Development of foamed Inorganic Polymeric Materials based on Perlite

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Abstract. This work deals with the development of lightweight geopolymeric boards for use in the construction sector utilizing a solid perlitic waste as the main raw material. Hydrogen peroxide ($H_2O_2$) was used for the foaming of geopolymeric pastes and the production of porous and lightweight inorganic polymeric materials. The effect of geopolymeric synthesis parameters, such as the composition of activator and the curing conditions, on paste’s properties that affect the foaming process, such as setting time and viscosity, were studied in detail. Finally, the effects of $H_2O_2$ concentration on the properties (apparent density and % cell volume) and the microstructure of foamed boards were also studied. The produced porous boards have effective densities in-between 540 – 900 Kg/m$^3$ and the thermal conductivity of the optimum product is 0.08 W/m.K. Based on their properties, the developed lightweight geopolymeric boards have high potential to be used as building elements in construction industry.

1. Introduction

Lightweight porous materials offer some significant advantages to the construction sector such as lighter high rise buildings, less structural steel and concrete consumptions, improved thermal efficiency and superior fire resistance as well as seismic performance. The market of lightweight porous materials is exclusively occupied by the autoclaved aerated concrete (AAC). AAC is produced by foaming OPC concrete through hydrogen gas that is produced when aluminum powder reacts with the alkaline water of concrete [1]. The hydrogen gas after the end of the foaming process escapes to the environment and is replaced by air. The AAC after foaming is very soft and in order to acquire satisfactory mechanical strength is placed in an autoclaved chamber at 180$^\circ$C-200$^\circ$C and 8-12 bars steam pressure [2, 3]. The AAC production suffers from some disadvantages such as increased plant precautions due to the explosive nature of hydrogen gas, difficulties in the production control and high energy consumption [4, 5].

The development of lightweight foamed inorganic polymeric materials based on perlitic wastes as alternatives of the autoclaved aerated concrete seems to be very attractive. Geopolymers can replace OPC with significant environmental (80-90% reduction in CO$_2$ emissions) and technical (improved resistance to aggressive chemicals and fire) benefits while at the same time have identical mechanical properties [6]. In addition, geopolymers are normally produced utilizing waste materials such as fly ashes, metallurgical slags and mine wastes [7-10] strengthening thus their environmental character and contributing towards a zero waste circular economy. In Europe the annual production of perlite was estimated about 1.835.000 tons for 2012 [11] while the perlite fine wastes were about 275.250 tons which equals almost 15% of the raw perlite. Perlite wastes have not been extensively studied as
potential aluminosilicate source for the synthesis of inorganic polymers through the geopolymerization technology. The geopolymerization process is based on an exothermic heterogeneous chemical reaction between a solid aluminosilicate raw material and an alkali metal silicate solution under atmospheric conditions and temperatures up to 100°C. The materials synthesized by this reaction present mainly an amorphous or semi-crystalline Si-O-Al and/or Si-O-Si backbone. Extended research activity in the field of geopolymeric synthesis the last decades has proven that geopolymers possess excellent mechanical and physicochemical properties [12-14] that render them ideal alternatives for many industrial applications, mainly in the construction sector.

Foaming process aims ideally at the formation of a large number of small individual voids (closed cells) or interconnected series of voids (open cells) inside a viscous material (paste or polymer). The control of the nature, size and distribution of voids is the most critical step in production of foamed materials, as the voids determine their density and strength [15]. Voids can be produced by two main methods: 1) by endogenous gas generation, which can be achieved by mixing gas-releasing agents such as H₂O₂ or fine aluminium or zinc powders in cement paste or mortar, or 2) by introducing a very large volume fraction of air bubbles, usually through the use of an organic foaming agent. Hydrogen peroxide (H₂O₂) is a widely known foaming agent which is thermodynamically unstable and therefore can be easily decomposed to water and oxygen gas (chemical equation (1)) with the latter playing the role of the blowing agent [16].

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]  

This paper deals with the development of lightweight foamed geopolymeric boards as alternatives to the marketable autoclaved aerated concrete. The geopolymeric pastes were prepared utilizing milling plants perlitic wastes as raw material and were foamed by using hydrogen peroxide as blowing agent. The effect of main synthesis parameters on the properties of geopolymeric pastes (setting time and viscosity) were studied in extent. In addition, the effect of the amount of added foaming agent on the final foamed board’s characteristics (apparent density and % cell volume) and microstructure was also studied.

2. Experimental

2.1 Materials

The raw materials used for the synthesis of geopolymeric paste were perlitic waste, sodium hydroxide and hydrogen peroxide. The perlitic waste originated from the milling plant of S&B Industrial Minerals S.A. in Greek island Milos. The chemical analysis in dry basis, determined by XEPOS X-ray Fluorescence diffractometer utilizing X-LAB software, is given in Table 1. The main chemical components of perlitic waste are silicon, aluminum, sodium and potassium while magnesium, calcium, titanium and manganese are minor constituents.

| Oxides (wt%) | Na₂O | MgO | Al₂O₃ | SiO₂ | K₂O | CaO | TiO₂ | Fe₂O₃ | MnO |
|--------------|------|-----|-------|------|-----|-----|------|-------|-----|
|              | 4.00 | 0.64| 11.80 | 72.29| 5.26| 0.90| 0.12 | 1.41  | 0.13|

The raw perlitic waste is extremely fine with mean particle size d₅₀ = 6.50 μm measured on a MALVERN Laser Particle Size Analyzer. The mineralogical analysis confirmed that perlitic waste is an amorphous volcanic alumino-silicate glass which contains some crystalline phases as illite, feldspars (albite and anorthite) and quartz.
2.2 Experimental procedure
The geopolymeric viscous paste was prepared by mixing perlite with the alkaline activating solution for 5 minutes until a homogeneous mixture was obtained. The NaOH concentration in the alkaline activating solution was varied in-between 2-12M while the solid/liquid ratio was kept constant at 1.2g/mL. The resulted paste was cured at four different temperatures (50°C, 70°C, 90°C, 100°C) and its setting time was determined by a MATEST Vicat apparatus according to the EN 196-3:2005. The viscosity of the geopolymeric pastes was measured immediately after their preparation at ambient temperature by Brookfield Viscometer LV+.

The geopolymeric foams were prepared by mixing the geopolymeric viscous paste (solid/liquid ratio =1.2 g/mL, CNaOH 8M) with hydrogen peroxide in a mechanical mixer for 5 minutes. The amount of added H$_2$O$_2$ was varied in-between 0.25-1.25%w/w. Then the mixture was molded in 15 x 15 x 4 mm molds and cured in three consecutive stages (stage 1: 90°C for 24h, stage 2: 50°C for 72 h, stage 3: 35°C for 24h). After curing the foamed boards were demolded and kept in a dry atmosphere for further evaluation. The % cell volume of the foamed boards was estimated through the equation (2) by measuring their apparent (ρ) and skeletal (d) densities [16]. The apparent density of foamed boards was determined by measuring the weight of cured boards with a precision balance as well as their dimensions with a precision electronic caliper. The skeletal density was determined by QUANTACHROME stereopycnometer.

$$C = \left(1 - \frac{ρ}{d}\right) \times 100$$ (2)

The microstructure of foamed boards was observed with SEM microscopy using JEOL 2100 HR Scanning Electron Microscope. Finally, the thermal conductivity of foamed boards was measured with the Netzsch HFM 436/3 Lamda, Heat flow meter.

3. Results and discussion

3.1 Synthesis and evaluation of the geopolymeric paste
The effect of initial NaOH concentration in the activating phase on the properties of geopolymeric pastes was studied in the region from 2M to 12M. The solid/liquid ratio was kept constant at 1.2 g/mL while the pastes cured at 50°C, 70°C, 90°C and 100°C. The results are shown in Figure 1 where the setting time of synthesized geopolymeric pastes at different temperatures is plotted versus the initial concentration of NaOH solution. The results showed a strong trend towards increase of setting time as a function of NaOH concentration. At 50°C and as the NaOH concentration rises from 2 to 6 M, the setting time rises from 20 to 120 hours indicating an increase of almost 6-fold, while for NaOH concentration higher than 6 M the setting time is invariable. It is observed that at 70°C the setting time is generally faster than at 50°C. The setting time is invariable in the region of NaOH concentration in-between 2-5M but the setting process is strongly decelerated when the NaOH concentration becomes higher than 5M reaching again a plateau after a NaOH concentration higher than 8M. The setting of the geopolymeric pastes is substantially accelerated at 90°C and 100°C. The results revealed that the geopolymeric perlitic pastes solidify faster under lower NaOH concentrations in the alkaline activating phase as well as at higher curing temperatures. The former of the above observations seems opposing to the common perception in the geopolymerization technology according to which geopolymerization is effective at high NaOH concentrations. Indeed as is seen in Figure 2, Si dissolution from perlitic waste after 24 hours retention time at 50°C increases as the initial NaOH concentration increases but the 10-fold increase of NaOH concentration (from 1M to 10M) causes only 2.5-fold increase on the silicon dissolution (from 10% to 25%) leaving, according to the dissolution reaction ( equation 3), a substantial excess amount of free NaOH and establishing lower SiO$_2$/Na$_2$O mass ratios in the aqueous phase. The lower SiO$_2$/Na$_2$O mass ratios favor the formation of monomer and oligomer Si species (Figure3) [17] and therefore inhibit the polycondensation phenomena prolonging the setting time of geopolymeric perlitic pastes.
SiO₂ + NaOH + H₂O SiO(OH)₃⁻ + Na⁺

(3)

The increase of temperature improves the dissolution reaction kinetics and therefore, decreases the excess amount of free NaOH and increases the SiO₂/Na₂O mass ratios in the aqueous phase accelerating the polycondensation phenomena (Figure 3) and making the geopolymeric paste setting faster (Figure 1).

In Figure 4, the effect of NaOH concentration on the viscosity of perlitic pastes is shown. The perlitic pastes are non-Newtonian shear thinning fluids that achieve substantially low viscosities at high shear stresses. Not significant dependence of NaOH concentration on viscosity was revealed, indicating that the early viscosity is more related to the density of suspended perlite particles in the paste rather than to the physical properties of the aqueous phase itself. An exception is the high viscosity values from 800.000 to 1.400.000 centipoise measured at spindle speed lower than 1 rpm for the paste composed with 2M NaOH solution as activator. This observation proves once more the faster polymerization and therefore solidification at 2M NaOH indicating that the polycondensation phenomena in the perlitic pastes are optimized under low NaOH concentration.

**Figure 1.** Setting time as a function of C₁NaOH

**Figure 2.** Silicon dissolution from perlitic waste in several NaOH solutions at 50°C, 24h and pulp density 16g/L

**Figure 3.** Qualitative interpretation of soluble silicate species equilibria in 1m aqueous silicate solution

**Figure 4.** Viscosity as a function of CNaOH

3.2 Synthesis and evaluation of foamed boards

In order for a large number of relatively small individual gas bubbles to be dispersed inside the geopolymeric paste, two main processes have to be appropriately controlled: a) bubble swelling and b) bubble upward movement. The former is mainly affected by the amount of blowing agent per volume.
of paste while the latter is affected by the viscosity of paste [18]. The highest the viscosity, the lowest
the bubble rise terminal velocity. Because the initial viscosity of the geopolymeric perlitic pastes
under ambient temperature (where the foaming is taking place) seems to be almost unaffected by
the composition of the aqueous phase, the most important parameter that determines the effective
entrainment of bubbles inside the paste is its setting time which is shorten substantially at temperatures
as high as 90°C. Therefore, the curing of perlitic pastes was decided to take place initially at 90°C for
24h for fast setting and then to lower temperatures (50°C for 72h and 35°C for 24h) for avoiding the
surface cracking.

The apparent density of the foamed boards as a function of the % H$_2$O$_2$ addition in the paste is
shown in Figure 5. The apparent density decreases substantially as the % H$_2$O$_2$ increases up to an
optimum value of 0.5% reaching a value which is slightly lower than 600 kg/m$^3$. Further addition of
H$_2$O$_2$ seems to have detrimental effect on the apparent density of foamed boards increasing it to a
value around 700 kg/m$^3$. The increase of the % H$_2$O$_2$ up to the optimum value of 0.5% increases the %
cell volume in the boards (Figure 6) as well as increases the size of cells and makes thinner their walls
(Figure 7a & b). Further increase of % H$_2$O$_2$ leads to the perforation of the very thin cell walls causing
coalesscence of neighboring cells (Figure 7c, d & e) and collapse of the foamed structure which has as
a consequence the decrease of % cell volume (Figure 6) and therefore the increase of the apparent
density (Figure 5).

![Figure 5. Apparent Density of foamed boards in function of H$_2$O$_2$ content in the paste](image1)

![Figure 6. %Cell Volume of foamed boards in function of H$_2$O$_2$ content in the paste](image2)

![Figure 7. Scanning Electron Microscopy pictures of geopolymeris foamed boards synthesized with different H$_2$O$_2$ content. a) 0.25%, b) 0.5%, c) 0.75%, d) 1% and e) 1.25% H$_2$O$_2$.](image3)

A comparison of the most important properties of aerated concrete, autoclaved aerated concrete and
developed geopolymer foams is given in Table 2. The developed geopolymer foamed boards have
directly comparable thermal conductivity and apparent density with the aerated concrete and
autoclaved aerated concrete and therefore have high potential to be used as lightweight construction
materials.
4. Conclusions
In this work, the development of lightweight geopolymeric boards was investigated. The evaluations of the geopolymeric paste’s properties that are important for the foaming process were performed. The concentration of sodium hydroxide in the liquid phase and the curing temperature of the pastes were proved as important synthesis parameters affecting substantially the geopolymeric paste’s setting time. Under the optimum synthesis conditions defined in this work, the perlite based inorganic polymeric pastes had setting time shorter than 2h. The produced pastes are viscoelastic fluids with viscosity values up to 1400 cp x 10^3 while their initial value is more determined by the density of suspended perlite particles in the paste rather than the physical properties of the aqueous phase itself. Hydrogen peroxide (H₂O₂) proved to be an effective foaming agent for this type of geopolymeric pastes. The foamed materials that came out were lightweight and porous and the foaming process proved to be more efficient at 0.5%(w/w) H₂O₂ addition in the geopolymeric paste. The best foamed boards produced had apparent density 540 Kg/m³, cell volume 70% and thermal conductivity 0.08 W/mK. In comparison with the other conventional lightweight materials (mainly AAC), the foamed boards from perlite have similar thermal properties and densities that render them potential lightweight materials for the construction sector.

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