

Article



Experimental Evaluation of Efficient Si Dissolution from Perlite at Low Level Activator's Concentration

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Abstract: This paper deals with the Si dissolution of fine perlite in alkaline solutions for the determination of the SiO₂/Na₂O mass ratio in the aqueous phase of geopolymer slurries. In the present work, the effect of the main synthesis parameters such as NaOH concentration and curing temperature on the setting time of the paste were studied. The obtained results showed that the inorganic polymer pastes present fast hardening at low concentrations of NaOH solutions for both 70 and 90 °C. This observation was also identified by the Si dissolution study of perlite pastes as a function of different concentrations of NaOH solutions and different solid to liquid ratios of the slurries, under a constant temperature. The optimum synthesis conditions for geopolymer pastes proved to be a low initial NaOH concentration in the alkaline phase (2–4 M NaOH), where the fast hardening of the paste was attributed to the high SiO₂/Na₂O mass ratio, enhancing the polycondensation phenomena and promoting the geopolymerization process.

Keywords: geopolymerization; inorganic; perlite; alkali activation

1. Introduction

Extended research activity in the field of geopolymer synthesis over the last decade has proved that geopolymers possess excellent mechanical and physicochemical properties. According to these properties, inorganic polymers are considered ideal alternatives for many industrial applications, mainly in the construction sector. Geopolymerization 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 frame. A variety of industrial solid residues or wastes such as fly ashes, metallurgical slags, and mine wastes, as well as industrial minerals such as kaolinite and feldspars [1–10], have been used for the synthesis of geopolymers. The produced materials exhibit remarkable properties, depending on the mix design and on the applications for which they are intended, such as high surface hardness, high mechanical strength, fire and chemical resistance, thermal stability, low density, and micro or nano porosity [11–18].

However, perlite has not been extensively studied as a potential aluminosilicate source for the synthesis of inorganic polymers through geopolymerization technology. The main reason for this is that perlite has been considered as an inefficient raw material for geopolymerization, resulting in final materials with a lack of mechanical properties [19]. Perlite deposits are normally exploited with low-cost open pit mining methods followed by in situ milling and screening. Greece and Turkey are the world's leading perlite producers, with an annual production for the year 2017 of 700,000 t and 1,100,000 t per country [20], while in Europe the annual production of perlite was estimated to be about 1,935,000 t for 2017 [20].

This paper deals with the investigation of perlite geopolymer paste's setting time, as a function of different NaOH solution concentrations, at two temperatures. The results were evaluated by the determination of the SiO_2/Na_2O mass ratio, which corresponds to the geopolymer pulps after two series of Si dissolution tests from perlite in an alkaline activator. In the first series, Si dissolution of perlite in NaOH solutions of different concentrations and temperatures was determined at a constant solid to liquid ratio. The second experimental series included Si dissolution tests of the perlite pulps as a function of different alkaline activator concentrations at different solid to liquid ratios for a constant temperature. Finally, the SiO_2/Na_2O mass ratio of the examined pulps was determined, indicating (after an extrapolation process) a possible SiO_2/Na_2O value for the real solid to liquid ratio of the geopolymer paste.

2. Materials and Methods

2.1. Materials

The raw materials used for the synthesis of geopolymer slurries consist of sodium hydroxide and expanded perlite wastes from the milling plant of Imerys on Milos Island, Greece. The chemical analysis with a dry basis, determined by a XEPOS X-ray fluorescence diffractometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany) utilizing the X-LAB software, is given as oxides in wt % in Table 1. Loss on ignition was determined after heating perlite for 1 h at 1100 °C.

Table 1.	Chemical	analysis	of p	perlite	waste.
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Oxides (%) <i>w/w</i>								
Na ₂ O	MgO	Al_2O_3	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	LOI	TOTAL
3.99	0.27	10.51	75.33	4.31	1.38	1.17	2.83	100

Fine raw perlite waste was measured on a MALVERN Laser Particle Size Analyzer with a mean particle size of d50: 26 μ m. Its specific surface area was measured to be 0.65 m²/g by a QUANTACHROME Nova–1200 Ver 5.01 porosimeter (Boynton Beach, FL, USA). Its skeletal density, measured with a QUANTACHROME stereopycnometer, was 2402 kg/m³. The mineralogical analysis showed that the perlite waste was mostly amorphous, with only a small proportion of crystalline phases such as quartz and feldspars.

The alkaline activator that was used for the synthesis of geopolymer pastes was an aqueous sodium hydroxide solution, prepared by dissolving sodium hydroxide pellets (Merck Chemicals, Darmstadt, Germany, 99% purity) in deionized water.

2.2. Paste Preparation

The geopolymer viscous paste was prepared by mixing perlite with the alkaline activating solution for 20 min, until a homogeneous mixture was obtained. The NaOH concentration varied between 2 and 10 M, while the solid/liquid ratio was kept constant at 2 g/mL. The produced paste was cured under two different temperatures (70 °C and 90 °C).

2.3. Characterization Methods

Primarily, the setting time of geopolymer pastes was determined using a MATEST Vicat apparatus (Treviolo, Italy) in accordance with BS EN 196-3:2005+A1:2008 Methods of Testing Cement. Determination of setting times and soundness [21]. In addition, the dissolution of silicon from perlite in sodium hydroxide solution was studied in a 400-mL autoclave reactor, equipped with a thermostatically controlled heating mantle that was connected to a mercury contact thermometer, a mechanical stirrer with speed control, and a glass condenser. The dissolution tests were performed at 50, 70, and 90 °C for a 24-h retention time under intensive agitation, with a solid to liquid ratio (S/L) of 0.02–1 g/mL and

a NaOH concentration of 2–6 M. At the end of each test, the suspension was filtered and the filtrate was further analyzed for its silicon content, using an inductively coupled plasma mass spectrometer (ICP–MS, Perkin Elmer, Waltham, MA, USA).

3. Results and Discussion

Characterization of Geopolymer Pastes Properties

The effect of the NaOH concentration on the setting time of geopolymer pastes was studied in the region from 2 M to 10 M. This characterization method is of high importance, as indicates the favorable conditions of the alkaline activator's synthesis in the aqueous phase which contribute to the effective geopolymerization of perlite. The results are shown in Figure 1.



Figure 1. Setting time of geopolymer paste as a function of NaOH concentration (S/L: 2 g/mL, Temperature: 70 and 90 °C).

Figure 1 reveals that perlite geopolymer pastes solidify faster under lower NaOH solution concentrations, as well as at higher curing temperatures. More specifically, it is observed that 2 and 4 M NaOH solution constitute the optimum concentrations of the activator, at 90 °C, as the paste solidifies after 5 and 8 h, respectively. The former of the above observations is in contrast to the common perception that geopolymerization is most effective at high NaOH concentrations [22–24].

The setting time of the geopolymer pastes is affected by the SiO_2/Na_2O mass ratio, which controls the polycondensation phenomena in the aqueous phase, as indicated by the semi-quantitative interpretation of soluble silicate species (Figure 2).



Figure 2. Semi-quantitative interpretation of soluble silicate species equilibria in 1 m aqueous silicate solution (Reproduced from Reference [25]).

The lower SiO₂/Na₂O mass ratios favor the formation of monomer and oligomer Si species [25–27], and therefore inhibit the polycondensation phenomena, slowing the setting time of perlite geopolymer pastes [27]. On the other hand, the higher SiO₂/Na₂O mass ratios favor the formation of large chains and complex polymer structures, indicating effective polycondensation phenomena as well as fast solidification of the pastes.

In order to define a suitable setting time of perlite pastes in low concentrations of the activator (as indicated by Figures 1 and 2), the kinetic study of the SiO_2/Na_2O mass ratios at the aqueous phase of the geopolymer slurries was performed as a function of their stirring time at a constant solid to liquid ratio (S/L: 0.02 g/mL). The NaOH solution concentrations and the temperatures selected for this study were as follows: [NaOH]: 2–6 M, Temperature: 50–90 °C. The results are shown in Figure 3.



Figure 3. SiO₂/Na₂O mass ratio (w/w) in the aqueous phase of geopolymer slurries as a function of stirring time and the concentration of NaOH solution at three different temperatures: (**a**) 90 °C; (**b**) 70 °C; (**c**) 50 °C ([NaOH]: 2, 4, and 6 M, S/L: 0.02 g/mL).

According to Figure 3a-c, it is observed that for each temperature, the SiO₂/Na₂O mass ratio increases inversely proportional to the concentration of NaOH solution in the aqueous phase. In addition, it is clearly seen that this ratio also increases as a function of the temperature, for the same alkalinity of solution and the same activation time, in accordance with similar studies of the literature [28–32]. Therefore, the higher curing temperatures of the geopolymer pastes as well as the lower NaOH concentrations of the solutions result in higher SiO₂/Na₂O mass ratios in the slurries. In this way, faster polycondensation is achieved, leading to a shorter setting time of the pastes (Figure 1).

Figure 3 also indicates that the highest SiO_2/Na_2O ratio, equal to 0.17 ([NaOH]: 2 M, Temperature: 90 °C), corresponds to the monosilicates and oligomers area of the semi-quantitative interpretation of soluble silicate species equilibria (Figure 2) [25–27]. This is possibly attributed to the low solid to liquid ratio of the geopolymer paste (S/L: 0.02 g/mL). Thus, an investigation of slurries with higher solid to liquid ratios was performed, in order to determine the real solid to liquid ratio of the geopolymer paste (S/L: 2 g/mL). The SiO₂/Na₂O mass ratio of the perlite pastes was studied at three different NaOH solution concentrations (2, 4, and 6 M) and three different solid to liquid ratios (0.2, 0.6, and 1 g/mL). The upper limit of the S/L ratio was equal to 1 g/mL due to the lack of the paste's workability (due to the intensive agitation conditions under temperature) at higher ratios. Temperature was kept constant at 70 °C, which was considered to be the most appropriate choice for the mild curing of geopolymers. The results are shown in the diagrams below (Figure 4).



Figure 4. SiO₂/Na₂O mass ratio (w/w) in the aqueous phase of geopolymer slurries as a function of stirring time at different concentrations of NaOH solution: (**a**) 2 M; (**b**) 4 M; (**c**) 6 M (Temperature: 70 °C, S/L: 0.02–1 g/mL).

From Figure 4a–c, it is concluded that the increase of the pulp's density at a constant concentration of NaOH solution leads to a higher SiO₂/Na₂O mass ratio in the aqueous phase of the slurry. According to Figure 4a, the highest SiO₂/Na₂O value (1.862 w/w) corresponds to the lowest concentration of NaOH solution in the aqueous phase (2 M NaOH), for the denser slurry (S/L: 1 g/mL) after 24 h of agitation at 70 °C. Slurries with 4 M NaOH solution concentration follow, reaching a SiO₂/Na₂O ratio equal to 1.683 w/w. Finally, the highest NaOH solution concentration slurries are observed with a value of 1.21 w/w. Therefore, it was found that the increased solid to liquid ratio of the geopolymer slurries results in higher SiO₂/Na₂O values, due to the efficient Si dissolution, promoting the polycondensation phenomena and rendering the geopolymerzation process.

In order for the SiO_2/Na_2O mass ratio of the real conditions in geopolymer slurries to be determined (S/L: 2 g/mL), a simple mathematical simulation of the experimental data shown in Figure 4 was employed. Thus, the mathematical trend of SiO_2/Na_2O mass evolution was determined in the solution, as a function of S/L ratio, for each value of stirring time that was studied (in order to obtain the necessary experimental data).

The mathematical equations used in all cases to adapt the experimental data is of the form:

$$y = \mathbf{a} \cdot x^{\mathsf{D}},\tag{1}$$

y: SiO₂/Na₂O mass ratio; *x*: solid to liquid ratio (S/L); and a, b are constants.

The mathematical adaptation equations and their R^2 values, on which the graphs of Figure 5 are based, are presented in Table 2.

Time h	2 M NaOH		4 M NaOH		6 M NaOH	
11110, 11	Equation	R^2	Equation	R^2	Equation	R^2
1	$y = 0.2398 \ x^{0.6282}$	0.9895	$y = 0.2627 \ x^{0.6592}$	0.8797	$y = 0.0716 \ x^{0.4798}$	0.8892
3	$y = 0.2927 \ x^{0.4964}$	0.9786	$y = 0.3162 \ x^{0.5944}$	0.9625	$y = 0.1651 \ x^{0.6244}$	0.9021
5	$y = 0.422 x^{0.519}$	0.9926	$y = 0.4598 \ x^{0.6072}$	0.9844	$y = 0.2925 \ x^{0.6434}$	0.9974
7	$y = 0.5128 \ x^{0.487}$	0.9994	$y = 0.6581 \ x^{0.6858}$	0.9948	$y = 0.4007 \ x^{0.6753}$	0.9964
24	$y = 2.0605 \ x^{0.6772}$	0.9959	$y = 1.939 \ x^{0.7345}$	0.9843	$y = 1.3525 \ x^{0.7237}$	0.9947

Table 2. Mathematical data adaptation equations from Figure 5.



Figure 5. Graphical representation of the mathematical equations employed to adapt the experimental data of Figure 4 in three different NaOH solution's concentrations: (**a**) 2 M NaOH; (**b**) 4 M NaOH; (**c**) 6 M NaOH.

Assuming that the mathematical adaption equations will apply to the case of S/L: 2 g/mL (no data support the truth of this hypothesis or not), by extrapolating the experimental data, the SiO_2/Na_2O values in the aqueous phase are obtained as a function of stirring time and NaOH solution concentration for S/L: 2 g/mL (Table 3 and Figure 6).

Table 3. Prediction of SiO_2/Na_2O mass ratio in the alkaline activator for geopolymer slurries with S/L: 2 g/mL as a function of stirring time and NaOH solution concentration, at 70 °C.

Time, h	2 M NaOH	4 M NaOH	6 M NaOH	
	SiO ₂ /Na ₂ O, w/w	SiO ₂ /Na ₂ O, w/w	$SiO_2/Na_2O, w/w$	
1	0.3706	0.4149	0.0999	
3	0.4129	0.4775	0.2545	
5	0.6047	0.7004	0.4569	
7	0.7188	1.0586	0.6399	
24	3.2948	3.2262	2.2335	



Figure 6. Prediction of SiO_2/Na_2O mass ratio in the alkaline activator for geopolymer slurries with S/L: 2 g/mL at 70 °C as a function of stirring time and NaOH solution concentration (2–6 M).

As shown in Figure 6, the SiO_2/Na_2O mass ratio at 70 °C for S/L: 2 g/mL is almost identical in the case of the alkaline solutions at concentrations of 2 and 4 M NaOH, while it is most noticeably

4. Conclusions

In this study, the efficient Si dissolution from perlite at alkaline solutions was determined, revealing high SiO_2/Na_2O mass ratios of the aqueous phase after treatment with low activator concentrations. The solid/liquid ratio was kept constant at 2 g/mL and the selected sodium hydroxide solution concentration varied between 2 and 10 M, presenting fast paste hardening at 70 °C and 90 °C for the low-level alkaline activator concentrations. Two series of dissolution tests were also performed at different NaOH concentrations, solid/liquid ratios, and temperature conditions, indicating that the actual amount of Si species that can be transferred into the solution is more than adequate, especially at low concentrations of NaOH solution (2 and 4 M NaOH). This makes them good potential raw materials for geopolymerization, a technology which could be ideally combined with appropriate foaming techniques for the production of lightweight insulating materials with a view to numerous applications in the construction field.

Author Contributions: Dimitrios Panias and Georgia-Maria Tsaousi conceived and designed the experiments; Georgia-Maria Tsaousi performed the experiments; Iliana Douni and Georgia-Maria Tsaousi analyzed the data; Georgia-Maria Tsaousi wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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