Development of vacuum carbonation curing technology for concrete at ambient conditions

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Abstract

In this thesis, a more practical methodology was conceived for the early-age carbonation of concrete. A widely published topic in recent years, the accelerated curing of concrete using CO_2 has managed to pique the interest of the building sector, with a number of outlets seeking to industrialize this technique. The challenge of implementing, however, lies in the need of elevated pressures to achieve effective CO_2 penetration within concrete. The overwhelming majority of curing chambers currently employed by the precast industry are incapable of withstanding such elevated pressures. Working with industrial partner Boehmers, this collaborative effort mainly sought to develop, and pilot-test, a carbonation approach that marginalizes the need for pressurized conditions, thus alleviating the need for expensive and impractical pressure vessels. The prescribed approach incorporated a vacuum pre-step such that a pressure-differential allowed carbonating concrete at sub-atmospheric gauge pressures, hence the term *vacuum-carbonation*. Proof-of-concept was first carried out in laboratory settings and then scaled to an industrial pilot. Concrete masonry units (CMU) were the targeted precast product for this study, with mix designs for both normal-weight and light-weight concrete. Parametric based testing was carried out to evaluate the effects of pre-conditioning (or drying), vacuum, and pressure-differential, on CO_2 uptake, compressive strength, phenolphthalein indication, pH, and carbonation depth. For normal weight concrete, vacuum carbonation curing at low vacuum and near ambient CO_2 pressures led to an average CO_2 uptake of 15.9 %, and a denser concrete with a one-day strength around 170% that of the benchmark control batch. With respect to lightweight concrete, while CO_2 uptake averaged 15.1%, an accelerated early-age strength gain was not observed. Nonetheless, the devised vacuum carbonation curing technique demonstrated its efficacy in curing concrete and its viability in replacing carbonation curing at elevated pressures.

Résumé

Au cours de cette thèse, une méthode pratique de carbonatation prématurée du béton a été conçue. Un sujet largement publié ces dernières années, la cure accélérée du béton utilisant le CO_2 a suscité l'intérêt du secteur du bâtiment, avec un nombre d'acteurs visant à industrialiser cette technique. Le défi que recèle la mise en œuvre de ce processus réside dans le besoin de pressions élevées pour assurer une pénétration efficace du CO_2 au sein du béton. La majorité des chambres de maturation actuellement adoptée par l'industrie du béton préfabriqué sont incapables de résister à de telles pressions élevées. Pour remédier à l'usage de récipients sous pression coûteux et peu pratique, une approche de carbonatation qui marginalise le besoin de pression élevée a été développée et testée à l'échelle pilote en collaboration avec le partenaire industriel Boehmers. Cette approche prescrite a incorporé une pré-étape sous-vide créant une différentielle de pression qui a permis la carbonatation du béton à une pression sous-atmosphérique intitulée *carbonatation sous-vide*. L'étude préliminaire destinée à valider le concept a d'abord été effectuée au laboratoire et ensuite exécutée à l'échelle pilote. Les blocs de maçonnerie en béton étaient le produit préfabriqué utilisé au cours de cette recherche avec des mélanges conçus pour des blocs de béton normal et léger. Des tests paramétriques ont été effectués afin d'évaluer l'effet du pré-conditionnement (séchage), de la séquestration du CO_2, de la résistance en compression, de l'indicateur de phénolphtaléine, des valeurs de pH et de la profondeur de carbonatation. Dans le cas du béton normal, la carbonatation sous vide à pression de CO_2 quasi-ambiante a permis l'absorption moyenne de 15.9% de CO_2 et un béton plus dense ayant une résistance d'un jour de 170% du spécimen de référence. Alors que le béton léger a entrainé une consommation moyenne de 15.1% de CO_2, un gain de force en âge précoce n'a pas été observé. Néanmoins, cette technologie conçue de carbonatation sous vide, a démontré son efficacité lors du mûrissement du béton et sa viabilité à remplacer les chambres de cure de béton à pression élevée.

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Table of Contents

List of Tables

List of Figures

List of Equations

List of abbreviations

GHG: greenhouse gas emissions

Mt: Million tons or megatonnes

CMU: Concrete Masonry Unit

RH: Relative humidity

TG: Thermogravimetric analysis

DTA: Differential thermal analysis

SEM: Scanning electron microscopy

w/c: water-to-cement ratio

Cement Chemistry Nomenclature:

CO_2: Carbon dioxide

$Ca(OH)_2$ or CH: Calcium hydroxide

$CaCO_3$: Calcium carbonates

C_2S: Dicalcium silicates

C_3S: Tricalcium silicates

C-S-H: calcium silicate hydrates where:

C = CaO

S = SiO_2

H = H_2O

Chapter 1 - Introduction

1.1. Overview

Concrete is the most widely used construction material in the world. Cement is the binding agent responsible for the performance of concrete, and, in fact, the most crucial building ingredient that defines our developed urban communities. The cement industry, however, is responsible for 5% of the world's total anthropogenic CO_2 emissions [1].

As of 2015, Canada's greenhouse gas (GHG) emissions were evaluated at 722 megatonnes (Mt) CO_2 equivalent [2]. Figure 1.1 shows that the heavy-industry sector accounted to 74.6 Mt of GHG emissions for that year, of which 4 Mt originated from cement operations. [2]. Carbon dioxide from cement manufacturing is in part generated from the calcination of limestone (~800 °C), and from the combustion required to achieve the high temperatures required for clinkering [3]. It is estimated that each ton of cement produced releases the equivalent of approximately 0.8 tons of carbon dioxide into the atmosphere.

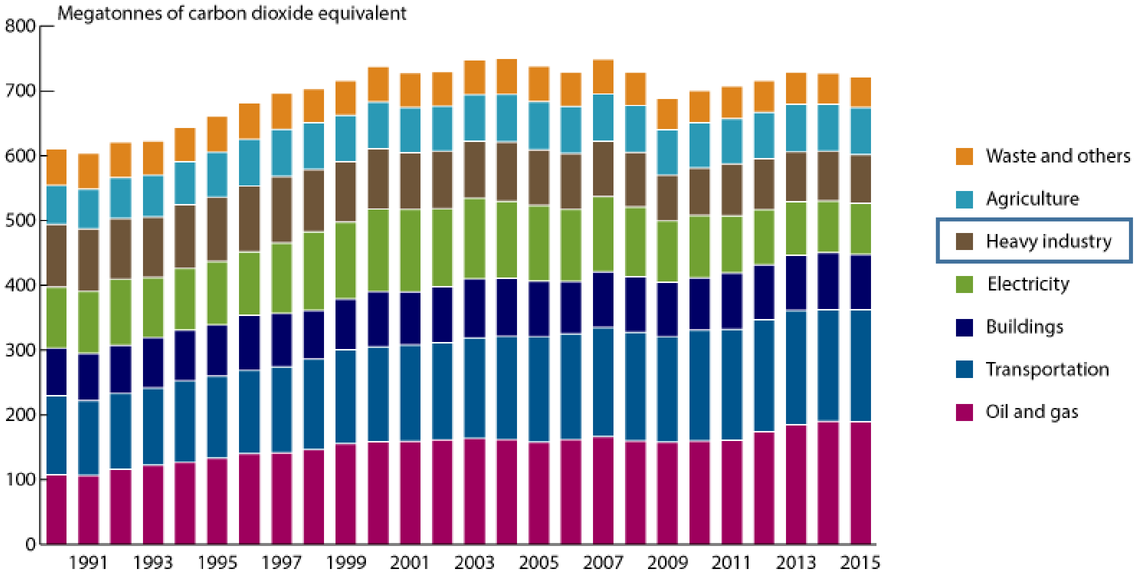


Figure 1.1: GHG emissions by Canadian economic sector, Canada, 1990 to 2015

In Canada, the government announced its plan to implement a carbon trading scheme by 2018, thus incentivising businesses to reduce their carbon footprints and thus incrementally contribute to the country's environmental and economic sustainability [4]. One pragmatic solution, specific to the concrete precast industry, to suitably fit such framework is the early carbonation curing of concrete [5].

Early carbonation curing is a method whereby fresh concrete is exposed to pure carbon dioxide under pressurized conditions. In the presence of water, the anhydrous components of the cement paste (C_2S and C_3S) react with the CO_2 to form calcium silicate hydrates (C-S-H) and calcium carbonates ($CaCO_3$) [5]. This reaction leads to a) a CO_2 consumption by the concrete, i.e. carbon sequestration, b) very rapid curing of the concrete, c) an accelerated early-age strength gain, d) improved mechanical properties, e) a less permeable concrete, and f) a more durable overall concrete arising from the associated densification of the outermost layer [6]. The elevated pressure acts as a driving force for enhanced CO_2 penetration within the concrete's pore structure. Consequently, it is generally understood that the use of pressure chambers is necessary for effective carbonation curing. This is how this technique is currently being carried out at most laboratory scale and proof-of-concepts works.

Concrete masonry units (CMUs) are ideal precast candidate products for early-age carbonation treatment, given the industry's rapid 24-hour production cycle and CMUs lack of embedded steel reinforcement.

Two types of curing processes are practiced by the concrete masonry industry in North America: high pressure steam curing, also called autoclaving, and ambient pressure steam curing, the most common process for its simplicity and lower capital and operational costs. In Canada, only two of the 23 masonry producers run autoclave curing installations [7]. Boehmers, operating under Hargest Blocks Ltd. of Kitchener, Ontario, is one of the masonry producers employing autoclaving systems designed to operate at pressures upwards of 800 kPa (120 psi) and temperatures of 180 °C [8]. Concrete is normally loaded in large air-tight autoclave pressure kilns and exposed to steam in sealed high temperature and pressure conditions [8]. Steam curing, on the other hand, processes fresh concrete units at an atmospheric pressure and temperatures within the range of 60 - 80°C.

This curing option does not require the use of expensive pressure vessels, but rather common aerated steam chambers.

While the masonry industry is an attractive candidate for carbonation curing, it becomes challenging to market this technology to the majority of producers that employ ordinary steam chambers that are neither air-tight nor capable of withstanding pressure. High capital cost and reduced practicality associated with the adoption of pressure kilns therefore limits the applicability of this curing method to autoclave operators and laboratory scale works. To promote the practical adoption of early-age carbonation curing to all masonry producers, it becomes imperative to develop an equally effective methodology that is pressure independent.

1.2. Research Objectives

This research presents an alternative methodology to conventional CO_2-curing of masonry articles through the development of vacuum carbonation, which allows curing to be conducted at near-ambient pressure conditions. The main feature of this approach was a vacuum pre-step meant to facilitate atmospheric displacement and create a pressure differential to serve as the carbonation reaction's driving force.

The objectives of this project were broken down into the following tasks:

1. Develop a vacuum carbonation methodology that allows curing at near-ambient pressures without the use of a pressure chamber. This was to be compared to positive pressure carbonation curing – the status quo that had been studied by previous research. The process parameters included concrete mix proportioning, optimal water content, vacuuming duration, and carbonation durations.
2. Produce laboratory concrete specimens to simulate commercial concrete masonry products. Ensuring proper concrete making is a crucial primary step. This will be done in accordance with mix proportions provided by industrial partner, Boehmers.
3. Study and quantify the effect of initial curing (pre-conditioning) on the proposed ambient carbonation, and compare results (CO_2 uptake, compressive strength) of produced concrete slabs to control slabs prepared via pressurized carbonation, and also normal hydration.
4. Characterize the differently processed concrete specimens using analytical techniques that include thermal pyrolysis (to quantify carbonation degree and cement reaction products), carbonation depth elucidation via phenolphthalein spraying, and pH gradient determination between core and surface regions along the cross-section of fractured specimens.
5. Conduct pilot-scale vacuum carbonation trials at the industrial sponsor's site.

Chapter 2 - Literature Review

Carbonation curing of concrete has been studied since the 1970's as a potential replacement to autoclave and steam curing [5, 9, 10]. Because of the high cost associated with piloting, the process was never adapted to industrial scale. Some 50 years later, the technology has received renewed interest due to its potential for carbon dioxide sequestration. A number of start-up initiatives are working on extending deployment of carbonation curing beyond the laboratory. This chapter gives a brief review of previous research on early carbonation curing and how vacuum may help attain pressure independency to make curing at ambient conditions possible.

2.1. Carbonation reaction

2.1.1. Weathering Carbonation

Weathering carbonation affects mature concrete in service and is a very slow process due to the low partial pressure of the CO_2 in the air [11]. Atmospheric CO_2 reacts with the hydration products of the cement paste, namely the $Ca(OH)_2$ and C-S-H. The CO_2 reacting with the $Ca(OH)_2$ forms $CaCO_3$ as per Equation 2.1, thereby reducing the hydroxide concentration of the concrete's pore solution. This will lead to a decrease in pH of the concrete from 13 to 9 which will promote the destruction of the passivation film and induce corrosion of the steel reinforcement [12, 13]. The C-S-H is also susceptible to decalcification in the presence of CO_2, producing $CaCO_3$ and silica gel following Equation 2.2 [6]. The silica gel decomposition product is vulnerable to polymerization-induced shrinkage [14]. Carbonation can also engage ettringite and monosulphoaluminate into reaction [15], however, these reactions will not be discussed further herein as they are beyond the focus of this thesis.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{Equation 2.1}$$

$$C\text{-}S\text{-}H + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \qquad \text{Equation 2.2}$$

It is therefore well understood that weathering carbonation inflicts detrimental effects on concrete that undermines its durability. The decalcification of cement paste weakens concrete's binding strength and increases susceptibility to shrinkage as a result of C-S-H decomposition; the associated lowering in alkalinity in part leads to corrosion cracking for reinforced concrete articles [14, 16].

2.1.2. Early-Age Carbonation Curing

2.1.2.1. Pressurized carbonation

Early age carbonation curing of concrete is the process of intentionally exposing fresh concrete to CO_2. Once subject to CO_2 and water, the minerals of the cement, namely, the dicalcium silicates (C_2S) and the tricalcium silicates (C_3S), react to from C-S-H and $CaCO_3$ according to equations 2.3 and 2.4 [5, 6]:

$$C_3S + (3\text{-}x)\ CO_2 + yH_2O \rightarrow C_xSH_y + (3\text{-}x)\ C_aCO_3 \qquad \text{Equation 2.3}$$

$$C_2S + (2\text{-}x)\ CO_2 + yH_2O \rightarrow C_xSH_y + (2\text{-}x)\ C_aCO_3 \qquad \text{Equation 2.4}$$

Unlike weathering carbonation, early carbonation curing is a very fast process that occurs within hours of casting. Moreover, the reaction mostly involves the anhydrous components (C_2S and C_3S) of the cement paste which would otherwise be engaged hydraulically with water. Although the dominant reactions of carbonation curing are shown by Equations 2.3 and 2.4, it is important to note that the reaction shown in Equation 2.2 can also occur to some extent during early age carbonation curing [5, 10]. A 3-minute carbonation of a C_3S paste was found to yield the same extent of reaction after 12 hours of hydration curing. Carbonation curing leads to rapid early strength gain, reportedly attaining over 45 MPa of compressive strength within 81 minutes of reaction. This curing method is also known to densify the outer layer of the concrete as this portion is heavily reacted due to direct CO_2 exposure [5].

Another important benefit of early age carbonation curing is its carbon storing capacity within concrete. Carbonation curing is entertained as an attractive CO_2 sequestration option to address climate change as carbon dioxide is chemically transformed to stable carbonates with no likelihood of leakage. Theoretically, it is presumed that Portland cement has the potential of absorbing the equivalent of 50% of its weight in CO_2 [16]. In practice, such high levels of CO_2 consumption have never been witnessed as the reaction is never truly 100% efficient [16]. Many factors affect the reaction between CO_2 and the cement minerals, such as: (1) capillary pores and optimal water content, (2) the purity of CO_2, (3) the pressure used during CO_2 curing, and (4) continued curing following carbonation curing, among others [17, 18]. These four factors are described below.

(1) The degree of carbonation is greatly dependent upon the moisture content and relative humidity (RH). The moisture content plays a crucial role as it is one of the reactants of the carbonation reaction. Excessive free water blocks the capillary pores and prevents CO_2 from diffusing into the concrete [19, 20]. To overcome this, an initial setting step called pre-conditioning is adopted prior to carbonation curing. Pre-conditioning involves drying the concrete in a controlled environment to optimize the residual water content such that enough is present for the reaction to occur and enough is lost to create space for gas diffusion. Both air drying and fan drying have previously been employed to facilitate diffusivity of CO_2 by removing free water and freeing capillary pores [20, 21].

    The optimal level of moisture content and internal RH to maximize the carbon reaction has been established between 50-60% [5, 22]. El-Hassan et al. (2013) monitored the internal relative humidity (RH) in parallel with moisture loss. Following 24 hours of pre-conditioning, they reported a 53% moisture loss and only an 87% RH. Their study concluded that attaining the optimal RH of 50% is not possible within 24 hours of initial curing [19, 20]. Thus, the degree of carbonation, or CO_2 uptake by the concrete, is to a certain extent directly proportional to the amount of free pore space. Prolonged drying past the optimal water content can lead to water starvation, and the eventual halt of the reaction. Pre-conditioning could also be detrimental for the development of late-strength due to insufficient residual water content for hydraulic activation following carbonation[20]. Thus, subsequent water compensation following carbonation curing is crucial to safeguard against this phenomenon. The pre-conditioning in this research was adopted using fan drying to expedite the initial curing process and respect the 24-hour CMU production cycle.

(2) Most research pertaining to early age carbonation curing has usually been conducted using pure CO_2 (99.5%) as opposed to flue gas (between 10-25% CO_2 content) for reasons

pertaining reaction efficiencies[23]. Generating pure carbon dioxide is quite energy extensive and costly, making early age carbonation curing economically challenging to pursue at an industrial scale [23]. Direct flue-gas carbonation has yet to be proved practical. Attempts have been made, for example with the help of a pseudo-dynamic carbonation process in one specific case [23]. The monetizing of CO_2 emissions, like in the case of Canada's Cap and Trade system, gives more merit for early age carbonation curing technologies as costs associated with the utilisation of pure gas can be recovered (or compensated) by such a taxing model. This research focused solely on the use of high purity CO_2.

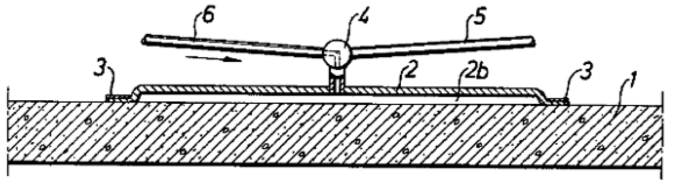
(3) Until now, early carbonation curing was only tested using high CO_2 pressures (> 100 kPa) as a minimal driving force is necessary for diffusing the gas into concrete pores. While this curing method proved quite successful, it has seldom been implemented at the industry level due to the high cost associated with the upscaling process, particularly, the need for pressure vessels. One of the main goals of this thesis was to develop of vacuum carbonation curing method that would allow to carbonate at near ambient pressure conditions.

(4) As mentioned previously, continuous curing through subsequent hydration following early age carbonation is critical to ensure further hydraulic reaction of unreacted cement grains and improved ultimate strength and durability of the concrete.

2.1.2.2. Vacuum carbonation

The purpose of this study was to develop a vacuum carbonation curing method with the goal of lowering the CO_2 pressure applied during the curing process and thus, alleviating the costs associated with the need for pressure vessels.

Vacuum carbonation curing was previously studied by Malinowski (1982), Hannawayya (1984) and Venhius (2001) with a similar purpose, however targeting different applications [24-26]. During carbonation, the exothermic nature of the reaction results in the evaporation of mix water, which occurs while the hydrated cement phases are being converted into carbonate minerals. The released water obstructs the concrete's open pore network thereby reducing the carbonation penetration depth. As such, a vacuum was used to lower the free water obstructing the capillary pores to facilitate CO_2 penetration into the concrete. Malinowski (1982) patented a vacuum carbonation method as shown in Figure 2.1 to cast concrete which uses a plate or mat to de-water and compact the concrete mass [24].



Where:
1. Concrete mass
2. Mat or plate

2b. Carbonation chamber

3. Mat or plate seals abutting the concrete
4. Two-way valve
5. Vacuum pressure applied through line 5
6. CO_2 gas supplied through line 6

Figure 2.1: Malinowski's patent schematic of concrete casting method

Hannawayya's (1984) vacuum curing of cement mortar led to a rapid early strength gain. After 38 minutes of CO_2 vacuum curing, the samples had achieved a strength of 48.15 MPa compared to the 28 days hydrated specimens which gave 28.63 MPa [26]. Later, Venhius (2001) developed a continuous vacuum carbonation system to address the pore closure problem and attempt the remove the water as it is being produced in order to enhance the CO_2 transfer into the concrete [25]. This near-vacuum carbonation setup required the use of a desiccant for water removal. His work specifically targeted the use of vacuum carbonation to create a protective layer around cementitious wasteforms in order to reduce the leachability of these hazardous substances [25]. While his research was successful in demonstrating increased carbonation penetration depths of up to 15 mm, the adopted laboratory vacuum carbonation setup consisted of a reaction vessel built out of stainless steel, and required curing periods in excess of 24 hours, making it rather impractical to pilot for the masonry industry.

El-Hassan (2012) and Rostami (2012) also vacuumed the carbonation chamber prior to carbonation curing to aid with lowering the amount of free water and enhancing CO_2 penetration [19, 27].

The use of a vacuum can therefore be exploited for early-age carbonation curing for the dual purpose of reducing processing pressures and enhancing the diffusion of CO_2 within the concrete.

2.1.2.3. Quantification of carbon dioxide uptake

The CO_2 content in the concrete was quantified using two methods: the mass gain approach and thermal pyrolysis.

As detailed in Equation 2.5, the CO_2 uptake is the difference in mass before and after the reaction, including the water lost during [28]. Early age carbonation curing is an exothermic reaction, thus releasing heat and water that usually condenses within the walls of the chamber.

$$CO_2\,uptake(\%) = \frac{(Mass_{after\ carb.} + Water_{lost}) - Mass_{before\ carb.}}{Mass_{cement}} \times 100\% \qquad \textit{Equation 2.5}$$

Early carbonation curing leads to an increase in mass of the concrete as the CO_2 gas is converted into carbonate minerals [25]. The overall CO_2 taken up by the concrete material during carbonation needs to be adjusted for the simultaneous water loss also being experienced by the concrete, where the net weight gain is expressed as a fraction of the initial cement content.

The CO_2 content was also measured through thermal pyrolysis, where mass loss of concrete is recorded after each predetermined holding temperatures. Mass loss experienced between room temperature (24°C) and 105 °C is normally attributed to the evaporation of free water, between 105 °C and 550 °C to the release of bound water as the result of hydrates decomposition, and between 550 °C and 1000 °C to the release of CO_2 arising from the decomposition of the calcium carbonates. Therefore, the CO_2 content can be determined following Equation 2.6 [15, 20, 29].

$$CO_2\,content(\%) = \frac{(Mass_{at\ 550\,°C} - Mass_{at\ 1000\,°C})}{Mass_{cement}} \times 100\% \qquad \textit{Equation 2.6}$$

The literature reveals mixed findings regarding the temperature ranges used for thermal decomposition. Research dating back to 1979 demonstrates that the weight difference between 105 °C and 350 °C is attributed to the loss of bound (combined) water, and between 350 °C and 1000 °C due to the decomposition of carbonates (equivalent to the CO_2 content) [30]. These findings were later dismissed on account of another more accurate method for the quantification of CO_2, thermogravimetric analysis (TG) [19]. It has been shown that the mass loss between 350 °C and

470 °C was in fact due to the decomposition of calcium hydroxides, while the loss between 470 °C and 950 °C a result of the decarbonation of calcium carbonates. Matsushita's findings suggest that the CO_2 content is represented by the weight loss between 600 °C and 800 °C [31]. Other research breakdown carbonates according to their crystallinity. With the aid of mass spectroscopy (MS), the CO_2 in low-crystalline $CaCO_3$ was detected between 415 °C and 565 °C and in high-crystalline $CaCO_3$ between 565 °C and 745 °C [32, 33].

Differential thermal analysis (DTA), and to some extent TG, conducted by Ramachandran and Beaudoin assigned temperature ranges for different thermal activities, summarized by Table 2.1 [29]:

Table 2.1: Mass loss classification based on DTA/TG

Temperature range	**Mass loss attribution to decomposition of the:**
Below 105 °C	Free (evaporable) water
105 °C - 200 °C	Free water in poorly formed C-S-H
200 °C - 420 °C	Bound water in well-formed C-S-H and C-A-H
420 °C – 550 °C	$Ca(OH)_2$
550 °C – 720 °C	CO_2 in the poorly-crystalline $CaCO_3$
720 °C – 950 °C	CO_2 in the well-crystalline $CaCO_3$

2.1.2.4. CO_2 storage and sequestration capacity

Whereas it is very challenging and near impossible to eliminate the CO_2 emissions from cement manufacturing, early age carbonation curing enables the utilization of a portion of these emissions during the production of concrete.

The total GHG emissions in Canada has been declining since 2005 – this reduction is mainly due to optimizations implemented by public utilities for power and electricity [2]. As the masonry industry in Canada is growing at an annual rate of 5%, there will be a proportional demand for cement, and hence an equal increase in emissions [7].

On a per masonry block basis, a normal-weight concrete unit weighing 18 kg, and containing 1.75 kg of ordinary Portland cement, is responsible for the emission of 1.4 kg of CO_2 into the atmosphere (since 0.8 kg CO_2 released per kg of cement). A lightweight masonry unit weighing 15 kg and containing 2 kg of cement by mass emits 1.6 kg of CO_2.

While it is very challenging to reduce the CO_2 emissions from the source (cement manufacturing plant), early age carbonation curing of concrete enables the recapturing of a portion of the emitted GHG back into the end-product (concrete masonry units).

Early age carbonation curing sequesters 350 g of CO_2 in a normal weight unit and 400 g for a lightweight concrete unit. This is equivalent to a 20% CO_2 uptake [20]. Given the average yearly production in Canada of 50 million blocks, and assuming half the production being normal weight concrete while the other half is lightweight concrete, 18.75 million kg of CO_2 could be sequestered per year.

2.2. Strength development through carbonatation of concrete

2.2.1. Early age strength

Rapid strength gain can be achieved through early age carbonation curing as the cementitious hydration mechanism is effectively accelerated [34]. A 5-minute carbonated Portland cement mortar sample produced higher compressive strengths than one-day hydrated specimens [35]. Moreover, C_2S and C_3S mortar samples carbonated for 81-minute yielded strength values three folds that of a one-day hydrated concrete reference batch [5]. The strength development observations were recorded for specimens that had the highest degree of carbonation confined to the outer surface. Vacuum carbonation had been shown to further enhance the CO_2 penetration within concrete specimens by reducing the free water content on the surface [25]. Mortar samples that underwent a vacuum carbonation process for 38 minutes yielded higher strength results than 28-day hydrated mortar references [26].

Lightweight concrete seems to exhibit a different strength behaviour than normal weight concrete in response to carbonation. Carbonated lightweight concrete was unable to achieve strength values higher than those of the 1-day hydrated references. The recorded values were either equal or slightly below the hydrated or steam-cured control batches [18]. This discrepancy may likely be due to a dynamic change in the water content and effective water-to-cement ratio incurred from CO_2 curing.

2.2.2. Late strength

In the case of normal weight concrete, continued hydration following early age carbonation curing proved beneficial in furthering ultimate strength gain. Furthermore, subsequent hydration replenishes water lost during carbonation such that unreacted cement grains become hydraulically engaged [36].

A pH test conducted on carbonated samples that had undergone 28days of subsequent hydration successfully demonstrated a rebound effect in alkalinity such that a $pH > 12$ was achieved, primarily due to the generation of CH from the hydration of unreacted cement grains. This rebound phenomenon is very useful for reinforced precast concrete susceptible to corrosion [20].

El-Hassan et al. reported that subsequent hydration of lightweight concrete slabs did not impart strength gain trends like in the case of normal-weight specimens. The hydrated-only lightweight control batch demonstrated a higher average compressive strength than the carbonated-only batch [36].

Phase II: On-site testing – Boehmers, Cambridge, Ontario

The CMU production process at Boehmers is entirely automated. Figure 2.2 is a schematic of the process. The components are first mixed and then molded in the block machine. The blocks are then racked and transferred to a drying area where they are pre-condition (dried) prior to curing., Boehmers employs an autoclave curing system. The company is seriously considering to convert its current operation to carbonation curing.

In the masonry industry, it is common-practice to accelerate the curing process of products to satisfy the preferable 24-hour product turnover criteria. Both steam and autoclave curing methods are highly energy intensive. A total energy balance for a normal weight CMU cured by steam reportedly consumes 2300 kJ of energy, while a lightweight steam cured CMU block consumes 2500 kJ [37]. Steam curing is typically conducted at atmospheric pressure and temperatures reaching an average maximum of 71 °C (160 °F) [38]. Autoclave curing is far more energy intensive as the masonry units are cured at pressures as high as 827 kPa and steam temperatures up to 180°C. Given these conditions, pressure vessels or industrial autoclaves are necessary. The

ASME Boiler and Pressure Vessel Code (BPVC) and the CSA B51-14 mandates the use of certified air-tight vessels for operations running at pressures above 100 kPa. These vessels also need to be periodically inspected for safety validation. The more complicated autoclave process and its higher capital and operating costs renders this technique the least popular nowadays among masonry producers, whereas steam curing is more economic and far more practical since pressure vessels are not required. While carbonation curing can be rather easily adapted to autocalve kilns, a novel methodology has yet to be developed for the more popular steam curing chambers, which are neither air-tight nor capable of being pressurized.

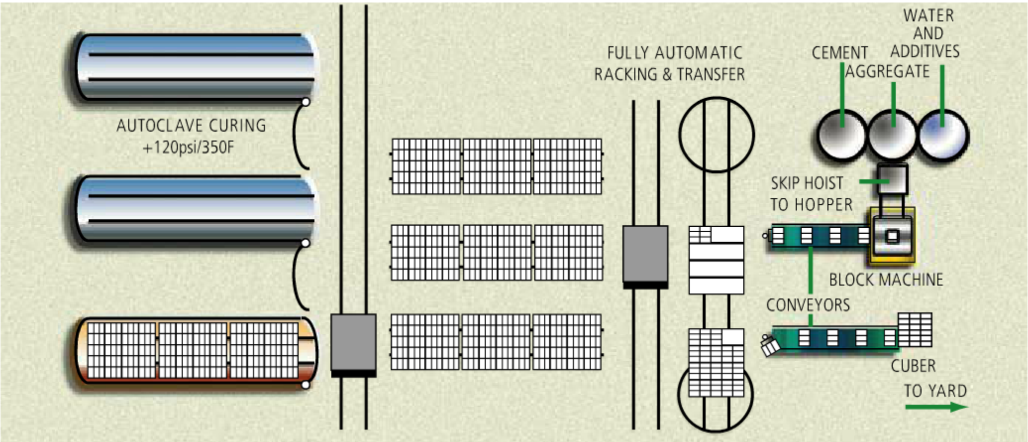


Figure 2.2: Boehmers automated block production process

Chapter 3 - Experimental Program

The flow chart shown in Figure 3.1 summarizes the laboratory and on-site experiments conducted. To accomplish the objective of demonstrating that vacuum carbonation curing can replace pressurized carbonation curing, various experiments where selected. For this research, both normal weight and lightweight concrete were considered.

In phase I, high pressurized early age carbonation curing of concrete was compared to vacuum carbonation curing and to a control hydrated concrete sample. A minimum of 3 slabs were casted for each batch in order to calculate a standard deviation, thus ensuring consistency between the results. In phase II, tests were conducted at Boehmers' facilities. Likewise, both normal weight and lightweight concrete were considered. On-site, only vacuum carbonation curing was carried out, where the resulting blocks were benched against pressure-carbonated blocks and hydrated blocks (autoclaved concrete reference) prepared using Boehmers' pressure kilns.

In all cases, 1 day and 28-day strengths were assessed in accordance with CSA A165-14 and ASTM C140 standards.

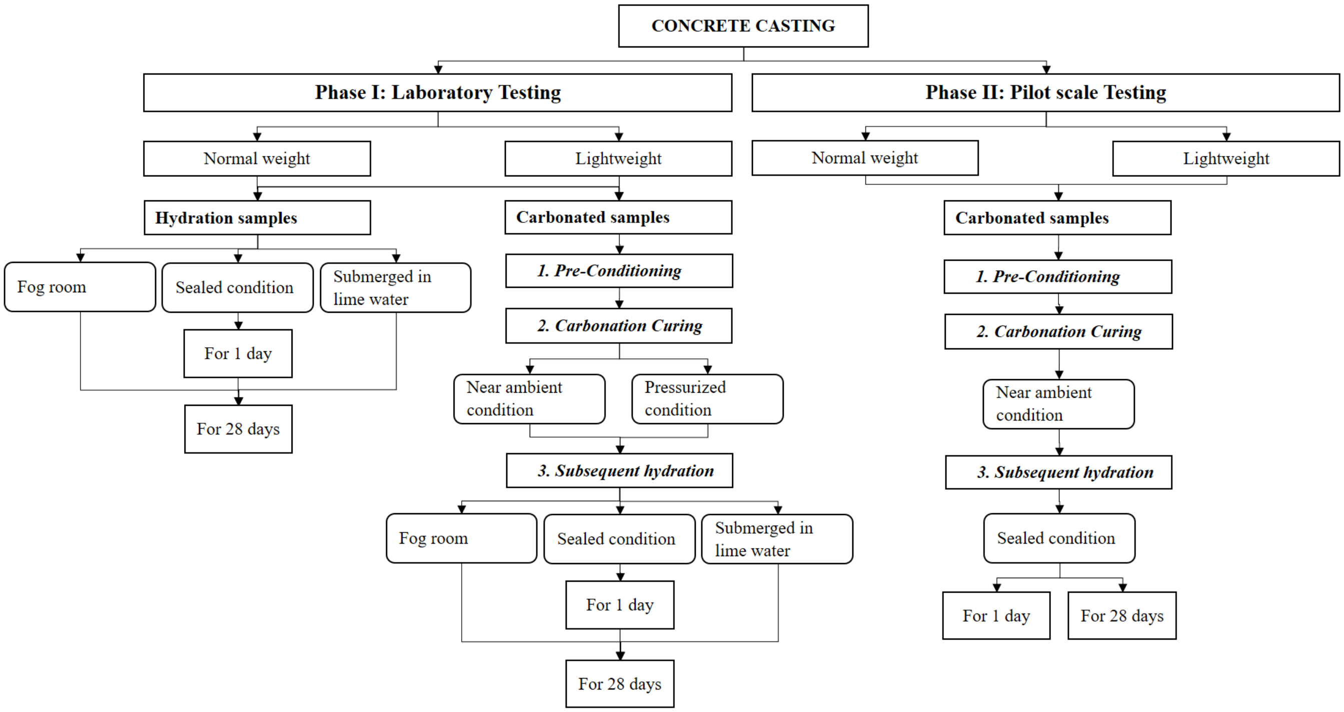


Figure 3.1: Flow chart of laboratory and on-site experiments

Phase I: Laboratory Testing

The laboratory testing followed the step-by-step procedure displayed in Figure 3.2. First, the aggregates, the ordinary Portland cement and the water was mixed using a concrete mixer. Then, the wet concrete was molded and compacted using a BOSCH hammer (11320VS). The concrete slabs were pre-conditioned to achieve a 50% water loss following which the samples were carbonated. Finally, the slabs were subsequently hydrated for 1 day and 28 days respectively.

Mixing | Casting in steel mold | Compaction | Pre-conditioning | Early-carbonation curing | Subsequent hydration

Figure 3.2: Step-by-step procedure of the concrete making process in the laboratory

3.1. Type of concrete

As mentioned above, two types of concrete were considered in accordance with the CMU's produced at Boehmers: (1) normal weight concrete and (2) lightweight concrete.

3.1.1. Normal Weight Concrete

For normal weight concrete, granite was used as both fine and coarse aggregates. The granite was received from the Bauval CCM query in Montreal, Canada. The fine aggregates ranged between 0-2 mm and the coarse aggregates ranged between 2-5 mm. It is important to note that the granite as-received was damp and was dried before use in the laboratory. Moreover, granite is known to have a 2% water absorption rate by mass of aggregates. As such, this additional water aside from the mixture water shown in table 3.1 was added to the previously dried granite to account for this absorption by the aggregates.

Ordinary Portland cement of type GU from Ciment Québec that complies with the CSA Standard A3000-13 requirements section A3001-13 was used throughout this research. The proportions of the materials are shown in table 3.1 and were chosen as such to respect that of the CMU's produced by Boehmers. The w/c was 0.35.

The mixing procedure followed these steps:

1. The fine and coarse aggregates were dried at room temperature.
2. Using a concrete mixer, the 2% additional water by mass of aggregates was mixed with the granite content for 2 minutes.
3. The aggregates were set aside for 10-20 minutes to allow the granites to absorb the water.
4. The ordinary Portland cement was then added and mixing resumed for 2 minutes.
5. The mixture water as shown in table 3.1 was added and further mixed for 2 minutes.

Table 3.1: Mixture proportion of concrete

Normal Weight Concrete		
	Slab (g/unit)	**Percent (%)**
OPC	54.3	9.7
Fine granite (0-2 mm)	324.8	58.0
Coarse granite (2-5 mm)	161.8	28.9
Water	19.0	3.4
Total sample	560.0	100.0
w/c = 0.35		

3.1.2. Lightweight Concrete

Table 3.2 shows the mixture used for lightweight concrete which follows that of Boehmers. For lightweight concrete, Litex^{TM} lightweight aggregates from Lafarge was used ranging between 0-6 mm in dimension. This aggregates is also called expanded slag and a by-product of iron-making. A small portion of Bomix® sand <1.25 mm in size was used as filler. Ordinary Portland cement of type GU from Ciment Québec was also used. The mixing procedure for lightweight concrete varied slightly from the normal weight concrete as the expanded slag aggregates had a higher absorption rate than the granite. Expanded slag aggregates absorbs 7% of water by weight and this type of aggregate takes longer to absorb the added water. Thus, the mixing process went as follow:

1. The Litex^{TM} aggregates were dried in the oven at 105 °C ± 5 °C for 24 hours.
2. 7% water by mass of expanded slag was added and the damp lightweight aggregates and were sealed in a container overnight in a 100% moisture room.

3. A 2% absorption was used for the small quantity of Bomix® sand which was added and set aside for 10-20 minutes.
4. Both the expanded slag and the sand were mixed using a concrete mixer for 2 minutes.
5. The ordinary Portland cement was added and further mixed for 2 minutes.
6. Finally, the mixture water as shown in table 3.2 was added and mixing resumed for 2 minutes.

It is important to note that the lightweight concrete demonstrated a “wetter” texture than the normal weight concrete. This is explained by the higher amount of absorption water added in the case of expanded slag aggregates. The w/c for the lightweight concrete was also 0.35.

Table 3.2: Lightweight concrete mixture

Lightweight concrete		
	Slab (g/unit)	**Percent (%)**
OPC	69.8	13.3
River sand (0-1.25 mm)	46.7	8.9
Exp. Slag Agg. (0-6 mm)	383.8	73.1
Water	24.7	4.7
Total sample	525.0	100.0
w/c = 0.35		

3.2.2. Sieve Analysis

The sieve analysis data is compiled in Tables 3.3 and 3.4 for the aggregates of normal weight and lightweight concrete, respectively. Figure 3.3 shows the gradation curves for both aggregate types. In general, the aggregate combination for the normal-weight concrete has a larger portion of finer aggregates.

Table 3.3: Sieve analysis of granite as-received from the Bauval query

Normal weight Concrete				
Sieve Opening	Mass retained (g)	Mass Passing (g)	% Passing	% Retained
0	0	0	0.0	0
0.08	30.4	14.5	0.0	6.2
0.16	43.9	44.9	0.1	8.9
0.315	60.1	88.8	0.2	12.2
0.63	71.1	148.9	0.3	14.4
1.25	105.9	220	0.4	21.4
2.5	150.9	325.9	0.7	30.5
5	17.3	476.8	1.0	3.5

Table 3.4: Sieve analysis of expanded slag as-received from Lafarge

Lightweight Concrete				
Sieve Opening	Mass retained (g)	Mass Passing (g)	% Passing	% Retained
0	0	0	0.0	0
0.08	3.1	1.6	0.3	0.6
0.16	12.2	4.7	0.9	2.4
0.315	57.9	16.9	3.4	11.6
0.63	131.1	74.8	15.0	26.2
1.25	181.7	205.9	41.2	36.3
2.5	102.2	387.6	77.5	20.4
5	10.1	489.8	98.0	2.0

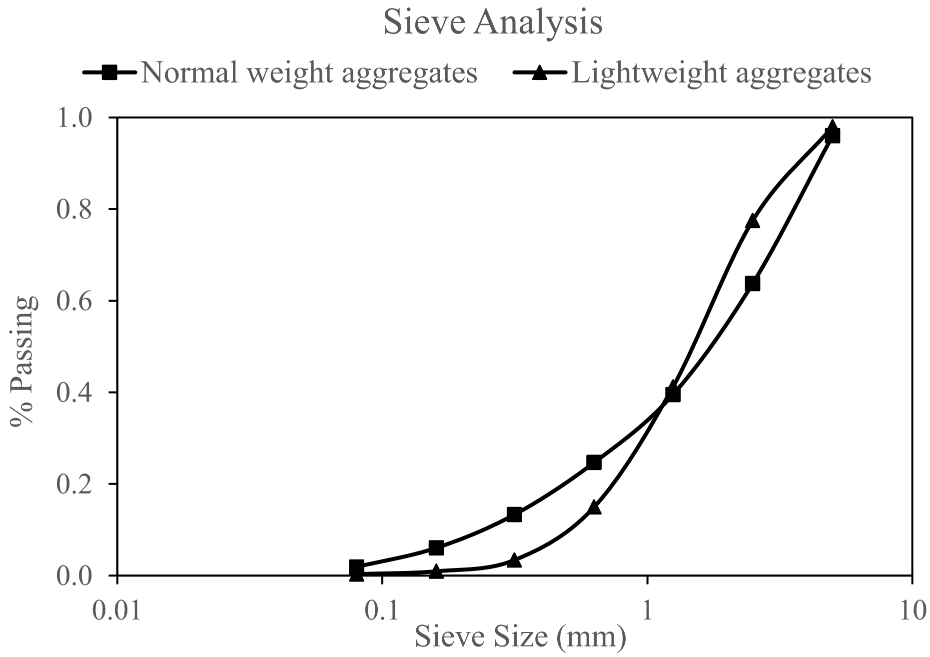


Figure 3.3: Gradation curves for the normal weight and lightweight aggregates

3.2. Laboratory casting procedure

The concrete slabs produced in the lab are 100 mm x 31 mm x 76 mm as shown in Figure 3.4. These dimensions were selected as such to mimic the wall thickness of a concrete masonry unit.

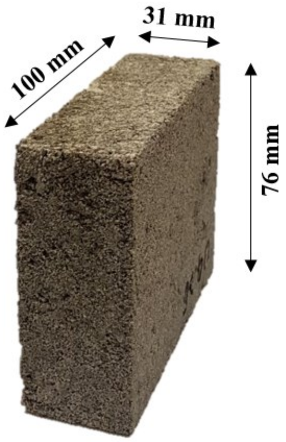


Figure 3.4: Laboratory specimen dimensions

3.3. Laboratory pre-conditioning

Prior to carbonation curing, the concrete slabs were pre-conditioned, or in other words, dried to allow for higher carbonation reaction. The slabs were dried in a controlled room at 50% RH and 24 °C. A fan was used to expedite the process. The target water removal (or water loss) was 50% of the total water in the concrete slabs. The total water includes the mixture water and the added absorption water. It took on average 2 hours to achieve 50% water loss for the normal weight concrete slabs and 4 hours for the lightweight concrete slabs. Two methods were employed to assess the water loss target: (1) mass monitoring using a digital balance and a (2) moisture meter. These approaches are discussed below.

3.3.1. Mass monitoring

First, the water loss was monitored using a digital balance. The weight loss profile as a function of time is shown in Figure 3.5. The lightweight concrete slabs took much longer to dry than the normal weight concrete. This is explained by the fact that the total water content in the lightweight concrete was far greater than in the normal weight concrete.

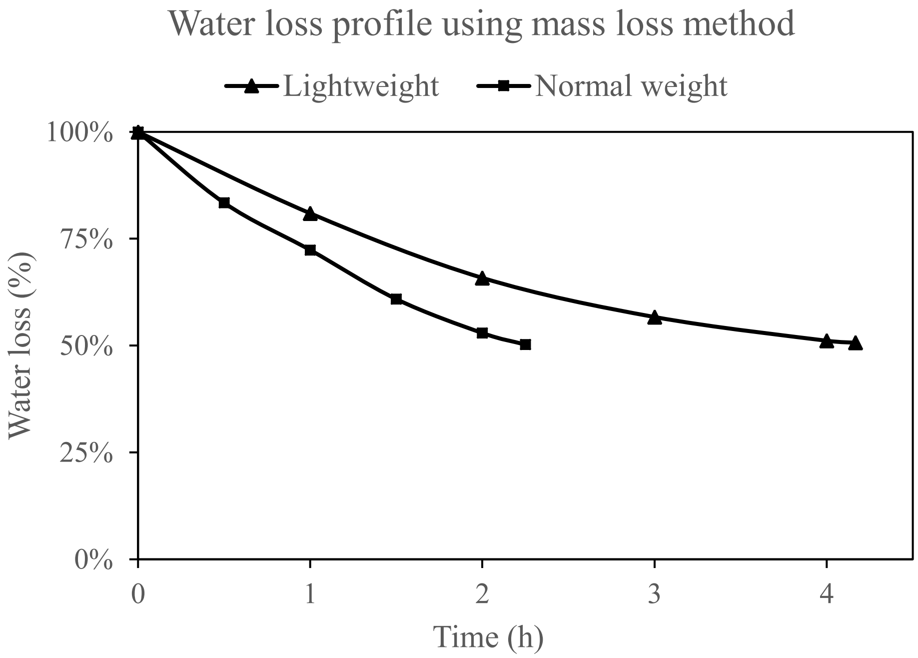


Figure 3.5: 50% water loss target as monitored in the laboratory

3.3.2. Moisture meter

Second, an Extech Instruments pinless moisture/humitidy meter + IR (Model MO290) was also used to assess the water loss of the sample. This device has an external pin probe that was placed against the concrete slab to give a moisture content reading. Once calibrated in the laboratory, this device was useful on-site as it allowed for a quick assessment of the water content without having to weigh the blocks.

3.4. Curing Methods

Tables 3.5 and 3.6 list the various carbonation curing regimes tested and compared against the traditional hydration curing methods for both normal weight and lightweight concrete respectively. The vacuum carbonation curing at ambient condition was developed and tested to replace the pressurized carbonation curing.

Table 3.5: Abbreviations used for different curing regimes for normal weight concrete

		Abbreviations used for various curing conditions	Batch	Vacuum kPa (psi)	Pressure kPa (psi)	Net range kPa (psi)
Carbonation curing	Pressurized Carbonation	No vacuum, high **P**ressure	NP	-	100 (14.5)	100 (14.5)
	Vacuum Carbonation	**H**igh **V**acuum, above atmospheric **P**ressure	NHVP	-76 (-11)	14 (2)	90 (13)
		Low **V**acuum, near atmospheric **P**ressure	NLVP	35 (-5)	3 (0.5)	38 (5.5)
Hydration curing	Hydrated References	**S**ealed container	-	-	-	-
		Fog room (100% humidity chamber)	-	-	-	-
		Submerged in **L**ime water (3% Calcium Hydroxide solution)	-	-	-	-

*N: Normal weight concrete

Table 3.6: Abbreviations used for different curing regimes for lightweight concrete

		Abbreviations used for various curing conditions	Batch	Vacuum kPa (psi)	Pressure kPa (psi)	Net range kPa (psi)
Carbonation curing	Pressurized Carbonation	No vacuum, high **P**ressure	LP	-	100 (14.5)	100 (14.5)
	Vacuum Carbonation	**H**igh **V**acuum, above atmospheric **P**ressure	LHVP	-76 (-11)	14 (2)	90 (13)
		Low **V**acuum, near atmospheric **P**ressure	LLVP	35 (-5)	3 (0.5)	38 (5.5)
Hydration curing	Hydrated References	**S**ealed container	-	-	-	-
		Fog room (100% humidity chamber)	-	-	-	-
		Submerged in **L**ime water (3% Calcium Hydroxide solution)	-	-	-	-

*L: Lightweight concrete

3.4.1. Carbonation Curing

Early carbonation curing was carried out using the setup shown in Figure 3.6. Pure CO_2 at 99.5% in gaseous form was used and all concrete samples were carbonated for 4 hours at constant pressure.

Three distinct carbonation curing regimes were tested using the set up in Figure 3.6:

1. Pressurized carbonation curing (batches NP and LP) with no vacuum and a CO_2 pressure of 100 kPa (14.5 psi).
2. Vacuum carbonation curing (batches NHVP and LHVP) with a high vacuum to -76 kPa (-11 psi) and an above atmospheric CO_2 pressure of 14 kPa (2 psi) yielding an overall net pressure of 90 (13 psi).
3. Vacuum carbonation curing (batches NLVP and LLVP) with a low vacuum to 35 kPa (-5 psi) and a near-ambient CO_2 pressure of 3 kPa (0.5 psi) representing an overall net pressure of 38 kPa (5.5 psi).

Following carbonation curing, the concrete slabs were subsequently hydrated for 1 day and 28 days. The 1 day specimens were kept in a sealed container. For the 28-day age testing, the three subsequent hydration methods described in Tables 3.5 and 3.6 were considered.

3.4.1.1. Pressurized carbonation curing

For pressure assisted carbonation curing, the CO_2 gas was injected without prior vacuuming of the chamber. In Figure 3.6, valve 1 remained closed and valve 2 was kept open through which the carbonation chamber was pressurized. The pressure was set at 100 kPa (14.5 psi) and held constant throughout the duration of curing. This regime served as the benchmark early carbonation curing previously adopted by a number of studies. Consequently, the pressurized carbonation samples (NP and LP) were used as a means of comparing positive pressure carbonation curing to ambient curing.

3.4.1.2. Vacuum carbonation curing

For vacuum carbonation curing a venturi pump as shown in Figure 3.6 was connected to an air compressor inlet which served as a vacuum. First, valve 1 was opened and the carbonation chamber was vacuumed to the target sub-pressure. In the laboratory, the desired negative vacuum pressures were achieved in under 5 minutes. The, valve 1 was closed and as the vacuum state was maintained in the carbonation chamber, pure CO_2 was injected by opening valve 2. The concrete slabs were carbonated at constant pressure for the duration of the test.

Two different vacuum carbonation curing conditions were tested, a high vacuum and a low vacuum scenario. From a practical perspective, it was challenging to create a system that can withstand elevated negative and positive pressures. Thus, attempting to minimize both the vacuum and the CO_2 pressures was key to conducting a successful pilot scale testing.

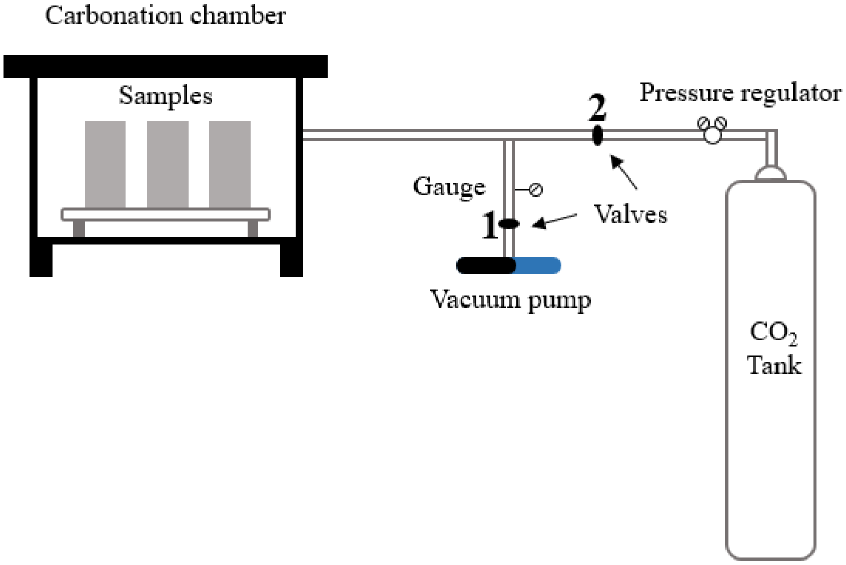


Figure 3.6: Schematic of laboratory carbonation curing setup

3.4.2. Hydration Curing

Hydration curing was conducted and used as reference or control samples. Both 1 day and 28-day slabs were tested. All 1 day concrete specimens were tested in a sealed container. In the case of 28-day specimens, three hydration curing methods were considered:

1. Curing of the concrete in a sealed container with constant spraying of water.
   The slabs were place in a sealed container and kept moist through constant water spraying for the duration of the hydration period.
2. Curing of the concrete in a 100% moisture room.
3. Curing of the concrete in a solution with 3% calcium hydroxide used to mimic lime water conditions. A container was filled with lime water which was created by mixing 3 g of CH per 100 mL of tap water. The concrete specimens were then submerged in this solution for the duration of the subsequent hydration curing period.

While all three reference curing methods were conducted, the first one is the most analogous of on-site procedures given that subsequent hydration is not performed on-site.

3.5. Quantification of carbon dioxide

The carbon dioxide captured in the concrete slabs was assessed and quantified using two different methods, a mass gain approach and a thermal pyrolysis analysis.

3.5.1. Mass gain

To estimate the mass gain, the concrete slabs were weighted prior and following the 4-hour carbonation period. As well, the water present in the chamber was collected using paper towels. The CO_2 absorbed by the concrete was represented by the water collected added to net change in the mass of the slab as a function of the cement content. A minimum of three concrete samples were casted per test to calculate the standard deviation.

3.5.2. Thermal pyrolysis

The second method used to quantify the CO_2 content in the concrete specimens was via thermal pyrolysis as shown in Figure 3.7. Approximately 50 grams of each sample was placed in a crucible and burned in a Muffle Furnace (Thermo Scientific Lindberg Blue M Muffle Furnace) at 105 °C, 550 °C and 1000 °C respectively. The mass change between 550 °C and 1000 °C as a function of the weight of cement represents the carbon dioxide content.

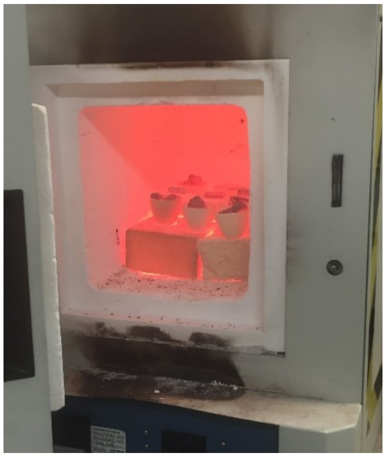


Figure 3.7: Muffle furnace used to perform thermal pyrolysis with caption taken at 1000 °C

3.6. Performance evaluation

3.6.1. Compressive strength

The 1-day and 28-day compressive strengths were tested using an MTS Sintech compression machine. The slabs were compressed along their weak axis as shown in Figure 3.8. The slab dimensions were measured using a digital vernier caliper.

Figure 3.8: Slabs compressed along weak axis using an MTS Sintech machine

3.6.2. Phenolphthalein

Phenolphthalein was sprayed on cut samples to determine depth of carbonation and as such, the extent of the reaction. A solution containing 5 g of phenolphthalein indicator per 100 mL deionized water was sprayed onto the sawn concrete surfaces, as shown in Figure 3.9, to determine the depth of carbonation. The concrete slabs were sawn using a Dewalt 575 7-1/4” circular saw. The solution turns dark pink in a highly alkaline (basic) medium and becomes colorless if the pH is reduced. Thus, a colorless region is indicative of the carbonation reaction. The carbonation depth can also be determined through this chemical, as in most cases, the phenolphthalein left an outer ring of colorless region and a darker pinkish core.

The concrete slabs were sawn following the compression and tested for both phenolphthalein and pH.

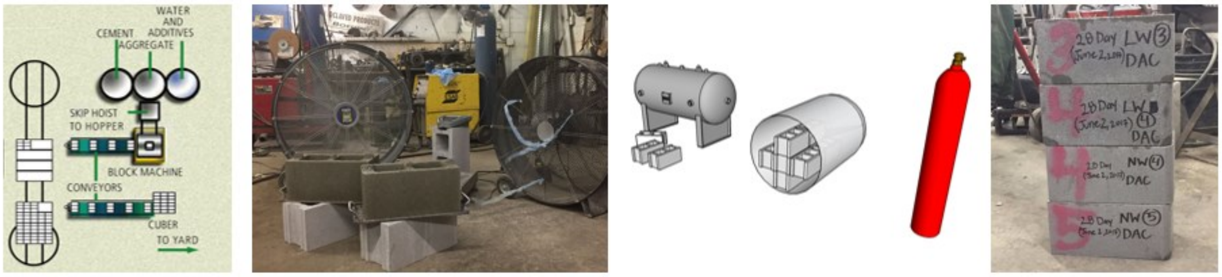
3.6.3. pH

An Extech pH meter (Extech PH110 model) was used to read the pH of the concrete at both the surface and the core of the slab. The pH meter was first calibrated in a solution with a pH = 10. A filter paper was placed against the sawn surface and deionized water was sprayed onto the paper. After a few minutes, the pH meter was placed against the filter paper to determine a pH reading.

Figure 3.9: Sawn surfaces of laboratory slabs for phenolphthalein and pH tests

Phase II: Pilot scale testing

The production of concrete on-site was automated. As such, the casting of the standard concrete masonry units followed Boehmers automated systems. The CMU's were then pre-conditioned, CO_2 cured and further hydrated as shown in Figure 3.10.



On-site mixing

Pilot scale pre-conditioning

Pilot scale early age vacuum carbonation curing

Subsequent hydration

Figure 3.10: Pilot scale step-by-step procedure of the concrete making process

3.7. Type of Concrete

The concrete slab casted in the laboratory followed Boehmers CMU mixture designs. As such, both the laboratory specimens and on-site specimen have the identical mixture proportions.

3.7.1. Normal weight concrete

The normal weight CMU followed the mixture design shown in table 3.7 and were casted at Boehmers facilities. The fine and coarse aggregates used on-site is granite. These aggregates were also pre-wetted to account for the water absorbed before usage.

Table 3.7: Normal weight concrete mixture

Normal Weight Concrete		
	CMU (g/unit)	Percent (%)
OPC	1737.0	9.7
Fine granite (0-2 mm)	10440.0	58.0
Coarse granite (2-5 mm)	5220.0	28.9
Water	603.0	3.4
Total sample	18000.0	100.0
w/c = 0.35		

3.7.2. Lightweight Concrete

The lightweight CMU followed the mixture design detailed in table 3.8 which is identical to the lightweight concrete slabs casted in the laboratory. The water absorbed by the expanded slag aggregate was also accounted for during the mixing process.

Table 3.8: Lightweight concrete mixture

Lightweight concrete		
	CMU (g/unit)	Percent (%)
OPC	1999.7	13.3
Sand (0-1.25 mm)	1332.9	8.9
Exp. Slag Agg. (0-6 mm)	10967.6	73.1
Water	699.8	4.7
Total sample	15000.0	100.0
w/c = 0.35		

3.8. On-site casting procedure

The blocks casted for the pilot scale were concrete masonry units of standard dimensions as shown in Figure 3.11 and prescribed in CSA A165.1.

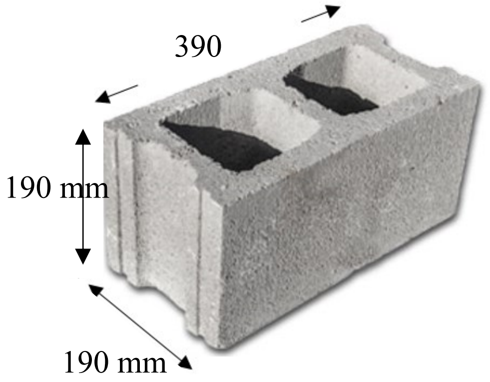


Figure 3.11: Standard concrete masonry unit dimensions casted on-site

3.9. Pilot scale pre-conditioning

Once casted, several CMU's were set aside for on-site prototype testing. They first underwent a pre-conditioning step to achieve the 50% water loss target. Fans were used (refer to Figure 3.10) to expedite the process. Both the mass monitoring method and the moisture meter method previously calibrated in the laboratory were used to track the water loss of the concrete blocks.

3.9.1. Mass monitoring

The plot of the water loss against time of the concrete blocks dried on-site is shown in Figure 3.12. The weights of the concrete blocks were recorded each hour.

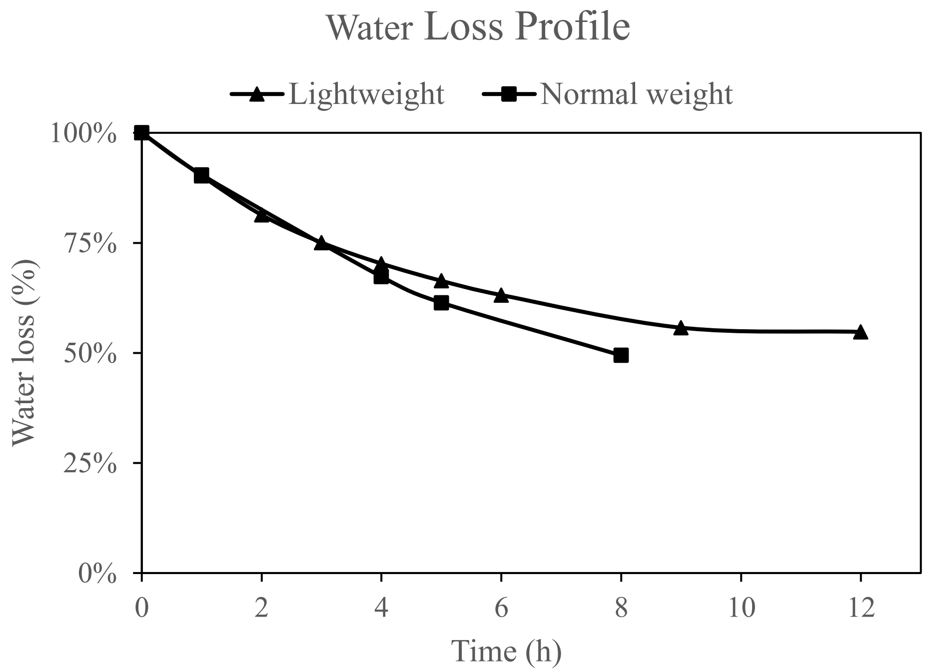


Figure 3.12: 50% water loss target as monitored on-site

3.9.2. Moisture meter

The moisture meter previously calibrated in the laboratory was also used to assess the water loss in the concrete blocks. Moisture meter readings were conducted at every hour until the water loss target was achieved.

3.10. Curing methods

Tables 3.9 and 3.10 list the details regarding the various curing methods adopted for the pilot scale. The carbonated and autoclave curing are currently being conducted at Boehmers. The low vacuum and low pressure (NLVP and LLVP) was added following the on-site testing as it was witnessed that creating a system that achieved high vacuum levels was somewhat challenging. Moreover, the on-site trials were important they demonstrated the potential to conduct early carbonation curing using a low vacuum pressure.

Table 3.9: Abbreviation used for different curing regimes for normal weight concrete

		Abbreviations used for various curing conditions	Batch	Vacuum kPa (psi)	Pressure kPa (psi)	Net range kPa (psi)
Carbonation curing	Pressurized carbonation	Carbonated	-	-	70 (10)	70 (10)
	Vacuum carbonation	**L**ow **V**acuum, near atmospheric **P**ressure	NLVP	-21 (-3)	3 (0.5)	24 (3.5)
Hydration curing	Hydrated References	Autoclave	-	-	-	-

Table 3.10: Abbreviation used for different curing regimes for lightweight concrete

		Abbreviations used for various curing conditions	Batch	Vacuum kPa (psi)	Pressure kPa (psi)	Net range kPa (psi)
Carbonation curing	Pressurized carbonation	Carbonated	-	-	70 (10)	70 (10)
	Vacuum carbonation	**L**ow **V**acuum, near atmospheric **P**ressure	LLVP	-21 (-3)	3 (0.5)	24 (3.5)
Hydration curing	Hydrated References	Autoclave	-	-	-	-

3.10.1. Hydration Curing

Traditionally, Boehmers used autoclaving as hydration curing of the CMU’s. This is a process whereby the concrete blocks are cured in pressure vessel 30.48 m (10 ft) long under high temperature and high pressure (177 °C and 827 kPa) as shown in Figure 3.13.

Figure 3.13: Autoclaves or pressure vessels traditionally used to cure the CMU's at Boehmers

3.10.2. Carbonation Curing

3.10.2.1. Pressure assisted carbonation curing

As autoclaving is slowly phasing out of concrete masonry industry, Boehmers is moving away from autoclave and towards carbon dioxide curing using a pressure of 70 kPa. Boehmers has installed a pressure tank containing pure carbon dioxide that feeds into the autoclave units (refer to Figure 3.14). As such, the CMU's no longer undergo high temperature and high pressure steam curing (autoclaving), but instead, pure CO_2 at 70 kPa is injected in the pressure vessels containing the concrete blocks.

Figure 3.14: Pure CO_2 pressure tank for the early carbonated curing process

3.10.2.2. Near ambient carbonation curing

Given that most concrete masonry block producers in Canada are not equipped with pressure vessels, a prototype system was developed to allow for on-site near ambient carbonation curing. Through the development of this enclosure, vacuum carbonation curing at near ambient pressure was possible. For confidentiality reasons, the details regarding the development of the enclosure cannot be revealed at this time. The system was first vacuumed to -21 kPa (- 3 psi) and a constant pressure of pure CO_2 gas at 3 kPa (0.5 psi) was applied for 10 hours. The pilot scale carbonation curing testing was carried out for a greater time span than the laboratory testing to account for the size effect between the slabs and the CMUs.

3.11. Quantification of carbon dioxide

The CO_2 uptake was calculated following the laboratory procedure described in section 3.5. through both the mass gain approach and thermal pyrolysis. In the latter case, the concrete masonry units were cut in the lab in order to conduct the furnace test.

3.12. Performance evaluation

3.12.1. Compressive strength

A sulfur capping was placed on the concrete masonry units prior to being tested for compressive strength to ensure uniformity of the distributed load. They were further tested for compressive strength at the Englobe Laboratory facilities in Kitchener following the CSA A165-14 and in accordance wit ASTM 140 as required in Section 9.1 of the CSA A 165.14 standard.

3.12.2. Phenolphthalein and pH

The concrete blocks were sawn as demonstrated in Figure 3.15 below and tested for phenolphthalein and pH as described in section 3.6.2. and 3.6.3. respectively.

Dimensions: 190 x 190 x 390 mm

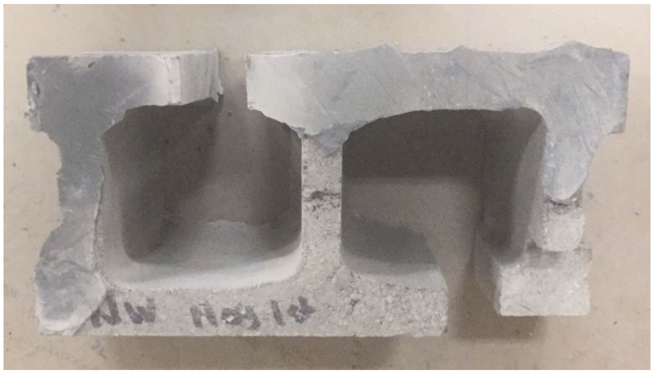


Figure 3.15: Sawn surfaces for phenolphthalein and pH tests

Chapter 4 - Results and Discussion

4.1 Effect of water content on degree of carbonation

As mentioned in the previous section, water loss was relative to the total water content of the concrete specimens, which included the mixture water and water absorbed by the aggregates. As such, the mixture water in a normal weight concrete slab was 19 g. The water absorption was 2% by mass of aggregates, thus amounting to 9.74 g. Consequently, the total water per slab was 28.74 grams as shown in table 4.2 below. The target water loss for the lightweight concrete was calculated in the same fashion, but water absorption by the expanded slag was 7%.

Table 4.1 tabulates various water loss targets tested prior to selecting the 50% water loss mark. These preliminary tests were conducted on normal weight concrete. All the samples were cured following the NHVP (high vacuum and above atmospheric pressure) carbonation curing method for 4 h.

From table 4.1 and Figure 4.1 it is clear that as the water loss target increased, the carbon uptake was slightly greater. It is important to notice the decline in carbon uptake at 60% water loss target. This is likely due to the length of pre-conditioning required to achieve 60% water loss. The samples dried for over 12 hours. As the drying took place, the water evaporation could have reduced the degree of hydration of the cement paste which resulted in a lower strength [37]. The highest 1 day compressive strength was found to be 23.05 MPa at the 50% water loss target. The decrease in compressive strength past 50% water loss could be an effect of over-drying (water starvation) of the samples. Furthermore, the specimens were pre-conditioned using a fan to expedite the process and this likely increased the moisture evaporation rate which could have led to plastic shrinkage cracking [37]. Following this preliminary testing, 50% water loss was found to be the most optimal point and was adopted for both normal weight and lightweight concrete.

Table 4.1: CO_2 uptake and strength for various water loss targets for normal weight concrete

Sample	Water loss achieved (%)	Carbon uptake (%)	1 day Strength (MPa)
NHVP-35	35	11.81 ± 0.49	21.73 ± 0.49
NHVP-40	40	12.95 ± 0.44	16.72 ± 1.03
NHVP-45	45	13.03 ± 0.08	21.88 ± 1.06
NHVP-50	50	14.07 ± 0.38	23.05 ± 1.95
NHVP-55	55	14.44 + 0.11	17.36 ± 1.00
NHVP-60	60	12.66 ± 0.15	16.44 ± 2.19

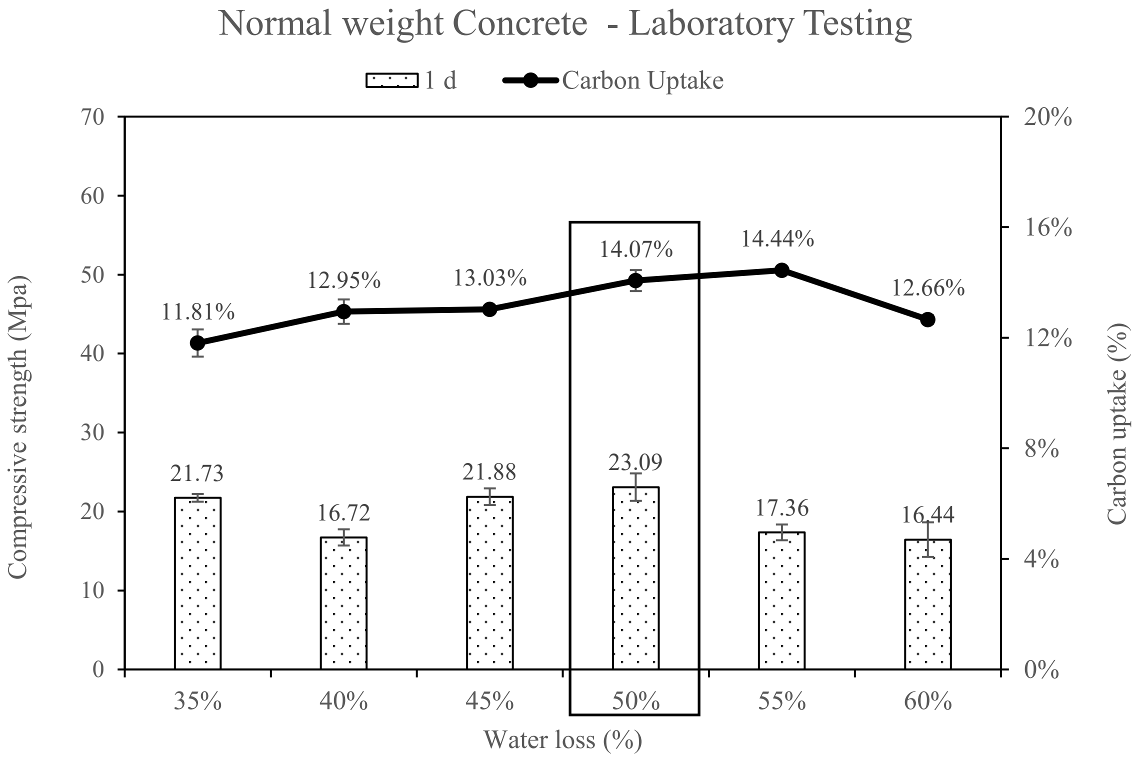


Figure 4.1: CO_2 uptake and 1 d strength for various water loss profiles tested with normal weight concrete

4.1.1. Water loss monitoring

Tables 4.2 and 4.3 compare both water loss methods for normal weight and lightweight respectively. The initial water mass at time 0 is the total water content prior to pre-conditioning as calculated in section 4.1.

It is important to note that the concrete units casted on site took far longer to achieve 50% water loss than the laboratory slabs. This is likely due to the difference in size. In the laboratory, the normal weight slabs took 2 hours to achieve 50% water loss while the lightweight samples took 4 hours. As for the site tests, the normal weight CMU took on average 8 hours to achieve their water loss target while the lightweight CMU pre-conditioned for almost 12 hours prior to carbonation. The moisture gun was calibrated using the laboratory slabs to moisture readings of 47.2% for a fresh normal weight samples and 52.2% for lightweight samples. At 50% water loss, the moisture readings were 24.6% and 17.9% respectively. The on-site specimens had similar moisture readings. Once on-site, the moisture gun was especially useful as the mass monitoring approach using a balance is highly impractical at such large-scale production (20,000 blocks/day). Overall, the lightweight samples did have a slightly higher initial moisture reading as their initial total water content was more significant than the normal weight concrete.

Table 4.2: Comparison of water loss monitoring for normal weight concrete

Normal weight concrete			
Laboratory Testing	Pre-conditioning Time (h)	Mass of water (g)	Moisture meter (%)
	0	28.74	47.2 ± 1.00
	2	14.37	24.6 ± 0.79
Site Testing	0	916.2	49.6 ± 0.90
	8	458.1	23.6 ± 0.66

Table 4.3: Comparison of water loss monitoring for lightweight concrete

Lightweight concrete			
Laboratory Testing	Pre-conditioning Time (h)	Mass of water (g)	Moisture meter (%)
	0	52.30	52.2 ± 1.50
	4	26.15	17.9 ± 1.01
Site Testing	0	1494.19	52.9 ± 0.64
	12	747.10	19.5 ± 1.04

4.2. CO_2 uptake

4.2.1. Mass gain method

In the case of normal weight concrete (Table 4.4), the samples that were cured using vacuum carbonation at near ambient condition (NHVP, NLVP) had a slightly lower carbon uptake than the specimens cured at a high CO_2 pressure (NP). Vacuum carbonation curing at ambient condition yielded an uptake of 12-14% in normal weight concrete. It was in the same order of magnitude (13-16%) for high pressure carbonation curing. Furthermore, the NLVP sample which was cured using a lower vacuum and with lower CO_2 pressure had a similar uptake to the NHVP sample. The pilot scale testing conducted on-site also yielded optimistic results with the NLVP specimen giving a carbon uptake of 17%, which was 1% higher than the carbonated sample. This is an important finding as upscaling a system to achieve low vacuum (NLVP) reduces the cost significantly as compared to high vacuum (NHVP).

In the case of lightweight concrete, the carbon uptake achieved with low vacuum (LLVP) was 4.38% less than the high vacuum specimen (LHVP). This can be explained by an inconsistent control of the vacuum and carbonation pressure during the curing period. Although the carbon uptake is reduced in the case of the LLVP sample, it is still within the range of the LHVP and LP specimens. Similarly, the pilot scale testing for lightweight concrete (LLVP) yielded a CO_2 uptake of 15% while the carbonated sample reached 16%. In general, lightweight concrete yields a higher net mass uptake of CO_2 than normal weight concrete. This is justified by a greater amount of CO_2 mineralization due to the lightweight mix design's higher cement content than the normal weight concrete.

Vacuum carbonation seems to be a viable alternative. Moreover, it was demonstrated through samples NLVP and LLVP that it is not necessary to cure at high vacuum or a high CO_2 pressure to achieve substantial CO_2 uptake results.

Table 4.4: Comparison of CO_2 uptake using mass gain and thermal pyrolysis on normal weight concrete

Normal weight Concrete			
Specimen		Mass gain method (%)	Thermal pyrolysis (%)
Laboratory Testing	NHVP	14.07	12.13
	NLVP	14.70	12.02
	NP	16.18	13.24
	NH	-	0.00
Site Testing	NLVP	17.09	15.77
	Carbonated	16.50	-

Table 4.5: Comparison of CO_2 uptake using mass gain and thermal pyrolysis on lightweight concrete

Lightweight Concrete			
Specimen		Mass gain method (%)	Thermal pyrolysis (%)
Laboratory Testing	LHVP	18.97	18.11
	LLVP	14.59	13.84
	LP	19.69	18.81
	LH	-	0.00
Site Testing	LLVP	15.70	13.98
	Carbonated	16.20	-

4.2.2. Thermal pyrolysis

The carbon content obtained through thermal pyrolysis was slightly below the carbon uptake values calculated by the mass gain approach. This is explained by the fact that the carbon dioxide in the low-crystalline $CaCO_3$ is being released between 415 °C and 565 °C while between 565 °C and 745 °C, the CO_2 in the high-crystalline $CaCO_3$ is being lost [32]. The thermal pyrolysis test underestimates the actual amount of carbon dioxide by assuming the weight loss between 550 °C and 1000 °C. Future research should consider the mass loss between 415 °C and 1000 °C as being more representative of the CO_2 content [19, 32].

Tables 4.6 represents the tabulated raw data collected during the thermal pyrolysis test for normal weight concrete. It shows the weight losses between the three holding temperatures of 105 °C, 550 °C and 1000 °C, with weight differentials in between representing the amount of free water, bound water, and carbon dioxide, respectively. As expected, the hydrated laboratory samples (NH) exhibited a greater free water and bound water content than the carbonated specimens (NHVP, NLVP and NP), which all indicated a more significant $CaCO_3$ content. Thus, in the case of normal weight concrete, it can be concluded that more carbonates were produced throughout the carbonation reaction as hydration products were being consumed.

Table 4.6: Weight loss data collected from the furnace test for normal weight concrete

Thermal Pyrolysis Data - Normal Weight Concrete											
Specimen		**Weight (g)**				**Weight loss at 105°C**		**Weight loss between 105°C - 550°C**		**Weight loss between 550°C - 1000°C**	
		Initial	**105°C**	**550°C**	**1000°C**	**(g)**	**(%)**	**(g)**	**(%)**	**(g)**	**(%)**
Laboratory	NHVP	38.42	38.27	37.95	37.29	0.15	0.39	0.32	0.83	0.66	1.72
	NLVP	48.01	47.71	47.32	46.5	0.3	0.62	0.39	0.81	0.82	1.71
	NP	29.57	29.46	29.23	28.69	0.11	0.37	0.23	0.78	0.54	1.83
	NH	42.46	42.03	41.59	41.36	0.43	1.01	0.44	1.04	0.23	0.54
Site	NLVP	72.37	71.83	70.11	49.80	0.54	0.75	1.72	2.38	20.31	28.06

Table 4.7 shows the carbon content calculated through thermal pyrolysis. The CO_2 content shown above are solely due to the carbonation reaction. The small amount of carbon present in the cement (control sample) was deducted from the carbonated specimens. The carbon content of the low vacuum low pressure laboratory specimen (NLVP) was 12.02% and the pilot scale specimen (NLVP) was almost 16%.

Table 4.7: Quantification of CO_2 uptake from thermal pyrolysis test for normal weight concrete

Thermal Pyrolysis - Normal Weight Concrete								
Specimen		**Weight loss between 550°C - 1000°C**			**Full weight of specimen**	**Cement content**	**Net CO_2 content**	
		(g)	**(%)**	**(Δ%) with NH**	**(g)**	**(g)**	**(g)**	**(%)**
Laboratory	NHVP	0.66	1.72	1.18	560	54.32	6.59	12.13
	NLVP	0.82	1.71	1.17	560	54.32	6.53	12.02
	NP	0.54	1.83	1.28	560	54.32	7.19	13.24
	NH	0.23	0.54	0.00	560	54.32	0.00	0.00
Site	NLVP	20.31	28.06	1.53	18170	1762.49	278.00	15.77

Table 4.8 summarizes the thermal pyrolysis results for the lightweight concrete specimens. Unlike normal weight concrete, the lightweight concrete indicated dissimilar chemical decomposition patterns. It is interesting to note that the vacuum carbonated samples (LHVP, LLVP) had a higher free water content at 1.34% and 2.28% (weight loss at 105 °C) than the control sample at 1.13% (LH). It seems the vacuum led to this outcome. Moreover, the carbonated specimens revealed a similar or higher bound water content (weight loss between 105 °C and 550 °C) as compared to the hydrated reference at 2.62%. This is indicative of a significant amount of hydration products within the carbonated lightweight specimens, and particularly, the presence of C-S-H gel [34, 39]. As expected, carbonates were present in large amounts in the CO_2 cured specimens (LHVP, LLVP and LP). Overall, it seems that, respective to lightweight concrete, the carbonation reaction is yielding significant amounts of both hydration (C-S-H) and carbonation ($CaCO_3$) products [34].

Table 4.8: Weight loss data collected from the furnace test for lightweight concrete

Thermal Pyrolysis Raw Data - Lightweight Concrete											
Specimen		**Weight (g)**				**Weight loss at 105°C**		**Weight loss between 105°C - 550°C**		**Weight loss between 550°C - 1000°C**	
		Initial	**105°C**	**550°C**	**1000°C**	**(g)**	**(%)**	**(g)**	**(%)**	**(g)**	**(%)**
Laboratory	LHVP	52.28	51.58	50.38	48.7	0.70	1.34	1.20	2.30	1.68	3.21
	LLVP	35.15	34.35	32.96	32.03	0.80	2.28	1.39	3.95	0.93	2.65
	LP	39.32	38.97	37.5	36.20	0.35	0.89	1.47	3.74	1.30	3.31
	LH	39.76	39.31	38.27	37.95	0.45	1.13	1.04	2.62	0.32	0.80
Site	LLVP	45.22	44.7	43.88	40.83	0.52	1.15	0.82	1.81	3.05	6.74

Table 4.9 below shows the carbon content of each specimen. Once again, the pre-existing carbonates in the cement (control sample) were subtracted from the carbonated specimens to achieve the actual (net) CO_2 content present in the concrete due to the carbonation curing reaction. The low vacuum laboratory and pilot scale specimens yielded a carbon content of 13.84% and 13.98% respectively.

Table 4.9: Quantification of CO_2 uptake from thermal pyrolysis test for lightweight concrete

Thermal Pyrolysis - Lightweight Concrete								
Specimen		**Weight loss between 550°C - 1000°C**			**Full weight of specimen**	**Cement Content**	**Net CO_2 content**	
		(g)	**(%)**	**(Δ%) with LH**	**(g)**	**(g)**	**(g)**	**(%)**
Laboratory	LHVP	1.68	3.21	2.41	525	69.83	12.65	18.11
	LLVP	0.93	2.65	1.84	525	69.83	9.67	13.84
	LP	1.30	3.31	2.50	525	69.83	13.13	18.81
	LH	0.32	0.80	0.00	525	69.83	0.00	0.00
Site	LLVP	3.05	6.74	1.86	14874	1978.24	276.66	13.98

4.3. Compressive strength

4.3.1. Laboratory testing

The 1 day and 28-day compressive strengths of the four laboratory specimen types for normal weight concrete are shown in Figure 4.2. Early carbonation curing of concrete does accelerate the hydration process yielding the 28-day hydrated strength in merely 1 day. In general, the 1day early carbonated specimens (NHVP, NLVP and NP) yielded a strength beyond 160% that of the 1 day hydrated reference sample. The 28-day samples were subsequently hydrated in a sealed condition with continuous water spraying to restore water lost during preconditioning and curing. The carbonated samples demonstrated a strength gain between 10% - 15% after 28 days of subsequent hydration. The control samples (NH) witnessed a x 1.5 gain in strength between the 1-day and 28-day mark. This once again exemplifies carbonation curing's effectiveness in rapid strength development.

It is interesting to note that early carbonation curing not only accelerates the hydration curing process, but also seemingly increases the ultimate strength of the normal weight concrete. The 28-day strength of the carbonated samples (NHVP, NLVP, NP) were significantly higher reaching values of up to 27.93 MPa versus 22.29 MPa for the control benchmark batch. This represents a 25% top-off in compressive strength.

The vacuum carbonated specimens had a comparable strength to the pressurized carbonated concrete, thus making it a viable alternative to pressurized carbonation curing based on the premises of comparable CO_2 uptakes and more resilient strength performance.

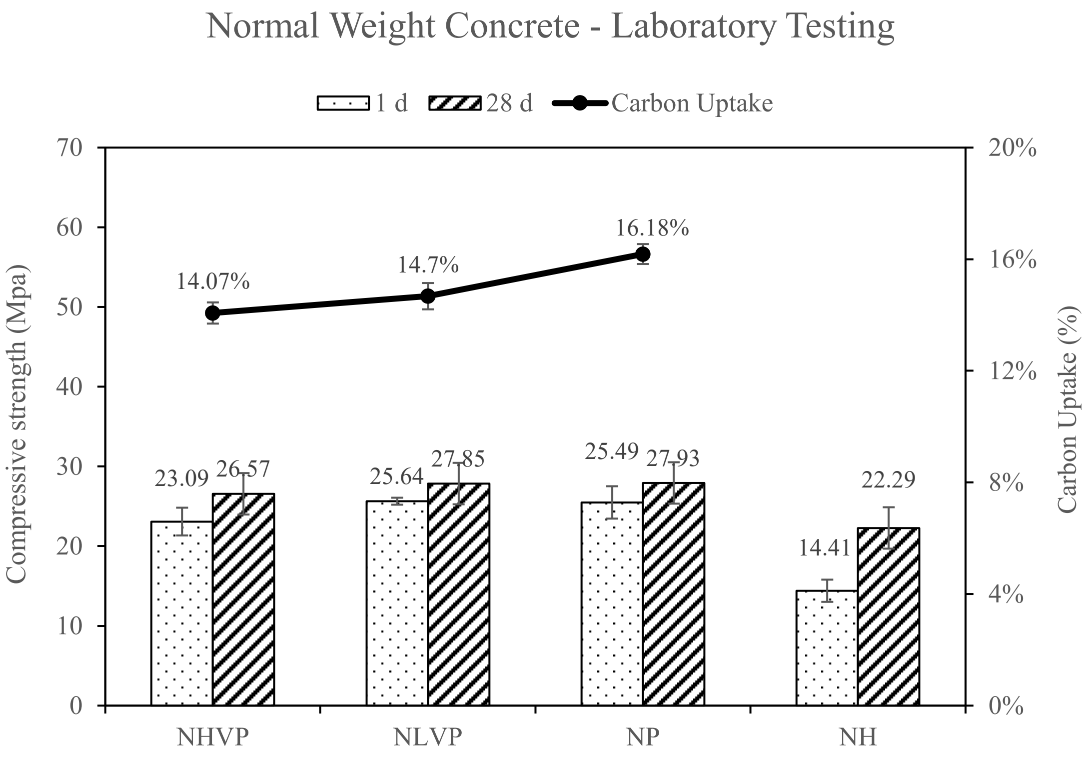


Figure 4.2: 1 d, 28 d strength and CO_2 uptake for the laboratory testing of normal weight concrete

Figure 4.3 demonstrates the 1 day and 28-day strengths for the different lightweight concrete batches. The 1 day strength for the carbonated samples (LHVP, LLVP and LP) were comparable to the 1 day hydrated reference. However, carbonation curing of lightweight concrete did not seem to accelerate the early age strength as no surge in strength is visible after 1 day when compared to the control sample. Moreover, the strength gain following subsequent hydration of the carbonated samples is minimal. As expected, the 28-day hydrated reference had yielded a strength of 24.70 MPa which is more than double that of the 1 day specimen at 11.18 MPa. Overall, early age carbonation curing of lightweight concrete seems to obstruct the development of strength beyond the 1-day values. The displayed maximum 28-day hydration strength of 24.70 MPa could not be achieved by any of the carbonated batches, even after being subject to subsequent hydration.

This phenomenon is not yet well understood. Nonetheless, the following hypotheses can be inferred:

1. This is likely due to the aggregates (the expanded slag) as this strength related problem is specific to lightweight concrete and not normal weight concrete.

2. It is known that the carbonation reaction leads to an almost instantaneous drop of the pH from 11 to 8 [39]. This low pH environment could be activating a reaction between the slag and the CO_2.
3. The early age carbonation curing reaction could be generating a greater volume of interfacial transition zones (ITZ) which would explain the lower strength values.
4. The strength could be governed by the inherently porous aggregates of the lightweight concrete

It is clear that a carbonation curing reaction is occurring as the lightweight specimens are yielding very high CO_2 uptakes. However, strength gain is being limited. Further research is required to properly determine the root cause as to why the 1 day carbonated lightweight concrete does not demonstrate an accelerated strength gain and why subsequent 28-day hydration does not yield strength levels comparable to the ultimate strength of the material.

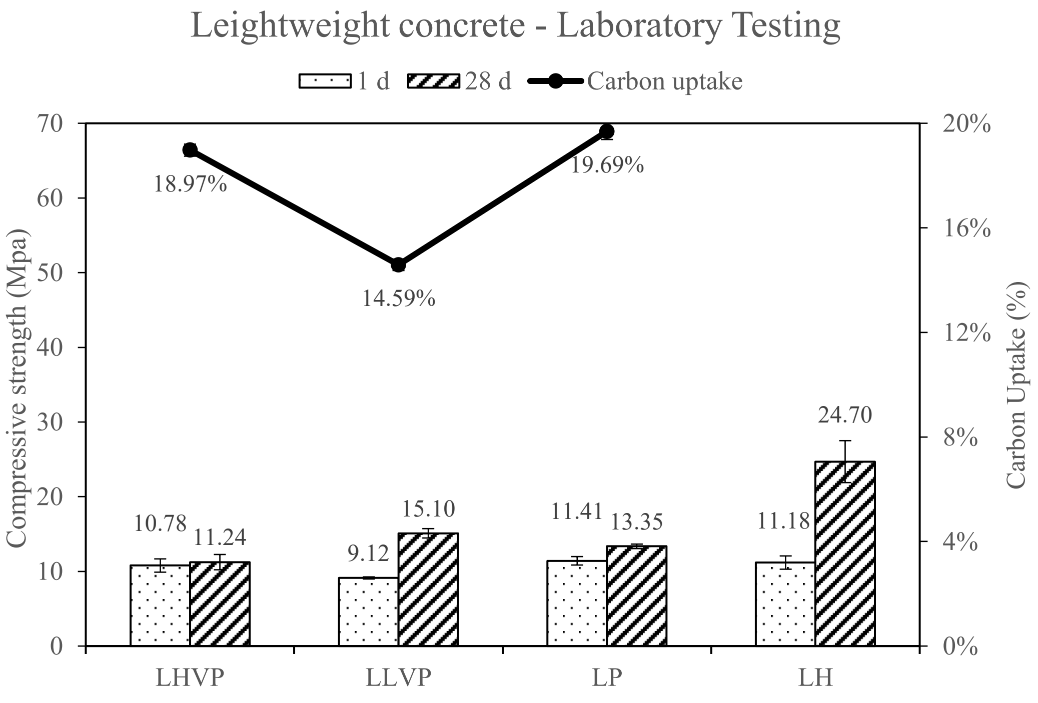


Figure 4.3: 1 d, 28 d strength and CO_2 uptake for the laboratory testing of lightweight concrete

Figure 4.4 demonstrates the different hydration curing methods that were assessed to determine the most optimal compressive strength for normal weight concrete. On average, all three methods yielded similar 28-day strengths. The samples submerged in 3% CH solution yielded a slightly higher increase in strength although not significant enough to conclude that this method is the most effective. The strengths obtained through sealed condition and 100% humidity room were near identical. This is expected as the specimens that were contained in a sealed environment remained hydrated through constant water spraying throughout the 28-day hardening period.

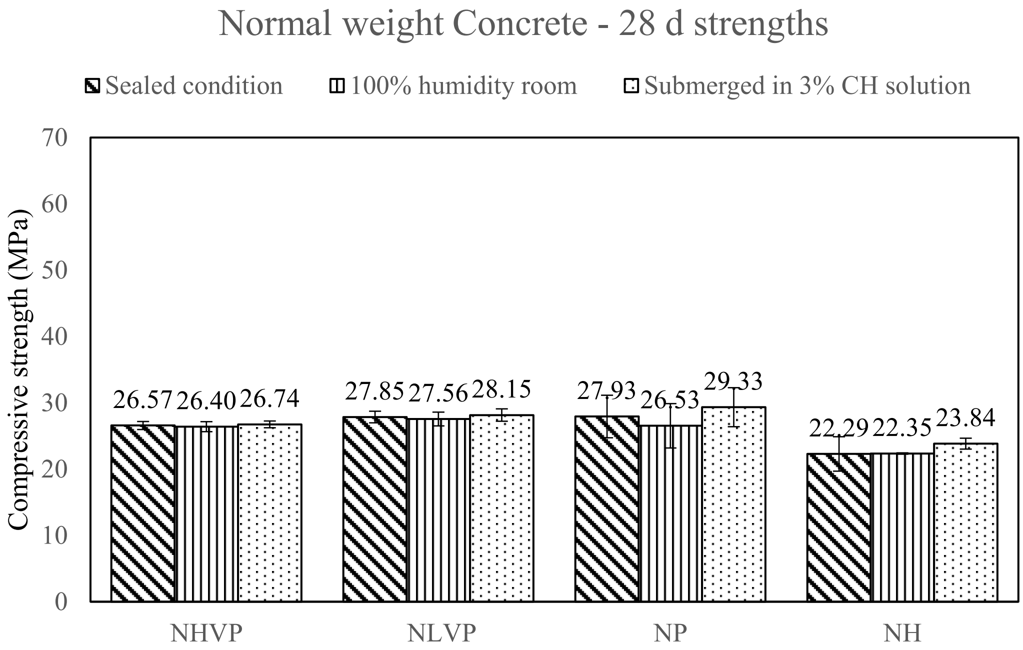


Figure 4.4: 28 d strength comparison of various subsequent hydration methods for normal weight concrete

Figure 4.5 shows the compressive strength of the different subsequent hydration curing methods with respect to the lightweight concrete specimens. Once again, these three different hydration regimes generated comparable strengths. Overall, the hydration in a sealed environment is the method that most closely relates to what is conducted on-site. The samples once cured are packaged and stored in a lot until they are sold and shipped.

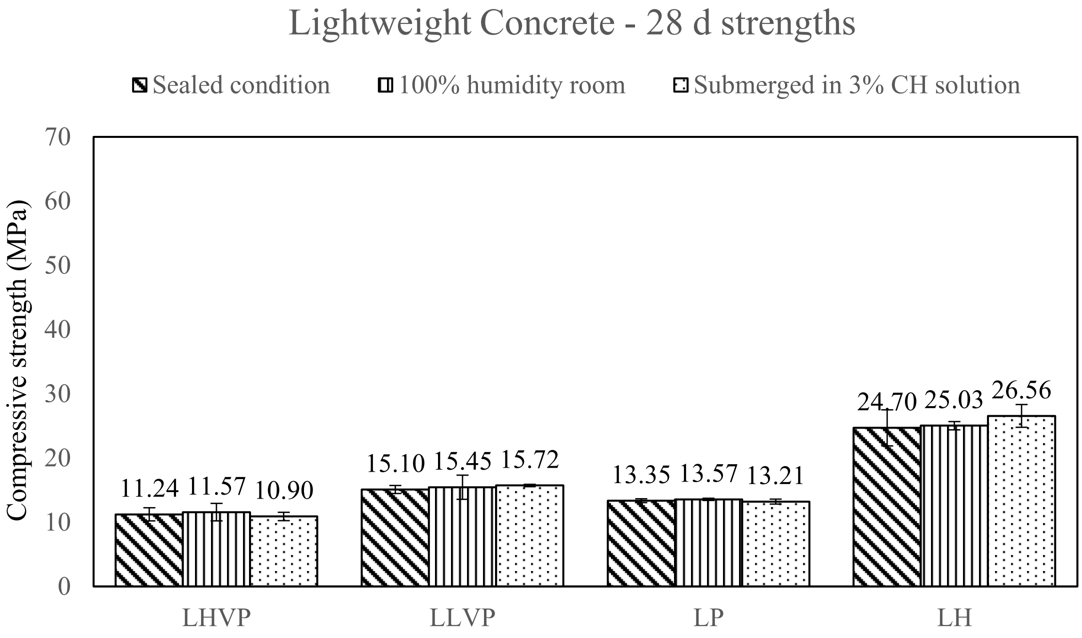


Figure 4.5: 28 d strength comparison of various subsequent hydration methods for lightweight concrete

4.3.2. On-site testing

Figure 4.6 shows the carbon uptake and compressive strength values for the pilot scale testing with full size CMU blocks. The low vacuum (NLVP) curing technique was developed on-site as an alternative to pressurized carbonation curing with the goal of making this technology accessible to all masonry producers including those not equipped with pressure vessels. An enclosure was developed to cure the masonry blocks at low vacuum and low pressure (NLVP). The carbonated and autoclaved data as shown in Figure 4.6 were used as received form full industrial scale testing. It is interesting to note the similarities in carbon uptake and compressive strength between both the NLVP and carbonated concrete blocks.

The laboratory findings are reciprocal to pilot scale testing. An accelerated strength gain was visible for the carbonated concrete units compared to the autoclave reference.

Vacuum carbonation curing of concrete at near-ambient pressure is as effective as carbonation curing at high pressures. NLVP demonstrates all the benefits of early age carbonation curing while being pressure independent. Thus, the development of this enclosure is key in ensuring feasibility of this system amongst most block producers in Canada whom are not equipped with pressure vessels.

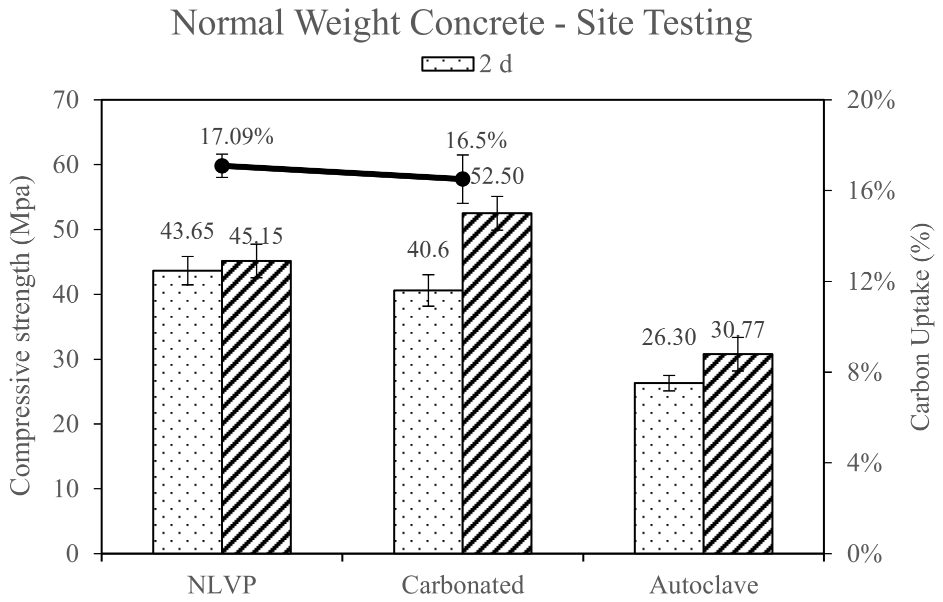


Figure 4.7: 1 d, 28 d strength and CO_2 uptake for pilot scale testing of normal weight concrete

The carbon uptake and compressive stregnth results for lightweight concrete are detailed in Figure 4.7. The compressive strength of the low vacuum concrete units (LLVP) are slightly higher than the carbonated specimens. As revealed with the lightweight laboratory samples, the carbonated site testing (LLVP, carbonated) are not indicative of an accelerated early age strength gain when compared to the autoclaved units.

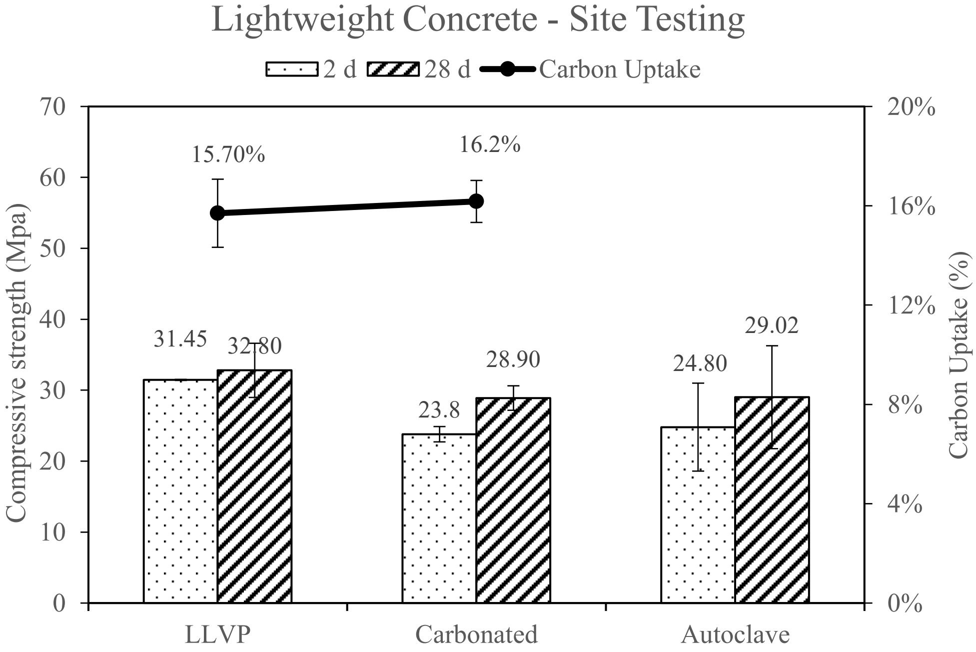


Figure 4.6: 1 d, 28 d strengths and CO_2 uptake for pilot scale testing of lightweight concrete

4.4. Phenolphthalein, pH and carbonation depth

4.4.1. Laboratory results

4.4.1.1. 1 day results

The phenolphthalein, pH and carbonation depth of all laboratory specimens at 1 day are shown in Figure 4.8. The hydrated reference for both lightweight and normal weight concrete turned pink in the presence of phenolphthalein as they contain CH and had a pH ranging between 12-13 as expected. The lightweight samples LP and LHVP showed a very light shade of pink. This is indicative of carbonation taking place throughout the full depth of the laboratory specimen. The pH ranged between 9.7 and 10. Specimen LLVP had a distinct carbonated region (11 mm inwards from the edge). The pH of the carbonated area was 10.64 while the pH in the core was 11.78. The distinction in carbonation between the lightweight samples is explained by the fact that the LLVP sample was carbonated at a significantly lower pressure (0.5 psi as compared to 14.5 psi and 2 psi). This could be a possible reason for sample LLVP not being fully carbonated for the entirety of its depth.

The carbonated normal weight concrete samples (NP, NHVP, NLVP) showed a carbonated depth ranging between 5-10 mm from the edge. The normal weight concrete mixture is less porous than the lightweight concrete mixture which would explain why the normal weight concrete samples were not carbonated throughout the full depth of the specimen. It is also interesting to note that the vacuum carbonated samples seemed to yield a larger carbonation depth than pressurized carbonation cured specimen. Moreover, as it was seen with the site specimens, the size of the concrete samples largely affects the carbonation depth.

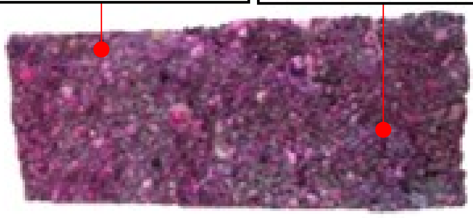
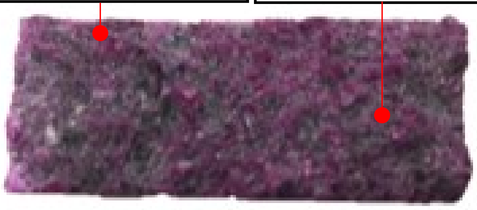
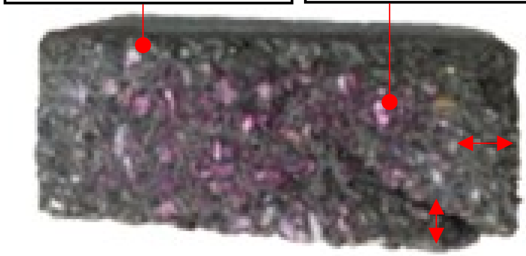
Lightweight concrete – Laboratory Testing	**Normal weight concrete – Laboratory Testing**
Hydrated specimen (LH) Edge: 12.19 ± 0.05 Core: 11.76 ± 0.06 	Hydrated specimen (NH) Edge: 13.06 ± 0.06 Core: 11.90 ± 0.09 
Pressurized specimen (LP) Edge: 9.85 ± 0.10 Core: 9.73 ± 0.09 	Pressurized specimen (NP) Edge: 9.78 ± 0.12 Core: 10.63 ± 0.05  Depth: 4-6 mm
High Vacuum, above atmospheric Pressure specimen (LHVP) Edge: 9.81 ± 0.18 Core: 10.08 ± 0.04 	High Vacuum, above atmospheric Pressure specimen (NHVP) Edge: 9.38 ± 0.13 Core: 10.41 ± 0.07  Depth: 6-11 mm
Low Vacuum, near atmospheric Pressure specimen (LLVP) Edge: 10.64 ± 0.22 Core: 11.78 ± 0.25  Depth: 5-11 mm	Low Vacuum, near atmospheric Pressure specimen (NLVP) Edge: 10.45 ± 0.06 Core: 11.54 ± 0.10  Depth: 5-11 mm

Figure 4.8: Phenolphtalein, pH and carbonation depth of 1 day laboratory specimens

4.4.1.2. 28-day results

The phenolphthalein and pH were also tested on all laboratory specimens following the 28-day subsequent hydration as shown in Figure 4.9.

While the phenolphthalein is not always representative in the pictures above, a clear rebound in the pH was witnessed following 28-day subsequent hydration. The pH of the lightweight carbonated samples ranged between 10.5 and 11.8. This is more than 1 point higher on the pH scale as compared to the 1 day lightweight concrete samples (refer to Figure 4.8). The normal weight concrete samples demonstrated a similar regain in pH following 28-day subsequent hydration, reaching a pH between 10.5 and11.5.

Concrete has a highly alkaline pore solution (pH above 12). This high pH environment acts as a protective barrier against the corrosion of steel rebars [39]. While this is not a major concern for most masonry products, this rise in pH after 28-day subsequent hydration presents a promising argument for precast products that do incorporate steel reinforcement, concrete pipes for example.

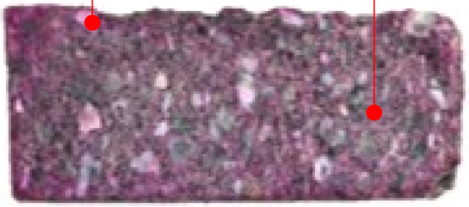
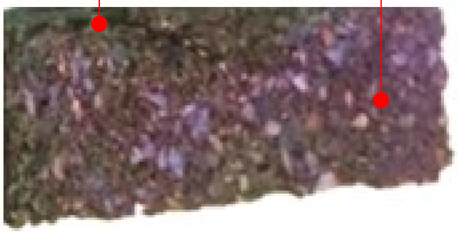
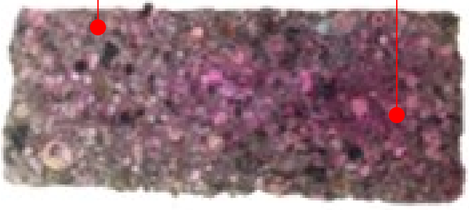
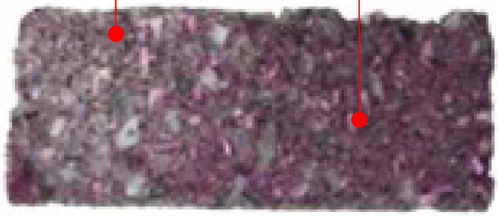
Lightweight concrete – Laboratory Testing	Normal weight concrete – Laboratory Testing
Hydrated specimen (LH) Edge: 12.19 ± 0.06 Core: 12.93 ± 0.06 	Hydrated specimen (NH) Edge: 12.29 ± 0.06 Core: 12.57 ± 0.09 
Pressurized specimen (LP) Edge: 10.61 ± 0.13 Core: 11.87 ± 0.04 	Pressurized specimen (NP) Edge: 10.61 ± 0.19 Core: 11.10 ± 0.07 
High Vacuum, above atmospheric Pressure specimen (LHVP) Edge: 10.56 ± 0.05 Core: 10.78 ± 0.27 	High Vacuum, above atmospheric Pressure specimen (NHVP) Edge: 10.52 ± 0.14 Core: 11.52 ± 0.42 
Low Vacuum, near atmospheric Pressure specimen (LLVP) Edge: 11.22 ± 0.29 Core: 12.24 ± 0.02 	Low Vacuum, near atmospheric Pressure specimen (NLVP) Edge: 11.17 ± 0.06 Core: 11.64 ± 0.04 

Figure 4.9: Phenolphthalein and pH of 28-day laboratory specimens

4.4.2. Pilot scale testing

4.4.2.1. 3 day results

The phenolphthalein and pH was tested on the CMU blocks produced on-site as shown in Figure 4.10. The carbonation depth is not as defined in the lightweight sawn surface compared to the normal weight concrete. Also, the core of the lightweight sample had a lighter pink color than the normal weight concrete. This suggests that carbonation did progress deep into the core of the lightweight sample. The pH ranged between 10.6 and 11.4. As mentioned in section 4.4.1.1. the pilot scale lightweight concrete blocks were not colorless, as observed for the laboratory sample. This could be due to the difference in size between both specimens or the fact that the on-site blocks were tested at a later age, giving rise to pH increase due to the continued hydration of cement. The normal weight concrete had a pH between 10.6 and 11.5 and demonstrated a visible carbonated region.

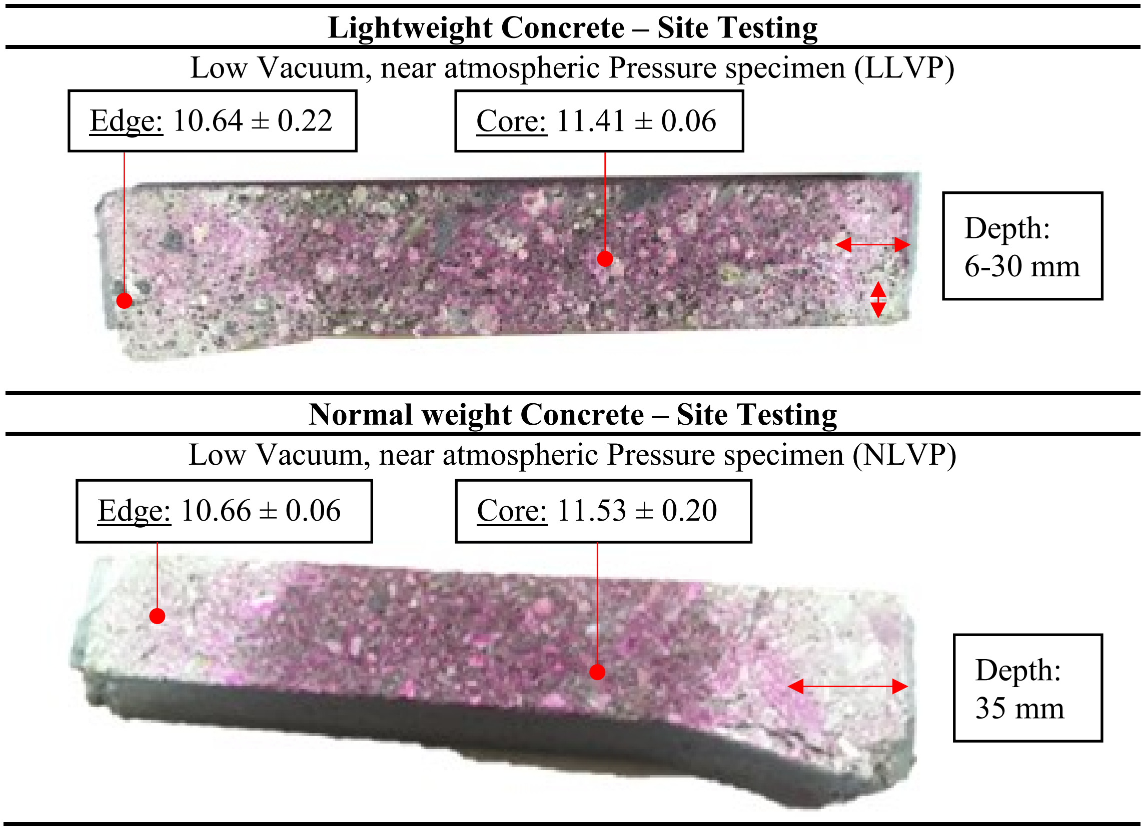


Figure 4.10: Phenolphtalein, pH and carbonation depth of 1 day site specimens

Chapter 5 - Conclusion and future work

5.1. Conclusions

The development of vacuum carbonation was successfully attempted by this thesis work, which had the primary intention of enabling the CO_2 curing of concrete at near-ambient pressures. In principle, this should facilitate the adoption of carbonation curing by the precast industry, since the presented methodology can be rather easily implemented within conventional steam curing processes, without incurring major modifications. The majority of masonry producers in Canada do not employ pressure vessels. Thus, to feasibly deploy carbonation curing, it became imperative that a pressure independent system be developed to increase the marketability of this approach.

Both normal weight and lightweight concrete were assessed for the laboratory scale and pilot scale testing portions of this study. Various net pressures were tested for the devised vacuum carbonation curing technique, which was compared to pressurized CO_2 curing at 100 kPa (14.5 psi) for laboratory tests and 70 kPa (10 psi) for the pilot tests. Hydrated specimens serving as the control reference batch were also tested and compared to all carbonated batches. The following main conclusions were drawn:

1. A pre-conditioning (drying) step was crucial for freeing spaces to promote gas penetration within concrete and maximise CO_2 uptake. The most optimal water loss was found to be 50% of the total water content of a specimen.

2. With respect to normal weight concrete, it was proven that vacuum carbonation curing at near-ambient conditions with an overall pressure of 38 kPa (specimen NLVP) can viably replace pressurized carbonation curing (specimen NP), based on results pertaining to carbon uptake and compressive strength. The average CO_2 storage potential, expressed as a fraction of cement content, was 14.7% for the laboratory specimens and 17.09% for the pilot specimens. This is equivalent to 301.21 g of sequestered carbon dioxide per masonry unit. The 1 day and 28-day strength values for the laboratory NLVP sample were 25.64 MPa and 27.85 MPa respectively. These results were similar to specimen processed under pressurized carbonation at 100 kPa (NP). An accelerated early age strength gain was also

visible as the hydrated reference reached a strength of 14.41 MPa after 1-day and 22.29 MPa after 28 days of hydration.

The pilot tests displayed the same behaviour. The 1 day and 28-day compressive strength of blocks processed via the developed enclosure (specimen NLVP) were 43.65 MPa and 45.1 MPa, respectively, while the control samples (autoclaved concrete units) only reached strength of 26.3 MPa and 30.77 MPa, respectively.

3. Results for lightweight concrete were not as conclusive as ones displayed by the normal weight concrete. Vacuum carbonation curing at ambient pressure (specimen LLVP) obtained an average CO_2 uptake of 14.59% for the laboratory specimens and 15.70% for the pilot specimens. This represented a carbon storage capacity of 310.58 g per lightweight masonry unit. While promising for CO_2 utilisation, the carbonation of lightweight concrete did not prove as effective in accelerating or increasing the strength potential. The 1-day carbonated strength values were comparable to the 1-day hydrated reference vales, ranging between 9.12 and 11.18 MPa. Moreover, following 28-day subsequent hydration, the LLVP samples achieved an average strength of 15.16 MPa whereas the control specimen reached 24.70 MPa.

   The pilot equivalent tests yielded 1-day and 28-day strength values of 31.45 MPa and 32.80 MPa. On the other hand, the 1 day and 28-day compressive strengths for the autoclave hydrated reference blocks were 24.8 MPa and 29.02 MPa. Although an accelerated early age strength gain was not plainly noticeable for the lightweight concrete, vacuum carbonation curing at ambient pressure conditions still presents a more practical alternative to CO_2 curing at elevated pressures. Strength results were comparable and well above the minimum standard requirements.

4. Phenolphthalein and pH measurements demonstrated that while early age carbonation curing leads to an immediate reduction in alkalinity, 28 days of subsequent hydration compensated for this dropin pH by an average 1 point increase on the pH scale. This presents promise to extending the applicability of carbonation curing to steel reinforced precast products.

5.2. Future work

Further research pertaining specifically to lightweight concrete is necessary to better understand what prohibits achieving an accelerated strength gain following carbonation, an observation that was consistently made for normal weight concrete. Below is a list of possible further investigations:

1. Further testing should be conducted on the initial curing step. The lightweight concrete could be experiencing water starvation as the 50% pre-conditioning level may be too high.
2. The use of a fan to expedite the drying process may be increasing the rate of evaporation of the moisture content which may need to be controlled as it could result in drying shrinkage and cracking of the specimens
3. Scanning electron microscopy (SEM) analysis would be useful to draw conclusions regarding the ITZ and highlighting the difference between the lightweight and normal weight specimens. The features and depth of the ITZ could relate to the interfacial bonding between the cement paste and aggregates, and therefore possibly explain why lightweight concrete does not display improvements in early age strength.
4. A more thorough examination of the expanded slag aggregates is required, specifically their interaction with water and CO_2.
5. Creating a system that uses flue gas as opposed to pure CO_2 could further reduce the costs of implementation. However, achieving similar CO_2 uptakes might be challenging as flue gas only contains 10-25% CO_2.
6. Developing a continuous vacuum carbonation curing technique (or dynamic system) could potentially increase the CO_2 uptake capacity per concrete block. Water is released throughout the carbonation reaction and some of it accumulates in the concrete pores. In fact, following curing, the concrete has noticeable water marks on the surface. This water is believed to block the pores and likely prevent further CO_2 from permeating into the concrete. As such, creating a dynamic vacuum carbonation system could alleviate pore blockage and allow for increased CO_2 penetration within the concrete pores.

References

[1] P. S. Taylor. (2016, 6 June). *Why Canada's cement industry is crumbling Climate change rules and new competition are creating big problems for Canada's cement industry*. Available: http://www.macleans.ca/economy/business/canadas-cement-industry-is-crumbling/

[2] (2017). *Environment and Climate Change Canada (2017) Canadian Environmental Sustainability Indicators: Greenhouse Gas Emissions*. Available: : www.ec.gc.ca/indicateurs-indicators/default.asp?lang=En&n=FBF8455E-1.

[3] Lafarge. (2017, 7 June). *All about Cement: Manufacturing Process*. Available: http://www.lafarge.com.ng/wps/portal/ng/2_2_1-Manufacturing_process#editoEncartVide0000000000019050

[4] C. Workman. (2016, 6 June). *Government of Canada Announces Pan-Canadian Pricing on Carbon Pollution*. Available: http://news.gc.ca/web/article-en.do?nid=1132149

[5] J. F. Young, R. L. Berger, and J. Breese, "ACCELERATED CURING OF COMPACTED CALCIUM SILICATE MORTARS ON EXPOSURE TO CO2," *Journal of the American Ceramic Society,* vol. 57, no. 9, pp. 394-397, 1974.

[6] C. J. Goodbrake, J. F. Young, and R. L. Berger, "REACTION OF HYDRAULIC CALCIUM SILICATES WITH CARBON-DIOXIDE AND WATER," *Journal of the American Ceramic Society,* vol. 62, no. 9-10, pp. 488-491, 1979 1979.

[7] C. C. M. P. Association. (2015, 1 May). *Producers*. Available: http://ccmpa.ca/producers/

[8] Boehmers. (2017, 1 May). *The Autoclave Curing System*. Available: http://www.boehmerblock.com/autoclave.asp

[9] W. A. Klemm and R. L. Berger, "CALCINATION AND CEMENTING PROPERTIES OF CACO3-SIO2 MIXTURES," *Journal of the American Ceramic Society,* vol. 55, no. 10, pp. 485-&, 1972 1972.

[10] R. L. Berger, J. F. Young, and K. Leung, "ACCELERATION OF HYDRATION OF CALCIUM SILICATES BY CARBON-DIOXIDE TREATMENT," *Nature-Physical Science,* vol. 240, no. 97, pp. 16-+, 1972 1972.

[11] J. M. Bukowski and R. L. Berger, "REACTIVITY AND STRENGTH DEVELOPMENT OF CO2 ACTIVATED NON-HYDRAULIC CALCIUM SILICATES," (in English), *Cement and Concrete Research,* Article vol. 9, no. 1, pp. 57-68, 1979.

[12] C.-F. Chang and J.-W. Chen, "The experimental investigation of concrete carbonation depth," *Cement and Concrete Research,* vol. 36, no. 9, pp. 1760-1767, Sep 2006.

[13] V. G. Papadakis, C. G. Vayenas, and M. N. Fardis, "EXPERIMENTAL INVESTIGATION AND MATHEMATICAL-MODELING OF THE CONCRETE CARBONATION PROBLEM," *Chemical Engineering Science,* vol. 46, no. 5-6, pp. 1333-1338, 1991.

[14] J. J. Chen, J. J. Thomas, and H. A. Jennings, "Decalcification shrinkage of cement paste," *Cement and Concrete Research,* vol. 36, no. 5, pp. 801-809, May 2006.

[15] D. Zhang, "Performance evaluation of precast reinforced concrete after earlyage carbonation curing," PhD, Civil Engineering and Applied Mechanics, McGill, Montreal, 2016.

[16] H. H. Steinour, "Some Effects of Carbon Dioxide on Mortars and Concrete," *Journal of American Concrete Institute,* vol. 30, no. 2, pp. 905-907, 1956.

[17] W. J. J. Huijgen, G. J. Ruijg, R. N. J. Comans, and G.-J. Witkamp, "Energy consumption and net CO2 sequestration of aqueous mineral carbonation," *Industrial & Engineering Chemistry Research,* vol. 45, no. 26, pp. 9184-9194, Dec 20 2006.

[18] C. J. Shi and Y. Z. Wu, "Studies on some factors affecting CO2 curing of lightweight concrete products," *Resources Conservation and Recycling,* vol. 52, no. 8-9, pp. 1087-1092, Jul 2008.

[19] H. El-Hassan, "Static and dynamic carbonation of lightweight concrete masonry units," PhD, Civil Engineering and Applied Mechanics, McGill, Montreal, 2012.

[20] H. El-Hassan, Y. X. Shao, and Z. Ghouleh, "Effect of Initial Curing on Carbonation of Lightweight Concrete Masonry Units," (in English), *Aci Materials Journal,* Article vol. 110, no. 4, pp. 441-450, Jul-Aug 2013.

[21] A. Z. Morshed and Y. Shao, "Influence of moisture content on CO2 uptake in lightweight concrete subject to early carbonation," (in English), *Journal of Sustainable Cement-Based Materials,* vol. 2, no. 2, pp. 144-160, 2013.

[22] G. J. Verbeck, "Carbonation of Hydrated Portland Cement," *Amer. Soc. Test. Mater.. Spec. Tech. Pub.,* no. 205, pp. 17-36, 1958.

[23] Y. Shao, A. Zhou, and M. Mahoutian, "Pseudo-dynamic carbonation for concrete curing and carbon storage," *International Journal of Materials and Structural Integrity,* vol. 9, no. 1/2/3, pp. 21-38, 2015.

[24] R. Malinowski, "Method of casting concrete," ed: Google Patents, 1982.

[25] M. A. Venhuis and E. J. Reardon, "Vacuum method for carbonation of cementitious wasteforms," *Environmental Science & Technology,* vol. 35, no. 20, pp. 4120-4125, Oct 15 2001.

[26] F. Hannawayya, "Microstructural Study of Accelerated Vacuum Curing of Cement Mortar with Carbon Dioxide - Part 1," *World Cement,* vol. 15, no. 9, pp. 326-334, 1984.

[27] V. Rostami, "Development of early carbonation curing to replace steam curing for precast drymix concrete," PhD, McGill, 2012.

[28] S. Monkman and Y. Shao, "Assessing the carbonation behavior of cementitious materials," *Journal of Materials in Civil Engineering,* vol. 18, no. 6, pp. 768-776, Nov-Dec 2006.

[29] V. S. Ramachandran and J. J. Beaudoin, "Handbook of analytical techniques in concrete science and technology," (in English), 2001.

[30] C. J. Goodbrake, J. F. Young, and R. L. Berger, "REACTION OF BETA-DICALCIUM SILICATE AND TRICALCIUM SILICATE WITH CARBON-DIOXIDE AND WATER-VAPOR," *Journal of the American Ceramic Society,* vol. 62, no. 3-4, pp. 168-171, 1979 1979.

[31] F. Matsushita, Y. Aono, and S. Shibata, "Carbonation degree of autoclaved aerated concrete," *Cement and Concrete Research,* vol. 30, no. 11, pp. 1741-1745, Nov 2000.

[32] Z. Ghouleh, R. I. L. Guthrie, and Y. X. Shao, "High-strength KOBM steel slag binder activated by carbonation," *Construction and Building Materials,* vol. 99, pp. 175-183, Nov 2015.

[33] S. Goto, K. Suenaga, T. Kado, and M. Fukuhara, "CALCIUM SILICATE CARBONATION PRODUCTS," (in English), *Journal of the American Ceramic Society,* Article vol. 78, no. 11, pp. 2867-2872, Nov 1995.

[34] Z. Al-Ghouleh, "Development of green concrete from industrial wastes and carbon dioxide," (in English), 2016.

[35] W. A. Klemm and R. L. Berger, "Accelerated curing of cementitious systems by carbon dioxide," *Cement and Concrete Research,* vol. 2, no. 5, pp. 567-576, 1972/09/01/ 1972.

[36] H. El-Hassan, Y. X. Shao, and Z. Ghouleh, "Reaction Products in Carbonation-Cured Lightweight Concrete," (in English), *Journal of Materials in Civil Engineering,* Article vol. 25, no. 6, pp. 799-809, Jun 2013.

[37] C. Shi, F. He, and Y. Wu, "Effect of pre-conditioning on CO2 curing of lightweight concrete blocks mixtures," *Construction and Building Materials,* vol. 26, no. 1, pp. 257-267, 2012.

[38] B. C. J. Gerwick, *Construction of Prestressed Concrete Structures, Second Edition*. New-York: John Wiley & Sons, Inc, 1993, pp. 19-23,91-94.

[39] M. Fernandez Bertos, S. J. Simons, C. D. Hills, and P. J. Carey, "A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2," *J Hazard Mater,* vol. 112, no. 3, pp. 193-205, Aug 30 2004.