Effect of calcium stearate based foam stabilizer on pore characteristics and thermal conductivity of geopolymer foam material

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ARTICLE INFO

ABSTRACT

Foam stabilizer plays a crucial role in the synthesis of geopolymer foam materials (GFMs). To better clarify the effects of calcium stearate based foam stabilizer (CSFS) on pore characteristics and thermal conductivity of materials, GFMs prepared with 0–2% CSFS were investigated for foam characterization, compressive strength, bulk density, geopolymerization products, pore distribution, and thermal conductivity. Results shows that (1) the foam time and initial setting time match optimally with 1.0% CSFS content. And at this point, the foam time and foam volume of GFMs were increased obviously by 42.8% and 28.6% respectively. (2) 28 d compressive strength of GFMs with a bulk density of 0.31 g/cm3 at 1.0% CSFS content were the lowest, 1.45 MPa, but still better than the standard of 1.0 MPa for 0.325 g/cm3 according to the Chinese National Standards GB11968-2006. (3) CSFS displayed limited effect on the quantity or type of geopolymerized products. (4) With CSFS/FA increasing from 0.5% to 2.0%, The quantity of macroscopic scale pores sized 10–100 μm rose considerably and then drop obviously, but still more than that of sample with free CSFS. The quantity of microscopic scale pores sized 10–100 nm grew stably. (5) Overall, 1.0% CSFS optimized pore characterization well with a largest porosity, 82%, where the thermal conductivity of GFMs reached a bottom point at 0.095 W/(m K). (6) The relationship between thermal conductivity and total porosity conforms to a Maxwell-Euchen or modified Cheng-Vachon model and the value of parameter t is determined as 1.1.

1. Introduction

Geopolymer foam materials (GFMs) are usually manufactured by introducing air (by chemical reaction or mechanical mixing) into activated-aluminsilicate material paste to form a homogenous porous material [1,2]. Due to the high volume of pores and voids, GFMs display good thermal insulating property in addition to their other desirable characteristics such as low shrinkage, superior heat resistance [3], and fire prevention [4]. These materials are gaining industry spotlight due to their excellent properties and characteristics. The global application of GFMs is expected to be in, but not limited to safety, energy-saving and environmental protection of building and engineering materials. In addition, a reduction of greater than 45% CO_2 emission and up to 60% energy consumption could be achieved by manufacturing geopolymers instead of ordinary Portland cement (OPC) [5].

Numerous factors can affect the performance of GFMs. These include the quality of raw materials, design of mix proportion, the content and type of foam agents/stabilizer, etc. [6–9]. Of particular importance is the foam stabilizer as a surfactant which could reduce the surface free energy of the bubble and enhance the toughness of the bubble, thereby reducing the burst and coalesce of bubble. So it shows a great effect on the stability, optimization and development of pore in GFMs. Moreover, pore characteristic, governed by the size, volume, and connectivity in GFMs plays a crucial role in determining the macro properties, such as bulk density, compressive strength, and thermal conductivity of GFMs [10,11]. The pores in GFMs can be classified into four groups according to sizes (1) interlayer pore/space (negligible pores present in N(C)-A-S-H gel with width < 1 nm), (2) gel pore between N(C)-A-S-H gels with width > 10 nm [11,12], (3) capillary pore (average radius of 5–100 nm), and (4) air void (width from several micrometers to 10 μm-2 mm [13]). Both the air voids in GFMs produced by deliberated entrained air and microscopic scale pore (mainly including capillary pore) of GFMs are decisive for their final formation and properties.

Many studies have been reported pertaining to the degree of reaction and the effect of pore characteristic on the compressive strength and thermal conductivity values of GFMs. The effect and amount of

alkali activator and H_2O_2, curing temperature [6–8,11], several foam stabilizers such as sunflower oil [14], polyoxyethylene and polyethylene [15] were applied and investigated. However, these studies on foam stabilizers were mainly concentrated on organic or polymeric based molecules and this type of foam stabilizer might result in poor pore structure with more connectivity. While anionic surfactant such as sodium dodecyl benzene sulfonate (SDBS) are known to be used as foam stabilizer in GFMs because of its hydrophobic non-polar long chain, the air entrainment of SDBS itself weakens its efficiency of foam stabilization, So, there still exist a great potential for further research on this class of surfactant type stabilizers. In particular, calcium stearate has two long chains different from the one long chain of SDBS. These two long chains make it effective to be as a foam stabilizer for GFMs [16,17].

This study thus aims to investigate properties of GFMs as affected by calcium stearate based foam stabilizer (CSFS) through analysis of the regular pattern of the foam characterization, compressive strength, bulk density, geopolymerization products, pore distribution, and thermal conductivity. Finally, the relationship between thermal conductivity and porosity of GFMs will be clarified. Obviously, the results obtained would provide an effective method for regulating the pore structure of porous materials.

2. Experimental investigations

2.1. Raw materials

Fly ash (FA) was circulating fluidized bed combustion coal fly ash supplied from Pingshuo power station in Shuozhou, China. The main chemical composition is given in Table 1, while SEM (A), XRD (B) and particle size distribution (C) of FA were shown in Fig. 1. The FA had an average particle size of 4.25 μm. Water glass (Red Star Co., Ltd, China, modulus 2.4, 54.2% of water), sodium hydroxide pellets (Beijing Chemical Works, China, 96 wt%) and water were mixed to produce the alkaline activator (AA) given in Table 2. Hydrogen peroxide (30 wt% H_2O_2) as a foam blowing agent and pure calcium stearate (99% of purity) as a foam stabilizer (CSFS, Fig. 2) were bought from Beijing Chemical Factory in China. Calcium stearate is effective in the range of − 20–145 °C [16,18].

2.2. Synthesis and preparation of GFMs

A series of five samples were prepared with CSFS/FA from 0% to 2.0%; each differing by 0.5%. Considering the preferred workability and mechanical property according to our previous experiments in laboratory, AA: FA and H_2O_2: FA were kept constant at 0.867 and 0.04 (by weight) respectively. AA consisted of water glass, NaOH and H_2O.

FA was homogenized with calcium stearate. AA solution was added to the powder mix and stirred for 5 min using a flat blade agitator to obtain a homogeneous slurry. H_2O_2 was added to the slurry and stirred for 30 s to obtain a consistent mixture with relatively high flow ability and viscosity. All the prepared samples are presented in Table 2. The foamed mixture was cast in triplet steel molds of 40 mm × 40 mm × 160 mm slabs for density and strength tests, and in 300 mm × 300 mm × 30 mm cuboids for thermal conductivity tests. All casted samples were sealed with polyethylene film and placed into a standard curing box, cured at 60 °C for 24 h. The samples were demolded thereafter subjected to further curing in air environment. The aged specimens

were tested and characterized at 7 and 28 days.

2.3. Characterization

The initial setting time was measured by ISO vicat apparatus according to GB/T 1346–2011. The prepared geopolymer pastes were poured into a conical mold and placed in a curing box with 60 °C. The first test was performed after 10 min curing. Then each test was performed every 2 min until the vicat needle was pointed to a distance of 4 ± 1 mm from the bottom plate. The foam time of H_2O_2 was obtained by an indirect method. 12 g H_2O_2 and 12 g water were both placed in an oven with 60 °C, and the mass of H_2O_2 and water was recorded at intervals of 2 min by electronic analytical balance with a sensitivity of 0.0001 g until the difference of the mass of H_2O_2 and water was constant. Three times of this process was performed to minimized the errors.

The surface tension of AA was measured by Wilhelmy plate method using Surface tensiometer (K100 from KRUSS, Germany) according to GB/T 22237-2008. All the measurements were recorded at 25 °C.

The initial volume and the finishing foam volume of slurry after different foaming times were recorded with 250 ml graduated cylinders.

Bulk density of specimens was obtained by the mass of specimen dividing by the volume of specimen. The mass of specimens was measured by electronic balance and the volume of specimens was calculated by the length, height and width of 40 mm × 40 mm × 160 mm specimens. Compressive strength of specimens was tested by a Universal Testing Machine (CS200, China) with a load rate of 0.05 kN/s according to GB/T 5486-2008. The specific strength was the ratio of compressive strength to bulk density at the same cured ages. All the reported apparent density and compressive strength were the average of 3 independent measurements.

Thermal conductivity was measured in accordance with GB/T 10294-2008, the standard test method for determining the steady state thermal transmission properties using a heat flow meter apparatus (DD300F-D15from Foreda, China). A tabulate specimen (300 mm × 300 mm × 30 mm) was placed between two plates, the temperatures of the hot and cold plates were set as 45 °C and 20 °C, respectively.

Mineral phases present in the powdered geopolymers specimens were determined via XRD analysis, recorded on an X'TRA high-performance powder X-ray diffractometer (ARL, Switzerland) with Cu Ka radiation generated at 40 mA and 40 kV. The XRD data was evaluated using MDI Jade 5.0 software based on the International Center for Diffraction Data (ICDD) PDF database 1998.

The chemical environments of molecular bonds were studied using Fourier transform infrared (FT-IR) absorption spectra. The spectra were recorded in the range $4000 − 400 \, cm^{-1}$ using FT-IR spectrometer (NICOLET iS10, USA) at a spectral resolution of $2 \, cm^{-1}$ and a scan speed of 0.2 cm/s.

Elemental composition of FA was determined by XRF spectroscopy on an AXIOS X-ray fluorescence spectrometer (PANalytical, the Netherlands). The loss on ignition (LOI) test was done at 960 °C.

The characteristic (distribution and porosities) of macroscale pore (> 10 μm) in GFMs caused by the decomposition of H_2O_2 [11] were carried out with an image analysis (IA) system consisting of an optical microscope (moticam2306) and Image-pro plus image analysis software. The procedure was as follow: Five images of fracture section of each sample were observed by optical microscope (25 ×). The black/white binarization of images were then treated by Image-pro plus image analysis software. Finally, the average pore size of five images of each sample were calculated by Image-pro plus image analysis software.

The distribution of mesoscale pore between 100 nm and 10 μm was not considered in this work as they are assumed to be insignificant in affecting the macro properties of GFMs according to [11,19]. The total porosities, φ, was calculated by the formula (1):

Table 1
Chemical composition of FA.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	TiO_2	K_2O	MgO	LOI[a]
wt%	43.35	35.77	6.33	8.76	2.43	1.96	0.37	0.56	5.37

[a] LOI, loss on ignition at 960 °C.