

Article

Recycling of Coal Combustion Waste through Production of Foamed Geopolymers with Improved Strength

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Abstract: Recycling of industrial waste into useful materials is a crucial aim for achieving sustainable development in materials science. The use of production waste in the manufacture of construction materials contributes to improving the environmental situation and reducing the cost of the final product. This article examines the utilization of coal combustion waste recycled into foamed geopolymers and ways of enhancing their strength properties through the introduction of strengthening additives. Eight compositions of foamed geopolymers containing different strengthening additives were synthesized. Inorganic substances (CaO, MgO, ZnO, TiO₂, Al₂O₃, SiC, and ZrO₂) were chosen as strengthening additives that were introduced in an amount of 3% (over 100%). The physical and mechanical properties (density, compressive strength, porosity, and pore size distribution) of the obtained samples were studied and compared. Magnesium oxide MgO and aluminum oxide Al₂O₃ were chosen as the best strengthening additives. Magnesium oxide allows geopolymer materials with the lowest density to be obtained. Aluminum oxide can significantly increase the strength of geopolymers. The phase composition of the samples contains new crystalline phases in the form of α -alumina and periclase. The porous structure is homogeneous and meets the requirements for foamed thermal insulation materials. The strengthening effect of the chosen additives was verified using geopolymers based on different waste from Novochoerkassk SDPP.

Keywords: coal combustion waste; foamed geopolymer; strengthening additives; foaming agent; Arctic zone; road construction



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1. Introduction

Coal energy has long served as a prominent electricity source, contributing over one-third of global electricity generation [1]. During the combustion of coal in power plant boilers, intricate physical and chemical processes transpire, forming various waste byproducts, including nitrogen oxides, sulfur oxides, carbon compounds, volatile organic substances, and substantial solid mineral residues. These solid residues encompass fly ash, fuel slag, and their mixtures, primarily arising from the inorganic impurities within coal, such as quartz, pyrite, and hematite. These minerals transform under high-temperature conditions within boilers. The worldwide annual production of waste resulting from coal combustion in thermal power plants exceeds one billion tons, necessitating the exploration of innovative waste utilization methods.

In the context of contemporary environmental concerns and a heightened focus on sustainable practices, the conversion of coal combustion waste into materials production offers a valuable avenue for resource optimization. It allows not only energy waste to be recycled but also reduces a share of the natural raw materials in production. All of this

aligns with sustainability goals by addressing the responsible management of technogenic byproducts and supporting the principles of a circular economy and resource efficiency.

Several countries have already identified limited applications for these waste materials, including their use in ceramic production and cement manufacturing, as concrete additives and ameliorants, for road and dam construction, etc. [1–3]. In terms of chemical composition, coal combustion wastes (CCWs) exhibit a complex matrix, containing oxides of silicon, aluminum, iron, magnesium, and others. Notably, SiO_2 and Al_2O_3 constitute a substantial portion, ranging from 55% to 90%, categorizing them as aluminosilicate materials [4].

The importance of finding new ways to utilize industrial waste into useful products is also of great significance for the sustainable development of the materials science field. One of the main challenges here is the limitation of natural raw material resources. The use of industrial waste in materials production contributes to sustainable resource conservation, the advancement of innovative research for obtaining a range of new environmentally friendly and sustainable materials, and, as a result, a reduction in negative impacts on the environment. Additionally, these initiatives contribute to the economic development of this industry by fostering the development of new technologies, products, and services.

Geopolymer production represents an innovative approach to repurposing waste derived from coal combustion [5,6]. Geopolymers are novel binding materials generated through the alkaline activation of aluminosilicate source materials. These source materials encompass both natural substances, such as feldspars and metakaolin, as well as anthropogenic materials, including residues from coal combustion (fly ash, boiler slag, and their mixtures), mining wastes, byproducts of metallurgical processes (blast furnace slag, steelmaking slag, slag from nonferrous metallurgy, and red mud), and others [7–13].

Geopolymers are characterized as inorganic polymers comprised of silicon–oxygen and aluminum–oxygen tetrahedra interconnected through bridging oxygen atoms, forming chains and rings that constitute the polymer matrix. In this molecular architecture, positive ions, typically represented by alkaline and alkaline earth metal atoms (such as Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc.), are balancing the negatively charged $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra.

The formation of geopolymers involves a multistep progression initiated by the interaction of aluminosilicate source materials with strong alkali solutions (e.g., NaOH and KOH). This interaction yields silicates and aluminates from silicon and aluminum oxides. Subsequently, the natural polymer structures disintegrate, giving rise to monomers. In the final phase, these resultant monomers undergo polymerization, resulting in the compaction and solidification of the reaction mixture [14].

Geopolymer materials exhibit technical and operational characteristics close to those of cement-based building materials. Notably, geopolymer production stands out for its superior environmental sustainability when compared to cement manufacturing. Geopolymer production minimizes carbon dioxide emissions and eliminates the need for energy-intensive high-temperature processes, which can reach up to $1500\text{ }^\circ\text{C}$ in cement production. Furthermore, the incorporation of technogenic waste materials into geopolymer production diminishes the consumption of precious and limited natural resources, rendering their production both carbon neutral and resource-efficient [15].

In the global research, substantial focus is placed on the exploration of geopolymer concretes founded on diverse natural and anthropogenic source materials [16–20]. There is a particular interest in foamed geopolymer materials distinguished by their intricate cellular structure, low density (below 1000 kg/m^3), and excellent thermal insulating properties. Foamed geopolymers also have many other advantages, such as low carbon emissions, good durability, and resistance to high temperatures. The synthesis of foamed geopolymers from coal combustion waste marks a significant stride toward sustainable material practices. The utilization of strengthening additives has notably enhanced the strength properties of these geopolymers, potentially extending their lifecycle and applicability across various industries. These materials exhibit promising traits such as a lower density, improved compressive strength, and a homogeneous porous structure, aligning with the requisites of eco-conscious and cost-effective construction materials. Geopolymer mate-

rials have demonstrated their ability to withstand more than 100 freeze-thaw cycles with resilience [21–23]. These attributes render foamed geopolymers suitable for application in Arctic conditions, such as serving as frost-protective layers for road surfaces.

Geopolymer materials consisting of 70% or more coal combustion waste are more economically advantageous compared to existing similar materials. This is primarily due to the low cost and large quantities of coal combustion waste, which, in some countries, has an extremely low percentage of recycling. Additionally, the significant content of waste in geopolymers will contribute to their high processing speed. As a result, this will reduce the pollution of groundwater near ash dumps and soil caused by the toxic components of coal combustion waste, such as heavy metals, with a subsequent use of this areas for agricultural purposes.

Enhancing the strength of foamed geopolymer materials is a significant research aim. Previous investigations [24] have unveiled the beneficial impact of incorporating glass powder on the mechanical properties of geopolymers. During the research, adjustments were made to the chemical composition of the ash and slag mixture, which initially lacked a sufficient amount of SiO_2 . The correction was carried out by introducing sand or glass powder into the mixture. It was found that glass powder is a preferable additive for strengthening geopolymer materials as it contains a reactive amorphous silicon dioxide capable of participating in the geopolymerization reaction. Other studies have also explored the effects of zirconium, magnesium, zinc, and aluminum oxide compounds on the strength of geopolymer concretes [25–29].

In the study [25], the researchers investigated the synthesis of geopolymer coatings modified with magnesium oxide. It was revealed that magnesium oxide, upon interaction with water, forms magnesium hydroxide, whose crystals expand and disperse in the geopolymer mixture, inhibiting the shrinkage process, enhancing crack resistance, and consequently, improving the strength of the final material. In the study [26], the authors explored the influence of nanoscale aluminum oxide on the strength properties of geopolymer materials. They found that aluminum oxide enhances the geopolymerization process by effectively participating in the chemical activation of aluminosilicate raw materials, leading to improved mechanical characteristics of the material.

The research [27] investigated the impact of titanium dioxide on the mechanical properties of geopolymer materials. It was identified that titanium dioxide particles contribute to the reduction in geopolymer concrete porosity, promoting matrix compaction and a dense microstructure formation, resulting in the increased strength properties of geopolymers. In the work [28], the authors studied the influence of zirconium dioxide on the strength properties of geopolymer concrete. They hypothesized that zirconium dioxide particles are incorporated into the geopolymer matrix, reducing the mobility of alkaline metal ions and enhancing strength. However, the authors claimed that an excess amount of zirconium dioxide (above 3%) has a detrimental effect on the continuity of the interpenetrating three-dimensional polysialate matrix.

In the study [29], the authors investigated the influence of zinc oxide particles on the mechanical properties of geopolymer concrete. They established that the addition of ZnO at a concentration of 2.5% is preferable as it allows material with the highest compressive strength to be obtained. The authors claim that a further increase in the quantity of zinc oxide leads to a reduction in the material's strength, weakening the condensation processes and the formation of geopolymer bonds.

The objective of this research is to examine the impact of strengthening additives on the properties of foamed geopolymer materials. As porous materials have low mechanical characteristics, the enhancement of their strength is essential and particularly relevant. Additionally, as mentioned earlier, previous studies have focused on improving the strength of monolithic geopolymer concretes. The enhancement of strength in foamed geopolymer materials has not received extensive attention, indicating the novelty of the presented research.

2. Materials and Methods

2.1. Raw Material

The main raw material in this study was a coal combustion waste (CCW) of Severodvinsk CHPP-1 (Severodvinsk, Arkhangelsk region, Russian Federation). Seven substances were selected as strengthening additives for geopolymer production: calcium oxide CaO (LenReactive, St. Petersburg, Leningrad region, Russian Federation), magnesium oxide MgO (LenReactive, St. Petersburg, Leningrad region, Russian Federation), zinc oxide ZnO (LenReactive, St. Petersburg, Leningrad region, Russian Federation), titanium dioxide TiO₂ (National Titanium Dioxide Production Company (Cristal), Jeddah, Saudi Arabia), aluminum oxide Al₂O₃ (LenReactive, St. Petersburg, Leningrad region Russian Federation), silicon carbide SiC (LLC "NPK Ermakhim", Moscow, Russian Federation), and zirconium dioxide ZrO₂ (LLC "Zircon", Novocherkassk, Russian Federation).

The following components were used to prepare a solution of an alkaline activator:

- Sodium waterglass (an aqueous solution of sodium silicates) was used. The content of the main substance in the solution was 45 wt.%, silicate modulus = 2 (manufacturer: Palitra LLC, St. Petersburg, Leningrad region, Russian Federation);
- In total, 12 M aqueous NaOH solution was prepared by dissolving granulated sodium hydroxide with the main substance content of 99 wt.% (producer: LLC SANTREID, Moscow, Russian Federation) in deionized water.

Polished aluminum powder of aPAP-1 grade (LLC PTK NeftePromKomplekt, Moscow, Russian Federation) was used as a foaming agent.

2.2. Synthesis of Foamed Geopolymer Materials with Strengthening Additives

Eight mixtures with different strengthening additives were developed for the study (Table 1).

Table 1. Compositions of foamed geopolymers with strengthening additives, wt.%.

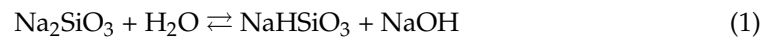
Sample	CCW	NaOH, 12 M Solution	Waterglass	Aluminum Powder *	CaO *	MgO *	ZnO *	TiO ₂ *	Al ₂ O ₃ *	SiC *	ZrO ₂ *
1 (WA)	70	5	25	2	-	-	-	-	-	-	-
2 (CaO)	70	5	25	2	3	-	-	-	-	-	-
3 (MgO)	70	5	25	2	-	3	-	-	-	-	-
4 (ZnO)	70	5	25	2	-	-	3	-	-	-	-
5 (TiO ₂)	70	5	25	2	-	-	-	3	-	-	-
6 (Al ₂ O ₃)	70	5	25	2	-	-	-	-	3	-	-
7 (SiC)	70	5	25	2	-	-	-	-	-	3	-
8 (ZrO ₂)	70	5	25	2	-	-	-	-	-	-	3

* These components of the mixture were introduced into the raw mixture over 100%.

A decision was made to introduce a 3 wt.% strengthening additive based on the analysis of previous research mentioned above. As established, some additives (such as ZnO, ZrO₂) in excess quantities lead to the deterioration of condensation and geopolymerization processes. Moreover, the significant introduction of a strengthening additive may negatively impact the final cost of the geopolymer material. The resource-saving factor also plays a significant role here as the production of some additives involves the use of rare raw materials, such as zircon mineral (zirconium orthosilicate), used in the production of ZrO₂.

The synthesis of foamed geopolymers was carried out using the following technology: CCW was dried at a temperature of 110 °C. Then, it was ground in a laboratory ball mill for 24 h until reaching particles smaller than 250 µm. A 12 M aqueous solution of sodium hydroxide was prepared in a separate container by dissolving NaOH granules in deionized water and stirring the solution for 5 min. The resulting aqueous alkali solution was mixed with waterglass (an aqueous solution of sodium silicate) for 10 min. As a result, a solution of an alkaline activator was obtained. The alkaline activator is a crucial component of the geopolymer mixture. The alkali within its composition contributes to the breakdown of

natural polymeric structures in aluminosilicate raw materials and the dissolution of silicon and aluminum oxides. Sodium metasilicate, the main component of sodium waterglass, acts as an adhesive, promoting the formation of a robust geopolymer framework after material drying. Additionally, sodium silicate contributes to the creation of an additional alkaline medium in the solution according to Reaction (1):



Prepared CCW was mixed with an alkaline activator solution in proportions described in Table 1. The mixture was stirred for 10 min until homogeneity. Afterward, a portion of a strengthening additive and a foaming agent-aluminum powder-was added to the mixture. The resulting mixture was thoroughly stirred for 5 min. The mixture was then poured into cubic molds with an edge size of 30 mm. Foaming of the reaction mixture occurred according to the scheme shown in Figure 1.

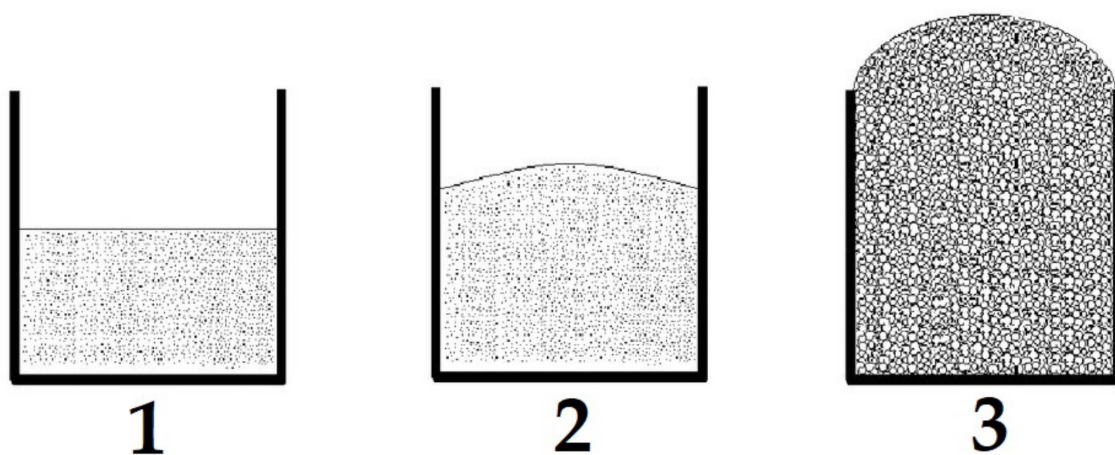


Figure 1. Scheme of the geopolymer mixture foaming: 1—molding; 2—the beginning of the foaming process; 3—the end of the foaming process and the final porous structure formation.

The molded foamed geopolymer was subjected to heat treatment at a temperature of 80 °C for 24 h. The significance of thermal treatment of geopolymer materials lies in accelerating the reactions of foaming and geopolymerization, intensifying the drying process, and, consequently, achieving a rapid increase in the mechanical strength of the material. It is necessary to remove moisture, harden the reaction mixture, and stabilize the cellular structure of the material. After the heat treatment process, the samples were subjected to mechanical processing and the study of their physical–mechanical properties.

2.3. Methods for Studying the Finished Materials

The density of the obtained samples was determined using sample mass (measured using OHAUS analytical balance (Ohaus Corporation, Parsippany, NJ, USA) with an accuracy of 0.0001 g) divided by its volume calculated as a product of its linear dimensions (measured using caliper with an accuracy of ± 0.1 mm). The compressive strength was determined using a breaking load, kN (measured by a TP-1-350 test press (TestPress, Misailovo village, Russia) divided by sample surface area. The porosity of the samples was calculated according to Formula (2):

$$P = (1 - d_b/d_t) \cdot 100,\% \quad (2)$$

where d_b is the sample bulk density, kg/m^3 ; d_t is the sample true density, kg/m^3 .

Resulting test values are the medium of 3 measurements. This decision allows the error of the study to be minimized, including the error of the control and measurement

instruments of the used equipment, leading to a more accurate medium result (about 4 times more precise than using 2 parallel measurements).

The phase composition of the samples was determined using an ARL X'TRA diffractometer (Thermo Fisher Scientific, Waltham, MA, USA), which is a part of the collective use center "Nanotechnologies" of SRSPU (NPI).

3. Results and Discussion

3.1. Composition and Structure of Coal Combustion Waste and Other Raw Materials

The chemical (oxide) composition of the studied CCW was determined using X-ray fluorescence analysis. The analysis was carried out on an Axios mAX vacuum spectrometer (PANalytical, Almelo, The Netherlands). The chemical (oxide) composition of the raw materials is presented in Table 2.

Table 2. Chemical (oxide) composition of CCW, wt.%.

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	CaO	TiO ₂	MnO	P ₂ O ₅	SO ₃	LOI
CCW from (Severodvinsk CHPP-1)	61.6	17.9	6.0	2.8	3.6	2.3	2.1	0.8	0.1	0.2	0.3	2.3
CCW from NovoCherkassk SDPP	51.2	18.8	10.3	2.1	0.9	3.0	3.1	0.8	0.1	0.1	0.3	9.2
Geopolymer	57.8	18.4	5.1	2.3	9.5	2.0	1.8	0.7	0.1	0.2	0.2	1.9

As can be seen from Table 2, the studied CCW contains a significant amount of SiO₂ (61.6 wt.%) and Al₂O₃ (17.9 wt.%). This allows the classification of the CCW as a aluminosilicate material suitable for geopolymer materials production. In addition, it is clear that the raw material contains more than 5 wt.% Fe₂O₃. It was probably formed during the oxidation of pyrite contained in the original coal. The CaO content in raw materials is less than 10 wt.%. This indicates that the studied CCW is a low-calcium material. An increased CaO content secures the curing of a slurry and impairs the geopolymerization.

The qualitative phase composition of the CCW was studied using X-ray phase analysis. An ARL X'TRA diffractometer (Thermo Fisher Scientific, USA) was used. The determination was carried out using the Bragg–Brentano method. The ICDD PDF 2 database was used for obtained data interpretation. Figure 2 presents the results of the X-ray phase analysis of the CCW from Severodvinsk CHPP-1.

As can be seen from Figure 2, the main crystalline phases in the raw material are high quartz (SiO₂, ICDD PDF# 82-0512) and mullite (3Al₂O₃·2SiO₂, ICDD PDF# 15-0776). A "halo" in the range of 20–36° shows a significant amount of the amorphous glassy phase. The true density of the CCW measured using the pycnometric method is 2034 kg/m³. Thus, the presented waste constitutes an amorphous material containing a small amount of a crystalline phase. As amorphous materials possess relatively high reactivity, the considered coal ash and slag waste are preferable for producing geopolymer materials.

The structure of the aluminum powder foaming agent was studied using a Micromed Polar microscope (Weber LLC, Moscow, Russia) at 250× magnification (Figure 3).

As can be seen from Figure 3, the structure of the aluminum powder is represented by spherical and cubic metal particles, as well as smaller scaly particles. The obtained microscopic image of the utilized aluminum powder reveals predominantly particles ranging from 5 to 10 μm, with some flaky inclusions of 1–5 μm. Thus, the aluminum powder exhibits high dispersity, promoting significant contact between the metal and liquid phase (alkaline activator solution) and, consequently, intensifying the foaming process of the geopolymer mixture.

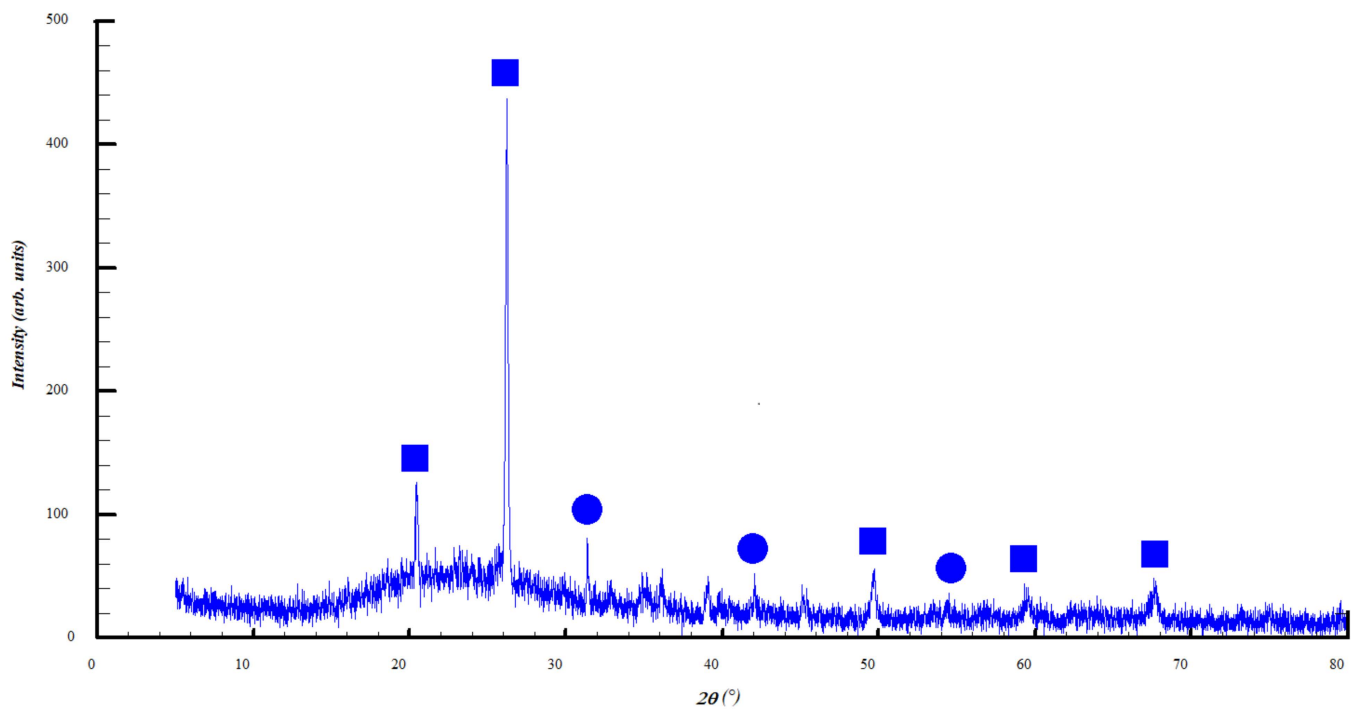


Figure 2. X-ray phase analysis of CCW from Severodvinsk CHPP-1; ■—high quartz (SiO_2), ●—mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

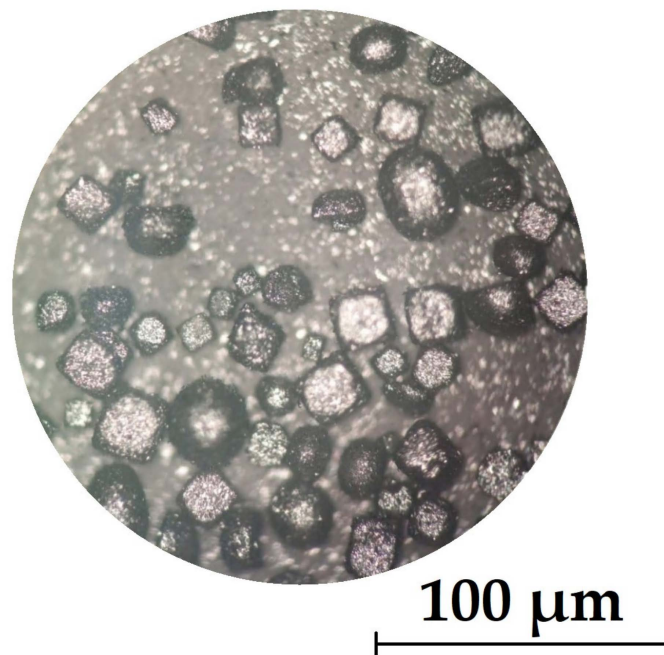


Figure 3. The structure of the aluminum powder foaming agent.

3.2. Investigation of the Properties of Synthesized Foamed Geopolymer Materials

The macrostructure of the synthesized foamed geopolymer material compositions is shown in Figure 4. Table 3 shows the properties of the studied foamed geopolymers.

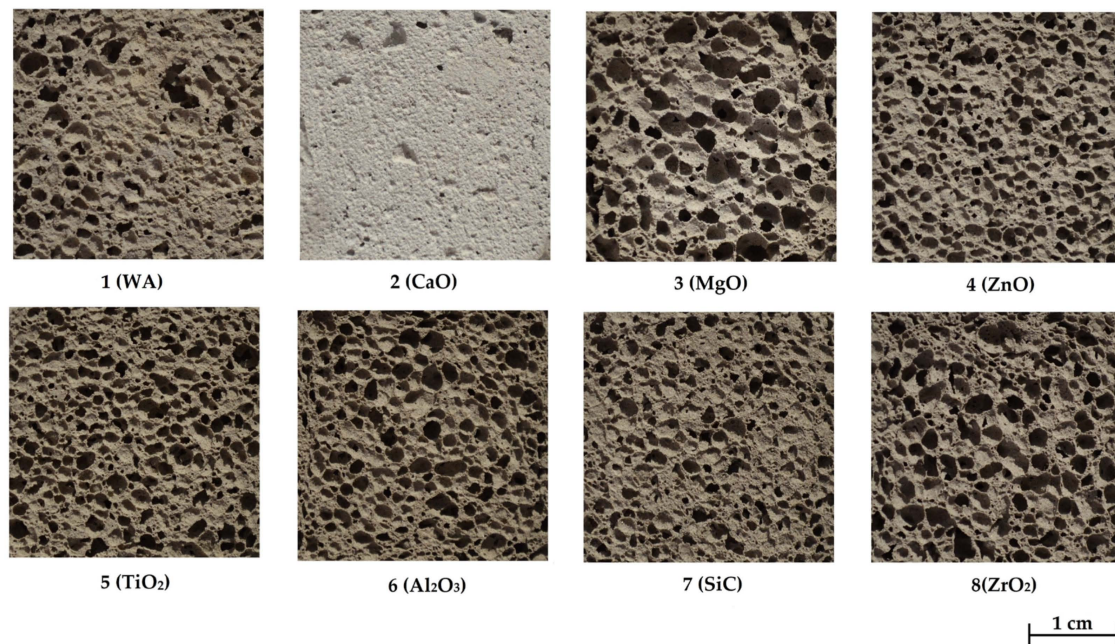


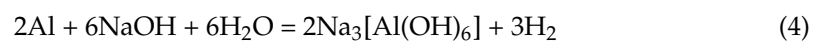
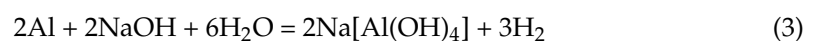
Figure 4. Macrostructure of synthesized samples of foamed geopolymer materials with strengthening additives.

Table 3. Properties of synthesized samples of foamed geopolymer materials.

Sample	Density, kg/m ³	Compressive Strength, MPa	Porosity, %	Relative Compressive Strength, m ² /s ² ·1000	Average Pore Size (D50), mm
1 (WA)	304 ± 9	1.52 ± 0.04	85.0 ± 2.5	5.00	0.26
2 (CaO)	658 ± 9	1.63 ± 0.05	68.1 ± 2.1	2.48	0.04
3 (MgO)	285 ± 8	1.35 ± 0.04	86.0 ± 2.6	4.74	0.41
4 (ZnO)	318 ± 9	1.42 ± 0.04	84.4 ± 2.5	4.47	0.33
5 (TiO ₂)	314 ± 9	1.92 ± 0.06	84.6 ± 2.5	6.11	0.39
6 (Al ₂ O ₃)	320 ± 9	1.94 ± 0.06	84.3 ± 2.5	6.06	0.42
7 (SiC)	371 ± 11	1.38 ± 0.04	81.8 ± 2.4	3.72	0.38
8 (ZrO ₂)	326 ± 10	2.03 ± 0.06	84.0 ± 2.5	6.23	0.44

In general, the foaming process does not directly participate in the geopolymerization process, but it plays a crucial role in forming the porous material. Foaming occurs due to the increase in gas volume generated on the surface of aluminum metal particles uniformly distributed in the volume of the geopolymer mixture.

As seen in Figure 1, the initial stage involves the molding of the reactive mixture into cubic shapes. At the second stage, gas formation begins, leading to the expansion of micro-pores formed due to the gas pressure on the pore walls and the adjacent liquid geopolymer mixture. As the reaction takes place in an aqueous medium, the formation of hydroxo-complexes occurs, with hydroxide ions (OH⁻) serving as ligands, as seen in Reactions (3) and (4):



Overall, the processes described above can be summarized by Reaction (5):



During these processes, forces act on the walls of gas pores, contributing to the creation of a porous structure in the geopolymer material. The resulting pores have shapes resembling either spheres or ellipsoids—elongated or fused bimodal pores. This final cellular structure of the material is solidified through the drying and curing processes.

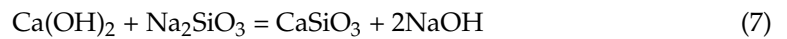
The hydrogen gas can escape from the pores of the foamed geopolymer replaced by air. This is due to the small radius of the hydrogen atom and its high penetrating ability [30]. The penetration of air into the pore space of the geopolymer is explained by the presence of mesopores in the inter-pore partitions of the material.

Sample 1 (WA, without additives) was synthesized for the purpose of facilitating a comparative assessment with samples with additives. It manifests a well-developed cellular structure. The pore sizes are in the range of 0.1–3 mm. However, its compressive strength is confined to a mere 1.52 MPa.

Sample 2 (CaO) with calcium oxide addition exhibits an elevated density and concurrently demonstrates an unsatisfactory cellular structure. Single pores measuring 1–2 mm are observed. Upon introducing CaO into the reaction mixture, it undergoes an interaction with water to form calcium hydroxide according to Reaction (6):



In turn, the formed calcium hydroxide reacts with sodium silicate, the main component of sodium liquid glass, resulting in the formation of insoluble calcium silicate according to Reaction (7):

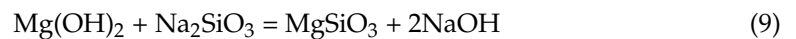


The formation of insoluble calcium silicate leads to the rapid densification and inhibits the geopolymerization reaction, indicating the impracticality of using CaO as a strengthening additive.

The addition of magnesium oxide to Sample 3 (MgO) allows samples with the lowest density to be synthesized. Probably, the effect of the addition of magnesium oxide on the density of the geopolymer is associated with the effect on the deformation behavior of the material as it reduces its shrinkage. Magnesium oxide is capable of reacting with free $[\text{SiO}_4]$ to form a magnesium silicate gel [31]. It is also possible for magnesium oxide to interact with water, forming sparingly soluble magnesium hydroxide according to Reaction (8):

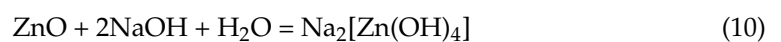


In turn, magnesium hydroxide can react with sodium silicate to form insoluble magnesium silicate according to Reaction (9):



The formation of carbonization products or magnesium hydroxide, which are often observed in hydrated MgO-containing Portland cement, are almost absent [32]. The resulting magnesium silicate gel, possessing a porous structure, likely contributes to the formation of the low-density final material.

The properties of Sample 4 (ZnO) reveal the detrimental influence of zinc oxide on the strength properties of the foamed geopolymer material, with a 7% decrease in strength. Presumably, this stems from zinc oxide's adverse effects on the geopolymer system, hindering the formation of geopolymer gels, polymerization, and condensation processes [33]. With the introduction of zinc oxide into the geopolymer mixture, a significant consumption of sodium hydroxide occurs through its interaction with ZnO according to Reaction (10):



The resulting sodium tetrahydroxozincate is a ballast substance in the geopolymer mixture as it does not participate in the geopolymerization processes. Furthermore, it reacts

with sodium silicate, consuming it to form insoluble sodium–zinc silicate according to Reaction (11):



Sample 5 (TiO_2), with titanium dioxide as an additive, exhibits a favorable impact on the strength characteristics of foamed geopolymer material, with a significant 21% strength increase. The inclusion of TiO_2 leads to the formation of nanocrystals within the geopolymer mixture, augmenting the material's strength properties. Furthermore, the incorporation of titanium dioxide holds promise for the production of photocatalytically active geopolymer materials [34]. However, the relatively high cost of titanium dioxide limits its widespread application. Moreover, there is a possibility of interaction between titanium dioxide and sodium hydroxide, leading to the formation of sodium hexahydroxotitanate according to Reaction (12):

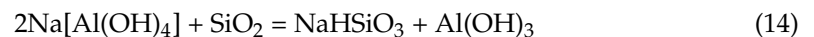


However, the formed complex has no impact on the strength properties of foamed geopolymer materials.

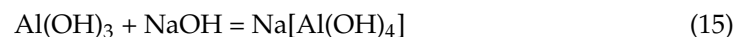
The properties of Sample 6 (Al_2O_3) illustrate that the incorporation of aluminum oxide yields a beneficial effect on the strength of foamed geopolymer materials, with a 22% increase in strength. This can be attributed to the formation of additional Si-O-Al bonds. Also, aluminum oxide has the capacity to interact with an alkaline activator solution (Reaction (13)), leading to the creation of an additional quantity of geopolymer gel:



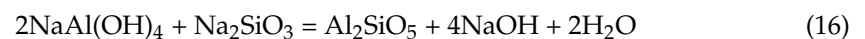
Furthermore, the sodium tetrahydroaluminate formed in these interactions can react with amorphous silicon dioxide, leading to the formation of sodium hydrosilicate solutions participating in the geopolymerization process and the precipitation of aluminum hydroxide according to Reaction (14):



The freshly precipitated aluminum hydroxide can undergo a secondary reaction with sodium hydroxide according to Reaction (15):



The newly formed hydroxo-complex can again react with amorphous silicon dioxide according to Reaction (14). Additionally, the considered hydroxo-complex can interact with sodium silicate, forming aluminum silicate according to Reaction (16):



These mechanisms indicate that the addition of aluminum oxide contributes to the transition of silicon dioxide into a solution and the formation of new components in the geopolymer mixture, so it enhances geopolymerization processes. Furthermore, it is worth noting that Al_2O_3 can also be sourced from natural materials, which tend to be more cost-effective compared to their synthetic counterparts.

The introduction of silicon carbide (Sample 7) had an adverse impact on the mechanical strength of geopolymer foams. There is a notable 10% reduction in strength. This phenomenon can be attributed to the remarkable chemical resistance of silicon carbide, coupled with its high particle hardness. Silicon carbide is highly chemically inert and does not interact with the components of the geopolymer mixture. Possessing high mechanical characteristics and good compatibility with the geopolymer matrix, silicon carbide is regarded as a reinforcing additive. As indicated by [35], the hydrophilicity of silicon carbide and the bonding with the inorganic polymer framework resulted in a strong interfacial

bond in the geopolymer concrete between the SiC filler and the geopolymer mass, leading to a 49% increase in material strength. This conclusion applies exclusively to monolithic geopolymers, as research has shown that silicon carbide has a negative impact on the strength of foamed geopolymer materials. It was observed that the abrasive particles of silicon carbide hinder the bonding of fine pore walls, significantly impairing the material's mechanical strength.

The addition of zirconium dioxide had the best effect on the strength properties of the test sample. Thus, for Sample 8 (ZrO_2), the strength increased by 26%, which is associated with the ability of zirconium dioxide to form bonds with three-dimensional polysialate chains. It leads to a decrease in the mobility of alkali metal ions. Hence, zirconium dioxide (ZrO_2) fails to participate in the geopolymerization reaction; instead, it becomes embedded within polysialate networks, contributing to the formation of a robust microstructure [36]. However, it is essential to acknowledge that zirconium dioxide ranks among the most expensive substances examined in this study, which imposes significant limitations on its practical applicability. According to [37], zirconium dioxide forms bonds with three-dimensional polysialate chains, reducing the mobility of sodium ions. It does not participate in geopolymerization reactions; rather, it acts as a filler penetrating between the polysialate networks, leading to the formation of a rigid microstructure of the material.

The obtained regularities are in accordance with previous studies. In [25], as previously mentioned, the effect of magnesium oxide on the properties of geopolymer concretes was conducted. These conclusions about the reduction in material shrinkage are generally valid and applicable to foamed geopolymer materials, which exhibit somewhat different properties compared to geopolymer concretes. In the work [38], it was found that the addition of aluminum oxide to geopolymer concretes based on metakaolin and volcanic ash increased the material's strength by 18%. Similarly, the addition of aluminum oxide was observed to increase the strength of foamed geopolymers by 22%.

In [29], the influence of zinc oxide nanoparticles on the properties of geopolymer concretes was studied. The authors claimed that the inclusion of 0.5% zinc oxide in the geopolymer mixture increased the material's strength by 26%. However, additions beyond 0.5% led to a deterioration in the properties of geopolymers, a finding corroborated by the present study. It was established that a 3% addition of zinc oxide adversely affects the strength of foamed geopolymer materials.

According to [36], the inclusion of 3% zirconium dioxide increased the strength of the developed geopolymer concrete by 30%. Overall, the impact of zirconium dioxide on the strength of foamed geopolymer materials is analogous, with an observed increase in material strength by 25%.

In the research [39], the authors claimed that a 5% addition of titanium dioxide increased the strength of their developed geopolymer materials by 52%. However, when using titanium dioxide to strengthen foamed geopolymer materials, the strength increased by only 21%.

Overall, a comparative analysis with other scientific studies primarily related to strengthening geopolymer concretes using similar additives shows that strengthening additives have a similar effect on foamed geopolymer materials compared to dense geopolymer concretes. However, there was an exception; silicon carbide worsens the properties of foamed geopolymers, but it enhances the strength of geopolymer concretes.

Considering the resulting properties, porous structure, and cost, the following additives influencing the physical and mechanical properties of foamed geopolymer materials were chosen for the following study: magnesium oxide MgO and aluminum oxide Al_2O_3 . Excluding expensive compounds (TiO_2 and ZrO_2), MgO and Al_2O_3 allow the highest relative strength and acceptable parameters of porous structure to be obtained. Moreover, MgO addition results in achieving materials with the lowest density, which is important for insulating properties. Consequently, Samples 3 (MgO) and 6 (Al_2O_3) emerge as the preferred choices for achieving the required geopolymer characteristics. These geopolymer materials meet the necessary operational properties: high strength, low density, and relative

cost-effectiveness of production. This allows their utilization in various fields, ranging from the construction and insulation of civil and industrial structures to the engineering of insulated pipelines, containers, reactors, road construction, etc. For instance, road construction in harsh climatic conditions requires thermal insulation materials with a strength of no less than 0.5 MPa. The developed foamed geopolymer materials with the chosen strengthening additives completely meet the necessary operational properties of thermal insulation materials for road construction.

3.3. Study of X-ray Phase Analysis and Microstructure of Samples with Chosen Additives

An X-ray phase analysis of Samples 3 (MgO) and 6 (Al₂O₃) was carried out. The results are shown in Figure 5.

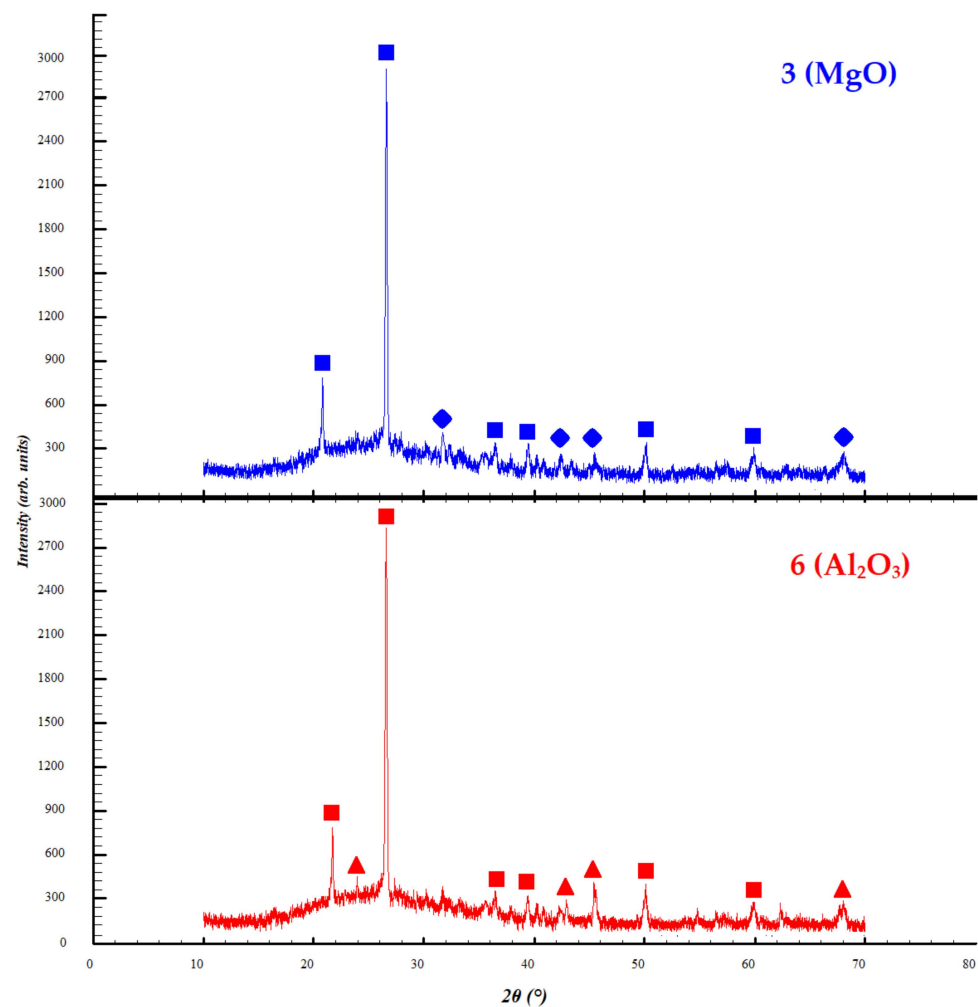


Figure 5. X-ray analysis of Samples 3 (MgO) and 6 (Al₂O₃); ■—high quartz (SiO₂); ◆—periclase (MgO); ▲—aluminum oxide (Al₂O₃).

As can be seen from Figure 5, Sample 3 (MgO) contains crystalline phases in the form of high quartz (content 24.3%) (PDF number: 010-75-8322) and periclase (content 5.1%) (PDF number: 010-77-2364). An amorphous glassy phase is also observed (content 70.6%). Sample 6 (Al₂O₃) contains a crystalline phase in the form of high quartz (content 25.6%) (PDF number: 010-75-8322) and α -alumina (content 8.4%) (PDF number: 010-79-8917). A significant amount of amorphous glassy phase (76.0%) is also observed.

Figure 6 shows the pore distribution in the studied samples 3 (MgO) and 6 (Al₂O₃).

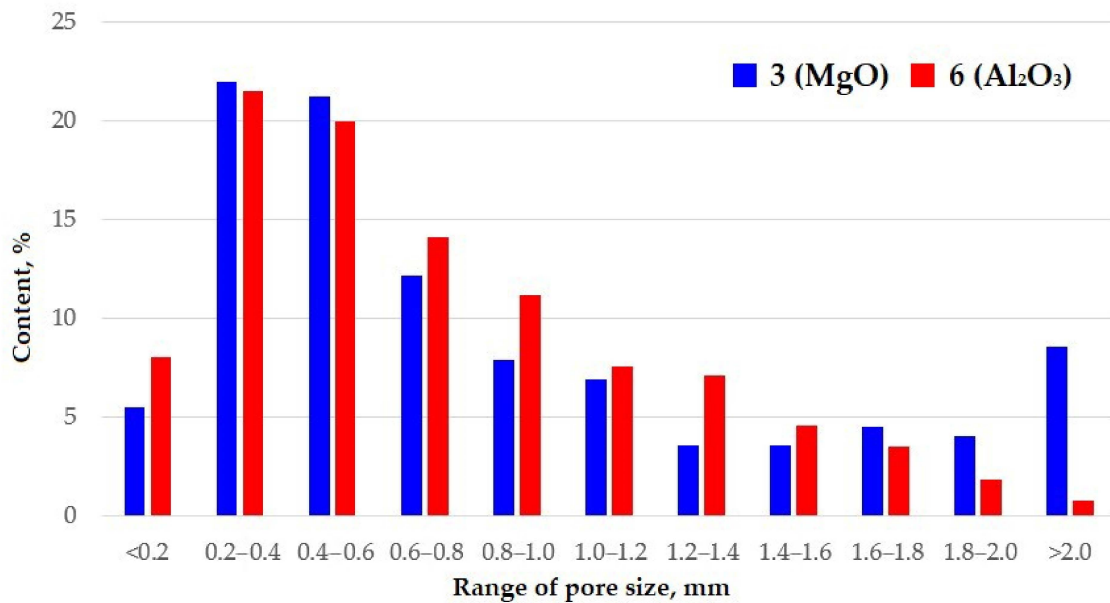


Figure 6. Pore distribution in Samples 3 (MgO) and 6 (Al₂O₃).

As can be seen from Figure 6, both samples contain a significant amount of macropores in the range of 0.2–0.6 mm (43.20% in Sample 3 (MgO) and 41.51% in Sample 6 (Al₂O₃)). Sample 3 (MgO) also contains 8.59% of pores larger than 2 mm. This clearly confirms that magnesium oxide reduces the shrinkage of the material, as the sample containing its additive contains larger macropores. The resulting histogram shows that the distribution of pores is homogeneous in both samples.

The microstructure of Samples 3 (MgO) and 6 (Al₂O₃) obtained using a scanning electron microscope is presented in Figure 7.

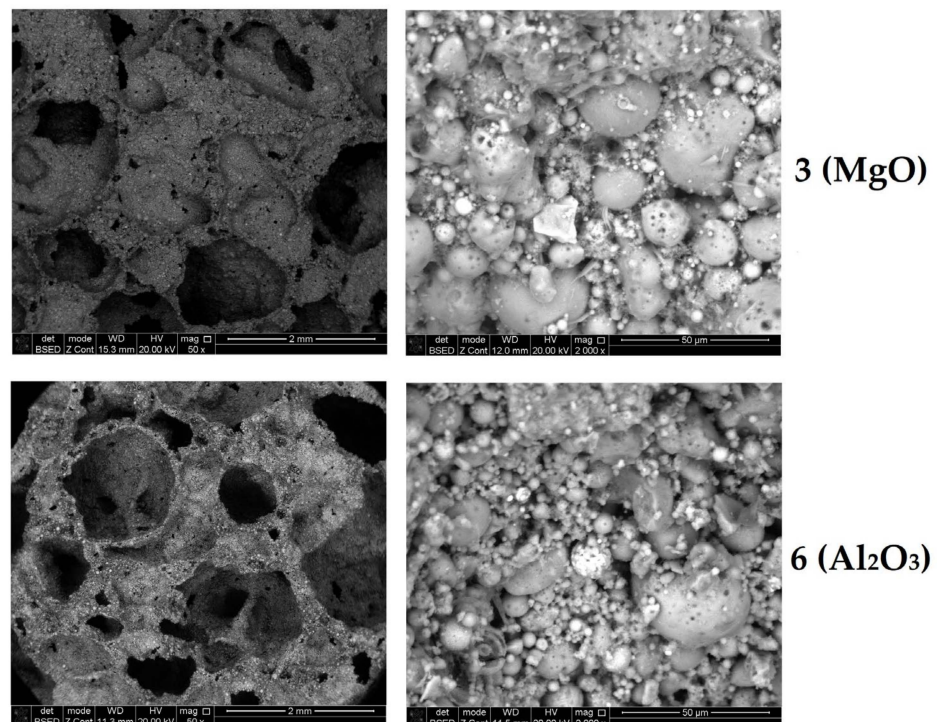


Figure 7. Microstructure of foamed geopolymer material samples 3 (MgO) and 6 (Al₂O₃).

As can be seen from Figure 7, the samples have a developed porous structure. Pores measuring 0.5–1.5 mm are observed. The structure of the material, as well as the pore walls, is composed of hollow aluminosilicate microspheres, with sizes ranging from 1 to 30 μm .

3.4. Study of the Influence of Additives on the Properties of Geopolymers Based on Other Raw Materials

To verify the discovered influence of strengthening additives, geopolymer mixtures based on a ash and slag mixture (ASM) of the Novochoerkassk State District Power Plant (SDPP) were synthesized. This type of waste is generated during the combustion of substantially different coals. The chemical and phase composition of the ASM at the Novochoerkassk State District Power Plant was previously studied [40]. Three series of samples were developed based on Compositions 1, 3, and 6 (Table 2). The “N” letter in composition name stands for the origin of ASM–Novochoerkassk SDPP. The macrostructure of the synthesized samples is shown in Figure 8. The properties of the obtained samples of foamed geopolymers are given in Table 4.

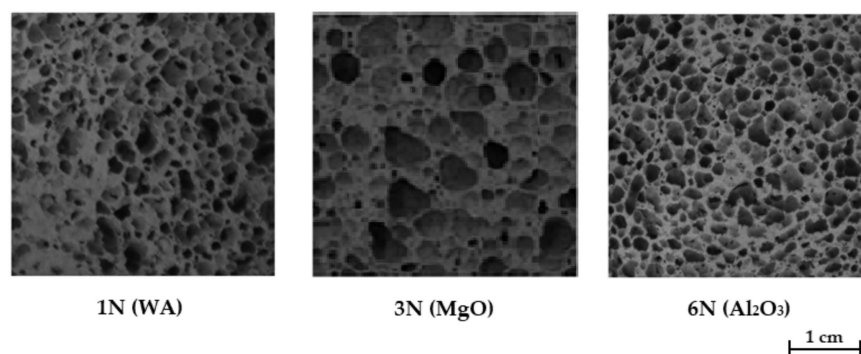


Figure 8. Macrostructure of synthesized samples based on ASM from Novochoerkassk SDPP.

Table 4. Properties of synthesized samples based on ASM from Novochoerkassk SDPP.

Sample	Density, kg/m^3	Compressive Strength, Mpa	Porosity, %	Relative Compressive Strength, $\text{m}^2/\text{s}^2 \cdot 1000$
1N (WA)	320 ± 9	1.36 ± 0.02	85.1 ± 2.5	4.25
3N (MgO)	296 ± 10	1.07 ± 0.02	87.7 ± 2.6	3.61
6N (Al ₂ O ₃)	332 ± 10	1.67 ± 0.03	86.3 ± 2.5	5.03

The results clearly indicate a similar effect of strengthening additives on the structure and properties of foamed geopolymers. The initial sample without additives has a density of $320 \text{ kg}/\text{m}^3$, with a compressive strength of 1.36 MPa. The addition of MgO leads to additional pore growth with a consequent density reduction. As mentioned earlier, this process occurs due to the formation of a porous gel of magnesium silicate, as well as the expansion of its crystals, leading to the inhibition of the shrinkage process. At the same time, structural changes with the magnesium oxide addition lead to an increase in relative strength. The addition of Al₂O₃ slightly increased the sample density but strongly improved its compressive strength. The relative strength of the alumina-containing sample exceeds $5000 \text{ m}^2/\text{s}^2$, which is more than a 15% increase. The Al₂O₃ addition had almost no effect on the porous structure compared with the sample without strengthening additives.

Thus, the positive influence of the chosen additives (MgO and Al₂O₃) on the strengthening of geopolymer materials based on coal combustion waste can be stated. Changes caused by the ASM chemical composition can be diminished using these strengthening substances at a relatively low cost, which allows porous geopolymers with elevated strength and low density to be synthesized.

4. Conclusions

Industrial waste recycling plays a pivotal role in advancing the goals of sustainable development and the preservation of finite nonrenewable mineral resources. Within this context, the potential of harnessing mineral waste derived from coal combustion to create foamed geopolymers represents a promising avenue for the development of carbon-neutral materials. The investigation centered on assessing the impact of strengthening additives on the physical and mechanical properties of foamed geopolymer materials derived from coal combustion waste (CCW) from Severodvinsk CHPP-1. Chemical, X-ray phase, and microstructural analyses of coal combustion waste (CCW) from the Severodvinsk CHPP-1 were conducted. The material was identified as an aluminosilicate structure containing a significant amount of an amorphous phase. The microstructure revealed a high presence of hollow aluminosilicate microspheres.

Eight series of samples with various strengthening additives (CaO, MgO, ZnO, TiO₂, Al₂O₃, SiC, and ZrO₂) were synthesized using this CCW. An investigation into the synthesized samples was carried out, determining their properties and examining the chemical processes occurring with each additive. The following additives were chosen for the study: Al₂O₃ (a density of 320 ± 9 kg/m³ with a compressive strength of 1.94 ± 0.06 MPa) and MgO (a density of 285 ± 8 kg/m³ with a compressive strength of 1.35 ± 0.04 MPa). X-ray phase analysis of the chosen compositions revealed the presence of the crystalline phases of high quartz and aluminum oxide or periclase. Microstructural analysis identified that the geopolymer samples consisted of hollow aluminosilicate microspheres and micropores sized 0.5–1.5 mm.

To confirm the obtained results, investigations were conducted on the impact of the chosen additives on the properties of geopolymers based on raw material from a different source—CCW from the Novocherkassk SDPP. Reproducibility of the earlier results was observed, indicating the potential application of strengthening additives for geopolymers based on various raw materials.

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