Microstructure and characterization of hydrothermal synthesis of Al-substituted tobermorite

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HIGHLIGHTS

- The suitable synthesis condition for tobermorite was 5 h in autoclave at 180 °C.
- Addition of aluminum resulted in an increased interlayer spacing.
- The tobermorite with the incorporated of aluminum had a longer mean chain length.
- The microstructure of tobermorite with aluminum had larger and more ordered foils.

ARTICLE INFO

ABSTRACT

Tobermorite is an important mineral analog of calcium silicate hydrate (C-S-H), the main phase formed by hydration of Portland cement, due to the structural similarity. As part of a broader study on the effect of aluminum substitution C-S-H, the synthesis and characterization of tobermorite with and without aluminum were conducted. The X-ray diffraction pattern indicated that a suitable synthesis time for tobermorite with or without aluminum was 5 h in an autoclave at 180 °C and saturated steam pressure around 1 MPa. In both samples the mineral is 11 Å-tobermorite. X-ray fluorescence showed that the sample with aluminum had a higher molar ratio of Ca/(Si + Al). Thermogravimetry-differential scanning calorimetry showed the same general changes, loss of free water at 55 °C, loss of interlayer water at 187 °C, dehydroxylation at 664 °C, and conversion to wollastonite at 841 °C. With the incorporation of aluminum, 29Si and 27Al magic angle spinning-nuclear magnetic resonance spectra showed aluminum addition increases the mean chain length, Al mainly occupies Q^2 bridging and Q^3 branching sites. Scanning electron micrographs indicated that tobermorite crystals are larger than those of sample without alumina. This work is beneficial for understanding the implication of the use of admixtures containing aluminum in concrete on its micro- and atomic-scale properties.

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1. Introduction

Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) is a natural mineral, first discovered by Heddle in 1880 at Tobermory, Scotland [1,2]. It is also an important mineral analog of the main phase of cement hydrate due to the structural similarity. Taylor et al. showed that natural tobermorite and "well-crystallized synthetic calcium silicate hydrate (I)" were essentially identical [3,4]. Tobermorite is the main constituent in autoclaved calcium silicate products such as sand-lime brick, autoclaved aerated concrete, thermal insulation board, fiber-reinforced calcium silicate sheets, and other similar building materials [5].

The main hydration product of Portland cement, calcium silicate hydrate (C-S-H), is known to be a major contributor to the performance of concrete. Researchers have paid high attention to the synthesis and characterization of C-S-H. However, a difficulty in the characterization lies in the fact that C-S-H does not have a well defined structure and properties. It is often referred to as a 'gel', the structure and properties of which exhibit significant local variations. Moreover, cement hydration is a complex set of chemical reactions that lead to a variety of species in the hardened paste. In a regular paste, C-S-H is therefore never found alone and is therefore difficult to probe or test directly. Another difficulty stems from the fact that concrete exhibits a complex heterogeneous microstructure, with heterogeneities that span orders of magni-

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tude, from the nanometer scale (for the gel porosity) to the centimeter scale (for the aggregates). This complex multiscale heterogeneity makes it difficult to identify the individual contribution of each constituent to the overall macroscopic behavior [6]. In order to obtain phase-pure materials, synthesis of C-S-H were explored in the laboratory has been explored by many researchers [7].

Avoiding carbonation is critical due to the structural changes that occur in C-S-H when it becomes carbonated. Carbonation causes the silicate ions to become protonated. A high degree of carbonation completely decomposes the double silicate chain such that silica gel and calcium carbonate are the only phases present [8]. In all synthesis methods it is very difficult to totally avoid CO_2 coming into contact with the C-S-H.

The C-S-H phase has a layer structure which ideally resembles the layer structure of crystalline tobermorite with the expected constitutional formulas. Tobermorite has been used as an important mineral analog of C-S-H. Tobermorite is a layer structure consisting of CaO_2 layers, with 7-fold coordinated Ca^{2+} ions, where the oxygens are shared with Si^{4+} in chains of SiO_4 tetrahedra in a "dreierketten" arrangement on both sides of the CaO_2 layers. Water molecules and additional Ca^{2+} ions are present between these layers [9].

The original technological significance of tobermorite arose from its close relationships with the C-S-H phases formed during the hydration processes of Portland cement and its role as the primary binder in autoclaved concrete and sand-lime masonry blocks [10–12]. Both of C-S-H and tobermorite has the similar microstructure [13]. Since then, natural and synthetic tobermorites have been studied extensively. Recently, particular interest in the structure and crystal chemistry of tobermorite synthesized from different kinds of industrial solid wastes/byproducts, such as blast furnace slag [14–16], trachyte rock [17], municipal incineration bottom ash [18], and newsprint recycling residue[19]. For these wastes higher temperature (above 150 °C) and longer period (usually several days) are necessary to form the porous tobermorite structures [20]. Therefore, some additives are usually adopted to accelerate the transformation. Reinik et al. [21] investigated the hydrothermal properties from oil shale ash in the presence of NaOH, suggesting that alkali ions could induce the formation of tobermorite. Subsequently attention has been drawn to the properties of tobermorite as a cation exchanger and its potential applications in catalysis, and in nuclear and hazardous waste disposal [22]. Coleman et al. [19] reported that Al-substituted 11 Å-tobermorite exhibits cation exchange properties and cation selectivity, and is effective in the exclusion of Cd^{2+}, Pb^{2+}, and Zn^{2+} from acidified aqueous wastes.

Utilization in concrete of mineral admixtures containing alumina requires understanding the effects of aluminum on formation and properties of C-S-H [23]. It was also proposed that aluminum could influence the generation of tobermorite to form Al-substituted tobermorite, in which Al substitution occurred at the Q^2 or Q^3 sites (symbol Q represents one SiO_4^{4-} tetrahedron and the superscript indicates the number of other Q units to which it is bonded) [24]. Shaw et al. [25] indicated that the presence of Al slows the initial formation of C-S-H by reducing the solubility of quartz, which then accelerates tobermorite formation from C-S-H. Matsui et al. [26] used in-situ time-resolved X-ray diffraction technology obtained that Al addition strongly affects the decrease of C-S-H phase and causes tobermorite formation to begin earlier. However, these processes are more complex, and the formation mechanism and chemical environmental of Al-substituted tobermorite is not thoroughly understood.

As part of a broader study on the effect of aluminum substitution on properties and microstructure of C-S-H [27], the synthesis and characterization of tobermorite with/without aluminum were conducted in this work. The effects of aluminum incorporation on

properties of tobermorite, including mineral composition, chemical composition, functional groups, thermal properties, and microstructures, were explored by methods of XRD (X-ray diffraction), XRF (X-ray fluorescence), TG-DSC (thermogravimetry and differential scanning calorimetry), ATR-IR (attenuated total reflectance-infrared spectroscopy), MAS-NMR (magic angle spinning-nuclear magnetic resonance), and SEM (scanning electron microscope). This work is aimed at better understanding the role of admixtures containing aluminum in concrete in a micro- and atomic-scale.

2. Experimental procedures

2.1. Synthesis

The tobermorite samples were synthesized from mixtures of reagent-grade chemicals obtained or prepared as follows. Fresh calcium oxide (CaO) was obtained by calcining calcium carbonate ($CaCO_3$, 99.0%, Sigma-Aldrich) at 1000 °C for 24 h, immediately after which it was stored under vacuum. Fumed silica powder (SiO_2, 0.007 μm, Sigma-Aldrich) was placed in an oven at 105 °C for 24 h to remove any water. Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Sigma-Aldrich) was used for aluminum substitution. Nanopure water was used as the mix water.

The mix ratios related to ideal composition of tobermorite are used. For the sample without Al, the designed molar ratio of Ca/Si is 0.83 which is according to ideal composition of tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$). For the sample with Al, molar ratio of Ca/(Si + Al) is 0.83, and the replacement molar ratio of Si by Al is 0.05 which could be calculated as molar ratio of Al/(Al + Si). The mass ratio of water/solid is 10.00. Samples were mixed and then placed directly in an autoclave (Cement-Menzel Boekel autoclave). The temperature was set at 180 °C, so the saturated steam pressure was around 1 MPa. The samples were held in this condition for the duration of the synthesis time. The samples without aluminum are marked as T-1 h, T-3 h, T-5 h, T-9 h, and T-24, and the samples with aluminum are T-A-1 h, T-A-3 h, T-A-5 h, T-A-9 h, and T-A-24 h, in which T means tobermorite, A means substitution with Al, and h means the synthesis time in hours.

The synthesized products were filtered using a Büchner funnel and 2.7-μm filter paper (Whatman Grade 50), then dried in an oven at 60 °C to a constant weight. The dried samples were then stored in a desiccator in which a saturated solution of lithium chloride (Sigma-Aldrich, ACS reagent, ⩾99%) was used for control of humidity of 11% relative humidity.

2.2. Characterization

For XRD, the samples were crushed, ground, and passed through a 45-μm screen. A Siemens-Bruker D5000 powder diffractometer with Cu-Kα radiation in the theta/ θ configuration was used for measurements. The diffractometer was operated at 40 kV and 30 mA. Measurements were made from 5° to 60° 2θ at a rate of 1°/min with a step size of 0.02° 2θ.

The XRF samples were ground. Then compositions of the samples were tested using a Bruker XRF SRS3400.

The TG-DSC testing utilized a SDT Q600 V20.9 Build 20 simultaneous thermal analyzer. The samples were tested at a heating rate 10 °C/min under flowing nitrogen from 20 to 1100 °C.

The PerkinElmer ATR-IR Spectrometer was used to test the synthesized samples. After the crystal area has been cleaned and the background collected, the solid powder samples is placed onto the small diamond crystal area to be tested directly. The pressure arm should be positioned over the crystal/sample area. Force is applied to the sample, pushing it onto the diamond surface. The