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Carbon dioxide as an admixture for better performance of OPC-based concrete

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ABSTRACT

This study explores a novel beneficial utilization of CO_2 in ordinary Portland cement (OPC) based concrete. In existing studies, CO_2 is mainly added into concrete through accelerated carbonation of fresh or hardened concrete, which is limited by the low diffusion of CO_2 into the concrete. In addition, a high CO_2 concentrated environment is needed to carbonate the concrete, making the existing methods only applicable to pre-cast concrete. Aiming to eliminate these limitations in the existing methods, this study proposes to directly add gaseous CO_2 into fresh concrete mix as an admixture through a two-step mixing approach, pre-carbonation method. In this method, CO_2 is first absorbed into a slurry of calcium-rich cementitious material in the first step, and then blended with the rest ingredients to produce concrete in the second step. This method can in-situ produce nano to sub-micro $CaCO_3$ particles in fresh concrete, providing extra heterogenous nucleation sites for the hydration of OPC. Therefore, the hydration of OPC can be greatly improved, as evidenced by the calorimetry testing result. The addition of CO_2 also produces more ettringite in the produced mortar, as revealed by X-Ray Diffraction and Thermogravimetric analysis. As a result, the overall volume of the hydration products of the OPC is increased, leading to denser microstructure of the mortar samples. For these reasons, the compressive strength of the cement mortar samples can be significantly improved by the proposed method.

1. Introduction

Concrete with Ordinary Portland cement (OPC) as the binder is the most widely used construction material. The global use of concrete is only second to water, accounting for 70% of all building and construction materials. Although OPC has many advantages such as ease of application, availability of the raw materials all over the world, the production of OPC releases large amount of green-house gases. One ton of cement clinker releases 0.98 tons of equivalent carbon dioxide, and cement industry accounts for 5% of global carbon dioxide emission [1,2].

Carbon dioxide emitted during the manufacturing of OPC is naturally reabsorbed in concrete products through a natural chemical reaction. However, the natural process is too slow and it can take hundreds of years to reabsorb all the emitted CO_2. In addition, carbonation is detrimental to concrete because it can cause corrosion of steel reinforcement. However, carbonating concrete at early age with highly concentrated and pressured CO_2 can significantly accelerate the strength development of the concrete, as shown in some early studies [3,4]. Now this fast carbonation curing technique is revisited [5–8] to accelerate reabsorbing of CO_2 in concrete. To this end, early age concrete specimens are cured in a closed chamber full of CO_2 gas [5]. After diffusing into the concrete specimen, CO_2 gas can react with the fresh concrete and transform into solid calcium carbonates ($CaCO_3$). Reabsorbing CO_2 in concrete is an application example of a general concept of storing CO_2 permanently in the form of thermodynamically stable carbonates through chemical reaction between CO_2 and reactive metal oxide feedstocks first suggested by Seifritz [9].

Many descendants of this method have also been developed [10–15]. For example, Mo et al. extended this method to fly ash and MgO blended cement system and found the compressive strength of blended the cement paste can be greatly enhanced by exposing the produced pastes under pressurized CO_2 [10]. Pan et al. [15] first carbonated circular fluidized bed fly ash with over 60% calcium content through high-gravity carbonation process, and then added the carbonated fly ash into concrete. Their study shows that the cement mortar containing 10% carbonated fly ash can even have higher compressive strength than the pure cement at 7 d [15]. In addition, binders hardening purely through carbonation have been explored over the past decades to store CO_2 [11–14].

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Although it is accelerated by using high concentrations of CO_2, carbonation speed is still the major obstacle of this technique. This is because the carbonation rate of early age concrete is determined by the diffusion of CO_2 into the concrete matrix, which is very slow. In addition, the carbonation products, $CaCO_3$ particles, can fill the pores in the concrete matrix, making the diffusion of CO_2 more difficult [16]. Therefore, existing studies on carbonation curing of concrete are limited to concrete specimens with a small thickness so that diffusion of CO_2 to the full depth of the specimen is possible in short period. In addition, the degree of carbonation varies at different depths from the surface and thereby affects the properties of the concrete. Excessive carbon curing can even destroy calcium silicate hydrate (C-S-H), the major hydration product and binding agent of OPC, and thereby reduce the strength of the concrete. Consequently, the theoretical CO_2 absorption of concrete can never be reached if the strength of concrete must be maintained. Since a closed curing chamber is needed, carbonation curing technology is only applicable to precast concrete.

Aiming to address the limitations in the existing methods summarized above, we propose a new method of utilizing CO_2 as an admixture for concrete to not only reduce the carbon footprint of the concrete, but also enhance the strength and durability of the concrete. To avoid the difficulty of CO_2 diffusion into concrete, the new method directly adds CO_2 into the mix of the concrete. However, CO_2 is in the gas phase in ambient environments, and therefore cannot be mixed with other ingredients to make concrete products. To overcome this difficulty, we propose to use absorbents to absorb CO_2 first, and then mix the absorbed CO_2 and absorbents with other ingredients to make concrete. Since the cementitious materials used in the concrete - both OPC and commonly used supplementary cementitious materials (SCMs) including high calcium fly ash, blast furnace slag, cement kiln dust, and slaked lime - are rich in calcium, CO_2 can be absorbed by these materials through reaction with calcium to produce a mix of calcium carbonate/bicarbonate. Therefore, these calcium-rich cementitious materials serve perfectly as CO_2 absorbents, and no extra absorbent is needed.

To implement this concept, a two-step mixing approach can be used, as shown in Fig. 1. In the first step of the mixing, calcium-rich cementitious material (can be OPC if no SCMs is used; otherwise, it should be SCMs) is mixed with mixing water to form a slurry. Then, carbon dioxide is bubbled into this slurry, which reacts with calcium ions in the slurry to form a mix of calcium carbonate/bicarbonate. In the second step, other ingredients of the concrete, including OPC, aggregates, and other admixtures as needed are added and mixed with the slurry produced in the first step to produce concrete.

It can be seen that the first step of the proposed technique is essentially a carbonation process in which the calcium-rich cementitious material is carbonated by CO_2. Since this carbonation occurs before the casting of concrete, we refer to this new approach as the pre-carbonation method. Since CO_2 is directly bubbled into the slurry in the pre-carbonation, the slow diffusion process through the concrete matrix is eliminated. Thereby the pre-carbonation method overcomes the major drawback of the existing carbonation curing technology and can be used to make bulky and large-size concrete products. This method is also applicable to in-situ casting of concrete because no closed curing chamber is needed. In addition, some mechanism can also be triggered by this method, as demonstrated by this study.

Table 1
Chemical composition of Type I/II Portland cement.

Oxide Composition	Type I/II Portland cement (%)
SiO_2	22.94
TiO_2	0.21
Al_2O_3	4.89
Fe_2O_3	2.57
MgO	3.52
CaO	64.85
Na_2O	0.20
K_2O	0.81
LOI	2.52

2. Materials and methods

2.1. Materials

Pure CO_2 gas, from Airgas, United States was used as carbonate source. Slaked lime from Montevallo Plant (owned by Lhoist North America) was used as calcium source. Type I/II OPC produced by Sakrete Inc. was used to make mortar/concrete samples. Its chemical composition is presented in Table 1. Based on Bogue calculation (ASTM C150 [17]), this cement has 53% C_3S, 25.7% C_2S, 8.6% C_3A, and 7.8% C_4AF. The fine aggregate was river sand with bulk specific gravity of 2.70 and water absorption capacity of 0.95%. The coarse aggregate was crushed limestone with dry specific gravity of 2.74 and water absorption capacity of 0.7%. The ground limestone powder, which contains 94% $CaCO_3$, was manufactured by Dudadiesel.

2.2. Pre-carbonating the slaked lime slurry

Although many calcium-rich minerals such as high calcium fly ash can be used to absorb CO_2, slaked lime was used in this study. This is because the carbonation reaction of the slaked lime slurry is very simple, making it easier for us to delve into the working mechanism of the pre-carbonation method. In this process, CO_2 gas first dissolves in water forming carbonic acid. Then carbonic acid dissociates to H^+ and $CO_3{}^{2-}$, which meet with Ca^{2-} released from the slaked lime to form calcium carbonate precipitate in nano to sub-micrometers. If more CO_2 is bubbled into the slurry, some of calcium carbonate will be dissolved to form calcium bicarbonate, which has much higher solubility in water. Therefore, the carbonated slaked lime slurry is rich in calcium carbonate particles, Ca^{2+}, $HCO_3{}^-$, and small portion of $CO_3{}^{2+}$. After mixing with OPC, $Ca(OH)_2$ produced by the hydration of OPC reacts with $HCO_3{}^-$ to produce calcium carbonate precipitants.

The slaked lime slurry was made by mixing the slaked lime with 500 mL deionized water in a 1 L glass beaker for 3 min. Two concentrations of the slaked lime slurries were made: 0.14 mol/L (1% by weight of water) and 0.52 mol/L (3% by weight of water). The slaked lime slurry was carbonated by directly bubbling CO_2 into the slurry through an air stone with a gas flow rate of 2 L/min. A magnetic stir was used to stir the slurry at a rate of 800 rpm during the carbonation. The pH value of the slaked lime slurry during the carbonation was continuously monitored to determine the carbonation duration needed to fully carbonate the slaked lime slurry. The determined carbonation duration was used to carbonate the slaked lime slurry to produce all the

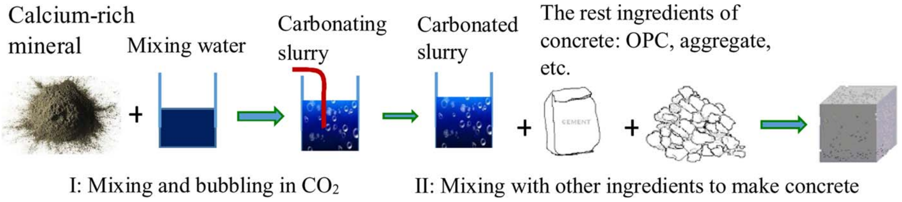

Fig. 1. Manufacturing concrete through the pre-carbonation method.