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Modeling Natural Carbon Sequestration Rates of Dry-Cast Manufactured Concrete Products

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ABSTRACT

Accurate quantification of the natural carbon sequestration of dry-cast manufactured concrete products is crucial for assessing their long-term environmental impact. Previously, test protocols for measuring carbon sequestration in manufactured dry-cast concrete products were developed, and the results on the amount and rate of sequestration of nine sets of concrete masonry units (CMU) from 1 to 6 months of age were reported. This paper presents a follow-up study that extends the analysis on the same nine sets of units to a 3-year period. Furthermore, experimental tests using crushed samples of the nine sets, exposed to the atmospheric conditions, provide an estimate of the maximum carbonation potential for dry-cast concrete. The results demonstrate that initial drying conditions during sample preparation play a crucial role in carbon uptake for dry-cast CMUs, with specimens dried at 45°C showing higher uptake at 28 days due to residual moisture enabling additional carbonation. However, this effect was not observed at 91 and 182 days, indicating that residual moisture's influence decreases over time. Additionally, crushed CMU samples reached a practical upper limit of 52%-55% of the maximum calcination carbon emission potential after four months of exposure. A proposed logarithmic model effectively captures the observed carbon uptake trends, aligning with the deceleration of carbonation over time due to pore blocking and the limited availability of reactive phases.

KEYWORDS

carbon uptake modeling, carbonation potential, CO_2 uptake modeling, concrete masonry unit (CMU), dry-cast, sequestration

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INTRODUCTION

The carbon uptake (also known as carbonation) of cement-based masonry products has garnered increasing attention due to their potential to mitigate CO_2 emissions from the calcination of the limestone feedstock during the manufacture of cement clinker. Previously, Walloch et al. [1], investigated the carbon sequestration potential of nine lots of dry-cast concrete masonry unit (CMU) samples manufactured at five different production facilities across North America by developing and refining test protocols to measure CO_2 uptake accurately. This previous paper included results of testing through six months after production. Given the porous nature and large surface-to-volume ratio of dry-cast CMU units, CMUs are expected to have a higher carbonation rate than a traditional wet-cast concrete. Using thermogravimetric analysis (TGA), the sequestered CO_2 was quantified at different ages. At 28 days post-production, the average CO_2 sequestered in the CMU was 21 kg/m^3 (1.30 lb/ft^3), which increased to a value of 34 kg/m^3 (2.12 lb/ft^3) at 6 months, a 63% increase. The study also found that integral water repellent admixtures had no significant impact on carbonation, while limestone aggregates introduced high variability in measurements due to their latent carbonate content.

The research established a repeatable and accurate testing protocol for assessing CO_2 uptake in dry-cast CMUs. The carbonation potential of cement phases (CPCP) was calculated by first using the Bogue calculations to estimate the amount of various cement phases and then calculating the amount of CO_2 that would be consumed by the hydration reaction products of all of the phases. Sequestration was expressed in multiple ways, including the percent of total weight, percent of cement weight, percent of CPCP, and CO_2 sequestered per square meter and cubic meter of concrete. The results indicated that dry-cast CMUs offer a promising approach to CO_2 sequestration of a significant portion of the CO_2 originally released during the calcination of the limestone in the manufacture of the cement clinker, with this process continuing well beyond the initial curing stage.

While this initial research demonstrated dry-cast CMU's ability to sequester more CO_2 than would be anticipated for conventional wet-cast concrete at early ages, it only quantified results through 6 months of exposure. Additional work was contemplated to quantify longer periods of exposure and to use this data to investigate modeling of the rate of carbon sequestration of CMU. Because the macro structure of dry-cast masonry products includes different levels of porosity, the capillary effects can significantly influence how CO_2 and moisture interact within the material. This phenomenon can potentially make the dry-cast carbon uptake behavior different from the wet-cast products. The maximum carbon uptake potential of dry-cast CMU could also be investigated. While numerous studies have evaluated the maximum carbon uptake potential of wet-cast concrete, this value is unknown in dry-cast concrete and may be influenced by the presence of relatively large quantities of unhydrated cement in low w/c dry-cast concrete.

The present study extends the testing of the nine sets beyond six months to analyze long-term sequestration trends. To refine the test protocol, this study also includes experimental studies evaluating the impact of using a higher initial temperature of 110ºC (230ºF) to dry the saw-cut specimens before TGA analysis. To determine maximum carbonation potential, experimental results are also provided for specimens from the initial nine sets that were crushed and exposed to the elements to determine maximum carbonation potential. To increase the utility and ease of use, the present study evaluates the extent of carbonation of the CMUs compared to the total calcination carbon emissions of the cement used in the production of the CMU, instead of comparing the results to the carbonation potential of cement phases (CPCP) that was used in the previous research. While calculating CPCP can be somewhat laborious and inherently approximate, the calcination carbon emissions can be taken directly from the environmental product declaration (EPD) of any cement.

The present study then models the rate of carbon sequestration (carbon uptake) of the nine sets by fitting non-linear curves to the data points over time expressed as a percentage of the calcination carbon emissions of the cements that were used in the manufacture of the units and expressed as the net carbonation potential defined by the carbon sequestration of the crushed samples. Mechanistic models based on the interaction of the unique structure of the dry-cast concrete and the cement hydration products are proposed to explain both the rapid sequestration rate at early ages followed by deceleration over time at later ages.

METHODOLOGY OF CARBONATION MEASUREMENT

Both the original study [1] and the present study used the same procedures for measuring the carbonation, except for the sample drying temperature, which will be discussed later in this paper. Once the designated curing interval had been reached, samples for carbonation testing were obtained from the face shell of a unit. Samples were saw-cut dry to avoid wetting and potentially accelerating the carbonation process artificially. Sample sizes were nominally 100 mm (4 in.) in length by 200 mm (8 in.) in height. The thickness of each face shell coupon was equal to the thickness of the face shell as produced, which for all sets was approximately 32 mm (1.26 in.). Once a face shell coupon was obtained, it was wrapped in shipping padding and vacuum sealed in a 0.15-mm (6-mil) clear polyethylene bag and shipped to the laboratory.

The samples remained vacuum-sealed at the laboratory until scheduled for analysis. Once the vacuum bag was opened, a thin slice, typically 6 mm (0.24 in.) thick, was cut from the full height of the CMU face shell at the center of the sample using a water-cooled tile saw with a thin blade. The thin slice was immediately placed in a drying oven at 45°C (113°F) to minimize any further carbonation of the coupons. Slices were dried overnight. Upon removal from the oven, they were ground in a ball mill to pass a 150 µm (#100) sieve and the resulting powder was sealed in a plastic bag. Approximately 3 g to 4 g of the blended powder was analyzed by TGA (thermal gravimetric analysis) using a LECO TGA701 that has the capacity to run 18 samples concurrently. This sample size is larger than the 0.05 to 1 g sample size typically used for cement analysis to help increase the sensitivity and repeatability (precession) of the test procedure.

The TGA program used in the original study was a typical program used for cement analysis which ramps the temperature from room temperature to 950°C with temperature plateaus at 45°C, 220°C, 550°C and 950°C. The TGA maintains a constant temperature at each plateau until the weight loss is complete and stabilized, at which point it ramps up to the next plateau. The typical program was modified to slow the ramp between 550°C and 950°C to 5°C/min. This slower ramp also helped increase the sensitivity and repeatability of the test procedure.

As detailed in the original study [1], once the cement hydrates in the concrete, other compounds are formed, principally the hydrated forms of calcium silicates (Ca_3SiO_5 and Ca_2SiO_4) and the associated calcium hydroxide [$Ca(OH)_2$] by-product along with other aluminum and iron containing hydrate products. All of these hydration products decompose at temperatures below 550°C.

When these cement hydration products are exposed to carbon dioxide from the atmosphere, they will sequester the carbon dioxide and form carbonated species, principally of calcium hydroxide (CH) and subsequently calcium silicate hydrate (CSH). These carbonated species decompose and release carbon dioxide in the 550°C and 950°C range.

Samples of each raw material (aggregates and cementitious materials) used in the manufacture of the CMU were analyzed in a similar manner to determine the 'background' CO_2 content in the raw materials. This was subtracted from the gross CO_2 weight loss of the CMU sample between 550°C and 950°C to yield the net CO_2 loss of the CMU due to the carbonation of the cement in the CMU.

The testing of the nine sets at 1-year and 2-years of age followed the protocol detailed above. The 3-year samples from these nine sets followed a similar protocol with a modification to the initial drying conditions. In the original study, the 6-mm slices that were cut from the face shell coupons using a water-cooled tile saw with a thin blade were subsequently dried overnight at 45°C before being ground prior to TGA analysis. For the 3-year samples, the slices were dried at 110°C for a minimum of 2 hours, which was twice as long as the preliminary drying study demonstrated was needed, to ensure that the samples reached equilibrium with no additional weight loss. This was done to minimize the potential for additional carbonation of the concrete matrix. Further discussion on the effect of initial drying conditions is included in the Experimental Results & Discussion section below.

ANALYTICAL EVALUATION AND CARBON UPTAKE REPORTING

The original study calculated the net carbon sequestration results for the nine sets from 28 days to 6 months by subtracting the 'background' CO_2 loss due to the raw materials from the gross CO_2 loss of the CMU samples as determined with the TGA. The results were reported in several formats:

- Percent of total weight: This is the amount of CO_2 sequestered into the concrete sample due to the carbonation of the cement, expressed as a percentage of the total weight of materials (aggregate and cement) in the sample. This is the net value that comes directly from the TGA data.
- Percent of cement weight: This is the amount of CO_2 sequestered expressed as a percentage of the weight of the cement in the sample. It is simply the "percent of total weight" multiplied by the percentage of cement in the total concrete matrix.
- Percent of potential: This is the amount of CO_2 sequestered expressed as a percentage of the potential amount of carbonation if all of the cement phases had totally carbonated. This is the "percent of cement weight" divided by the carbonation potential of cement phases (CPCP) that was calculated for that cement. Further discussion on the percentage of potential is included in the next section
- Based on kg of CO_2/m^3 (lb of CO_2/ft^3) of concrete: This is the amount of CO_2 that would be sequestered at the test age per volume of concrete. It is simply the "percent of total weight" multiplied by the average oven-dry density of the CMU as determined using ASTM C140/C140M [2]. This is the global warming potential (GWP) value that would typically be reported on an EPD.

Because of its usefulness for reporting the natural carbon sequestration on an EPD, the original paper focused on reporting that the average CO_2 sequestered was 21 kg/m^3 at 28 days post-production, which increased to a value of 34 kg/m^3 at 6 months, a 63% increase.

Although focusing on kg/m^3 is attractive as it is directly related to the reporting units in an EPD, this is not the best way to compare the data between sets because the various sets of CMUs had different oven-dry densities. For the nine sets in the original study, the oven-dry densities ranged from 1554 to 2166 kg/m^3 (97.0 to 135.2 lb/ft^3). For the data reported for the nine sets in the original study, the coefficient of variation (COV), which represents the overall scatter in the CO_2 sequestration values expressed in kg/m^3 was 24%.

A more accurate way to compare the data is to correlate the amount of carbon uptake to the percent of potential of the cement as represented by CPCP because this takes out the complicating effect of the oven-dry density of the CMU. This can be seen in the reduced scatter and lower COV of 17% when the data in the original study is expressed as CPCP.

Another way to express the carbon uptake is as a percentage of the Calcination Carbon Emissions of the Cement that was used in the CMU. This is essentially the CO_2 that was released from the limestone feedstock that went through the kiln process to form the clinker.

There are a number of ways that the calcination carbon emissions of the portland cement can be determined. This paper uses estimations of the calcination carbon emissions for each cement using the Global Cement and Concrete Association (GCCA) Detailed Output Method B2 [3], which is the method that cement companies need to follow when calculating the emissions listed on their EPDs. According to this method, the calculation of the calcination carbon emissions incorporates magnesium (MgO) in addition to calcium oxide (CaO) contents of the clinker.

EXPERIMENTAL RESULTS & DISCUSSION

Impact of initial drying condition on carbon uptake - 45°C vs 110°C

The initial drying conditions of concrete samples play a crucial role in determining their early-stage carbon uptake as they influence the moisture availability necessary for carbonation reactions. In the original study, after the face shell specimens were removed from their sealed vacuum bags, a thin (nominal 6-mm) slice was cut out with a wet saw, and the slices were oven-dried overnight at 45°C following standard petrographic protocol for studying concrete specimens.

The goal of the oven-drying regime is to remove residual water from the slices to prevent any further carbonation and hydration of the specimens so that the measured carbonation level of each slice is representative of the sample when the face shell was harvested and vacuum-sealed at a given age. In the current study, to determine if the 45°C overnight drying regime was sufficient to prevent further carbonation of the slices, a small experiment was run with two new CMU sets.

Prior to the experiment, a drying study was conducted to determine how long it would take to dry a 6-mm thick slice wet-cut from a CMU at 110°C. The slices appeared surface-dry within 20 minutes and were completely dry by 1 hour, with no further weight loss observed thereafter. A minimum oven-drying time of 2 hours at 110°C was chosen for the study to be safe and to ensure that all specimens would be thoroughly dry.

For the oven-drying experiment, six face shell coupons (three from each set) were tested at 28 days of age and four face shell coupons (two from each set) were tested at 91 days of age with an additional four face shell coupons (two for each set) being tested at 182 days of age. For each face shell coupon, two 6-mm slices were cut with one of the slices being oven-dried overnight (21 hours) at 45°C and the other companion slice being oven-dried for a minimum of 2 hours at 110°C. The relative results of the two companion slices were compared for all sets tested.

As shown in Fig.1, the specimens dried at the lower temperature of 45°C overnight for 21 hours exhibited higher carbon uptake at 28 days compared to those dried at 110°C for 2 hours. Compared to the 110°C dried specimens, the companion 45°C dried specimens averaged 111% relative uptake, with values ranging from 103% to 121% for the individual companion slices. This increase in carbon uptake indicates that additional carbonation occurs in the 45 °C-dried specimens. Consequently, the 21 hours of 45°C drying did not totally dry the sample and preserved a higher residual moisture content, enabling more favorable conditions for further carbonation of the slice.

Unlike the 28-day specimens, the 91-day and 182-day specimens dried for 21 hours at 45°C did not show an increase in carbon uptake compared to their companion specimens dried for 2 hours at 110°C. At 91 days of age, compared to the 110°C dried specimens, the 45°C dried specimens averaged 100% relative uptake with values ranging from 91% to 112% for the individual companion slices. At 182 days of age, compared to the 110°C dried specimens, the 45°C dried specimens averaged 101% relative uptake with values ranging from 98% to 105% for the individual companion slices. The error bars shown in Fig. 1 represent a 95% confidence interval range for the respective ages.

The additional carbonation that occurred in the 28-day specimens dried at 45°C, is most likely due to latent calcium hydroxide ($Ca(OH)_2$) that built up in the specimen pores after they were vacuum sealed. Even though they were sealed, there was residual moisture in the samples, which could continue the hydration process. At early ages, the first phase of the cement to hydrate is the tricalcium silicate (C_3S), which releases 3 moles of calcium hydroxide byproduct for every mole of calcium silicate hydrate gel (CSH) formed. The next phase to hydrate is dicalcium silicate (C_2S), which releases 1 mole of calcium hydroxide byproduct for every mole of CSH gel formed. This calcium hydroxide, in the presence of moisture and carbon dioxide, gets carbonated. The carbonation process causes the formation of various types of calcium carbonates. In total, the carbonation of the calcium hydroxide byproducts represents about 40% of the total potential carbonation of the cement, with the other 60% representing the carbonation of the CSH gel and aluminate phases at later ages [1].

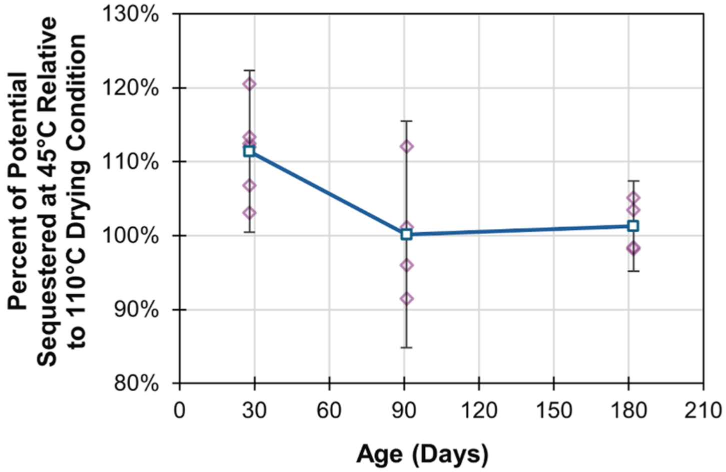

Figure 1. Carbon uptake as a percentage of the potential sequestered for different initial drying conditions: 45°C Relative to 110°C

It is logical that the early age specimens would be more susceptible to the build-up of latent calcium hydroxide in the pores, which could continue to carbonate if the specimen slices are not thoroughly dried after being saw-cut from the face shell coupons. At later ages, the calcium hydroxide that was originally produced during the cement hydration process would have already been carbonated before the face shell coupons were cut up and would not be as available for further carbonation if the slices were not thoroughly dried. Therefore, at 28 days, a correction factor of 10% was applied to adjust the carbon uptake results in the original study that were obtained from the samples subjected to a lower initial drying temperature. The adjusted results better reflect the expected carbonation level of concrete at that early age. However, at later ages, no modification is applied, as the carbon uptake values from both drying conditions are essentially the same. This approach ensures that the results accurately represent the natural progression of CO_2 uptake in concrete while still addressing early-stage inconsistencies caused by variations in initial drying conditions.

Carbon uptake of crushed CMU samples

Because of the nature of the dry-cast concrete used to manufacture CMU, it is usually not possible to disperse the cement particles in the mixture to the degree that is typical in wet-cast concrete. This is a direct result of the need to limit the addition of water to the mix so that the dry-cast CMUs do not slump when they are released from the molds before curing. The result is that in dry-cast concrete, a significant amount of the cement remains as agglomerations of multiple cement particles. During the cement hydration process, the cement particles on the surface of the agglomerations are exposed to water and can hydrate normally to form a shell of hydration products, leaving a kernel of unhydrated cement particles inside of the agglomeration. Research has shown the residual unhydrated cement contents range from 6% to 36% depending on the w/c ratio with higher unhydrated cement contents at lower w/c ratios [4]. The fraction of unhydrated cement in dry-cast CMU is typically estimated to be between 25% and 35% [5]. These unhydrated cement particles do not have the capacity to participate in the subsequent natural carbonation of the concrete. This limits the practical upper limit on how much carbon uptake a CMU can achieve over its lifetime.

To estimate the practical upper limit for carbon uptake of the nine sets of CMU in the study, a part of CMU from each set was crushed at 1.5 to 2 years of age and stored outside in exposed conditions. The resulting gradations of the crushed material had an average fineness modulus (FM) of 3.66 and ranged from 3.27 to 4.09, which is typical of what would be obtained with a commercial crushing operation. The crushed samples were tested three times for carbon uptake after approximately 4 months, 14 months, and 20 months of crushing and subsequent exposure. The testing corresponded to approximately 24 months, 34 months, and 40 months after original production. The results are shown in Fig. 2. The legend refers to the identification number and density classification for each set. For example, '1 – MW' was medium weight CMU with identification number 1. Similarly, LW and NW represent light weight and normal weight CMU. Additional details on the sets can be found in Walloch et al. [1]. The results were fairly consistent for all sets and averaged 52%-55% of the maximum calcination carbon emission potential. Additionally, it is observed that the uptake of the crushed samples remained approximately the same over time, indicating that the samples have reached the maximum practical carbon uptake at 4 months of exposure.

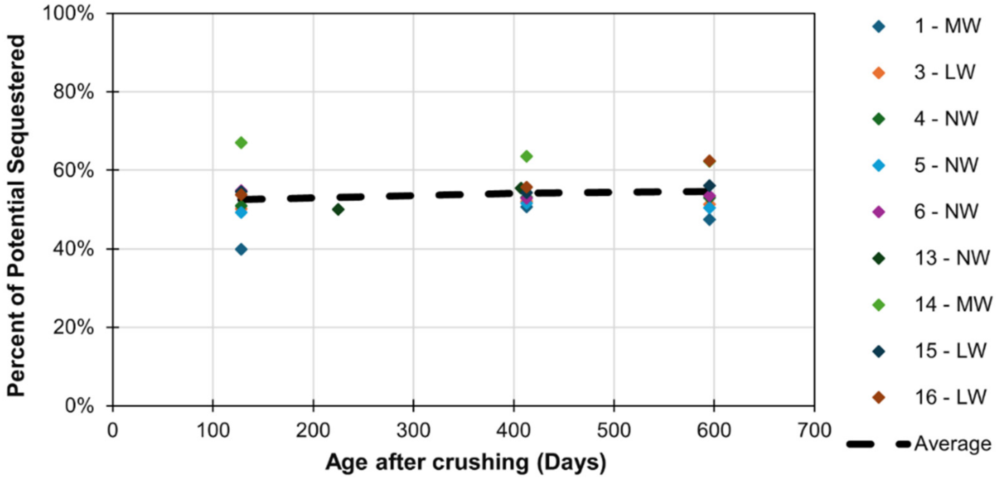

Figure 2. Carbon uptake of crushed CMU samples as a percentage of the calcination carbon emissions potential

The findings suggest that although crushing concrete enhances carbon uptake, fully neutralizing the calcination carbon emissions potential remains challenging for dry-cast CMUs, even under exposed outdoor conditions. The complete neutralization of calcination carbon emissions assumes that all calcium oxide (CaO) and magnesium oxide (MgO) in the clinker will undergo carbonation, disregarding the actual mechanisms of carbon uptake reactions. It represents the total calcination carbon emissions from the kiln production process. By comparison, the degree of carbonation (DOC) factor for crushed exposed wet-cast concrete is typically assumed to be 80% [6], which is the practical limit of how much of the calcination carbon emissions can be captured over time.

Another factor contributing to the maximum potential difference of crushed CMU compared to crushed exposed wet-cast concrete is due to the relatively large amount of unhydrated cement particles inside the cement agglomerations in dry-cast concrete, as discussed above. While even wet-cast concrete will have some unhydrated cement, it is interesting to note that the ratio of the dry-cast crushed samples is about 68%-73% of the DOC value for wet-cast crushed concrete. This is consistent with the typical estimation that 25%-35% of unhydrated cement is in dry-cast concrete and indicates that the crushing operation is not intense enough to expose the unhydrated cement particles inside the cement agglomerations.

Proposed carbon uptake model for dry cast masonry units

The carbon uptake model for the nine sets of CMU follows a logarithmic trend when expressed in terms of both uptake relative to the maximum sequestration potential and net uptake relative to crushed sample uptake. Compared to wet-case carbon uptake, which follows Fick's law of diffusion and progresses as a function of the square root of time, this shape indicates a more rapid initial uptake followed by a gradual deceleration over time.

Percent of Calcination Carbon Emission Potential (CCEP):

Fig. 3 presents the proposed model that can be used to determine the carbon uptake for the dry-cast CMU samples expressed as the percent of calcination carbon emissions of the cement. It presents the individual results for the nine sets up to three years of exposure and the curve for the average of the nine sets over time. The figure also shows the fitted logarithmic curve for the data, along with the 95% confidence interval. The equation for the proposed curve for the model is presented with an R^2 of 0.60 for the fitted data. This modest R^2 value indicates that while there is a good correlation between the data and the model, there is significant scatter in the data due to differences in the sets with respect to the mix design and constituent materials and the fact that only one specimen was tested at each age for each set with no replicate samples or duplicate measurements. On the other hand, the soundness of the model can be seen when plotting the average of the nine sets at each age as the correlation increases significantly with an R^2 of 0.94.

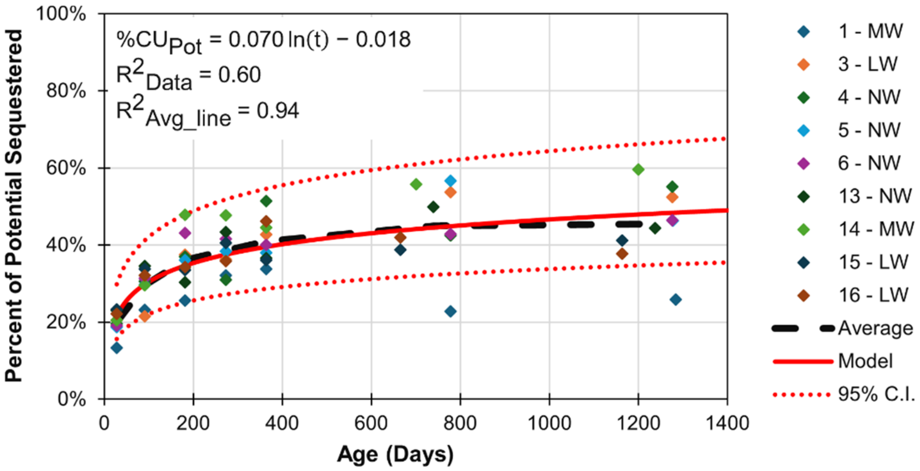

Figure 3. Proposed carbon uptake model for dry cast CMU units as a percentage of the calcination carbon emission potential

As in the original study, the nine sets of units in this study were stored outside without protection until the designated curing interval had been reached, at which time a coupon sample was saw-cut from the face shell of the unit. While uncontrolled, this storage condition was intentional to simulate the environmental exposure conditions the units would see in service, which in turn influence the rate of carbonation.

Specimens were stored in northern Virginia, the location of the Concrete Masonry and Hardscapes Association (CMHA) Research and Development Laboratory. The annual weather conditions in northern Virginia were considered a representative average weather pattern for North America, being neither extreme of precipitation nor temperature.

When a dry-cast CMU is exposed to rainwater or wet environments, its pores can become fully saturated, effectively blocking CO_2 diffusion and slowing carbonation. While capillary action initially aids moisture penetration, prolonged saturation restricts gas transport, limiting carbonation depth. However, under outdoor conditions, where the block experiences frequent wetting and drying cycles, capillary forces draw moisture into the pores during wet periods, while subsequent drying allows CO_2 to penetrate deeper into the material. This cyclical process enhances carbonation at greater depths over time. The carbonation rates are much higher in dry-cast CMU compared to wet-cast concrete because of the relatively larger inter-connect voids in the dry-cast concrete allow water and CO_2 to penetrate faster and deeper than is possible with the wet-cast concrete that only contains smaller capillaries in the paste and mortar fractions.

The repeated interaction between moisture uptake and drying-driven CO_2 ingress may contribute to the logarithmic trend of carbonation depth. Initially, carbonation progresses rapidly as CO_2 readily reacts with available calcium hydroxide that is produced as a byproduct of the hydration of the calcium silicate phases in the cement. However, as cycles continue, the carbonation gradually slows due to the blocking of some of the smaller pores with carbonation reaction products and the slower kinetics of the carbonation reactions with the calcium silicate gel and aluminate phases in the cement. This dynamic explains why carbonation rate slows over time, aligning with observed logarithmic trends in long-term carbonation studies of dry-cast CMU units.

Net Potential: Percent of Crushed (NP)

Fig. 4 presents a proposed model that can be used to determine the net carbon uptake for the dry-cast CMU samples. It compares the carbon uptake of the CMU samples to the crushed samples of the same set over time. As explained above, the crushed samples represent the practical limit of the degree of carbonation of the dry-cast concrete. The model essentially shows the carbon uptake of the CMU over time as compared to its practical limit.

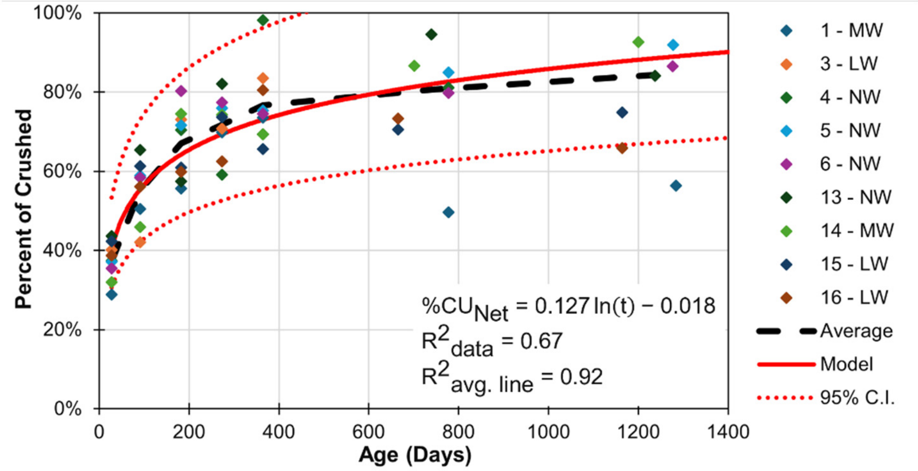

Figure 4. Proposed net carbon uptake model for dry cast CMU units with respect to the crushed samples.

Fig. 4 presents the individual results for the nine sets up to three years of exposure and the curve for the average of the nine sets over time. The figure also shows the fitted logarithmic curve for the data along with the 95% confidence interval. The equation for the proposed curve for the model is presented with an R^2 of 0.67 for the fitted data. This modest R^2 value indicates while there is good correlation between the data and the model there is significant scatter in the data due to difference in the sets and the fact that only one CMU specimen was tested at each age for each set with no replicate samples or duplicate measurements. On the other hand, the soundness of the model can be seen when plotting the average of the nine sets at each age as the correlation increases significantly with an R^2 of 0.92.

A similar logarithmic curve emerges, with crushed samples serving as a comparative benchmark for sequestration efficiency. This logarithmic behavior aligns with the physical constraints of carbonation. The crushed samples represent a theoretical upper bound, and the model indicates that the CMUs have achieved about 85% of their net potential uptake over a three-year period. The logarithmic trend effectively describes the relationship, as it mirrors the deceleration of CO_2 sequestration rates due to progressive pore blocking and declining availability of reactive phases in the CMU, as well as the steady carbon uptake of the crushed samples.

The predictive model for carbon uptake of CMU can be described by the following equation:

$$(1)\ \%CU_i = A \times ln(t) + B$$

where '$\%CU$' is the carbon uptake as a percent of potential, 't' is in days, and 'A' and 'B' are coefficients established based on the experimental data and the type of model (i), as shown in Table 1. Table 1 includes the models for CCEP and NP as well as a model for CPCP, which is not discussed in this paper. It is included for comparison as it was the carbon uptake protocol used in the original paper [1]. It was derived by fitting a logarithmic curve to the data through 3 years of exposure in a similar approach as the CCEP model discussed in this paper.

Table 1: Carbon Uptake Model Coefficients

Model Type (i)	**CPCP**	**CCEP**	**NP**
Coefficient A	0.080	0.070	0.127
Coefficient B	-0.018	-0.018	-0.018

Table 2 shows the values for carbon uptake predicted by the various models presented above as compared to the experimentally determined average values. As can be seen from this table, the value of carbon uptake (in kg/m^3) from all models is the same and correlates very closely to the experimentally determined average results.

Table 2: Summary of Results of Carbon Uptake Models

Age		Carbon Uptake, Percent of Potential			Carbon Uptake, kg/m^3	
Days	Years	CPCP	CCEP	NP	CPCP & CCEP Models	Experimental Averages
28	0.08	25	22	41	20	19
91	0.25	34	30	55	28	28
182	0.5	40	35	64	32	34
366	1.0	45	40	73	37	39
740	2.0	51	44	82	42	42
1,240	3.4	55	48	89	45	42

Of the three models and values presented in Tables 1 and 2, CCEP is the most useful for applications in EPDs because it is directly related to the calcination carbon emissions that are listed on a cement EPD and reported in CMU EPDs. Moreover, Life Cycle Assessment (LCA) practitioners can use the CCEP model to calculate the natural carbon uptake of a particular CMU for use in developing a product-specific EPD for that CMU. To calculate the amount of natural carbon sequestration of the CMU at a given number of days, one needs to first calculate the carbon uptake as a percent of potential at that age ($\%CU_{CCEP}$) using Eq. 1 with the coefficients A and B for CCEP from Table 1. Next, the practitioner should multiply this value by the calcination carbon emissions value shown on the CMU EPD that is attributable to the cement used in the production of the CMU. (The calcination carbon emissions of the cement used in a CMU are calculated by multiplying the value from the cement EPD by the cement content in the CMU, which is the product of the cement percentage and the CMU's density.) For example, at 28 days of age, $\%CU_{CCEP}$ equals $[0.070 \times \ln(28) - 0.018]$ or 0.215. The calcination carbon emissions attributable to the cement used in the production of a normal weight CMU (set 5-NW) is 90 kg CO_2e per m^3 of concrete, then at 28 days of exposure, the natural sequestration at 28 days of age equals [0.215 x 90] or 19.4 kg CO_2 e per m^3 of concrete.

It should be noted that the CCEP model was developed based on the carbon uptake of CMU mixes manufactured with Ordinary Portland Cement (OPC) (ASTM C150/C150M) [7] and without supplementary cementitious materials (SCM). Portland-Limestone Cement (PLC) (ASTM C595/C595 Type IL) [8] was not readily available when the CMU in this study were manufactured in 2021, however, the CCEP model is also applicable for CMU manufactured with PLC since there is no reactive Ca-rich products other than those in the clinker. The difference is that PLC has less clinker than OPC and limestone additions of up to 15% versus the maximum 5% limit for OPC. Although the clinker content in PLC is lower than in OPC, the CCEP model accounts for this because the calcination carbon emissions of the cement are directly related to the clinker content. However, the use of SCMs in CMU may result in larger total amounts of carbon sequestration than is calculated based solely on the calcination carbon emissions of the cement, especially when high calcium containing SCMs such as slag cement are used. Further investigation of the impact of using SCM mixtures on dry cast carbon uptake is needed.

CONCLUSIONS

Based on the results of the study presented here, the following conclusions are offered:

- Experimental results show that CMU sequesters CO_2 soon after production at a rate much faster than other concrete products. Carbonation continues throughout the lifetime of CMU, although the rate decelerates over time.

- The rate of carbon sequestration can be predicted using a logarithmic model based on the age of the CMU. At 3 years of age, the CCEP model shows that CMU sequesters approximately 48% of the potential maximum amount that could be sequestered based on the calcination carbon emissions of the cement.
- The CCEP model is directly related to the calcination carbon emissions that are listed on cement EPDs. As such, it is the model that should be used to estimate the carbon sequestration amounts for CMU at various ages.
- The results of CMU samples crushed and left exposed to the environment indicates a maximum carbonation potential of 52-55% for these dry-cast units.

FUTURE WORK

The following topics are offered as potential future work related to carbon uptake and sequestration of concrete masonry.

- Future studies – To improve robustness and reduce scatter of results, replicate samples and duplicate measurements should be incorporated in any future studies.
- Mix Design – The CMU mixes used in the present study did not contain SCMs. Further experimental investigation on SCM mixes may help in modifying the models to account for variation in carbonation due to the presence of SCMs with a high calcium content.
- Exposure conditions – This study has looked at carbon uptake for units exposed to typical weather outside in Northern Virginia. The impact of different exposure conditions on the carbon uptake of typical concrete masonry walls could be studied.
- Impact of coatings/surface treatments – The CMU in this study did not have any coatings or sealants applied. A future study could evaluate how the presence of typical coatings applied to exposed concrete masonry impacts the intensity and extent of carbon uptake.
- Depth of carbonation – The current study measured the carbon uptake based on samples from the entire depth of a CMU face shell. It is known that carbon uptake generally occurs from the exterior to the interior. To further enhance the modeling of dry-cast CMUs, it is proposed to conduct an experimental analysis to generate the carbonation coefficient and degree of carbonation as a function of depth over time. The data can be used for universal carbon uptake measurement and move toward a more material-agnostic approach, including a larger scope of masonry products.

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REFERENCES

[1] Walloch, C., Powers, L., Broton, D. and Thompson, J.(2022), "Conceptual Test Protocols for Measuring Carbon Sequestration of Manufactured Dry-Cast Concrete Products", *Masonry 2022: Advancing Masonry Technology,* ASTM International, West Conshohocken, PA. https://doi.org/10.1520/STP164020210112.

[2] ASTM C140/C140M-24a, "Standard Test Methods for Sampling and Testing Concrete Masonry Units and Related Units", ASTM International (approved December 15, 2024), West Conshohocken, PA. https://doi.org/10.1520/C0140_C0140M-24A.

[3] Global Cement and Concrete Association (GCCP). "CO2 and Energy Accounting and Reporting Standard for the Cement Industry, v3.1", https://www.cement-co2-protocol.org

[4] Kulisch, D.; Katz, A.; Zhutovsky, S. Quantification of Residual Unhydrated Cement Content in Cement Pastes as a Potential for Recovery. *Sustainability* 2023, 15, 263. https://doi.org/10.3390/su15010263.

[5] L. Powers, Personal communication, March 3, 2025.

[6] BS EN 16757 (2022). Sustainability of Construction Works – Environmental Product Declarations – Product Category Rules for Concrete and Concrete Elements. British Standards Institution, London UK.

[7] ASTM C150/C150M-24, "Standard Specification for Blended Portland Cement", ASTM International (approved July 1, 2024), West Conshohocken, PA. https://doi.org/10.1520/C0150_C0150M-24.

[8] ASTM C595/C595M-24, "Standard Specification for Blended Hydraulic Cement", ASTM International (approved July 1, 2024), West Conshohocken, PA. https://doi.org/10.1520/C0595_C0595M-24