

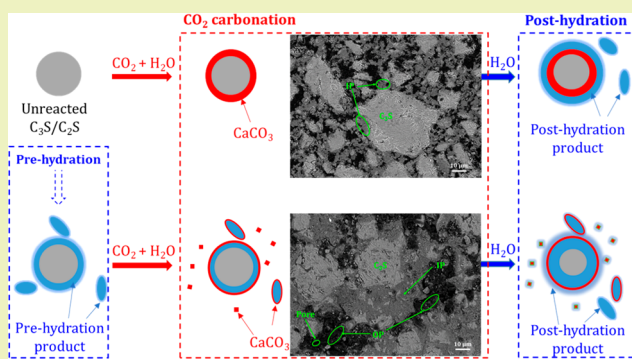
Optimal Pre-hydration Age for CO₂ Sequestration through Portland Cement CarbonationDuo Zhang,¹ Victor C. Li, and Brian R. Ellis^{*,1}

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Supporting Information

ABSTRACT: An emerging technology of CO₂ sequestration in Portland cement (PC) is through accelerated carbonation, where PC is intentionally carbonated at early hydration age and reinitiates long-term hydration upon completion of carbonation. However, the current literature has overlooked a fact that different PC hydration ages prior to carbonation (pre-hydration) could lead to distinct carbonation efficiencies and subsequent hydration behaviors (post-hydration). Here, we examine the effects of length of pre-hydration period on CO₂ uptake and on the hydration extent and final strength at 28 days. The CO₂ and H₂O profiles in the carbonated PC were examined with thermogravimetric analysis/derivative thermogravimetric analysis. The pre-hydration path was traced with isothermal calorimetry. Experimental results suggested that extension of pre-hydration decreased CO₂ uptake, but enhanced the extent of PC hydration at 28 days. It was found that a pre-hydration beyond the late deceleration period of PC hydration (where heat generation is slowing down) led to a higher hydrate content of cement paste, hence forming a higher compressive strength of mortar compared to the noncarbonated benchmarks at 28 days. The lesser carbonation-induced water loss and the nucleation seeding enabled by calcium carbonate are likely responsible for this effect. The finding reported here should be useful for fine-tuning PC carbonation process for CO₂ sequestration in concrete.

KEYWORDS: CO₂ Sequestration, Portland cement, Carbonation, Hydration, Compressive strength, Thermogravimetric analysis/derivative thermogravimetric analysis



INTRODUCTION

The cement industry contributes 5–8% of global CO₂ emissions. CO₂ sequestration in cement offers a pathway for reducing net CO₂ footprint and approaching a closed loop of carbon flow for a sustainable construction industry. It is generally agreed that cement-based materials possess a substantial potential through transforming CO₂ into carbonate minerals whereby the CO₂ can be safely stored.^{1,2} Recent research demonstrated that CO₂ could add technical benefits to a hydrating cement, thus opening new opportunities for beneficial use of CO₂ in producing cement-based construction materials.³ The process is usually completed within a few hours to days after the casting. The effect of CO₂ on cement-based materials is found 3-fold: (i) accelerating the early age strength gain of cement,⁴ (ii) enhancing durability properties of the cement-based materials, e.g., resistance to sulfate attack, chloride permeation and freeze–thaw damage,^{5–7} and (iii) stabilizing and recycling contaminated waste or soil in cement.^{8–10} More recently, the technology of cement carbonation has been further developed in the concrete industry including applications such as carbonation curing of precast concrete^{11–13} and CO₂ activation of waste-derived and alternative binder.^{10,14–16} The substantial volume of the

concrete industry makes this emerging technology a promising strategy for CO₂ utilization and sequestration.

Despite extensive research related to cement carbonation, one key parameter that affects the reactants, that is, the timing of CO₂ exposure with respect to cement hydration age, has been overlooked in the design process. Simply put, previous studies lack a consistency on how long the cement should be allowed to hydrate before introducing deliberate carbonation (i.e., pre-hydration). Portland cement (PC), which comprises 90% of the cement market,¹⁷ is studied here as an example. The hydraulic behavior of PC rapidly alters the phase assemblage of early age PC paste. In fact, roughly 50% of the initially mixed PC can be reacted and transform to the hydrated phases in the first 24 h.^{18,19} As such, the hydrated phases gain an increasing chance to be carbonated after a longer pre-hydration. This effect, however, has not been evaluated in the current literature. Table S1 in the Supporting Information lists carbonation processes reported in previous work.^{5,12,20–25} The reason for the inconsistency in length of pre-hydration is associated with the philosophy of design for

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cement carbonation processes. In cement and concrete technology, cement is normally mixed with an excessive amount of water (more than needed for complete hydration) to achieve a sufficient workability of the fresh concrete mixture.²⁶ Because the water would impede the diffusion path of CO₂ at the pore scale, a water removal process is usually applied prior to carbonation. In addition, the samples need to gain sufficient strength for demolding to be fully exposed to CO₂. Consequently, the length of pre-hydration is usually dictated by the time required to demold and achieve the desired water removal in samples, which varies significantly with the mixture type and conditioning environment. Such variation of the length of pre-hydration introduces uncertainties in the carbonation efficiency and engineering property of the carbonated material.

The purpose of this Letter is to promote discussion regarding the “pre-hydration age” as a controlling parameter for CO₂ sequestration through PC carbonation. On the basis of laboratory experiment and state-of-art PC hydration research, we aim to articulate the effect of the timing of CO₂ exposure (i.e., pre-hydration) on the efficiency of cement carbonation and subsequent hydration (i.e., post-hydration) of the carbonated cement. Note that, unlike other CO₂ sequestration methods, PC carbonation transforms CO₂ into engineering products (e.g., building materials) that are expected to have sufficient mechanical integrity and durability to be widely used in infrastructure applications. As such, the compressive strength and hydration profile of the carbonated PC were characterized until the standard curing age of 28 d with assistance of mortar compression and thermogravimetric analysis (TGA). Isothermal calorimetry was used to identify the pre-hydration path. The findings of this research would be useful to fine-tune the carbonation process for enhanced carbonation efficiency and material longevity, and should provide useful guidelines for effective early age carbonation for CO₂ sequestration in the concrete industry.

MATERIALS AND METHODS

Pre-hydration, Carbonation and Post-hydration. Ordinary Portland cement, Ottawa silica sand and deionized water were used in this study. The cement chemical composition and mixing protocol are listed in [Supporting Information](#) (Section 2). In order to exclude the water's effect on CO₂ diffusion and carbonation efficiency, an ideal dry mix was formulated.^{4,10,21,27} Because of the reactive transport nature of cement CO₂ carbonation, a low moisture condition was necessary to create a porous path for CO₂ diffusion. As such, the dry mix with a water-to-cement ratio of 0.15 allowed for effective cement carbonation to occur both immediately upon mixing and after a pre-hydration with an equal total water content of the sample. Samples were compacted to disks (diameter, 50 mm; thickness, 6 mm) for cement paste and cylinders (diameter, 50 mm; height, 50 mm) for mortars. Although the chemical reactions in cement pastes are the main focus of this study, compression test was conducted using mortar samples as a general protocol that includes the effect of paste-aggregate interfacial transition zone.

The experiment followed a three-step sequence: (i) pre-hydration, (ii) high-purity CO₂ carbonation, and (iii) post-hydration until the age of 28 days. The pre-hydration of cement was conducted in a sealed plastic bag set in a water-sealed container at room temperature (23 °C). The samples were assumed to have no water evaporation and the cement hydration was the sole contributor responsible for free water reduction during the pre-hydration. Five pre-hydration ages were designed in conjunction with the time frame of industrial manufacture turnover, including 0, 5, 11, 23 and 71 h. At each age, the samples were fully exposed and transferred to a carbonation chamber.

Pure CO₂ gas was injected and kept at one atmospheric pressure over the reaction period. The carbonation was carried out for 1 h with the cement paste and for 3 h for the mortar. Upon completion of carbonation, the samples were retrieved from the chamber and were compensated with deionized water to enable the post-hydration. The samples were properly wrapped with an impermeable membrane and stored in the water-sealed container to minimize water evaporation. The post-hydration proceeded until the 28th day after mixing. Compression test was performed in triplicate on mortar samples at a constant loading rate of 0.25 MPa/s. The averaged compressive strength is reported.

PC hydration typically follows four primary stages, which can be identified by the flow rate of the heat of hydration measured by an isothermal calorimeter.²⁸ The four stages of PC hydration include (1) initial reaction, i.e., early mineral dissolution, (2) induction period, i.e., a dormant stage with a low heat evolution, (3) acceleration period, in which nucleation and growth of hydration products are rapidly occurring, and (4) deceleration period, in which precipitation of hydration products slows down. Here, a Calmetrix I-Cal 8000 isothermal calorimeter was used to mark the pre-hydration of PC used in this experiment. Cement paste for the isothermal calorimetry was prepared following the same mix design and protocol as that for the carbonated samples. The isothermal calorimetry was carried out with 30 g of cement paste at 23 °C and lasted for 72 h. These samples were exclusively used to recognize the pre-hydration process and were not intentionally exposed to CO₂.

TGA-Based Hydrate and Carbonate Characterization. The hydration and carbonation products in PC decompose at high temperatures (up to 950 °C) to release H₂O and CO₂, hence decreasing the mass of the solid cement paste. By simultaneously heating and weighing the solid sample, TGA is able to quantitatively capture thermal decompositions of primary phases in cement pastes, which are useful for understanding the mechanisms of PC hydration and carbonation. In this experiment, TGA was conducted using the cement pastes on completions of the carbonation and post-hydration, respectively. The hardened cement pastes were manually crushed to small pieces with the largest dimension below 10 mm, and were soaked in isopropyl alcohol for 7 d. The purpose of this treatment is to arrest the cement hydration for further characterization through extracting free water in porous space of the hydrated cement paste. Isopropyl alcohol soaking was chosen for its low impact on mineralogical composition and microstructure of hydrated cement.^{29,30} The soaked samples were dried in a vacuum desiccator for 24 h before being pulverized and passed through a 100 μm sieve. Approximately 100 mg powdered sample was mounted into an aluminum crucible for TGA (Equipment: Netzsch TASC 413 Instrument). The crucible was heated at a rate of 10 °C/min to 950 °C. The furnace was purged with pure N₂ gas during the heating process with a flow of 50 mL/min. All TGA results, i.e., bound water content and CO₂ uptake, were rescaled to the ignited mass at 950 °C. To supply insights into evolutions of different hydration products, a breakdown of the total bound water was presented corresponding to C-S-H/AFt/AFm dehydrations mass loss (bound water I) at 30–300 °C and CH dehydroxylation mass loss (bound water II) at 400–500 °C (see [Figure S3](#)). Microstructures of carbonated cement pastes were investigated using scanning electron microscopy (SEM, equipment: Jeol IT500) with a backscattered electron (BSE) detector. The cement paste samples were impregnated in epoxy and polished at an applied force of 25 N. Isopropyl alcohol was used as a lubricant during the polishing process.

RESULTS AND DISCUSSION

Carbonation in Relation to Pre-hydration. [Figure 1](#) shows CO₂ uptake and mass increase of cement pastes scaled to the ignited mass. The PC carbonation is an exothermic process, wherein the free water is evaporated from the sample driven by the heat of reaction. The carbonation-induced water evaporation is plotted in [Figure 1](#). It was found that the CO₂ uptake was slowing as the pre-hydration extended from 0 to

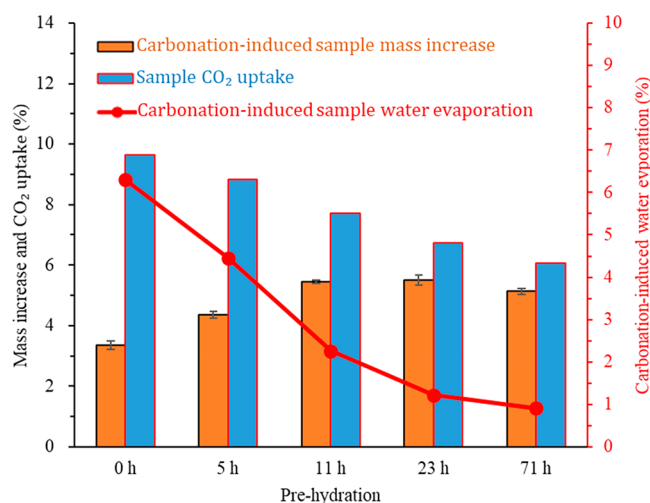


Figure 1. Carbonation-induced sample mass increase and CO₂ uptake varied with different pre-hydration ages. Measurements are performed immediately after CO₂ carbonation. All data are regulated to ignited masses. Carbonation-induced sample mass increase is measured at a precision of 0.001 g; sample CO₂ uptake is determined with TGA immediately after CO₂ carbonation; carbonation-induced sample water evaporation is determined by subtracting the carbonation-induced sample mass increase from the corresponding CO₂ uptake.

71 h. Over the same period, the carbonation-induced sample's mass increase was rising while the carbonation-induced water evaporation was declining. The profiles of CO₂ uptake and evaporated water collectively suggest that a longer pre-hydration lessened the efficiency of PC carbonation. A short pre-hydration, however, favored a faster carbonation reaction but led to a severe water loss in cement paste. The role of pre-hydration age in PC carbonation was 2-fold:

- Water reduction:** the water from the initial mixture of cement paste was consumed along with pre-hydration. In fact, the TGA result shows that the free water was rapidly reduced to ~84% at 1 h and ~46% at 72 h with respect to the originally mixed water (Table S3). Yet cement carbonation occurs only in an aquatic medium with water as an essential reactant. Hence, the limited availability of free water in cement paste after a longer pre-hydration limited the CO₂ dissolution and carbonation extent.
- Phase change:** in pre-hydration, the phase assemblage of cement paste was progressively varying with the anhydrous phases (i.e., C₃S, C₂S, C₃A and C₄AF) consumed to form the hydrates (i.e., C-S-H, CH, Aft and AFm). Consequently, the latter gain an increasing chance of being carbonated. Figure 2 shows the hydrate-bound water content of the carbonated and non-carbonated samples in relation to the pre-hydration of which the four main PC hydration stages were identified with calorimetric heat flow. Apparently, the two curves of hydrate-bound water content crossed at a pre-hydration age of ~11 h. In other words, the carbonation increased the hydrate-bound water content when CO₂ exposure began prior to ~11 h and decreased the hydrate-bound water content after ~11 h. This transition indicated that the CO₂ carbonation with a pre-hydration beyond 11 h was likely dictated by dehydration and decalcification of the hydrated phases.

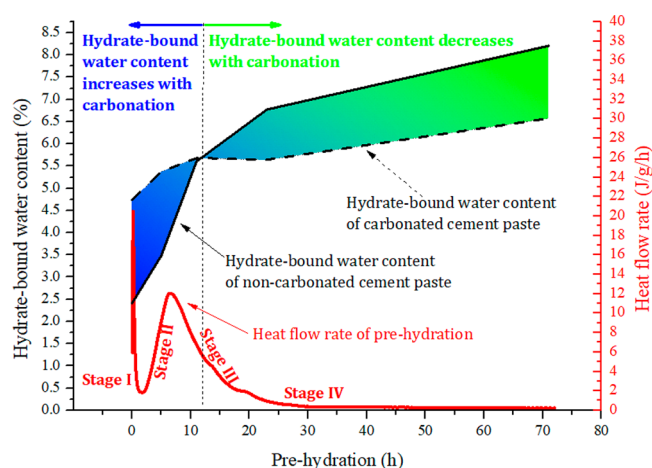


Figure 2. Impact of carbonation on hydrate-bound water content in relation to pre-hydration ages. Extending pre-hydration shifts hydrate-bound water from “increasing” to “decreasing” during CO₂ carbonation. Measurements are performed immediately after CO₂ carbonation.

Post-hydration in Relation to Pre-hydration. Figure 3 shows the 28 d's hydrate-bound water contents and mortar

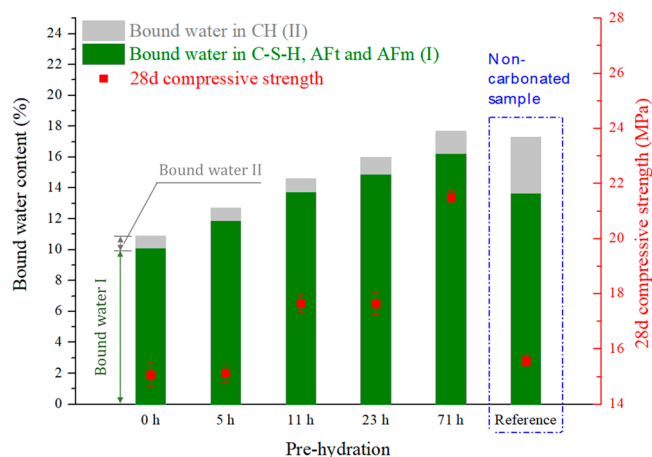


Figure 3. Effect of pre-hydration on hydrate-bound water and compressive strength stabilized at 28 days. Bound water I and II correspond to dehydration mass loss of C-S-H/Aft/AFm at 30–300 °C and CH at 400–500 °C, respectively. Derivative thermogravimetric analysis curves are given in Figure S3.

compressive strengths as a function of the pre-hydration age. It was found that the 28 d's bound water content in C-S-H, Aft and AFm phases (bound water I) in the carbonated samples increased with the pre-hydration age. This is likely attributed to a lesser carbonation degree after a longer pre-hydration that leaves a higher portion of cement to be subsequently hydrated. However, it was interesting that the content of bound water I of the noncarbonated sample was close to that of the carbonated sample with ~11 h pre-hydration. Indeed, as shown in Figure 3, the bound water in C-S-H, Aft and AFm of the carbonated sample surpassed the noncarbonated counterpart with a pre-hydration beyond ~11 h. This indicates that the carbonation posed an impact on the post-hydration, which likely varied with the pre-hydration age. The profile of compressive strength at 28 d was consistent with the profile

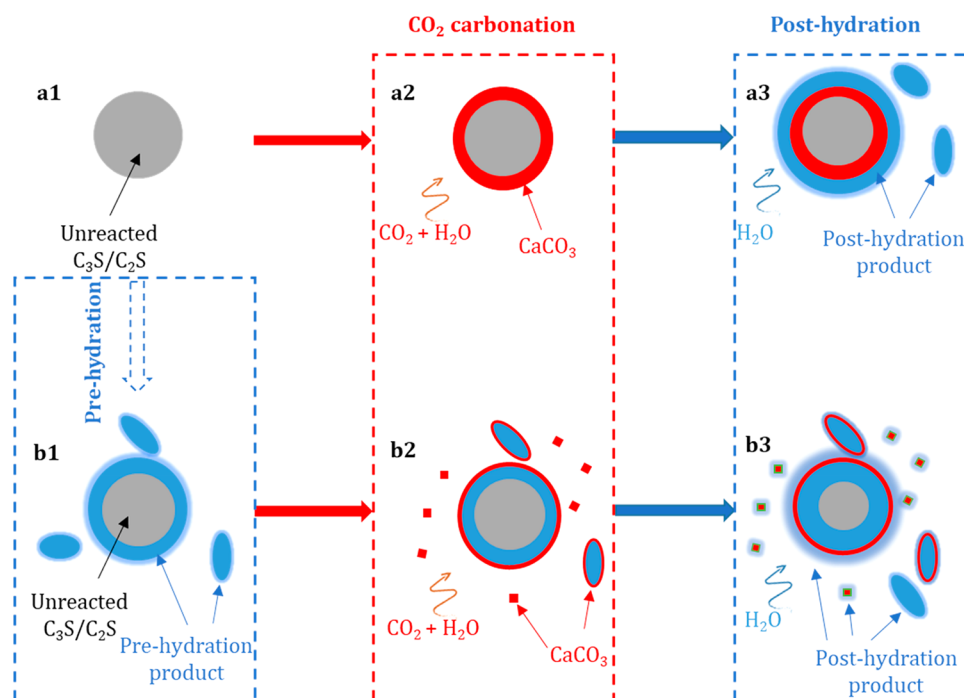


Figure 4. Proposed microscale model depicting the relative effect of pre-hydration on carbonation and post-hydration of a hydrating Portland cement. The drawings are not strictly to scale. For the cement paste with no pre-hydration, States a1, a2 and a3 denote the microstructural appearances before carbonation, after carbonation and after post-hydration, respectively. For the cement paste with a pre-hydration, States b1, b2 and b3 denote the microstructural appearances after pre-hydration, after carbonation and after post-hydration, respectively. Portland cement is represented by C_3S and C_2S . Carbonation of minor phases, including ettringite, monosulfoaluminate are not considered.

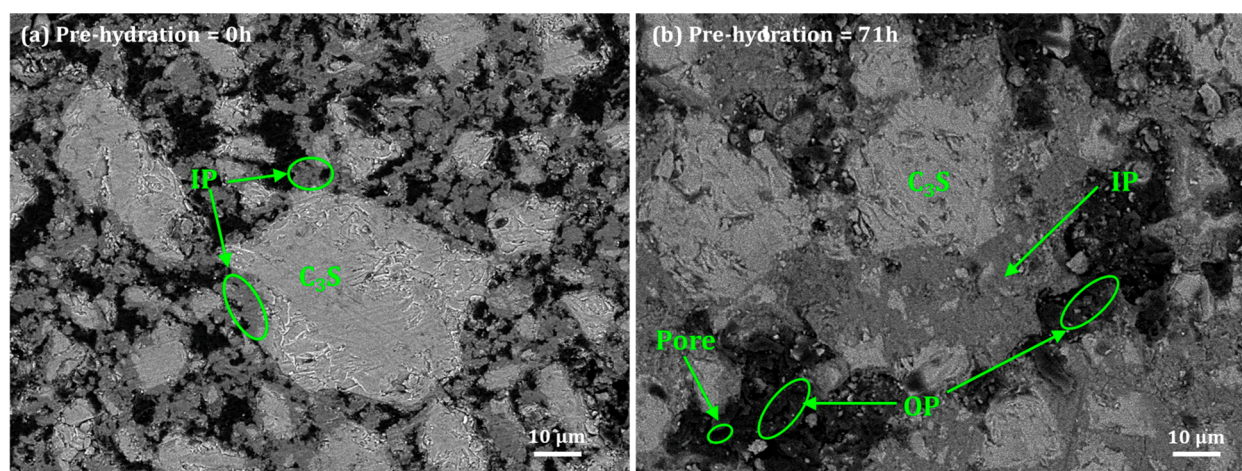


Figure 5. SEM/BSE images of early age cement pastes carbonated at pre-hydration of (a) 0 h, and (b) 71 h. Hydration of the cement paste samples was stopped immediately after 1 h of carbonation. IP, inner hydration/carbonation product; OP, outer hydration/carbonation product.

of bound water in C-S-H, AFt and AFm, which comprise the major constituents accounting for PC's bonding property.

Another water-bearing phase is the CH, which is responsible for the alkalinity of pore fluid in a hydrated cement paste. Despite that the 28 d's CH content was likely increasing to a slight extent along with the pre-hydration age, the CH content of all carbonated samples was unanimously lower compared to that of the noncarbonated reference.

Microscale Model. Figure 4 describes a simplified microscale model to demonstrate the role of pre-hydration in the carbonation and post-hydration of PC. The model concerns the carbonation and hydration products of C_3S and C_2S , which are the main carbonatable clinker phases in PC.

When no pre-hydration is applied (state-a1), the C_3S/C_2S particles are simultaneously exposed to CO_2 and H_2O . The TGA result suggests that the carbonation at this time causes severe water evaporation with rapid carbonate precipitation. The Ca^{2+} ions dissolved from C_3S/C_2S would not have sufficient time to disperse in the pore fluid before being carbonated and precipitating on the rim of C_3S/C_2S particles (state-a2). Microstructure of the carbonated cement paste at this state is shown in Figure 5a by SEM/BSE, in which the carbonation products were found mostly attached to the surface of C_3S particles as CO_2 and H_2O were concomitantly introduced (i.e., pre-hydration = 0 h). The heat of carbonation reaction leads to a relatively dry condition by evaporating free

water, and the precipitated calcium carbonate (Cc) limits the pathway of externally compensated water to the unreacted part of C_3S/C_2S for post-hydration. The Stage I and Stage II of the normal PC hydration have liberated abundant Ca^{2+} ions in the pore fluid of a cement paste, which would not largely precipitate until Stage III. The evolution of Ca^{2+} ion concentration in pore fluids can be found in a previous study by Rothstein et al., who observed an initial increase in Ca^{2+} concentration in the first few hours followed by a drastic reduction at ~ 12 h.³¹ The ion activity product for C-S-H and portlandite saturation index peaked simultaneously.³¹ The easy availability of Ca^{2+} ions in the pore fluid favors the formation and precipitation of Cc when exposed to CO_2 , thus promoting higher CO_2 uptake and carbonation efficiency as observed in Figure 1.

The carbonation will follow a different mechanism if the cement paste is allowed to sufficiently hydrate prior to the CO_2 exposure. Because the dissolved Ca^{2+} and SiO_3^{2-} ions would precipitate equally in the porous space and on the C_3S/C_2S rim,³² the pre-hydration products of C_3S/C_2S tend to spread out in the microstructure of cement paste, hence exposed to CO_2 equally as the anhydrous C_3S/C_2S (state-b1). As such, the Cc likely precipitates in close proximity to both hydrated and anhydrous phases (state-b2). Figure 5b shows microstructure of the cement paste carbonated at 71 h of pre-hydration, when a partially hydrated micromorphology comprising both inner and outer products has been established. Hydration products precipitate around C_3S particles (inner product) and fill up microscale pores (outer product), thus increasing the possibility of interacting with CO_2 and losing bound water due to carbonation. Carbonation products (mainly Cc) can therefore spread over a wider area where hydration products were located. Due to the small crystal size, dispersed Cc could enable a seeding effect by providing more surface area for the post-hydration products to reside (state-b3). Though the CO_2 uptake is lower with a longer pre-hydration, the sequestered CO_2 can function in a beneficial way, in which the post-hydration of the unreacted C_3S/C_2S can be expedited.

Implication for Beneficial Utilization of CO_2 in PC.

The experimental results and microscale model in prior sections collectively state one fact that, in order to benefit the post-hydration, the precipitation of Cc needs to spread out to avoid coating on the surface of anhydrous C_3S/C_2S . The Cc precipitated during early age PC carbonation is generally recognized as calcite with crystal size below $1\ \mu m$.³ These small Cc crystals potentially serve as nucleation seeds by providing additional solid surface area for precipitation of hydration products, thereby expediting the process of post-hydration. We postulate that the Cc solids precipitated from CO_2 carbonation are analogous to the naturally sourced limestone filler as a mineral additive in PC, which is well-known to enable the nucleation seeding effect when ground to a particle size below $2\ \mu m$.^{33,34} Investigation of additional factors relevant to the effect of Cc on post-hydration, such as interparticle distance³⁴ and surface chemistry,³⁵ are beyond the scope of this Letter. Accelerated post-hydration has also been observed in previous studies even with no pre-hydration applied,^{36–38} as long as the CO_2 uptake is limited such that the Cc does not effectively coat C_3S/C_2S particles. This opens plausible opportunities for CO_2 utilization in ready-mix PC-based concrete at fresh state, demonstrating a vast potential for CO_2 capture and sequestration in the construction market.

On the other hand, our findings also favor the cement carbonation after an intentional period for in-mold and water removal process, which is more commonly seen in practice for CO_2 sequestration in the precast industry. For this type of CO_2 sequestration, however, we suggest the process should include a pre-hydration stage until at least the late deceleration stage of PC hydration, as far as the long-term hydration property is concerned. Preparations for CO_2 exposure, such as demolding, conditioning and drying processes, can fit within this time frame. As a control of the CO_2 uptake and the carbonated material quality, the pre-hydration age needs to be documented and kept consistent in the process. Further investigations should examine the pore structure and durability of the carbonated cement with different pre-hydration ages.

Although reinforced application is out of scope of this study, it is worth noting that carbonation at a significant intensity would adversely affect the longevity of reinforced concrete due to increased risk of reinforcing steel corrosion posed by low alkalinity pore fluids after carbonation. The low calcium hydroxide content in the carbonated PC even after post-hydration emphasizes this concern. Further studies should evaluate general viability of CO_2 sequestration in reinforced applications, with particular focus on corrosion-related durability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.8b03699](https://doi.org/10.1021/acssuschemeng.8b03699).

Pre-hydration ages adopted in literature, sample preparation protocol, compression test method and procedure, TGA data (PDF)

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Notes

The authors declare no competing financial interest.

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■ CEMENT NOTATION

A = Al_2O_3
C = CaO
c = CO_2
F = Fe_2O_3
H = H_2O
S = SiO_2

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