



Carbonation activated binders from pure calcium silicates: Reaction kinetics and performance controlling factors

Warda Ashraf^{a,*}, Jan Olek^b

^a Department of Civil and Environmental Engineering, University of Maine, 314 Boardman Hall, Orono, ME, 04469-5711, USA

^b Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN, 47907, USA

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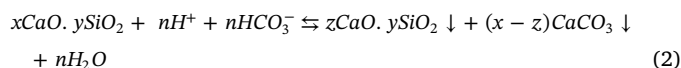
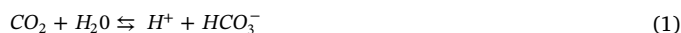
ABSTRACT

This paper presents a study on the carbonation activated binders prepared from pure calcium silicate phases, which included tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$, [C_3S]), β -dicalcium silicate ($\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$, [$\beta\text{-C}_2\text{S}$]), γ -dicalcium silicate ($\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$, [$\gamma\text{-C}_2\text{S}$]), tricalcium disilicate (rankinite, $3\text{CaO}\cdot 2\text{SiO}_2$, [C_3S_2]), and monocalcium silicate (wollastonite, $\text{CaO}\cdot\text{SiO}_2$, [CS]). The overall study consisted of three experimental parts, with individual focus on the following issues: (i) reaction kinetics, (ii) mechanical performance at the microscale, and (iii) mechanical performance at the macroscale. Carbonation of calcium silicate phases was found to occur in two distinct stages, namely: phase boundary controlled stage and product layer diffusion controlled stage. Theoretical solid-state reaction approach, including contracting volume model and Jander's equations were used to determine the carbonation rate constants for the calcium silicate phases. Phase boundary controlled stage was found to be dominantly dependent on the type of the starting calcium silicate phases. On the other hand, during the diffusion controlled stage the reaction rate constants were found to depend on the type of carbonation products (in this case Ca-modified silica gel and calcium carbonate). The mechanical properties of the individual microscopic phases were evaluated using nanoindentation test whereas the overall strength of the carbonated paste was evaluated using macroscale three-point bending test. Correlations between the mechanical performances and microstructural characteristics revealed the performance controlling factors of the carbonation activated binders. The higher bound water contents of the carbonated matrix tend to increase the short-term (up to 3 h) creep deformation of the matrix when subjected to constant stress. The presence of a higher proportion of poorly-crystalline forms of calcium carbonates (i.e., vaterite and amorphous calcium carbonate) were observed to increase the flexural strength but decrease the elastic modulus of the carbonated matrix.

1. Introduction

In recent years, the high carbon footprint of ordinary portland cement (OPC) drove the demand for development of alternative sustainable binder systems. Accordingly, during the past several decades, a number of alternative cementitious systems with low carbon footprint have been developed. Examples include alkali activated materials [1,2], reactive belite [3,4], waste metallic powder [5], magnesia [6], carbonate binders [7–9], etc. A new addition to these alternative cementitious systems is the carbonation activated low-lime calcium silicate binder composed mostly of wollastonite ($\text{CaO}\cdot\text{SiO}_2$, [CS]), pseudo-wollastonite ($\text{CaO}\cdot\text{SiO}_2$, [CS]), and rankinite ($3\text{CaO}\cdot 2\text{SiO}_2$, [C_3S_2]) phases [10]. Since these low-lime phases are non-hydraulic, they are generally not utilized in OPC. However, these low-lime calcium silicates exhibit enhanced reactivity in the presence of CO_2 [11–13]. Utilization

of these low-lime calcium silicates can reduce the carbon footprint of cement (compared to the production of OPC) by reducing the amount of limestone and lowering the temperature (up to 250°C) required to produce clinker. In general, the carbonation of calcium silicate phases occurs in two steps:



As seen from Equations (1) and (2), during the carbonation process, the calcium silicate phases produce Ca-modified silica gel (amorphous) and calcium carbonate (both, crystalline and amorphous forms) [14,15]. Most of the studies on carbonation kinetics of cementitious materials have focused on the carbonation of well-hydrated systems,

* Corresponding author.

E-mail address: warda.ashraf@maine.edu (W. Ashraf).

where the reaction rate is governed by the diffusion rate of CO₂ through the dense microstructure [16,17]. However, in case of low-calcium silicate binders, the samples are subjected to carbonation immediately after mixing with water. In such cases, the chemical kinetics of carbonation is expected to play a vital role [18].

Goodbrake et al. [19,20] investigated the carbonation kinetics of hydraulic calcium silicate phases (C₃S and β-C₂S) and suggested that the same type of equation (in the general form: degree of reaction = constant × log (reaction duration) or $\alpha = K' \log t$) can be used to describe the kinetics of both, hydration of cement and the carbonation of wet samples, even though carbonation occurs over much shorter time compared to hydration. In these studies [19,20], the initial (i.e., fast) carbonation stage was not considered in the evaluation of the kinetics of the process. Rather, it was assumed that the complete carbonation was diffusion controlled. Although Bukowski and Berger [12] reported that it is possible to carbonate the non-hydraulic calcium silicates, the reaction kinetics of these phases are yet to be explored. Furthermore, depending on their chemical composition, the crystallographic structures of the calcium silicate phases of interest will be significantly different. As an example, the C₃S and C₂S phases belong to orthosilicate group of minerals and consist of isolated silicate tetrahedrons [21,22]. On the other hand, the rankinite (C₃S₂) and wollastonite (CS) minerals belong to, respectively, sorosilicate (consisting of isolated double silicate tetrahedra) and inosilicate (consisting of chain of silicate tetrahedra) groups [21,22]. It is therefore expected that such structural differences in these calcium silicate phases will influence their carbonation reaction kinetics.

Unlike for the case of reaction kinetics, the microstructures of the carbonation activated pure calcium silicate phases have been extensively investigated and the results can be found in several publications [11,14,19,22–27]. These studies have revealed several interesting aspects of carbonation activated binders as given below:

1. The morphology of the CaCO₃ formed during the carbonation reaction was found to vary, depending on the composition of the starting calcium silicate phase [22,27]. Specifically, it has been observed that during the carbonation of C₃S, C₂S, and C₃S₂, higher proportions of metastable polymorphs (i.e., aragonite, vaterite, and amorphous calcium carbonate (ACC)) are formed in comparison to those formed during carbonation of the CS under the same environmental conditions (i.e., RH, temperature and water to solid ratio) [22].
2. The degree of silicate polymerization of the Ca-modified silica gel is substantially higher than that of the calcium silicate hydrate (C-S-H) gel present in hydrated OPC system. Specifically, based on the findings from the ²⁹Si NMR tests, the C-S-H is reported to primarily consist of Q₁ (dimers, end of silicate chain groups) and Q₂ (middle of silicate chain, bridging and pairing sites) [28,29]. However, Ca-modified silica gel consist mostly of Q₃ (cross linked silicate tetrahedrons or hydroxylated surface sites) and Q₄ (fully polymerized silicate sites) [22,23,25,29].
3. In binders with similar particle size distributions, the maximum levels of CaCO₃ that formed during carbonation of any of the previously mentioned calcium silicate phases (i.e., the degree of carbonation) were all very similar (~5% variation by mass). Carbonated matrixes prepared from the binders with higher initial lime content contained higher amounts of unreacted grains compared to binders prepared with low-lime calcium silicates at the same level of CaCO₃ formation. This phenomena has been confirmed using stoichiometric equations [11] and ²⁹Si NMR analysis [22].
4. The degree of polymerization of the Ca-modified silica gel phases formed during the carbonation was nearly the same for all of the calcium silicate phases (except for the carbonated C₃S, which had slightly lower degree of polymerization) [11,22]. However, the amount of bound water present in the gel phase of the carbonated systems varied, depending on the composition of the starting

calcium silicate phases [11,19,22].

Even though this line of research first started in 1970s and subsequently regained interest in 2000s with the development of ‘carbonate binders’, gaps still exist in the fundamental understanding of these systems. Specifically, it is not clear how the carbonation rates vary depending on the starting calcium silicate phase or which microscopic phase/feature plays the dominant role in controlling the performance of these systems. Accordingly, the primary objective of this paper is to address following issues: (i) how the structural differences of the calcium silicate phases influence their carbonation kinetics, and (ii) how microscopic phases formed during the carbonation process contribute to the mechanical performance of these materials. To achieve these goals, the overall study was divided into three parts. The goal of the first part was to address the carbonation kinetics of pure calcium silicates. The micro and macro-scale mechanical performances of the fully carbonated systems were investigated in, respectively, the second and the third parts of the study.

2. Materials and methods

2.1. Sample preparation

All of the calcium silicates used in the study (i.e., C₃S, β-C₂S, γ-C₂S, C₃S₂) were synthesized in the laboratory. The only exception was wollastonite (CS) which was used in its natural (i.e., mineral) form. All of the synthesized calcium silicate phases were prepared by heating the stoichiometric mixtures of CaO and amorphous (fumed) silica (SiO₂). The C₃S phase was prepared by heating 3:1 M mixture of CaO and fumed silica at a temperature of 1510 °C for 4 h and then leaving the melt in the furnace until it cooled down to a room temperature. The resulting material was ground (using mortar and pestle), sieved using # 200 (75 μm) sieve and re-sintered (three times in total) to maximize the potential for chemical reaction between the available lime and silica. After each grinding, small amount of the powdered sample was examined using X-ray diffraction (XRD) method to check for the presence of any free lime. Similar process was followed for preparing γ-C₂S, except the molar ratio of CaO and fumed silica was 2:1 and the heating temperature was 1400 °C. The β-C₂S phase was obtained by heating the previously prepared γ-C₂S for 4 h at a temperature of 1300 °C. This was followed by a rapid cooling process using de-ionized water. In case of C₃S₂, the molar ratio of CaO and fumed silica was 3:2 and the heating temperature was 1250 °C. The specific surface areas of the powdered samples were determined using the laser particle size analyzer and were found to be in the range of 0.4–1.8 m²/g. The details regarding the sources of raw materials, synthesis method, X-ray diffraction patterns, and particle size distributions of the calcium silicates used in this study can be found in a previous paper [11]. As mentioned earlier, this study was divided into three separate parts, each utilizing specimens prepared using different methods, as discussed below.

2.1.1. Sample preparation for carbonation kinetics (Part-1: thermogravimetric test)

The carbonation kinetics part of the study was performed using paste specimens prepared by hand mixing of calcium silicate powder and deionized water (water to solid ratio = 0.4) for a period of 2 min. Immediately after mixing, about 10–15 g of the paste was spread on plastic plates which were then placed in the carbonation chamber. For these set of samples, compaction was intentionally avoided to eliminate the diffusion effect of CO₂ through the sample cross-section. The samples prepared by this method had a maximum thickness of up to 2 mm. These samples were subjected to carbonation in the atmosphere of 15% CO₂ and 94% RH for a period of up to 145 h. The carbonation was performed at three different temperatures (35 °C, 45 °C, and 60 °C). At regular intervals (i.e., 0.5, 3, 6, 12, 24, 72, 145 h), small amounts of material (~1 g m) were removed from the larger test specimen and

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