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Impact of amorphous micro silica on the C-S-H phase formation in porous calcium silicates

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ABSTRACT

Amorphous micro silica (MS) is used as a raw material in the production of porous calcium silicate. MS is a by-product from the silicon and silicon-alloy production, and strongly influences the properties of porous calcium silicate products. We investigate the kinetics of the formation of calcium silicate hydrate (C-S-H) gel from the reaction between quicklime and MS based on two types of MS (MS97.5 and MS92.8, which have 97.5 and 92.8 wt% SiO_2, respectively). The C-S-H gel is found to be amorphous, but with short- and medium range order similar to tobermorite for the two types of MS. MS97.5 is found to react faster than MS92.8. The activation energy is determined to be 76 kJ/mol for MS97.5 and 103 kJ/mol for MS92.8. For comparable surface area of MS, the C-S-H formation mechanism is strongly affected by metallic or metal oxide impurities in two ways. First, the positively charged metal ions are attached to the negatively charged hydroxyl groups at the MS surface, resulting in less available hydroxyl groups for MS-quicklime reaction, and in lower solubility of MS. Second, impurities react with the calcium silicate network, making less raw material available for the reaction.

1. Introduction

Porous calcium silicates are widely used as insulation materials in high temperature applications, in buildings, and as passive fire protection [1–3]. Calcium silicate is prepared through reaction between reactive CaO and SiO_2 resulting in calcium-silicate-hydrate (C-S-H) gel followed by high pressure hydrothermal treatments for crystallization. The reaction kinetics and mechanism of C-S-H gel formation, as well as the structure, are complex and not fully understood [4–6].

Quicklime (CaO, from calcination of $CaCO_3$) and micro silica (MS) (SiO_2, a by-product from the silicon and silicon-alloy production) are used in the production of calcium silicates [7]. Quicklime and MS are mixed in water, leading to their chemical reaction forming amorphous C-S-H gel, and this reaction is referred to as the pre-reaction. Then, the reaction slurry is pressed into boards, autoclaved at temperatures above 180 °C for crystallization [8], and finally a porous product is obtained upon drying. Important properties of the product are low density, low thermal conductivity, high compressive and bending strength, and low shrinkage upon heating. These product properties are found to be influenced by the raw materials used in the production, pre-reaction, the processing conditions, and the reaction stoichiometry [9]. The chemical composition of the MS highly influences the thermal stability and crystallization of the calcium silicate material. Especially iron is found to highly impact the product shrinkage upon heating and crystal formation [10].

The C-S-H gel formed in the pre-reaction is an amorphous phase similar to the hydration phases found in cements [5,6,11,12]. The C-S-H structure formed during pre-reaction with Ca/Si < 1 corresponds to the tobermorite structure in terms of both the short-range and the medium range order [5,13,14]. The structure of C-S-H with Ca/Si > 1 was believed to match the jennite structure [13] found from FTIR analysis, however, recent studies suggest that only a tobermorite like structure is present even at Ca/Si > 1 [15] and that the disorder degree increases with an increase in Ca/Si ratio [16]. The tobermorite structure consists of $[SiO_4]$ tetrahedral chains in a dreierketten configuration, with CaO polyhedral layers with Ca^{2+} and H_2O in the interlayer [17]. The length of the unit cell c-axis varies with the number of water molecules, with the minimum spacing of ~0.98 nm, expanding up to 1.1 nm and 1.4 nm with increasing number of water molecules. The silica tetrahedra are buildup of mainly Q^2 Si sites (Q^n represents the silica tetrahedron and n denotes the number of bridging oxygen-silicon sites per tetrahedron). From NMR studies it is found, that the tobermorite with spacing of 1.1 nm is more polymerized than that with 1.4 nm [13]. The jennite structure is related to tobermorite, but with every other silica chain replaced by Ca-OH, and can be distinguished using FTIR [13].

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In the reaction between SiO_2 and CaO, the rate determining step is found to be the dissolution of silica [18]. Therefore, amorphous silica (e.g. MS) is advantageous compared to crystalline silica (e.g. quartz), as it dissolves easier [19,20]. The dissolution proceeds as shown in the equation:

$$SiO_2(s) + 2H_2O \leftrightarrow H_3SiO_4^-(aq) + H^+ \tag{1}$$

The dissolution of silica in water is dependent on pH, temperature, specific surface area, and the presence of ions [21]. MS is covered with surface hydroxyl groups, which deprotonate when dispersed in water resulting in negatively charged particle surfaces. The silica surface charge can be influenced by positively charged counter metal ions [22].

MS, as a by-product from the silicon and silicon alloy production, can vary greatly in chemical composition, particle size distribution, crystalline impurities etc. [23–25]. Type and quality of MS highly influences the properties of the final calcium silicate product. Changing from one type of MS in the calcium silicate production to another can result in e.g. changed bulk density, strength and thermal stability of the calcium silicate products. In the industrial production, it is a challenge to ensure stable quality of calcium silicate products. To control the production process of calcium silicates, it is of great importance to know the reaction kinetics of different types of MS in reaction with quicklime.

The reaction kinetics of calcium silicate formation is only briefly described in previous studies [9,18]. The reaction kinetics of MS is important for the understanding and optimization of the calcium silicate production process. Here we study two types of MS with same particle size distribution, but originated from two different production sites (silicon plant and ferro silicon plant) concerning the activation energy, the structure of the C-S-H gel, and the chemical bond formation during the reaction among MS, lime and water.

2. Experimental

2.1. Micro silica

Two types of MS with different chemical composition were tested, one from the silicon industry (97.5 wt% SiO_2) and one from the ferro silicon industry (92.8 wt% SiO_2). Their chemical compositions and names are listed in Table 1. Size and zeta potential of the MS were determined using ZetaSizer Nano ZS (Malvern). Prior to measurements, MS was dispersed in deionized water under sonication (Ultrasonic processor 500W, model CV334). The suspension was diluted and transferred to a folded capillary cell (DTS1070, Malvern). Two samples were scanned three times each for size determination. 6 measurements were carried out on each MS, the average size was calculated. The average zeta potential was determined from three scans on the same sample.

2.2. Synthesis of C-S-H gel

In all synthesis, quicklime and MS were obtained from commercial sources. The Ca/Si molar ratio was kept constant at 1:1 and the water/solid ratio was kept constant at 1:10, by mass. The reaction kinetics between MS and quicklime is investigated at the reaction temperatures: 60, 70, 80, 90, and 95 °C, for each type of MS. After reaction, the samples obtained from MS97.5 were referred to as CS97.5, while those from MS92.8 were referred to as CS92.8. Prior to the reaction, quicklime was slaked in demineralized water for 1 h at the reaction temperature. MS was dispersed in demineralized water using ultra sonication (Branson, 2510) for 1 h before reaction. The MS suspension was heated to the reaction temperature and then added into the slaked suspension of quicklime. For Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analysis, samples were taken from the reaction mixture, filtered, and dried in a vacuum oven at 40 °C.

Table 1
Chemical composition (wt%) of the two types of MS, determined from XRF.

	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O
MS92.8	92.8	0.81	0.36	2.24	1.40	0.98	0.41
MS97.5	97.5	0.20	0.20	0.10	0.49	0.20	0.20

2.3. Characterization of C-S-H gel

The electrical conductivity (Mettler Toledo, SevenMulti) measurements were conducted on a diluted reaction mixture. 1.0 mL reaction mixture was diluted to 100 mL with demineralized water, and the electrical conductivity was measured. It was assumed that Ca^{2+} ions were the only contributor to electrical conductivity [18], and hence a standard curve was plotted for converting the electrical conductivity to Ca^{2+} concentration.

The FTIR spectroscopy (Agilent Technologies, Cary 670 FTIR) was used to determine bindings in the C-S-H gel. The samples for FTIR measurements were prepared by mixing 1 mg of C-S-H sample with 200 mg of potassium bromide (KBr), drying in vacuum oven at 40 °C, and finally the mixture was pressed to self-supporting pellets. The measurements were performed in transmittance mode.

The crystal structures in CS95.7 and CS92.8 were determined using an X-ray diffractometer (XRD) (Empyrean, PANalytical) with the voltage and working current of 45 kV and 40 mA, respectively, and with a 2θ scan range of 5° to 70° and a step size of 0.013°. Each measurement was repeated 4 times on the same sample. Before measurement, the samples were powdered using a mortar. The crystalline phases in the samples were identified by comparing the Bragg peak positions with diffraction patterns in the Joint Committee on Powder Diffraction Standards (JCPDS) data files using the HighScore software (PANalytical).

3. Results

3.1. Characterization of MS

Table 2 shows the size and zeta potential measured on MS dispersed in water. It is seen that MS92.8 and MS97.5 possess comparable particle sizes, and hence the comparable surface areas. MS92.8 has a zeta potential slightly lower than MS97.5, however, the difference is not significant.

3.2. Kinetics of C-S-H gel

Fig. 1 shows the concentration of the Ca^{2+} ions in the solution as a function of reaction time at different temperatures, for both MS97.5 and MS92.8. It can be observed that the concentration exponentially decreases with increased time. Further, the development in concentration of Ca^{2+} is measured at different temperatures, and it is clearly seen that the reactions progress faster at higher temperatures. The data set is fitted to the following equation:

$$\frac{C(t)}{C_0} = \frac{C_\infty}{C_0} + \left(1 - \frac{C_\infty}{C_0}\right)\exp\left(-\frac{t}{\tau}\right) \tag{2}$$

where $C(t)$ is the concentration of Ca^{2+} in the reacting suspension at

Table 2
Average size (± 4 nm) and zeta potential(ZP) (± 0.5 mV) of MS dispersed in demineralized water using ultrasonication.

	Size (nm)	ZP (mV)
MS92.8	206	− 38.7
MS97.5	200	− 40.1