Impact of minor iron content on crystal structure and properties of porous calcium silicates during synthesis

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HIGHLIGHTS

- Minor amount of iron prevents calcium silicate from crystallizing into xonotlite.
- Hence, the iron lowers the thermal stability of porous calcium silicates.
- Their compressive strength first decreases with iron content and then increases.
- The chemical mechanism of the impact of iron on crystallization is discussed.
- The results are useful for selecting raw materials for porous calcium silicates.

ARTICLE INFO

ABSTRACT

We investigate the impact of minor iron content on the crystallization behavior and thermal stability of hydrothermally treated calcium silicates for insulation at high temperatures. The impurity content of the raw materials (micro silica and quicklime), particularly iron, varies greatly with the production site and method. In this work the porous calcium silicate is synthesized with a Ca/Si molar ratio of 1. To systematically study the iron impact on crystallization during synthesis of calcium silicates, we introduce different amounts of iron (Fe/Si = 0 to 0.013) into the reactants. Using Fourier transform infrared spectroscopy we find a pronounced decrease in the number of 3-bridging oxygen coordinated Si sites in the calcium silicate with increasing iron content. The X-ray diffraction results revealed that the fractions of tobermorite, calcite, and amorphous phases increase with iron content, whereas the fraction of xonotlite phase decreases. These phase changes affect the compressive strength and thermal shrinkage of the calcium silicates. The compressive strength decreases with increasing iron content until amorphous phase becomes dominant, and then it increases again. The shrinkage increases from 1.3% at 1050 °C for the reference sample, to 30.4% for the sample with Fe/Si = 0.01. We discuss why such a small amount of iron can greatly affect the crystal structure of calcium silicates and deteriorate the physical performances of final products. Therefore, the iron contamination of raw materials should be avoided to ensure high temperature stability of porous calcium silicates.

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1. Introduction

Porous calcium silicates are widely used as an insulating material for high temperature applications, insulation and passive fire protection in buildings [1,2]. Their important properties for thermal insulation are low thermal conductivity, low shrinkage upon heating, and high mechanical strength. These properties are strongly influenced by impurities such as Al^{3+}, Ca^{2+}, and Na^+ in the raw materials [3–6].

As for the production of porous calcium silicates, quicklime (CaO), from thermal decomposition of limestone ($CaCO_3$) and micro silica (SiO_2) have been used as key raw materials [7–12]. Micro silica is a by-product from the production of silicon and silicon alloys. The concentration of impurities are highly dependent on the type of raw materials used in the silicon and silicon alloy production and on the production method [13,14]. Today, to the largest extent, micro silica is a by-product originating from the production of ferro silicon (FeSi) [15].

In the production of porous calcium silicates, CaO and SiO_2 are mixed in water, where they react forming a calcium silicate hydroxide (C-S-H) gel. After reaction the slurry is pressed into boards and autoclaved. During autoclaving minerals of tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) and xonotlite ($Ca_6Si_6O_{17}(OH)_2$) form, which contribute to strength and thermal stability of the material. The flake-like tobermorite crystal is formed with the molar Ca/Si ratio of 0.83 [2,16,17]. The needle-like xonotlite forms at Ca/Si = 1 [1,8,18]. Upon heating the structure of tobermorite and xonotlite transforms into the mineral wollastonite ($CaSiO_3$), which is also needle shaped [16,19]. Xonotlite is associated with less shrinkage upon heating, compared to tobermorite, due to its similar crystal structure to wollastonite and less crystal water released upon heating [20]. Xonotlite is, therefore, the mostly desired crystal phase for insulation materials applied in high temperature environments.

The crystal structure of calcium silicate is strongly influenced by impurities present during gel formation and crystallization [3,9,21]. Nocun-Wczelik [9] found that the addition of aluminum promote the formation of tobermorite, and hinders its further crystallization into xonotlite. Using NMR, it was shown that Al substitutes Si in the tobermorite structure of calcium silicate [4]. Ke et al. [3] found that such substitution in the crystal lattice leads to expansion of the unit cell, since Al is larger than Si. SO_4^{2-} is also found to enhance the tobermorite formation by replacing the SiO_4^{2-} tetrahedral, the unit cell is not found to be influenced by this substitution [3]. Sodium is also found to influence the crystal formation of calcium silicate [4]. The presence of sodium enhances the formation of poorly crystalline phases in the calcium silicate, the xonotlite crystallization is, however, still possible with the presence of Na_2O [9,22].

The influence of iron on porous calcium silicate properties has not been investigated to our best knowledge. It is indicated by Rayment and Majumdar [23] that iron in Portland cement replaces Si in the C-S-H structure. But how this replacement influences the structure of the C-S-H phase, and the further crystallization in the autoclave of the porous calcium silicate material is still unknown. Since the largest volume of micro silica originates from the FeSi production, it is of great interest to investigate the influence of iron on the structure and properties of porous calcium silicate products. In this work we approach this by synthesizing calcium silicate with varying concentrations of Fe. We analyze the chemical structure using x-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR), and determine the crystal structure using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Furthermore, we will investigate the phase transition behavior of the material by performing differential scanning calorimetery (DSC) measurements. We also measure the density, compressive strength, and thermal stability of products.

2. Experimental

2.1. Synthesis of calcium silicate

In all synthesis quicklime and micro silica (MS) were obtained from commercial sources and used as-received. The SiO_2 content in the MS was 97 mass % and the Fe_2O_3 was 0.1 mass % given by the manufacturer.

Calcium silicate was prepared using equimolar quantity of quicklime and silica. The MS was dispersed in water using ultrasonication. The dispersed MS was mixed with water and quicklime under magnetic stirring. After reaction wood pulp was added to the mixture. The mixture was pressed on a filter to remove water and autoclaved at 200 °C. Finally, the boards were dried at 105 °C for 24 h. This sample was used as reference.

Samples with iron were prepared by adding $Fe(NO_3)_3 \cdot 9H_2O$

(VWR, CAS 7782-61-8) to the MS before preparing the dispersion. Preparation of calcium silicate boards with iron followed the same procedure as for the reference sample. The Fe/Si molar ratios used for production of calcium silicate samples as well as the sample names are listed in Table 1. The slurry of sample Fe1.3 blocked the filter during pressing, and a very poor sample was prepared. Therefore, it was not possible to determine shrinkage, compressive strength and the density of this sample.

2.2. Characterization of calcium silicates

The chemical composition of the calcium silicate samples was investigated using XRF (Epsilon 3x, PANalytical). Approximately 0.5 g of dried calcium silicate was added to 6.0 g of Lithium borates ($Li_2B_4O_7$ and $LiBO_2$, Claisse), and the mixture was melted at 1100 °C. Loss on ignition (LOI) was determined for each calcium silicate.

The surface morphology of the calcium silicates was determined using SEM (Zeiss 1540 XB). The SEM images were obtained on Au coated calcium silicates at 10 kV.

The crystal structure of the prepared calcium silicate samples was determined by XRD (Empyrean, PANalytical). The voltage and working current were 45 kV and 40 mA, respectively, with a 2θ scan range of 5°—70° under a step size of 0.013°. Each measurement was repeated 6 times on the same sample. Before measurement the samples were powdered using a pestle and a mortar. The identification of phases in the samples was performed by comparing peak positions with diffraction patterns in the Joint Committee on Powder Diffraction Standards (JCPDS) data files using the Highscore software (PANalytical). Rietveld refinement was performed for quantitative phase determination, and quartz was used as an external standard. The crystallographic information files (CIF) used in the Rietveld refinement were obtained from Churakov and Mandaliev [1] for xonotlite with the space group *P-1*, from Hamid et al. [24] for tobermorite with the space group *Imm2* and from Post et al. [25] for calcite with the space group *R-3cH*.

FTIR spectroscopic measurements were conducted using a spectrometer (Agilent Technologies, Cary 670 FTIR). The samples were prepared by mixing 3 mg of calcium silicate sample with 200 mg of KBr, the mixture was pressed to self-supporting pellets. The measurements were performed in transmittance mode.

The phase transition behavior was monitored using DSC (STA Jupiter 449C, Netzsch) in argon atmosphere. A baseline (blank) and a reference sample (sapphire) were measured. Firstly approx. 10 mg of crushed calcium silicate was transferred to an alumina crucible. The sample was heated to 1000 °C at 20 K/min, and subsequently downscanned at 20 K/min to 400 °C. Two separate scans were performed on each sample.

Compressive strength measurements (UCT 10 kN, Bent Tram, Denmark) were performed on samples cut into 40 × 40 × 21 mm, two test specimens were prepared for each calcium silicate sample. The compression was performed with a speed of 10 mm/s until a deformation of 10% or breakage. The highest value obtained was reported as the compressive strength. Prior to tests, the density of

Table 1
The Fe/Si ratio used in the synthesis of calcium silicates, and abbreviations of sample names.

Fe/Si	Abbreviation
0	Ref
0.001	Fe0.1
0.005	Fe0.5
0.007	Fe0.7
0.010	Fe1.0
0.013	Fe1.3