Review article

Review on carbonation curing of cement-based materials

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ABSTRACT

Carbonation for the curing of cement-based materials has been gaining increased attention in recent years, especially in light of emerging initiatives regarding carbon emissions. This article reviews the status quo of the carbonation curing process with insight into the approach's scientific premise, industrial scalability, and commercial spin-offs. Calcium-silicate-based binders, such as Portland cement and its lower energy alternatives, experience very rapid hardening when adequately moistened and exposed to high concentrations of carbon dioxide. Concretes processed as such display improved physical performance and better overall resistance to freeze-thaw cycles, sulfate salts, and acids. In addition to binder activation, carbonation's valorizing potential can also be exploited to recycle suitable industrial wastes into raw building materials. The perpetual fixation of carbon dioxide in building products conduces a more sustainable stance for the concrete industry as it fulfills mandates for lower carbon footprint. In this article, topics relevant to carbonation curing including reaction mechanisms, processing and impacts on material performance and sustainability are comprehensively reviewed. Further laboratory and industrial research are also proposed.

1. Introduction

The role of carbon dioxide (CO$_2$) in building materials is not new. In fact, it dates back to Ancient Rome, where mortar prepared from lime, sand, and water was found to exhibit improved binding strength after slowly reacting with CO$_2$ in the atmosphere. A similar enhancing effect was experienced by mortar used in the construction of the Great Wall of China. Forwarding to the early 19th century, the introduction of Portland cement (PC) set a new standard for hydraulic binders, one which today's behemoth concrete industry was founded upon. Simply stated, PC binds by generating strength-inducing hydration products when mixed with water. Unlike its role in ancient lime mortar, CO$_2$ is unfavorable for PC as it gradually decomposes hydration products over time. Carbonation is generally regarded as a deterioration mechanism for concrete. The main binding component of cement, the calcium-silicate-hydrate (C-S-H), is believed to decalcify upon extended exposure to atmospheric CO$_2$, eventually becoming a silica gel in the process and losing its binding capability as a consequence. Meanwhile, carbonation also induces a neutralizing effect to the highly alkaline environment provided by PC hydration (pH above 13 in pore solution), thereby increasing the vulnerability of embedded reinforcing steel to corrosion. The deleterious effect of atmospheric CO$_2$ on modern concretes and mortars is known as 'weathering carbonation'.

Curing of freshly cast concrete allows for rapid cement hydration, which influences early-age performance development as well as durability properties in service life. This is an important processing step adopted by the precast industry in order to ensure product turn-over is met. Steam is conventionally used during curing so that an environment of elevated temperature (50–70 °C) and relative humidity (above 95%) is maintained. Although the rate of strength development is increased with steam curing, other less desirable side effects may appear in the long term. Moreover, steam curing is an energy-intensive process due to its steam generating component. Nonetheless, it remains the most widely used approach for precast curing, and even mandatory for specific alternative cementing materials that require hydrothermal processing, such as alkaline activated binders.

The idea of using CO$_2$ for curing was initially proposed in the 1970s and has not been adopted until recently. This method has been reluctantly deliberated because of expensive production of pure CO$_2$ and apparent negative effects of weathering carbonation. The urgency of mitigating greenhouse gas emissions, however, re-ignited interest in carbonation curing, particularly after the 2000s. Dramatically rapid strength gain has been observed for CO$_2$-cured PC. Increased product resilience and improved durability performance have also been demonstrated by carbonation curing. Broader studies have shown that a binder-like consolidation can also be activated when carbonating certain minerals otherwise known to exhibit weak to no hydraulic reactivity (e.g. mono-calcium-silicates, di-calcium-silicates). Certain

industrial wastes meet this mineral composition criteria, leading many studies to explore the use of such waste materials in construction, and envisioning alternative concrete raw materials that embody a negative carbon footprint.

Unlike weathering carbonation where hydration products are undermined by atmospheric CO_2, early-age carbonation engages anhydrous binder minerals directly to form the binding matrix. The CO_2 gas acts as a reactant, rather than a catalyst, yielding a binding matrix distinct from that obtained from conventional hydration. To distinguish from deleterious weathering carbonation, the term 'early-age carbonation curing' is used. This type of curing is normally finalized within a time frame of a few hours to days.
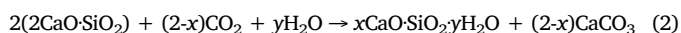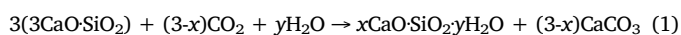
Weathering carbonation of cement-based materials has been extensively investigated. Laboratory studies have been conducted on hardened cement pastes and concretes (hydrated for 28 days or longer) subject to accelerated carbonation environments to mimic long term weathering. Similar onsite testing was performed on existing structures. In the early 2000, Bertos et al. presented an elaborate overview on the use of carbonation for treating industrial wastes and attaining CO_2 sequestration [1]. In a more recent study, Ashraf presented a general perspective on the carbonation of cements and concretes [2]. Jang et al. narrowed the scope down to focus on CO_2 sequestration by cement-based materials [3]. Apart from those works, this article reviews the application of carbonation as a curing approach, with topics covering the reaction mechanism, process of implementation, final product performance, economic feasibility, and environmental impacts. The carbonation curing on PC, alternative binders, and artificial aggregates are comprehensively examined.

## 2. Chemical reactions of early-age carbonation

2.1. Calcium silicate system

2.1.1. Reaction mechanism

Calcium silicates and their hydrate products constitute more than 60% the volume of hydrated PC, the fraction primarily responsible for the engineering properties of concrete products. Fig. 1 identifies the different phases of the CaO-SiO$_2$-Al$_2$O$_3$ ternary system and their CO_2 reactivity. Anhydrous minerals alite (3CaO·SiO$_2$, or C$_3$S) and belite (2CaO·SiO$_2$, or C$_2$S), of different polymorphs, are known to be reactive to CO_2 and follow Eqs. (1) and (2) below [4].

$$3(3CaO\cdot SiO_2) + (3\text{-}x)CO_2 + yH_2O \rightarrow xCaO\cdot SiO_2 \cdot yH_2O + (3\text{-}x)CaCO_3 \quad (1)$$

$$2(2CaO\cdot SiO_2) + (2\text{-}x)CO_2 + yH_2O \rightarrow xCaO\cdot SiO_2 \cdot yH_2O + (2\text{-}x)CaCO_3 \quad (2)$$

Calcium silicates react with CO_2 in aqueous conditions to generate calcium silicate hydrate ($xCaO\cdot SiO_2 \cdot yH_2O$, or C-S-H) and calcium carbonate (CaCO$_3$) [4,5]. During normal hydration, calcium hydroxide (Ca(OH)$_2$) is generated instead of calcium carbonate [4,5]. The stoichiometry of the products (x and y in Eqs. (1)–(2)) vary with the extent of the reactions, which are exothermic in nature and accompany the partial evaporation of mixing water. Extensive carbonation of C-S-H associates a decalcification effect and an eventual transformation to silica gel (SiO$_2$) and CaCO$_3$ following Eq. (3) [6,7]. The carbonation of adequately moistened C$_2$S and C$_3$S occurs rapidly within a few minutes to hours, where the equally rapid generation of C-S-H explains the associated strength gain.

$$C\text{-}S\text{-}H + CO_2 \rightarrow CaCO_3 + SiO_2 + H_2O \quad (3)$$
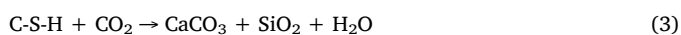
Short-term carbonation doesn't fully react all C$_2$S and C$_3$S grains, therefore continued exposure to moist or humid environments post-carbonation allows for the subsequent hydration of residual unreacted portion [8]. The microstructure of the final paste matrix generated from dual carbonation/hydration curing presents an intermixture of C$_2$S, C$_3$S, C-S-H, CaCO$_3$ and Ca(OH)$_2$.

2.1.2. Reaction products

Carbonation of calcium silicates is essentially a CO_2 sequestering process. Gaseous CO_2 is converted into mineral CaCO$_3$, which can be precipitated as one or a combination of different polymorphs. Table 1 summarizes the reaction products obtained from the carbonation of different cement-based preparations, as identified by various studies. Calcite seems to be the most dominant crystalline CaCO$_3$ polymorph when carbonating C$_3$S and β-C$_2$S, with a crystal size confined to ~ 1 μm [5]. Aragonite is reported for a few circumstances, while the formation of vaterite is seemingly not favored. Interestingly, however, non-hydraulic belite, γ-C$_2$S, yields both calcite and vaterite after carbonation [9–11].

Formation of C-S-H from carbonation alone is widely debated, but strong evidence seems to suggest a gel-like amorphous phase with a lower CaO/SiO$_2$ ratio than that of hydraulically generated C-S-H from calcium silicates [4,6,12–14]. A number of studies refer to this gel phase as decalcified C-S-H or polymerized silica gel [13], exhibiting morphological similarities to C-S-H obtained from C$_3$S hydration [15]. Another study suggests the presence of an amorphous calcium silicate hydrocarbonate, with CaCO$_3$ impregnated [12]. More recently, evidence from ^{29}Si magic-angle spinning nuclear magnetic resonance (NMR) demonstrates increased silicate polymerization from a higher degree of carbonation [11,13]. Peak intensities representing silicate chains of C-S-H in lightly carbonated β-C$_2$S (CO_2 uptake of 9.3%, shown in Fig. 2) vanish as the material is subjected to more vigorous carbonation (CO_2 uptake of 48%, shown in Fig. 3a). The result is that the primary peak progressively shifts to Q^4 sites, typical of highly polymerized silica gel [11,13].

A lower degree of carbonation on PC (CO_2 uptake ~ 8.2%) over a short period (2 h) does not indicate the generation of silica gel [16]. The same insights are reflected from Fourier transform infrared spectroscopy (FTIR) results [14]. Under such circumstances, the resulting binding phase is depicted as small crystallites of CaCO$_3$ incorporated into an enveloping C-S-H nanostructure [16]. However, conclusive depictions are premature in the absence of precise characterization with Transmission electron microscopy (TEM) [17,18] and high-energy X-ray diffraction [19,20].

2.1.3. Carbonation of non-hydraulic calcium silicate minerals

C$_2$S has five subsiding polymorphs among which only γ-C$_2$S is non-hydraulic. Regardless, all polymorphs can be activated by CO_2 for strength gain as per Eq. (2). Relevant studies have been initially conducted by Bukowski and Berger [9] and complemented later by NMR and FTIR in recent years [11,21]. In contrast to β-C$_2$S, γ-C$_2$S shows a CO_2 reactivity that is twice as high, but forms only half the binding compressive strength [11]. Belite-rich cements and compositionally-suitable industrial wastes are the topic of the following section. In addition to C$_2$S and C$_3$S, other minerals in the calcium silicate system can react with CO_2 and H$_2$O to gain strength as well. One example is wollastonite (CaO·SiO$_2$, or CS) as indicated in Fig. 1. Investigations on the carbonation of CS suggest that C-S-H formation is absent [14,22]. Instead, CaCO$_3$ and silica gel are indicated as the main binding phases that contribute to strength values in the range of 60–80 MPa [9,14], giving birth to the emerging wollastonite-based cements.

2.2. Calcium aluminate and sulfoaluminate system

Unlike calcium silicate phases, calcium aluminates record minimal to no reactivity to CO_2. Carbonation seemingly offers no contributions to strength development of C$_3$A (3CaCO$_3$·Al$_2$O$_3$) and C$_{12}$A$_7$ (12CaCO$_3$·7Al$_2$O$_3$) [23]. However, aluminium dissolved from C$_3$A might be incorporated into the polymerized silicate chains of carbonated PC [13]. The primary phase of calcium aluminum cement (CAC), monocalcium aluminate (3CaCO$_3$·Al$_2$O$_3$, or CA), was studied by reacting with supercritical CO_2 after a short period of hydration [24,25]. Products of the reaction were identified as calcium aluminate hydrate,