materials proceedings

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A Study of Fly Ash-Based Geopolymers with Basalt Flour Addition †

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† Presented at the 10th MATBUD'2023 Scientific-Technical Conference "Building Materials Engineering and Innovative Sustainable Materials", Cracow, Poland, 19–21 April 2023.

Abstract: The purpose of this study is to evaluate the effect of basalt flour addition, replacing quartz sand, and its proportion on fly ash-based geopolymers' properties. As a base material, F-grade fly ash was used. The activation process was carried out using a 10 mol solution of sodium hydroxide and an aqueous solution of sodium silicate. The tests included measurements of density, compressive and flexural strength, abrasion resistance, and observation of the microstructure of geopolymers. The results of the study showed that basalt flour significantly increases compressive strength and causes a slight increase in flexural strength—by about 106% and 11%, respectively—and it allows for the reduction of the size of voids and the share of porosity in the structure of the tested geopolymers. Basalt flour has an application potential in geopolymer materials to make them more useful in construction.

Keywords: fly ash; quartz sand; basalt flour; geopolymer; abrasion resistance; strength properties

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Citation: Kozub, B.; Miernik, K.; Gądek, S. A Study of Fly Ash-Based Geopolymers with Basalt Flour Addition. *Mater. Proc.* **2023**, *13*, 3. https://doi.org/10.3390/materproc2023013003

Academic Editors: Katarzyna Mróz, Tomasz Tracz, Tomasz Zdeb and Izabela Hager

Published: 13 February 2023

1. Introduction

Geopolymers, by definition, are included in the third-generation lime cement and ordinary Portland cement. They are amorphous synthetic alkali aluminosilicates belonging to the group of inorganic polymers, the properties of which depend mainly on the type of base material used, the type and amount of activator used during their production, as well as external factors of the polycondensation process, such as temperature and heating time. In the face of global trends and challenges, developing binders for the manufacture of geopolymer concrete has become a hot topic in construction science [1–5].

Geopolymers are widely regarded as substitute materials for Portland cement. This is due to their good strength and thermal properties, as well as their very good corrosion resistance. These materials are widely used in various industries [6].

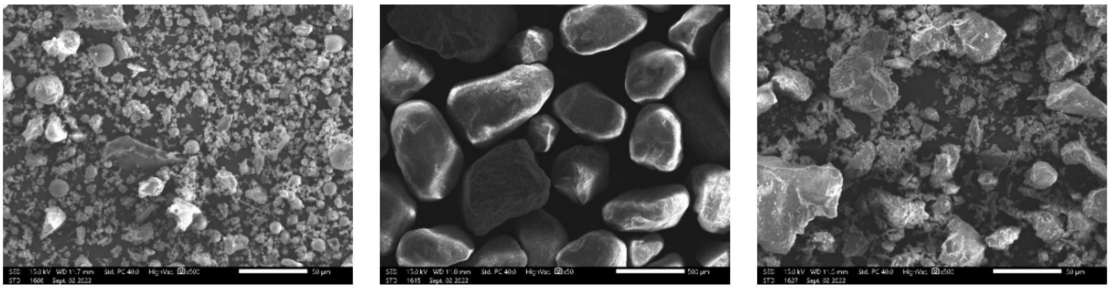
One of the most commonly used raw materials in geopolymer production is fly ash. Standard EN-450-1:2012 [7] defines fly ash as fine-grained dust resulting from the combustion of coal dust, which consists mainly of glassy, spheroidal particles.

Basalts, as basic minerals, include intermediate plagioclase feldspars, as well as augite pyroxene with or without olivine, magnetite, and variable amounts of glass. Natural large deposits of basaltic rocks, which are used as aggregate for concrete, are found in Egypt. During the process of crushing and grinding basalt rock, large amounts of basalt powder are produced as a byproduct. Numerous works have investigated the activity of basalt and the possibilities of its use. The reactivity of basalt mainly depends on the surface area of its particles, the content of silica and alteration minerals, as well as the content of volcanic glass [8–13].

The purpose of this study is to investigate the possibility of using basalt flour as a substitute raw material for quartz sand during the production of fly ash-based geopolymers. The effect of the addition of basalt flour and its proportion on the strength properties of the produced geopolymers was evaluated. The scope of the research conducted includes density measurements, compressive and flexural strength tests, abrasion resistance, and microstructure studies using a scanning electron microscope (SEM).

2. Material

The base material from which the test samples were made was fly ash from coal combustion (Figure 1a) from the Skawina Combined Heat and Power Plant (Skawina, Poland). The ash used is classified as class F. Obtained by XRD analysis on an X-ray diffractometer from Panalytical Aeris (Malvern PANalytical, Lelyweg 1, Almelo, the Netherlands), the proportion of phases comprising the fly ash used in the study is shown in Figure 2. The main components are quartz and mullite, with a small proportion of hematite and magnetite, not exceeding 4%. Quantitative analysis was carried out using the Rietveld method in HighScore Plus software (version: 4.8, Malvern PANalytical B.V, Almelo, the Netherlands) with a PDF-4+ database.



(**a**) (**b**) (**c**)

Figure 1. SEM micrographs of (**a**) fly ash, (**b**) quartz sand, (**c**) basalt flour.

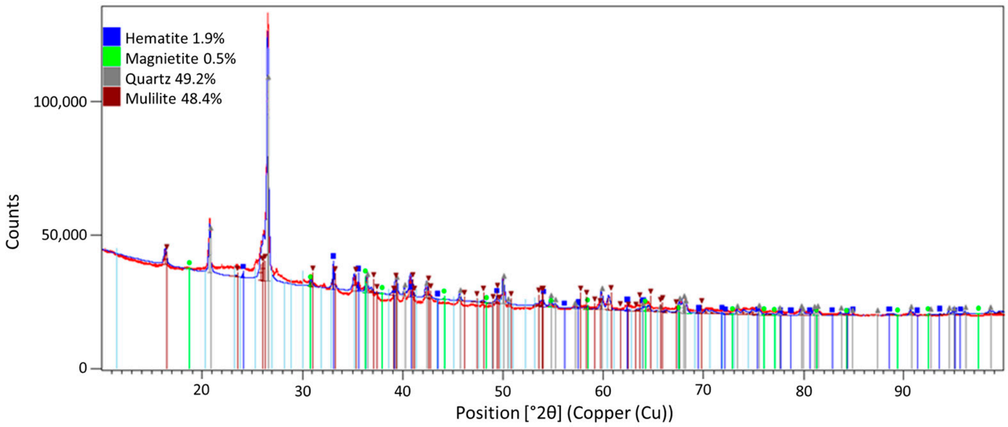


Figure 2. Diffractogram for fly ash.

Materials added in different proportions to the fly ash were quartz sand (Figure 1b) and basalt flour (Figure 1c). Basalt is a volcanic rock that is formed from magma melted in the Earth's mantle. Basalt flour is produced as a result of processing during the extraction of the raw material. The oxide compositions of the fly ash, quartz sand, and basalt powder used for the tests, which were determined with the use of the JEOL JSM-820 scanning electron microscope (IXR Inc., Austin, TX, USA) with the EDS attachment, are shown in Table 1.

Table 1. Oxide composition of raw materials.

Oxides [wt.%]	Fly Ash	Basalt Flour	Quartz Sand
Silica (SiO_2)	53.83 ± 0.38	51.89 ± 0.35	94.24 ± 0.49
Aluminum oxide (Al_2O_3)	28.12 ± 0.24	17.40 ± 0.19	4.81 ± 0.11
Calcium oxide (CaO)	3.16 ± 0.10	10.33 ± 0.16	0.95 ± 0.12
Magnesium oxide (MgO)	2.15 ± 0.07	5.10 ± 0.10	-
Sodium oxide (Na_2O)	2.06 ± 0.07	4.17 ± 0.09	-
Iron oxide (FeO)	6.73 ± 0.22	9.69 ± 0.25	-
Potassium oxide (K_2O)	3.94 ± 0.10	1.42 ± 0.06	-

The summary plots of particle size distribution and cumulative curves for ash, sand, and basalt meal are shown in Figure 3a,b, respectively. Particle size distribution tests were carried out using an instrument from Anton Paar GmbH (Graz, Austria).

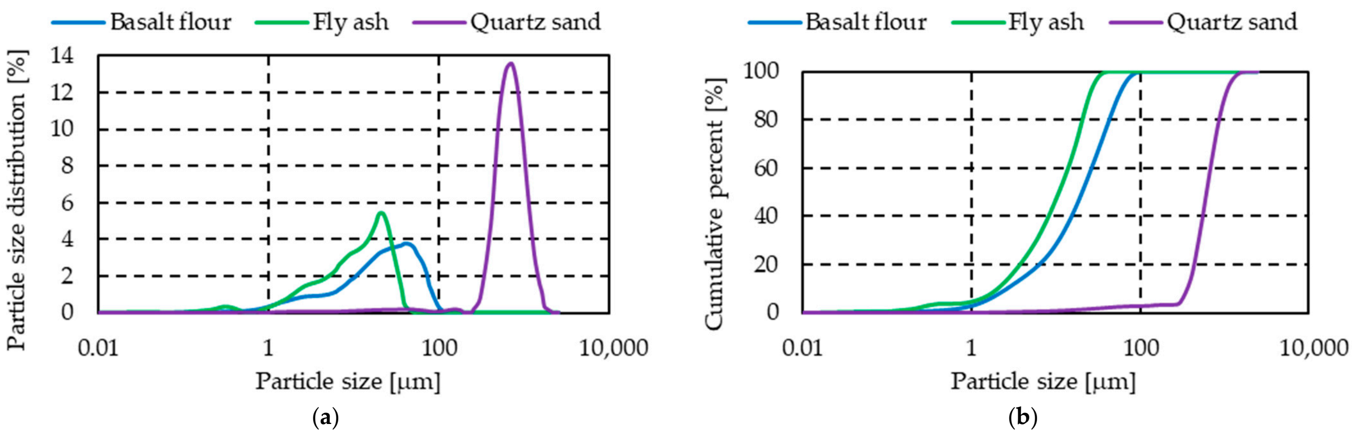


Figure 3. (**a**) The particle size distribution curves for fly ash, quartz sand, and basalt flour; (**b**) the cumulative curves for fly ash, quartz sand, and basalt flour.

3. Sample Preparation

The first step in the preparation of the geopolymer mortar was to mix dry ingredients in a GEOLAB cement mortar mixer (GEOLAB, Warsaw, Poland), which were previously weighed in the appropriate proportions for each mixture according to Table 2, which shows the composition of the mixtures used for the geopolymers, along with sample determinations.

Table 2. Percentage of individual dry components in the mixtures used to produce geopolymers, along with designations.

Mixture No.	Fly Ash [wt.%]	Basalt Flour [wt.%]	Quartz Sand [wt.%]	Sample ID
Mixture I	50	50	-	BF_0
Mixture II	50	37.5	12.5	BF_12.5
Mixture III	50	25	25	BF_25
Mixture IV	50	12.5	37.5	BF_37.5
Mixture V	50	-	50	BF_50

Then, an alkaline 10 mol solution of sodium hydroxide and an aqueous solution of sodium silicate R-145, whose mass ratio was 1:2.5, was prepared and used to activate the prepared mixtures. The dry ingredients with the addition of an alkaline solution were mixed until a uniform paste was obtained. The ratio of dry ingredients to the solution was 0.4. The prepared geopolymer paste was poured into molds, which were then cured in an SLW 750 STD laboratory oven (POL-EKO-APARATURA, Wodzislaw Slaski, Poland) at 75 °C for 24 h. The samples were seasoned under laboratory conditions for 28 days.

4. Methods

The density of the produced geopolymers was measured using a geometric method—measurements were made of the volume and weight of the samples made for compressive strength tests.

Compressive strength and flexural strength measurements were carried out in accordance with PN-EN 196-1:2016-07 [14]. The tests were performed on a Matest 3000 kN testing machine (Matest, Treviolo, Italy) equipped with heads for compressive and flexural strength measurements. For compressive strength tests, six perpendicular specimens of $50 \times 50 \times 50$ mm^3 each were prepared. In contrast, four $50 \times 50 \times 200$ mm^3 specimens were made for flexural strength testing. The specimens were made in accordance with PN-EN 12390-1:2021-12.

The abrasion resistance of the produced geopolymers was determined using the Boehme method. The test was carried out in accordance with PN-EN 14157:2017-11 [15]. The samples prepared for the measurements had dimensions of $71 \times 71 \times 71$ mm^3. The abrasive used during the test was alumina (20 g was used for each sample pass). The clamping force of the sample to the disc was equal to 294 N. For each specimen (three specimens were abraded for each compound), 16 cycles were performed for 20 rotations of the disc per cycle. After the cycle was completed, the sample was rotated 90° and another cycle was started. One of the methods described in the standard for determining abrasion resistance is the method for measuring sample height loss, which was used in this study. This method involves measuring the height of the sample before and after the test and determining their difference. Based on the literature [16], the classification of the tested geopolymers in terms of abrasion resistance was made.

The standard deviation was determined for all obtained results, which was plotted on graphs in the form of error bars.

The microstructure of the fabricated geopolymers was also observed using a JEOL JSM-820 scanning electron microscope (IXR Inc., Austin, TX, USA). A JOEL DII-29030SCTR vacuum coating machine (IXR Inc., Austin, TX, USA) was used to sputter gold onto the samples.

5. Results and Discussion

Analyzing the results of density measurements of the tested geopolymers (Figure 4), it can be observed that the replacement of quartz sand with basalt flour has a slight effect on the obtained values—a slight increase in density can be observed with an increase in the share of basalt meal in the mixture. This is related to the approximate densities of sand and basalt flour. The obtained results do not differ from the values of densities of fly ash-based geopolymers presented in the literature [2,4,17].

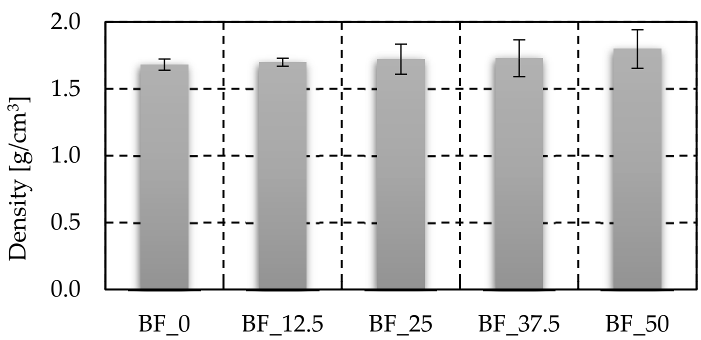


Figure 4. The density of the tested geopolymers.

As can be observed in Figure 5a,b, replacing quartz sand with basalt flour has a favorable effect on the strength properties of the produced geopolymers. As the proportion of basalt meal in the mix increases, there is a significant increase in compressive strength and a gentle increase in flexural strength. The highest values of compressive strength and flexural strength were obtained for the sample which was made from a mixture consisting of fly ash and basalt flour in a ratio of 1:1. The recorded increase in these values relative to the reference sample, made from a mixture of fly ash and sand in a ratio of 1:1, was about as high as 106% and 11% for compressive strength and flexural strength, respectively. It is also worth noting that for samples with 37.5% and 50% basalt meal, the resulting compressive strengths are higher than the compressive strengths of average concretes used in residential and commercial construction, typically ranging between 17 MPa and 28 MPa [18]. The particles of basalt powder are small, so they can fill the voids in the geopolymer structure, which is confirmed by SEM images, and thus effectively improve the strength properties of the tested composites. In addition, the particles of basalt powder dispersed in the geopolymer structure can contribute to passivation and stress dissipation, which allows the delay of the appearance of plastic deformation and the appearance of cracks, which increases the bending strength [19,20].

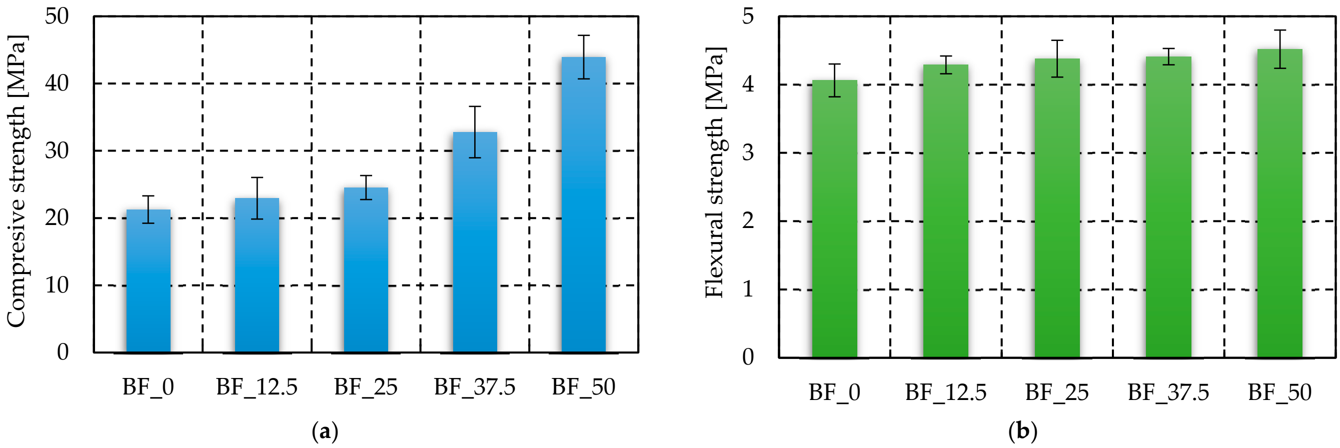


Figure 5. Results for tested geopolymers of (**a**) compressive strength test, (**b**) flexural strength.

The obtained results of compressive strength are also higher in comparison with the results from measurements of compressive strength of geopolymers produced on the basis of basalt meal activated with aqueous sodium hydroxide solution, as presented by Saray et al. [21].

In their work, Venyite et al. [22] studied geopolymers produced based on a mixture of metakaolin, calcined laterite, and basalt flour activated with a 6 mol sodium hydroxide solution and cured at room temperature. The authors showed that the incorporation of basalt into geopolymers based on calcined laterite and metakaolin resulted in compressive strengths of 41.14, 34.46, 40.46, and 24.93 MPa for 20, 30, 40, and 50 wt.% basalt addition.

Beskopylny et al. [23] studied, among other things, the statistical compressive and flexural strengths of fine-grained geopolymer concrete with different types of stone flours. They obtained compressive strength values between 34.1 MPa and 52.2 MPa, and values between 4 MPa and 6.7 MPa for flexural strength for the produced geopolymers.

Figure 6 shows the values of height loss for all tested geopolymers after abrasion tests. Analyzing the results obtained, it can be concluded that all the geopolymers produced are very hard-to-wear materials, as evidenced by the height loss not exceeding the value of 2.5 mm. The highest abrasion resistance was demonstrated by samples made from a mixture consisting of fly ash and basalt flour in a ratio of 1:1, for which the measured average value of sample height loss was 0.81 mm.

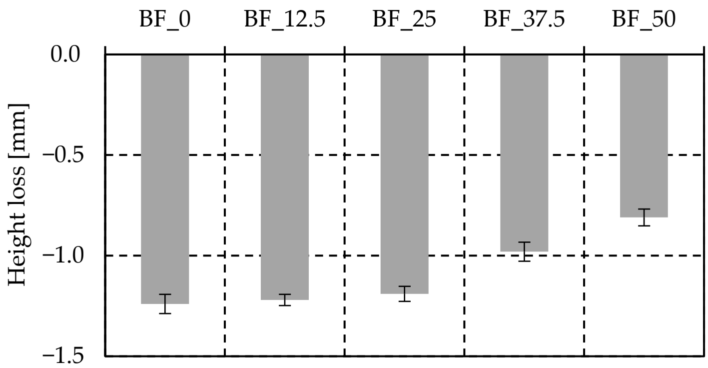


Figure 6. The height loss of tested geopolymers due to abrasion test.

Similar results for a geopolymer made from a mixture based on fly ash and quartz sand, also activated with a 10 mol sodium hydroxide solution, were obtained by Bazan et al. [24], where the average value of sample height loss after abrasion tests was 0.9 ± 0.02 mm, which also classifies the tested material as very difficult to abrade.

Figure 7 shows microphotographs of the structures of the produced geopolymers. For all samples, typical features of the structure of geopolymers produced based on fly ash [25] can be observed, including unreacted spheroidal fly ash particles and dissolved fly ash particles. In addition, it is possible to observe the presence of sand and basalt particles, present in the geopolymer gel in the samples for the production of which they were used. During the study of the structure of the tested geopolymer composites, the influence of the proportion of basalt flour on porosity could be observed—with the increase in the proportion of basalt flour in the mixture, the size of the voids, as well as their share in the structure, decreases.

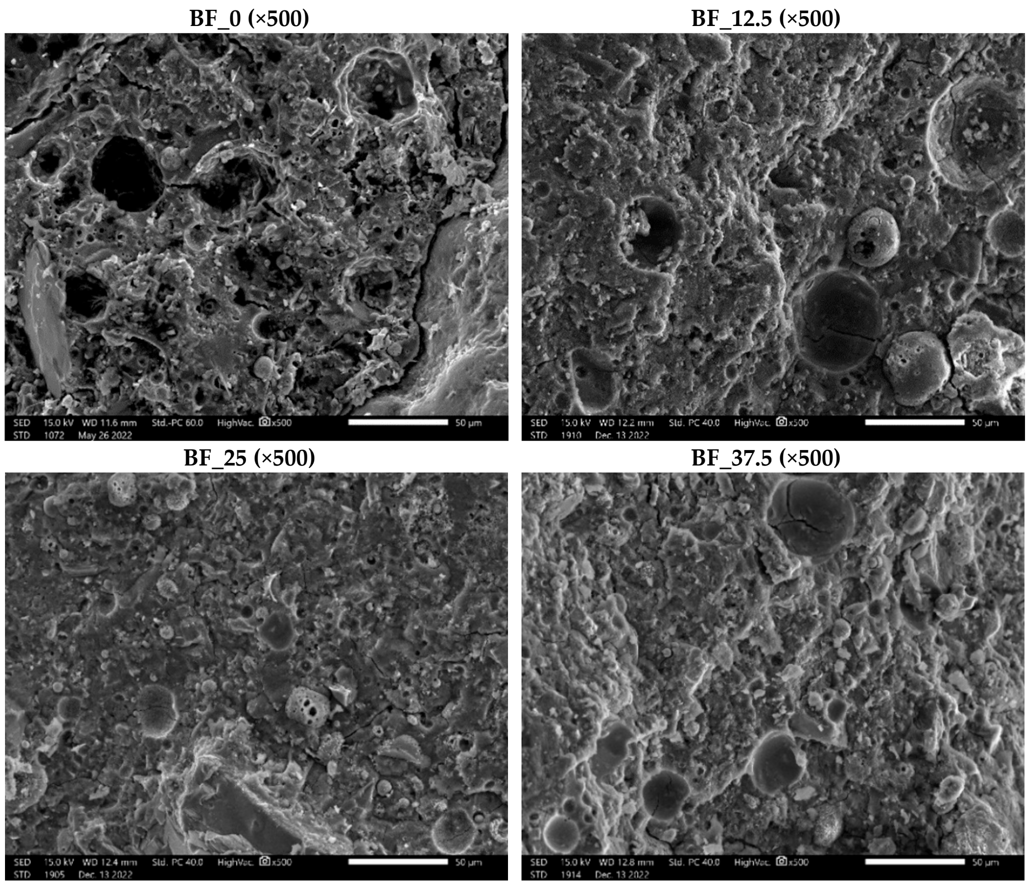


Figure 7. *Cont.*

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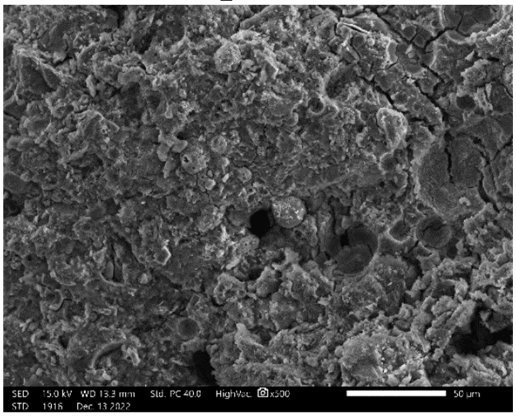

Figure 7. The microstructure SEM photography of produced geopolymers.

6. Conclusions

The study investigated the possibility of using basalt flour as a substitute raw material for quartz sand during the production of fly ash-based geopolymers. The effect of the addition of basalt flour and its proportion on the durability properties of the produced geopolymers was evaluated. Based on the analysis of the obtained test results, the following conclusions can be formulated:

- Basalt flour can be successfully used as a substitute for quartz sand in the production of geopolymer mortars;
- Replacement of quartz sand with basalt flour has a slight effect on the density of geopolymers—a small increase in density can be observed as the proportion of basalt flour in the mixture increases;
- The use of an additive in the form of basalt flour allows a significant improvement in compressive strength and a slight increase in flexural strength, by about 106% and 11%, respectively, compared to geopolymers made based on fly ash with the addition of quartz sand in a ratio of 1:1;
- The addition of basalt powder allows for the reduction of the size of voids and the porosity in the structure of the tested geopolymers.

Basalt flour can be successfully used as a replacement for quartz river sand during the production of fly ash-based geopolymers which have application potential in construction.

Author Contributions: Conceptualization, B.K.; methodology, B.K.; validation, B.K.; formal analysis, B.K. and K.M.; investigation, B.K.; resources, B.K.; data curation, B.K.; writing—original draft preparation, B.K. and S.G.; writing—review and editing, B.K., S.G. and K.M.; visualization, B.K.; supervision, B.K. All authors have read and agreed to the published version of the manuscript.

Funding: The publication cost of this paper was covered with funds from the Polish National Agency for Academic Exchange (NAWA): "MATBUD'2023—Developing international scientific cooperation in the field of building materials engineering" BPI/WTP/2021/1/00002, MATBUD'2023.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work has been supported by the National Centre for Research and Development in Poland in the framework of the project SMART-G Smart Geopolymers (ERA-MIN2-3/SMART-G/1/2022).

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

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