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Microscopic features of non-hydraulic calcium silicate cement paste and mortar

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ABSTRACT

Non-hydraulic calcium silicate-based cement (CSC) is a newly developed binder that hardens upon carbonation reaction. The primary components of CSC are low-lime calcium silicates, including rankinite, wollastonite and pseudo-wollastonite. During the carbonation, CSC binder forms Ca-modified silica gel and $CaCO_3$. Microscopic evaluation of the carbonated CSC paste using the ^{29}Si {^1H} CP-MAS NMR revealed that the Ca-modified silica gel phase consists primarily of Q^3 and Q^4 species, indicating a substantially higher degree of polymerization in comparison to that of the C-S-H. The elastic modulus and hardness of this gel phase were found to be close to those of the high density C-S-H. A composite phase, formed by the intermixing of Ca-modified silica gel and $CaCO_3$, was also identified using SEM X-ray microanalysis and nanoindentations. The distribution of the microscopic phases in ITZ was similar to that observed in the bulk paste region for this system.

1. Introduction

In terms of total volume of the material, concrete is the second largest commodity (after water) consumed annually by any society [1]. Due to the combined effects of high volume of consumption and high CO_2 emissions accompanying the production process of ordinary portland cement (OPC), concrete industry is currently responsible for about 5% of total global anthropogenic carbon emissions [2,3]. Approximately, 4200 million metric tons of cement were produced globally in 2016 [4] and that amount is projected to increase by about 2.5% annually [5]. Accordingly, finding an alternative cementitious binder system, with lower CO_2 footprint compared to OPC, is one of the major challenges for cement and concrete industry. Options to reduce the concrete's CO_2 footprint involve utilization of clinker substitutions (i.e., use of supplementary cementitious materials (SCMs)), use of alternative fuels, carbon capture and storage, or production of alternative cements. Consequently, during the last decade, development of few alternative cementitious material systems with low carbon footprint has been reported [6]. The most recent addition to these low CO_2 footprint alternative cement and concrete systems is the non-hydraulic calcium silicate cement (CSC), also known as Solidia Cement™ (patented in 2015 [7]). This binder is primarily composed of non-hydraulic low-lime calcium silicate minerals, such as wollastonite/pseudo-wollastonite ($CaO{\cdot}SiO_2$) and rankinite ($3CaO{\cdot}2SiO_2$) [8].

Since their production requires lower clinkering temperature and lower amount of limestone, the low-lime calcium silicates offer a good potential for reduction of carbon footprint when compared to OPC, in which the main reactive component is alite, a high-lime calcium silicate ($3CaO{\cdot}SiO_2$). However, due to their lack of hydraulic reactivity compared to alite, until now the low-lime calcium silicates (especially wollastonite and rankinite) have been considered undesirable as components of the OPC. On the other hand, low-lime calcium silicates were found to exhibit enhanced reactivity in the presence of CO_2 [9–11]. As such, these materials can potentially be used to produce low CO_2 footprint binders (such as belite-rich cement [12] or CSC [8]), which would require carbonation curing for faster strength gain. The required production temperature of CSC (~1200 °C) is about 250 °C lower than that of the OPC.

As already mentioned, the hardening and strength generation of the CSC system will require carbonation of the calcium silicate phases. The carbonation process will involve chemical reactions as shown in Eqs. (1) and (2).

$$CO_2 + H_20 \leftrightarrows H^+ + HCO_3^- \quad (1)$$

$$Ca_xSi_yO_{(x+2y)} + xH^+ + xHCO_3^- \rightarrow ySiO_2\downarrow + xCaCO_3\downarrow + xH_2O \quad (2)$$

When subjected to carbonation, the CSC paste can store up to 17% (by mass) of CO_2 in the form of stable carbonates [13]. Considering its CO_2 storing capacity, along with lower production temperature and reduced limestone requirements, the overall CO_2 footprint of

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carbonated calcium silicate cement (CCSC) concrete has been reported to be about 70% less than that of OPC concrete [8]. The theoretical enthalpy of formation of 1 ton CSC clinker is around 1.051 GJ, which is approximately 0.706 GJ lower than that required for the formation of 1 ton of Portland cement clinker (around 1.757 GJ) [8]. The structural elements made from CCSC were also found to have satisfactory resistance to freeze-thaw exposure [14] and high temperature environment [15].

Since all of the above-mentioned characteristics imply that the carbonation-activated binders have a definite potential to offer an effective solution to the current CO_2-related challenges facing the cement industry, it is essential to develop a thorough understanding of the binding phases present in this novel binder system. Development of this information will be critical with respect to wide-ranging acceptance and further development of such materials. Therefore, the aim of this paper is to utilize multi-technique approaches to reveal the chemical and mechanical aspects of the microscopic phases present in CCSC paste and mortar samples. Specifically, the objectives of this paper are: (i) to identify the carbonation reaction products of CSC, (ii) to reveal the chemical composition, structural information as well as the mechanical properties of the microscopic phases present in CCSC paste, and (iii) to characterize the interfacial transition zone (ITZ) between sand particles and paste matrix present in CCSC mortars.

2. Materials and methods

2.1. Materials

The particle size distribution of CSC was obtained using Malvern Mastersizer 2000 particle size analyzer with a refractive index of the cement powder assumed to be 1.63. De-ionized water was used as the dispersant. The particle size distribution of the CSC powder is given in Fig. 1. Using the information presented in Fig. 1, the specific surface area of the cement powders found to be 883 m^2/kg with a mean particle size (D50) of 13 µm. The oxides content of the CSC was determined using X-ray fluorescence (XRF) analysis and the results are presented in Table 1. The X-ray diffraction (XRD) patterns of the CSC were recorded with Cu K_α radiation on a Siemens D-500 diffractometer. The diffraction pattern was obtained for the range of 2θ angles from 10° to 80 using the step size of 0.02°. From the XRD pattern (Fig. 2), it can be seen that the primary ingredients of CSC are wollastonite/pseudowollastonite, rankinite, and belite. In addition, this CSC also contained minor amounts of quartz and melilite (i.e., akermanite/gehlenite) phases, which are non-reactive during the carbonation process.

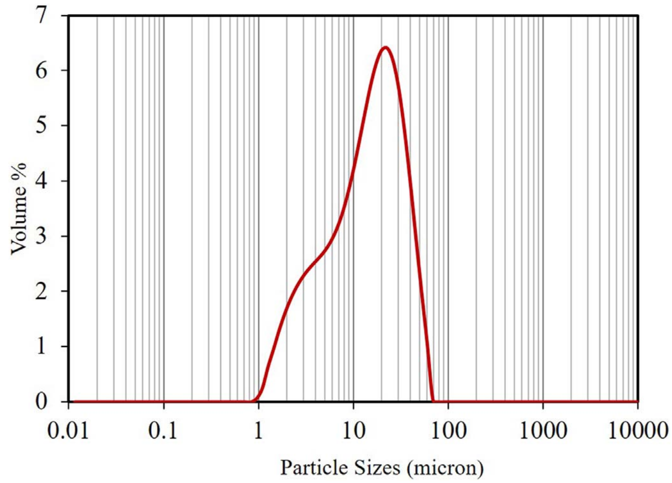

Fig. 1. Particle size distribution of the (CSC) binder.

Table 1
Oxide contents of the CSC as measured by XRF.

Oxides	Content (wt%)
SiO_2	44.02
Al_2O_3	5.13
Fe_2O_3	1.79
CaO	43.64
MgO	1.15
SO_3	0.16
Na_2O	0.33
K_2O	1.94
TiO_2	0.22
P_2O_5	0.06
Mn_2O_3	0.04
SrO	0.12
Cr_2O_3	0.01
ZnO	0.01
BaO	0.03

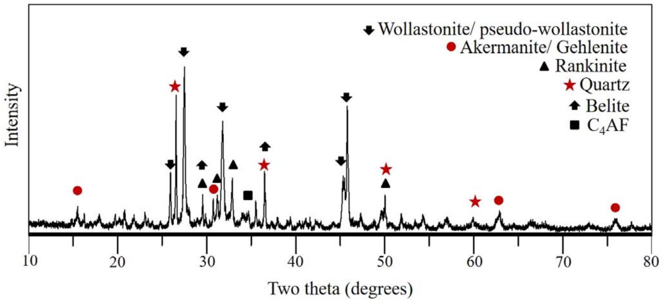

Fig. 2. XRD pattern of the calcium silicate cement (CSC).

2.2. Preparation of the test specimens

The desired curing scenario for the production of CCSC concrete is similar to that previously used for the accelerated carbonation curing of the OPC concrete [16–19]. At the present time, the primary use of this material is limited to precast concrete products. Once the carbonation process is completed, the microstructure of the CCSC concrete does not change over time. The degree of carbonation of the CCSC paste and mortar samples used in this study was about 60%, (i.e., 30% $CaCO_3$ formation by mass) which is similar to the degree of carbonation encountered in the typical prefabricated members prepared from the same material.

The paste samples were prepared by mixing 1200 g of CSC powder with 420 g of water (water to cement ratio was 0.35) in a regular Hobart mixer. The cement and water were mixed together for 1 min at low speed. The material on the blade and from the sides of mixer was scrapped off with rubber spatula and the mix was allowed to sit for 1 min. Finally, the paste was mixed further at medium speed for 1 min and then compacted into 50 mm cubes using vibrating table. The mortar samples were prepared using cement-to-sand (ASTM C 778 standard sand) ratio of 2.75 and the water-to-cement ratio of 0.35 (i.e., the same as that used for the paste samples). After mixing, the mortar samples were also compacted into 50 mm cubes using a vibrating table. Both paste and mortar samples were subjected to carbonation curing immediately after mixing. Carbonation curing was performed in a custom build carbonation chamber operated at the temperature 65 °C, 60% relative humidity and at atmospheric pressure. The concentration of CO_2 in the chamber was about 100%. The samples were removed from the chamber after 24 h of carbonations, demolded, and re-inserted back into the chamber for up to 72 h of curing. It should be noted that although relatively high (i.e., 65 °C) curing temperature was used in this particular study, using of such elevated temperature is not mandatory for the hardening of CSC. In fact, the CSC mortar/paste samples could also be cured at more moderate temperatures (i.e., 20 to 60 °C)