Research Article

Synthesis and Characterization of Porous Fly Ash-Based Geopolymers Using Si as Foaming Agent

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This paper concerns the synthesis of foamed geopolymers using fly ash and metallic Si as the binder and the porogent agent, respectively. The Taguchi approach was applied in order to study the effect of some significant synthesis parameters such as the Si foaming agent content (% w/w fly ash based), the alkali type (R : Na or K), and the alkalinity (R/Al molar ratio) of the activation solution on the compressive strength and apparent density of the foamed geopolymers. The final products were characterized by means of XRD, FTIR, and SEM, while optical microscopy was applied for the evaluation of the porosity. Lightweight geopolymers with a compressive strength of 2.08–14.88 MPa and an apparent density of 0.84–1.55 g/cm³ were prepared by introducing a Si content up to 0.2% w/w on fly ash basis.

1. Introduction

Geopolymers are a class of inorganic materials which comprises a three-dimensional polymeric-type structure [1]. They are formed by the reaction of an alkaline solution with an aluminosilicate material at ambient or slightly elevated temperature [2–4]. The synthesis and chemical composition of geopolymers are similar to those of zeolites, but their microstructure is amorphous to semicrystalline. The aluminosilicate source is usually an industrial mineral, waste, or by-product where silicon and aluminum ions are preferably located in amorphous phases [5–10]. Fly ash produced at coal-fired thermal plants has, recently, attracted a lot of research attention on its alkali activation and transformation into cementitious materials (geopolymer) [11–15]. The fly ash exploitation in geopolymer technology leads to the reuse of this material and the drastic reduction of soil, water, and air pollution.

Geopolymers have a very low embodied energy and CO₂ footprint compared to conventional building materials [16, 17], but their greatest advantage is that based on the choice of the raw materials and the design of the processing, geopolymers can meet a variety of requirements. This flexibility of geopolymer synthesis is of great importance when products with specific properties are required.

The application of geopolymers as insulating materials for construction sector is a new research field. The main challenge on inorganic insulation materials' development is related to the production of a high porous material with sufficient mechanical properties. Geopolymer foams can be produced by the introduction of foaming agents such as hydrogen peroxide [18–21], metal powders [22–24], or silica fumes [25–27]. Their foaming action is due to the oxygen or hydrogen formation in alkaline conditions according to the following reactions:

The major advantage of the inorganic foaming is its suitability to produce ceramic foams without utilizing high temperature treatments (such as burn out of organics and sintering) in contrast to the conventional production of macroporous ceramics [28].

On the other hand, the lightweight geopolymers developed through the chemical reaction of foaming agents usually exhibit limited mechanical behavior because of the large pore size distribution (in the range of 0.5–3.0 mm).

If the pore size distribution is efficiently controlled, the mechanical properties of the foamed geopolymers can be improved [24].

Factors such as the mineral and chemical composition of raw materials, the curing conditions and the ratios of the starting materials, strongly affect the structure and properties of geopolymers. Therefore, the optimization of the synthesis is mandatory prior to any development of geopolymeric material.

This paper presents a study on the synthesis of foamed geopolymers. The synthesis optimization was performed via the Taguchi experimental design method that provides a simple and efficient tool for optimizing parameters in complicated systems [29–33]. Fly ash was used as the aluminosilicate precursor and Si was added as the foaming agent. The aim of this work is to record the combined effect of some significant synthesis parameters such as the Si foaming agent content (% w/w fly ash based), the alkali type (R : Na or K), and the alkalinity (R/Al molar ratio) of the activation solution on the compressive strength, the apparent density, and the porosity development of the foamed fly ash-based geopolymers.

2. Experimental

2.1. Materials and Methods. The fly ash used in this study comes from the power station of Megalopolis in Greece. This material can be classified as calcareous fly ash (Type W) according to EN 197-1, as it contains CaO between 10 and 15% w/w and SiO₂ higher than 25% w/w. Fly ash was previously ground and its mean particle size (d_{50}) was approximately 20 μ m. This is a typical fineness of fly ash when used as the main constituent in blended cements. The chemical composition of fly ash is presented in Table 1. Silicon metal powder (99+%, 325 mesh, CAS No. 7440-21-3) was used as the foaming agent.

The synthesis of the foamed geopolymers includes three steps: (a) the preparation of the activation solution, (b) the mixing of the raw materials (fly ash and foaming agent) with the activation solution, and (c) the molding and the curing of the specimens. The activation solution contains soluble Si in the form of alkali silicates (Na₂SiO₃ with SiO₂ = 27.56–28.39% w/w and Na₂O = 8.53–8.79% w/w, K₂SiO₃ with SiO₂ = 27.67–28.47% w/w and Na₂O = 14.03–14.83% w/w, Multiplass SA, Greece) and NaOH ($\geq$ 98.0%, CAS No. 1310-73-2) or KOH ($\geq$ 85.0%, CAS No. 1310-58-3) in order to provide the alkaline environment that is necessary for the activation of the geopolymerization reactions. The activation solutions were stored for a minimum of 24 h prior to use to allow equilibrium. The foaming agent was effectively mixed with the fly ash in order to obtain a homogenous blend. Then, this blend and the activation solution were mechanically mixed (standard mortar mixer: Controls 65-L0005) to form an homogenous slurry that was transferred into 50 × 50 × 50 mm cubic molds and mildly vibrated. In all mixtures, the silicon to aluminum (Si/Al) molar ratio in the starting mixture and the solids to liquids (s/l) mass ratio were kept constant to 2.4 and 2.8, respectively [32]. The specimens were left at room

TABLE 1: Chemical composition of fly ash (% w/w).

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	L.O.I.
45.52	22.13	8.99	14.75	2.84	1.55	0.72	1.69	1.49

temperature for 2 h and then were transferred to an oven at 80°C for 24 h. Compression tests were carried out on a Toni-technik uniaxial testing press, 7 days after the specimens' preparation (load rate 1.5 kN/s, according to the EN196-1 requirements). The apparent density of the geopolymers was measured by the specimens' dimensions and mass. The presented value for each synthesis is the average density value of three specimens.

The final products were characterized by means of XRD, FTIR, SEM, and optical microscopy. The phase distribution of the powders was investigated by X-ray diffraction, on a Bruker D8 ADVANCE X-ray diffractometer. The data were collected in a 2 θ range 2–70° with 0.02° step size and 0.2 sec per step and were evaluated using DiffraC.Eva v3.1 software.

FTIR measurements were carried out using a Fourier Transform IR Spectrophotometer (Jasco 4200 Type A). The FTIR spectra were obtained by the KBr pellet technique in the wavenumber range from 400 to 4000 cm⁻¹ and resolution 4 cm⁻¹. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample: KBr equals to 1 : 200 approximately) at 7.5 t/cm².

The morphology as well as the phase stoichiometry of the products was examined using a JEOL JSM-5600 scanning electron microscope equipped with an OXFORD LINK ISIS 300 energy dispersive X-ray spectrometer (EDX). The samples were examined as powders or cross sections and in all cases were gold or graphite coated prior to the measurement. In order to evaluate the morphology and porosity of the products by image analysis, a Zeiss Stemi 2000 C high resolution optical microscope equipped with an Axio Cam ErcS5 digital camera was used. The samples were carefully cut down into 3 cross sections of specified dimensions (50 × 50 × 10 mm) by the use of a Buhler IsoMet™ low-speed precision cutter equipped with a diamond saw disk. The cross section of the samples was mildly polished by the use of appropriate emery papers (Grade: P220, P80).

2.2. Image Analysis. Image analysis was applied in order to evaluate the porosity of the samples. In this study, image analysis was carried out using the ImageJ® software.

The specimens (3 cross sections for each sample) were scanned using an optical microscope, and images were generated. The images were converted into grayscale 8-bit files, and the threshold adjustment took place. In any image, the dark-colored areas account for the pores of the sample while the bright ones indicate the geopolymer matrix. Through threshold adjustment, the area of dark objects was computed in pixels, and the porosity was calculated based on the area of the pores and the total area of the image. As representative pore size of the samples, the pore areas with diameter greater than 0.1 mm were chosen. This choice was adopted as image processing records a large number of features with diameter less than 0.1 mm, and their

consideration in the analysis results in unrealistic values of porosity. The circularity of the pores was kept above 0.2.

2.3. Experimental Design. Geopolymerization is a complicated and dynamic process, and in the case of a full factorial design, the experiments are numerous and practically, as well as economically, not possible to be carried out. In the Taguchi method [30], the implementation of a multi-factorial experimental designing model allows the investigation of the combining effect of selected parameters by conducting the minimum number of experiments. This method involves the use of a special set of arrays called orthogonal arrays to arrange the factors affecting the product/process as well as the levels at which the selected factors are varied. The selection of the array is related with the number and the variation level of the tested factors.

After conducting the experimental designing model, the collected data are analyzed by means of ANOVA (ANalysis Of VAriance) in order to determine the percent contribution of each factor on the chosen quality performance characteristics of the product or process. In this work, the studied characteristics are the compressive strength and the apparent density of the produced geopolymers.

The factors selected to be investigated are (i) the foaming agent content (Si% w/w on fly ash basis), (ii) the alkali to aluminum molar ratio (R/Al, R : Na or K) that associates the alkali quantity in the activation solution with the aluminum content of the raw material, and (iii) the (Na/(Na + K)) ratio which is related to the kind of alkali in the activation solution. The experimental design involved the variation of the above factors in four levels selected according to physical and chemical restrictions as well as to the previously published literature [32, 34]. The variation levels of the selected factors are presented in Table 2. A full factorial design requires the conduction of 64 experiments (3 factors, 4 levels per factor, experiments = (levels)^(factors) = 4³ = 64). The application of a L16 orthogonal array, based on Taguchi method, reduces the number of the experiments to 16.

3. Results and Discussion

3.1. Synthesis Optimization. The results of the Taguchi model are presented in Table 3 which shows the synthesis parameters along with the compressive strength and apparent density of the corresponding geopolymers. In each experiment, three specimens were prepared and tested under compression. In case a value varies by more than $\pm 10\%$ from the mean, the result is discarded and new specimens are prepared. Table 3 also presents the maximum % variation from the mean and the standard deviation of the compressive strength measurements. The maximum % variation from the mean and the standard deviation of the apparent density are near zero and thus are not presented in Table 3. As it is seen, the produced geopolymers have a wide variation of strength and apparent density. More specifically, the foams exhibit compressive strength from 2.08 to 14.88 MPa and apparent density from 0.84 to 1.55 g/cm³. The wide variation of the strength and the apparent density indicates

TABLE 2: Parameters and their variation levels.

Parameters	Level 1	Level 2	Level 3	Level 4
Silicon content (Si% w/w)	0.050	0.085	0.120	0.150
Alkali to aluminum ratio (R/Al)	0.8	1.2	1.6	2.0
Alkali species (Na/(Na + K))	0.00	0.35	0.65	1.00

that the chosen parameters strongly affect these properties. The reference geopolymer prepared with no Si addition (Si/Al = 2.4, R/Al = 0.8, (Na/(Na + K)) = 1.00, and $s/l = 2.8$) possesses enhanced strength and apparent density values (53.70 MPa and 1.77 g/cm³).

The effect of each parameter on the measured properties is presented in Figure 1 which has been based on the processing of the data presented in Table 3. For example the compressive strength corresponding to Factor 1, Level 1 (0.050% w/w Si) is the average strength of all samples containing 0.050% w/w Si. The impact of each factor on the development of compressive strength and apparent density was estimated through ANOVA and is presented in Table 4.

The factor with the greatest impact on both properties is the alkali to aluminum molar ratio. The increase of the R/Al ratio from 0.8 to 1.2 leads to the drastic reduction of both strength and density. Further addition of alkali (R/Al > 1.2) does not have a major effect on compressive strength while in the case of the apparent density, the produced foams are more compact. It seems that the alkali environment of geopolymer paste promotes the foaming action of Si powder, with R/Al = 1.2 being the optimal level. Higher alkalinity (R/Al > 1.2) creates mixing problems between the fly ash and the activation solutions, leading to the drastic coagulation of the geopolymeric pastes and therefore the limited action of the foaming agent.

The second more influential parameter is the foaming agent content (Si% w/w). An increase in the Si metal content (from 0.050 to 0.120% w/w) causes a decrease of the compressive strength and apparent density values by 50 and 20%, respectively. This is expected since higher foaming agent content leads to higher H₂ formation and therefore to higher porosity and lower compressive strength. The kind of the alkali ion (Na/(Na + K)) has only a marginal effect on the geopolymers' properties.

The optimal synthesis conditions for achieving the highest strength are Si% w/w = 0.050, R/Al = 0.8, and (Na/(Na + K)) = 0.35, while those for the lowest apparent density are Si% w/w = 0.120, R/Al = 1.2, and (Na/(Na + K)) = 0.00. The optimized value of the compressive strength and apparent density for a 95% confidence interval was predicted to be 12.42 ± 1.44 MPa and 0.7342 ± 0.0699 g/cm³, respectively. In order to confirm the model prediction geopolymer specimens with Si% w/w = 0.050, R/Al = 0.8, (Na/(Na + K)) = 0.35, and Si% w/w = 0.120, R/Al = 1.2, (Na/(Na + K)) = 0.00 were prepared appropriately cured for 7 days and subjected to compression and density measurements. The compressive strength (mean of 3 specimens) of the first synthesis was found to be 11.04 MPa while the apparent density of the

TABLE 3: Synthesis parameters, compressive strength, and apparent density of Si foamed geopolymers.

Experiment	Si% w/w	R/Al	(Na/(Na + K))	Compressive strength (MPa)						Apparent density (g/cm ³)
				(1)	(2)	(3)	Mean	Maximum variation from mean (%)	Standard deviation	
1	0.050	0.8	0.00	13.49	16.32	14.82	14.88	9.32	1.42	1.30
2	0.050	1.2	0.35	6.40	5.88	6.45	6.24	5.78	0.31	1.10
3	0.050	1.6	0.65	6.26	6.11	6.90	6.43	7.43	0.42	1.25
4	0.050	2.0	1.00	3.82	4.11	3.48	3.80	8.56	0.32	1.55
5	0.085	0.8	0.35	9.73	10.66	9.73	10.04	6.17	0.54	1.18
6	0.085	1.2	0.00	2.36	2.41	2.72	2.50	8.87	0.19	0.84
7	0.085	1.6	1.00	5.47	5.63	5.20	5.43	4.29	0.22	1.44
8	0.085	2.0	0.65	4.23	4.24	4.19	4.22	0.71	0.03	1.35
9	0.120	0.8	0.65	6.79	6.84	6.83	6.82	0.43	0.03	1.05
10	0.120	1.2	1.00	3.80	4.06	4.42	4.09	7.94	0.31	0.86
11	0.120	1.6	0.00	2.19	2.03	2.02	2.08	5.38	0.10	0.98
12	0.120	2.0	0.35	3.32	3.42	3.45	3.40	2.32	0.07	1.26
13	0.150	0.8	1.00	6.20	6.46	7.21	6.62	8.88	0.53	0.98
14	0.150	1.2	0.65	4.18	4.14	4.08	4.13	0.16	0.05	0.94
15	0.150	1.6	0.35	3.73	3.98	4.40	4.04	9.12	0.34	1.21
16	0.150	2.0	0.00	2.62	2.90	3.13	2.88	9.13	0.26	1.14

FIGURE 1: Effect of the studied parameters on the development of the compressive strength and apparent density.

TABLE 4: Contribution (%) of the studied parameters on the development of the compressive strength and apparent density.

Parameters	Si content	R/Al	(Na/(Na + K))
Compressive strength	26.9	71.7	1.4
Apparent density	32.0	59.5	8.5

second synthesis was found to be 0.72 g/cm³. Both values fall within the predicting range confirming in this way the validity of the used experimental design model.

The above results show, as it was expected, that the compressive strength of foamed geopolymers is in close relationship with the apparent density: the higher the density, the higher the compressive strength. The Taguchi

approach can be very useful in practice since it allows the optimization of the synthesis on the basis of specific requirements that must be met by the final products (e.g., strength and density). When a lightweight geopolymer must be designed for a specific application, it is recommended to define the optimum synthesis parameters using multicriteria analysis and introducing appropriate weighting factors for each criterion (strength, density).

3.2. Characterization of Geopolymers. The XRD patterns of the fly ash and some representative foamed geopolymers are presented in Figure 2. The selection of the XRD patterns was made on the basis of the R/Al ratio and the Si% w/w, which were defined by the Taguchi method as the most influential parameters. The main crystallographic phases in the fly ash pattern are quartz ($d = 3.34 \text{ \AA}$), cristobalite ($d = 4.04 \text{ \AA}$), feldspars ($d = 3.19 \text{ \AA}$), gehlenite ($d = 2.85 \text{ \AA}$), maghemite ($d = 2.52 \text{ \AA}$), and anhydrite ($d = 3.49 \text{ \AA}$). Moreover the broad peak between 20 and 40° indicates the presence of an amorphous phase. In the XRD patterns of the geopolymeric products, anhydrite and cristobalite phases are consumed while the other phases of fly ash are still present. The 20–40° broad peak becomes more intense, indicating the formation of the amorphous geopolymer phase. As R/Al ratio is increased, the formation of zeolitic phases is favored. Particularly, exp. 3 (R/Al = 1.6) contains small amounts of hydroxysodalite while in exp. 4 (R/Al = 2.0) high amounts of hydroxysodalite and hydroxycancrinite are identified. Besides, it is observed that the increase of R/Al rate favors the formation of alkali carbonates. The gradual introduction of the foaming agent does not affect the crystallographic phases as it can be seen by the pattern of exp. 13.

Figure 3 shows the FTIR spectra of fly ash and selected geopolymer samples. The grouping of the samples is the

FIGURE 2: XRD patterns of fly ash and selected Si foamed geopolymers. 1: quartz (PDF: 46-1045), 2: albite (PDF: 20-0554), 3: anhydrate (PDF: 03-0377), 4: maghemite (PDF: 04-0755), 5: ghelenite (PDF: 04-0690), 6: cristobalite (PDF: 03-0276), 7: hydroxysodalite (PDF: 89-9098), 8: hydroxycancrinite (PDF: 31-1272), 9: natrite (PDF: 37-0451), 10: calcite (PDF: 47-1743), 11: potassium carbonate (PDF: 70-0292), 12: sodium bicarbonate (PDF: 15-0475), and 13: potassium bicarbonate (PDF: 70-0995).

FIGURE 3: FTIR spectra of the fly ash and Si foamed geopolymers.

same as in the case of XRD analysis. The fly ash spectrum exhibits, relatively, shapeless peaks due to the semicrystalline state of this material. The region of interest in both fly ash and geopolymer products lies in the range between 800 and

1300 cm^{-1} . This broad hump exhibits overlapped peaks which are associated with the asymmetric stretching vibrations of Si-O-T (T: tetrahedral Si or Al) bonds. In the case of the fly ash, the maximum of this hump is at around 1110 cm^{-1} while in the case of the geopolymers this hump becomes narrower and shifts to lower wavenumbers ($\sim 1000\text{ cm}^{-1}$). This alteration is directly linked with the substitution of Si by tetrahedral Al and therefore the formation of an aluminosilicate network [35]. The Si-O-T asymmetric bending vibrations at $\sim 460\text{ cm}^{-1}$ are not as sensitive as the stretching vibrations to changes of the aluminosilicate network. The band at $\sim 1635\text{ cm}^{-1}$ is related to O-H bending vibrations of molecular water. All samples contain carbonate species pointed out by the presence of the band at around 1450 cm^{-1} , related to antisymmetric vibrations of CO_3^{2-} ions. Samples with high R/Al ratios (exp. 3 and exp. 4) tend to exhibit more pronounced carbonate ion vibrations. This observation is in well accordance with the XRD results which showed that samples of high alkalinity contain carbonate phases such as natrite, calcite, and potassium carbonate. The absorbance at 875 cm^{-1} is related to symmetric stretching vibrations of Al-O and it constitutes sign of geopolymerization. As for 800 , 780 , and 685 cm^{-1} peaks, these are connected with symmetric stretching vibrations of Si-O-T bonds. In case of geopolymeric products, the latter band is located at higher wavenumbers in relation to the fly ash showing the enrichment of the aluminosilicate network in silicon [35]. In all geopolymeric products, a vibration at 620 cm^{-1} is observed. This absorbance peak is assigned to hexasilicate ring vibrations. This network formation indicates the participation of silicon in a more organized structure than the fly ash and refers to nanocrystalline zeolitic phase formation into geopolymeric matrix [36]. In the case of the geopolymer with high alkali content (exp. 4), there is a peak at $\sim 565\text{ cm}^{-1}$ which indicates

FIGURE 4: SEM images of selected geopolymer samples. (a, b) Reference geopolymer; (c, d) exp. 1; (e, f, g) exp. 4.

the double ring vibrations and characteristics of zeolite formation.

Figure 4 shows SEM images of selected samples. In particular, Figures 4(a)–4(b) present the microstructure of the reference geopolymer ($\text{Si}/\text{Al}=2.4$, $\text{R}/\text{Al}=0.8$, $(\text{Na}/(\text{Na} + \text{K}))=0.00$, and $s/l=2.8$) which was prepared with the same synthetic parameters as exp. 1 but without any foaming agent.

As it is seen, there are unreacted particles of fly ash well embodied in the geopolymer matrix. The reference geopolymer exhibits microstructure homogeneity and constitutes a very compact material. Figures 4(c)–4(d) correspond to exp. 1–geopolymer which contains 0.050% w/w Si. In contrast to the reference geopolymer, this material (exp. 1) possesses a very porous structure with the size of pores being approximately $350\text{ }\mu\text{m}$. A more intense study of the sample shows its good homogenous microstructure. The pore shape

is regular, while the dispersion of the pores seems to be uniform. However, the lightweight products differ in the coherence of the binding material and the quantity of the unreacted fly ash particles. In every case the compressive strength and the density are close related to the microstructure of the final products. In Figures 4(e)–4(g), SEM images of the exp. 4 are presented. This geopolymer differs from the exp. 1 in the extent of the alkali ions ($\text{R}/\text{Al}=2.0$). A comparison with the exp. 1 shows that this material is more compact and its microstructure is rather heterogeneous. This can be clarified by Figures 4(f)–4(g) that were taken from different points of sample's surface. In one point, the sample exhibit polygonal shape of particles while in the other the particles are prismatic.

The reduced porosity of the exp. 4–geopolymer is in well accordance with its apparent density value which is the highest among the Si geopolymer series. As it is shown by

FIGURE 5: Optical microscope images of foamed geopolymers. (a) exp. 5 ($R/Al = 0.8$, $Si = 0.085\%$); (b) exp. 6 ($R/Al = 1.2$, $Si = 0.085\%$); (c) exp. 7 ($R/Al = 1.6$, $Si = 0.085\%$); (d) exp. 8 ($R/Al = 2.0$, $Si = 0.085\%$); (e) exp. 2 ($R/Al = 1.2$, $Si = 0.050\%$ w/w); (f) exp. 6 ($R/Al = 1.2$, $Si = 0.085\%$ w/w); (g) exp. 10 ($R/Al = 1.2$, $Si = 0.120\%$ w/w); (h) exp. 14 ($R/Al = 1.2$, $Si = 0.150\%$ w/w).

XRD and FTIR measurements, the high alkalinity of the starting mixture favors the formation of crystalline phases (zeolites and alkali carbonates) which inhibit the geopolymerization reaction. Furthermore, high R/Al ratios tend to produce more compact pastes, limiting in this way the foaming action of Si.

The foamed geopolymers were examined by means of a high resolution optical microscope in order to evaluate the porosity of the samples. Figure 5 presents images of selected Si foamed geopolymers. Particularly, Figures 5(a)–5(d) show geopolymers with varying R/Al ratios and constant foaming agent content (0.085% w/w Si), while those from e to h correspond to geopolymers with varying foaming agent content and constant R/Al ratio ($R/Al = 1.2$). Once more the grouping of materials was chosen keeping in

mind the most influential parameters of Taguchi model (R/Al and Si %w/w).

An increase of the alkalinity of the samples leads to a drastic expansion of pores till the $R/Al = 1.2$ (Figure 5(b)). Further increase of the alkali content has a negative effect on the porosity of the samples (Figures 5(c)–5(d)). As it was stated before, the presence of alkali ions promotes the foaming reaction, producing geopolymers with increased porosity. However, high alkali contents ($R/Al > 1.2$) create drastic coagulation of the pastes and therefore restrain the foaming agent action. These observations are in well accordance with the Taguchi results where the optimum R/Al value for the preparation of lightweight products was found to be 1.2. In general, the high alkali content tends to produce compact materials. The increase of the foaming agent

FIGURE 6: Steps of image analysis. (a) Cross-sectional image; (b) grayscale 8-bit image adjusted by the threshold option; (c) drawing of the pores.

FIGURE 7: Effect of the studied parameters on the porosity of the Si foams.

content in these samples does not have any significant effect on the porosity.

The gradual incorporation of metallic Si into the pastes leads to the increase of the number of pores and therefore the overall pore volume (Figures 5(e)–5(h)). At the same time the size of the pores shows a tendency to decrease. This copes well with the fact that Si rich samples exhibit the lowest values of apparent density and compressive strength. For the whole Si foam series, the shape of the pores seems to be spherical. However, an increase in silicon content changes the shape of pores from spherical to irregular, possibly, due to the more intense conditions of the gaseous hydrogen release.

Image analysis was applied in order to have a semi-quantitative evaluation of the porosity. The image processing correlates the surface of the pores and 2-d porosity of the samples and converts this correlation to a percentage of the total surface of the image. As an example Figure 6 presents images of the exp. 9 before and after the image processing. In particular, Figure 6(a) stands for the cross section of the exp. 9 before analysis, Figure 6(b) presents the grayscale image generated after threshold adjustment, and Figure 6(c) shows a drawing of the pores which took place in the porosity calculation (pores with diameter higher than 0.1 mm

TABLE 5: Contribution (%) of the studied parameters to the pore area and pore diameter of the samples.

Parameters	Si% w/w	R/Al	(Na/(Na + K))
Pore area	12.7	71.9	15.4
Pore diameter	19.5	70.9	9.6

and circularity above 0.2). Corresponding images were generated for all the samples.

The image processing showed that Si foamed geopolymer exhibit pore area and pore diameter in the range of 1–21% and 0.34–0.90 mm, respectively. The collected data were analyzed by means of ANOVA analysis as in the case of the compressive strength and apparent density values. The effect of each parameter on the pore area and pore diameter is presented in Figure 7, while their contribution to the measured properties is shown in Table 5.

The alkali content is the most significant factor for both the pore area (71.9%) and pore diameter (70.9%). Particularly, the increase of R/Al ratio up to 1.2 leads to a boost of the pore area by almost 50% (Figure 7). The enhancement of the pore diameter is even higher and close to 60%. However, further increase of the alkali content leads to a considerable reduction of the pore area and size. The foaming agent content has a contradictory effect on the pore area and the pore size. The increase of Si content increases the porosity of the sample and at the same time decreases the mean pore size. The increase of the Si content from 0.050 to 0.150% w/w results in a 125% increase of the pore surface while the pore diameter is reduced by 32% (Figure 7). The alkali selection has a limited effect on porosity. In any case, the potassium anions tend to produce more porous structures in relation to sodium anions. This observation is related to the effect of each ion on pastes' workability. It is well known that potassium ions exhibit greater levels of reactivity due to their higher basicity, and they produce more workable pastes in relation to the sodium ions [37].

The pore size distribution was also evaluated through the image analysis of the samples. Figure 8 shows the pore size distribution of Si foams in relation to the R/Al (a, b, and c) and in relation to the Si content (d, e, and f). Histograms (a) to (c) of Figure 8 reveal the effect of R/Al molar ratio on the

FIGURE 8: Pore size distribution of Si samples in relation to the R/Al molar ratio (a, b, and c) and the foaming agent content (d, e, and f). (a) exp. 5 (R/Al = 0.8, Si = 0.085%); (b) exp. 6 (R/Al = 1.2, Si = 0.085%); (c) exp. 8 (R/Al = 2.0, Si = 0.085%); (d) exp. 1 (R/Al = 0.8, Si = 0.050%); (e) exp. 5 (R/Al = 0.8, Si = 0.085% w/w); (f) exp. 13 (R/Al = 0.8, Si = 0.150% w/w).

pore size distribution. Samples of modest alkalinity (Figure 8(a)) exhibit wide distributions with the peak size being located in low values (47% of pores below 0.39 mm for the exp. 5). When R/Al ratio equals to 1.2 (Figure 8(b)), the size distribution remains wide but at the same time shifts to higher diameters. Identically, for the exp. 6, the peak of pore diameter (40%) lies beneath 1.00 and 1.19 mm. Higher alkali contents ($R/Al > 1.2$) increase the viscosity of the paste, inhibit the foaming agent action, and generate narrower distributions shifted to smaller diameters (Figure 8(c)).

The pore size distribution of the samples with varying Si content (Figures 8(d)–(f)) show that increasing the Si incorporation, the distributions become gradually narrower and shift to lower pore diameters. It seems that the introduction of more Si to geopolymer pastes produces foams of enhanced porosity based on small and more homogenous pores.

4. Conclusions

This work came up with the following results:

- (i) Fly ash (Type W, EN 197-1) was successfully recycled into the production of lightweight geopolymers. Metallic silicon, added in the starting mixture even in small quantities, acts effectively as a foaming agent. Lightweight geopolymers with a compressive strength of 2.08–14.88 MPa and an apparent density of 0.84–1.55 g/cm³ were prepared by introducing a Si content up to 0.2 % w/w on fly ash basis. This wide range of properties values reveals the great applicability potential of geopolymer foams in the building sector.
- (ii) The compressive strength of the foamed geopolymers is in close relation with the porosity of the final products, but even in the case of highly porous structures, compressive strength higher than 2 MPa can be easily achieved.
- (iii) Apart from the foaming agent's content in the raw mixture, the development of the porosity and strength is also affected by the synthesis parameters of the geopolymer matrix. The alkali to aluminum molar ratio (R/Al) in the starting mixture is the most influential factor, while the kind of the alkali (Na or K) has only a marginal effect on foams' properties.
- (iv) The Taguchi design methodology was applied in order to evaluate the impact of the synthesis parameters on the development of the porosity and strength. The Taguchi approach can also be very useful in practice since it allows the optimization of the synthesis on the basis of specific requirements that must be met by the final products.
- (v) The applied analytic techniques (XRD, FTIR, and SEM) led to the complete characterization of the foamed geopolymers. As it is shown, the introduction of the foaming agent does not affect the mineral composition of the geopolymer matrix, while the increase of the alkali content in the starting mixture favors the formation of zeolites and alkali carbonates.
- (vi) Optical microscope image analysis provided an estimation of the pore size distribution. The R/Al molar ratio has an effect on the pore size. An increase in the alkali content till 1.2 value leads to the expansion of the pores. Higher alkalinity ($R/Al > 1.2$) tends to reduce the workability of the pastes having as a consequence the restrain of pores formation. Metallic Si seems to affect the total number of the pores. High introduction levels produce foams with increased number of pores.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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