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Micro-nanostructures of tobermorite hydrothermal-synthesized from fly ash and municipal solid waste incineration fly ash

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HIGHLIGHTS

- The optimum Ca/Si for hydrothermal synthesis of tobermorite was 1.0.
- The mass ratio of MSWIFA/(FA + MSWIFA) was up to 62.6%.
- MSWIFA impeded the synthesis of silicon tetrahedron chain of fibrous tobermorite.
- Aluminum mainly appeared in form of substituting the silicon of silicon tetrahedron.

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ABSTRACT

Tobermorite has attracted extensive attention as the main hydrothermal product of autoclaved aerated concrete. The optimum hydrothermal synthesis conditions, micro-nanostructure and properties of the solid wastes-based tobermorite were analyzed using XRD, SEM, XRF, TG-DSC, FT-IR, MAS-NMR and nano-indentation. The results indicated that the optimum molar ratio of Ca/Si was 1.0, the mix mass ratio of MSWIFA/(FA + MSWIFA) was up to 62.6%; The incorporation of MSWIFA reduced the degree of polymerization and micromechanical properties of tobermorite, impeded the synthesis of silicon tetrahedron chain and the formation of fibrous tobermorite, and resulted in a low hardness and elastic modulus of tobermorite.

1. Introduction

With the rapid development of technology and the acceleration of industrialization, the human beings have continuously enriched the social wealth, at the same time a large amount of industrial and solid wastes have been produced, which continuously destroys living space and seriously endangers the sustainable survival of mankind. The utilization of solid wastes as green building materials has become a hot topic among researchers.

In 1845, Schafhat carried out the hydrothermal synthesis of minerals [1]. In the past 200 years, hydrothermal technology had been continuously developed. With the application and research of autoclaved curing in the aerated concrete in depth, hydrothermal synthesis and autoclave curing have been gradually recognized. Tobemorite as the main hydrothermal product of autoclaved aerated concrete (AAC) will affect its properties. Autoclaved temperature, autoclaved time and the molar ratio of Ca/Si have an effect on the performance of tobermorite [2–4], which in turn affects the properties of AAC. In recent years, hydrothermal curing, especially subcritical hydrothermal reaction, has attracted much attention to the disposal of solid wastes, and it is considered as one of the most promising ways of the utilization of solid wastes [5].

For the past few years, the technology of waste incineration has become a major means of handling municipal solid waste. Incineration ash is from the grate of the waste incinerator and flue gas dust collector, waste heat boiler and other collected emissions, they are mainly non-combustible inorganic and unburned organic matter. Municipal solid waste incineration fly ash (MSWIFA) is the residue which is collected by the flue gas purification system, accounting for about 10% - 20% of incineration ash. The main components of MSWIFA are very close to blast furnace slag and fly ash (FA), they all belong to the system of SiO_2-CaO-Al_2O_3-Fe_2O_3 [6]. As MSWIFA contains high concentration harmful heavy metals, there

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are soluble Cd^{2+}, Pb^{2+}, and Cr^{3+} which can be leached by water. It also contains dioxins, furan and other organic matter. Some scholars [7,8] studied the hydrothermal treatment of MSWIFA, they found that the hydrothermal treatment can well solidify heavy metals and decompose dioxins in MSWIFA.

Currently, material of coal-fired power is usually dominated by coal in China, this leads that FA emissions of power plant are increasing year by year. Data shows that the total amount of FA emissions which has not been used has reached more than 2.5 billion tons over the years. And with the increasing demand for electricity, emissions of FA are also increasing, from 480 million tons in 2010 to 580 million tons in 2015, FA has become one of the largest cumulative amount and occupation of cultivated land of industrial waste in China [9,10]. Therefore, reasonable and effective use of FA, turning waste into treasure, has become an urgent problem to be solved. The comprehensive utilization of FA mainly have brick making, road construction [11,12], as admixture in the concrete [13], selecting the floating beads, improving soil, etc. [14,15] at home and abroad. Relatively speaking, these can partially solve the stacking problem of FA, but this still can't be all absorbed.

FA and MSWIFA contain CaO, SiO_2, Al_2O_3 and other ingredients, which have the potential to be used to hydrothermally synthesize tobermorite. In this paper, the solid wastes-based tobermorite was synthesized by hydrothermal synthesis from FA and MSWIFA, of which FA was used as silicon source and MSWIFA was used as calcium source. The optimum proportion of MSWIFA was determined by controlling the molar ratio of Ca/Si. The micro-nanostructures and viscoelastic behaviors of the synthesized products were also characterized. This will lay a theoretical foundation for the utilization of solid wastes and provides the corresponding support of data for AAC.

2. Experimental

2.1. Raw materials

The chemical compositions of MSWIFA are listed in Table 1. The total content of SiO_2 and Al_2O_3 is 28.9%, the content of CaO is 33.3%, and the molar ratio of Ca/Si is 2.03. Its XRD pattern, as shown in Fig. 1(A), shows that the main phases comprise sylvite (KCl), calcium chloride hydroxide (CaClOH) as well as some other minerals.

The chemical compositions of FA are also listed in Table 1. As a comparison the total content of SiO_2 and Al_2O_3 is 63.1%, the content of CaO is 9.5%, the molar ratio of Ca/Si is 0.25, which is belong to Class C fly ash closely. The average particle size of FA is 25 μm. The main minerals (Fig. 1(B)) are quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), and calcium oxide (CaO).

In this experiment, the alkaline reagent is analytical purity NaOH, this can be used to adjust alkali concentration of the reaction system.

2.2. Method

The FA based tobermorite synthesized by hydrothermal synthesis was served as the control sample (sample FA-T). The solid wastes-based tobermorite from FA and MSWIFA was synthesized by hydrothermal synthesis, of which the FA was used as a silicon source and MSWIFA was used as a source of calcium. During this process, analytical purity NaOH was chosen as the alkaline admixture. The mix ratio of FA and MSWIFA was changed by adjusting the molar ratio of Ca/Si, and the optimum solid wastes-based tobermorite was selected through XRD and other characterization methods. The designed molar ratio of Ca/Si was 0.7–1.2. The effect of the different mix mass ratio of FA and MSWIFA on the hydrothermal product was studied. Mix mass ratios were shown in Table 2. The reaction conditions based on our previous work were as follows [16]: liquid-solid ratio was 25 ml/g, the concentration of alkali was 0.2 mol/L, the reaction was continued for 10 h at 220 °C, and the filling degree (Volume of the sample/The total volume of kettle) was 70%.

The FA based tobermorite (sample FA-T) and the optimum FA-MSWIFA based tobermorite (sample FM-T) through hydrothermal synthesis were selected. Then the micro-nanostructures of the synthesized products were characterized. X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetry and differential scanning calorimetry (TG-DSC) and fourier transform infrared spectroscopy (FT-IR) were used to study mineral compositions, chemical compositions, thermal properties, and functional group characteristics. Through magic angle spinning-nuclear magnetic resonance (MAS-NMR), the complexing way of silicon tetrahedron and the average chain length of silicon tetrahedron chain of hydrothermal products were studied by sub-peak fitting technique; Scanning electron microscopy (SEM) was used to analyze the microstructure; The micro-mechanical properties such as hardness and elastic modulus of the product were analyzed by nanoindentation.

The mineral composition of the raw materials and the products were qualitatively analyzed by a Bruker AXS D8 ADVANCE powder X-ray diffractometer with Cu-Kα radiation in the theta/ θ configuration. During this process, the samples were grinded and passed through a 10-μm sieve. The diffractometer was operated at 40 kV and the scanning speed was set to 10°/min.

A Bruker XRF SRS3400 was used to analyze the chemical composition of the samples. The XRF samples should be dried, grinded and passed through a 75-μm sieve.

A FT-IR 380 infrared spectrometer of Thermo Fisher Scientific was utilized for the FT-IR testing. The scanning range was set to 400–4000 cm^{-1} and the scanning frequency was 3 in the resolution of 4 cm^{-1}. The samples were dried, grinded and passed through a 75-μm sieve, then taking 2 g.

The TG-DSC samples were ground, the samples were tested at a heating rate 10 °C/min under flowing nitrogen from 20 to 1000 °C through using SDT Q600 V20.9 simultaneous thermal analyzer.

For ^{29}Si and ^{27}Al MAS-NMR, the samples were dried, grinded to less than 1 mm. A Bruker Avance III 400 MHz NMR was used. Proton resonance frequency was 400.13 MHz and the main magnetic field was 9.4 Tesla (superconducting). CP/MAS broadband solid probe was adopted, it can detect the range of 31P-15 N and the variable range of temperature was from −50 °C to 100 °C, the rotating speed was not more than 15 KHz.

SEM was performed to characterize micro-nanostructure and morphology of the samples using Hitachi S-4800. The samples with

Table 1
Chemical compositions of municipal solid waste incineration fly ash (MSWIFA) and fly ash (FA)/%.

Chemical compositions	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	P_2O_5	SO_3	K_2O	Cl	MgO	TiO_2
MSWIFA	17.6	11.3	3.5	33.3	5.9	0.5	4.4	4.0	16.1	–	–
FA	40.7	22.4	5.3	9.5	0.5	0.7	2.2	–	–	0.8	1.2