CO$_2$ Utilization in Concrete

Yixin Shao[1*] and Hilal El-Hassan[2]

[1]*McGill University, Canada*
[2]*American University of Dubai, UAE*
[*]Department of Civil Engineering, McGill University, Montreal, Canada H3A 2K6
Yixin.shao@mcgill.ca
hilal.el-hassan@mail.mcgill.ca

ABSTRACT

Flue gas carbon dioxide collected from cement kiln can be beneficially utilized in precast concrete production to reduce carbon emission, accelerate early strength, and improve durability of the products. It is accomplished through a carbonation curing of precast products at very early age. This paper summarizes a recent study on optimization of the reaction conditions at which carbon uptake can be maximized, performance of the products is competitive and the process can be implemented in large scale. It is found that initial curing plays a critical role in reaction efficiency. In reference to cement content, carbon uptake in 4-hour carbonation reaches 8 -12% by zero initial curing, 22% by 4 to 8 hours initial curing and 24% by 18 hours initial curing. CO$_2$ curing process can replace steam to reduce embodied energy in concrete products, utilize sufficient amount of carbon dioxide in the vicinity of CO$_2$ sources, and produce the final products with equivalent performance.

Keywords. CO$_2$ utilization, carbonation curing, precast concrete, CO$_2$ uptake.

INTRODUCTION

A significant fraction of the CO$_2$ discharged to the atmosphere comes from point sources, such as thermal power plants and cement plants. The current strategy on CO$_2$ mitigation is focused on the removal, recovery and disposal of CO$_2$ at the control sources. While carbon capture and storage (CCS) in geologic formation is promising, carbon capture and utilization (CCU) appears to be more rewarding. Utilization of CO$_2$ recovered from stack gases has been explored for urea production and enhanced oil recovery (IPCC, 2005). More commercial use of CO$_2$ will further increase the value of carbon dioxide. It is also critically important for the area where CCS in geologic formation is not possible.

Carbonation of concrete is a CO$_2$ uptake process (Shao, et al 2006). It is the dicalcium silicate (C$_2$S) and triclacium silicate (C$_3$S) that react with CO$_2$ producing C-S-H and CaCO$_3$. This is well known as an accelerated carbonation curing (Young, et al 1974; Goodbrake, et al, 1979). The governing reactions are shown by Eqs (1-2). The carbonation reaction

products are a hybrid of calcium-silicate-hydrate (C-S-H) and calcium carbonate ($CaCO_3$). High early strength can be obtained within a few minutes to a few hours.

$$C_3S+(3-x)CO_2+yH_2O \rightarrow C_xSH_y+(3-x)CaCO_3 \qquad (1)$$

$$C_2S+(2-x)CO_2+yH_2O \rightarrow C_xSH_y+(2-x)CaCO_3 \qquad (2)$$

The carbonation reaction could also occur in hardened concrete (Eqs. 3-4). It is the reaction between carbon dioxide and hydration products, such as calcium hydroxide (CH) and calcium silicate hydrate (C-S-H), forming $CaCO_3$ and silica gel (Papadakis, et al 1991). This process is usually considered as detrimental since C-S-H is decomposed and strength will get reduced. However if this process takes place at early age, it could be beneficial for CO_2 utilization and performance improvement. The durability of concrete can also be improved (Rostami, et al, 2011).

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

$$C\text{-}S\text{-}H + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \qquad (4)$$

This paper presents a study on the development of a new process that introduces initial curing prior to early carbonation to promote degree of carbonation reaction. High purity CO_2 (99.5%) will be used to simulate the recovered cement kiln flue gas carbon dioxide. The goal is to shorten the carbonation duration to 2 to 4 hours with the help of initial curing ranging from 0 to 18 hours. The effect of initial curing on degree of carbonation reaction is evaluated to promote maximum possible carbon uptake in concrete. The carbon uptake is estimated using mass gain and thermal analysis. Early age and 28-day performance of carbonated concrete are examined in terms of carbon uptake and strength gain. Concrete masonry unit (CMU) is used as an example of precast concrete product for CO_2 utilization. The results gained from CMU are applicable to other precast products.

EXPERIMENTAL

Sample preparation. Lightweight concrete masonry units are used in this paper as precast concrete example to study the CO_2 utilization. The lightweight concrete used expanded blast furnace slag as lightweight aggregates which is not sensitive to carbonation. The bulk density of dry expanded slag aggregate was 0.95 g/cc and maximum aggregate size was 6 mm. Slag aggregate was used as saturated surface dry (SSD) with 5% water in aggregates. The industry mixture proportion was followed by the ratio of cement: wet slag aggregate: water = 1: 6.2: 0.4. The LW concrete weighed 1840 kg/m^3. The carbonation curing parameters will be studied using rectangular slab concrete samples of 38 mm thick to simulate the typical web or face shell of a hollow concrete masonry unit (CMU). Each sample weighed approximately 680 grams (1.5 lb) with a density of 1850 kg/m^3. Raw materials were mixed in a pan mixer, cast into 127 x 76 x 38 mm mold and compact formed using a vibrating hammer to simulate the industry production of CMU. Because of the dry mix, concrete was demolded right after casting for initial curing.

Curing procedure. Carbonation curing was carried out together with conventional sealed hydration and steam curing as comparison. Steam curing took place in a steam cooker for a period of 4 hours with maximum temperature of 80°C and relative humidity of 95%. Initial curing of 0, 4, 6, and 8 hours at 22°C at relative humidity of 80% was applied prior to steam. Carbonation curing setup is shown in Fig. 1. Initial curing was performed on fresh concrete by 0, 4, 6, 8, 18, 336 hours respectively in an environmental chamber at a relative humidity

of 50% and a temperature of 25°C. The purpose of initial curing was to reduce the free water on the surface and allow diffusion of carbon dioxide. Initial curing of 0 hour was actually immediate carbonation of fresh concrete and served as reference. Initial curing of 18 hours was to simulate an overnight curing and was likely the longest preset that can be accepted by commercial production. Initial curing of carbonation for 96 hours (4 days) was designed to push for theoretical limit (Shideler, 1955). At full carbonation, theoretical maximum of CO_2 uptake could reach to 50% by the mass of cement (Stienour, 1959). Concrete slab samples after initial curing were placed in a sealed chamber in Fig. 1, which was then vacuumed to about 0.7 bars and filled with carbon dioxide gas to a pressure of 1 bar. The chamber was placed on a digital balance to obtain the mass curve of concrete during carbonation. The carbonation duration varied from 2 to 4 hours. A period of 96 hours was also investigated to study the effect of extreme exposure time. The effect of initial curing and carbonation curing were evaluated based on water loss, carbon uptake, and compressive strength. To compensate the water loss during initial curing and carbonation curing, water spray was applied to carbonated concrete right after carbonation to restore the original water content and examine its effect on subsequent hydration. The temperature, relative humidity, pressure, samples' initial and final mass, and mass of water condensed on the wall of the chamber were recorded. Control concrete as reference to carbonation underwent same initial curing of 0, 4, 6, 8, and 18 hours in an environmental chamber at a 50% RH and a 25°C for each hydration control batch.
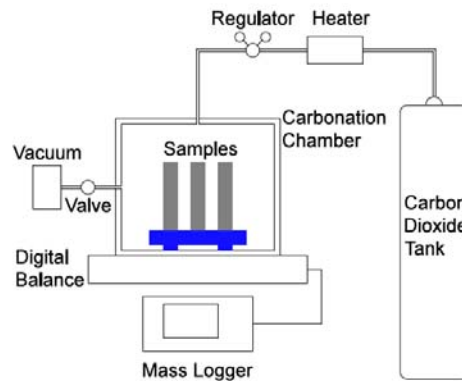

Fig. 1: Concrete carbonation setup

CO_2 uptake quantification. Both mass gain and mass curve methods were used in quantifying CO_2 uptake. Mass gain method estimates CO_2 uptake in concrete by comparing mass of samples before and after carbonation (Eq. 5). Carbonation-induced water loss was collected by absorbent paper and added to the final mass. By treating the system as a closed system, it was imperative to include the evaporated water, which was initially inside the samples prior to carbonation.

$$CO_2 \text{ uptake } (\%) = \frac{Final\ mass + Mass\ of\ water\ loss - Initial\ mass}{Mass\ of\ cement} \qquad (5)$$

Mass curve method was executed by placing the carbonation setup on a digital balance, which was zeroed after vacuuming the chamber. A mass curve was recorded as mass versus time until the end of the process at which time CO_2 was released and the residual mass, M, was measured. The system was calibrated by repeating the tests using CO_2-insensitive

styrofoam samples of the same volume to obtain second residual mass, m. The difference between M and m represented the CO_2 uptake by concrete (Eq. 6). Data collected by mass gain and mass curve methods are two simultaneous measurements from the same process and therefore should be comparable. They are independent from any carbon content existing before carbonation.

$$CO_2 \text{ uptake } (\%) = \frac{M - m}{Mass\ of\ cement} \tag{6}$$

The compressive strength was measured at 1 and 28 days after casting. Three samples per batch were tested and averaged. Compressive strength was compared between carbonated and hydrated concrete at 1 day and 28 days.

RESULTS

CO_2 Uptake. Degree of carbonation is characterized by carbon uptake. The results from mass gain method and mass curve method are presented in Table 1 along with their averages. The two methods appeared to be in good agreement. Two groups of data are presented in Table 1. First group includes the first 5 batches with constant carbonation time of 4 hours and varied initial curing of 0, 4, 6, 8 and 18 hours to study the effect of initial curing. The second group involves the last three batches with constant initial curing of 18 hours and varied carbonation duration of 2, 4 and 96 hours to investigate the effect of carbonation time.

Table 1: CO_2 uptake (%) in carbonated concretes

Condition	Mass Gain	Mass Curve	Average
0a + 4c	7.5 ± 1.8	9	8.3
4a + 4c	21.3 ± 1.4	22.1	21.7
6a + 4c	22.8 ± 1.8	23.6	23.2
8a + 4c	23.5 ± 1.6	24.0	23.7
18a + 4c	24.2 ± 0.35	24.4	24.3
18a + 2c	20.4 ± 0.4	21.7	21.1
18a + 96c	34.9 ± 1.6	35.2	35.1

In first group with 4-hour carbonation, immediate carbonation with no initial curing resulted in a carbon uptake of 8.3%. It was indicative of a low degree of reaction. Immediate carbonation was impeded by saturated surface. Initial air curing of 4, 6, 8 and 18 hours removed free water by 32%, 33%, 33% and 52% respectively based on total water. The subsequent 4-hour carbonation led to a significant increase in average carbon uptake. It was 21.7, 23.2, 23.7 and 24.3% respectively based on cement content in mix. Initial curing reduces free water, making room for gas diffusion and calcium carbonate precipitation. It seemed that prolonged initial curing was not directly beneficial to reaction efficiency.

In the second group, initial curing was fixed at 18 hours. When 2-hour carbonation was compared with 4-hour carbonation, longer carbonation promoted higher carbon uptake. In

prolonged carbonation, carbon uptake by 96 hours carbonation was increased by 44% in comparison to that by 4 hours. A carbon uptake of 35.1% in 4-day carbonation represented a degree of carbonation of nearly 70%, if full carbonation is considered as 100%. Longer carbonation time could promote carbon uptake and enhance the carbon storage capacity of concrete, although practically it is not feasible for industry scale production.

Compressive Strength. The accelerated strength gain of concrete 4 hours after casting without initial curing is shown in Fig. 2. In comparison to hydration reference of 1.9 MPa, carbonation strength reached 5.6 MPa and steam strength 6.3 MPa. Early strength was significantly improved by accelerated curing. It seemed steam was slightly more effective than carbonation.
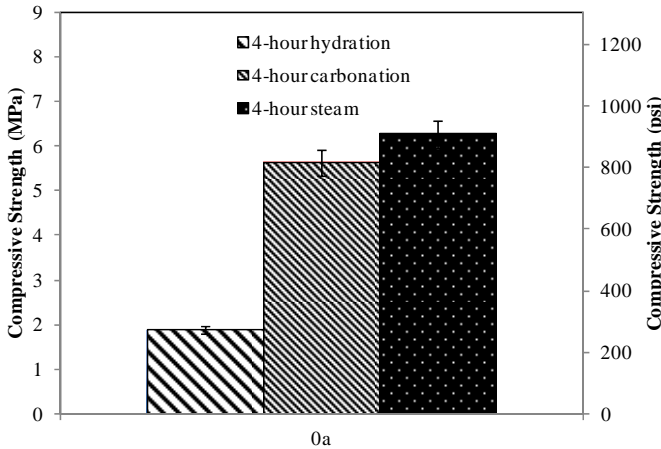

Fig. 2: Comparison of 4-hour strength after accelerated curing

Compressive strengths at 28-day are shown in Fig. 3 and 4. Fig. 3 shows effect of initial curing on 28-day strength and Fig. 4 demonstrates effect of carbonation time. Four-hour carbonation strength reached 15.0 MPa without initial curing and 14.2 MPa with 18-hour initial curing. The best hydration strength was 17.0 MPa for the reference and steam cured samples. It was noticed that 4-hour carbonation produced lower 28-day strength than hydration reference. This was because of the water loss during the initial curing. The subsequent hydration was affected due to the lack of water for hydration. However the extensive carbonation of 4-day produced a higher 28-day strength than the best references. In an attempt to improve the compressive strength of short-term carbonated concrete, water compensation by surface spray after carbonation was adopted to restore the lost water during early curing. Water was slowly added until surface saturation. The process could last a few days until the lost water were all compensated. The results are summarized in Table 2. The best reference is the hydration without initial curing. Water compensation increased the compressive strength by 20-25% in comparison to carbonation without spray. This increase in strength is associated with the high bound water and carbonate content. The 28-day strength of 18a+4c after spraying was 17.2 MPa, which was comparable to the hydration strength (0a) of 17.2 MPa, and steam strength (4a+4s) of 17.4 MPa. The results show that

carbonation followed by water compensation is beneficial to compressive strength. It is clear that early carbonation does not hinder subsequent hydration. It is the water loss during carbonation that reduces hydration degree. With water compensation through spray, it is possible to make carbonation strength comparable to the best hydration reference.
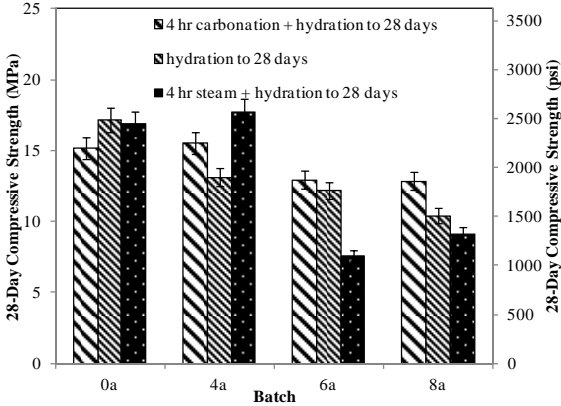

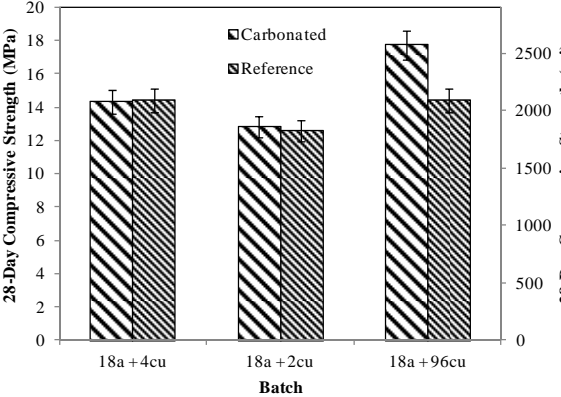Fig. 3: Effect of initial curing on carbonation strength

Fig. 4: Effect of carbonation time on compressive strength

The Market. Reaction of cement with carbon dioxide at early age is a CO_2 sequestration process. If one 20cm block with a mass of 15 kg contains 13% cement could have a CO_2 uptake of 24% based on cement, one block has the capacity to store 0.47 kg of CO_2 in a thermodynamically stable calcium carbonate form. Assuming every block or brick has the same carbon storage capacity, the projected annual production of 4.3 billion units in US market (Freedoniap Group 2010) can thus consume 2 million tons of CO_2 per year. The capacity for carbon capture and storage (CCS) in geologic formation is approximately 1 million ton per year per site (IPCC, 2005). CO_2 utilization in concrete blocks and bricks production is equivalent to carbon sequestration in two geologic formation sites. The cement annual production in the United State is about 100 million tons with CO_2 emission of 80 million tons. If all block and brick plants adopt carbonation curing with the same carbon uptake rate, CO_2 utilization in their production lines alone could reduce carbon emission by 2.5% for cement industry.

CO_2 utilization in concrete is not only beneficial to environment. It has also shown technical advantages. In terms of durability, the carbonation treatment led to more resistance to surface air permeability and chloride diffusion compared to steam cured concrete. It was also found that the carbonation curing technique increased surface electrical resistivity and sulfate resistance due to the chemically and physically modified microstructure. The enhanced durability performance of carbonated concrete is attributed to the low CH content. Nevertheless pH of carbonated concrete could be still maintained above corrosion threshold value of 10.5. With the controlled carbonation, it is expected a heavily carbonation surface layer could be produced to serve as protective layer for enhanced durability while high alkalinity could be kept around reinforcement (Rostami et al, 2012).

Table 2: Compressive strength (MPa) after water compensation

Batch	After 1 Day	After 28 Days
0a + 4c	9.5 ± 0.7	15.2 ± 1.5
0a + 4c^W	10.0 ± 0.7	15.9 ± 1.7
0a	11.1 ± 1.0	17.2 ± 1.3
4a + 4c	7.9 ± 0.6	15.5 ± 1.6
4a + 4c^W	8.1 ± 0.6	15.8 ± 1.3
4a	4.4 ± 0.3	13.2 ± 1.4
18a + 4c	8.8 ± 0.6	14.3 ± 1.2
18a + 4c^W	12.3 ± 1.2	17.2 ± 1.4
18a	5.2 ± 0.5	14.4 ± 1.2

W – Water compensation by surface water spray right after carbonation

CONCLUSIONS

1. A new carbonation process was developed to incorporate initial curing prior to carbonation. The process had significantly increased carbon uptake capacity for concretes exposed to an early carbonation. However, initial curing could be detrimental to late strength development because of water loss. Therefore, initial curing shall be minimized to secure the performance and reduce the process cost. With water compensation immediately after carbonation, high early strength, equivalent late strength, and superior carbon uptake can be achieved.
2. Water content is a more important process parameter than relative humidity. Traditional believe that relative humidity is the dominant parameter for carbonation is not correct. It works only for weathering carbonation of hardened concrete. For early carbonation targeted in the first 24 hours after casting, it is not possible to reduce the internal relative humidity to an ideal level of 50-60%. No matter what drying process is used, internal RH remains higher than 80% within 24 hours. Water content is a better parameter to justify the condition for carbonation.
3. Carbon uptake capacity by concrete is dependent on initial curing. Taking cement content in concrete as reference, the carbon uptake in 4-hour carbonation treatment reached approximately 8.5% by zero initial curing, 22% by 4 to 8 hours initial curing and 24% by 18 hours initial curing. Longer carbonation time of 96 hours could promote carbon uptake to 35%. It is corresponding to a degree of carbonation of 70%.

4. If all block and brick plants In US and Canada could adopt carbonation curing with the carbon uptake of 24% based on cement, CO_2 utilization in block production lines alone could reduce carbon emission by 2.5% for cement industry. If more concrete products are produced by this carbonation process, CO_2 utilization market can be considerably increased.

ACKNOWLEDGMENTS

REFERECES

Freedonia Group, (2010) "Brick and block demand to reach 12.4 billion units, $8 billion by 2014", *Journal of Concrete Products*, Freedonia Group Study, Issue 2652.

Goodbrake, C. J. and Young, J. F. (1979), "Reaction of Beta-Dicalcium Silicate and Tricalcium Silicate with Carbon Dioxide and Water Vapor", *Journal of the American Ceramic Society*, 168-171

IPCC (2005), "IPCC Special Report on Carbon Dioxide Capture and Storage", Cambridge.

Papadakis V G, Vayenas C G, Fardis M N. (1991), "Fundamental modeling and experimental investigation of concrete carbonation". ACI Mater J, 88(5):363-373

Rostami V., Shao, Y., and Boyd, A. (2011). "Durability of concrete pipes subjected to combined steam and carbonation curing," *Construction and Building Materials*, 25, 3345-3355.

Rostami, V., Shao, Y. and Boyd, A. (2012), "Carbonation curing versus steam curing for precast concrete production", Journal of Materials in Civil Engineering, 24(9), 1221-1229.

Shao, Y., Mirza, M. S., and Wu, X., (2006), "CO_2 Sequestration using calcium-silicate concrete", *Canadian Journal of Civil Engineering*, 33, 776-784.

Shideler, J. J., "Investigation of the Moisture-Volume Stability of Concrete Masonry Units", *Portland Cement Association Research and Development Laboratories*, 1955, Bulletin D3.

Steinour, H. H., (1959). "Some Effects of Carbon Dioxide on Mortars and Concrete - A Discussi*on," Journal of American Concrete Institute*, Vol. 55, No. 2, 905-907

Young, J. F., Berger R. L., and Breese J., (1974) "Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO_2", *Journal of the American Ceramic Society*, Vol. 57, No. 9, 394-397.