Calculating Sustainability Impacts of CarbonCure Ready Mix

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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_2 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_2 emissions that exceed 63,000 tons as of January 2020.

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EXECUTIVE SUMMARY

Concrete is the world's most important and widely used construction material. Carbon dioxide utilization in the production of ready mixed concrete was investigated through the injection of an optimal amount of CO_2 during batching and mixing. The carbon dioxide improved the concrete compressive strength with minimal impact on fresh air content or workability. Three-way comparisons between a reference batch, reduced binder batch and reduced binder batch with CO_2 addition, confirmed that the carbon dioxide could allow for a 5-8% reduction in binder loading without compromising strength. A model case shows that integrating a CO_2 utilization step into conventional concrete production can, net of process emissions, reduce the carbon footprint of the concrete by 4.6%. The direct utilization is amplified to attain a carbon footprint improvement that is more than 35 times larger than the amount of carbon dioxide required. One year production at a medium sized producer would use about 24 tonnes of carbon dioxide to achieve nearly 897 tonnes of CO_2 absorbed and avoided.

Keywords: concrete, carbon footprint, construction materials, environmental impact; carbon dioxide utilization

1. INTRODUCTION

Concrete is the world's most widely used material. Annual cement production has surpassed an estimated 4.6 Gt (CEMBUREAU, 2016). It is a versatile and economical building material and demand is ever increasing (Scrivener, 2014). Cement production in 1950 amounted to 133 million tonnes (Fig. 1) thereby creating about 0.4 tonnes of concrete per person. By 2015, global cement production had seen a nearly 35-fold increase while the per capita concrete production had increased more than 12-fold. Considering that a generic concrete mix contains about 300 kg cement per cubic meter and global population exceeds 7.4 billion (Population Reference Bureau (PRB), 2016), it is evident that the annual global production of concrete is currently around 2.1 m3 per person. At a density of 2.3 tonnes per cubic meter there are about 4.8 tonnes of concrete produced annually for each person.

The carbon impact of the cement and concrete industry has been the subject of increasing attention. The production of cement involves the calcination of limestone ($CaCO_3$) to create reactive calcium silicates; carbon dioxide is a by-product (Barcelo et al., 2014). Cement production is responsible for 5.6% of emissions from fossil fuel and industry and is the largest industrial emitter (Le Quéré et al., 2016). The industry is facing a challenge to meet demand yet address carbon emissions. The cement and concrete industry worked with the International Energy Agency to outline the ambitious effort that would be required to reduce industry emissions to 50% below 2006 levels by 2050 (IEA, 2009); the target is consistent with the "blue map scenario" (International Energy Agency, 2008) wherein atmospheric CO_2 is limited to a level commensurate with atmospheric warming of þ3 C (IPCC, 2007). It was concluded that a projected 0.79 Gt of CO_2 reduction from the BAU baseline 2050 emissions needed to be achieved and would be addressable by four approaches:

(1) Reducing CO_2 emissions for the manufacture of Portland based cements through the increased use of alternative fuels and/or alternative raw materials (potentially 24% of the required reduction)
(2) Improving the energy efficiency of cement kilns (10%)
(3) Increasing clinker substitution through the increased use of low-carbon supplementary cementitious materials (SCMs) (10%)
(4) Capture and sequestration (CCS) of the carbon dioxide emissions released from cement plants (56%)

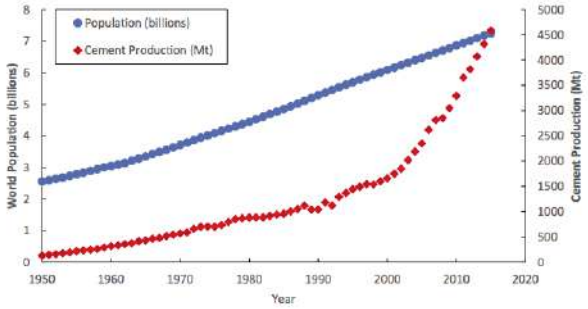

Fig. 1. Global population growth and cement production from 1950 to 2015 (population data from (U.S. Census Bureau, 2016), cement data to 2013 from (U.S. Geological Survey, 2016), cement data after 2013 from (CEMBUREAU, 2016)).

Traditional levers to reduce the carbon footprint of concrete (approaches 1 to 3) have practical limits whether it is the finite supply of viable supplementary cementitious material (SCMs) (Scrivener, 2014) or the realistic understanding of the potential to reduce the energy required to produce cement (Madlool et al., 2013). As a result, the greatest proportion of the projected carbon reduction depends upon the implementation of carbon sequestration technologies that are as-yet undefined solutions developed outside the industry. The time that has elapsed since the IEA roadmap was published in 2009 has allowed thinking to evolve and finds that, arguably, CCS is no longer the most promising technology for the reduction of CO_2 emissions related to cement based materials (Scrivener et al., 2016). Research has demonstrated that CO_2 utilization concepts can contribute to the creation of lower carbon concrete products (Ashraf, 2016; Jang et al., 2016). Methods rooted in CCS-style approaches focus upon maximizing the amount of CO_2 that can be sequestered and stored within useful building products. The necessity to contain the supplied CO_2 gas during the reaction has meant that efforts have largely focused on precast and/or masonry concrete applications wherein closed curing is feasible (El-Hassan and Shao, 2015; Wang et al., 2017; Zhan et al., 2016). Further applications have focused on the development of building products produced using carbon dioxide activated binder systems (Ashraf and Olek, 2016; Mahoutian and Shao, 2016; Vance et al., 2015), partly due to the limited amount of CO_2 that Portland cement can absorb. The potential for such applications to achieve large sustainability improvements within the niche

of addressable compatible concrete is promising, but carbon dioxide utilization solutions are required for the ready mixed concrete market segment, which consumes about 70% of the cement produced in the United States (U.S. Geological Survey, 2016) and is associated with 60% of concrete industry revenue.[1]

Recent work has identified the potential for CO_2 to unlock a performance benefit in cast-in-place concrete without impacting durability (Monkman et al., 2016). A carbon dioxide utilization method that can be integrated as a retrofit into typical concrete production and use normal Portland cement presents an attractive route to lessen the environmental impact of concrete while upcycling one industry waste (carbon dioxide) with the main industry output (ready mixed concrete).

The objective of this research was to test the hypothesis that the carbon dioxide utilization could improve the compressive strength of concrete so-produced and whether said improvement could be leveraged to improve the carbon footprint of the concrete and produce a more sustainable concrete mix. The work involved a retrofit CO_2 injection system installed at a ready mix concrete producer. Carbon dioxide was injected into the concrete while it was being batched and mixed. A model examines the potential process benefits and the net impact on the carbon footprint of concrete so-produced.

2. MATERIALS AND EXPERIMENTAL

A carbon dioxide utilization approach for ready mix concrete production was designed to be implementable as a retrofit technology. If the concept is shown to be technically viable through the realization of performance benefits and improvements in concrete sustainability then successful integration must respect incumbent practices and conform with existing equipment, sequences and process. A mixer injection approach demonstrated for masonry block production (Monkman and MacDonald, 2016) established a template for a central CO_2 injection approach for ready mix concrete.

Concrete was produced whereby carbon dioxide was injected during batching. A metering system fed a controlled supply of pressurized liquid CO_2 through to a discharge conduit. The liquid was converted into a mixture of CO_2 gas and finely divided solid carbon dioxide particles (commonly referred to as CO_2 "snow") once it reached the atmosphere upon discharge (liquid carbon dioxide is not stable at atmospheric temperature and pressure; the phase transition is spontaneous upon depressurization of the liquid). The carbon dioxide 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. CO_2 was injected directly into the central mixer prior to the discharge of the concrete into the truck. The carbon dioxide rapidly reacts with calcium ions, produced by the hydrating cement, to form calcium carbonate. The reacted CO_2 is chemically bound in the concrete as a solid phase; no gaseous carbon dioxide persists in the concrete.

The concrete was then subjected to assessment and testing. Industrially produced concrete was tested in the fresh state in terms of slump (ASTM C143 Standard Test Method for Slump of Hydraulic-Cement Concrete), air content (ASTM C231 Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method), unit weight and temperature. Hardened concrete cylinders were assessed in terms of compressive strength (ASTM C39 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens) at various ages and test conditions.

Preliminary proof-of-concept testing established that the addition of the carbon dioxide could produce a compressive strength benefit. The present investigation paired the strength-boosting CO_2 injection with a mix design optimization wherein the concrete mix was redesigned to have a reduced binder content. The intention was to produce a concrete with the same target strength but with a reduced carbon footprint. The cement reduction testing considered five cases across which comparisons could be made with both historical data (quality control data provided by the producer) and reference data produced at the same time. The dose of CO_2 varied slightly from batch to batch but can be generalized as 0.15% by weight of cement. The five cases were:

[1] The concrete industry can be divided into three segments. An expected total 2016 US revenue of $44.5B can be divided according to $26.9B for ready mix (Ulama, 2016), $10.6B for precast (Masterson, 2016a) and $7.0B for concrete pipe and block (Masterson, 2016b).

1. A three-way comparison using mix 30RT - a 3000 psi (21 MPa) residential mix design with a ternary blend of 50% cement, 25% slag, 25% class F fly ash. Batches representing a control (reference), reduced binder, and reduced binder + CO_2 were compared both with and without air entrainment. The nominal binder adjustments were a reduction of 7% for the non-air entrained comparison, and 8% for the air entrained comparison.
2. Extended production using Mix 30RT wherein batches using CO_2 included a cement reduction of about 5.7% or 11 kg/m^3. The binder further had a 1.4%increase in class F fly ash and 7.2%reduction in slag for an overall binder reduction of 4.3%.
3. Mix 30CF – a 3000 psi (21 MPa) general commercial use non air-entrained fly ash mix, with a total binder loading of 320 kg/m^3 comprised of 74% cement and 26% class F fly ash. The modified batch used an average cement reduction of 4.5% or 14 kg/m^3. The fly ash loading was not changed. The reduction as a proportion of the total binder reduction was 3.5%.
4. Mix 50HE – a 5000 psi (35 MPa) non-air entrained high early strength mix design with a total binder loading of 419 kg/m^3. The entirety of the binder was Type III cement. The modified batch used an average cement reduction of 6.7% or 28 kg/m^3.
5. Mix 80T – an 8000 psi (55 MPa) structural mix design, with a total binder loading of 575 kg/m^3 comprised of 52% cement, 12% class F fly ash and 36% slag. The modified batch used an average cement reduction of 6.0% or 18 kg/m^3. The fly ash and slag loadings were not changed.

The binder reductions were accompanied by small adjustments of fine aggregate loadings to ensure that yield was maintained.

2. MATERIALS AND EXPERIMENTAL

3.1. THREE WAY COMPARISON - MIX 30RT

The binder adjustments for the batches produced in this study are detailed in Table 1. The modified mix design for the non-air entrained concrete reduced the overall binder by 7% via a 3% reduction in cement and a 19% reduction in slag. The modified mix design for the air entrained concrete used an overall binder reduction of 8% with the cement reduced 12%, slag reduced 21% and fly ash increased 18%.

An overview of the fresh properties for the loads produced during the three-way comparison is presented in Table 2. In general, the fresh properties were found to be comparable and within the range of normal batch-to-batch variation. No adjustments in mix water volume, admixture dose or batching process were made to accommodate the modified binder loadings, nor in response to the use of CO_2. Thus, in addition to a reduction in paste volume, the reduced binder mixes were observed to have slightly increased water to cementitious ratios and admix loadings per unit of binder. The former is expected to have a negative impact on strength development while the latter is expected to have a neutral impact.

The average compressive strength measured for each non-air entrained batch at three test ages is summarized in Fig. 2. The binder modification lead

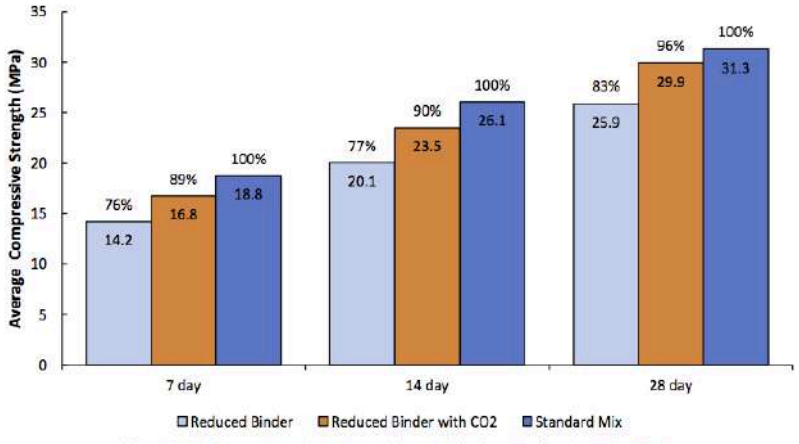

Fig. 2. Mix 30RT Three way comparison - Compressive strength development of non air entrained batches.

to a 17% drop in 28 day compressive strength. the strength of the reduced binder batch 18% at 1 day, 17% at 7 days and 16% at 28 days. Ultimately the strength of the batch with CO_2 and the 7% reduced binder content was within 4% of the reference at 28 days. The trial represented the first attempt at an optimized mix design and it was concluded that further tweaks to the binder loading and/or CO_2 dose should establish that the CO_2 addition can achieve at least equivalent performance at all ages.

The average compressive strength measured for each air entrained batch at three test ages is summarized in Fig. 3. The binder reduction in the air entrained batch resulted in an 11-13% drop in compressive strength. The addition of the carbon dioxide improved the strength of the reduced binder concrete by 15% at 1 day, 10% at 7 days and 13% at 28 days. The strength of the batch with 8% less binder and the CO_2 addition was equivalent to the reference at all three test ages.

A useful assessment of the mix design modifications can be developed using the concept of binder intensity and CO_2 intensity (Damineli et al., 2010). These metrics allow broad comparisons to be made between mix designs in terms of their functional and environmental performance. For the non air entrained batches the binder intensity relevant to compressive strength (bic_S) for the reference condition was 10.2 kg binder m^{-3} MPa^{-1}, 11.4 for the reduced cement batch and 9.9 for the batch produced with CO_2. The binder modification initially increased the bic_S by 11% but the addition of the carbon dioxide

However, the addition of carbon dioxide improved resulted in a net 9% decrease. With the air entrained batches the three calculated indices were 11.4, 11.9 and 10.4 kg binder m^{-3} MPa^{-1}. The binder modification increased the factor slightly (4%) whereas the addition of CO_2 decreased the factor by 9%.

An approximate CO_2 intensity calculation uses an emission factor of 915 kg CO_2/tonne of cement (as communicated by the cement supplier) and no emissions associated with the SCMs. For the non air entrained batches the carbon intensity (*ci*) is 4.5, 5.2 and 4.5 kg CO_2 m^3 MPa^{-1} for the reference, cement cut and cement cut with CO_2 batches respectively. The *ci* increased 16% due to the cement cut, but the carbon dioxide restored it to be equivalent to the baseline. For the air entrained batches the carbon intensities for the three conditions were 5.4, 5.4 and 4.8 kg CO_2 m^{-3} MPa^{-1}. The cement cut had no impact but the addition of CO_2 caused a 12% reduction.

The results of the three way comparison tests prompted subsequent mix design modifications to be made with only a two way comparison – reference control mix and modified mix design that included the CO_2 injection.

3.1.1. PRODUCTION CASE - MIX 30RT

A production run was conducted employing mix 30RT. Ten batches were produced during the run; eight batches were made using the CO_2 injection alongside two complementary control batches. The average slump was 145 mm for the reference data

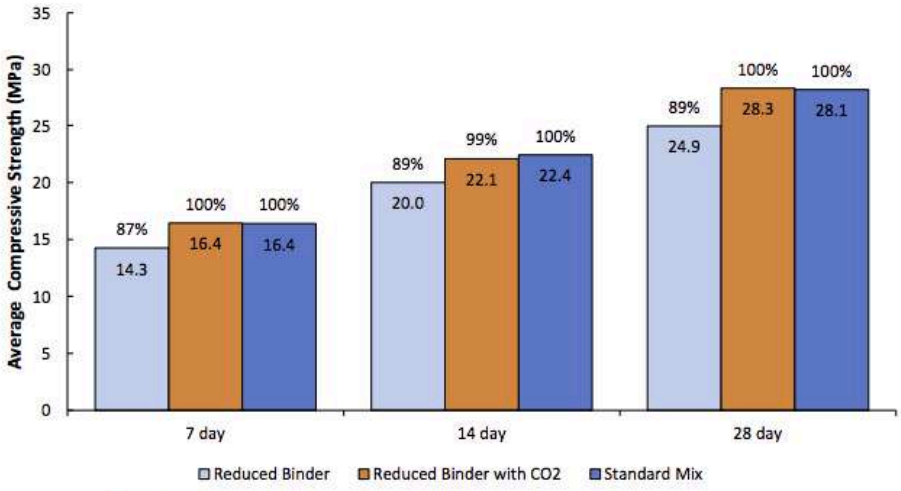

Fig. 3. Mix 30RT Three way comparison - Compressive strength development of air entrained batches.

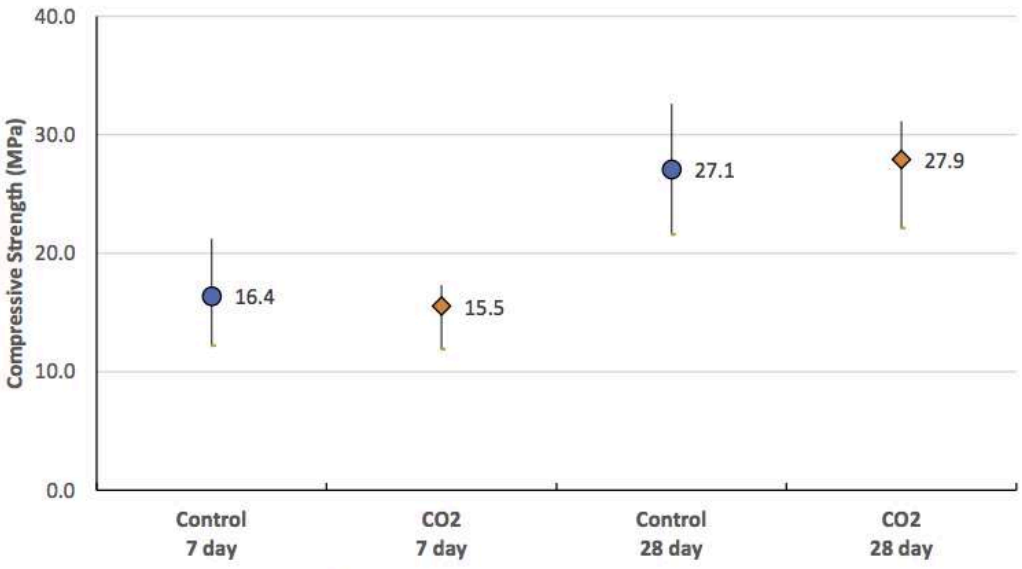

Fig. 4. Compressive strength development (7 and 28 days) of Mix 30RT produced with a CO_2 addition and an average cement reduction of 5.7%. Historical data (n = 9 including the co-produced control batches) and the CO_2 batch data (n = 8) are presented with the average strength as a point and error bars representing the range of the observed data.

(total 9 batches including two created within the same production, standard deviation 19 mm, coefficient of variation 13%) and 165 mm for the CO_2 batches. The compressive strength was tested at 7 and 28 days and compared against the reference data. A chart presents the average values for each condition at each age with error bars indicating the overall range of the collected data (Fig. 4). The control mix design averaged 16.4 MPa at 7 days (and ranged between a minimum of 12.2 MPa and a maximum 21.2 MPa, standard deviation 3.5 MPa, coefficient of variation 21%). The eight batches produced with the 5.7% reduced binder loading and a CO_2 addition averaged 15.5 MPa (ranging between a minimum of 11.9 MPa and maximum 17.3 MPa psi). At 28 days the historical performance was an average of 27.1 MPa, with a minimum of 21.6 MPa and maximum of 32.6 MPa (standard deviation 3.5 MPa, coefficient of variation 13%). The CO_2 production data was observed to average 27.9 MPa, and ranged between 22.1 and 31.1 MPa.

The average strength of the CO_2 treated batches with reduced binder was 95% of the typical historical strength at 7 days, and 103% of the typical historical strength at 28 days. The production variation was comparable to what was observed with the regular production data. The bics and *ci* were reduced by 7% (from 11.5 to 10.6 kg binder m^{-3} MPa^{-1}) and 9% (from 5.3 to 4.8 kg CO_2 m^{-3} MPa^{-1}) respectively.

3.1.2. PRODUCTION CASE - MIX 30CF

A production using Mix 30CF created four CO_2 treated batches with reduced binder. The 7 and 28 day compressive strength results are plotted in Fig. 5 with the control data comprising the performance of 31 historical reference batches (including the one batch created within the same production). The unaltered mix design typically averaged 19.7 MPa at 7 days (ranging between 15.0 MPa and 25.2 MPa, standard deviation 2.7 MPa and coefficient of variation 13%). The four batches produced with the reduced binder loading and a CO_2 addition averaged 19.1 MPa (minimum 16.7 MPa and maximum 23.5 MPa). At 28 days the historical performance was an average of 28.3 MPa, with tests as low as 23.7 MPa and as high as 34.6 MPa, standard deviation 3.0 MPa and coefficient of variation 11%. The CO_2 production data was observed to average 26.1 MPa, and range between 23.7 and 31.1 MPa. The binder and carbon intensity indices slightly increased. The bics increased 5% (11.3 to 11.9 kg binder m^{-3} MPa^{-1}) and the *ci* increased 3% (7.6 to 7.9 kg CO_2 m^{-3} MPa^{-1}).

The average strength of the reduced binder CO_2 batches was slightly lower than the historical averages (within 3% at 7 days and 8% at 28 days) but the overall variation was consistent with performance of the unmodified mix. The acceptable production of batches using the CO_2 and a reduced binder loading was assured.

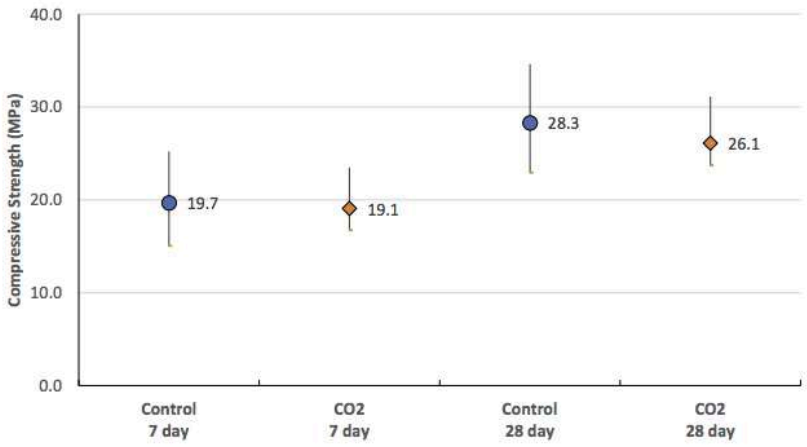

Fig. 5. Compressive strength development (7 and 28 days) of Mix 30CF produced with a CO_2 addition and an average cement reduction of 4.5%. Historical data (n = 31 including the co-produced control batches) and the CO_2 batch data (n = 4) are presented with the average strength as a point and error bars representing the range of the observed data.

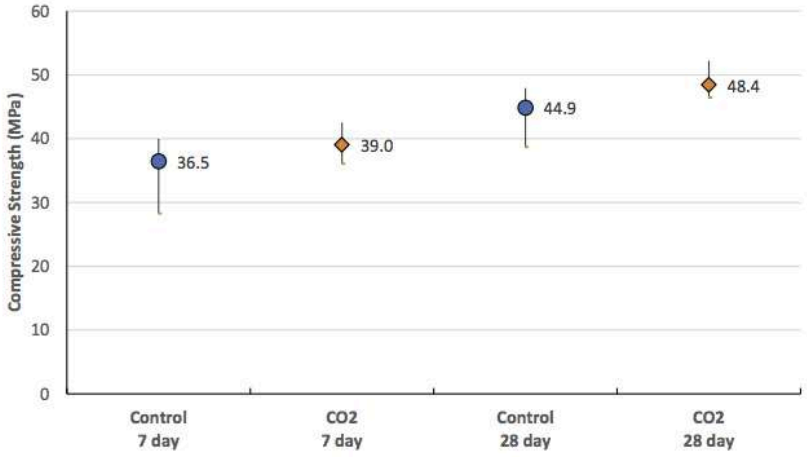

Fig. 6. Compressive strength development (7 and 28 days) of Mix 50HE produced with a CO_2 addition and an average cement reduction of 6.7%. Historical data (n = 30 batches) and the CO_2 batch data (n = 6) are presented with the average strength as a point and error bars representing the range of the observed data.

3.1.3. PRODUCTION CASE - MIX 50HE

The compressive strength results suggested compressive strengths that clearly exceeded the historical performance (**Fig. 6**). The historical data set comprised 30 batches. The baseline performance was an average strength of 36.5 MPa, standard deviation of 3.1 MPa, and coefficient of variation 8% at 7 days and an average strength average of 44.9 MPa, standard deviation of 2.1 MPa, and coefficient of variation 5% at 28 days. The strength of the CO_2 batches averaged 39.0 MPa at 7 days (overall 7% increase). At 28 days the batches produced using CO_2 were 8% stronger at 48.4 MPa. The increased strength accompanying a cement decrease of nearly 7% may indicate that the carbon dioxide has a particular synergy with the chemistry and/or high fineness of the Type III cement. Both the binder and carbon intensity indices decreased 22%. The bi_{CS} decreased from 9.9 to 7.8 kg binder m^{-3} MPa^{-1} while the *ci* decreased from 9.1 to 7.1 kg CO_2 m^{-3} MPa^{-1}.

3.1.4. PRODUCTION CASE - MIX 80T

The compressive strength of the batches using CO_2 compared favourably to the historical data (**Fig. 7**). The historical data set comprised 30 batches. The baseline performance was an average strength of 52.1 MPa, standard deviation of 6.0 MPa, and coefficient of variation 12% at 7 days and an average strength of 67.5 MPa, standard deviation of 6.5 MPa, and coefficient of variation 10% at 28 days. The strength of the CO_2 batches averaged 57.9 MPa at 7 days (overall 11% increase) and 73.9 MPa at 28 days (10% increase) albeit using 6% less cement.

The 80T mix had the lowest binder and carbon intensities at 8.5 kg binder m^{-3} MPa^{-1} and 4.0 kg CO_2 m^{-3} MPa^{-1} but the addition of the carbon dioxide allowed for a 12% reduction to the binder intensity (to 7.5) and 14% reduction to the carbon intensity (to 3.5).

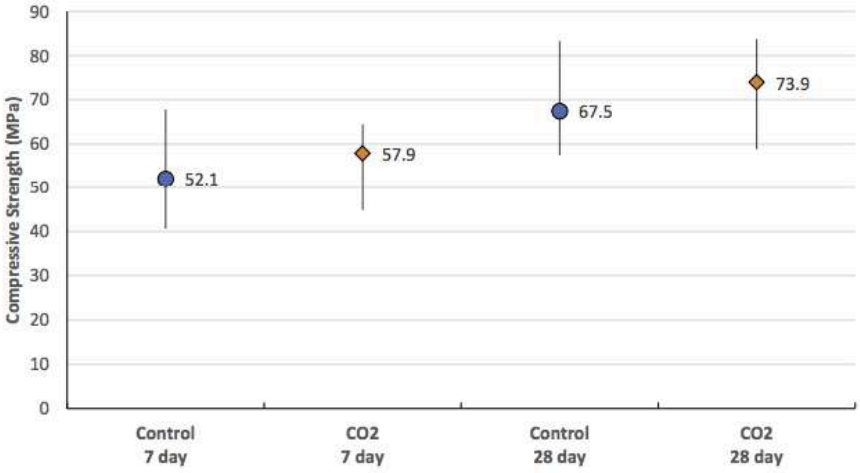

Fig. 7. Compressive strength development (7 and 28 days) of Mix 80T produced with a CO_2 addition and an average cement reduction of 6.0%. Historical data (n = 30) and the CO_2 batch data (n = 3) are presented with the average strength as a point and error bars representing the range of the observed data.

4. DISCUSSION

4.1. PROCESS BENEFITS

The compressive strength benefit results confirmed two major outcomes.

1. A reduction in the binder loading contributed to a reduction in the compressive strength
2. The strength reduction could be offset through the introduction of an optimized dose of CO_2 into the concrete while it is batched and mixed

The conclusions were confirmed in three-way comparison testing and supported through extended production.

The carbon dioxide utilization can be a platform for further producer actions according to their specific motivation whether it be to improve the economic, performance, or environmental characteristics of the concrete so produced. A producer that is economically motivated may seek to reduce the overall amount of binder to save money. The reduction of the most expensive components can be prioritized. If performance benefits are the most important consideration, then an improvement in early strength development can allow for increased proportioning of slower-hydrating slag and/or fly ash and thereby target the durability benefits that may arise. If the motivation is environmental, then a strength boost that allows for a reduction in the cement usage will consequently lead to avoiding the associated CO_2 emissions and thereby result in a reduction in the carbon footprint of the mix.

4.2. MODEL ENVIRONMENTAL IMPACT

The Sustainable Concrete Plant Guidelines (RMC Research and Education Foundation, 2011), published in 2011 in conjunction with the National Ready Mixed Concrete Association, outlined industry targets for improving the sustainability of ready mixed concrete. The stated goal to improve the carbon footprint of concrete, relative to 2007, was a 20% reduction by 2020, and a 30% reduction by 2030. In this context, the carbon footprint of concrete is the total amount of CO_2 emitted due to concrete production and encompasses raw material extraction, production, delivery to job sites, and eventual disposal or reuse. A 2016 industry survey concluded that the NRMCA benchmark carbon footprint for a generic 4000 psi (27.6 MPa) concrete was 393 kg CO_2e/m^3 (Athena Sustainable Materials Institute, 2016). On average, the cement used in a concrete mix represents over 85% of the embodied energy and up to 96% of greenhouse gas (GHG) emissions per unit volume of concrete produced (Marceau et al., 2007). Thus, the most important lever to reducing the carbon footprint of concrete will be to reduce the carbon contribution of the cement. The impact of the described approach to improve the sustainability characteristics of concrete can be assessed through an environmental analysis.

The calculations are considered in terms of one m^3 of concrete. The baseline process considers the raw materials required to make the concrete, the operational inputs to produce concrete, and greenhouse gas outputs associated with transporting materials, using electricity, and burning fuels. A generic model concrete mix can be based upon benchmark data compiled by the National Ready Mixed Concrete with a target compressive strength

of 4000 psi (27.6 MPa) a baseline cement loading of 570 lb/yd^3 (338 kg/m^3). Additional process elements are included when the concrete is produced with the addition of carbon dioxide: the capture and liquefaction of the carbon dioxide, the carbon dioxide transport, and the production and operation of the carbon dioxide injection hardware. Additionally, a model 5% cement reduction is achieved (a reduction of 17 kg to 321 kg/m^3). The environmental footprint of the process considers:

1. The baseline CO_2 emissions related to conventional concrete production
2. The net impact of mix design changes on CO_2 emissions
3. CO_2 emitted during the capture and compression of the CO_2
4. CO_2 emitted during the transportation of the CO_2
5. CO_2 emitted during the production of the gas injection equipment
6. CO_2 emitted during the transportation of the gas equipment
7. CO_2 absorbed through the utilization step
8. CO_2 emissions avoided due to the reduction in the cement content

The calculations are reported in terms of creating one cubic meter of concrete. The CO_2 dosage used in the model is 0.15% by weight of cement or 482 g CO_2 per cubic meter of generic concrete.

4.2.1. GAS PRODUCTION AND GAS TRANSPORT IMPACTS

The industrial gas processing to create liquid CO_2 from an emissions stream requires on the order of 200 kWh/tonne CO_2 (Haring, 2008) with emissions that are dependent upon the electrical grid emissions rate at the location where the work is performed. The 2014 average CO_2 emission rate for electrical power produced in the United States was 1130.2 lb CO_2e/MWh (512.6 g CO_2e/kWh) (US Environmental Protection Agency, 2017). Thus, the industrial processing to produce a tonne of liquid CO_2 would involve the emissions of 102.5 kg of carbon dioxide. Given a carbon dioxide dose of 482 g/m3 concrete, the CO_2 emissions associated with gas processing are estimated to be 49.4 g/m^3 concrete. This compares favourably to the GHG emissions impact of producing a typical plasticizing concrete admixture; 1.88 kg CO_2e per kg of admixture produced (European Federation of Concrete Admixtures Associations Ltd. (EFCA), 2015) or 160 g CO_2e/m^3 concrete according to the generic loading of 3 oz/m^3 concrete reported in the NRMCA benchmark data.

The carbon dioxide would be transported from the industrial source to the concrete producer. Transport emissions can be modeled using an emissions rate of 1.430 kg CO_2/vehicle·mile of freight using medium to heavy duty trucks (EPA Center for CEMBUREAU, 2016) and a single bulk load mass of 25 tons (22.7 tonnes). The emissions are then 0.063 kg CO_2/tonne·mile. If a roundtrip transport distance of 200 miles (322 km) is used then the gas transport emissions are calculated to be 6.1 g CO_2/m^3 concrete produced.

4.2.2. EQUIPMENT PRODUCTION, TRANSPORT AND OPERATION IMPACTS

The gas injection equipment is comprised of steel, brass and plastic. Considering the amounts used and CO_2 emissions factors associated with the production of these materials (calculated as generic examples of OHF steel, generic brass, and polypropylene plastic) results in an estimated CO_2 emission of 80.7 kg (**Table 3**). The transportation of the equipment is estimated as the truck freight transport of 61.2 kg (equipment totaling 43.1 kg and contained within a crate of 18.1 kg) over a generic single trip distance of 1250 miles. The transport emissions would be a partial load shipment with an emissions rate of 146 g CO_2/ton·mile (EPA Center for CEMBUREAU, 2016). The transport emissions associated with the delivery of one gas injection system total 12.3 kg CO_2.

Table 3
Process emissions – equipment.

Component	Amount (kg)	Emissions Factor (kg CO_2/kg)	Emissions (kg CO_2)
Steel	31.8	1.72 (IPCC, 2016)	54.6
Brass	2.3	4.66 (Muthu, 2014)	10.6
Plastic	9.1	1.71 (EPA, 2015)	15.5
Total	43.1	–	80.7

If the total equipment production and transport emissions (93.0 kg CO_2) are amortized over a 20-year operational life and an annual production of 50,000 m^3 concrete, then the associated emissions are 0.09 g of CO_2 per m^3 concrete (comprising 0.08 g from the production and 0.01 from the transport). The power demand of the hardware has been estimated to be 0.037 kWh/kg CO_2 injected. For the carbon dioxide dosed into a cubic meter of concrete the corresponding power consumption is 0.018 kWh. According to the generic carbon intensity for power generation there is an anticipated 9.2 g CO_2 emitted. The overall emission for the production, transport and operation of the equipment is 9.3 g CO_2/m^3 concrete.

4.2.3. DIRECT CO_2 ABSORPTION

Direct quantification of the absorbed carbon dioxide is difficult (the dose of 482 g is applied to concrete with a nominal density of 2300 kg/m3 which is equivalent to an abundance on the order of about 200 ppm). The carbon dioxide applied to the concrete is about 50% solid and 50% gas. If the solid fraction, directly observed to adhere to the wet concrete, is incorporated into the concrete with a high efficiency (say 90%) while the gas, which is heavier than air but otherwise above the mixing concrete, is incorporated at a low efficiency (say 30%) then the combined overall absorption efficiency can be estimated at 60%. The 482 g total dosage/m^3 concrete absorbed at a rate of 60% would result in about 289 g of CO_2 being fixed. This would mean an estimated 2.3 kg of CO_2 are absorbed in an 8 m^3 truck load of concrete, and 14.4 tonnes over an annual production of 50,000 m^3 concrete.

4.2.4. CHANGES TO MATERIAL FLOWS

The addition of the carbon dioxide allows for a reduction in the cement loading in the concrete. The cement in turn has a carbon impact that is directly avoided both through the material reduction and the associated transportation that is not required. Additionally, the fine aggregate (sand) loading in the mix design may be increased to compensate for the volume of the removed cement. If the specific gravities of cement and sand are taken to be 3.15 and 2.61 respectively, then for a given unit mass of cement removed then the equivalent volume would be filled by 0.85 units of sand.

The 5% cement reduction means that 16.9 kg of cement are removed per m^3 of concrete. Conversely, the sand would be increased by 14.0 kg. This would be a relative sand increase of 1.8% in the model mix design.

The transportation distances of the raw materials can be used to model a total GHG impact for materials transport. The NRCMA reports average values for distances between the suppliers of each of the mix components and the concrete producer (Athena Sustainable Materials Institute, 2016). Applying the previously identified emissions rate for bulk freight transport can determine the transport GHG impact for the components of the baseline (**Table 4**) and modified (**Table 5**) mix designs. It was calculated that the modified mix design would result in a net reduction in transport emissions of 124 g CO_2e/ m^3 concrete, or a 1.6% reduction. The plant operations are not anticipated to change in response to the mix design modification. The inputs of fuel and electricity, and the output of concrete wash water are unchanged.

Table 4
Transport Emissions – Materials per m^3 concrete, Baseline mix.

Component	Distance (km)	Freight (kg)	Emissions (g CO_2)
Cement	117.6	338	3117
Fly Ash	107.0	65	547
Slag	52.5	15	61
Coarse Aggregate	31.6	930	2305
Fine Aggregate	31.1	778	1899
Total			7932

Table 5
Transport Emissions – Materials per m^3 concrete, Modified mix.

Component	Distance (km)	Freight (kg)	Emissions (g CO_2)
Cement	117.6	321	2961
Fly Ash	107.0	65	547
Slag	52.5	15	61
Coarse Aggregate	31.6	930	2305
Fine Aggregate	31.1	792	1934
Total			7808

4.2.5. OVERALL PROCESS FLOW

A process flow diagram (**Fig. 8**) outlines the overall inputs and outputs of concrete production using the carbon dioxide injection approach. Compared to the baseline approach there is the addition of the CO_2 capture and utilization portion, a reduction in the cement usage (17 kg), an increase in the sand usage (14 kg) and a reduction in the overall material transport emissions (124 g CO_2).

4.2.6. TOTAL NET PROCESS IMPACTS

The environmental impacts are summarized in **Table 6**. The total process emissions (CO_2 processing, CO_2 transport, equipment production, equipment transport and equipment operation) are estimated to be 64.7 g CO_2/m^3 concrete. This equates to 22% of the modeled absorbed CO_2. By this metric an estimated 78% of the modeled absorbed CO_2 would represent a net storage of CO_2.

Industrially-sourced CO_2 is typically the byproduct of an industrial process. Consequently, CO_2 captured from such a source would have been atmospheric carbon emissions if not for having been captured and transported to address a market demand in an economically viable fashion. The environmental analysis considers that any CO_2 leakage at the injection site does not represent a net increase of CO_2

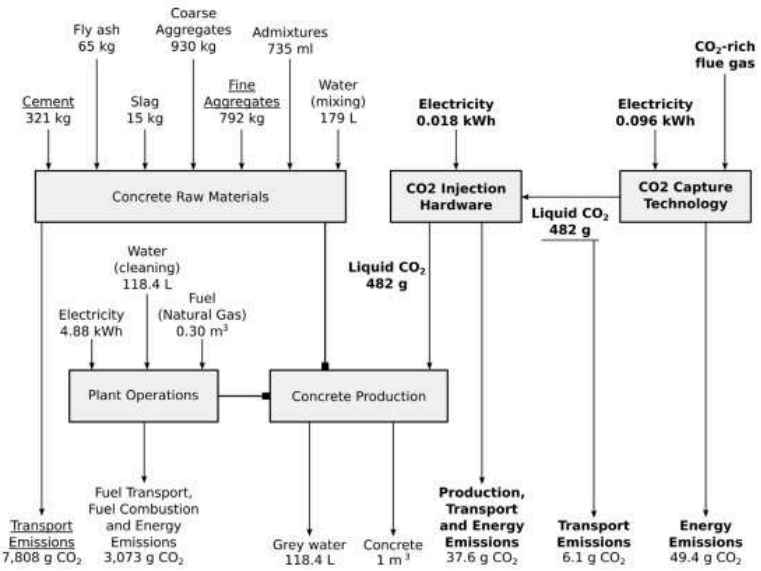

Fig. 8. Process Flow Diagram for CO_2 utilization in ready mixed concrete production. Items specific to the CO_2 utilization step are in bold. Underlined items are present in the default case but changed when the CO_2 utilization is implemented.

in the atmosphere since the injected carbon dioxide is comprised of industrial process emissions that were displaced prior to being utilized/absorbed/lost.

Table 6
Summary of the Environmental Impact on 1 cubic meter of concrete.

Factor	g CO_2/m^3 concrete
Emissions – CO_2 from gas processing	49.4
Emissions – CO_2 from gas transport	6.1
Emissions – CO_2 from equipment production	0.1
Emissions – CO_2 from equipment transport	0.0
Emissions – CO_2 from equipment operation	9.2
Emissions – Avoided CO_2 from materials transport	−123.6
CO2AB: CO_2 absorbed	−289.1
CO2AV: Avoided CO_2 emissions from cement	−17584.8
Total CO_2 avoided and absorbed	−17997.4
CO2EM: Total CO2 produced	64.7
Net CO_2 reduction	−17932.7

4.2.7. IMPACT MODEL - SENSITIVITY ANALYSIS

A sensitivity analysis is presented in Fig. 9 to consider the impact of changes to different inputs. The analysis considers factors that may vary with location and factors associated with technologies employed: electrical grid carbon intensity, the energy to capture CO2, the transport distance of the CO2, and the energy to operate the gas injection hardware. The analysis considers alternative cases for the energy use from electric grids (US National average of 513 kg CO2e/kWh), industrial gas energy requirements (200 kWh/ tonne CO2), CO2, gas transport distances (100 miles one way), and injection hardware energy requirement (0.037 kWh/kg CO2). The plot shows reasonable variation ranges for the various factors. The grid emissions are considered between two United States examples – the second highest (Wyoming) and second lowest (Idaho) carbon intensity power grids in the US (US Environmental Protection Agency, 2017). The gas processing energy requirement was changed ±25%, the gas transport distance was considered from 50% to þ100%, while the hardware energy requirement was changed ±50%.

It is shown that the overall process emissions are most sensitive to the electrical grid CO2 emissions associated with the CO2 capture and processing. A 25% change in the electrical grid emissions results in a 23% change in the overall emissions. This factor can vary widely according to location. If the capture took place in the second highest carbon intensity US electrical grid then the overall emissions would increase 69% to 109.7 g CO_2/m^3 concrete. Conversely, if in a location with the second lowest carbon intensity power grid, then the emissions would be 79% lower at 13.8 g CO_2/m^3 concrete.

The process emissions were next most sensitive to the CO2 capture energy; a 25% change in the gas capture energy resulted in a 19% change in the overall emissions. While considering an alternate electrical grid intensity is simple considering the breadth of grid emissions rates, proposing alternate gas capture strategies is less clear. The analysis is open to the possibility that a newer technique (e.g. membrane technology (Giordano et al., 2016) or cryogenic carbon capture (Jensen et al., 2015)) may achieve a sizably lower specific energy than the incumbent industrial gas processing approach.

Changing the CO2 transport distance and injection hardware energy had the least effect with a 25% variation to each factor resulting in an impact to the

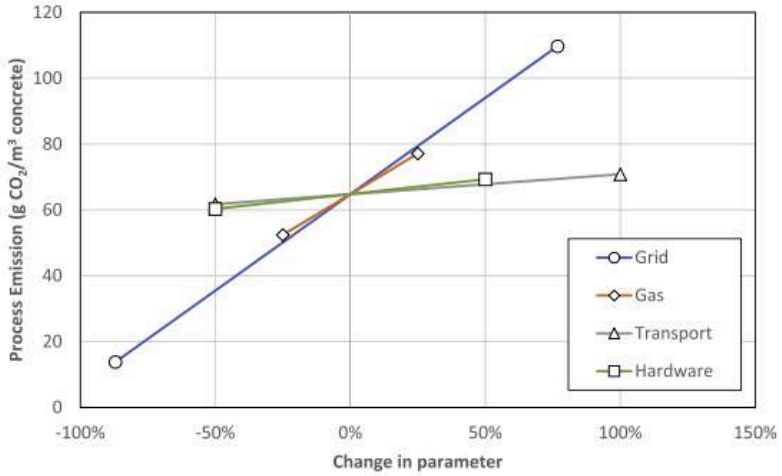

Fig. 9. Process emissions sensitivity modelling considering changes to electrical grid CO_2 emissions rate (Grid), energy requirement for industrial gas processing (Gas), CO_2 transport distance (Transport) and injection hardware energy demand (Hardware).

overall process emissions of ±3.4% and ±2.4% respectively.

4.2.8. OVERALL IMPACT ON CARBON FOOTPRINT

The strength increase produced by the small amount of CO_2 utilized can be leveraged into reductions in cement loading. The environmental benefit associated with using less cement is an order of magnitude greater than the calculated direct CO_2 absorption. A generic cement in the United States has an emissions intensity of 1040 kg CO_2/tonne of finished cement (Portland Cement Association, 2016). The cement reduction has a net environmental impact on the process given the avoided carbon dioxide emissions associated with cement production. There are 17.6 kg of CO_2 associated with the 16.9 kg of cement removed from each cubic meter of concrete. The overall net environmental impact would also include 289.1 g of CO_2 absorbed, 123.6 g of CO_2 avoided (materials transport) and 64.7 g of CO_2 emitted to result in a net CO_2 footprint reduction of 17.933 kg CO_2/m^3 concrete. The avoided cement emissions would be responsible for 97.7% of the net environmental impact. The environmental impact of the cement removal is over 60 times the net direct CO_2 absorption. In comparison to the baseline carbon footprint of 393 kg CO_2e/m^3 concrete the overall impact would be a 4.6% reduction. A facility with an annual production of 50,000 m^3 of concrete could see an annual direct CO_2 utilization of about 24 tonnes, of which about 14 tonnes would be absorbed and leveraged to achieve a total net absorbed and avoided CO_2 of 897 tonnes.

The small scale of the process emissions (64.7 g CO_2/m^3 concrete) can be placed into context by comparing them to the environmental impact of a cement reduction. The process emissions would be offset by the avoided emissions for a cement reduction of 0.062 kg cement/m^3 concrete or 0.02% of the baseline loading of 338 kg/m^3.

If carbon accounting would conclude that the CO_2 that is dosed but unreacted represents emissions associated with the concrete plant rather than the original industrial emitter then the process emissions are increased by 193 g to 258 g CO_2/m^3 concrete. (While the small amount of carbon dioxide absorbed suggests this the concept is not accurately positioned as a sequestration technology it is likely that the emissions would be counted this way if adhering to carbon accounting guidelines for geological storage approaches (IPCC, 2006)). The process becomes environmentally neutral if the cement reduction exceeds 0.248 kg/m^3 concrete, or 0.07 of the baseline cement loading.

The upper bound of the process emissions would occur in a case where both the absorption of CO_2 is minimal (i.e. assumed in calculation as 0% of the dose) and the carbon accounting classed the unabsorbed CO_2 as concrete plant emissions. The process emissions would increase to 547 g CO_2/m^3 concrete. This is equivalent to the emissions from 526 g of cement and thus the process is carbon neutral once the cement reduction reaches 0.16% of the baseline loading. The relative scale of the process emissions to the impact of the cement loading means that only miniscule cement reductions are required to produce a net carbon benefit.

The equipment emissions of 93 kg CO_2 have been amortized over 20 years of production, but alternately can be considered as a one-time implementation penalty. The equipment emissions are equivalent to the CO_2 avoided through a cumulative cement reduction of 89 kg. This amount is less than the cumulative cement reduction observed after producing one truckload of concrete (8 m^3 load with a 17 kg/m^3 cement reduction). The implementation emissions are rapidly surpassed by the accumulating environmental benefit.

The required dosage of carbon dioxide is small and, thusly, so is the direct CO_2 absorption. However, the utilization approach can be leveraged to achieve the cement reduction. In a comparative sense, the dosage is about 3% of the net carbon impact. Alternatively, the utilization of one unit of CO_2 can unlock a carbon benefit 36 times greater.

4. CONCLUSIONS

Industrial scale integration of a carbon dioxide injection into ready mixed concrete has demonstrated a means to beneficially use carbon dioxide to improve concrete performance and create more sustainable concrete. The performance improvement can be the basis to reduce binder loadings without compromising on compressive strength. Three way comparisons confirmed that removing 7-8% of binder from a concrete mix would lead to a reduction in strength, but the addition of CO_2 had the potential to restore the compressive strength performance.

The modified binder loadings result in a concrete with a reduced carbon footprint. A small amount of carbon dioxide is absorbed directly but a larger amount of CO_2 emissions would be avoided by reducing the cement loading. A generic case suggests that a 4.6% reduction in the carbon footprint is feasible. The energy and materials required to implement the approach (building the equipment, capturing the carbon dioxide, transporting the equipment and the carbon dioxide) result in a small emission of CO_2 that is less than the amount of absorbed CO_2 or otherwise quickly outstripped by the environmental impact associated with the mix optimization.

Cement producers would then be able to put their waste CO_2 to beneficial use in concrete production thereby upcycling a portion of their primary waste product and using resources in a manner consistent with circular economy principles.

FUNDING

Compliance with ethical standards.

CONFLICT OF INTEREST

The author acknowledges that the research was conducted in the course of commercial technology development.

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Ready Mix Technology Case Studies

CarbonCure Ready Mix Technology Case Studies

DECEMBER 2016

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SVP Technology Development
CarbonCure Technologies

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_2 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_2 emissions that exceed 63,000 tons as of January 2020.

EXECUTIVE SUMMARY

The CarbonCure Ready Mix Concrete Technology is being implemented by concrete producers across the United States and Canada to improve the compressive strength and environmental footprint of their concrete products. This case study examines data provided by a CarbonCure producer partner who installed the CarbonCure technology and used the system to produce concrete with an optimized dosage of CO_2.

Concrete prepared using the CO_2 injection system was shown to deliver comparable compressive strength performance with a 5-8% reduction in binder loading while having a neutral impact on fresh properties, including air, slump, and temperature. Roughly 45 000 yd^3 of concrete were produced over an 10 month period using a 5% binder reduction in conjunction with an optimized dose of CO_2. The estimated cement savings exceeded 600 tons and more than 550 tons of CO_2 emissions were avoided. The use of the technology did not impact the producer's cycle time; all operations continued as normal throughout this assessment.

The action of the CO_2 is discussed in terms of nanomaterial impacts. The injection of carbon dioxide into the concrete mix forms well dispersed calcium carbonate nanoparticles, which allows concrete producers to realize the understood benefits of nanoparticle additions while avoiding common technical or economic barriers. The technology delivers value to the concrete producer while reducing the concrete's environmental impact.

Introduction

This case study analyzes data collected by a CarbonCure producer utilizing the CarbonCure Ready Mix Technology to inject CO_2 during normal concrete operations. The CarbonCure technology controlled the carbon dioxide delivery into the ready mix concrete truck during the initial batching and mixing. The carbon dioxide was bound as solid and stable carbonate reaction products in the cement matrix and provided a positive impact on the concrete properties.

Methods

The fresh concrete was assessed via on-site measurement of slump, temperature, air content and unit weight. The concrete was then cast into 4" x 8" cylinders for compressive strength testing at 7, 14 and 28 days after batching. All concrete specimens were prepared and tested in accordance with the relevant ASTM and ACI standards.

The CarbonCure Ready Mix Technology controlled the delivery of CO_2 into the concrete. In a process that resembles the introduction of a chemical admixture, a tank of liquid CO_2 was connected to the CarbonCure injection system. The liquid was metered to deliver an optimum dose of CO_2 into the drum of the ready mix truck at the same time as the concrete was loaded. Upon entering the mixing drum, the liquid carbon dioxide converted into a mixture of CO_2 gas and solid carbon dioxide snow whereupon it reacted with the hydrating cement to form solid calcium carbonate particles. The concrete was then subjected to assessment and testing.

All samples were collected from trucks carrying 9 yd^3 of a residential mix with design strength of 3000 psi. The concrete mix design used a ternary binder system of Portland cement, class F fly ash and slag.

To illustrate the potential of CO_2 in mix design optimization, a three-way comparison was conducted between a standard mix, a mix with reduced binder content, and a reduced binder mix that used an optimized dose of CO_2. Two mix designs, including/excluding air entrainment admixtures, were examined. The relevant binder loadings for the mix designs are summarised in Table 1. Small adjustments of fine aggregate loadings were also included to ensure that yield was maintained following a reduction in binder loading.

The binder reduction leads to a decrease in paste volume, but can also serve to slightly increase the water to cementitious ratio and admix loading per unit of binder. The former is expected to have a negative impact on strength development while the latter is expected to have a neutral impact.

Strength Enhancement Results

An overview of the fresh properties for the loads produced during the production run is presented in Table 2.

Table 1: Binder loadings for four mix design variations.

Mix Type	Type	Cement (lbs/yd³)	Class F Fly Ash (lbs/yd³)	Slag (lbs/yd³)	Total Binder (lbs/yd³)
Non Air Entrained	Standard Mix				
	Reduced Binder	258	132	149	539
	Mix Relative	249	132	119	500
	Change	-4%	n/a	-20%	-7%
Air Entrained	Reduced Binder	281	109	151	540
	Mix Relative	248	129	119	496
	Change	-12%	+18%	-21%	-8%

Table 2: Production variables, CO_2 settings and fresh results.

Mix	Type	Slump (in)	Air (%)	Unit Wt (lbs/ft³)	Temp (°F)
Non Air Entrained	Reduced Binder	5	2.5	146.6	84
	Reduced Binder with CO_2	4	2.5	147.2	84
	CO_2 Standard Mix	4	2.5	147.2	84
Air Entrained	Reduced Binder	6	4.2	144.4	84
	Reduced Binder with CO_2	5	3.4	147.2	81
	CO_2 Standard Mix	6	3.5	146.0	84

The average compressive strength measured for each batch at three test ages is summarized in Figure 1.

The binder modification in the non-air entrained batch lead a strength reduction at all ages including a 17% drop in 28 day compressive strength. However, when the carbon dioxide was added the strength of the reduced binder batch improved to be within 4% of the reference at 28 days. The trial represented the first attempt at an optimized mix design and it was observed that further tweaks of the modified mix design and/or CO_2 dose should establish that the CO_2 addition can result in at least equivalent performance at all ages. The 28 day data suggested that a CO_2 injection in conjunction with a binder reduction on the order of 7% can create concrete without compromising performance.

The binder reduction in the air entrained batch lead to an 11-13% drop in compressive strength across the three test ages.

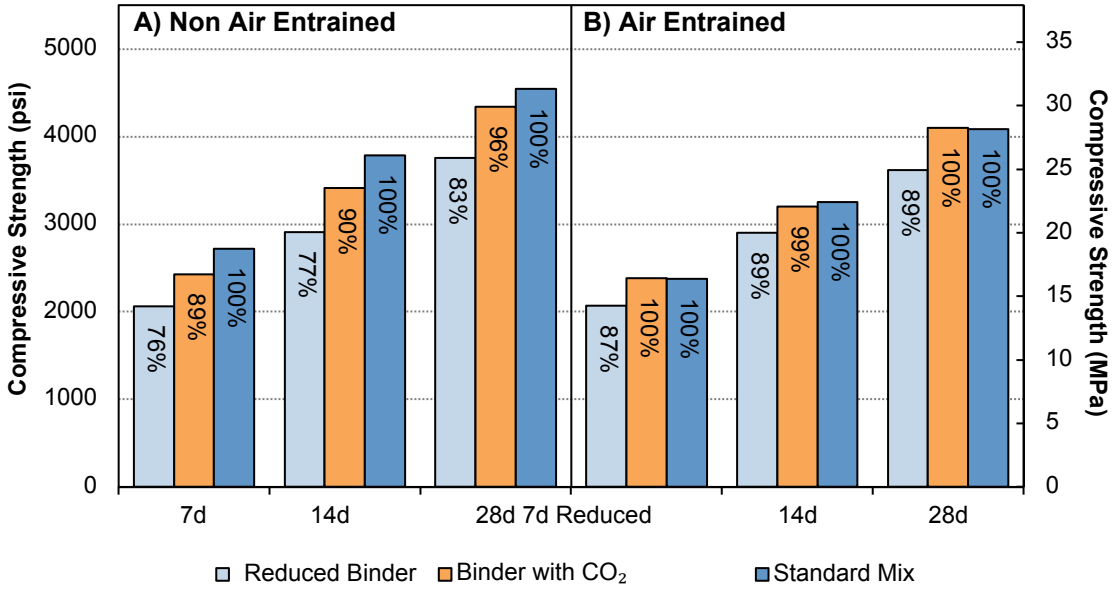

Figure 1: Compressive strength development of non air entrained (A) and air entrained (B) concrete test loads. For each mix the customer compared 3 cases: A standard mix (dark blue), the standard mix with a reduction in binder loading (light blue), and the standard mix with a reduction in binder loading that further incorporated the addition of an optimized dose of CO_2 (orange). The binder reductions were 8% and 7% for the non air entrained and air entrained variations respectively.

However, when the carbon dioxide was added the strength of the reduced binder batch improved to be equivalent to the standard mix.

The strength benefit results confirmed two major outcomes:

1) A reduction in the binder loading leads to a reduction in the compressive strength
2) The strength reduction could be offset through the introduction of CO_2 into the concrete mix during batching

The conclusion was examined in extended production.

Extended Production Results

Three mix designs were selected for expanded testing to assess the performance enhancement of CO_2 across a range of concrete strength classes. . The compressive strength development of mixes with 28 day design strengths of 3000, 5500 and 8000 psi were assessed when using CO_2 alongside reductions in binder loading of 4.5%, 4.4% and 3.1% respectively. The 7 and 28 day compressive strength results for each mix design are plotted in Figures 2-4 against graphical ranges of historical data representing the average, 10th percentile and 90th percentile results for the unmodified mix.

In each case the addition of an optimized dosage of CO_2 was shown to bring the performance of the concrete mix deign with a reduced binder loading within the expected performance range based on historical data. The average and the variation of the reduced binder CO_2 batches were consistent with the historical data of the unmodified mix. The acceptable production of batches using the CO_2 and a reduced binder loading across a range of strength classes was assured.

The success of these two assessments encouraged the ready mix concrete producer to apply the CarbonCure Ready Mix Concrete Technology across their concrete production. Over a 10-month period, spanning March to Decemnber, CO_2 was injected into roughly 56,000 yd^3 of concrete with an average cement reduction of 5%. The extended implementation of the technology resulted in 600 tons of cement savings and, according to emissions information specific to the cement, 530 tons of avoided CO_2 emissions (Figure 5).

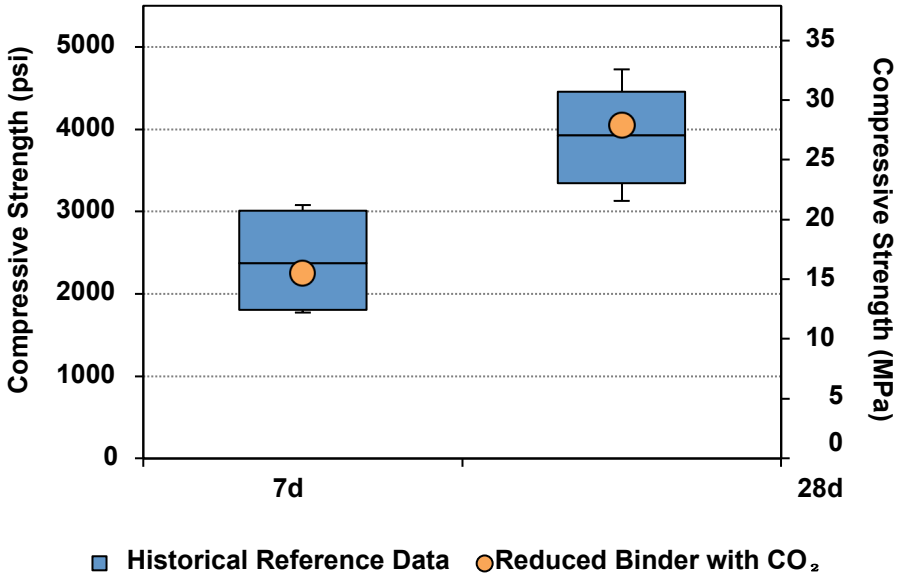

Figure 2: Compressive strength development of a 3000 psi air entrained mix. The blue boxes represent the historical compressive strength performance range (10th to 90th percentile) while the orange circles represent the compressive strengths of loads of the mix prepared with a 4.3% reduction in binder content (5.7% reduction in cement content) and an optimized dose of CO_2. Whiskers indicate the historical data maximum and minimums.

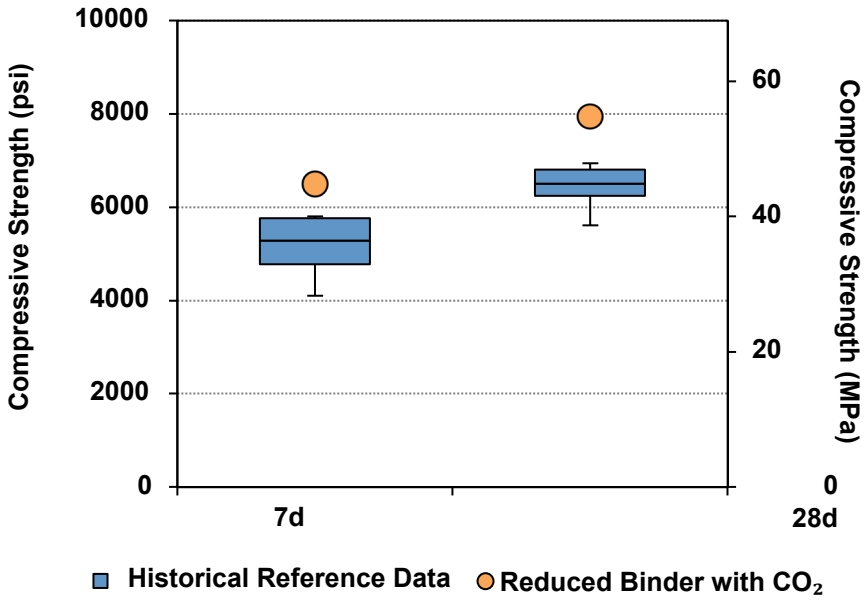

Figure 3: Compressive strength development of a 5500 psi mix designed for high early strength applications. The blue boxes represent the historical compressive strength performance range (10th to 90th percentile) while the orange circles represent the compressive strengths of loads of the mix prepared with a 4.4% reduction in binder content (4.4% reduction in cement content) and an optimized dose of CO_2. Whiskers indicate the historical data maximum and minimums.

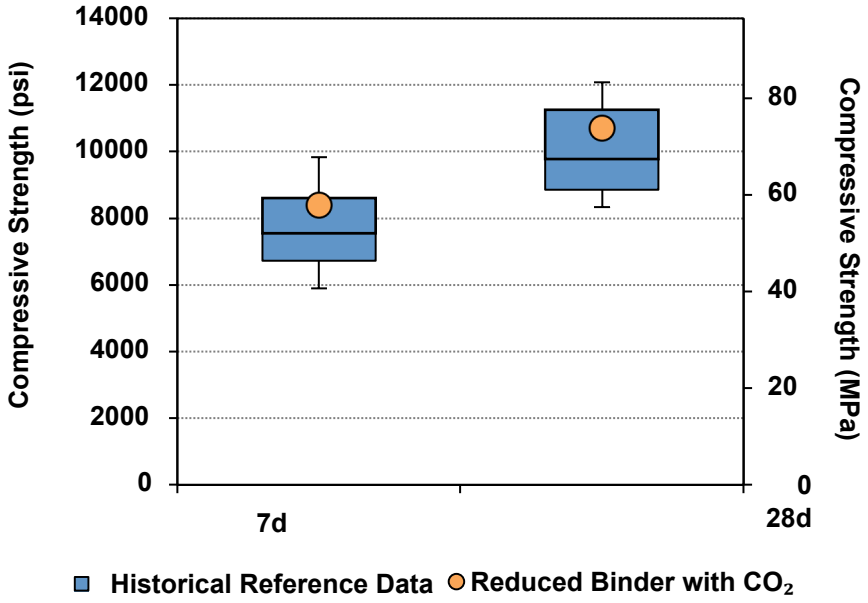

Figure 4: Compressive strength development of a 8000 psi mix. The blue boxes represent the historical compressive strength performance range (10th to 90th percentile) while the orange circles represent the compressive strengths of loads of the mix prepared with a 3.1% reduction in binder content (6.0% reduction in cement content) and an optimized dose of CO_2. Whiskers indicate the historical data maximum and minimums.

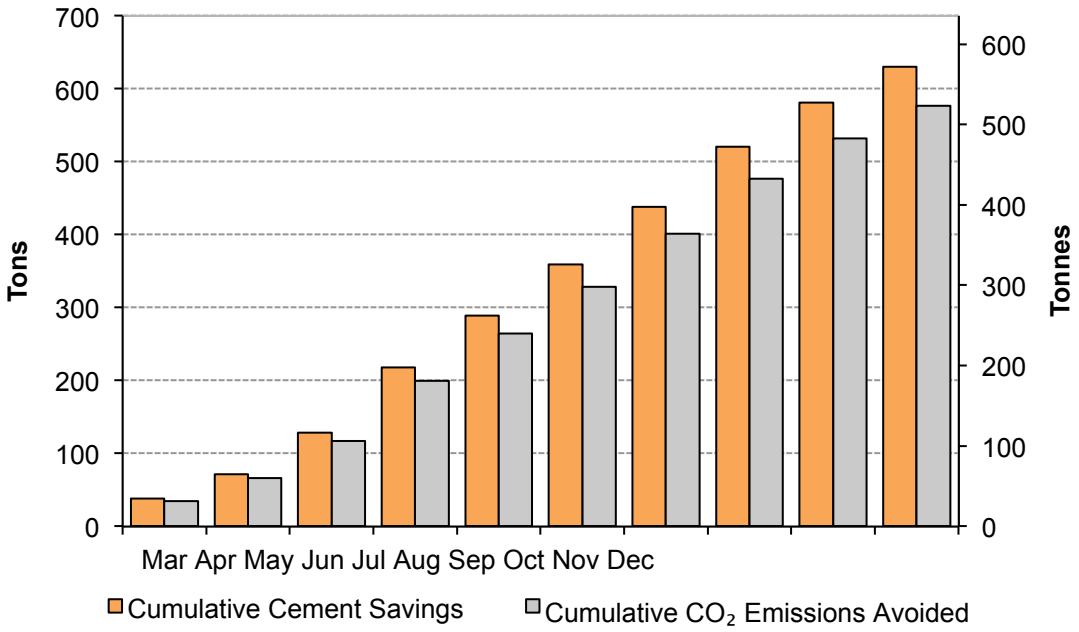

Figure 5: Cumulative cement savings (orange) and avoided CO_2 emissions (gray) for a producer using the CarbonCure Ready Mix Technology in conjunction with a 5% cement reduction over an 10 month period. These reductions were totalled through the production of approximately 56 000 yd^3 of concrete.

This customer data provides verification that producers can leverage the strength enhancing effect of the CO_2 to achieve binder adjustments with diverse motivations:

- Economic – reducing the overall amount of binder can save money. The reduction of the most expensive components can be prioritized.
- Performance – durability benefits related to increased binder proportioning of slag and/or fly ash can be targeted while not compromising on the early strength development.
- Environmental – reducing cement usage directly leads to avoiding CO_2 emissions thereby allowing for a reduction in the carbon footprint of the mix.

Mechanism

When liquefied CO_2 is injected into wet concrete the CO_2 chemically reacts with calcium ions released from cement to form solid, nano-sized calcium carbonate particles that become permanently bound within the concrete.

The main cement phases, tricalcium silicate and dicalcium silicate, are known to react with carbon dioxide in the presence of water to form calcium carbonate[1]. The reaction proceeds in the aqueous state when calcium ions from the cementitious phases meet carbonate ions from the applied CO_2.

The reaction of carbon dioxide with hardened concrete 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, carbon dioxide utilization in concrete production reacts CO_2 with freshly hydrating cement, rather than the hydration phases present in mature concrete, and does not have the same effects. Consequently durability is not affected[2]. By virtue of adding CO_2 to freshly mixing concrete the carbonate reaction products are formed within the concrete mix at the nano-scale and homogenously distributed. Figure 6 shows an example of a nano-scale reaction product formed following the introduction of CO_2 into a hydrating cement sample produced in an associated laboratory test.

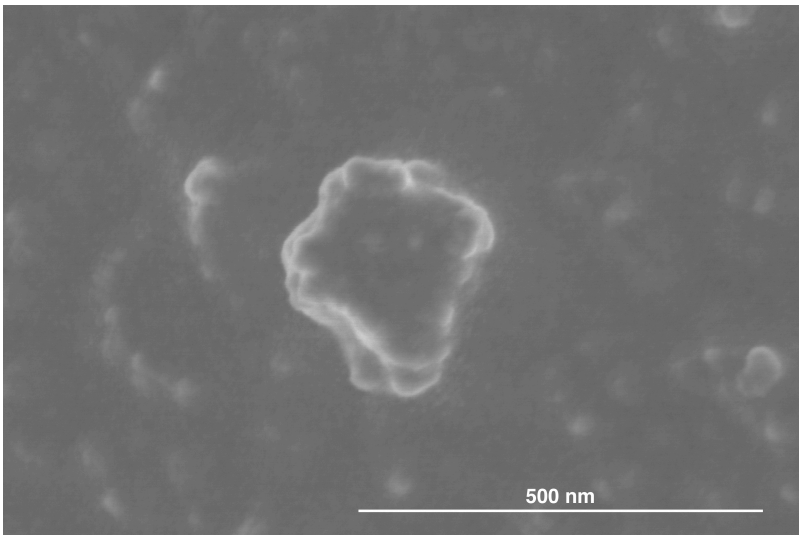

Figure 6: Nano-scale (100-150 nm) calcium carbonate reaction products produced through carbonating freshly hydrating cement as imaged by scanning electron microscopy.

While it is known that the addition of nano-sized calcium carbonate particles can be used to impact the hydration of cement[3], concrete producers attempting to add nanoparticles to a concrete mix often run into technical (e.g. difficulty achieving homogeneous dispersion), operational (e.g. availability and/or quality of supply) and economic (e.g. cost) barriers[4]. The addition of liquefied CO_2 injected into the concrete mix enables concrete producers to manufacture nano-$CaCO_3$ within the concrete mixture at the time of production, thus permitting the producer to realize the benefits of nano-$CaCO_3$ while avoiding these common barriers.

Conclusions

Industrial scale integration of the CarbonCure ready mix concrete system into a concrete production environment has demonstrated the ability to leverage CO_2 as a new tool in mix design optimization. By combining the strength enhancing properties of an optimized dose of CO_2 with reduced binder loadings concrete producers are able to achieve equivalent 28-day compressive strength performance with a reduced environmental footprint.

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CARBON CURE™

Durability of CO_2 Mineralized Concrete

Durability of CO_2 Mineralized Concrete

JUNE 2016

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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_2 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_2 emissions that exceed 63,000 tons as of January 2020.

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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_2) 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_2 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_2 is a viable admixture to improve concrete performance.

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

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_2 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 ap-proaches are sought that can be a part of a portfolio strategy.

One approach that many 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):

$$3CaO{\cdot}SiO_2 + (3\text{-}x)CO_2 + yH_2O \rightarrow xCaO{\cdot}SiO_3{\cdot}y\,H_2O + (3\text{-}x)\,CaCO_3 \quad (1)$$

$$2CaO{\cdot}SiO_2 + (2\text{-}x)CO_2 + yH_2O \rightarrow xCaO{\cdot}SiO_3{\cdot}yH_2O + (2\text{-}x)\,CaCO_3 \quad (2)$$

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

$$Ca(OH)_2 + CO_2 + \rightarrow CaCO_3 + H_2O \quad (3)$$

The carbonation reactions are exothermic. The reaction pro-ceeds in the aqueous state when Ca^{2+} ions from the cementitious phases interact with CO_3^{2-} ions from the applied gas.

The carbonation heats of reaction for the main calcium silicate phases are 347 kJ/mol for C_3S, 184 kJ/mol for b-C_2S [4] and 74 kJ/mol for Ca(OH)2 [5]. When the calcium silicates carbonate, the $CaCO_3$ 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_2S and C_3S exposed to a 100% CO_2 at 1 atm according to the observation that the amount of carbonate that forms does not exactly corre-spond 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 carbon-ation induced corrosion. In contrast, a carbonation reaction integrated into concrete production reacts CO_2 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_2 to freshly mixing concrete the carbonate reaction products are anticipated to form in situ, are of nano-scale and homogenously 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_2 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_2 gas and solid carbon dioxide (snow). The CO_2 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 acceler-ating 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^3) of concrete were batched according to the producer's standard operating proced-ures. 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.

The production personnel verified that the consistency of the concrete met expectations prior to continuing with the testing. For the batches without the CO_2 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_2 injection.

The batches were sampled to test the fresh properties of the concrete mixture and to prepare specimens for analysis via calo-rimetry, 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_2 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.

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

Admixture	Accelerated	Reference	CO2-1	CO2-2	CO2-3
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_2 (%/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_2-1 batch and at the reduced level for the two higher CO_2 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 sieved mortar was also used for time of set testing.

Concrete from each truck load was used to cast 100x 200 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_2 (mm)	Slump after CO_2 (mm)	Air content before CO_2 (%)	Air content after CO_2 (%)	Temperature (°C)	Unit weight (kg/m^3)
Reference	150	e	6.2	e	20.4	2372
Accelerated	135	e	5.4	e	21.0	2376
CO2e1	125	130	5.1	5.0	20.1	2376
CO2e2	140	120	5.9	6.2	21.4	2369
CO2e3	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 fives 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 CO2-1 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_2. Relative comparisons between the latter two CO_2 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 CO2-1 batch, however, is more problematic given that the CO_2 batch contained a higher amount of the retarding admixture.

All three injection doses of CO_2 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_2 provided the greatest acceleration benefit amongst the carbon dioxide treated batches. However, it is thought that the CO2-1 batch would have provided the most potent acceleration among the CO_2 batches, if not all the batches, if it had been pro-duced 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.

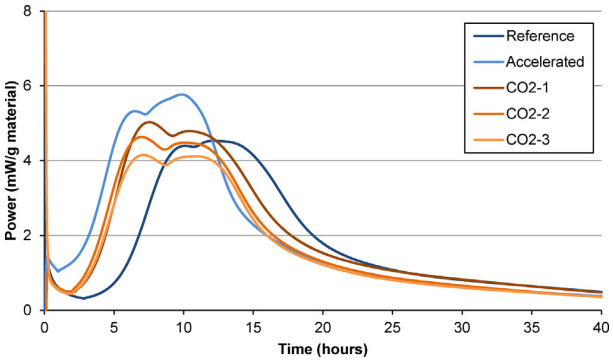

Fig. 1. Conduction calorimetry (power curves) of sieved mortar samples.

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%
CO2e1	5:33		78%	6:34		79%
CO2e2	5:10		72%	6:12		75%
CO2e3	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_2 on the onset of hydration was similar for all dosages, the maximum energy release observed was seen to decrease with increasing CO_2 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_3S hydration. In the non-CO_2 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_2 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.

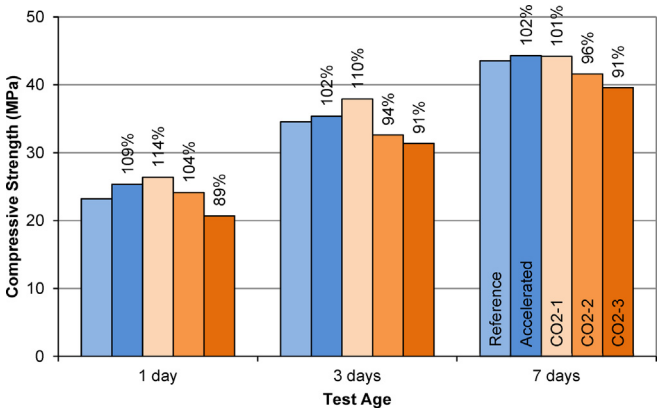

Fig. 2. Early age compressive strengths at 1, 3 and 7 days.

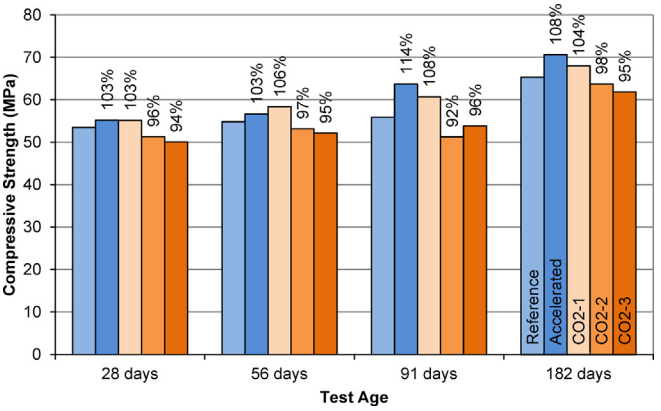

Fig. 3. Later age compressive strengths at 28, 56, 91 and 182 days.

Compressive strength measurements of the CO_2-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 fat 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_2 dose was increased. The strength of the concrete with the highest dose of CO_2 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_2 for strength development would be lower than 0.30% and likely on the order of 0.05%e0.15%. The dif-ferences in the strengths of the concrete produced with the different doses of CO_2 reflect the potential level of sensitivity of the interaction between the carbon dioxide and the binder system. Further adjustments of the CO_2 dose around the identified opti-mum 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_2 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_2 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 exam-ined 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^{-1})	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 will 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 tests results indicated that the carbon dioxide in-jection 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^2/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

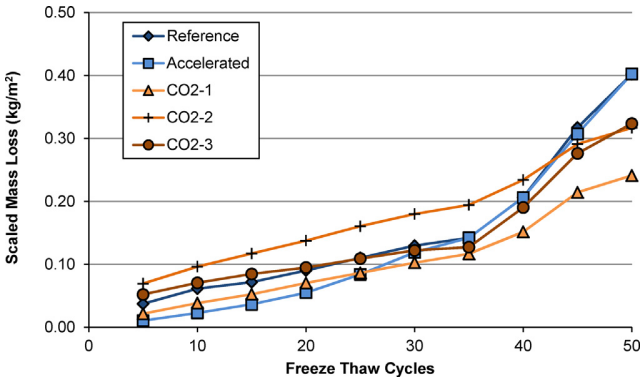

Fig. 4. Freeze thaw deicing salt scaling mass loss according to OPS LS-412 testing.

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_2 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_2 exhibited the least scaling with a 40% reduction over the two non-CO_2 batches. It can be noted, however, that none of the samples approached the OPS scaling limit of 0.80 kg/m^2.

The data from the ASTM C666 testing is presented in Table 10. All of the durability factors calculated from loss in dynamicmodulus 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_2-injection. It was observed that the two batches treated with CO_2 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_2 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 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-Hlay er should offer less resistance to hydration and shorten the induction period.

The results suggested that the concrete strength decreased slightly with increasing 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 CO_3^{-} ions in solution and the Ca^{2+} may not be replenished at the rate it is being consumed. The later-reacting carbon dioxide may combine with 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 CO_2 dosage.

The additional reaction products formed from higher dosages of 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 hy-dration (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 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 CO_2-process. It should also be stated that the concrete resulting from the 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 50e80%. The injection of liquid 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 CO_2 is associated with the reaction of roughly 0.025% CO_2 by weight of cement, or, according to molar weights, 0.057% $CaCO_3$. 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 C_3S [12].

Ex-situ additions of nano-$CaCO_3$ have been observed to achieve accelerated hydration and strength improvements [13e15]. However, cost notwithstanding, the obstacle to integrating nano-$CaCO_3$ additions into conventional concrete is effective dispersion [16]. The in-situ production of nano-scale calcium carbonate reaction products via 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_2 has triggered the nucleation and acceleration stage there is no appreciable dif-ference in the subsequent hydration chemistry and only a differ-ence observed in hydration kinetics. Conversely, such an assumption is not valid for non-chloride accelerators, such as cal-cium 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 gener-ated 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 CO2-1 dose correlates better to the strength (14% energy increase and 14% strength increase) than it did for the batch with the acceler-ating admixture (19% energy increase and 9% strength increase). The shapes of the heat of hydration curves showed that with the CO_2 treated concrete there was an increase in the activity of the C_3S (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_3A hydration having a lower heat of hydration per unit of space-filling capacity [20].

The identified acceleration effect of the carbon dioxide, com-bined 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 per-formed. Assuming a generic material cost of $385 (US) per tonne of industrial carbon dioxide then the raw cost of the CO_2 used in trial would range from $0.48 to $2.85 per truckload (8 m^3) 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 truck-load, 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 eco-nomics would potentially dictate the prospect of employing CO_2 or exploring a combination of CO_2 and a reduced dose of the existing accelerator.

The utilization of carbon dioxide in concrete production has potential sustainability impacts. The CO_2 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_2, 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^3 concrete mixtures were produced in concrete trucks using injection of carbon dioxide during their mixing. The injection of waste CO_2 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_2 injection accelerated early hydration re-actions 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_2 but interpretation was complicated by differences in air content (however, other trials have suggested that a strength benefit is readily achievable outcome).

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The batches with the two higher doses of CO_2 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_2-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_2-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_2 injection does not appear to be as potent, lending thought towards using it in combination with a reduced dose of accelerator.

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APPENDIX A

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