



Effect of microsilica addition on properties of geopolymer composites

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ABSTRACT

Purpose: Geopolymers are modern, inorganic aluminosilicate materials that, through their high mechanical properties, are used in many industries and can be an excellent alternative to Portland cement-based concrete. The study aims to determine the effect of adding microsilica on the properties of geopolymer composites.

Design/methodology/approach: Reference samples were made by mixing pozzolanic material such as fly ash (50 wt.%) with sand (50% wt.%). The effect of the additive was analysed by introducing microsilica (T180) into the material in shares of 5%, 10% and 15% by weight, each time replacing part of the fly ash with microsilica. The samples were activated with a 10 M sodium hydroxide solution mixed with an aqueous sodium silicate solution. Laser particle size analysis, mineralogical analysis and SEM observations were carried out on the raw materials. Phase identification analysis, SEM observations, density tests, compressive and flexural strength tests, water absorption and thermal conductivity tests were carried out on the produced geopolymer composites.

Findings: The results obtained based on the compressive strength test showed that the strength of the material decreases with the increase of the silica content in the material. Increasing the silica addition by each subsequent 5% resulted in a decrease in strength of about 20-30%—addition of silica at 5 wt.% resulted in a decrease in flexural strength compared to the reference sample of over 15%. However, adding 10% and 15% causes a decrease in flexural strength by more than 50% compared to the value for the reference sample. The thermal conductivity coefficient decreases with increasing silica content in the composite, which means introducing this additive improves the thermal insulation properties of geopolymer composites.

Practical implications: Adding microsilica introduced into the geopolymer matrix in 10% ensures a good correlation between thermal conductivity and strength. The compressive strength of this composite is over 25 MPa, which makes it a construction material with improved thermal insulation by approximately 15% compared to the reference material. The investigated materials are dedicated to application in the construction industry.

Originality/value: The article provides a new voice in a discussion connected with the role of microsilica in geopolymers because microsilica was not previously investigated as an additive for the fly ash used by the authors.

Keywords: Amorphous materials, Geopolymer, Microsilica, Fly ash



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MATERIALS**1. Introduction**

The term geopolymer was introduced into scientific terminology in the 1970s by Professor Joseph Davidovits and was used to describe inorganic aluminosilicate polymers with an amorphous structure having certain properties [1,2]. Internally, geopolymers can be divided into groups depending on the synthesis process that is used for their receipt: alkaline environment (NaOH, Na₂Si₂O₃, KOH, K₂Si₂O₃, rice husk (RSH), etc.) and acid environment (aluminium phosphate or phosphoric acid) [3,4]. Geopolymers as materials are solids, most often hard and with high mechanical resistance, which makes them comparable to materials such as concrete or stone [5].

Geopolymers originally gained importance due to their refractory properties. They were used to create composites with a wooden core in order to ensure the fire resistance of the materials [2,6]. Due to further research, geopolymers were used in construction because of their similarity in properties to concretes. They began to compare the materials, and they noticed ecological advantages. Unlike cement-based concretes, which require much less energy in production and emit less greenhouse gases, including CO₂ [7,8]. Moreover, using fly ashes, a by-product of the incineration process of coal power plants or other industrial by-products in geopolymerisation, brings additional environmental benefits [3,9].

Various raw materials can be used to produce geopolymers based on aluminosilicates, including metakaolin, volcanic turf, fly ash, mine tailings, blast furnace slags, etc. [1,10,11]. Among the materials, especially fly ashes, are of interest due to the lack of necessity of pretreatment, the good strength properties of geopolymers obtained on their base and the ecological aspect of using it as a feedstock [8,10,12]. The production of geopolymers also uses aggregates, reinforcement materials, and fillers, whose role is similar to that of traditional concrete. There are different goals for applying such a type of additive, including manipulating the density of the material, obtaining or improving its other properties or reducing the price of the obtained composite [10,13].

One of the additives for geopolymer materials can be microsilica. The material, which is microsilica, is formed as a by-product. As a result, the treatment of silicon or

aluminium alloys in arc furnaces [14]. It consists mainly of SiO₂. Structurally, the material should contain spherical particles with a diameter of the order of 150 nm. It has pozzolanic and cementing (binding) properties. The addition of microsilica caused the properties and the strength of concrete for compression to increase [14,15].

Additionally, the reinforcement mechanism can be achieved by improving material microstructure. The very small specific surface area particles oscillate in the range of 13,000 to 20,000 m²/kg, allowing them to fill the gaps created in the structure of concrete [15]. The two phenomena caused microsilica to be widely used as an additive to producing ultra-high-performance concretes. However, the solution also has disadvantages; the most important is that micro silica additives decrease the workability of the concrete paste, especially [14,15].

Considering the influence of microsilica on the properties of concretes, it is expected to have a similar influence on geopolymer materials. However, the research shows that this mechanism is not so obvious in the case of geopolymers, and different scientific results have been reported [16,17]. Besides, the amount of microsilica that has a positive influence is unclear, and the values between a few per cent to dozens per cent were investigated [16,18,19]. Most of the research also shows that with the addition of microsilica, material properties increase to a certain value. Usually about 10% (sometimes 20%), and then they decrease [16, 20-22]. On the other side, Wang et al. [23] proved that the influence of microsilica is dependent on the used matrix [23]. For this research, adding up to 20% silica fume caused an increase in the strength of geopolymers based on low-calcium fly ash but decreased the properties of the matrix based on calcium aluminosilicate cement [23]. The same research also showed that a small amount of silica fume – up to 10%, caused an increase in flowability [23]. The topic analysis shows that such a kind of investigation can give very different results depending on the feedstock used for geopolymer production.

It is worth noticing that if the micro silica increases the mechanical strength, this effect is also in extreme environments, including acid environments [20,24,25] and elevated temperatures [26]. Another positive influence of microsilica was observed by Zhang et al. [27]. They show that micro silica can prevent the drying shrinkage behaviour

of geopolymer composite by up to 50% by reducing the relative content of pores inside the material [27]. The changes in morphology and the more compacting structure of geopolymer can also influence material durability in changeable conditions [28,29]. Wang et al. [29] proved in the research higher material resistance on freeze–thawing cycles when the 10% addition of silica fume was applied [29]. It also should be mentioned that in recent times some investigation with microsilica has been conducted by using it in geopolymers in a slightly different form, as a silica source for alkali solution, in the same way as previously used rice husk [30-32]. Such an approach can be especially valuable from the environmental point of view because the environmental analysis shows that this element has the highest environmental burden in the case of geopolymer materials [33-35].

Discrepancies in the existing literature data, particularly concerning determining the influence of microsilica on the properties and structure of geopolymers, were the main motivation to undertake research in the given field. The presented research works were cognitive and sought to define reasons for such behaviour of the material by determining changes in the microstructure material. The article presents work to investigate the influence of microsilica on the properties and structure of geopolymers, depending on the percentage of silica, including physical and mechanical properties, microstructure, water adsorption, and thermal conductivity. The articles provide a new voice in discussion connected with the role of microsilica in geopolymers. The provided research partly confirms the previous experiments, but they also show contrary conclusions to some previously described in the literature. However, the microsilica was tested for some kinds of fly-ashes; it is also worth stressing that the microsilica was not previously investigated as an additive for the fly-ash used by the authors. The results of the work have potential applications in the construction industry. They can be used as an aid in determining the suitability of the use of microsilica additives to improve the material's properties to potentially enhance the advantages of geopolymers as alternatives to concrete based on Portland cement.

2. Materials and methods

2.1. Materials

The fly ash used to make the geopolymer comes from the Skawina power plant (Skawina, Poland). Such fly ash has an oxygen composition that is coherent with class F requirements [33,36]. It has a large amount of silica and

aluminium, which is an advantage in the polymerisation process.

River sand was used to produce the geopolymer. The sand plays the role of fine aggregate in the geopolymer composition, allowing it to obtain better mechanical properties.

The microsilica used to produce the geopolymer has the designation T180. (HRT Polska, Kołobrzeg, Poland).

2.2. Sample preparation

The sample preparation process began with the preparation of solution 10 molar alkaline base, consisting of water glass (Avantor Performance Materials, Gliwice, Poland) hydroxide sodium (R-145, a molar module of 2.5, ChemiKam, Będzin, Poland) and tap water, which was used as an activator in the geopolymerisation process. The ratio of sodium hydroxide solution to sodium water glass was 1:2.5. The resulting solution was then equilibrated overnight. After 24 hours, the preparation of the paste began. The dry ingredients (fly ash, sand and microsilica) were first mixed in a GEOLAB mixer (Geolab, Warsaw, Poland) for about 5 min. Microsilica was applied in 5, 10 and 15% as a replacement for fly ash. The amount of alkali activator was selected experimentally to obtain the paste that was possible to process. Next, the activator was applied, and mixing was continued (about 10 min.) to obtain adequate consistency that allowed pouring into moulds. The proportion of the prepared samples is presented in Table 1.

Table 1.
Samples designation

Designation	Sand, kg	Fly ash, kg	Microsilica, kg	Alkali activator, dm ³
GP0	2.5	2.5	0	1
GP1	2.5	2.375	0.125	1
GP2	2.5	2.250	0.250	1.61
GP3	2.5	2.125	0.375	2.1

Then, the samples were placed in a SLW 750 STD oven (Pol-Eko-Aparatura, Wodzisław Śląski, Poland) and held at 75°C for 24 hours. The samples were then taken out of the oven and demoulded. Before the testing, they were matured for 28 days after the tests were carried out.

Samples for bending were then tested with dimensions of 5×5×20 cm in the amount of 3 samples. Prepared 8 samples measuring 5×5×5 cm; 5 samples were used, and the remaining 3 were used in water adsorption studies. The last prepared samples had dimensions of 15×15×2 cm; one for each geopolymer was made and used for testing thermal insulation properties.

2.3. Methods

Particle size analysis in the work case was performed by an analyser called Anton Paar PSA 1190 LD (AntonPaar GmbH, Graz, Austria). Laser diffraction analysis for size study particles uses the phenomenon of diffraction. Using a bundled laser, the analyser can make more accurate measurements for the particles in a large range, from 0.1 to 3000 μm .

X-ray diffraction (XRD) analysis was performed using PANalytical AERIS (PAN-alytical, Almelo, The Netherlands). Materials in the form of powder were used for the tests. The copper lamp was used for the test, and a nickel filter was placed on the lamp. Samples were scanned in the range from 10° to 100° (2θ) at 0.003° (2θ) step size and a time per step of 340 s. After the measurements were completed, the data were then analysed using the HighScore Plus software, which uses a database ICDD (International Center for Diffraction Data, PDF4+) and crystallographic database (Newtown Square, PA, USA).

Scanning electron microscopy was made on a JEOL JSM-IT200 scanning electron microscope (JEOL, Tokyo, Japan). The study was carried out on raw materials and samples of materials after testing strength. The prepared test samples were placed on a stand carbon pot and covered with a layer of gold (DII-29030SCTR Smart Coater, JEOL, Tokyo, Japan) to ensure proper conduction, which is necessary to make proper conductivity during SEM observations.

A geometric method was used to test the density of geopolymer samples by calculating it from laboratory measurements made on prepared samples. For measuring the dimensions of the tested samples geopolymers, a calliper and the average value for at least three were used, excluding statistically insignificant results. Measurement weights of geopolymer samples were made with an electric balance with an accuracy of 1 order 0.01 g. The final density result is given by dividing mass by volume.

The mechanical properties were investigated using a MATEST 3000 kN test machine (Matest, Treviolo, Italy). Two types of tests were carried out:

- Compressive strength: PN-EN 12390-3:2019-07 – Testing Hardened Concrete – Part 3: Compressive Strength of Test Specimens.
- Flexural strength: PN-EN 12390-5:2019-08 – Testing Hardened Concrete – Part 5: Flexural Strength of Test Specimens.

The sample setup for compressive and flexural strength tests is shown in Figure 1.

Water adsorption tests are aimed at checking the behaviour of the sample in a wet environment. For the test purpose, adsorption was observed and measured by the

percentage of adsorbed substance to the starting mass of the tested material, including the case of geopolymer in atmospheric humidity conditions. Measurement was made by determining the increase in sample weight over time.

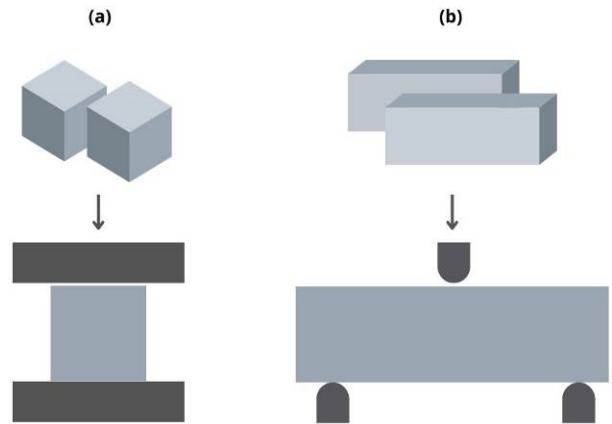


Fig. 1. Schematic of the sample setup for (a) compressive and (b) flexural strength tests

The study examined thermal conductivity, i.e. the ability to transport energy in the form of heat through the test mass of the sample as a result of external difference temperatures, geopolymers, was provided by using HZM 446 Lambda Smal plate apparatus (NEZTSCH, Selb, Germany). Thermocouples were centrally attached to the prepared sample to collect temperature readings. The sample was then placed in a device between the hot and cold plates, separating the geopolymer from the plates at heat flow conductors. After placing the sample and running the device, heating the geopolymer through the hot plate begins until temperature equilibrium is reached, which ends the test.

3. Results and discussion

3.1. Raw materials

Fly ash

Firstly, the fly ash was tested for mineralogical composition, as shown in Figure 2 and Table 2.

According to the above analysis of the diffractogram, it was possible to determine that the fly ash used in the geopolymer consisted mainly of quartz (54.6%) and mullite (40.9%). The results of fly ash analysis in the given respect coincide with other tests, where the content of quartz and mullite is over 90% of the composition of the fly ash [12,37,38]. Such a kind of fly ash can be used in geopolymerisation.

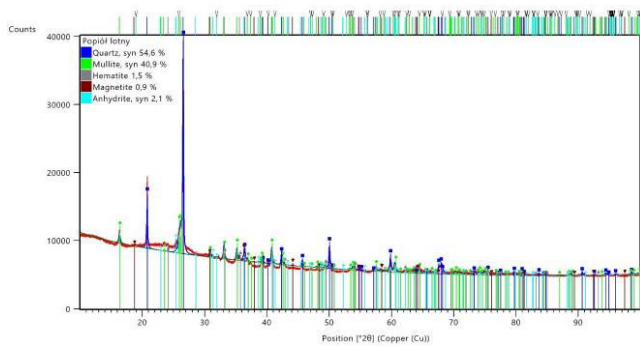


Fig. 2. Mineralogical phase identification in fly ash by using XRD

Table 2. Mineralogical composition of fly ash

Name	Phase Chemical composition	Percentage, %
Quartz	SiO ₂	54.6
Mullite	Al ₆ Si ₂ O ₁₃	40.9
Hematite	Fe ₂ O ₃	1.5
Magnetite	Fe ₃ O ₄	0.9
Anhydrite	CaSO ₄	2.1

In the next step, particle size analysis was conducted – Table 3 and Figure 3.

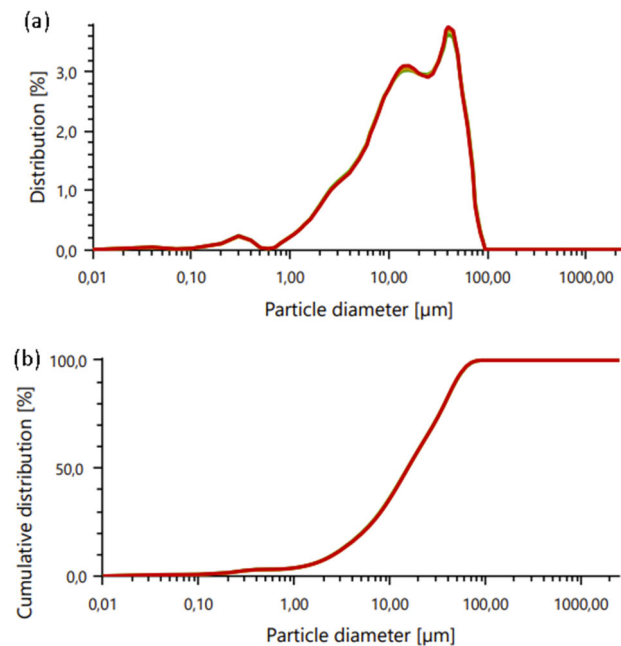


Fig. 3. Particle size analysis of fly ash: a) distribution (volume); b) Cumulative distribution (volume) – undersize

Table 3. Particle size distribution of fly ash.

Name	D ₁₀ , µm	D ₅₀ , µm	D ₉₀ , µm	Mean size, µm	Span
Sample 1	2.554	15.273	48.747	22.220	3.042
Sample 2	2.604	15.379	48.534	22.265	2.987
Sample 3	2.600	15.383	48.339	22.225	2.973
Mean	2.586	15.345	48.539	22.237	2.995

The particles of fly have a relatively small size mean value of 22.237 µm. The grain size is quite favourable for geopolymer production [33].

Also, the microstructure analysis was provided using scanning electron microscopy (SEM) – Figure 4.

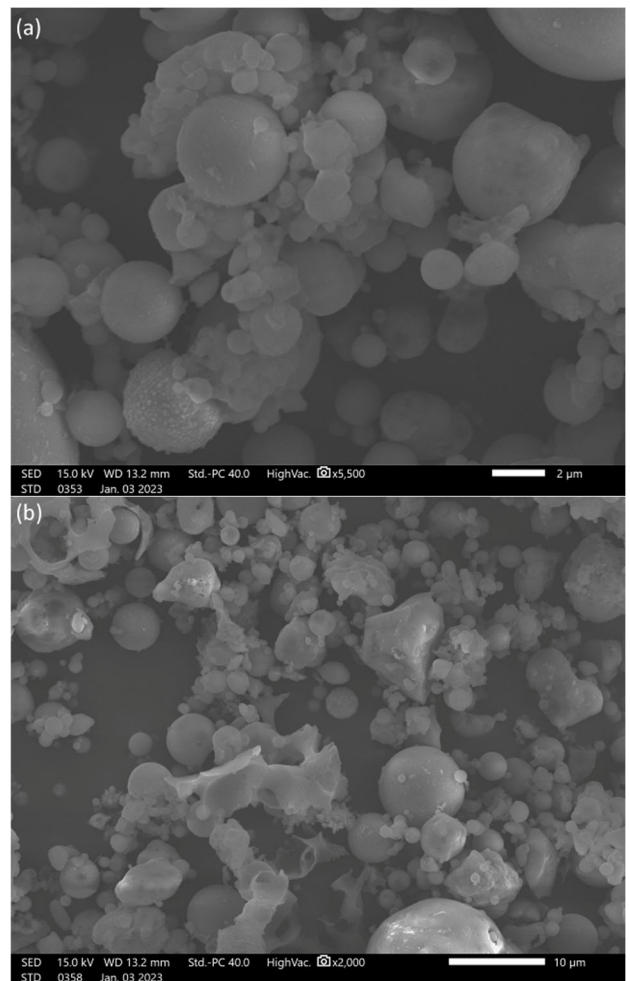


Fig. 4. SEM images of fly ash: (a) magnification 5 500×; (b) magnification 2 000×

The morphology of ash particles, where the occurrence of particles with regularly spherical shapes, improves workability and rheological properties [12,36].

Sand

Firstly, sand was tested for mineral composition – Figure 5 and Table 4.

According to the diffraction pattern analysis, it was possible to determine that the sand used in the geopolymer consisted entirely of quartz, according to expectations.

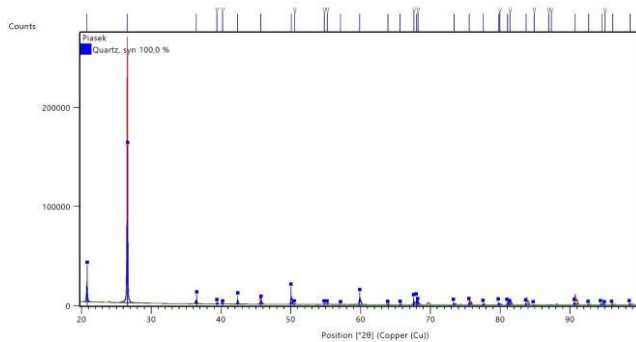


Fig. 5. Mineralogical phase identification in sand by using XRD

Table 4. Mineralogical composition of sand

Name	Phase	Percentage, %
Name	Chemical composition	%
Quartz	SiO ₂	100

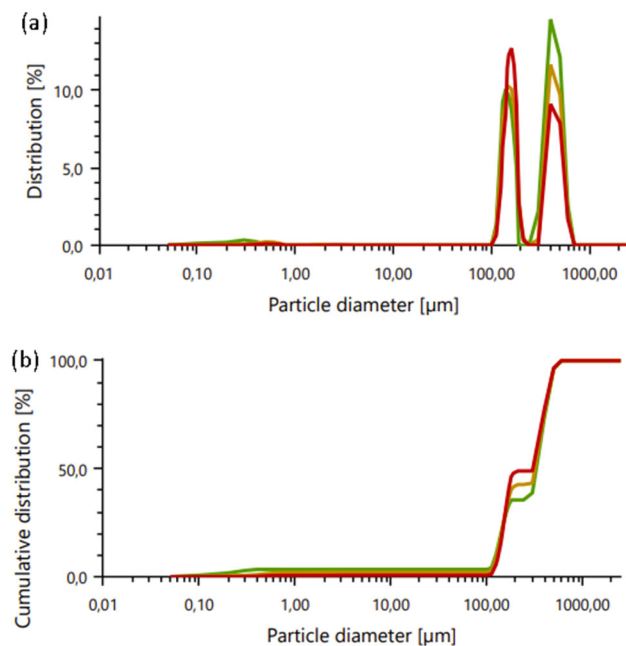


Fig. 6. Particle size analysis of sand a) distribution (volume); b) Cumulative distribution (volume) – undersize

In the next step, the particle size analysis was performed, as shown in Figure 6 and Table 5.

The mean value for the sand is definitively different than for fly ash. It is about 318.55 μm compared to 22.237 μm for the fly ash.

Table 5. Particle size distribution of sand

Name	D ₁₀ , μm	D ₅₀ , μm	D ₉₀ , μm	Mean size, μm	Span
Sample 1	124.560	329.125	470.765	331.958	1.052
Sample 2	127.513	318.439	467.049	318.571	1.066
Sample 3	132.486	303.183	462.886	305.143	1.090
Mean	128.186	316.916	466.900	318.557	1.069

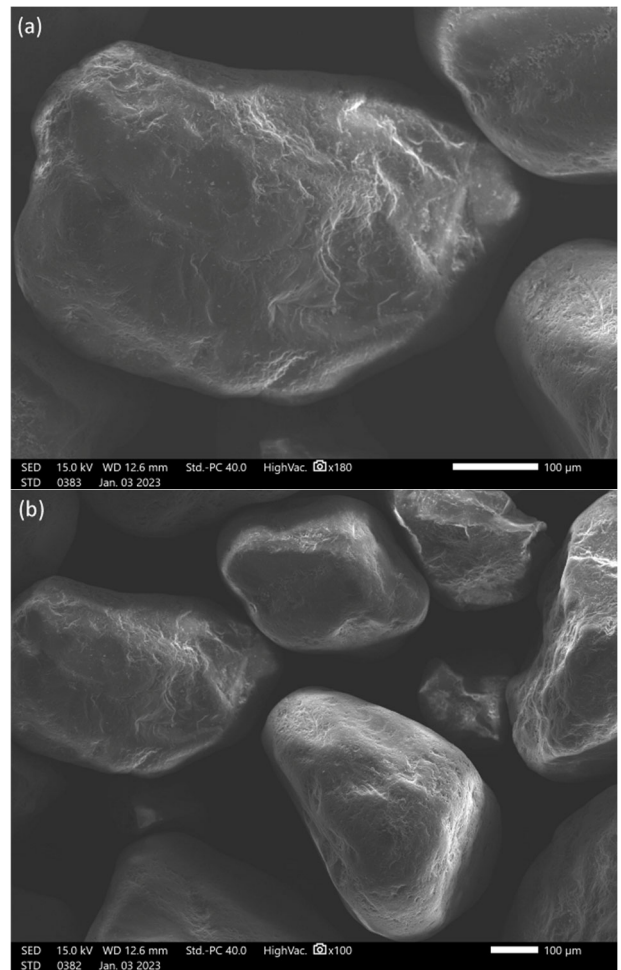


Fig. 7. SEM images of sand: (a) magnification 180×; (b) magnification 100×

Moreover, the SEM observation was conducted for the sand – Figure 7. SEM analysis of sand shows that it has a

structure in the form of irregularly shaped particles with smooth edges and a rough structure on grains of sand. It is also worth paying attention to the size of the images, which confirms the grain size analysis results and shows significant differences in size between the tested materials – sand and fly ash.

Microsilica

Similarly, as other raw materials, microsilica was tested for mineral composition – Table 6 and Figure 8.

Table 6. Mineralogical composition of misrosilica

Name	Phase	Percentage, %
Silica oxide	SiO ₂	99.9
Rutile	TiO ₂	0.1

According to the diffraction pattern analysis above, it was possible to establish that microsilica consisted of 99.9% oxide cream and only 0.1% of rutile, which may be an impurity coming from the manufacturing process of the material.

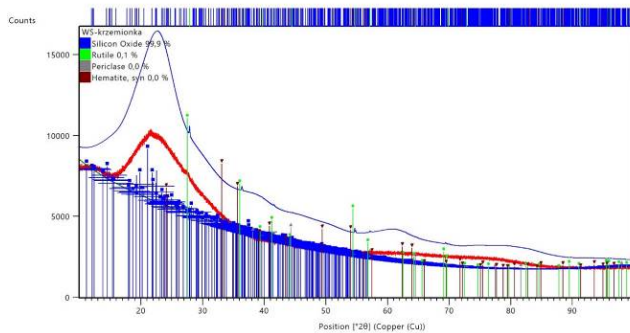


Fig. 8. Mineralogical phase identification in microsilica by using XRD

In the next step, particle size analysis was conducted – Figure 9 and Table 7.

Table 7. Particle size distribution of microsilica

Name	D ₁₀ , μm	D ₅₀ , μm	D ₉₀ , μm	Mean size, μm	Span
Sample 1	7.057	20.300	41.863	23.784	1.715
Sample 2	6.956	20.219	41.539	23.627	1.710
Sample 3	6.934	20.138	41.155	23.481	1.699
Mean	6.982	20.219	41.519	23.631	1.708

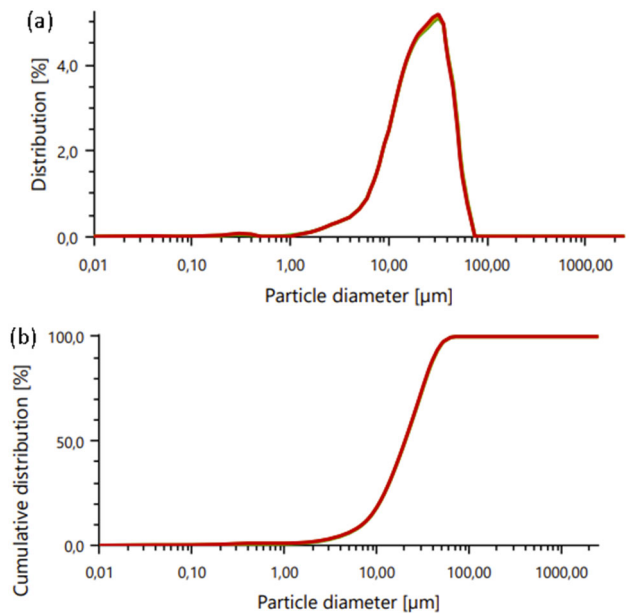


Fig. 9. Particle size analysis of microsilica a) distribution (volume); b) Cumulative distribution (volume) – undersize

The particle size analysis shows a lack of significant difference between the particle size of fly ash and applied microsilica. They are both similar sizes. Meanwhile, the sand is much larger.

Also, the SEM analysis for microsilica was conducted – Figure 10. The shape of microsilica was not coherent with previous expectations based on literature data [15]. The shape of the particles was irregular, with sharp edges.

Given the research of all three raw materials in which each possesses a different size of grains, they should form a “tight” structure (well packed), increasing both density and properties strength. However, it must also be considered that the particles possess different shapes, which may interfere with obtaining the desired properties of the material.

3.2. Geopolymer composites

Mineralogical analysis

The diffractograms for four types of prepared materials are presented in Figure 11, and the information about mineralogical composition is presented in Table 8.

A large amount of quartz is present in the produced geopolymers, which should ensure good mechanical properties of the materials, in particular compressive strength [36]. The other phases present are mullite and albite, typical of geopolymer materials. The obtained results do not correlate with the addition of microsilica due to the qualitative nature of the research.

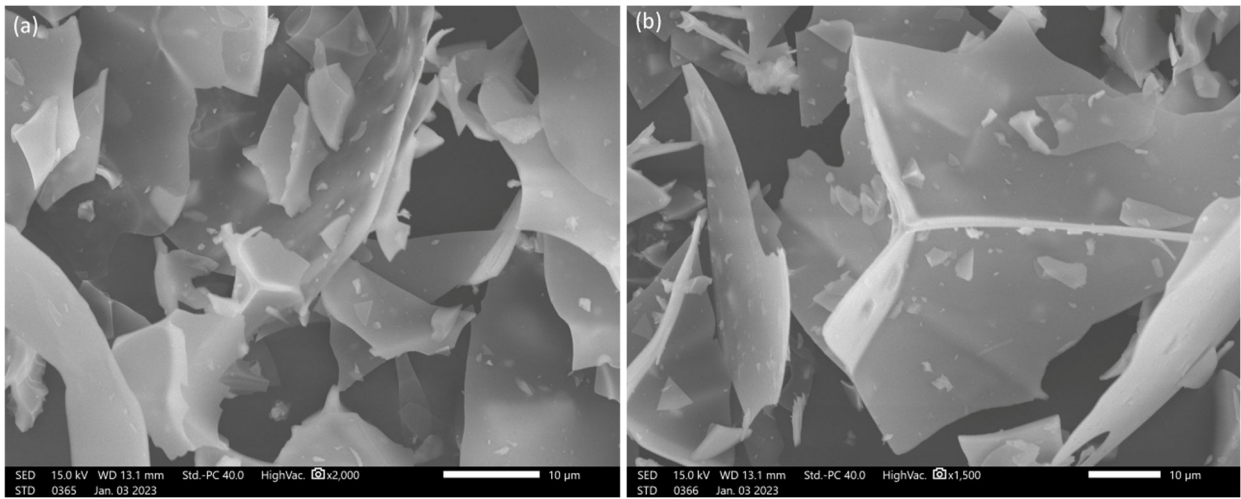


Fig. 10. SEM images of microsilica: (a) magnification 2 000×; (b) magnification 1 500×.

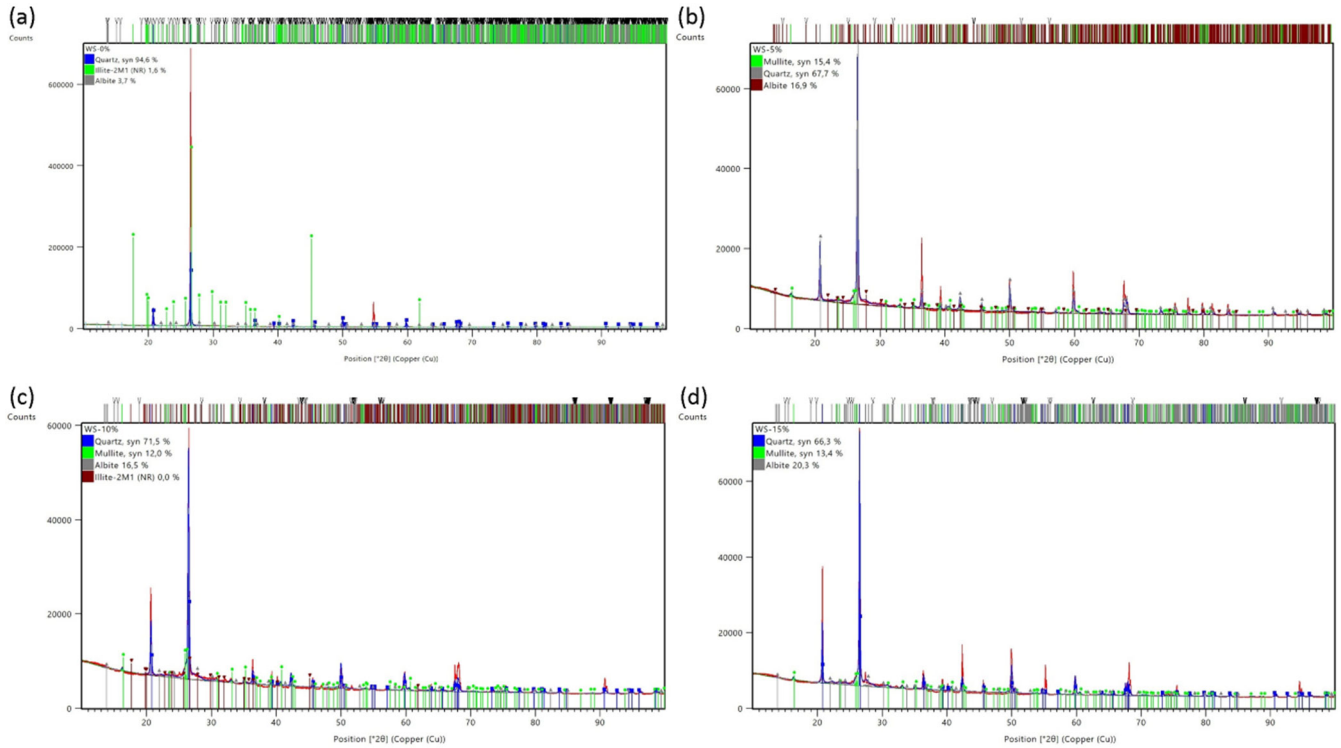


Fig. 11. X-ray diffractogram for geopolymers: (a) GP0; (b) GP1; (c) GP2; (d) GP3

Table 8. Comparison of mineralogical composition for geopolymer samples

Name	Chemical formula	GP0	GP1	GP2	GP3
Quartz	SiO ₂	94.6	67.7	71.5	66.3
Mullite	Al ₆ Si ₂ O ₁₃	1.6	15.4	12	13.4
Albite	NaAlSi ₃ O ₈	3.7	16.9	16.5	20.3

Density

The measurements of density are presented in Figure 12.

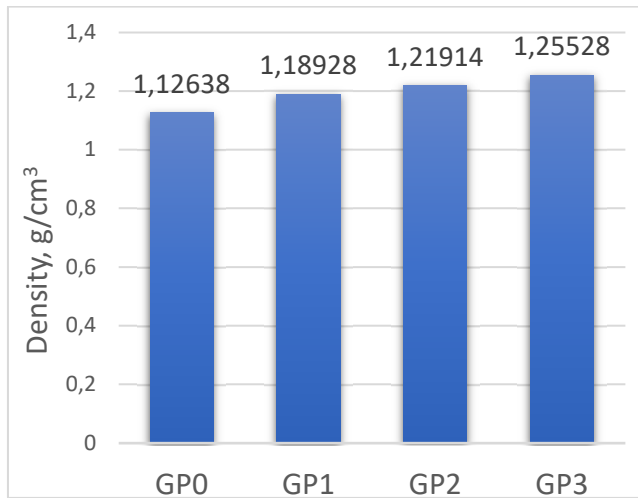


Fig. 12. Comparison of density of geopolymers

The density of geopolymers increases with the addition of microsilica. According to data from the manufacturer, microsilica should have a specific gravity of approximately 2.1 g/cm³ and low bulk density – about 0.2 g/cm³. In the case of mixture preparation, geopolymer's specific gravity plays an important role. The higher liquid requirement, which is visible during the process of geopolymer preparation and a mechanism where microsilica is placed between the sand grains (which is included in empty spaces not occupied by fly ash), caused the increasing material density. However, the differences in density between particular compositions are not huge.

Mechanical properties – compressive and flexural strength

The results of the mechanical properties test are presented in Table 9.

Table 9.

Mechanical properties for geopolymer samples

Name	Compressive strength, MPa	Flexural strength, MPa
GP0	42.29	7.23
GP1	30.53	6.02
GP2	25.43	3.53
GP3	18.75	2.35

In the case of compressive and flexural strength, their decrease is visible along with the addition of microsilica. It is not a standard behaviour of materials because mechanical

properties tend to increase with density [9,41]. However, in the presented investigation, a reverse tendency has been noted. Such anomaly can be caused by the microstructure of microsilica that has sharp edges and can cause a decrease in mechanical properties by creating the cumulation of stress in certain points of the material and causing the tendency for microcracking propagation under the forces. Despite the weakness of the material, it is worth noticing that the material with 5 and 10% microsilica addition still fulfils the requirements for their application to many construction purposes, including bricks or pavements [41].

Jaradat et al. [40] compared geopolymers' compressive strength with different microsilica shares. The authors noted that adding microsilica in amounts of 5% and 10% by weight increased the strength of composites cured at room temperature. When an elevated temperature was used, adding micro-silica decreased the compressive strength.

The decrease in compressive strength may be due to an increase in silica to alumina ratio. Both the properties and microstructure of geopolymers are highly dependent on the silica and alumina content [40]. The authors obtained optimal mechanical properties for composites with Si/Al ratios in the range of 3.0-3.8. Raising the Si/Al ratio beyond this range lowers the compressive strength. Curing geopolymers at elevated temperatures increases the solubility of Si from microsilica, causing the formation of silicates in the pores. Increasing the proportion of microsilica leads to an increase in the number of unreacted silicate oligomers in the geopolymer matrix, decreasing mechanical properties [41]. Therefore, sample GP3 obtained the lowest strength values because its composition contained the highest share of micro-silica among all the analysed variants.

Figure 13 illustrates the reasons for the decrease in the strength of the geopolymer after the introduction of microsilica.

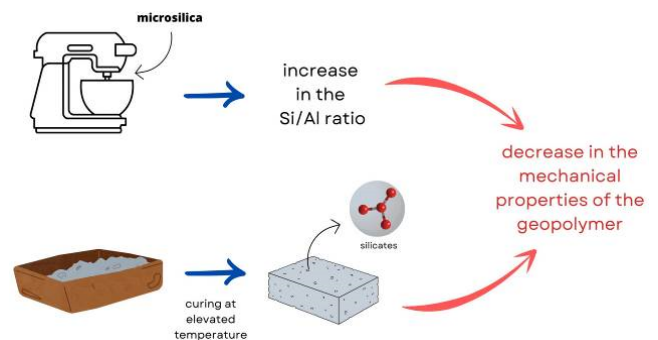


Fig. 13. Possible reasons for the decrease in geopolymer mechanical properties after the introduction of microsilica

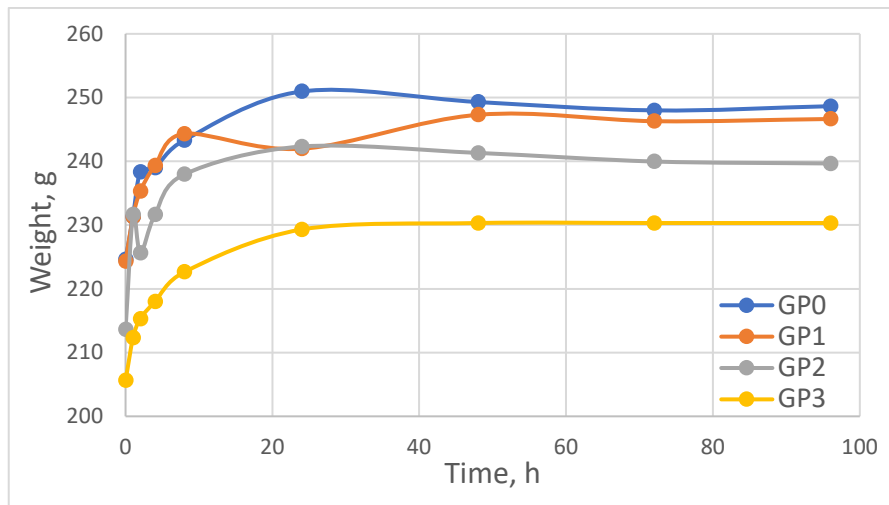


Fig. 14. Water absorption

Water absorption

The results of the measurement of water absorption at the time are presented in Figure 14.

The behaviour of all samples is quite similar according to the water absorption. The most intensive absorption is noted in the first 24 hours, and the weight stays at the same level the next. The small deviations from this stage can be caused by inaccuracy of the measurements.

The final values obtained for the absorption test are presented in Table 10.

Table 10.
Water absorption

Name	Water absorption, %
GP0	10.758
GP1	9.949
GP2	12.166
GP3	11.990

Table 10 shows that the adsorption of geopolymers increases, as a general tendency, with the addition of microsilica. However, some exceptions were noted for the values. In the case of 5% addition, the adsorption is lower than for reference samples and lower values were noted for 15% microsilica addition compared to 10%. It is also worth noting that the increase in sorption usually decreases with increasing material density [38]. No such correlation was obtained in the conducted studies. The phenomena can be caused by some voids inside the materials caused by irregular distribution of microsilica, which can confirm

some incoherences with material behaviour. According to the literature [42], amorphous silica particles tend to aggregate and agglomerate during production processes. It is worth noting that the differences between the tested materials are small, which may also be caused by a measurement error.

Microstructure

The SEM study allowed us to determine the appearance of geopolymer microstructures and determination of the permeable effect of microsilica on changes in the structure material. Some exemplary structures are presented in Figure 15.

The observed structure is typical for fly ash based geopolymers [36,39]. In the presented figures, some microsilica inclusion was not retrieved in the geopolymerisation process (Figure 15 a-c). Also, in the material structure, some grain coming from undissolved elements of fly ash can be observed (Figure 15b). However, the microscope investigation does not show any significant discontinuity in the matrix; existing cracks were connected with the sample preparation process, and it is worth observing that most of them seem to be connected with cracks connected with microsilica grains. Microsilica is probably the weakest part of the material structure, confirming the mechanical properties of the research results.

Thermal properties

The results of the measurement for thermal conductivity are presented in Table 11.

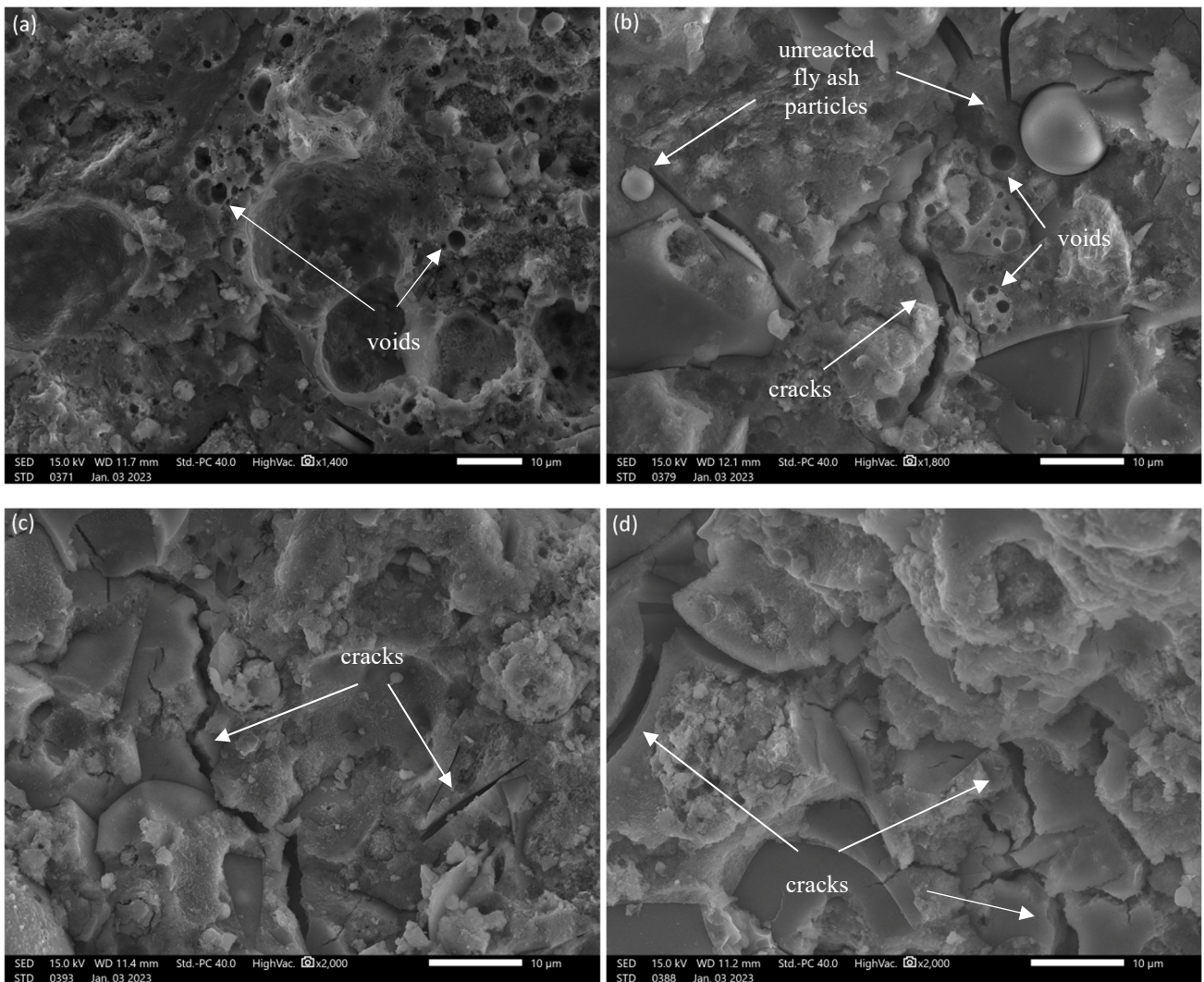


Fig. 15. SEM images of geopolymers: (a) GP0 in magnification 1 400×; (b) GP1 in magnification 1 800×; (c) GP2 in magnification 2 000×; (d) GP3 in magnification 2 000×

Table 11.
Mechanical properties for geopolymer samples

Name	Density ρ , g/cm^3	Thermal conductivity λ , $\text{W/m}^*\text{K}$
GP0	1.13	0.99207
GP1	1.19	0.97513
GP2	1.22	0.83020
GP3	1.26	0.78797

The thermal conductivity of geopolymers systematically decreases with an increasing percentage of microsilica, which means that the thermal insulation values grow. Notably, the measurements also have an inverse correlation with density measurements, which increased with the

addition of microsilica. It is not a typical phenomenon because materials with a lower density are usually characterized by better-insulating properties [9,43,44]. Considering the specificity of building materials, the obtained thermal conductivity values are close to those of ceramic bricks. The results align with the other research in the given area [6,45].

4. Conclusions

The addition of microsilica to geopolymer influenced its characteristics to a large degree. Mechanical durability was greatly reduced; with a 15% addition of microsilica, it dropped by over 50%. Characteristics such as thermal

conductivity were also lowered in contrast to density and sorption properties that both increased. As a result of the research carried out, it was established that microsilica additions to geo-polymers have the following influence.

- Increasing the amount of micro silica in paste requires a larger amount of alkali activator to obtain the proper liquid of paste, which is possible to process.
- XRD tests showed the presence of quartz, albite and mullite in the structure of the obtained geopolymer. They are typical phases present in geopolymers.
- The addition of microsilica causes an increase in the density of geopolymers.
- Strength properties significantly decrease with the addition of microsilica. For the 15% of microsilica addition, both compressive and flexural strength drops more than 50%. However, the obtained values still allow application in the building industry for materials with 5 and 10% of microsilica additives.
- Geopolymers with microsilica absorb more water, which is a disadvantage when considering their application in civil engineering.
- The microstructure of the composite is typical for geopolymers, with visible microsilica inclusions.
- The value of the thermal conductivity of geopolymers decreases with the addition of microsilica, which means that adding silica improves the properties of thermal insulation geopolymers. It is an advantage in application in many building products. It may contribute to reducing energy consumption and increasing the energy efficiency of buildings.

According to the PN-EN 206+A1:2016-12 standard, concrete for structural applications should have a minimum compressive strength of 20 MPa. Therefore, adding silica in the amount of 15% reduces the compressive strength of the geopolymer to a value suggesting non-structural applications. Introducing microsilica in the share of 10% into the geopolymer matrix raises the strength to about 25 MPa while increasing the thermal insulation properties by approximately 15%. It makes the composite a construction material with better thermal insulation, which ultimately increases the energy efficiency of the building.

It is worth stressing that adding silica is not the only factor that influences the properties of the final geopolymer composition. The strong influence on the material properties could have many other factors, such as molarity, alkaline liquid/binder ratio, and sodium hydroxide/sodium silicate ratio. The article did not investigate the factors which focused on microsilica influence with other parameters unchanged.

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References

- [1] H.U. Ahmed, L.J. Mahmood, M.A. Muhammad, R.H. Faraj, S.M.A. Qaidi, N.H. Sor, A.S. Mohammed, A.A. Mohammed, Geopolymer concrete as a cleaner construction material: An overview on materials and structural performances, *Cleaner Materials* 5 (2022) 100111. DOI: <https://doi.org/10.1016/j.clema.2022.100111>
- [2] K. Korniejenko, B. Figiela, C. Ziejewska, J. Marczyk, P. Bazan, M. Hebda, M. Choiniska, W.T. Lin, Fracture Behavior of Long Fiber Reinforced Geopolymer Composites at Different Operating Temperatures, *Materials* 15/2 (2022) 482. DOI: <https://doi.org/10.3390/ma15020482>
- [3] R.S. Krishna, J. Mishra, M. Zribi, F. Adeniyi, S. Saha, S. Baklouti, F.U. Ahmed Shaikh, H.S. Gökçe, A review on developments of environmentally friendly geopolymer technology, *Materialia* 20 (2021) 101212. DOI: <https://doi.org/10.1016/j.mtla.2021.101212>
- [4] A.B. Elhag, A. Raza, Q.Z. Khan, M. Abid, B. Masood, M. Arshad, A.F. Deifalla, A critical review on mechanical, durability, and microstructural properties of industrial by-product-based geopolymer composites, *Reviews on Advanced Materials Science* 62/1 (2023) 20220306. DOI: <https://doi.org/10.1515/rams-2022-0306>
- [5] T.V. Lam, M.H. Nguyen, Incorporating Industrial By-Products into Geopolymer Mortar: Effects on Strength and Durability, *Materials* 16/12 (2023) 4406. DOI: <https://doi.org/10.3390/ma16124406>
- [6] V.S. Le, V.V. Nguyen, A. Sharko, R. Ercoli, T.X. Nguyen, D.H. Tran, P. Łoś, K.E. Buczkowska, S. Mitura, T. Špirek, P. Louda, Fire Resistance of Geopolymer Foams Layered on Polystyrene Boards, *Polymers* 14/10 (2022) 1945. DOI: <https://doi.org/10.3390/polym14101945>
- [7] J. Mishra, B. Nanda, S.K. Patro, R.S. Krishna, Sustainable Fly Ash Based Geopolymer Binders: A Review on Compressive Strength and Microstructure

- Properties, Sustainability 14/22 (2022) 15062. DOI: <https://doi.org/10.3390/su142215062>
- [8] D. Mierzwiński, J. Walter, D. Wanat, Possibilities of Checking Water Content in Porous Geopolymer Materials Using Impedance Spectroscopy Methods, Materials 16/14 (2023) 5190. DOI: <https://doi.org/10.3390/ma16145190>
- [9] B. Kozub, J. Castro-Gomes, An investigation of the ground walnut shells' addition effect on the properties of the fly ash-based geopolymer, Materials 15/11 (2022) 3936. DOI: <https://doi.org/10.3390/ma15113936>
- [10] A. Danish, T. Ozbakkaloglu, M.A. Mosaberpanah, M.U. Salim, M. Bayram, J.H. Yeon, K. Jafar, Sustainability benefits and commercialization challenges and strategies of geopolymer concrete: A review, Journal of Building Engineering 58 (2022) 105005. DOI: <https://doi.org/10.1016/j.jobe.2022.105005>
- [11] J. Marczyk, K. Pławecka, M. Hebdowska-Krupa, M. Nykiel, M. Łach, Research on diatomite from Polish deposits and the possibilities of its use, Journal of Achievements in Materials and Manufacturing Engineering 115/1 (2022) 5-15. DOI: <https://doi.org/10.5604/01.3001.0016.2337>
- [12] L.J.J. Nieves, F. Elyseu, S. Goulart, M. de Souza Pereira, E.Z. Valvassoir, A.M. Bernardin, Use of fly and bottom ashes from a thermoelectrical plant in the synthesis of geopolymers: Evaluation of reaction efficiency, Energy Geoscience 2/2 (2021) 167-173. DOI: <https://doi.org/10.1016/j.engeos.2020.09.004>
- [13] B.S. Thomas, J. Yang, A. Bahurudeen, S.N. Chinnu, J.A. Abdalla, R.A. Hawileh, H.M. Hamada, Geopolymer concrete incorporating recycled aggregates: A comprehensive review, Cleaner Materials 3 (2022) 1000056. DOI: <https://doi.org/10.1016/j.clema.2022.100056>
- [14] U. Sharma, A. Khatri, A. Kanoungo, Use of Microsilica as Additive to Concrete-state of Art, International Journal of Civil Engineering Research 5/1 (2014) 9-12.
- [15] H.U. Ahmed, A.S. Mohammed, R.H. Faraj, S.M.A. Qaidi, A.A. Mohammed, Compressive strength of geopolymer concrete modified with nano-silica: Experimental and modeling investigations, Case Studies in Construction Materials 16 (2022) e01036. DOI: <https://doi.org/10.1016/j.cscm.2022.e01036>
- [16] A.K. Chishi, L. Gautam, Sustainable use of silica fume in green cement concrete production: a review, Innovative Infrastructure Solutions 8 (2023) 195. DOI: <https://doi.org/10.1007/s41062-023-01164-z>
- [17] H.M. Hamada, F. Abed, H.Y. Binti Katman, A.M. Humada, M.S. Al Jawahery, A. Majdi, S.T. Yousif, B. Skariah Thomas, Effect of silica fume on the properties of sustainable cement concrete, Journal of Materials Research and Technology 24 (2023) 8887-8908. DOI: <https://doi.org/10.1016/j.jmrt.2023.05.147>
- [18] R.P. Singh, K.R. Vanapalli, V.R. Sankar Cheela, S.R. Peddireddy, H.B. Sharma, B. Mohanty, Fly ash, GGBS, and silica fume based geopolymer concrete with recycled aggregates: Properties and environmental impacts, Construction and Building Materials 378 (2023) 131168. DOI: <https://doi.org/10.1016/j.conbuildmat.2023.131168>
- [19] M. Heikal, M.E.A. Zaki, S.M. Ibrahim, Preparation, physico-mechanical characteristics and durability of eco-alkali-activated binder from blast-furnace slag, cement kiln-by-pass dust and microsilica ternary system, Construction and Building Materials 260 (2020) 119947. DOI: <https://doi.org/10.1016/j.conbuildmat.2020.119947>
- [20] H. Assaedi, T. Alomayri, F. Shaikh, I.M. Low, Influence of Nano Silica Particles on Durability of Flax Fabric Reinforced Geopolymer Composites, Materials 12/9 (2019) 1459. DOI: <https://doi.org/10.3390/ma12091459>
- [21] A.M. Rashad, Silica Fume as a Part of Precursor/An Additive, in: Silica Fume in Geopolymers, Springer Briefs in Applied Sciences and Technology, Springer, Cham, 2023, 9-83. DOI: https://doi.org/10.1007/978-3-031-33219-7_2
- [22] W. Chen, J. Li, Effects of Different Silicon Sources on the Properties of Geopolymer Planting Concrete Mixed with Red Mud, Sustainability 15/5 (2023) 4427. DOI: <https://doi.org/10.3390/su15054427>
- [23] F. Wang, X. Sun, Z. Tao, Z. Pan, Effect of silica fume on compressive strength of ultra-high-performance concrete made of calcium aluminate cement/fly ash based geopolymer, Journal of Building Engineering 62 (2022) 105398. DOI: <https://doi.org/10.1016/j.jobe.2022.105398>
- [24] F.N. Okoye, S. Prakash, N.B. Singh, Durability of fly ash based geopolymer concrete in the presence of silica fume, Journal of Cleaner Production 149 (2017) 1062-1067. DOI: <https://doi.org/10.1016/j.jclepro.2017.02.176>
- [25] O. Vogt, N. Ukrainczyk, E. Koenders, Effect of Silica Fume on Metakaolin Geopolymers' Sulfuric Acid Resistance, Materials 14/18 (2021) 5396. DOI: <https://doi.org/10.3390/ma14185396>
- [26] W. Dai, Y. Wang, Silica fume enhances the mechanical strength of alkali-activated slag/fly ash pastes subjected to elevated temperatures, Fire 6/7 (2023) 252. DOI: <https://doi.org/10.3390/fire6070252>
- [27] Y. Zhang, H. Liu, T. Ma, G. Gu, C. Chen, J. Hu, Understanding the changes in engineering behaviors and microstructure of FA-GBFS based geopolymer paste with addition of silica fume, Journal of Building Engineering 70 (2023) 106450. DOI: <https://doi.org/10.1016/j.jobe.2023.106450>
- [28] J. Zhao, Y. Wang, Microstructure Evaluation of Fly Ash Geopolymers Alkali-Activated by Binary

- Composite Activators, *Minerals* 13/7 (2023) 910. DOI: <https://doi.org/10.3390/min13070910>
- [29] S. Wang, Y. Liang, D. Mo, C. Zhang, J. Xue, X. Song, Y. Wang, Doping Silica Fume Enhances the Mechanical Strength of Slag/Fly Ash Geopolymer Paste under Frost Attack, *Minerals* 13/7 (2023) 925. DOI: <https://doi.org/10.3390/min13070925>
- [30] B.O. Adaleke, J.M. Kinuthia, J. Oti, M. Ebailila, Physico-mechanical evaluation of geopolymer concrete activated by sodium hydroxide and silica fume-synthesised sodium silicate solution, *Materials* 16/6 (2023) 2400. DOI: <https://doi.org/10.3390/ma16062400>
- [31] M.F. Alnahhal, T. Kim, A. Hajimohammadi, Waste-derived activators for alkali-activated materials: a review, *Cement and Concrete Composites* 118 (2021) 103980. DOI: <https://doi.org/10.1016/j.cemconcomp.2021.103980>
- [32] D.Q. A'yuni, A. Subagio, H. Hadiyanto, A.C. Kumoro, M. Djaeni, Microstructure silica leached by NaOH from semi-burned rice husk ash for moisture adsorbent, *Archives of Materials Science and Engineering* 108/1 (2021) 5-15. DOI: <https://doi.org/10.5604/01.3001.0015.0248>
- [33] B. Kozub, K. Pławecka, B. Figiela, K. Korniejenko, Geopolymer fly ash composites modified with cotton fibre, *Archives of Materials Science and Engineering* 121/2 (2023) 60-70. DOI: <https://doi.org/10.5604/01.3001.0053.8487>
- [34] K. Korniejenko, K. Pławecka, A. Bulut, B. Şahin, G. Azizağaoğlu, B. Figiela, Development of lightweight geopolymer composites containing perlite and vermiculite, *Journal of Achievements in Materials and Manufacturing Engineering* 117/2 (2023) 49-56. DOI: <https://doi.org/10.5604/01.3001.0053.6696>
- [35] Q. Munir, M. Abdulkareem, M. Horttanainen, T.A. Kärki, A comparative cradle-to-gate life cycle assessment of geopolymer concrete produced from industrial side streams in comparison with traditional concrete, *Science of The Total Environment* 865 (2023) 161230. DOI: <https://doi.org/10.1016/j.scitotenv.2022.161230>
- [36] K. Pławecka, P. Bazan, W.-T. Lin, K. Korniejenko, M. Sitarz, M. Nykiel, Development of Geopolymers Based on Fly Ashes from Different Combustion Processes, *Polymers* 14/10 (2022) 1954. DOI: <https://doi.org/10.3390/polym14101954>
- [37] N. Arunachalam, J. Maheswaran, M. Chellapandian, G. Murali, N.I. Vatin, Development of High-Strength Geopolymer Concrete Incorporating High-Volume Copper Slag and Micro Silica, *Sustainability* 14/13 (2022) 7601. DOI: <https://doi.org/10.3390/su14137601>
- [38] K. Korniejenko, B. Figiela, B. Kozub, V. Azzopardi, M. Łach, Environmental degradation of foamed geopolymers, *Continuum Mechanics and Thermodynamics* 54 (2022) 7601. DOI: <https://doi.org/10.1007/s00161-022-01102-x>
- [39] K. Korniejenko, M. Łach, J. Mikula, The Influence of Short Coir, Glass and Carbon Fibers on the Properties of Composites with Geopolymer Matrix, *Materials* 14/16 (2021) 4599. DOI: <https://doi.org/10.3390/ma14164599>
- [40] Y. Jaradat, F. Matalkah, Effects of micro silica on the compressive strength and absorption characteristics of olive biomass ash-based geopolymer, *Case Studies in Construction Materials* 18 (2023) e01870. DOI: <https://doi.org/10.1016/j.cscm.2023.e01870>
- [41] S. Yaseri, G. Hajiaghaci, F. Mohammadi, R. Farokhzad, The role of synthesis parameters on the workability, setting and strength properties of binary binder based geopolymer paste, *Construction and Building Materials* 157 (2017) 534-545. DOI: <https://doi.org/10.1016/j.conbuildmat.2017.09.102>
- [42] P.J. De Temmerman, E. Van Doren, E. Verleysen, Y. Van der Stede, M.A.D. Francisco, J. Mast, Quantitative characterization of agglomerates and aggregates of pyrogenic and precipitated amorphous silica nanomaterials by transmission electron microscopy, *Journal of Nanobiotechnology* 10 (2012) 24. DOI: <https://doi.org/10.1186/1477-3155-10-24>
- [43] Z. Buliński, S. Pawlak, T. Krysiński, W. Adamczyk, R. Białecki, Application of the ASTM D5470 standard test method for thermal conductivity measurements of high thermal conductive materials, *Journal of Achievements in Materials and Manufacturing Engineering* 95/2 (2019) 57-63. DOI: <https://doi.org/10.5604/01.3001.0013.7915>
- [44] M. Kujawa, R. Suwak, L.A. Dobrzański, A. Gerle, B. Tomiczek, Thermal characterization of halloysite materials for porous ceramic preforms, *Archives of Materials Science and Engineering* 107/1 (2021) 5-15. DOI: <https://doi.org/10.5604/01.3001.0014.8189>
- [45] V.S. Le, A. Sharko, O. Sharko, D. Stepanchikov, R. Ercoli, T.X. Nguyen, D.H. Tran, K.E. Buczkowska, P. Dancova, P. Łos, P. Louda, Multi-criteria optimization of geopolymer foam composition, *Journal of Materials Research and Technology* 26 (2023) 9049-9062. DOI: <https://doi.org/10.1016/j.jmrt.2023.09.199>



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