Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 34 (2014) 3133–3137

www.elsevier.com/locate/jeurceramsoc

Short Communication

Open cell geopolymer foams by a novel saponification/peroxide/gelcasting combined route

Marcelo Strozi Cilla [a,b,*], Márcio Raymundo Morelli [a], Paolo Colombo [b,c]

[a] Graduate Program on Materials Science and Engineering, Federal University of São Carlos, Via Washington Luiz, km 235, São Carlos, SP, Brazil
[b] Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, Via Marzolo, 9, Padova, Italy
[c] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

Received 19 February 2014; received in revised form 31 March 2014; accepted 4 April 2014
Available online 2 May 2014

Abstract

Using a novel saponification/peroxide/gelcasting combined route it was possible to produce geopolymer foams with a total porosity of ~85 vol%, open porosity as high as ~70 vol%, average cell size (D50) of 318 μm, and possessing a specific surface area of 50 m^2/g. The in situ formation of surfactants by the saponification reaction of oil in the geopolymer alkaline environment led to increased total and open porosity in comparison to alternative methods for the fabrication of geopolymer foams.

Keywords: Combined route; Geopolymer foams; Saponification; Peroxide; Gelcasting

1. Introduction

The term geopolymer indicates a class of inorganic materials with chemical composition similar to that of zeolite and a variable microstructure (amorphous to semi-crystalline), which are obtained by the reaction of aluminosilicates with a highly alkaline medium, leading to the formation of a continuous three dimensional network.[1] These materials can consolidate at low temperature (about 80 °C) and, for selected compositions, can be used at high temperature (up to 1200 °C and above). Because of their ease of shaping from an aqueous slurry and the possibility of setting the component via the geopolymerization reactions, thereby enabling the retention of the produced shape, geopolymers offer the possibility of efficiently producing highly porous ceramic components. Several papers describe the production of porous components based on geopolymers, typically following approaches similar to those employed in the cement industry (i.e. in situ generation of gas[2–5]), leading to the creation of mainly closed cell foams. For filtration or adsorption applications, a fully interconnected cellular network is required, and therefore novel processing strategies need to be developed. The saponification reaction, recently proposed for the production of micro-/meso-porous geopolymers with high specific surface area,[6,7] has been here exploited for the first time in association with gelcasting for the generation of macrocellular open cell geopolymer foams.[8]

2. Experimental procedure

For these experiments, the samples were produced using the same raw materials described in reference[8]; the geopolymer mixture (GP) was prepared considering the three oxide molar ratios as follows: $SiO_2/Al_2O_3 = 3.78$, $K_2O/SiO_2 = 0.24$ and $H_2O/K_2O = 16$. The first step in the preparation the geopolymer foams was the preparation of a 15 M KOH solution, which should be used after 24 h.[9] Then, a solution of potassium-based activators and distilled water was prepared in a mixer (500 rpm, 30 min, Ika-Werke Ost Basic, Staufen, Germany). To this solution, Dolapix CE-64 (Zschimmer & Schwarz) was

* Corresponding author at: Graduate Program on Materials Science and Engineering, Federal University of São Carlos, Via Washington Luiz, km 235, São Carlos, SP, Brazil. Tel.: +55 16 33518245.
E-mail addresses: marcelocilla@ufscar.br, marceloscilla@gmail.com (M.S. Cilla), morelli@power.ufscar.br (M.R. Morelli), paolo.colombo@unipd.it (P. Colombo).

http://dx.doi.org/10.1016/j.jeurceramsoc.2014.04.001
0955-2219/

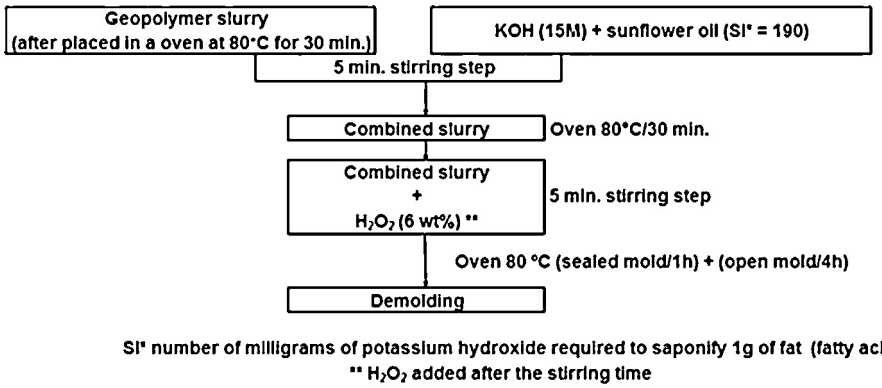

Fig. 1. Schematic flowchart for the production of geopolymer foams by the saponification/peroxide/gelcasting combined route.

added (0.32 wt% of the total weight). Metakaolin and fly ash were then added at room temperature to the activator solution, stirring at 1000 rpm for 30 min, producing suspensions with a solid content of 68 wt%. The GP suspension was placed in an oven at 80 °C for 30 min to accelerate the geopolymerization reaction, which is the key to enabling the retention of porous morphology of the wet foam subsequently produced. Thereafter, the suspension was removed from the oven and then 25 wt% of a commercial sunflower oil (SO Dolix, IN'S Mercato SpA, Pianiga, Italy), saponification index (SI) of 190 and the respective quantity of KOH solution considering the SI of sunflower oil were added, mixing at 500 rpm for 5 min. Thereafter, the combined suspension was placed in an oven at 80 °C for 30 min, being stirred again at 1500 rpm for 5 min, and then 6 wt% of hydrogen peroxide (Gabbiano Spa, Virgilio, Italy) was added. Finally, the geopolymer foam was cast in a polystyrene mold and placed for 1 h at 80 °C into an oven after sealing it into a plastic bag, and then removed from the plastic bag and left at 80 °C for further 4 h. The process is illustrated in Fig. 1 (saponification/peroxide/gelcasting route). For comparison, samples were also produced with the addition of oil but no hydrogen peroxide (saponification route) and with the addition of hydrogen peroxide but no oil (peroxide route). Hydrogen peroxide and sunflower oil were added always in the same amounts specified previously.

Prior to the characterization, the glycerol generated by the saponification reaction was extracted by hot water exchanging it every 30 min until it remained clear, visually indicating complete extraction. This step of the extraction of glycerol can also be used to confirm the extent of the geopolymerization reaction, since non-fully condensed geopolymer materials are sensitive to water and undergo swelling or complete destruction.[5] The bulk density and porosity of the geopolymer foams was determined by weight-to-volume ratio, dividing the mass of foam cut into a parallelepiped by its geometric volume measured with a caliper, and taking into account the true (skeleton) density of the pore-free solid material, measured with an helium pycnometer (Accupyc 1330, Micromeritics, Norcross, GA).[10] The open porosity was quantified by the Archimedes Principle using water as the infiltrating fluid. The Brunauer–Emmett–Teller specific surface area (SSA) was determined by multipoint BET method using the adsorption data in the relative pressure (P/P_0) range 0.05–0.3 obtained by a Quantachrome Nova Station A (Quantachrome Instruments, Boynton Beach, USA). All the samples were degassed at 300 °C prior to nitrogen adsorption measurements. The morphology of the foams was investigated using an optical stereoscope (Wild Heerbrugg, Type 376788, coupled with a digital camera) and a Scanning Electron Microscope FEI Quanta 200 (FEI Company, Hillsboro, OR, USA). The pore size distribution was evaluated from the acquired images using the Axio Vision 4.8.2 LE image processing software (Carl Zeiss, Oberkochen, Germany). Values obtained by image analysis were converted to 3D values using the stereological equation $D_{sphere} = D_{circle}/0.785$,[11] to determine the actual cell-size.

The air-permeation behavior of porous geopolymers was investigated at room temperature using a laboratory-made air permeator at the Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Legnaro (INFN-LNL), Italy, which is based on an action-response device, making a correlation between the pressure drop applied across a porous medium and the resulting flow rate or velocity of the fluid output.[12] Experiments were carried out on disk-shaped samples, which were tightly fixed with rubber rings inside the sample holder that provided a useful flow diameter of 1.99 mm with air flow, allowed to flow upward through the disk, at room temperature (20–24 °C) and atmospheric pressure (1 atm). Pressure drop (ΔP) across the disk was measured by either one of two digital manometers (GMH 3161-01, range 0–25 mbar, resolution of 0.01 mbar and GMH 3161-13, range 0–2000 mbar, resolution of 1 mbar, Greisinger Electronic GmbH, Regenstauf, DE) and the resulting volumetric air flow rate across the disk was measured by a laboratory made soap-bubble flow meter with useful volume of 50 mL and resolution of 0.1 mL. At least 20 sets of pressure drop and flow rate curves were acquired in steady-state conditions to ensure an accurate fitting analysis.

The compressive strength was determined (5 specimens) using a Universal Testing Machine (Instron 1121, Canton, MA, USA), with a constant crosshead displacement of 1 mm/min.

3. Results and discussion

When the vegetable oil is added to the highly alkaline geopolymer suspension (pH ~9.5), it generates in situ