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The Influence of Composition and Recipe Dosage on the Strength Characteristics of New Geopolymer Concrete with the Use of Stone Flour

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Abstract: Currently, considering global trends and challenges, as well as the UN sustainable development goals and the ESG plan, the development of geopolymer binders for the production of geopolymer concrete has become an urgent area of construction science. This study aimed to reveal the influence of the component composition and recipe dosage on the characteristics of fine-grained geopolymer concrete with the use of stone flour. Eleven compositions of geopolymer fine-grained concrete were made from which samples of the mixture were obtained for testing at the beginning and end of setting and models in the form of beams and cubes for testing the compressive strength tensile strength in bending. It was found that the considered types of stone flour can be successfully used as an additive in the manufacture of geopolymer concrete. An analysis of the setting time measurements showed that stone flour could accelerate the hardening of the geopolymer composite. It was found that the addition of stone waste significantly improves the compressive strength of geopolymers in comparison with a geopolymer composite containing only quartz sand. The maximum compressive strength of 52.2 MPa and the tensile strength in bending of 6.7 MPa provide the introduction of potassium feldspar in an amount of 15% of the binder mass. Microstructural analysis of the geopolymer composite was carried out, confirming the effectiveness of the recipe techniques implemented in this study.

Keywords: geopolymer concrete; compressive strength; tensile strength; optimal composition; temperature treatment; sodium silicate

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1. Introduction

The structure formation concept of geopolymer materials was proposed in 1979 by the French researcher Davidovits [1–3] and actively developed in recent years.

The interest of scientists and engineers in geopolymers is explained by these materials' technological and operational characteristics. In the early stages of the development of geopolymers, they were used to create expensive materials with high performance for aviation, automotive, and other industries. Later, geopolymerization processes began to be used to synthesize inexpensive building materials based on ashes from thermal power plants, slags, waste from mining, and processing of rocks and other industrial debris. Geopolymer binders are currently considered as a developing alternative to Portland cement—the main binder in modern construction [4–6].

Geopolymers are most actively studied in countries with a high level of scientific and technological development and significant volumes of mineral waste generated in various industries. These countries include France, the USA, Australia, Germany, the Czech Republic, China, India, Japan, etc.

1.1. The Relevance of Research

The relevance of geopolymer binders' usage appears in a wide range of construction industries due to the high-performance characteristics, which can be predicted and managed at all stages of designing the composition of the raw mixture and at the hardening stage gaining strength of the geopolymer composite. Therefore, it is advisable to create a copy of the geopolymer binder by changing the components of the raw mixture and technological parameters with the given physical and mechanical characteristics that satisfy the technical, economic, and operational indicators.

At present, considering global trends and challenges and the UN sustainable development goals, and the ESG agenda, world science, and industry are devoted to solving problems arising in society and people's lives jointly.

One of these problems within the indicated urgent challenges and trends is the deteriorating environmental situation, a high carbon footprint in the extraction, production of building materials, and the construction of new buildings and structures. For this reason, the world community is working to find comprehensive solutions to these problems. For example, one of the scientific problems is a high percentage of carbon footprint in the production of Portland cement. As one of the primary binders in the world construction industry, with all its apparent advantages, it has disadvantages, primarily reflected in environmental pollution during its production.

For this reason, recently, and especially over the past five years, the development of special binders to produce geopolymer concrete has become a topical area of construction science. In this concept, this article considers the development of clinker-free binders. When making concrete based on these binders, a significant ecological effect can be obtained during the production process and reduce the burden on the environment.

1.2. Literature Review

Many known studies in which the mechanical and microstructural efficiency of geopolymer pastes reinforced with different types of fibers and different percentages of sodium nanodioxide were considered. Based on the results of the tests carried out, the authors determined that using sodium nanodioxide in an amount of 3% was the most effective for improving the mechanical, microstructural properties, and fracture characteristics of geopolymers [7–10].

The influence of mono (single type) and hybrid (mixed type) fibers on workability, strength properties, and viscosity parameters of a geopolymer solution based on fly ash was also studied. It was found that the workability of the mortar decreased more when using polypropylene fibers due to their higher dispersion in the geopolymer solution compared to bonded fibers from alkali-resistant glass and polyvinyl alcohol. On the other hand, the compressive strength increased by 14% using 1% steel fibers with 0.5% polypropylene fibers compared with a control mixture of 48 MPa. In geopolymer solutions based on fly ash with a high sand-to-binder ratio, it is possible to achieve hardening with extensive cracking and sagging by using steel fibers in mono- or hybrid forms with fibers from alkali-resistant glass and polyvinyl alcohol [8].

The effect of carbide slag, nickel–laterite waste, and various concentrations of NaOH on the physical and mechanical properties of geopolymer composites based on fly ash was studied in [11]. The research results showed that, in general, the inclusion of a carbide slag additive provides a higher rate of the chemical reaction and a higher rate of pore formation when exposed to a higher temperature and reduces the shrinkage of the composite upon drying. It was determined that the molarity of $NaOH_{12}M$ provides the optimal rate of the geopolymerization process. However, the low concentration of sodium hydroxide in the alkaline activator solution limited the dissolution of fly ash and incomplete filling of the interparticle volumes of the participating gels, and the excessive amount of Na + ions during geopolymerization at 14 M led to the process being incomplete, which reduced the strength of the aggregate [12–14].

Geopolymers based on metakaolin are also quite popular in modern research. The authors studied the effect of the K/Al ratio at elevated temperatures on the thermomechanical properties of metakaolinite-based geopolymers filled with chamotte. Therefore, it was found that with an increase in the K/Al ratio, the crystallization temperature of new phases (leucite and kalsilite) and the temperature of the onset of the primary shrinkage decreased [15–21].

The effect of glass waste on the mechanical characteristics and microstructure of geopolymers was also investigated. Therefore, the authors have developed geopolymer mixtures with different percentages and a diverse range of sizes of grains of waste glass. The decrease in mechanical properties with increasing glass waste content was less evident for thinner glassy powders, but a value of about 4–5 MPa indicated their potential use as non-structural materials [16].

Several authors have considered the effect of small aggregate particles on the mechanical properties of a geopolymer solution based on fly ash. It was found that the fluidity index of the solution is approximately linearly proportional to the modulus of the size of the sands. Geopolymer mortar has the best fluidity when the gradation of sand belongs to the I and II categories. The compressive and flexural strength of the geopolymer solution improves with an increase in the dispersion modulus of the sands, while the specific surface area and voidness are opposite. Additionally, the tensile strength first increases and then decreases as the modulus of size increases [17].

At the same time, geopolymer concrete obtained by various technologies was studied according to physical and mechanical parameters, such as strength, crack resistance, and different mechanical properties adjustable by various methods. Additionally, several types of industrial waste used for the manufacture of geopolymer concretes and their impact on the quality indicators of the finished product were considered [7–14,16,17,22–28].

In all studies considered, an emphasis was placed on the development and achievements in the field of environmental friendliness of geopolymer concrete and resource conservation in its production [1–29].

To summarize the literature review results, it should be highlighted that the choice of environmentally friendly components for geopolymer concrete and correct composition adjustment is crucial from the technological point of view. Therefore, the formulation and determination of concrete composition's qualitative and quantitative features for environmentally friendly construction, research on a macro and micro level of relationships between recipe and technological factors, and structure formation and properties in geopolymer concrete are fundamental. Thus, having determined the lack of scientific research on the chosen topic, this article develops its plan and methodology for conducting experimental research and analysis.

1.3. Prospects for the Use of Geopolymer Binders in the Production of Building Materials and Analysis of Raw Materials Used to Obtain Geopolymer Binders

As a particular case of alkaline activation binders, geopolymer materials represent a separate class of cementless building binders. The areas of their practical application can significantly increase in the nearest future.

From a technological point of view, geopolymer materials have several advantages over traditional binders based on Portland cement. First, it is related to the peculiarities of their production. The reducing stages of technological processing of the initial raw materials, which, in turn, reduce the number of greenhouse gases emitted into the environment and significantly reduce the energy intensity of production, which also makes it possible to obtain materials with a lower cost.

By varying the ratio of raw materials and adjusting the conditions for the synthesis of geopolymer binders, it is possible to produce materials with different properties and characteristics. The most important are increased strength indicators, low shrinkage deformations, resistance to high temperatures, the ability to adjust the setting time, low thermal conductivity, etc. [1–27].

The main components necessary for the synthesis of geopolymer binders are activating agents that provide an alkaline medium and substances of aluminosilicate composition of various origins.

Choosing raw materials, which is the basis to produce geopolymer binders, is necessary to be guided by several essential parameters. The volume of reserves, the availability of extraction, and use are the main parameters. The activity of the raw materials, in particular the mixing agent, and the constancy of the composition capable of ensuring the stability of the physicochemical characteristics of the final product without changing the production technology are also crucial [1–6,10,21,23,27].

For the synthesis of geopolymers, as various alkaline binders, essential components are used: an aluminosilicate component, predominantly acidic, and an alkaline activator.

1.3.1. Activating Component

Among the most common activating agents used in synthesizing geopolymer binders, a wide range of alkali metal hydroxides and salts provide a high pH value. For geopolymer systems based on fly ash, alkaline agents such as NaOH, Na_2SiO_3 are often used, with concentrations in the range of 25–100% and 38–55%, respectively, as well as their compositions. The use of Na_2SiO_3 contributes to the intensification of the hardening processes and reduces the time for the curing of composites. The exothermic properties of NaOH contribute to the intensification of the processes of dissolution of the aluminosilicate component and subsequent polymerization.

1.3.2. Aluminosilicate Component

Potentially possible and practically used, aluminosilicate components for the synthesis of geopolymers are classified into three categories: technogenic, synthetic, and natural.

Technogenic Aluminosilicates

To take advantage of the most common types of technogenic aluminosilicate raw materials, it is necessary to determine the amount of waste from metallurgical (e.g., blast furnace slag, steel-making slag) and fuel (e.g., ash and fly ash from TPPs) industries.

In the modern world, there is an acute issue of disposal of metallurgical and ash and slag waste (ASW), which require large areas for their placement and storage. The use of human-made waste and by-products of aluminosilicate composition (blast furnace slag, fly ash, etc.) in the production of geopolymer binders can be an alternative to Portland cement in terms of environmental and economic efficiency [28,29].

However, the limited application of the technogenic variety of aluminosilicates is explained by the fact that their main properties, structure, mineral, and chemical compositions largely depend on the components of the mineral part of the fuel, the mode, and conditions of the technological process. Additionally, the methods of disposal and storage, etc., cause significant fluctuations in the chemical and mineral composition and the morphology of the constituent particles, leading to instability of its quality as a raw material component.

Synthetic Aluminosilicates

As a synthetic raw material in the production of geopolymers, metakaolin ($Al_2Si_2O_7$) is used as the main raw material component, which is of considerable interest to material scientists. The formation of the metakaolin structure occurs as a result of firing kaolinite at a temperature of 550–900 °C for up to 24 h. Regardless of the manufacturer, the resulting aluminosilicate material is characterized by the constancy of the chemical composition, morphology, and dispersion of particles, which provides it with high quality as a raw material [6,10,15–21,23].

Natural Aluminosilicates

The use of natural sources of aluminosilicate raw materials has become more widespread than synthetic analogs due to the wide variety of the raw material base, the presence of large nature reserves, and the relative constancy of the chemical and mineral composition in comparison with technogenic analogs.

The classification of natural aluminosilicates is presented in the form of a block diagram in Figure 1.

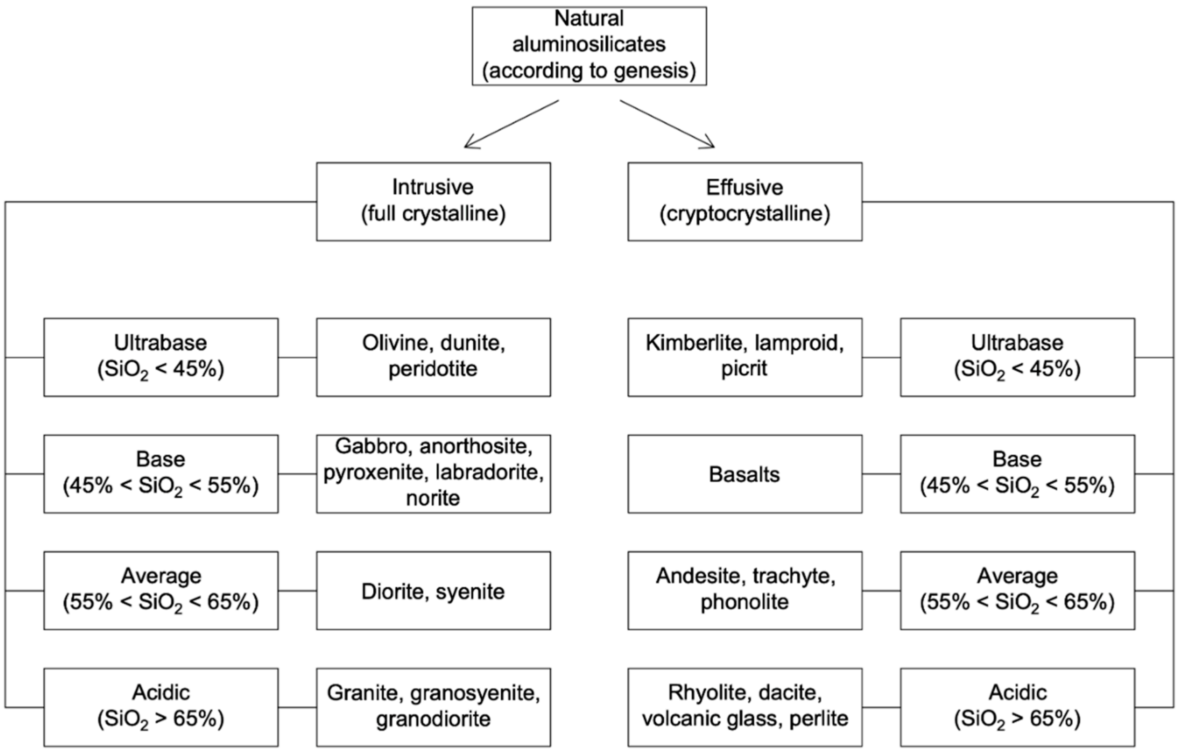


Figure 1. Classification of natural aluminosilicates.

There are significant reserves of mineral raw materials in Russia and a developed mining industry, which is associated with forming a considerable amount of waste. The bulk of this waste is not used and stored in dumps, creating environmental issues in their storage places. Only a small part of mining waste is used as aggregate for concrete and mortar, as well as soil dumping.

It was found that crushed igneous rocks of aluminosilicate composition with alkaline activation are capable of gaining a strength of 40–80 MPa. According to the technologies existing at precast concrete factories, structural concrete with a strength of 20–40 MPa can be obtained based on such binders. The advantage of these binders is their production technology's energy and resource-saving potential. These advantages are because the leading share of raw materials—waste from the mining industry of aluminosilicate composition—does not require heat treatment, and the raw material is a large-tonnage waste, the utilization of which allows you to save mineral resources for future generations [6,10,21,23,28,29].

During the extraction of stone rocks and the production of large aggregate for concrete, 22–28% of waste is formed in the form of crushing screenings fr. 0–5 mm, a significant part of which is not used and is stored in dumps. This waste contains a considerable amount of dust fraction, with 0–0.3 mm, which is of the greatest value for developing an energy-saving technology. Due to the fact that the crushing screenings can contain 5–20% of dust-like fractions, the use of this crushing waste without washing is not effective [28,29].

A promising area of application of dispersed crushed stone crushing wastes is the production of geopolymer materials based on crushed igneous rocks, which are the main component of the binder.

1.4. Purpose, Objectives, and Scientific Novelty of the Research

In this study, the object was geopolymer concrete with the use of stone flour, and the subject of the study was the characteristics of such concrete. The aim was to reveal the component composition and prescription dosage influence on these characteristics.

The following tasks were performed during the study:

- A literature review, in particular over the past 5 years, on the most progressive developments in the field of geopolymer concrete, taking into account the regional factor;
- Drawing up a research program, in which it was necessary to identify the factors affecting the characteristics of concrete and to identify the degree of this influence. To this end, it was necessary to determine the materials and methods, as well as to set up a phenomenological approach;
- Conducting experimental studies to obtain data on the influence of prescription and technological factors on the properties of a new type of geopolymer fine-grained concrete;
- Analysis of the results, their interpretation, and processing to develop proposals for the practical implementation of the research results in the construction industry and determine the further prospects of the chosen scientific direction.

The scientific novelty of this research is obtaining new knowledge about previously unknown compositions in terms of components and recipe dosage. Therefore, the quantitative and qualitative characteristics for new types of geopolymer concrete, particularly the use of stone flour obtained from raw materials of various kinds, are essential. Furthermore, considering the regional factor, this research may be helpful from the point of view of practice and implementation of this concrete composition in the construction materials industry in various regions in which the specified raw materials are contained in large quantities. This will significantly reduce the burden on the environment and significantly reduce the cost of obtaining new types of binder and concrete.

As a scientific novelty, the development of previously known theoretical directions in the field of clinker-free binders and concrete based on them should also be noted.

The practical application based on research results consists of obtaining information about the behavior and changes in the strength characteristics of new materials, which will be highly functional and suitable for those construction industries where the use of fine-grained concrete is developed. Furthermore, the analytical part of the article allows the scientific sector to use these studies for further research in terms of rationalizing the compositions of geopolymer concrete and helps to understand better the nature of this attractive, relevant, and promising material.

2. Materials and Methods

2.1. Materials

When conducting research in the framework of this work, potassium hydroxide KOH produced by OOO Soda-Chlorate (Berezniki, Perm Region, Russia) [30] and sodium liquid glass $Na_2O\ (SiO_2)_n$ produced by JSC Kubanzheldormash (Armavir, Russia) were used according to [31].

Quartz sand was used as a fine aggregate, the physical characteristics of which are presented in Table 1.

Table 1. Physical characteristics of dense fine aggregate.

Grain Composition							Pass-Through a Sieve With Mesh No. 0.16, wt %	Size Module	Content of Dust and Clay Particles, %	True Density, kg/m^3	Bulk Density kg/m^3
Sieve Hole Sizes, mm											
Sieve Residual		Private and Total Sieve Residual, %									
10	5	2.5	1.25	0.63	0.315	0.16					
0	0	0.17 0.17	1.39 1.56	8.86 10.42	45.80 56.21	41.03 97.25	2.49 99.74	1.66	1.1	2650	1438

Metakaolin produced by OOO RossPolymer (Noginsk, Moscow Region, Russia) was used as the main component of the geopolymer binder. The chemical composition of metakaolin and its physical characteristics are presented in Tables 2 and 3.

Table 2. Chemical composition of metakaolin RossPolymer "MetaKaolin 1400".

Title	Value
Aluminium oxide Al_2O_3, wt %	42
Silicon oxide SiO_2, wt %	51
Iron oxide Fe_2O_3, wt %	0.5
Loss on ignition, %	1
pH in 10% aqueous suspension	5.5

Table 3. Physical characteristics of metakaolin.

Title	Value
Sieve residue No. 0063, wt %	0.2
Average particle size (D50), no more, µm	10
Specific surface, m^2/g	18
Bulk density, kg/m^3	265

Water for laboratory research was used tap water that fully meets the requirements [32].

Additionally, in this study, two types of stone flour were used—namely, potassium feldspar, grade FK-100, produced by Malyshevskoye Ore Administration JSC (Malyshev settlement, Sverdlovsk Region, Russia) and micro calcite, grade Km-2, produced by Koelgamramor (Koelga village, Chelyabinskaya Region, Russia) according to [33].

The chemical composition and physical properties of potassium feldspar and its granulometric characteristics following the manufacturer's specification are presented in Tables 4 and 5 and Figure 2. These data are provided by the manufacturer.

Table 4. Chemical composition of FK-100 potassium feldspar.

Chemical Composition, %	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	Fe_2O_3	TiO_2	MgO	L.O.I
	68.60	17.00	11.20	2.15	0.45	0.09	0.02	0.04	0.45

Table 5. Physical properties of FK-100 potassium feldspar.

Density, g/cm^3	2.65
Bulk Density, g/cm^3	1.1
Humidity, %	0.5

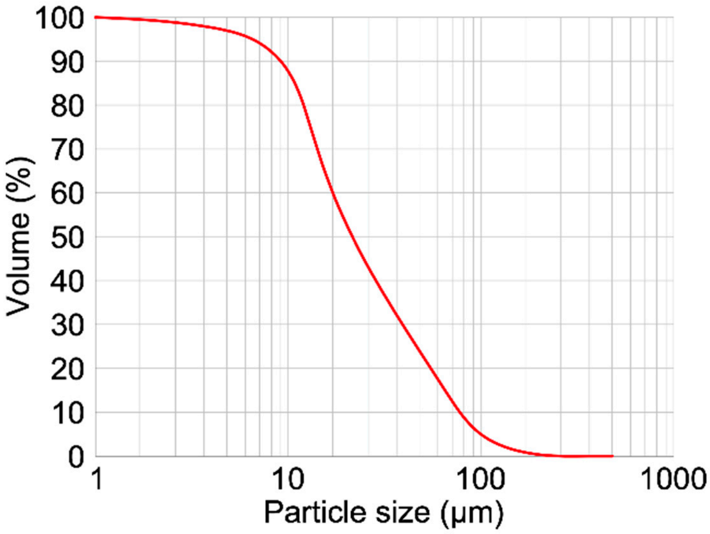


Figure 2. The size distribution curve of potassium feldspar grade FK-100.

The chemical composition and physical properties of Km-2 grade micro calcite and its granulometric characteristics in accordance with the manufacturer's specification are presented in Table 6 and Figure 3.

Table 6. Chemical composition and physical properties of micro calcite grade Km-2.

Chemical Composition	$CaCO_3$, %	98.07
	MgO, %	0.35
	SiO_2, %	0.06
	Fe2O_3 + Al_2O_3, %	0.07
	Insoluble substances in HCl, %	max 0.3
	Volatiles, wt. %	max 0.3
	Substances soluble in H_2O	max 0.3
	pH aqueous suspension	8–10
Physical Properties	Density, g/cm^3	2.68
	Bulk density, kg/m^3	510
	Humidity, %	max 0.2

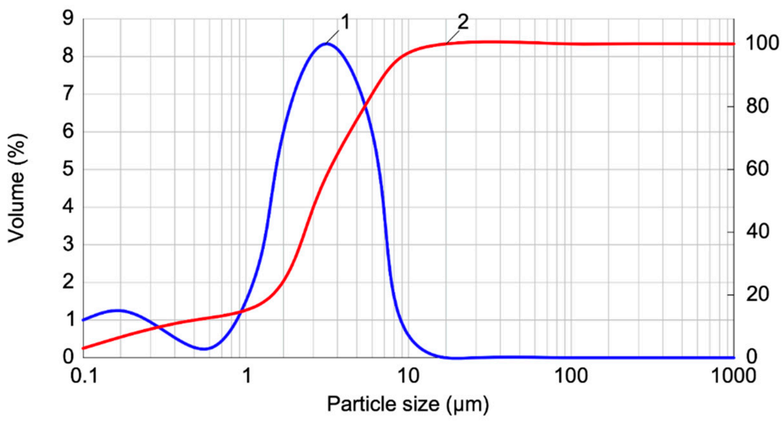


Figure 3. Curve of distribution of Km-2 grade micro calcite particles by size: 1—curve of the partial distribution of particles of a certain size (particle size) in percentage (along the left ordinate); 2—curve of the total distribution of particles as a percentage (on the right axis of ordinates).

2.2. Methods

The step-by-step algorithm of the research methodology is presented in the form of a block diagram (Figure 4).

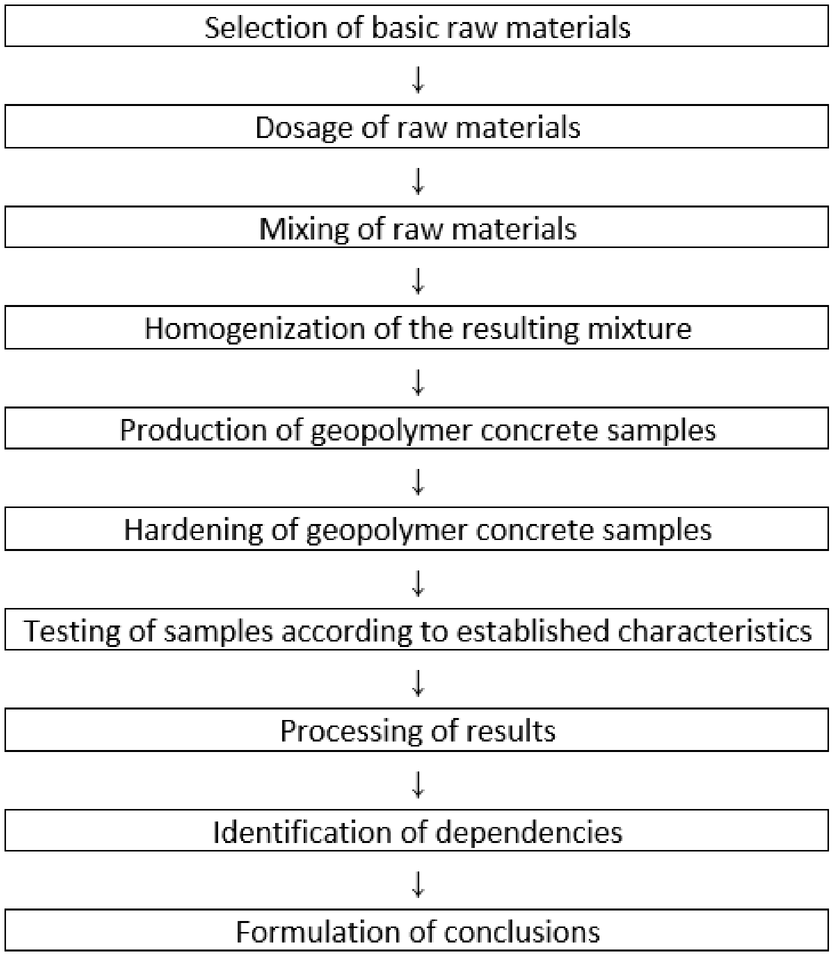


Figure 4. Step-by-step algorithm of the research methodology.

First, metakaolin was mixed with an aqueous alkaline solution (SiO_2/K_2O = 1.4, H_2O/K_2O = 12) using a laboratory mortar mixer for 30 min, and then quartz sand was added to the resulting geopolymer matrix. The introduction of stone flour (micro calcite or potassium feldspar) was carried out in an amount of 5%, 10%, 15%, 20%, and 25% of the mass of metakaolin. Before being introduced into the geopolymer matrix, micro calcite (A) and potassium feldspar (B) were pre-mixed with sand. Experimental compositions of geopolymer fine-grained concrete are shown in Table 7. The number of tests and samples is presented in Table 8.

Homogenization of the geopolymer mixture was carried out for 10 min. Then, the geopolymer mass was poured into molds 40 × 40 × 160 mm and 100 × 100 × 100 mm in size, which was subjected to vibration (5 min) to remove unwanted air bubbles. The molds were protected from water evaporation for 24 h using a polyethylene film. Thereafter, the solid samples were removed from the mold and stored for 28 days in plastic bags.

Tensile bending tests were performed using the same load model as described in GOST 30,744 "Cements. Methods of testing with using polyfraction standard sand" [34].

Table 7. Experimental compositions of geopolymer fine-grained concrete.

Composition Title	Metakaolin, g	Sand, g	Activator, g	Micro Calcite, g	Potassium Feldspar, g
C	800	1900	1000	-	-
1A	760	1900	1000	40	-
2A	720	1900	1000	80	-
3A	680	1900	1000	120	-
4A	640	1900	1000	160	-
5A	600	1900	1000	200	-
6B	760	1900	1000	-	40
7B	720	1900	1000	-	80
8B	680	1900	1000	-	120
9B	640	1900	1000	-	160
10B	600	1900	1000	-	200

Table 8. Number of tests and samples of geopolymer concrete.

Composition Title	Number of Tests, pcs	Number of Samples, pcs.		
		Beams	Halves of Beams	Cubes
	Setting Time	Bending Tensile Strength	Compressive Strength	Softening Coefficient
C	2	3	6	6
1A	2	3	6	6
2A	2	3	6	6
3A	2	3	6	6
4A	2	3	6	6
5A	2	3	6	6
6B	2	3	6	6
7B	2	3	6	6
8B	2	3	6	6
9B	2	3	6	6
10B	2	3	6	6
Total	22	33	66	66

The flexural strength R_{btb}, MPa, of a separate sample beam was calculated using Equation (1) as follows:

$$R_{btb} = \frac{1.5Fl}{b^3} \tag{1}$$

where F is the breaking load, N; b is the size of the side of the square section of the sample beam (mm); l is the distance between support axes (mm).

The bending strength was taken as the arithmetic mean of the test results of three samples. The calculation result is rounded to the nearest 0.1 MPa.

The compressive strength R_b (MPa) of an individual half of the sample beam was calculated by Equation (2) as follows:

$$R_b = \frac{F}{S} \tag{2}$$

where F is the breaking load (N); S is the area of the working surface of the pressure plate (mm^2).

The compressive strength was taken as the arithmetic mean of the test results of six halves of the beams. The calculation result is rounded to the nearest 0.1 MPa.

The water resistance was determined by the value of the softening coefficient (K_{soft}). Sample cubes were pre-dried for 24 h at a temperature of 70 °C to remove excess unbound water from the material's structure, then immersed in a hermetically sealed container with water and kept for two days. Across the established time interval, the samples were removed from the water, wiped off with a dry towel, and dried in the air, in the laboratory, for 2–3 h. Afterward, the samples were subjected to compression tests, to determine the strength characteristics [35].

The softening coefficient was determined from the change in the strength of the sample saturated with water to the strength of the sample in the dry state as follows:

$$K_{soft} = R_{b,hum} / R_{b,dry} \quad (3)$$

where $R_{b,hum}$ is the compressive strength of the sample after water saturation (MPa); $R_{b,dry}$ is the compressive strength of the sample after heat treatment (MPa).

Additionally, for each experimental composition, the setting time was determined. Determination of the setting time was carried out in accordance with the requirements of GOST 310.3 "Cements. Methods for determination of standard consistency, times of setting and soundness" [36].

The following devices were applied in this study:

- Technological equipment—laboratory concrete mixer BL-10 (ZZBO LLC, Zlatoust, Chelyabinsk region, Russia); laboratory vibrating platform SMZh-539-220A (LLC "IMASH", Armavir, Russia);
- Testing equipment—hydraulic press IP-1000 (OOO NPK TEKHMASH, Neftekamsk, Russia); Vika device (LLC GK "ERMAK", Yekaterinburg, Russia);
- Measuring instruments—measuring metal ruler 500 mm; laboratory scales [37–41].

3. Results

After the tests were carried out, all the results obtained were analyzed. Flexural tensile tests were carried out first, followed by compression tests of half specimens. A total of 33 bar specimens were tested in flexural tensile tests, 66 halves in compression tests, and 66 cube specimens when determining the water-resistance index. All these tests were carried out after 28 days of hardening.

Figure 5 shows a photo of the manufacture of samples beams of geopolymer fine-grained concrete in the process of vibration compaction.

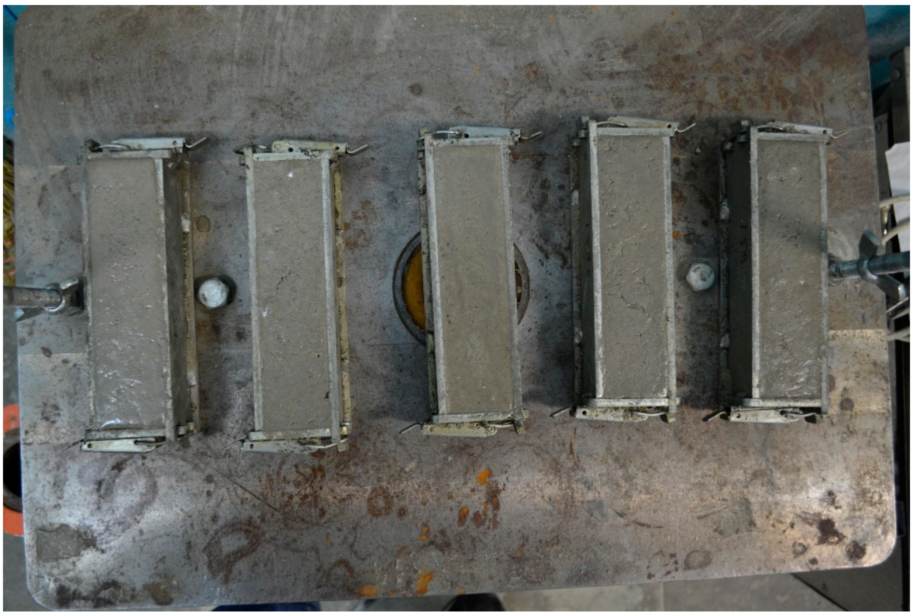


Figure 5. The process of vibration compaction of samples of geopolymer fine-grained concrete.

Table 9 shows the results of the start and end times of the setting of geopolymer composites of all test formulations. For comparison, the values of the control composition were taken without the addition of stone flour (C).

Table 9. Setting parameters of geopolymer composites with different types of stone flour.

Composition Title	IST, min	FST, min
C	550	690
1A	380	485
2A	290	370
3A	275	325
4A	270	300
5A	255	300
6B	480	595
7B	440	515
8B	410	495
9B	400	475
10B	390	450

IST—initial setting time, FST—final setting time.

According to the results of the studies, it can be seen that the longest IST was observed in the control composition and was 550 min, and the shortest, in the composition of type 5A, with 255 min. In general, type A and B formulations had shorter onset times, compared with the control formulation. It follows from this that the introduction of potassium feldspar and micro calcite promotes an increase in the rate of geopolymer reaction. The effect of the dosage of the added stone flour additives should also be highlighted. From the graphical dependence shown in Figure 6, it can be seen that an increase in the content of additives from 5% to 25% increased the rate of geopolymer reaction and, as a consequence, decreased the value of the time of the beginning and end of the setting.

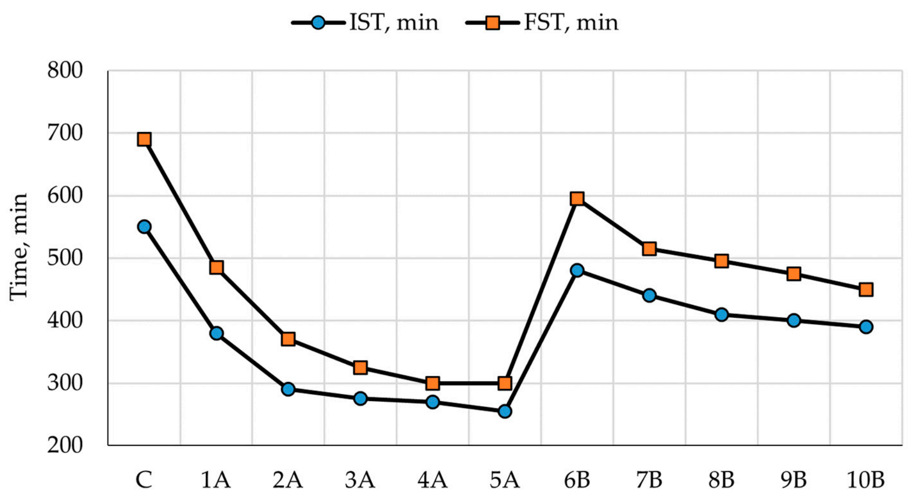


Figure 6. Dependence of changes in IST and FST on the content of stone flour: IST—initial setting time, FST—final setting time, C—control composition (without stone flour content), 1A–5A—marking of formulations with the addition of stone flour in the form of micro calcite, 6B–10B—marking of formulations with the addition of stone flour in the form of potassium feldspar.

Figures 7 and 8, respectively, show the statistical compressive strength and bending strength values for all seven types of fine-grained geopolymer concrete with various types of stone flour.

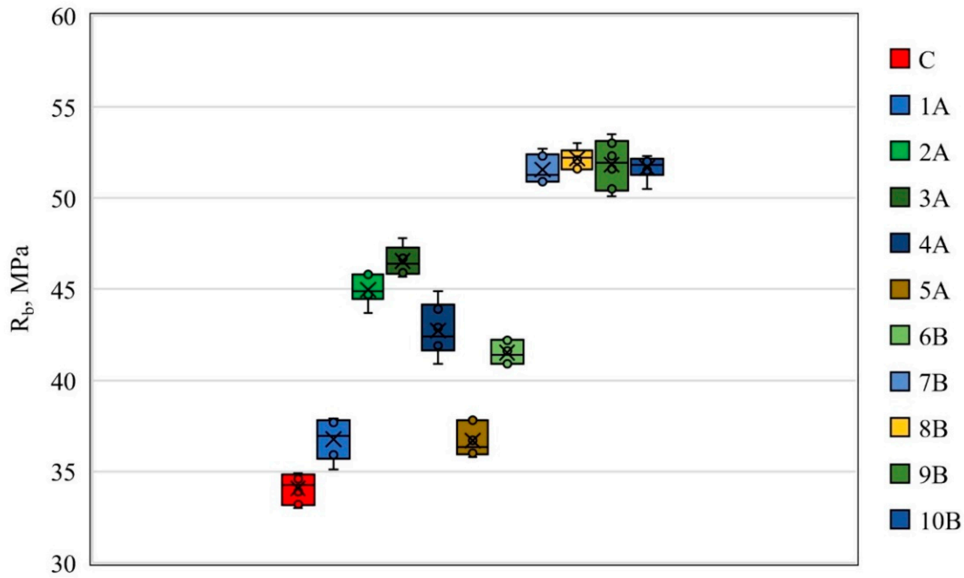


Figure 7. Compressive strength of fine-grained geopolymer concrete.

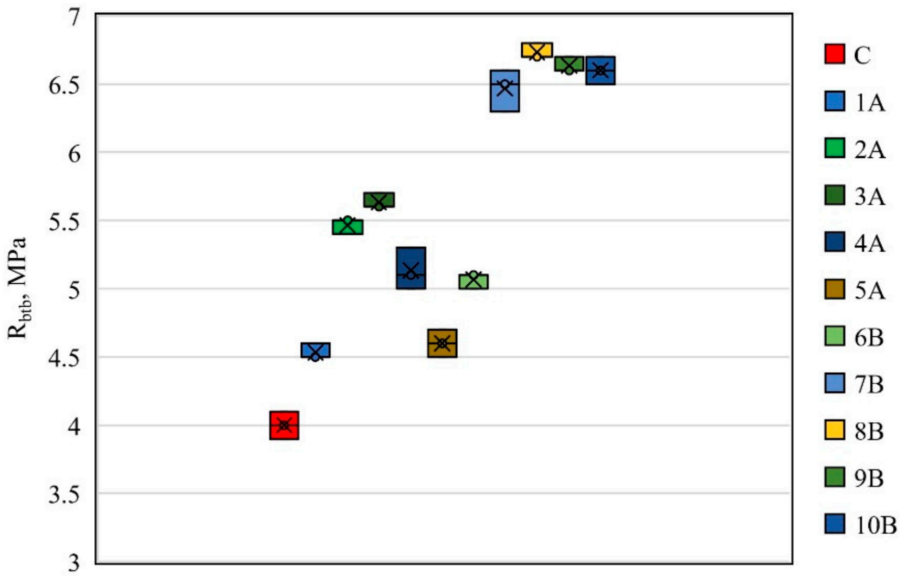


Figure 8. Bending tensile strength of fine-grained geopolymer concrete.

As shown in Figure 7, the maximum compressive strength of 52.2 MPa was observed for the geopolymer composite of the 8B type. The lowest compressive strength value of 34.1 MPa was recorded for the samples of geopolymer concrete of the control composition. Analyzing compositions of type 1A, 2A, and 3A, a tendency of increasing compressive strength was clearly visible. Therefore, the introduction of micro calcite additive in an amount of 5% of the binder mass led to an increase in compressive strength up to 36.8 MPa, and with the introduction of the same additive in an amount of 10% and 15%, a more intense increase in strength was observed; however, the difference between these compositions was insignificant—for a composition of type 2A, the value strength was 45 MPa, and for a composition of the type, 46.6 MPa. However, with the addition of micro calcite in the amount of 20% and 25%, instead of metakaolin, a drop in compressive strength was observed, so for the composition of type 4A, the value of the compressive strength was 42.7 MPa, and for the composition of type 5A, 36.7 MPa. A decrease can explain this result in the aluminosilicate component in the geopolymer composite.

In type B compositions, the pattern of changes in compressive strength differs compared to changes in the strength of type A compositions. Additionally, note that, in general, the addition of potassium feldspar provides higher values of compressive strength compared to type A compositions, where the addition of micro calcite was used. Therefore, when replacing a part of the binder with the addition of potassium feldspar in the amount of 5%, the compressive strength value increased from 34.1 MPa to 41.5 MPa. As for the compositions of the 7B, 8B, 9B, and 10B types, the values of their strengths changed insignificantly and were equal to 51.6 MPa, 52.2 MPa, 51.8 MPa, and 51.7 MPa, respectively, but, as in the first case, the maximum value of the compressive strength was recorded for the geopolymer composite where part of the binder was replaced with 15% potassium feldspar additive. A further increase in the dosage of this additive may be irrational due to the fact that the Si/Al ratio remains practically unchanged, leaving the strength indicators at the same level or less than at a dosage of 15%.

As shown in Figure 8, the maximum tensile strength of 6.7 MPa in bending was observed similarly to the compressive strength of the 8B composition, and the geopolymer composite of the control composition had the lowest bending tensile strength of 4.0 MPa. In general, the pattern of changes in tensile strength in bending is the same as for compressive strength. Therefore, for compositions of types 1A, 2A, 3A, 4A, and 5A, the tensile strength values in bending were 4.5 MPa, 5.5 MPa, 5.6 MPa, 5.1 MPa, and 4.6 MPa, respectively. Additionally, for compositions of types 6B, 7B, 9B, and 10B, the tensile strength values in bending were 5.1 MPa, 6.5 MPa, 6.6 MPa, and 6.6 MPa, respectively.

An increase in the strength characteristics of a geopolymer composite with the use of various types of stone flour is ensured by an increase in the rate of the geopolymerization reaction, which contributes to the accelerated dissolution of the aluminosilicate component and the formation of an aluminosilicate gel and the chemical interaction of an aluminosilicate gel with particles of undissolved aluminosilicate, leading to the formation of complexes of "gel-like layer–undissolved material grain".

Thus, the introduction of micro calcite and potassium feldspar additives into the composition of fine-grained geopolymer concrete led to increases in strength characteristics (ΔR_b and ΔR_{btb}), which are indicated in Table 10.

Table 10. Increases in strength characteristics of fine-grained geopolymer concrete depending on the dosage of micro calcite and potassium feldspar.

Composition Title	R_b, MPa	R_{btb}, MPa	ΔR_b, %	ΔR_{btb}, %
C	34.1	4.0	0	0
1A	36.8	4.5	+8	+12
2A	45	5.5	+32	+37
3A	46.6	5.6	+36	+40
4A	42.7	5.1	+25	+28
5A	36.7	4.6	+8	+15
6B	41.5	5.1	+22	+27
7B	51.6	6.5	+51	+62
8B	52.2	6.7	+53	+68
9B	51.8	6.6	+52	+65
10B	51.7	6.6	+51	+65

Figures 9 and 10 show the values of the test results for cube specimens in terms of "compressive strength".

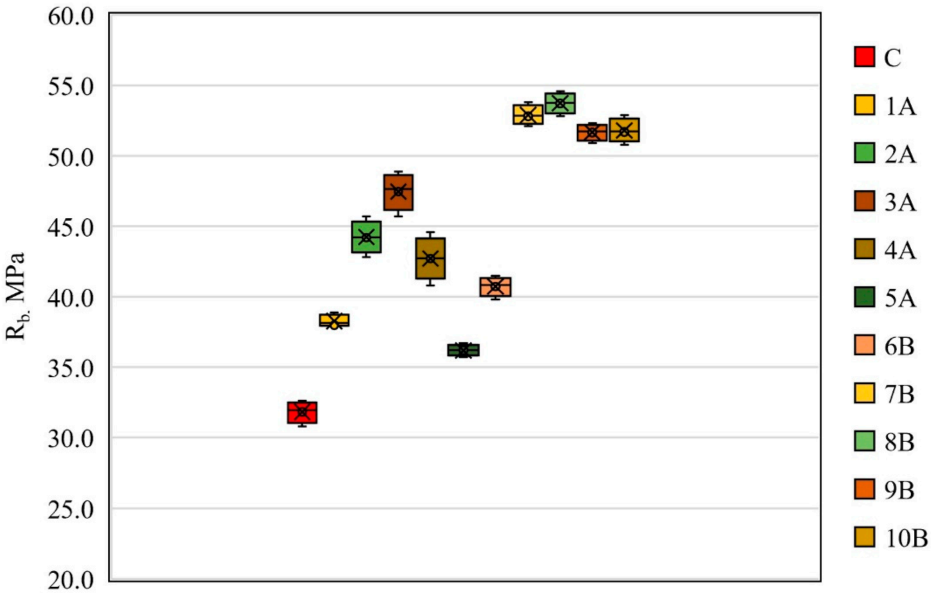


Figure 9. Strength of sample cubes after heat treatment (drying).

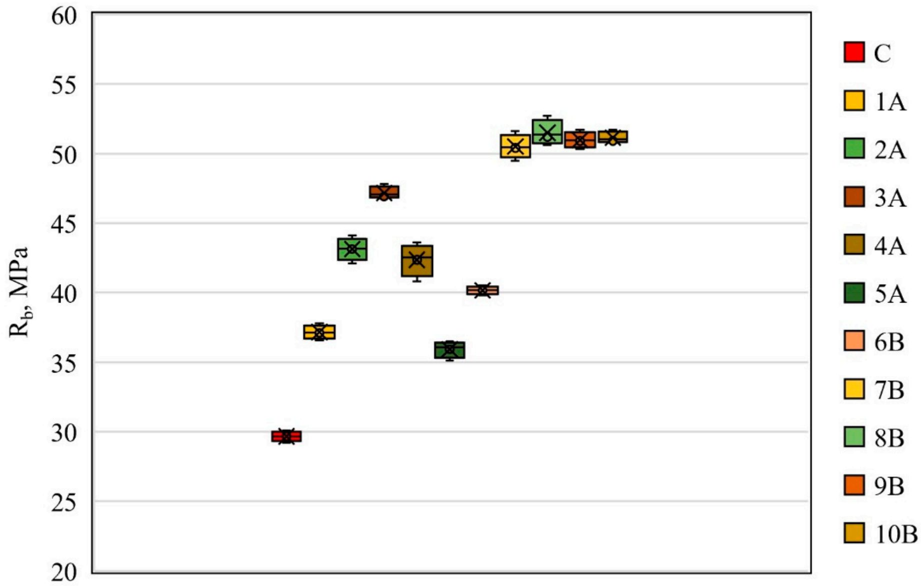


Figure 10. Strength of sample cubes after water saturation.

The values of the calculated softening factors are presented in the form of a diagram in Figure 11.

According to the data obtained, samples of experimental fine-grained geopolymer concrete with various types and dosages of stone flour demonstrated almost identical results of the softening coefficient. At the same time, the values of K_{soft} were close to 1, which indicates that there was no negative effect of the aquatic environment on the strength characteristics of the geopolymer composite.

To identify the features of structure-forming processes in geopolymer binder, an analysis of the microstructure of the geopolymer composite of the control composition (C) and the geopolymer composite of the 8B type was carried out.

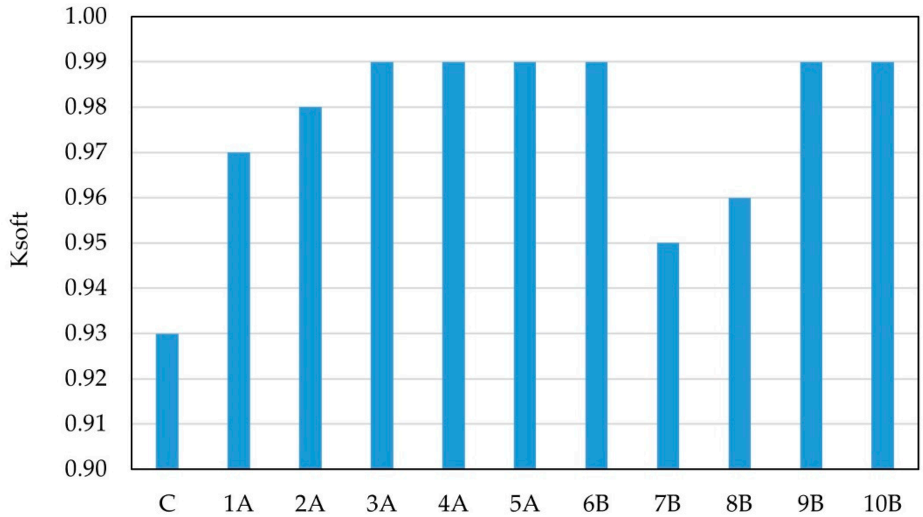
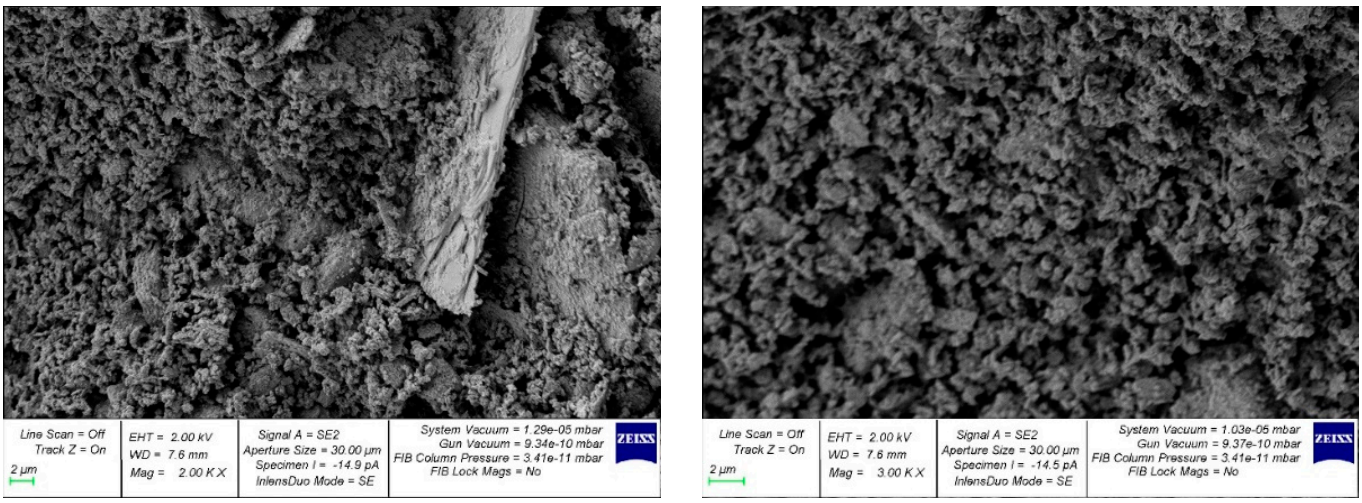


Figure 11. Softening coefficients of experimental compositions of geopolymer fine-grained concrete.

According to the data of microstructural studies (Figure 12), the structure of a type 8B geopolymer composite sample was characterized by the presence of an amorphous substance dissolved in an alkali aluminosilicate component, confirming the course of geopolymerization processes and the formation of a strong structure.



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

Figure 12. Microstructure of the geopolymer composite at the age of 28 days: (**a**) composition of type C; (**b**) composition of type 8B.

In addition, in the structure of the type 8B geopolymer composite, rounded particles of incompletely reacted metakaolin with an almost indistinguishable contact zone at the interface were observed, which indicates the following two facts:

- Unfinished polymerization process, i.e., the aluminosilicate component dissolved with the subsequent formation of an aluminosilicate gel;
- The presence of high adhesion between the newly formed phases and unreacted particles of the aluminosilicate component provided high strength values and low water absorption values of the hardened geopolymer stone.

As for the composition of type C, the amorphous component was present in a smaller amount, compared with the composition of type 8B; it also contained separate flocculent formations, indicating a lower density of the geopolymer composite, and as a consequence, its lower strength.

4. Discussion

In order to assess the scientific novelty, scientific significance, and reasonable prospects of the research, experiments were carried out. It is necessary to compare the results obtained with the results of other authors. In the case of geopolymer concrete, it is quite difficult to compare results due to a large number of developments of completely different compositions based on entirely different initial components that have a different nature of structure formation and formation of properties. A methodological set should be specified, in order to designate the research vector in the context of composition → structure → properties. We decided to consider the emerging structure of a new highly functional geopolymer concrete in the form of the system "gel-like layer–undissolved material grain" in the process of alkaline activation. This phenomenological model is shown in Figure 13 and is consistent with a similar model previously proposed by the authors [21].

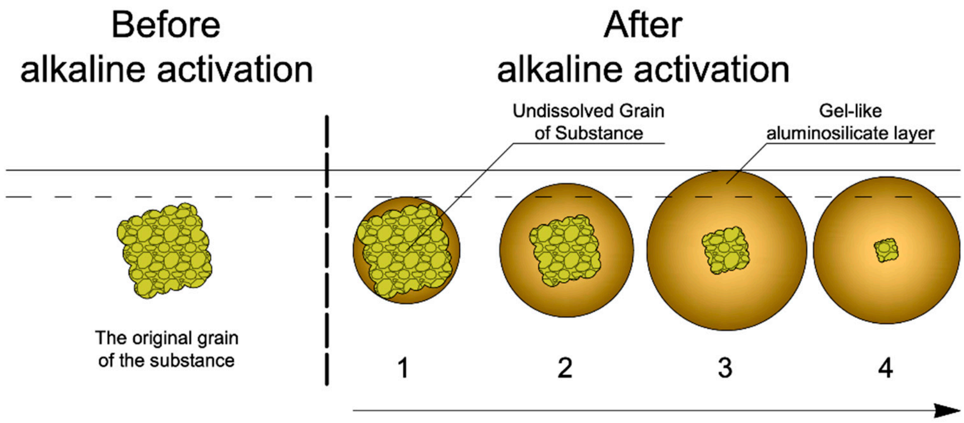


Figure 13. Phenomenological model of the formation of the system "gel layer–undissolved grain of material" in the process of alkaline activation.

According to the proposed model, in the process of alkaline activation of aluminosilicates, two processes occur simultaneously: The dissolution of the aluminosilicate component and the formation of an aluminosilicate gel and the chemical interaction of the aluminosilicate gel with particles of undissolved aluminosilicate with the formation of complexes of "gel-like layer–undissolved grain of material". The lower the degree of crystallinity of the aluminosilicate, the more intense the process of dissolution of aluminosilicate particles, and the greater the thickness of the surface gel-like layer in the resulting complex.

Thus, the hypothesis regarding the phenomenological model was experimentally and analytically confirmed. Next, a comparison should be made in terms of recipe and technological aspects. In terms of technology, our research is based on the principles and postulates of minimum energy intensity and maximum environmental friendliness in accordance with the set goal—reducing the carbon footprint and other harmful effects on the environment. In terms of recipe factors, for the first time, unlike the authors of [1–29], we applied an approach to studying the differences between two types of stone flour from two separate initial components. The comparison was carried out in terms of its technological properties and obtaining a solid composite, but by its mechanical, and more specifically, strength characteristics.

Therefore, for the first time, we achieved a scientific result through the use of new additives of micro calcite and potassium feldspar instead of part of metakaolin, and ultimately, based on the results of experimental studies, a rational, optimal composition was selected, including a dosage of potassium feldspar in an amount of 15% of the mass of metakaolin.

Therefore, this article proposed a qualitative and quantitative picture to form new knowledge about the obtained material. Further, the prospects for developing this direction in the selection of compositions, testing new raw materials, and reducing the labor intensity of the technological process with further greening of production were outlined.

5. Conclusions

The main conclusions of the presented results can be summarized as follows:

- The types of stone flour considered in this work can be successfully used as an additive in the manufacture of geopolymer concrete. The resulting composites are hard, resistant, and insoluble in water;
- Setting time measurements showed that stone powder can be used to accelerate the hardening of geopolymer composite. The shortest time of the beginning of setting (255 min) and the end of setting (300 min) was recorded for the composition containing the addition of micro calcite in the amount of 15% of the mass of metakaolin;
- Additives of stone waste significantly improve the compressive strength of geopolymers in comparison with a geopolymer composite containing only quartz sand. Maximum strength characteristics (compressive strength of 52.2 MPa and tensile strength in bending of 6.7 MPa) provide the introduction of potassium feldspar in an amount of 15% of the binder weight;
- A microstructural analysis of the geopolymer composite was carried out, confirming the effectiveness of the recipe techniques implemented in this study;
- A phenomenological model of the formation of the system "gel-like layer–undissolved grain of material" in a highly alkaline environment was proposed.

Further research by the authors is directed toward the selection of compositions, testing of new raw materials, and reducing the labor intensity of the technological process with further greening of production.

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References

1. Davidovits, J. Geopolymers: Ceramic-Like Inorganic Polymers. *J. Ceram. Sci. Technol.* **2017**, *8*, 335–350. [CrossRef]
2. Davidovits, J.; Davidovits, R. U.S. Patent 7229491, C04B 12/04, CO1B 33/26, 12 June 2007. Red Lion Cement Technology Limited, Road Town, Tortola (VG) No. WO03/099738; Publ. 12.06.2007, 7p. Available online: https://patents.google.com/patent/US7229491B2/en (accessed on 10 November 2021).

3. Davidovits, J. Global Worming Impact on the Cement and Aggregates Industries. *World Resour. Rev.* **1994**, *6*, 263–278. Available online: https://www.researchgate.net/publication/236503901 (accessed on 8 January 2022).
4. Rakhimov, R.Z.; Rakhimova, N.R.; Stoyanov, O.V. Geopolymers. *Bull. Kazan Technol. Univ.* **2014**, *17*, 189–196. Available online: https://www.elibrary.ru/download/elibrary_22671040_83776986.pdf (accessed on 8 January 2022).
5. Chekmarev, A.S.; Skvortsov, A.V.; Egorova, K.G. Geopolymer Concrete Based on Clay Raw Materials from the Republic of Tatarstan. *Bull. Kazan Technol. Univ.* **2014**, *17*, 45–48. Available online: https://www.elibrary.ru/download/elibrary_21636747_67301614.pdf (accessed on 8 January 2022).
6. Eroshkina, N.A.; Korovkin, M.O. Kinetics of Hardening of Geopolymer Binder Based on Rocks. *Eng. J. Don* **2016**, *7*. Available online: https://ivdon.ru/en/magazine/archive/n4y2016/3864 (accessed on 8 January 2022).
7. Rashedi, A.; Marzouki, R.; Raza, A.; Rawi, N.F.M.; Naveen, J. Mechanical, Fracture, and Microstructural Assessment of Carbon-Fiber-Reinforced Geopolymer Composites Containing Na_2O. *Polymers* **2021**, *13*, 3852. [CrossRef]
8. Junior, J.; Saha, A.K.; Sarker, P.K.; Pramanik, A. Workability and Flexural Properties of Fibre-Reinforced Geopolymer Using Different Mono and Hybrid Fibres. *Materials* **2021**, *14*, 4447. [CrossRef] [PubMed]
9. Abousnina, R.; Alsalmi, H.I.; Manalo, A.; Allister, R.L.; Alajarmeh, O.; Ferdous, W.; Jlassi, K. Effect of Short Fibres in the Mechanical Properties of Geopolymer Mortar Containing Oil-Contaminated Sand. *Polymers* **2021**, *13*, 3008. [CrossRef]
10. Eroshkina, N.A.; Korovkin, M.O.; Chamurliev, M.J. Application of Polypropylene Microfiber in Technology of Geopolymer Fine Grained Concrete. *Eng. J. Don* **2018**, *8*.
11. Zhao, X.; Wang, H.; Jiang, L.; Meng, L.; Zhou, B.; Zhang, J. Long-Term Physical and Mechanical Properties and Microstructures of Fly-Ash-Based Geopolymer Composite Incorporating Carbide Slag. *Materials* **2021**, *14*, 6692. [CrossRef]
12. Lei, J.; Fu, J.; Yang, E.-H. Alkali-Silica Reaction Resistance and Pore Solution Composition of Low-Calcium Fly Ash-Based Geopolymer Concrete. *Infrastructures* **2020**, *5*, 96. [CrossRef]
13. Longos, A., Jr.; Tigue, A.A.; Dollente, I.J.; Malenab, R.A.; Bernardo-Arugay, I.; Hinode, H.; Kurniawan, W.; Promentilla, M.A. Optimization of the Mix Formulation of Geopolymer Using Nickel-Laterite Mine Waste and Coal Fly Ash. *Minerals* **2020**, *10*, 1144. [CrossRef]
14. Abdullah, A.; Hussin, K.; Abdullah, M.M.A.B.; Yahya, Z.; Sochacki, W.; Razak, R.A.; Błoch, K.; Fansuri, H. The Effects of Various Concentrations of NaOH on the Inter-Particle Gelation of a Fly Ash Geopolymer Aggregate. *Materials* **2021**, *14*, 1111. [CrossRef]
15. Kohout, J.; Koutník, P.; Hájková, P.; Kohoutová, E.; Soukup, A. Effect of K/Al Molar Ratio on the Thermo-Mechanical Properties of Metakaolinite-Based Geopolymer Composites. *Polymers* **2021**, *13*, 3754. [CrossRef] [PubMed]
16. Dal Poggetto, G.; Catauro, M.; Crescente, G.; Leonelli, C. Efficient Addition of Waste Glass in MK-Based Geopolymers: Microstructure, Antibacterial and Cytotoxicity Investigation. *Polymers* **2021**, *13*, 1493. [CrossRef] [PubMed]
17. Ma, G.; Bai, C.; Wang, M.; He, P. Effects of Si/Al Ratios on the Bulk-Type Zeolite Formation Using Synthetic Metakaolin-Based Geopolymer with Designated Composition. *Crystals* **2021**, *11*, 1310. [CrossRef]
18. Perná, I.; Novotná, M.; Řimnáčová, D.; Šupová, M. New Metakaolin-Based Geopolymers with the Addition of Different Types of Waste Stone Powder. *Crystals* **2021**, *11*, 983. [CrossRef]
19. Chen, L.; Wang, Z.; Wang, Y.; Feng, J. Preparation and Properties of Alkali Activated Metakaolin-Based Geopolymer. *Materials* **2016**, *9*, 767. [CrossRef] [PubMed]
20. Fazli, H.; Yan, D.; Zhang, Y.; Zeng, Q. Effect of Size of Coarse Aggregate on Mechanical Properties of Metakaolin-Based Geopolymer Concrete and Ordinary Concrete. *Materials* **2021**, *14*, 3316. [CrossRef]
21. Kozhukhova, N.I.; Fomina, E.V.; Zhernovsky, I.V.; Strokova, V.V.; Chizhov, R.V. The Utilization Efficiency of Natural Alumosilicates in Composite Binders. *Appl. Mech. Mater.* **2014**, *670–671*, 182–186. [CrossRef]
22. Hsieh, Y.-C.; Lee, W.-H.; Liao, P.-H. Using Geopolymer Technology on Synthesizing Leucite Ceramics. *Polymers* **2021**, *13*, 3621. [CrossRef]
23. Eroshkina, N.A.; Korovkin, M.O.; Korovchenko, I.V. Resource-Saving Effectiveness of Technologies Geopolymer Binders Based on Magmatic Rocks. *Modern Sci. Res. Innov.* **2015**, *3*, 50975. Available online: https://web.snauka.ru/issues/2015/03/50975 (accessed on 8 January 2022).
24. Dao, D.V.; Ly, H.-B.; Trinh, S.H.; Le, T.-T.; Pham, B.T. Artificial Intelligence Approaches for Prediction of Compressive Strength of Geopolymer Concrete. *Materials* **2019**, *12*, 983. [CrossRef]
25. Ding, Y.; Bai, Y.-L.; Dai, J.-G.; Shi, C.-J. An Investigation of Softening Laws and Fracture Toughness of Slag-Based Geopolymer Concrete and Mortar. *Materials* **2020**, *13*, 5200. [CrossRef]
26. Mohammed, A.A.; Ahmed, H.U.; Mosavi, A. Survey of Mechanical Properties of Geopolymer Concrete: A Comprehensive Review and Data Analysis. *Materials* **2021**, *14*, 4690. [CrossRef]
27. Rudnov, V.S.; Gerasimova, E.S. Geopolymers Properties Regulating Methods. *Eng. J. Don* **2020**, *7*. Available online: https://ivdon.ru/en/magazine/archive/n7y2020/6545 (accessed on 8 January 2022).
28. Azad, N.M.; Samarakoon, S.M.S.M.K. Utilization of Industrial By-Products/Waste to Manufacture Geopolymer Cement/Concrete. *Sustainability* **2021**, *13*, 873. [CrossRef]
29. Imtiaz, L.; Rehman, S.K.U.; Ali Memon, S.; Khizar Khan, M.; Faisal Javed, M. A Review of Recent Developments and Advances in Eco-Friendly Geopolymer Concrete. *Appl. Sci.* **2020**, *10*, 7838. [CrossRef]
30. GOST 24363-80 Reagents. Potassium Hydroxide. Specifications. Available online: https://docs.cntd.ru/document/1200017451 (accessed on 12 November 2021).

31. GOST 13078-81 Sodium Silicate Solute. Specifications. Available online: https://docs.cntd.ru/document/1200019060 (accessed on 12 November 2021).
32. GOST 23732-2011 Water for Concrete and Mortars. Specifications. Available online: https://docs.cntd.ru/document/1200093835 (accessed on 12 November 2021).
33. GOST R 56775-2015 Microcalcite for Construction Materials. Specifications. Available online: https://docs.cntd.ru/document/1200127456 (accessed on 12 November 2021).
34. GOST 30744-2001 CEMENTS. Methods of Testing with Using Polyfraction Standard Sand. Available online: https://docs.cntd.ru/document/1200011363 (accessed on 12 November 2021).
35. GOST 30629-2011 Facing Materials and Products Made of Natural Stone. Test Methods. Available online: https://docs.cntd.ru/document/1200093394 (accessed on 12 November 2021).
36. GOST 310.3-76 Cements. Methods for Determination of Standard Consistency, Times of Setting and Soundness. Available online: https://docs.cntd.ru/document/871001226 (accessed on 12 November 2021).
37. Mailyan, L.R.; Beskopylny, A.N.; Meskhi, B.; Stel′makh, S.A.; Shcherban, E.M.; Ananova, O. Optimization of Composition and Technological Factors for the Lightweight Fiber-Reinforced Concrete Production on a Combined Aggregate with an Increased Coefficient of Structural Quality. *Appl. Sci.* **2021**, *11*, 7284. [CrossRef]
38. Stel'makh, S.A.; Shcherban′, E.M.; Beskopylny, A.N.; Mailyan, L.R.; Meskhi, B.; Butko, D.; Smolyanichenko, A.S. Influence of Composition and Technological Factors on Variatropic Efficiency and Constructive Quality Coefficients of Lightweight Vibro-Centrifuged Concrete with Alkalized Mixing Water. *Appl. Sci.* **2021**, *11*, 9293. [CrossRef]
39. Mailyan, L.R.; Beskopylny, A.N.; Meskhi, B.; Shilov, A.V.; Stel′makh, S.A.; Shcherban′, E.M.; Smolyanichenko, A.S.; El′shaeva, D. Improving the Structural Characteristics of Heavy Concrete by Combined Disperse Reinforcement. *Appl. Sci.* **2021**, *11*, 6031. [CrossRef]
40. Shcherban′, E.M.; Stel′makh, S.A.; Beskopylny, A.; Mailyan, L.R.; Meskhi, B. Influence of Mechanochemical Activation of Concrete Components on the Properties of Vibro-Centrifugated Heavy Concrete. *Appl. Sci.* **2021**, *11*, 10647. [CrossRef]
41. Beskopylny, A.; Kadomtseva, E.; Strelnikov, G.; Morgun, L.; Berdnik, Y.; Morgun, V. Model of Heterogeneous Reinforced Fiber Foam Concrete in Bending. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *365*, 032023. [CrossRef]