Multiscale characterization of carbonated wollastonite paste and application of homogenization schemes to predict its effective elastic modulus

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ABSTRACT

This paper describes the multiscale characterization of the carbonated wollastonite paste using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), and statistical nanoindentation (SNI, also known as 'grid indentation') methods as well as micromechanical homogenization models. Wollastonite ($CaSiO_3$) fibers are commonly used as filler in ceramics or plastics. However, wollastonite can also be regarded as non-hydraulic binder material since upon carbonation it forms a heterogeneous matrix with mechanical properties similar to those of the conventional hydrated cement pastes. Carbonation reaction of wollastonite results in the formation of two main products: calcium carbonate ($CaCO_3$) and amorphous silica gel (SiO_2). The SEM/EDS microanalysis performed on this system revealed that the average calcium to silica (Ca/Si) atomic ratio of the silica gel phase was around 0.40. Three individual carbonated wollastonite paste samples, each representing a different degree of carbonation were selected for nanoindentation tests. The obtained elastic moduli for silica gel, calcium carbonate, and unreacted wollastonite grains were, respectively, 41.7 GPa, 67.3 GPa, and 134.7 GPa. The micromechanical homogenization models were then utilized to predict the effective (also referred to as 'homogenized') elastic moduli of the carbonated wollastonite paste. The predicted values of the effective elastic moduli of carbonated wollastonite pastes were found to be in the range of corresponding values for hydrated high to ultra-high performance cement pastes. Additionally, the values of the effective elastic moduli of the carbonated wollastonite pastes were observed to increase with the increase in the degree of carbonation.

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1. Introduction

Reduction of the CO_2 footprint of conventional cement based materials represents one of the major challenges for the construction industry. This is because the production of the ordinary portland cement (OPC) accounts for approximately 5% of the total man-made CO_2 emissions [1,2]. Utilization of low lime calcium silicates such as wollastonite and rankinite as alternative binders can substantially reduce the CO_2 footprint of cement-based materials because of their lower (in comparison to the OPC) production temperature [3,4]. These low lime calcium silicates, though non-hydraulic, but reacts in the presence of CO_2 and moisture [5].
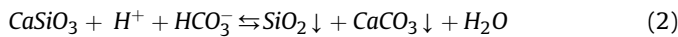
Accordingly, few recent studies [6,7] showed that these non-hydraulic, low lime calcium silicates can be utilized as an active component of the carbonation activated binders with substantially lower CO_2 footprint. Complementing the growing interests [8] on the carbonation activated binders, this paper focuses on the multiscale characterization of carbonated wollastonite, considering it as the model material for such alternative binder systems.

Wollastonite is generally used in ceramic and plastic matrixes [9,10] because of its good fluxing properties, low content of volatile components, and needle-like shape which gives it a reinforcing capability. Due to the presence of calcium oxide (CaO) [11] and rapid dissolution rate [12], wollastonite is also considered to be one of the most suitable minerals for geological sequestration of CO_2. The CO_2 is sequestered in wollastonite by the process of mineral carbonation [13] where this calcium-silicate material reacts with CO_2 to form calcium carbonate and silica gel [12,14,15]. The

following general set of equations can be used to explain the carbonation reaction of wollastonite ($CaSiO_3$):

$$CO_2 + H_2O \leftrightharpoons H^+ + HCO_3^- \tag{1}$$

$$CaSiO_3 + H^+ + HCO_3^- \leftrightharpoons SiO_2\downarrow + CaCO_3\downarrow + H_2O \tag{2}$$

The similarities of mechanical properties between the matrix formed by the carbonation of wollastonite (composed of calcium carbonate and amorphous silica gel) and the matrix formed during the hydration of OPC (consisting mainly of calcium-silicate-hydrate (C−S−H) and calcium hydroxide (CH)) suggest that carbonated wollastonite can be regarded as a viable component of carbonation activated binders [16,17]. Bukowski and Berger [17] studied the mechanical properties of the mortar samples prepared using wollastonite as the sole binder phase and revealed that this system can achieve compressive strength as high as 35 MPa within 1140 min from casting when subjected to carbonation. Recently, another group of researchers reported [16] to have obtained a compressive strength of more than 70 MPa from carbonated wollastonite mortars. Hence, wollastonite based binders can constitute a feasible alternative to the conventional cement systems. At this point, it should be noted that although wollastonite mineral can be found in nature, its availability is limited. However, similar non-hydraulic low-lime calcium silicate binder (i.e., wollastonite, pseudo-wollastonite, rankinite, etc.) can be manufactured from the same raw materials as those used for the production of the OPC, but at temperatures about 250 °C lower [18] than those required for the production of hydraulic (i.e., OPC) binder.

This paper aims to present an extensive microstructural characterization of the matrix of carbonated wollastonite using advanced experimental techniques including SEM/EDS, XRD, and nanoindentations. While SEM/EDS and XRD helped to delineate the chemical composition of the microscopic phases, the nanoindentation revealed the elastic properties of these phases. Nanoindentation based microscopic investigation of the composite microstructures has gained wide popularity in the last decade [19–25]. These initial efforts were further expanded with the introduction of SNI (or grid indentation) [26,27] method. This method not only yields the values of mechanical properties of the microstructural phases of heterogeneous materials, but it also allows for the determination of the relative volume fractions of those phases. Application of the nanoindentation method has so far revealed the intrinsic elastic modulus of several microstructural phases of hydrated cement pastes, including low-density C−S−H, high-density C−S−H [22,28], ultra high-density C−S−H [19,29], portlandite [30,31], calcium carbonate [32], and unreacted grains of cement [28]. Furthermore, knowing both, the mechanical properties and volume fractions of the individual microstructural phases of a heterogeneous composite, the effective elastic properties of the composite can be determined from micromechanical models. The approach of coupling micromechanical homogenization models with nanoindentation results to predict the macroscopic properties has been previously successfully applied to several heterogeneous composites [33–35]. Such approach also provided satisfactory correlation when compared with the results from the macroscopic examination of the hydrated cementitious matrixes [36].

Within the broader theme of multiscale characterization of the carbonated wollastonite matrix, the objectives of this paper are as follows: (i) to reveal the chemical and morphological properties of the microstructural phases using XRD and SEM techniques, (ii) to determine the elastic modulus and hardness values of the microstructural phases present in the carbonated wollastonite matrix using nanoindentation technique, (iii) to predict the effective elastic modulus of the carbonated wollastonite matrix and its variation with the degree of carbonation by coupling nano-indentation results with micromechanical homogenization models, and (iv) to compare the effective elastic modulus of the carbonated wollastonite with that of the conventional hydrated cement paste. Though this paper is primarily dedicated to the characterization techniques, it also attempts to address the probability of utilizing this novel, wollastonite-based, calcium silicate binder in cement and concrete industry as an option to reduce the CO_2 footprint.

2. Materials and methods

2.1. Paste sample preparation

Powdered natural wollastonite used in this study was supplied by Solidia Technologies, NJ, USA. The Particle size distribution (Fig. 1) of this wollastonite powder was obtained using Malvern Mastersizer 2000 particle size analyzer with previously determined refractive index of the powder of 1.63.

To prepare the paste test samples, wollastonite powder was first mixed with a small amount of water (water to solid ratio ~ 0.35) and compacted in 50 mm cube molds. These compacted cubes were then exposed to pure CO_2 (99.99% concentration) at the temperature of 60 °C and relative humidity (RH) of about 94%. A schematic of the carbonation setup used in this study is given in Fig. 2. A shallow pan filled with water was used to prevent the drop in RH due to the flow of CO_2 gas. Carbonated wollastonite paste specimens (50 mm cubes) prepared in this method had achieved around 60 MPa−80 MPa compressive strengths after 60−75 h of carbonation.

Thermogravimetric analysis (TGA) was utilized to quantify the amount of $CaCO_3$ formed during the carbonation of wollastonite. For this test, the carbonated samples were crushed manually (using mortar and pestle) and then sieved through number 200 sieve (0.074 mm opening). Using a commercially available TGA instrument (TA instruments, model: 2050), the powdered sample was first kept in isothermal condition for 10 min and then the temperature was raised at the rate of 10 °C per minute up to 1000 °C. Approximately 35−50 mg of powder was tested for each carbonated paste sample. Nitrogen (N_2) was used as purge gas during TGA tests. An example of the TGA curve obtained from one of the carbonated wollastonite paste samples is given in Fig. 3. The amounts of $CaCO_3$ were determined from the sample weight loss
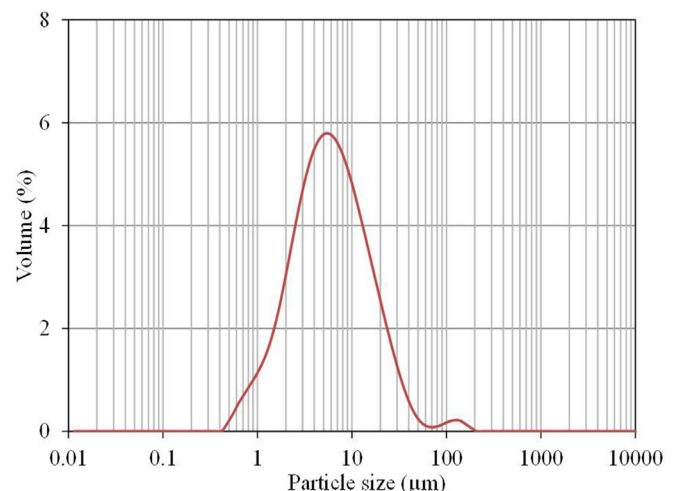

Fig. 1. Particle size distribution of wollastonite powder.