



**CARBON  
CURE™**

## Durability of CO<sub>2</sub> Mineralized Concrete

# *Durability of CO<sub>2</sub> Mineralized Concrete*

**JUNE 2016**

Sean Monkman, CarbonCure Technologies  
Mark MacDonald, CarbonCure Technologies  
Doug Hooton, University of Toronto  
Paul Sandberg, Calmetrix

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 CO<sub>2</sub> 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 CO<sub>2</sub> emissions that exceed 63,000 tons as of January 2020.

### **ABSTRACT**

Carbon dioxide was investigated for use as a beneficial admixture to concrete as it was truck mixed. The reaction between the carbon dioxide (CO<sub>2</sub>) and the hydrating cement creates finely distributed calcium carbonate reaction products that thereby influence the subsequent hydration. Comparisons of the fresh, hardened and durability properties were made between a reference concrete batch, a batch that contained a conventional accelerating admixture, and three batches subjected to a carbon dioxide addition. The optimum dose of carbon dioxide was found to reduce the time to initial set by 40% and increase the one and three day compressive strengths by 14% and 10% respectively. In comparison to the CO<sub>2</sub> batch, the conventional accelerator provided greater reductions in set time but lower early strength. Concrete durability test results indicated that the carbon dioxide process did not compromise the expected durability performance of the treated concrete. CO<sub>2</sub> is a viable admixture to improve concrete performance.

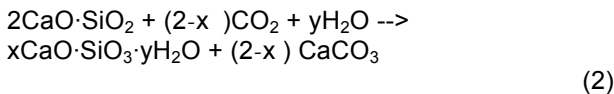
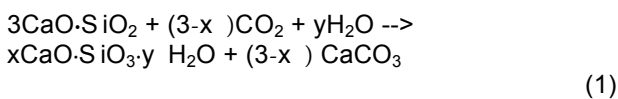
*Keywords:* Concrete, Carbon dioxide, Admixtures, Durability, Industrial trial, Sustainability

A version of this paper was published in Cement  
Concrete Composites 74 in 2016:  
<http://dx.doi.org/10.1016/j.cemconcomp.2016.10.007>

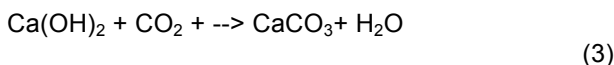
## 1. INTRODUCTION

Carbon dioxide emissions are recognized as a significant issue relating to cement production and the use of concrete as a building material. It is estimated that 5% of the world's annual CO<sub>2</sub> emissions are attributable to cement production [1]. The industry has previously recognized a number of approaches to reduce the emissions intensity of the cement produced and used in concrete with the industry goal to reduce emissions 50% below 2006 levels by 2050 [2]. It is clear, however, that practical limits on the impacts of these measures mean that meeting the goal will be difficult [3]. Innovative approaches are sought and are likely to be a part of a portfolio strategy. The most significant improvements in production efficiency and cement substitution with supplementary cementitious materials are already known and available. Future emissions improvements will likely be incremental. Therefore, innovative approaches are sought that can be a part of a portfolio strategy.

One approach that may be relevant is the beneficial use of carbon dioxide to make concrete products. The mechanism of carbonation of freshly hydrating cement was systematically studied in the 1970s at the University of Illinois [4]. The main calcium silicate phases in cement were shown to react with carbon dioxide, in the presence of water, to form calcium carbonate and calcium silicate hydrate gel as shown in Equations (1) and (2):



Further, any calcium hydroxide present in the cement paste will react, in the presence of water, with carbon dioxide, as shown in Equation (3):



The carbonation reactions are exothermic. The reaction proceeds in the aqueous state when Ca<sup>2+</sup> ions from the cementitious phases interact with CO<sub>3</sub><sup>2-</sup> ions from the applied gas.

The carbonation heats of reaction for the main calcium silicate phases are 347 kJ/mol for C<sub>3</sub>S, 184 kJ/mol for b-C<sub>2</sub>S [4] and 74 kJ/mol for Ca(OH)<sub>2</sub> [5]. When the calcium silicates carbonate, the CaCO<sub>3</sub> that forms is understood to be mixed with calcium silicate hydrate (C-S-H) gel [6]. C-S-H gel formation occurs even in an ideal case of b-C<sub>2</sub>S and C<sub>3</sub>S exposed to a 100% CO<sub>2</sub> at 1 atm according to the observation that the amount of carbonate that forms does not exactly correspond to the amount of calcium silicate involved in the reaction [4].

The reaction of carbon dioxide with a mature concrete micro-structure is conventionally acknowledged to be a durability issue due to such effects such as reduced pore solution pH, and carbonation induced corrosion. In contrast, a carbonation reaction integrated into concrete production reacts CO<sub>2</sub> with freshly hydrating cement, rather than the hydration phases present in mature concrete, and does not have the same effects. Rather, by virtue of adding gaseous CO<sub>2</sub> to freshly mixing concrete the carbonate reaction products are anticipated to form in situ, are of nano-scale and homogeneously distributed.

Earlier work had pursued reacting carbon dioxide with ready-mixed concrete to maximize the carbon dioxide absorption [7]. A limited reaction time and effects on workability were identified as challenges to overcome. Subsequent lab work using isothermal calorimetry identified the potential performance benefit of using an optimized low dose of carbon dioxide to promote the development of finely distributed carbonate reaction products. It was concluded that a small dose of carbon dioxide could feasibly be used to provide performance benefits in ready-mixed concrete.

## 2. EXPERIMENTAL

Industrial experiments were conducted whereby carbon dioxide was delivered to ready-mixed concrete immediately after batching. A tank of liquid CO<sub>2</sub> was connected to a gas control system and injector. The liquid was metered for injection into the truck whereupon it converted into a mixture of CO<sub>2</sub> gas and solid carbon dioxide (snow). The CO<sub>2</sub> was delivered into the fresh concrete, at a specified flow rate over a fixed injection interval, whereupon it reacted with the hydrating cement during initial mixing.

The concrete was then subjected to assessment and testing. Five truck loads of concrete were tested: a reference mixture, a reference mixture that used a proprietary non-chloride accelerating admixture, and three truck loads that were treated with increasing doses of carbon dioxide delivered over periods of 60, 90 and 120 s. The injection took place while the truck was paused at the wash rack for cleaning. Partial loads (4 m<sup>3</sup>) of concrete were batched according to the producer's standard operating procedures. The mix design used in the trial was designed to achieve a 35 MPa compressive strength at 28 days and used a binder with 20% slag replacement of cement. The mix design called for 1070 kg coarse aggregate, 756 kg sand, 308 kg cement, and 77 kg slag per cubic meter of concrete. Three admixtures were used: a retarding water reducer, a high range water reducer and an air entrainer. The w/cm was 0.39. The admixture dosages used in the five batches are summarized in Table 1. Batches are presented in their order of production. The quantities of the admixtures are in terms of 100 kg of cementitious materials while the carbon dioxide doses are in terms of weight of carbon dioxide by weight of cement.

**Table 1**  
Overview of the admixture loadings in the batches tested during the trial.

Admixture	Accelerated	Reference	CO <sub>2</sub> -1	CO <sub>2</sub> -2	CO <sub>2</sub> -3
Retarding WR (ml/100 kg cm)	125	220	220	125	125
HRWR (ml/100 kg cm)	175	200	175	175	175
Air entrainer (ml/100 kg cm)	23	23	23	25	25
Set accelerator (ml/100 kg cm)	1000	e	e	e	e
CO <sub>2</sub> (%) (cement)	e	e	0.05%	0.15%	0.30%

The first truck prepared during the trial was intended to be a reference batch but it was excluded from testing due to a slump that exceeded the target level. The retarding water reducer was decreased for the batch containing the accelerator according to the producer's batching policy. This admixture was further used at the default level for the CO<sub>2</sub><sup>-1</sup> batch and at the reduced level for the two higher CO<sub>2</sub> doses. The retarding water reducer is typically anticipated to improve the concrete compressive strength.

The high range water reducer dosage was slightly higher in the reference mix than in the other four batches and, according to the manufacturer, this is anticipated to improve its early compressive strength and ultimate compressive strength. The dosage of air entraining admixture was adjusted over the course of the trial in response to observed fresh properties in a manner consistent with normal production.

The production personnel verified that the consistency of the concrete met expectations prior to continuing with the testing. For the batches without the CO<sub>2</sub> injection this assessment was completed when the truck arrived at the wash rack whereas for the other batches the testing was completed after the CO<sub>2</sub> injection.

The batches were sampled to test the fresh properties of the concrete mixture and to prepare specimens for analysis via calorimetry, compressive strength, and various durability tests. For the three batches treated with carbon dioxide the fresh properties were assessed both before and after the CO<sub>2</sub> addition to directly evaluate the immediate impact of the treatment.

The fresh concrete was assessed in terms of slump, air content, plastic density, temperature, initial set and final set. Isothermal calorimetry data was collected by taking 6 grams of mortar from the concrete by wet sieving under vibration through a 4.75 mm screen and measuring the mortar's heat of hydration with a TAM Air Calorimeter.

The sieved mortar was also used for time of set testing.

Concrete from each truck load was used to cast 100x200 mm cylinders for compressive strength testing at ages of 1, 3, 7, 28, 56, 91 and 182 days. Further, test specimens for the rapid chloride penetration test (ASTM C1202), rapid chloride migration test (Nordtest NT 492), bulk resistivity, deicing salt scaling resistance (OPS LS-412: a modification of ASTM C672), freeze-thaw durability (ASTM C666), linear shrinkage (OPS LS-435: similar to ASTM C157 with 28 days drying at 50% RH after 7 days of moist curing), and hardened air void characteristics were cast. Note that the OPS designation indicates Ontario Provincial Standards, used by the highway agency in Ontario, Canada.



**Table 2**

Fresh concrete properties.

Batch	Slump before CO <sub>2</sub> (mm)	Slump after CO <sub>2</sub> (mm)	Air content before CO <sub>2</sub> (%)	Air content after CO <sub>2</sub> (%)	Temperature (°C)	Unit weight (kg/m <sup>3</sup> )
Reference	150	e	6.2	e	20.4	2372
Accelerated	135	e	5.4	e	21.0	2376
CO <sub>2</sub> e1	125	130	5.1	5.0	20.1	2376
CO <sub>2</sub> e2	140	120	5.9	6.2	21.4	2369
CO <sub>2</sub> e3	110	115	5.5	6.2	20.1	2366

### 3. RESULTS

#### 3.1 FRESH PROPERTIES

##### 3.1.1. PLASTIC PROPERTIES

An overview of the fresh properties of each of the five batches can be found in Table 2. The slumps, air contents, temperatures and unit weights were deemed to be acceptable, with the observed differences consistent with normal production variation. The reference batch had the highest slump as anticipated given that it had the highest dosage of high range water reducer. In all cases the scale of the changes in fresh properties was small enough that the carbon dioxide treated samples of concrete were deemed to have performed equivalently to the reference batch. The use of carbon dioxide did not produce any change to the fresh concrete properties.

The results of the time of set testing are presented in Table 3. For each condition, the initial and final set are presented along with comparisons to the reference both in terms of the actual differences (in minutes) and as a relative comparison.

The two dosages of set retarding water reducer suggest that three types of comparisons are valid. A comparison between the reference batch and the accelerated batch includes a reduction in the retarding water reducer but nonetheless represents the conventional industrial case. A comparison between the reference and CO<sub>2</sub>-1 batch can be made wherein equal doses of the set retarding admixture were used and differences are directly attributable to the action of the CO<sub>2</sub>. Relative comparisons between the latter two CO<sub>2</sub> doses and the accelerated batch are possible given that the retarding admixture reduction was made in all three. A direct comparison between

the accelerated and the CO<sub>2</sub>-1 batch, however, is more problematic given that the CO<sub>2</sub> batch contained a higher amount of the retarding admixture.

All three injection doses of CO<sub>2</sub> provided set acceleration although not to the same extent as the conventional accelerating admixture. The conventional accelerating admixture reduced the time of initial set by 173 min (a 40% reduction) and the final set by 162 min (a 33% reduction). The carbon dioxide doses reduced the time of initial set between 95 and 118 min (22e28% reduction) and the final set by 104e126 min (21e25% reduction). The middle dose of CO<sub>2</sub> provided the greatest acceleration benefit amongst the carbon dioxide treated batches. However, it is thought that the CO<sub>2</sub>-1 batch would have provided the most potent acceleration among the CO<sub>2</sub> batches, if not all the batches, if it had been produced with the 40% reduction in the retarding water reducer to be consistent with the other non-reference batches.

##### 3.1.3. CALORIMETRY RESULTS

The isothermal conduction calorimetry heat flow/power curves are presented in Fig. 1.

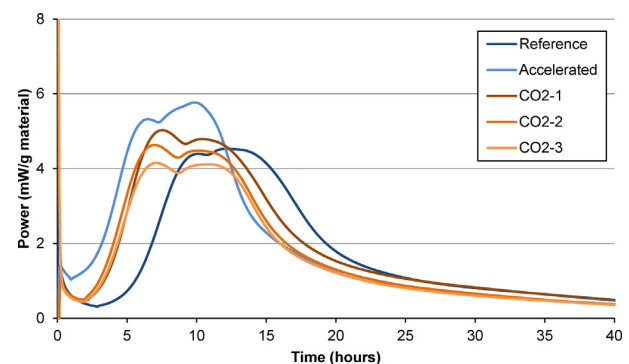


Fig. 1. Conduction calorimetry (power curves) of sieved mortar samples.

**Table 3**

Times of set.

Batch	Initial set			Final set		
	Time (h)	Difference (min)	Relative to reference	Time (h)	Difference (min)	Relative to reference
Reference	7:08	e	100%	8:18	e	100%
Accelerated	4:15		60%	5:36		67%
CO <sub>2</sub> e1	5:33		78%	6:34		79%
CO <sub>2</sub> e2	5:10		72%	6:12		75%
CO <sub>2</sub> e3	5:28		77%	6:27		78%

From the power curves it can be seen that the onset of hydration after the induction period occurs earlier for all the carbon dioxide treated batches than for the control and the subsequent hydration rate is comparable to both the control and the accelerated case following the end of the induction period. While the effect of CO<sub>2</sub> on the onset of hydration was similar for all dosages, the maximum energy release observed was seen to decrease with increasing CO<sub>2</sub> dose. The peak energy release for the middle dose was about equivalent to that of the reference batch. The onset of the heat evolution of the accelerated batch occurs earlier than for the carbonated batches. The shapes of the heat energy curves can allow for some inferred conclusions [8]. In the carbonated batches the energy release for the main silicate hydration peak is greater than it is for the subsequent aluminate activity peak suggesting a modification of C<sub>3</sub>S hydration. In the non-CO<sub>2</sub> injected batches, the aluminate peak is higher than the main hydration peak with a large enhancement being observed where the accelerating admixture was used.

The integration of the power curves provides the cumulative heat of hydration. The heats of hydration (presented both as J/g and relative to the reference concrete) are summarized in Table 4.

The total hydration was increased most by the accelerated batch, but the lowest dose of carbon dioxide was close behind. It is notable that these two conditions were close even though the accelerated batch contained less of the retarding water reducer. The amount of hydration after the 0.15% dose of CO<sub>2</sub> was essentially equivalent to that observed in the reference concrete, while the highest dose showed a slight decrease in total hydration at 40 h.

## 3.2 HARDENED PROPERTIES

### 3.2.1. COMPRESSIVE STRENGTH RESULTS

The results of the compressive strength testing are presented in Figs. 2 and 3. For each condition the strength values represent the average of three specimens.

The concrete containing the non-chloride accelerator was 9% stronger than the reference at 1 day, ranged between 2 and 3% up to 56 days, and was 8e14% stronger at later ages. The industrial case has determined that the dosage of the set retarding water reducer is decreased when using the accelerator, thereby the anticipated later age strength enhancement associated with the former

should be considered when interpreting the results. The 91 and 182 day strength benefit in this case is potentially even greater in light of the admixture reduction.

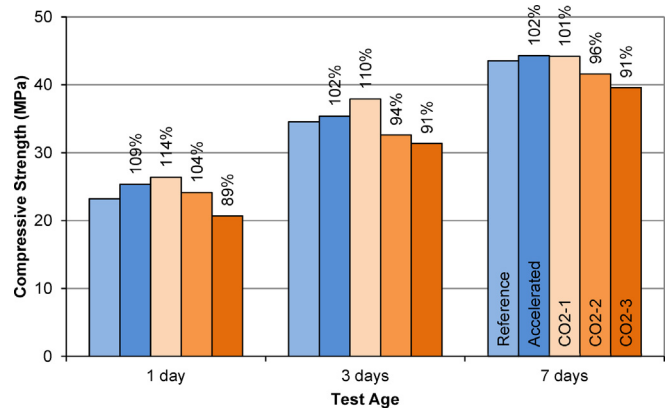


Fig. 2. Early age compressive strengths at 1, 3 and 7 days.

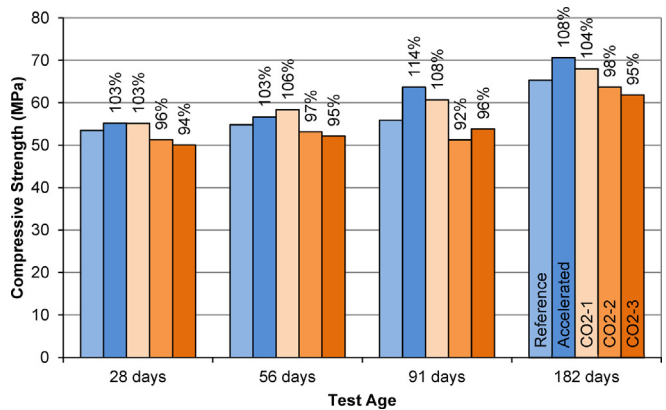


Fig. 3. Later age compressive strengths at 28, 56, 91 and 182 days.

Compressive strength measurements of the CO<sub>2</sub>-injected con-crete batches revealed that the best results came from the lowest dose, which provided a 14% improvement of the compressive strength for the cylinders tested at 1 day and 10% at 3 days. It was functionally equivalent to the reference at ages beyond 7 days where the benefit varied between 1 and 8%.

At all ages, except for 91 days, the strength decreased as the CO<sub>2</sub> dose was increased. The strength of the concrete with the highest dose of CO<sub>2</sub> ranged from 5 to 11% lower than the reference across the test period although the increased usage of the strength-enhancing/retarding water reducer in the reference likely played a role.

The ranges of dosages used in the different batches indicates that an optimal dose of CO<sub>2</sub> for strength development would be lower than 0.30% and likely on the order of 0.05% to 0.15%. The differences in the strengths of the concrete produced with the different doses of CO<sub>2</sub> reflect the potential level of sensitivity of the interaction between the carbon dioxide and the binder system. Further adjustments of the CO<sub>2</sub> dose around the identified optimum level, in addition to fine tuning of the normal admixture dosages, would be required to conclusively determine the optimum dose and conclusively establish a potential strength benefit.

The concrete with the lowest dose of CO<sub>2</sub> proved to have a higher strength than concrete produced with the conventional accelerator at 1 and 3 days. Thereafter there was little difference between the two batches until the latter showed a 14% benefit at 91 days and 8% at 182 days. It is noted that the difference in the retarding water reducer may account for some of the difference.

The CO<sub>2</sub> utilization approach has been developed through trials at more than a dozen industrial locations. The average strength improvements observed through a limited first-pass optimization (e.g. the dosage ramp presented here) were 10% at one day, 12% at three days, 11% at 7 days and 8% at 28 days [9]. The testing examined a range of cements and SCMs and can attest to the promise of a strength benefit associated with the approach.

### 3.2.2. LINEAR SHRINKAGE

The linear shrinkage tests, according to OPS LS 435, are reported in Table 5.

**Table 5**  
Linear shrinkage test results (OPS LS 435).

	1 day	3 days	7 days	14 days	28 days
Reference		-0.009	-0.016		
Accelerated		-0.011	-0.019	-0.026	-0.035
CO2-1		-0.010	-0.017	-0.025	-0.034
CO2-3		-0.012	-0.020		

Concrete from the CO2-2 batch was not tested due to a lack of prism moulds. All batches were found to have linear shrinkage lower than the optional CSA A23.1 limit for low-shrinkage concrete of 0.04% after 28-days drying at 50% RH. The concrete with the highest carbon dioxide dose did show a small increase in linear shrinkage but this is likely within the scatter of the data.

**Table 6**  
Hardened air void analysis results.

	Air content (%)	Specific surface (mm <sup>-1</sup> )	Spacing factor (mm)
Reference	4.9	38.19	0.119
Accelerated	5.0	33.33	0.134
CO2-1	4.3	38.49	0.130
CO2-2	6.1	40.84	0.111
CO2-3	4.6	46.05	0.111

### 3.2.3. HARDENED AIR VOIDS

The results of the hardened air void analysis are presented in Table 6.

The hardened air content and air void characteristics were acceptable for each of the batches with all values well below the CSA A23.1 maximum air void spacing factor limit of 0.230 mm.

A combined analysis of both the fresh and hardened air contents suggests that one caveat is applicable to the interpretation of the compressive strength. The air content (both in the fresh and hardened states) of batch CO2-1 was observed to be lower than in the reference. The strength benefits observed for this batch, as well as for the accelerated batch that had a lower fresh air content than did the reference, were possibly associated with the reductions in the air content in relation to the reference mixture.

### 3.2.4. TRANSPORT PROPERTIES

The RCPT test results (ASTM C1202) are presented in Table 7, bulk resistivity results are presented in Table 8, the rapid chloride migration test results (NT 492) are presented in Table 9.

Each of the test results indicated that the carbon dioxide injection did not negatively impact the predicted transport properties of the concrete. The RCPT results suggested that the chloride ion penetrability would be low for all concretes at 28 and 56 days and very low at 180 days. The resistivity results indicate that all five batches were on the cusp between moderate and low risk of chloride penetration at 28 days and low at 56 days. The non-steady state rapid chloride migration testing indicated that all the CO2-injected mixtures had lower chloride migration values than the reference mixture at 28 days, with 2 of 3 migration values lower at 56 days.

**Table 7**

Charge passed (coulombs) in the Rapid Chloride Permeability Test (RCPT).

Batch	28 days	56 days	180 days
Reference	1563	1061	841
Accelerated	1653	1385	906
CO2-1	1433	1126	965
CO2-2	1597	1161	900
CO2-3	1507	1114	836

**Table 8**

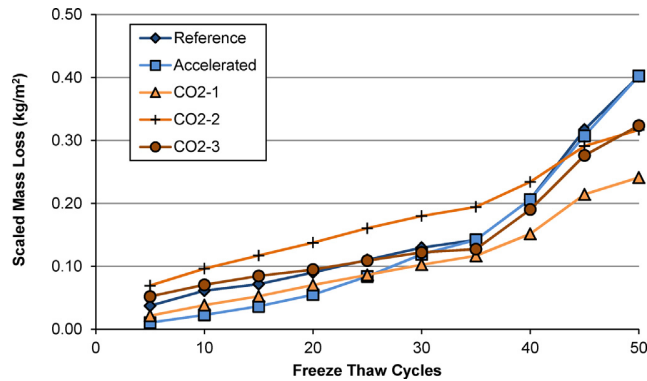
Bulk resistivity test results (kU -cm).

Batch	28 days	56 days
Reference	10.0	12.9
Accelerated	10.3	13.4
CO2-1	9.9	13.3
CO2-2	9.6	12.6
CO2-3	10.1	13.0

**Table 9**

Rapid chloride migration (NT 492) test results ( $10^{-12}$  m<sup>2</sup>/s).

Batch	28 days	56 days
Reference	8.2	6.3
Accelerated	5.6	5.8
CO2-1	7.0	6.7
CO2-2	7.1	6.0
CO2-3	6.4	4.8

**Fig. 4.** Freeze thaw deicing salt scaling mass loss according to OPS LS-412 testing.**Table 10**

Freeze/thaw durability (ASTM C666) test results.

Batch	ASTM C666 Durability factor	ASTM C666 mass loss
Reference	43.2%	1.66%
Accelerated	45.5%	1.65%
CO2-1	44.5%	0.84%
CO2-2	n/a	n/a
CO2-3	56.9%	0.79%

### 3.2.5. FREEZE-THAW AND SALT SCALING RESISTANCE

The data from the salt scaling testing are presented in Fig. 4.

By the conclusion of the scaling test it was observed that the three batches treated with CO<sub>2</sub> exhibited lower scaling than did the two batches without carbon dioxide. The performance of the reference and accelerated batches was identical from 35 cycles onward. The batch with the lowest dose of CO<sub>2</sub> exhibited the least scaling with a 40% reduction over the two non-CO<sub>2</sub> batches. It can be noted, however, that none of the samples approached the OPS scaling limit of 0.80 kg/m<sup>2</sup>.

The data from the ASTM C666 testing is presented in Table 10. All of the durability factors calculated from loss in dynamic modulus were low, in spite of good air void spacing factors, and likely due to the low hardened air contents, as shown in Table 6. However, there was no negative impact of the CO<sub>2</sub>-injection. It was observed that the two batches treated with CO<sub>2</sub> exhibited lower mass loss in ASTM C666 than did the reference batch (concrete from the CO2-2 batch was not tested under C666 due to a shortage of moulds). The durability factor was comparable for the two batches without carbon dioxide and the CO2-1 batch but it was improved for the CO2-3 batch. The mass loss observed on the two carbon dioxide batches tested was about half of that in the un-treated batches and indicated superior scaling performance.

## 4. DISCUSSION

The injection of carbon dioxide into concrete while mixing was associated with an increase in the heat of hydration observed through isothermal calorimetry, a reduction in the concrete set time, a neutral effect on compressive strength, and no negative effect on the durability properties.

The observed acceleration of time-of-set and early strength development with all doses of CO<sub>2</sub> may result from one or a combination of two causes. The formation of nanoscale carbon-ation reaction products may serve as heterogeneous nucleation sites for the precipitation of hydration products from pore solution. Seed particles acting as nuclei at a distance from cement particle surfaces have been identified as producing accelerating effects.

Research investigating the additions of C-S-H (1-4% by weight) to hydrating cement systems suggested that increases in the early hydration rate and total amount of early hydration were attributable to the creation of new nano calcium carbonate nucleation sites within the pore solution rather than upon the cement particle surfaces [10]. Such a mechanism is particularly relevant to the reactions at hand.

Alternately or additionally, the reaction of carbon dioxide in solution with calcium ions (and, as per a corresponding development of silicate hydrate) causes additional dissolution of clinker species (i.e. Ca, Si, and Al) into pore solution. The previously presented chemical equations (1) and (2) suggest that C-S-H gel formation, according to a driving force associated with balancing the ionic activity related to  $\text{Ca}^{2+}$

consumption, is expected alongside the calcium carbonate development. The net result is that the gel forms with a lower calcium content than it otherwise would have. It has been observed that a gel phase with a lower Ca/Si ratio has a lower density [11]. If the duration of the induction period is related to the action of a relatively impermeable C-S-H growing on the hydrating grains, then a less dense or thinner C-S-H layer should offer less resistance to hydration and shorten the induction period.

The results suggested that the concrete strength decreased slightly with increasing  $\text{CO}_2$  dose (although differences in admixture dosages and air content are also expected to have played a role). An optimum dose of carbon dioxide may impart a well-balanced addition of nuclei to the system whereas an excessive dose may compromise the subsequent hydration. Potentially the reaction would initially take place in the pore solution but upon continued addition of carbon dioxide there are more  $\text{CO}_3^{2-}$  ions in solution and the  $\text{Ca}^{2+}$  may not be replenished at the rate it is being consumed. The later-reacting carbon dioxide may combine with  $\text{Ca}^{2+}$  preferentially located close to or atop active dissolution sites rather than at a distance and in solution.

This interpretation is supported by the calorimetric observation that the rate of hydration is unchanged but the intensity of the silicate hydration peak decreases with increasing  $\text{CO}_2$  dosage.

The additional reaction products formed from higher dosages of  $\text{CO}_2$  serve to decrease the available active surface area of the cement while the remaining, exposed cement proceeds to hydrate at a rate consistent with the reference case. The decline in the heat of hydration (both at 24 and 40 h) with an increase in carbon dioxide dose suggests a transition between an optimal and non-optimal dosage.

Based on the tests conducted, the  $\text{CO}_2$ -injection process had a neutral to positive effect on concrete durability. Indicators of chloride penetration resistance (ASTM C1202, NT492 and bulk resistivity) as well as drying shrinkage and freeze-thaw and de-icer salt scaling resistance were not negatively impacted by the  $\text{CO}_2$ -process. It should also be stated that the concrete resulting from the  $\text{CO}_2$  injection process does not result in carbonated concrete and raises no concern regarding steel corrosion. The uniformly-dispersed initial nanocarbonates that form simply act as nucleation sites that accelerate subsequent normal hydration and do not impact the later development of pore solution alkalinity.

It is likely that the absorption efficiency of the carbon dioxide into the concrete is on the order of 50-80%. The injection of liquid  $\text{CO}_2$  into the truck was effectively a delivery of a two phase mixture (approximately 50/50) of solid carbon dioxide "snow" and gas. The liquid is not stable at atmospheric temperature and pressure and converts to the two phase mixture immediately upon delivery from the injection hardware. The acceleration for the lowest dose of  $\text{CO}_2$  is associated with the reaction of roughly 0.025%  $\text{CO}_2$  by weight of cement, or, according to molar weights, 0.057%  $\text{CaCO}_3$ . While this amount is small it is consistent with the physical action of finely divided silica which has been observed to achieve calorimetric acceleration effects in tricalcium silicate at doses as low as 0.05% by weight  $\text{C}_3\text{S}$  [12].

Ex-situ additions of nano- $\text{CaCO}_3$  have been observed to achieve accelerated hydration and strength improvements [13-15]. However, cost notwithstanding, the obstacle to integrating nano- $\text{CaCO}_3$  additions into conventional concrete is effective dispersion [16]. The in-situ production of nano-scale calcium carbonate reaction products via  $\text{CO}_2$  injection addresses this challenge.



It is known that the amount of heat released by the concrete can be used as a proxy for the development of mechanical properties (including compressive strength) for ages between the time of set and a few days of hydration [17]. This concept is similar to the well known use of maturity to predict early strength development of a given, fixed mix design [18]. The underlying assumption in the present analysis is that once the small amount of CO<sub>2</sub> has triggered the nucleation and acceleration stage there is no appreciable difference in the subsequent hydration chemistry and only a difference observed in hydration kinetics. Conversely, such an assumption is not valid for non-chloride accelerators, such as calcium nitrate, that are known to accelerate the hydration of the aluminate phases. In such case there is a change in the hydration chemistry and there is an increase in the heat of hydration generated by the aluminate reaction [19].

When examining the calorimetry results alongside the early strength data it can be observed that at 24 h the energy for the CO<sub>2</sub>-1 dose correlates better to the strength (14% energy increase and 14% strength increase) than it did for the batch with the accelerating admixture (19% energy increase and 9% strength increase). The shapes of the heat of hydration curves showed that with the CO<sub>2</sub> treated concrete there was an increase in the activity of the C<sub>3</sub>S (thereby producing more C-S-H gel) while in the batch with the accelerating admixture the aluminate activity increased (thereby producing more ettringite). The ratio of heat of hydration to product volume (i.e. pore filling capacity, strength) for those two reactants differs with the products of C<sub>3</sub>A hydration having a lower heat of hydration per unit of space-filling capacity [20].

The identified acceleration effect of the carbon dioxide, combined with lack of impact on the durability, offers an interesting prospect for use of a carbon dioxide injection alongside or instead of an accelerating admixture. An illustrative analysis can be performed. Assuming a generic material cost of \$385 (US) per tonne of industrial carbon dioxide then the raw cost of the CO<sub>2</sub> used in trial would range from \$0.48 to \$2.85 per truckload (8 m<sup>3</sup>) of concrete. As a comparison, a non-chloride accelerator cost can be estimated. The raw material cost of calcium nitrate (a typical ingredient in non-chloride accelerators) can be taken as \$143 (US) per tonne. An admixture cost can be estimated as 3 to 4 times the raw material cost (herein assumed as 3.5 times).

The typical admixture dosage rate can be taken as 1e2% by weight of cement. The cost to the concrete producer of a conventional non-chloride accelerator, across the typical dosage range and for one truckload, would be \$12.36 to \$24.72. Based upon a simple comparison of consumables, the carbon dioxide could offer an economic advantage over a non-chloride accelerator. It was observed for these mixtures that the commercial non-chloride accelerator was a more potent accelerator than was the carbon dioxide, but economics would potentially dictate the prospect of employing CO<sub>2</sub> or exploring a combination of CO<sub>2</sub> and a reduced dose of the existing accelerator.

The utilization of carbon dioxide in concrete production has potential sustainability impacts. The CO<sub>2</sub> must be captured from industrial process (in this case it was a by-product from a urea/fertilizer process), be liquefied and transported to the place of use. The net benefit is sensitive to the uptake rate of the CO<sub>2</sub>, the specific electrical grid emissions and transportation distance, but it can be conducted in a way that offers a net reduction in carbon emissions [21].

## 5. CONCLUSIONS

A series of 4 m<sup>3</sup> concrete mixtures were produced in concrete trucks using injection of carbon dioxide during their mixing. The injection of waste CO<sub>2</sub> into the concrete mixtures accelerated the hydration and strength development without affecting the fresh properties. The time to initial set was accelerated by 95e118 min (an average 25% time reduction) and the final set was accelerated by 103e126 min (an average 23% time reduction). The mixture batched with the conventional non-chloride accelerator offered 173 and 162 min improvements to the times of initial and final set, respectively. Isothermal calorimetry further supported the conclusion that the CO<sub>2</sub> injection accelerated early hydration reactions and indicated that the carbon dioxide reacted with the silicate phases whereas the non-chloride accelerator is normally considered to react with the aluminate phases.

A compressive strength benefit was observed for the concrete that received the lowest dose of CO<sub>2</sub> but interpretation was complicated by differences in air content (however, other trials have suggested that a strength benefit is readily achievable outcome).

CaCO<sub>3</sub> additions into conventional concrete is effective dispersion [16]. The in-situ production of nano-scale calcium carbonate reaction products via CO<sub>2</sub> injection addresses this challenge.

It is known that the amount of heat released by the concrete can be used as a proxy for the development of mechanical properties (including compressive strength) for ages between the time of set and a few days of hydration [17]. This concept is similar to the well known use of maturity to predict early strength development of a given, fixed mix design [18]. The underlying assumption in the present analysis is that once the small amount of CO<sub>2</sub> has triggered the nucleation and acceleration stage there is no appreciable difference in the subsequent hydration chemistry and only a difference observed in hydration kinetics. Conversely, such an assumption is not valid for non-chloride accelerators, such as calcium nitrate, that are known to accelerate the hydration of the aluminate phases. In such case there is a change in the hydration chemistry and there is an increase in the heat of hydration generated by the aluminate reaction [19].

When examining the calorimetry results alongside the early strength data it can be observed that at 24 h the energy for the CO<sub>2</sub>-1 dose correlates better to the strength (14% energy increase and 14% strength increase) than it did for the batch with the accelerating admixture (19% energy increase and 9% strength increase). The shapes of the heat of hydration curves showed that with the CO<sub>2</sub> treated concrete there was an increase in the activity of the C<sub>3</sub>S (thereby producing more C-S-H gel) while in the batch with the accelerating admixture the aluminate activity increased (thereby producing more ettringite). The ratio of heat of hydration to product volume (i.e. pore filling capacity, strength) for those two reactants differs with the products of C<sub>3</sub>A hydration having a lower heat of hydration per unit of space-filling capacity [20].

The identified acceleration effect of the carbon dioxide, combined with lack of impact on the durability, offers an interesting prospect for use of a carbon dioxide injection alongside or instead of an accelerating admixture. An illustrative analysis can be performed. Assuming a generic material cost of \$385 (US) per tonne of industrial carbon dioxide then the raw cost of the CO<sub>2</sub> used in trial would range from \$0.48 to \$2.85 per truckload (8 m<sup>3</sup>) of concrete. As a comparison, a non-chloride accelerator cost can be estimated. The raw material cost of calcium nitrate (a typical ingredient in non-chloride accelerators) can be taken as \$143 (US) per tonne. An admixture cost can be estimated as 3 to 4 times the raw material cost (herein assumed as 3.5 times).

The typical admixture dosage rate can be taken as 1e2% by weight of cement. The cost to the concrete producer of a conventional non-chloride accelerator, across the typical dosage range and for one truckload, would be \$12.36 to \$24.72. Based upon a simple comparison of consumables, the carbon dioxide could offer an economic advantage over a non-chloride accelerator. It was observed for these mixtures that the commercial non-chloride accelerator was a more potent accelerator than was the carbon dioxide, but economics would potentially dictate the prospect of employing CO<sub>2</sub> or exploring a combination of CO<sub>2</sub> and a reduced dose of the existing accelerator.

The utilization of carbon dioxide in concrete production has potential sustainability impacts. The CO<sub>2</sub> must be captured from industrial process (in this case it was a by-product from a urea/fertilizer process), be liquefied and transported to the place of use. The net benefit is sensitive to the uptake rate of the CO<sub>2</sub>, the specific electrical grid emissions and transportation distance, but it can be conducted in a way that offers a net reduction in carbon emissions [21].

## 5. CONCLUSIONS

A series of 4 m<sup>3</sup> concrete mixtures were produced in concrete trucks using injection of carbon dioxide during their mixing. The injection of waste CO<sub>2</sub> into the concrete mixtures accelerated the hydration and strength development without affecting the fresh properties. The time to initial set was accelerated by 95e118 min (an average 25% time reduction) and the final set was accelerated by 103e126 min (an average 23% time reduction). The mixture batched with the conventional non-chloride accelerator offered 173 and 162 min improvements to the times of initial and final set, respectively. Isothermal calorimetry further supported the conclusion that the CO<sub>2</sub> injection accelerated early hydration reactions and indicated that the carbon dioxide reacted with the silicate phases whereas the non-chloride accelerator is normally considered to react with the aluminate phases.

A compressive strength benefit was observed for the concrete that received the lowest dose of CO<sub>2</sub> but interpretation was complicated by differences in air content (however, other trials have suggested that a strength benefit is readily achievable outcome). The batches with the two higher doses of CO<sub>2</sub> did not show a strength benefit but the reference concrete contained a greater addition of a strength enhancing

The batches with the two higher doses of CO<sub>2</sub> did not show a strength benefit but the reference concrete contained a greater addition of a strength enhancing/retarding water reducer. The durability testing showed that the CO<sub>2</sub>-injection process had a neutral to positive effect on concrete durability. Suitable chloride penetration resistance, drying shrinkage, freeze-thaw, and de-icer salt scaling resistance performance of the CO<sub>2</sub>-treated concrete was assured through testing.

The acceleration benefits are associated with the in-situ development of uniformly distributed nano-carbonate reaction products. The products act as nuclei during early hydration and/or the lower Ca/Si silicate hydrate gel that forms alongside the carbonate products is less dense.

The economics of using an injection of carbon dioxide as a set accelerator are favourable as compared to use of a non-chloride accelerator. However, the acceleration effect of the CO<sub>2</sub> injection does not appear to be as potent, lending thought towards using it in combination with a reduced dose of accelerator.

## ACKNOWLEDGMENTS

The authors thank Phil Zacarias and Stephen Parkes of CBM (Canada Building Materials) for supporting the work through hosting the trial and collecting the data. Further assistance provided by University of Toronto students Gita Charmchi and Soley Einarsdottir was greatly appreciated. Research funding was received from Sustainable Development Technology Canada (SDTC)(project number SDTC-2010-B-1782R) and the National Research Council's Industrial Research Assistance Program (IRAP Project 837459). The funding sources had no input into the experimental design or analysis.

## APPENDIX A

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.cemconcomp.2016.10.007>.

## REFERENCES

- [1] J.S. Damtoft, J. Lukasik, D. Herfort, D. Sorrentino, E.M. Gartner, Sustainable development and climate change initiatives, *Spec. Issue d 12th Int. Congr. Chem. Cem. Montr. Can.* 38 (2008) (July 8-13 2007) 115e127, <http://dx.doi.org/10.1016/j.cemconres.2007.09.008>.
- [2] IEA, Cement Technology Roadmap: Carbon Emissions Reductions up to 2050, OECD Publishing, 2009. [http://www.oecd-ilibrary.org/energy/cement-technology-roadmap-carbon-emissions-reductions-up-to-2050\\_9789264088061-en](http://www.oecd-ilibrary.org/energy/cement-technology-roadmap-carbon-emissions-reductions-up-to-2050_9789264088061-en) (accessed October 15, 2014).
- [3] L. Barcelo, J. Kline, G. Walenta, E. Gartner, Cement and carbon emissions, *Mater. Struct.* 47 (2014) 1055e1065, <http://dx.doi.org/10.1617/s11527-013-0114-5>.
- [4] C.J. Goodbrake, J.F. Young, R.L. Berger, Reaction of beta-dicalcium silicate and tricalcium silicate with carbon dioxide and water vapor, *J. Am. Ceram. Soc.* 62 (1979) 168e171, <http://dx.doi.org/10.1111/j.1151-2916.1979.tb19046.x>.
- [5] D.R. Moorehead, Cementation by the carbonation of hydrated lime, *Cem. Concr. Res.* 16 (1986) 700e708, [http://dx.doi.org/10.1016/0008-8846\(86\)90044-X](http://dx.doi.org/10.1016/0008-8846(86)90044-X).
- [6] R.L. Berger, J.F. Young, K. Leung, Acceleration of hydration of calcium silicates by carbon-dioxide treatment, *Nat. Phys. Sci.* 240 (1972) 16e18, <http://dx.doi.org/10.1038/physci240016a0>.
- [7] S. Monkman, in: Carbon Dioxide Utilization in Fresh Industrially Produced Ready Mixed Concrete, Presented at the 2014 NRMCA International Concrete Sustainability Conference, May 12-15, 2014, NRMCA, Boston, USA, 2014. <http://www.nrmcaevents.org/?nav%4display&file%4653>.
- [8] D. Jansen, J. Neubauer, F. Goetz-Neunhoeffler, R. Haerzschel, W.-D. Hergeth, Change in reaction kinetics of a Portland cement caused by a superplasticizer d Calculation of heat flow curves from XRD data, *Cem. Concr. Res.* 42 (2012) 327e332, <http://dx.doi.org/10.1016/j.cemconres.2011.10.005>.
- [9] S. Monkman, M. MacDonald, R.D. Hooton, in: Carbon Dioxide Utilization in Ready-mixed Concrete Production, Presented at the ACI 2015 Fall Convention, Nov 9, 2015, ACI, Denver, CO, 2015.
- [10] J.J. Thomas, H.M. Jennings, J.J. Chen, Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, *J. Phys. Chem. C* 113 (2009) 4327e4334, <http://dx.doi.org/10.1021/jp809811w>.
- [11] J.J. Thomas, H.M. Jennings, A.J. Allen, Relationships between composition and density of tobermorite, jennite, and nanoscale CaO–SiO<sub>2</sub>–H<sub>2</sub>O, *J. Phys. Chem. C* 114 (2010) 7594e7601, <http://dx.doi.org/10.1021/jp910733x>.
- [12] W. Nocun-Wczelik, in: The Hydration of Tricalcium Silicate with Active Silica, in: *Proc. 4th CANMETACI Int. Conf. Use Fly Ash Silica Fume Slag Nat. Pozzolans Concr.*, Istanbul, Turkey, 1992, pp. 485e492.
- [13] T. Sato, F. Diallo, Seeding effect of nano-CaCO<sub>3</sub> on the hydration of tricalcium silicate, *Transp. Res. Rec. J. Transp. Res. Board* 2141 (2010) 61e67, <http://dx.doi.org/10.3141/2141-11>.
- [14] T. Sato, J.J. Beaudoin, Effect of nano-CaCO<sub>3</sub> on hydration of cement containing supplementary cementitious materials, *Adv. Cem. Res.* 23 (2011) 33e43, <http://dx.doi.org/10.1680/adcr.9.00016>.
- [15] D.P. Bentz, T. Sato, I. de la Varga, W.J. Weiss, Fine limestone additions to regulate setting in high volume fly ash mixtures, *Cem. Concr. Compos* 34 (2012) 11e17, <http://dx.doi.org/10.1016/j.cemconcomp.2011.09.004>.
- [16] S. Kawashima, P. Hou, D.J. Corr, S.P. Shah, Modification of cement-based materials with nanoparticles, *Cem. Concr. Compos* 36 (2013) 8e15, <http://dx.doi.org/10.1016/j.cemconcomp.2012.06.012>.
- [17] Z. Ge, K. Wang, P.J. Sandberg, J.M. Ruiz, Characterization and performance prediction of cement-based materials using a simple isothermal calorimeter, *J. Adv. Concr. Technol.* 7 (2009) 355e366, <http://dx.doi.org/10.3151/jact.7.355>.
- [18] G. Chengju, Maturity of concrete: method for predicting early-stage strength, *ACI Mater. J.* 86 (1989) 341e353.
- [19] P.J. Sandberg, C. Porteneuve, F. Serafin, J. Boomer, N. Loconte, V. Gupta, B. Dragovic, F. Doncaster, T. Vogt, L. Alioto, Effect of admixture on cement hydration kinetics by synchrotron XRD and isothermal calorimetry, in: *Proc. 12th Int. Congr. Chem. Cem.*, Montreal, Quebec, Canada, 2007.
- [20] D.P. Bentz, T. Barrett, I. De la Varga, W.J. Weiss, Relating compressive strength to heat release in mortars, *Adv. Civ. Eng. Mater* 1 (2012), <http://dx.doi.org/10.1520/ACEM20120002>.
- [21] S. Monkman, M. MacDonald, Carbon dioxide upcycling into industrially produced concrete blocks, *Constr. Build. Mater* 124 (2016) 127e132, <http://dx.doi.org/10.1016/j.conbuildmat.2016.07.046>.