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Article

Physical, Mechanical and Microstructural Characteristics of Perlite-Based Geopolymers Modified with Mineral Additives

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Abstract: One of the promising raw materials for the synthesis of geopolymers is perlite, which is a natural low-calcium aluminosilicate. This research studied the physical, mechanical and microstructural characteristics of perlite-based geopolymers modified with different mineral additives that were prepared using different methods of introducing the alkali components and curing conditions. The experimental results of the consolidated perlite-based geopolymer pastes showed that curing conditions and the method of introducing the alkali component into the geopolymer matrix had a minimal effect on the average density while demonstrating a significant boost in compressive strength. So, after thermal treatment, the compressive strength increased by 0.63 to 11.4 times for the mixes when fresh alkali solution was used and by 0.72 to 12.8 times for the mixes with the 24 h conditioned alkali solution. Maximum-strength spikes from 1.1 MPa to 13.2 MPa and from 0.7 MPa to 9.7 MPa were observed for the mixes with kaolin when prepared with fresh and conditioned alkali solutions, respectively. It was also observed that thermal treatment facilitates the compaction of the matrix structure by 18% and 1% for the non-modified mix and the mix modified with Portland cement. Perlite-based geopolymers modified with Portland cement and citrogypsum demonstrated a significant reduction in the initial and final setting times with both methods of introducing the alkali solution. On the surface of mixes modified with citrogypsum, regardless of the curing conditions and method of introducing the alkali component, an efflorescence substance was observed. The microstructural analysis of the consolidated geopolymer perlite-based pastes containing citrogypsum demonstrated a loose structure and the presence of efflorescence, which can be associated with a retardation in interaction processes between alkali cations and the aluminosilicate component. EDS analysis demonstrated that the presence of such elements as oxygen, sodium and sulfur may indicate the efflorescence of unreacted sodium hydroxide (NaOH), citrogypsum ($CaSO_4$) and the products of their interaction in the form of crystalline hydrates of sodium sulfate (Na_2SO_4).

Keywords: perlite; geopolymer; mineral additive; Portland cement; kaolin; metakaolin; citrogypsum; physical and mechanical characteristics; efflorescence; microstructure

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1. Introduction

The current tendency to reorient the building materials industry towards eco-friendly technologies and the development of alternatives to cement binders [1–4] are primarily caused by the continuous increase in emissions of pollutants into the environment due to the activities of industrial production around the world. Cement production is considered one of the most popular polluting industries in the construction sector. The development of the construction industry is growing steadily. This is leading to an increase in demand for Portland cement (PC) as a key component for building materials. At the same time, in accordance with existing global restrictions, there are extremely unfavorable conditions for cement producers, which complicate the production process and significantly increase the cost of the final product, making it uncompetitive and unattractive to the consumer. Thus, the current situation forces scientists around the world to simultaneously solve several of the following urgent problems:

- The development of zero waste production methods [5];
- The utilization of industrial and household waste in the production process [6–8];
- The production of alternative free-of-cement binders [2–4];
- The development and application of environmentally friendly production technologies [9,10].

As of now, Much research has been conducted with a focus on the above four problems. Many of the developments have already found their practical applications.

One of the promising materials, which allows for the mitigation of all the above mentioned industrial problems, is geopolymer binders. Today, there is much scientific research focused on the use of natural raw materials, as well as industrial and household waste in geopolymer materials.

The most common raw material for the synthesis of geopolymers is industrial waste products, such as fly ash [11], fuel slag [12] and metallurgical slag [13].

However, despite the undeniable advantages of using industrial waste in geopolymer production, it also has significant drawbacks, which include the considerable variability of the chemical and mineral composition as well as the quantitative content of constituents. Usually, this is due not only to the characteristics of the feedstock (coals, ore, etc.) but also to different parameters of the technological process of formation and the subsequent storage of this waste. This fact greatly complicates waste utilization and, therefore, significantly limits the scope of its practical application.

Natural raw materials that can be used as the main components of binders include aluminosilicate rocks of various origins [14]. From the point of view of composition uniformity and the stability of properties, natural raw materials are preferable. The authors of reference [15] proposed the use of laterite as the main raw material for the synthesis of eco-friendly and stable high-strength geopolymer composites, porous matrices for filtration, the removal of heavy metals or their encapsulation, membranes for catalysis, etc. According to the authors, laterite is associated with iron minerals that have a disordered structure or a low level of crystallization and, therefore, exhibit good solubility in a highly concentrated alkaline solution.

At the same time, the microstructure is characterized by rather large pores and microcracks, as well as weak flexural strength. Lateritic geopolymers are activated and cured at room temperature in the same way as those based on metakaolin.

In another study [16], kaolinic clays were considered a natural aluminosilicate for the synthesis of geopolymers. The research results showed that consolidated geopolymer pastes can achieve a compressive strength from 11.9 to 36.4 MPa. However, kaolinic clays require high-temperature treatment from 450 to 700 °C before use for geopolymer synthesis. In addition, even with calcined kaolinic clay, it takes up to 21 days for the geopolymer pastes to set.

Allahverdi A. et al. [17] established the possibility of obtaining geopolymers by activating natural pozzolans with solutions of NaOH and Na_2SiO_3. The resulting geopolymer pastes demonstrated suitable workability and 28-day compressive strengths of up to 63 MPa.

Volcanic ash or natural pyroclastic pozzolan is a material formed after the cooling of magma during volcanic eruptions. Pyroclastic materials are of great importance for the synthesis of geopolymers due to their high content of amorphous silica. In some works, such as [18,19], studies were aimed at the use of volcanic ash in alkali-activated materials.

Some studies have examined and proven the effectiveness of using perlite as an aluminosilicate raw material for the synthesis of geopolymers with compact [20–22] and porous [23] structures. Depending on the type of alkaline activator and curing conditions, the compressive strength can reach 15–50 MPa; flexural strength up to 5 MPa, when samples are cured in a dry oven at 65–120 °C; and compressive strength 30–40 MPa, when samples are cured at room temperature.

To valorize industrial and natural aluminosilicates for the synthesis of geopolymer materials, additives of different origins and different purposes are used. In [24], the authors talk about the positive effect of the addition of metakaolin in the composition of a natural clay-based geopolymer. In [25], calcined kaolinic clay as a source of reactive aluminum was added to perlite-based geopolymer. It was found that the addition of 10% calcined kaolinic clay leads to improvement in the physical and mechanical properties of geopolymer binder cured at room temperature. Another work [26] is devoted to the study of the effect of the crushed peel of ripe bananas on the properties of calcined halloysite activated with an alkaline silicate solution. It has been established that the introduction of up to 10% powdered banana peel in geopolymer paste immediately leads to an improvement in some following characteristics: an increase in compressive strength and average density due to a more efficient flow of chemical interaction between the components. At the same time, an increase in the setting time of the binder system is observed due to additional alkali cations, such as K^+ and Na^+, in the powdered banana peel.

There have also been several studies on replacing aluminosilicate powders with silica-rich agricultural waste to optimize the SiO_2/Na_2O molar ratio, which is a key parameter for improving the reactivity, physical and chemical properties and durability of geopolymer cement. For example, Tchakoute et al. [27] synthesized sodium silicate from rice husk ash mixed with sodium hydroxide. This made it possible to achieve good mechanical characteristics of the final products.

Also, in some works devoted to the modification of geopolymers, the use of calcium-based components is considered. One of the features of the effective hardening of geopolymers is the use of temperature treatment. In the study [28], to improve the processes of structure formation at room temperature, PC was introduced as an additive into a metakaolin-based geopolymer binder. The results showed that the addition of up to 20% PC significantly improved the compressive strength from 9.9 to 30.5 MPa and the tensile strength from 1.2 to 2.2 MPa. In the work [29], the authors investigated the influence of lime and gypsum as a mineral modifier on the properties of metakaolin-based geopolymers and found that the use of lime increases the fluidity of the mixture, while the addition of gypsum decreases the fluidity. Also, the introduction of 10 % lime increases compressive strength up to 210 %. In the reference [30], the authors investigated the modification of metakaolin-based geopolymer with silicon phosphate to provide waterproof characteristics. Reference [31] is devoted to the combination of fly ash and various mineral additives (Portland cement, metakaolin, kaolin, citrogypsum) and the study of their effect on mechanical, thermal and physical characteristics of geopolymer cement. The literature review showed that scientific research focused on the study of geopolymers based on natural aluminosilicates is widespread. However, very little information is provided about perlite-based geopolymers: their properties, production technologies and the use of modifying components.

The subject of the current research was to study the combined effect of different production methods and different curing conditions on physical, mechanical and structural characteristics of perlite-based geopolymer paste modified with different mineral additives.

The results obtained in this research are valuable for expanding the raw material spectrum for the production of geopolymers, as well as for attaining a deeper understanding of the potential for geopolymer materials as an alternative to PC.

2. Materials and Methods

Commercial perlite (P) from Perlite OJSC deposits in Russia were used as the basic aluminosilicate component. The following products were used as mineral additives: Portland cement CEM I 42.5 (PC), commercial kaolin (K) from Plast-Rifey LLC, Russia, laboratory-synthesized metakaolin (MK) and citrogypsum (CG) from Citrobel Company, Russia. Visual appearances of these products are presented in Figure 1.

Figure 1. Used mineral raw materials (**a**) P (perlite); (**b**) K (kaolin); (**c**) MK (metakaolin); (**d**) PC (Portland cement); (**e**) CG (citrogypsum).

Citrogypsum is a waste product of the biochemical production of citric acid. Visually, it is a finely dispersed gray powder.

Sodium hydroxide (NaOH) (98% purity) as an aqueous solution was used as an alkaline activating agent.

Despite the fact that perlite proves to be a suitable aluminosilicate precursor for geopolymers, the production of perlite-based geopolymer has some constraints that limit its use, which are a very long setting time, slow strength development and low ultimate strength characteristics when geopolymer paste is cured at room temperature. This requires application of thermal treatment of at least 40 °C. Therefore, the choice of modifying components of different origins and properties is aimed at studying the effectiveness of addressing each of the above-mentioned limitations in perlite-based geopolymer binders. Thus, the authors suggest that PC and citrogypsum can accelerate setting time and further hardening of the geopolymer at ambient conditions.

Metakaolin is used as a source of highly reactive alumina, capable of intensifying geopolymerization processes at room temperature. However, taking into account energy-intensive process of metakaolin production (i.e., calcination of kaolinite at 600–800 °C), its high cost should be noted. Therefore, in this research, the original component, kaolin, was used as an additional modified additive to compare its effectiveness with metakaolin.

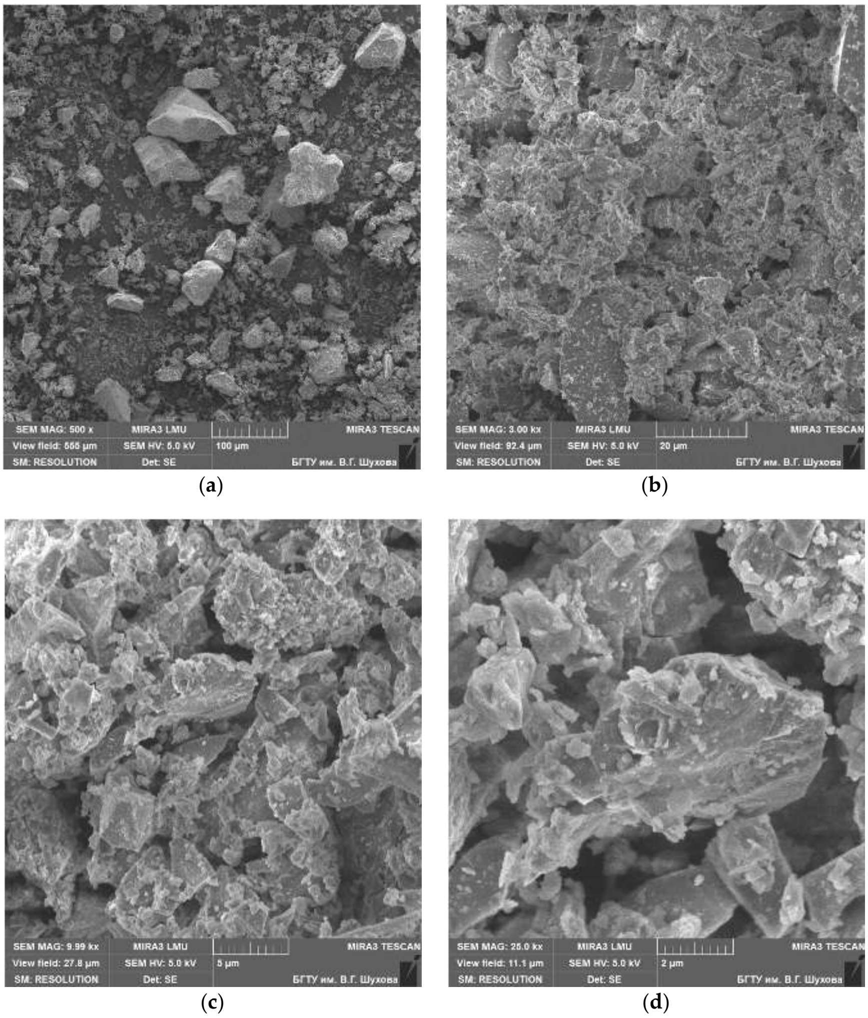
Perlite crushed stone with a fraction of 5–10 mm was used as the original raw material. Therefore, prior to its use for synthesis of geopolymer pastes, it was subject to crushing followed by grinding process. For crushing perlite stone, a laboratory jaw crusher ShD-6

(Vibrotechnic) was used. The average particle size of the crushed perlite product at the minimum gap between the jaws was 0.5–1 mm.

Grinding of crushed perlite stone was carried out in a laboratory ball mill RMSh-12 (Russia) with a volume of 15 L. Preliminary studies have shown that grinding for longer than 2.5 h in this mill is not effective because the increase in perlite dispersion is practically not observed. Therefore, in this research work, the grinding process was carried out for 2.5 h. The specific surface area (SSA) of perlite after grinding was 482.2 m^2/kg. Uralite cylinders 35 × 35 mm in size were used as grinding bodies. The ratio of grinding media to ground material was 3:1.

The microstructure of particles of crushed perlite and samples of perlite-based geopolymer with different mineral modifiers was studied using scanning electron microscopy (SEM). A scanning electron microscope (Tescan, Czech Republic) operated in the high vacuum mode (InBeam) with a high-brightness Schottky cathode applied. Before analysis, all test samples were pre-coated with a thin layer of chrome (Cr) for better conductivity.

To be able to assess the efficiency of chemical processes in experimental samples of geopolymer binder, Figure 2 shows the microstructure of dispersed perlite.



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

Figure 2. Microstructure of perlite after grinding in a ball mill (SSA = 482.2 m^2/kg) at different resolution: (**a**) ×500; (**b**) ×3000; (**c**) ×10,000; (**d**) ×25,000.

On the presented SEM images a wide range of particle size distributions is observed, from dust-like up to large ones, which are in the size range from 200 nm to 100 microns. Moreover, the content of fine and dust-like particles is much higher than that of large particles.

From the point of view of particle morphology, an angular anisometric shape (Figure 2a) characterizes both coarse and fine particles.

At higher resolution (Figure 2b–d), one can see the morphology of dust-like particles, which are characterized by a lamellar and flaky shape, as well as a smooth surface, which is explained by the vitreous structure of perlite and the conchoidal fracture characteristic of such rocks. It should also be noted that there is a significant concentration of aggregates of particles smaller than 1 micron, which evenly cover the surface of larger grains.

Thus, based on Figures 1 and 2, all mineral components used are finely dispersed powders. Their chemical composition and some physical characteristics are presented in Tables 1 and 2, respectively.

Table 1. Oxide composition of mineral components.

Component	Oxides Content, (wt.%)									
	SiO_2	Al_2O_3	P_2O_5	K_2O	Na_2O	CaO	Fe_2O_3	MgO	TiO_2	SO_3
P	71.3	16.0	–	3.76	5.5	1.05	1.26	0.38	0.16	–
PC	19.1	5.21	–	0.60	–	65.4	3.58	1.28	0.32	–
K	53.8	43.4	0.06	0.56	–	0.01	1.02	0.21	0.58	–
MK	53.1	42.8	–	0.90	–	0.15	0.70	–	0.30	–
CG	0.54	0.13	0.08	0.03	–	43.3	0.15	0.06	–	55.5

Table 2. Physical characteristics of mineral components.

Component	Parameter	
	Specific Gravity	Specific Surface Area (SSA), m^2/kg
P	2.38	482
PC	3.05	320
K	2.61	1091
MK	2.52	1170
CG	2.36	361

The fluorescence components on the surface of geopolymer samples were assessed visually and with scanning electron microscope (Tescan, Czech Republic) using Energy Dispersive Spectrometry (EDS) analysis.

Setting time test of perlite-based geopolymers was realized using the VICAT apparatus according to the ASTM C 191-21 [32].

3. Sample Preparation

For the research experiment, two series of samples of perlite-based geopolymer pastes were prepared. For the first series, a freshly prepared aqueous solution of NaOH was used. For the second series of samples, an aqueous solution of NaOH was conditioned for 24 h before use. The conditioning process was realized with the cooling of a freshly prepared aqueous solution of NaOH at room temperature for 24 h.

The mineral modifier was introduced as a replacement in the amount of 40% by weight of perlite. Two series of experimental geopolymer paste mixes were exposed to two types of curing conditions:

- *Type A*: thermal drying in a laboratory oven according to the following regime: curing at a temperature of 22 ± 3 C and a relative humidity (RH) of 34–38% for 24 h → heating to a temperature of 70 °C for 2 h → isothermal curing at a temperature of 70 °C for 24 h → cooling to a temperature of 22 ± 3 °C for 4 h → demolding and curing at temperature of 22 ± 3 °C and a RH of 34–38% until testing procedure;
- *Type B*: curing at ambient conditions: temperature of 22 ± 3 °C and an RH of 34–38% for 3 days → demolding and curing at a temperature of 22 ± 3 °C and an RH of 34–38% until the testing procedure.

Perlite-based geopolymer paste (PGP), modifier-free, was used as a reference mix.

Mix designs of the experimental geopolymer pastes and their corresponding IDs, which will be used further in the manuscript, are presented in Table 3.

Table 3. Mix design of the geopolymer pastes.

Mix ID	Components, %						
	Perlite	**NaOH**	**Water**	**PC**	**K**	**MK**	**CG**
PGP	73.3	6.1	20.6	–	–	–	–
P-PC	39.0	6.7	28.3	26.0	–	–	–
P-K	38.8	6.7	28.6	–	25.9	–	–
P-MK	37.8	6.5	30.4	–	–	25.2	–
P-CG	41.5	7.2	23.6	–	–	–	27.7

Experimental mixes were prepared with constant flowability: 110–120 mm, according to the cone flow diameter test. Such characteristics as average density and compressive strength were studied for consolidated geopolymer pastes in the form of cubes of $2 \times 2 \times 2$ cm.

The average density (ρ) of experimental samples was determined using the following formula:

$$\rho = \frac{m}{V},$$

where m is the average mass of the experimental cube sample, kg; V is the average volume of the experimental cube, m^3.

The measurement of compressive strength (R) was carried out on a laboratory hydraulic press PGM 100MG4 (with a maximum load limit of 100 kN) according to the following formula:

$$R = \frac{F}{A}, \tag{1}$$

where F is failure load, kN; A is load application area, cm^3.

For each mix, three experimental samples have been prepared. The standard deviations of the presented result for average density and compressive strength were 2–4% and 5–9%, respectively.

To study the microstructural characteristics, chips of freshly crushed geopolymer samples were used.

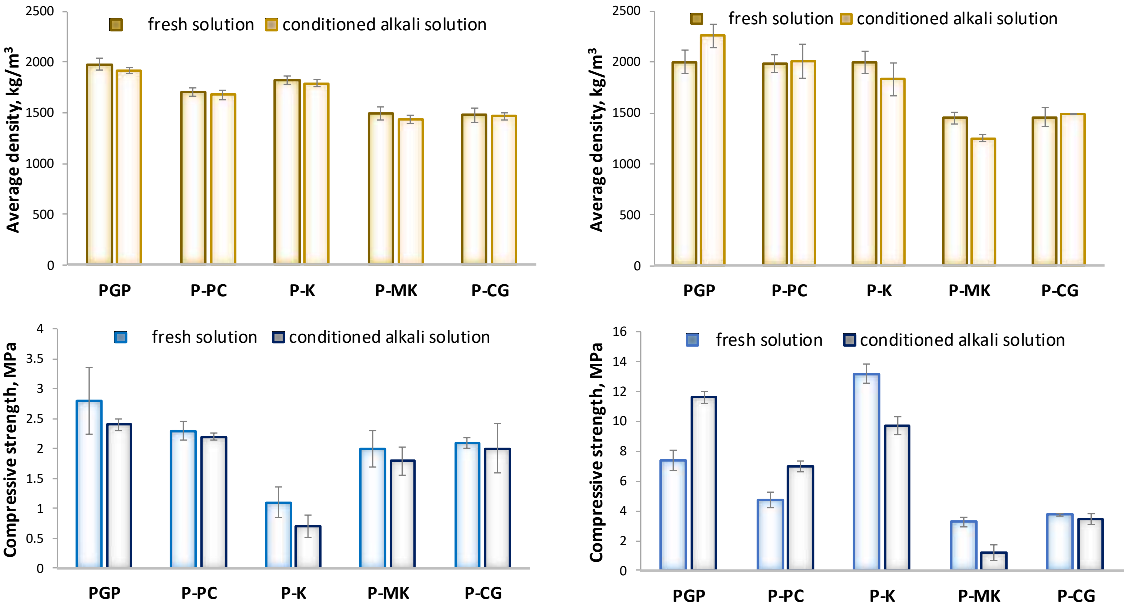
Average density and compressive strength tests, as well as microstructural characteristics, were studied for perlite-based geopolymers after 7 days of consolidation.

4. Results and Discussion

4.1. Compressive Strength and Average Density

Figure 3 illustrates the results of the average density and compressive strength of two series of modified perlite-based geopolymer pastes cured in ambient conditions (Figure 3a) and with thermal treatment (Figure 3b).

The effect of the method of introducing the alkaline activator in geopolymer pastes, cured in ambient conditions, on the values of average density is almost not observed (Figure 3a). At the same time, geopolymer mixes PGP, P-K and P-MK, cured at 70 °C, showed a more noticeable difference in density depending on the method of NaOH solution introduction. However, the trend of this parameter, depending on the mix, is different (Figure 3b). For example, in the reference mix PGP and P-PC mix, the use of a 24 h conditioned alkali solution initiates the compaction of the geopolymer matrix by 13% and 10%, respectively. In the mixes containing kaolin and metakaolin (P-K and P-MK, respectively), on the contrary, the 24 h conditioned alkali solution leads to decompaction of the geopolymer structure by 8.5% and 13%. In the mix modified with citrogypsum (P-CG), there are no significant changes in the average density values, as in the case of the mixes cured in ambient conditions.



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

Figure 3. Physical and mechanical characteristics of perlite-based geopolymer pastes with different mineral modifiers after (**a**) treatment in ambient conditions and (**b**) thermal treatment at 70 °C.

As for compressive strength, in ambient curing conditions, the use of fresh alkali solution provides a stronger geopolymer matrix for all experimental mixes compared to similar values for the 24 h conditioned alkali solution (Figure 3a). The difference in strength indicators ranges from 4% to 36%.

Thermal drying at 70 °C (Figure 3b) generally leads to an increase in compressive strength for all mixes regardless of the method of introducing NaOH. But under temperature conditions for PGP and P-PC mixes, the introduction of 24 h conditioned alkali solution vs. fresh one is most effective. The increase in strength in this case is 57% and 48% for PGP and P-PC, respectively.

According to Figure 3, the introduction of a modifying component into a perlite-based geopolymer matrix leads to a decrease in average density vs. reference PGP in the following sequence, regardless of curing conditions:

$$PGP \rightarrow P\text{-}K \rightarrow P\text{-}PC \rightarrow P\text{-}CG \rightarrow P\text{-}MK,$$

The introduction of a modifying component into a perlite-based geopolymer matrix also leads to a decrease in compressive strength vs. reference PGP in the following sequence:

- In ambient curing conditions: *PGP → P-PC → P-CG → P-MK → P-K*;
- Thermal treatment at 70 °C: *PGP → P-K → P-PC → P-CG → P-MK*.

A comparison of the compressive strength values of perlite-based geopolymer pastes modified by different mineral components showed that the mix modified with kaolin (P-K) forms the weakest matrix in ambient curing conditions, but the strongest matrix was observed for the mixes cured with thermal treatment.

Thus, curing conditions and the method of introducing alkali components into the geopolymer matrix showed almost no effect on average density. However, they affected compressive strength significantly, i.e., provided an increase in compressive strength from 0.63 to 11.4 times for the mixes using a fresh alkali solution and from 0.72 to 12.8 times for the mixes using a 24 h conditioned alkali solution.

However, for mixing P-MK using a 24 h conditioned alkali solution, thermal treatment negatively affects its hardening, resulting in a 33% reduction in compressive strength.

This mineral modifying component, i.e., MK (among the mineral additives studied in this work), leads to a decrease in the values of average density and compressive strength. However, geopolymer paste containing a kaolin modifier cured th thermal treatment, and using fresh alkali solution provides a radical increase in compressive strength, which is as much as 11 times greater than a similar mix, but this was cured in ambient conditions. Moreover, the compressive strength was 3.8 times greater than a reference mix cured in similar conditions (see Figure 3b).

The mechanical characteristics of experimental perlite-based geopolymers showed that when cured in ambient conditions, a metakaolin-modified mix (P-MK) demonstrates higher compressive strength with up to 2 MPa vs. a kaolin-based mix (P-K) with up to 1.1 MPa.

However, with thermal treatment, kaolin demonstrates significantly higher reactivity in the geopolymer matrix and provides a strengthening effect with a compressive strength of up to 13.2 MPa compared to metakaolin used, where the compressive strength was up to 9.7 MPa. Thus, with thermal treatment, kaolin manifests itself as a more reactive modifying additive than metakaolin.

4.2. Setting Time

To study the effect of PC and citrogypsum as mineral additives on the intensification of the structure formation of perlite-based geopolymers cured in ambient conditions, a setting time test was carried out for freshly prepared pastes of experimental geopolymer mixes. The results obtained are shown in Table 4.

Table 4. Setting times of perlite-based geopolymers.

Mix ID	**Fresh Alkali Solution**		**24 h Conditioned Alkali Solution**	
	Setting Time, min			
	Initial	**Final**	**Initial**	**Final**
PGP	More than 3 days		More than 3 days	
P-PC	44	115	79	96
P-K	More than 3 days		More than 3 days	
P-MK	More than 3 days		More than 3 days	
P-CG	39	159	1090	1360

Results of the setting time test (Table 4) showed that the following mixes of perlite-based geopolymers, PGP, P-K and P-MK, do not start setting for more than 3 days. On the other hand, P-PC and P-CG mixes demonstrated a significant reduction in the initial and final setting times with both methods of introducing alkali solution: fresh and 24 h conditioned ones. However, P-PC and P-CG mixes activated by fresh alkali solution are characterized by shorter initial (44 min and 39 min) and final (115 min and 159 min) setting times, respectively, compared to activation by 24 h conditioned solution: initial times are 79 min and 1090 min and final times are 96 min and 1360 min for P-PC and P-CG mixes, respectively.

Thus, the obtained results confirm that mineral additives such as PC and citrogypsum help accelerate the consolidation of perlite-based geopolymers when cured in ambient conditions.

4.3. Efflorescence Effect

In the process of consolidating experimental samples of perlite-based geopolymer pastes, it was revealed that after 30 min of the molding procedure, on the surface of the mix modified with citrogypsum (P-CG), the appearance of a white weak crust is observed, which is probably a product of efflorescence. Efflorescence substance is observed on P-CG cubes regardless of the method by which the NaOH was introduced (Figures 4 and 5) and curing conditions (Figures 4 and 6). However, it is interesting to note that the efflorescence components are formed to a greater extent on the surface of the P-CG sample where a 24 h conditioned alkali solution was used (Figures 4e and 5b).

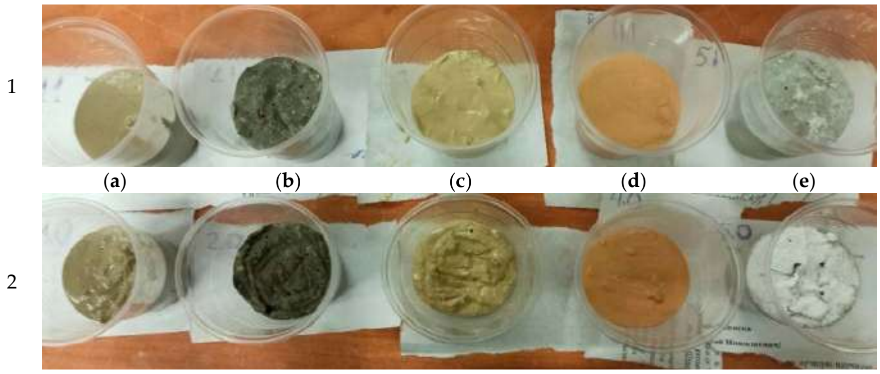


Figure 4. Appearance of perlite-based geopolymer pastes with different mineral modifiers after curing in ambient conditions: (**a**) PGP; (**b**) P-PC; (**c**) P-K; (**d**) P-MK; (**e**) P-CG. 1—fresh alkali solution; 2—24 h conditioned alkali solution. *Note: this image was made 30 min after molding procedure.*

At the same time, the surfaces of perlite-based geopolymer paste P-CG, cured with thermal treatment at 70 °C and with different methods of NaOH, look the same and are characterized by the presence of efflorescence substance covering the entire surface of the samples in the form of a thin weak crust (Figure 6e, red squares).

Probably, the formation of efflorescence components is one of the reasons for the lower compressive strength and average density for P-CG vs. PGP samples (Figure 3). A more clearly undesirable effect of the CG modifier is observed in the P-CG mix after thermal treatment at 70 °C.

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

Figure 5. Efflorescence substance on the surface of mix P-CG, activated with (**a**) fresh alkali solution; (**b**) 24 h conditioned alkali solution. Treatment type—ambient conditions.

On the surface of P-PC samples (Figure 4b), minor areas with efflorescence components are also observed with both methods of NaOH introduction. On the other hand, for PGP, P-K and P-MK mixes, efflorescence components are not observed, regardless of the method of NaOH introduction (Figure 4a,c,d) and curing conditions (Figure 6a,c,d).

The supposed reason for such an intense formation of efflorescence components in P-CG mix, as well as its insignificant manifestation in P-PC mix, may be the presence in the geopolymer matrix of an excessive amount of alkali cations due to the additional introduction of Ca^{2+}, which are in large quantities contained in mineral modifying components PC and CG (at least 60% in PC and at least 90% in CG).

So, perlite-based geopolymer mixes P-PC and P-CG contain alkaline cations Na^{+} and Ca^{2+} in quantities greater than those required for reaction with solid-phase components. In turn, extra alkali is in an unbound state in the binder matrix and begins to actively react with atmospheric CO_2, i.e., the carbonization process takes place.


(**a**) (**b**) (**c**) (**d**) (**e**)

Figure 6. Appearance of perlite-based geopolymer pastes with different mineral modifiers after thermal treatment at 70 °C: (**a**) PGP; (**b**) P-PC; (**c**) P-K; (**d**) P-MK; (**e**) P-CG. Upper level—fresh alkali solution; lower level—24 h conditioned alkali solution.

Thus, the carbonation products are efflorescence components on the sample surface. Considering that the content of efflorescence substance is higher and the compressive strength values are lower in geopolymer pastes prepared with 24 h conditioned alkali NaOH solution, it can be assumed that perlite and the studied modifying components are more reactive under fresh alkali NaOH solution exposure.

4.4. SEM Analysis

To study the manifestation of efflorescence components in P-PC and P-CG not only on the surface but also in the volume of modified perlite-based geopolymer pastes, their microstructure was studied on SEM-images and compared with the microstructure of the reference PGP (Figure 7).

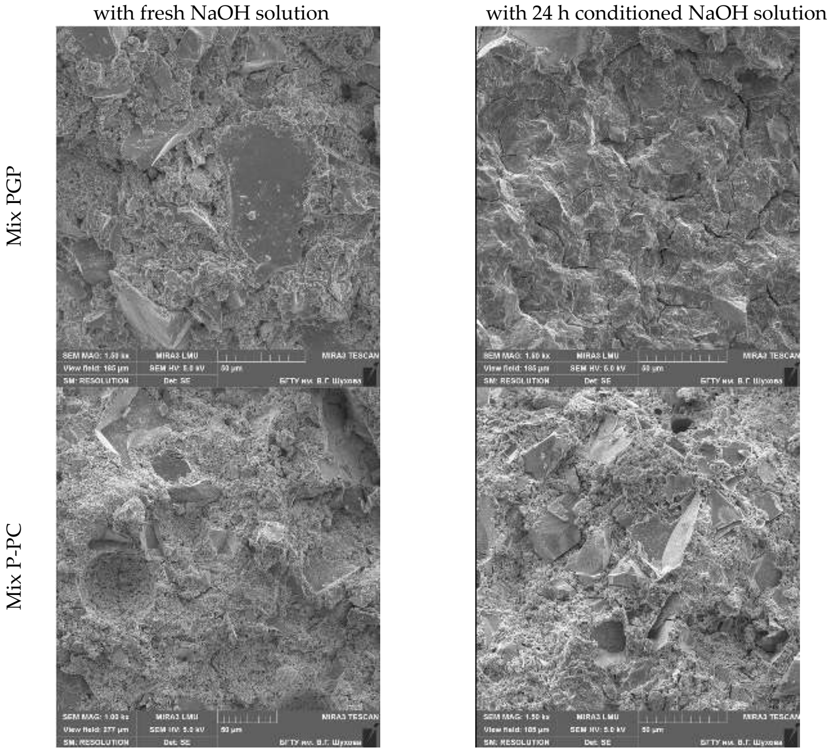


Figure 7. *Cont.*

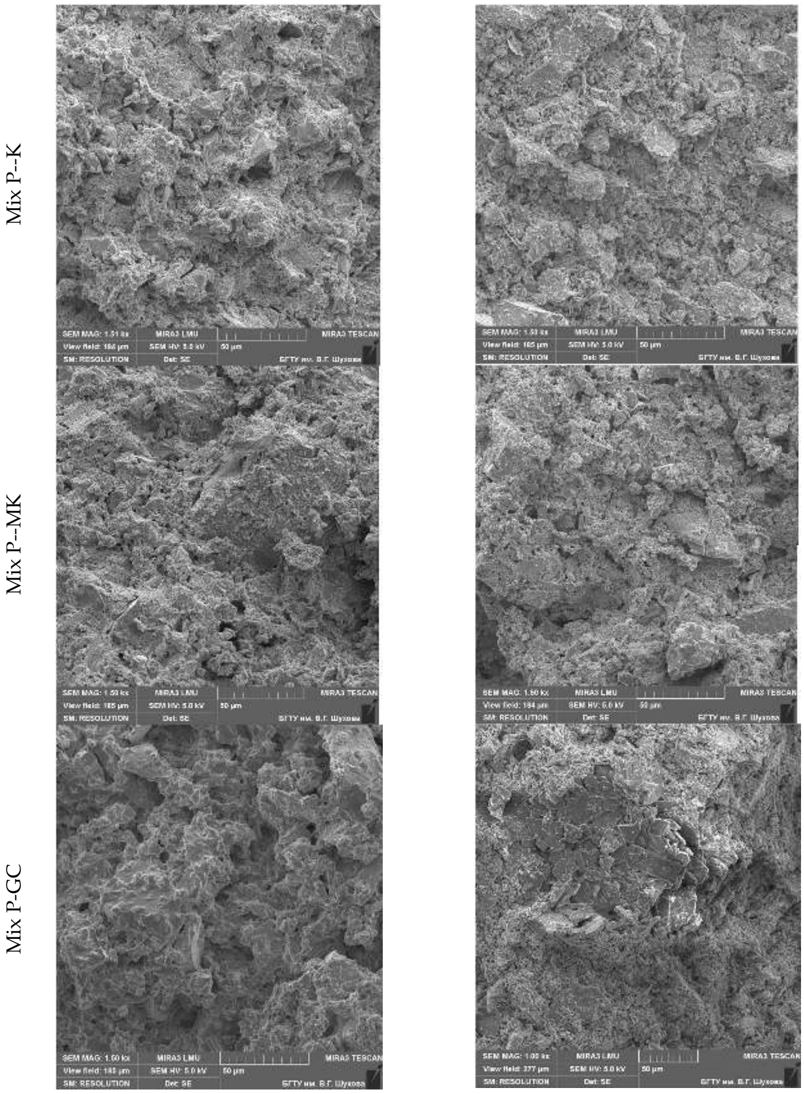


Figure 7. Microstructure of perlite-based geopolymer mixes.

When compared with the microstructure of the reference mix PGP, where clearly defined «perlite grain–monolithic substance» interfaces occur, the structure of mix P-CG obtained using a fresh solution of NaOH looks more monolithic and reflects a high degree of geopolymerization.

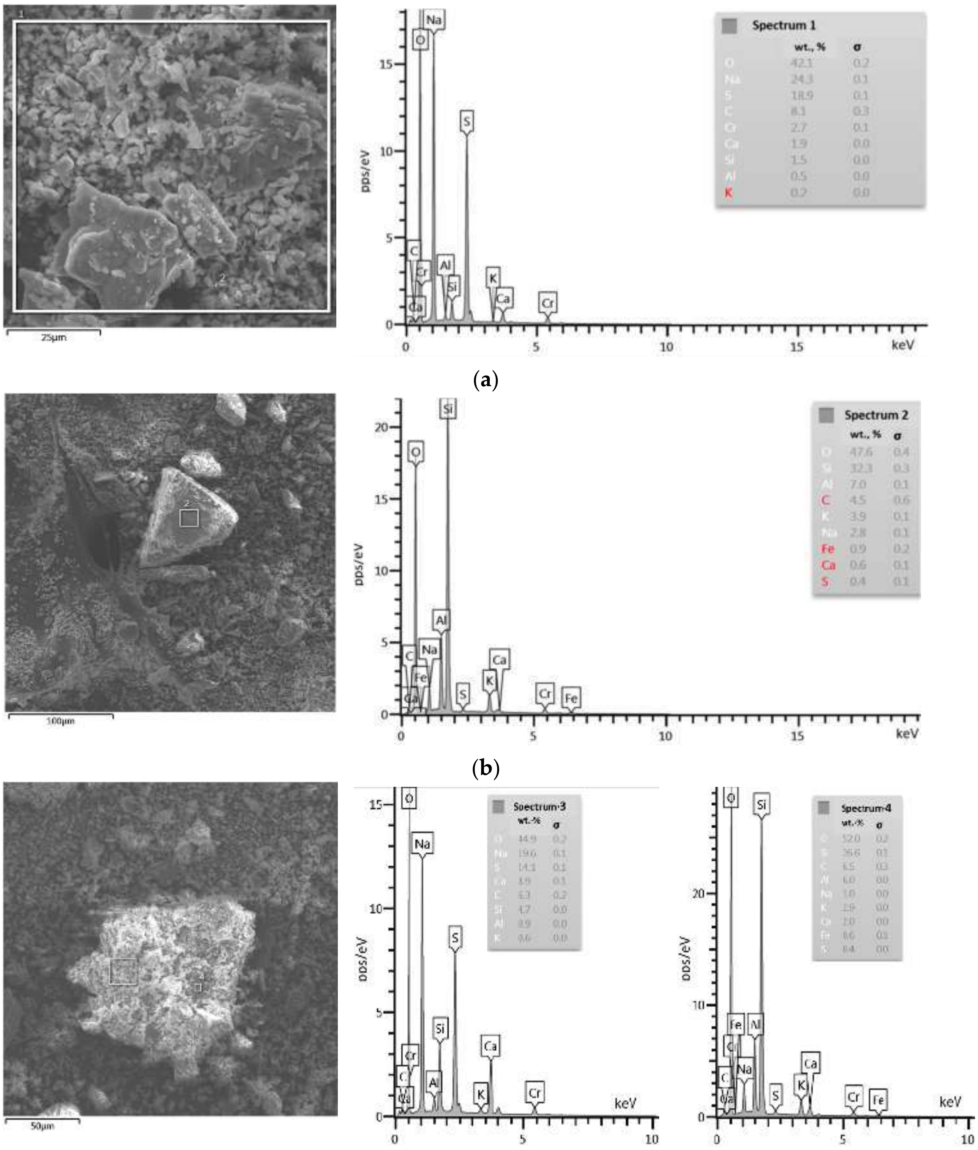
On the other hand, there is a pronounced loose structure of the same mix but with a 24 h conditioned alkali solution, where the unreacted citrogypsum crystals and a loose substance can be observed. Most likely, a loose substance can be associated with particles of unreacted perlite and efflorescence substance due to the slow processes of chemical interactions between the components of the binder system. Also, for this mix, there are no monolithic areas responsible for the products of the copolymerization process.

The microstructures of the P-PC mix obtained using both methods of NaOH introduction, fresh and 24 h conditioned ones, are identical to each other, despite the presence and different contents of surface efflorescence components for samples using 24 h conditioned alkali solution (Figure 4).

Thus, the presence of efflorescence components in the volume of geopolymer samples is more likely to take place $^{+}$.

4.5. EDS-Analysis

To identify the qualitative composition of efflorescence substance on the surface of the P-CG mix, a certain amount of the resulting white weak crust was taken from the samples, cured in ambient conditions (Figure 5b) and underwent thermal treatment at 70 °C (Figure 6e). Selected samples of efflorescence components were analyzed using EDS (Figure 8). The choice of the P-CG mix for carrying out EDS analysis is explained by the largest amount of efflorescence components on the surface of the experimental cube samples.



(**a**)

(**b**)

(**c**)

Figure 8. EDS spectra of efflorescence components taken from the surface of P-CG mix, cured (**a**) in ambient conditions; (**b**,**c**) with thermal treatment.

EDS spectra showed that on the surface of the P-CG mix cured in ambient conditions (Figure 8a), the formed efflorescence components mainly consist of elements such as oxygen (O), sodium (Na) and sulfur (S).

These elements indicate that the efflorescence substance probably consists of unreacted sodium hydroxide (NaOH), a modifying component; citrogypsum ($CaSO_4$) and the product of their interaction in the form of crystalline hydrates of sodium sulfate (Na_2SO_4).

The efflorescence component from the P-CG mix, cured with thermal treatment at 70 °C, also contains Na_2SO_4 (Figure 8c, Spectrum 3), as well as Si and Al elements associated with perlite (Figure 8b, Spectrum 2). The presence of an aluminosilicate component in the efflorescence substance may be a confirmation of the ineffective occurrence of geopolymerization processes, which leads to the presence of unreacted raw material components in the system, as well as the formation of a weaker geopolymer matrix, in accordance with the compressive strength data, depicted in Figure 3.

During sample preparation, geopolymer samples were attached to the substrate for fixation using electrically conducting carbon tape. This is probably why carbon is present in the samples.

5. Conclusions

The novelty of the research is the estimation of relationships between physical, mechanical and structural characteristics of perlite-based geopolymer paste and the combined effect of such parameters as different production methods, different curing conditions and the modification of geopolymers with different mineral additives.

It has been established that curing conditions and method of introducing an alkali component into the geopolymer matrix had almost no effect on average density, while they effected compressive strength significantly. This is confirmed by an increase in compressive strength by 0.63 to 11.4 times for mixes using fresh alkali solution and by 0.72 to 12.8 times for mixes using 24 h conditioned alkali solution. In the first case, the maximum increase in strength is observed for the mix containing kaolin (increase by 1.1 MPa to 13.2 MPa); in the second case, this is also observed for a mix containing kaolin (increase by 0.7 MPa to 9.7 MPa). Also, thermal treatment promotes the compaction of the structure by 18% and 1% for non-modified mix and mix modified with Portland cement.

The type of mineral modifying component (among the mineral representatives studied in the manuscript) leads to a decrease in average density and compressive strength. However, geopolymer paste containing a kaolin modifier under thermal treatment conditions and using fresh alkali solution provides a radical increase in compressive strength: 11 times vs. a similar composition (from 1.1 MPa to 13.2 MPa) but hardening under ambient curing conditions and 78% vs. the reference mix under thermal treatment (from 7.4 MPa to 13.2 MPa).

Based on the results obtained in the study, it should be noted that thermal treatment is a preferable consolidation regime over ambient conditions for a perlite-based geopolymer, regardless of the presence/absence of a modifying component. Thus, with thermal treatment, the highest compressive strength and denser structure are provided by the non-modified perlite-based geopolymer, as well as the geopolymer modified by kaolin. Moreover, it is better to activate non-modified perlite-based geopolymer with a fresh alkali solution, while for the geopolymer modified with kaolin, it is best to use a 24 h conditioned alkali solution.

With thermal treatment, kaolin demonstrates significantly higher reactivity in the geopolymer matrix and provides a strengthening effect with a compressive strength of up to 13.2 MPa compared to metakaolin used, where the compressive strength was up to 9.7 MPa. Thus, with thermal treatment, kaolin manifests itself as a more reactive modifying additive than metakaolin.

Portland cement and citrogypsum initiate a decrease in compressive strength and average density regardless of the introduction methods of alkali components. However, these additives help accelerate the consolidation of perlite-based geopolymers when cured in ambient conditions.

A study of perlite-based geopolymer pastes containing different mineral modifiers showed that efflorescence is observed in geopolymers containing Portland cement (to a lesser extent) and citrogypsum (to a greater extent).

Microstructure in the consolidated geopolymer perlite-based pastes containing Portland cement and citrogypsum demonstrates that the 24 h conditioned aqueous solution of NaOH tends to slow down the processes of interaction between alkali cations and the aluminosilicate component, which leads to the formation of a loose structure. At the same time, the method of introducing an alkaline activator did not affect the microstructure of the geopolymer mix containing Portland cement.

The efflorescence component could consist of unreacted alkaline activator NaOH, a modifying component citrogypsum $CaSO_4$ and the product of their interaction in the form of crystalline hydrates of sodium sulfate Na_2SO_4. This is evidenced by the presence in the efflorescence component of such elements as oxygen, sodium and sulfur. The presence of an aluminosilicate component in the efflorescence substance for thermally cured geopolymer mix may be evidence of ineffective geopolymerization processes, which leads to the presence of unreacted raw materials in the system, as well as the formation of a weak geopolymer matrix.

Thus, the most negative effect was demonstrated by citrogypsum, the introduction of which into the perlite-based geopolymer led not only to a significant decrease in compressive strength and average density but also to the formation of an aggressive alkaline efflorescence substance.

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