

## Article

# Utilization of Anthropogenic and Natural Waste to Produce Construction Raw Materials

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**Abstract:** The concept of the sustainable development of the world economy is currently aimed at achieving carbon neutrality, and this is due to the global warming of the planet. Energy and construction make a significant contribution to the release of carbon emissions into the environment and atmosphere. According to statistics, simply burning one ton of Portland cement clinker provokes the release of at least half a ton of carbon dioxide. In this study, the prepared samples were subjected to electron diffraction studies, as well as the X-ray phase analysis of the zone (XRF) using an ARLX'TRA diffractometer. Studies of macro- and microstructures were carried out using a Quanta 3D 200i scanning microscope. The obtained spectra were processed using EDAX TEAM software. The study of the microstructure of the samples showed that the bulk of the heterogeneous systems consisted of volumetric aggregates and intergrowths, i.e., small accumulations on their surfaces with pronounced cleavage, features of the microstructure indicating mineral formation processes. Therefore, the development of low-carbon construction models will make it possible to make a contribution and open an effective path to the implementation of climate policy through the rational use of natural resources and the involvement of industrial waste and nature-like technologies in the production process. In this regard, one of the options for solving the identified problems is to revise existing technologies and develop low-carbon, low-clinker binders using industrial waste and substandard raw materials.

**Keywords:** alkaline activation; volcanic additives; cement waste; liquid glass; structure; activity; mechatronic activation



Academic Editor: Antonio Caggiano

Received: 29 January 2025

Revised: 24 February 2025

Accepted: 27 February 2025

Published: 21 March 2025

**Citation:** Sarsenbayev, B.; Murtazaev, S.-A.; Salamanova, M.; Kuldeyev, E.; Saidumov, M.; Sarsenbayev, N.; Auyesbek, S.; Sauganova, G.; Abduova, A. Utilization of Anthropogenic and Natural Waste to Produce Construction Raw Materials. *Sustainability* **2025**, *17*, 2791. <https://doi.org/10.3390/su17072791>

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## 1. Introduction

Global warming, associated with greenhouse gas emissions, requires urgent measures to improve the planet's environmental situation [1,2]. Against the background of natural changes, the concept of the sustainable development of the world economy is currently aimed at achieving carbon neutrality, which is possible only at the level of international cooperation and technological exchange [3,4]. It is a well-known fact that sectors such as energy and construction make a significant contribution to carbon emissions into the environment and the atmosphere [5,6]. According to the European Cement Organization, simply burning one ton of Portland cement clinker provokes the emission of at least half a ton of carbon dioxide [7,8].

Therefore, the development of low-carbon construction models will contribute to and open an effective path to the implementation of climate policy through the rational use of natural resources and the involvement of industrial waste and nature-like technologies in production processes [9,10]. In this regard, one of the options for solving the identified problems is the revision of existing technologies and the development of low-carbon geopolymer binders using industrial waste and substandard raw materials [11,12].

It is difficult to call this direction new, as the analysis of foreign works has shown that, in as early as 1862, E. Langin proposed to activate ferrous metallurgy slags with an alkaline solution, and the resulting artificial stone was characterized by fairly high technical and operational indicators [13]. Slag–alkali cement and the concretes based on it are competitive materials and are widely used in construction in many European countries and the USA [14]. The regulatory documentation titled “European Standard of Slag-alkali Cement” was introduced, finding full applications for millions of tons of industrial waste: granulated slags, caprolactam, alkaline sodium production, alumina, sodium sulfide, etc. [15].

Despite the positive foreign experience of using alkali concrete, Portland cement has replaced this promising material from the domestic construction market. However, most developed countries, such as Japan, Great Britain, the Netherlands, Germany, and Singapore, pursuing the priority of abandoning carbonate technology and CO<sub>2</sub> emissions, are developing this direction and obtaining high-quality products with unique characteristics [9–12]—high strength and chemical resistance, low exothermy, good formability, resistance to chlorides, and adjustable setting times—without the use of expensive and energy-intensive clinker [16–19].

Geopolymer binders are characterized by the “aluminosilicate component–alkaline activator” bond—alkali metal compounds in solution form interacting with the solid phase of the aluminosilicate composition—which contributes to the synthesis of water-resistant and durable hydrated alkaline neoplasms. The theoretical justification is that the processes occurring in alkaline systems are, in many ways, similar to the formation of minerals in the Earth’s crust (aqueous and anhydrous modifications of silicates and aluminosilicates of calcium, sodium, or potassium), whereby natural zeolites of sedimentary origin (chabasite, analcime, garronite, mordenite, phillipsite, epidesmine, heulandite, harmotome, gismondite, natrolite, etc.) formed in the Earth’s crust as a result of hydrothermal reactions under low-temperature conditions and, depending on the concentration of alkali, the material and chemical composition of the minerals changed.

For a more complete understanding of the effect of the alkaline activation of metallurgical slags, the oxide composition of aluminosilicates, shown in Table 1, presents the dependence of binder composition on the type of alkaline binder, with a dry matter content of Na<sub>2</sub>O in the range of 3–5% [20].

The explanation for this is the high solubility and degree of dissociation of alkali silicates and aluminates in aqueous solutions, in contrast to which alkaline aluminosilicate compounds are characterized by a weak alkaline reaction. Consequently, alkaline compounds, like alkaline earth compounds, exhibit hydration hardening.

Depending on the material composition of the alkaline grouting fluid, it is possible to obtain concrete of various classes from B7.5 to B140. High strength can be achieved by activating with alkaline silicates—sodium metasilicate and disilicate. In all cases, the resulting concrete stone was characterized by increased corrosion resistance, lower exothermy and contraction, and the processes of setting and hardening occurring even at negative temperatures [21–23].

**Table 1.** Activity of the binder “slag–alkaline solution” depending on the binder type, MPa [20].

| Alkaline Metal Compounds                                            | Activity, MPa |
|---------------------------------------------------------------------|---------------|
| H <sub>2</sub> O                                                    | 7.5           |
| NaOH                                                                | 80            |
| Na <sub>2</sub> CO <sub>3</sub>                                     | 80            |
| Na <sub>2</sub> NO <sub>2</sub>                                     | 55            |
| NaF                                                                 | 85            |
| Na <sub>2</sub> S                                                   | 60            |
| Na <sub>2</sub> SiO <sub>3</sub>                                    | 130           |
| Na <sub>2</sub> O·2SiO <sub>2</sub>                                 | 160           |
| 4Na <sub>2</sub> O·SiO <sub>2</sub>                                 | 23            |
| Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> | 10            |
| Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·8SiO <sub>2</sub> | 6.5           |
| Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub>                    | 67            |

Industrial use of slag–alkali and geopolymer concretes is frequent, but the mechanism of the structure formation processes is still being studied [24,25]. Metallurgical waste is a by-product whose composition and properties are not stable. Moreover, for many regions of the country, they are a scarce and economically unprofitable raw material due to logistics. It is necessary to adhere to the concept of “geopolymers” [16], based on the alkaline contact of monomeric Si–O–Si and Al–O–Si groups included in the composition of rocks or technogenic waste with an amorphous or semi-crystalline structure, resulting in the dispersion of aluminosilicate chains with subsequent transformations into unstable colloidal structures and with the further synthesis of complex compacted substances to develop clinker-free research directions.

The process of geopolymer structure formation can be characterized by the following simplified model:

1. Dispersion of Si–O–Si and Al–O–Si groups in a highly concentrated alkaline solution and colloidal dispersed system formation.
2. Increase in the concentration of the dispersed colloidal system.
3. Compaction of the structure in the existing volume: due to autogenous shrinkage, the rings and chains of the tetrahedrons [SiO<sub>4</sub>]<sup>4−</sup> and [AlO<sub>4</sub>]<sup>5−</sup> close with the formation of three-dimensional aluminosilicate structures  $M \cdot [-(Si-O)_z-Al-O-]_n \cdot wH_2O$ .

The hydration products of the geopolymer binder are calcium hydrosilicates, CaO–SiO<sub>2</sub>–H<sub>2</sub>O; calcium and sodium hydroaluminosilicates, Na<sub>2</sub>O–CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O; and sodium hydroaluminosilicates, Na<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O (zeolites), of variable compositions [17].

In this regard, the work’s aim was to develop formulations and study the properties of a geopolymer binder using technogenic and natural raw materials activated by an alkaline solution. The scientific novelty of this research lies in the development of theoretical foundations for obtaining geopolymer binders; it was found that the alkaline activation of natural and secondary raw materials of aluminosilicate origin leads to the synthesis of a hydroaluminosilicate zeolite phase of variable composition, which contributes to the creation of concrete and mortar composites with improved physical, mechanical, technical, and economic indicators. The conducted research and the results will allow for the expanding of the raw material base and the range of cement products, thereby filling the gaps in the development sector of the resource-saving clinker-free direction.

## 2. Materials and Methods

### Materials

To study the possibility of synthesizing a geopolymer binder, both natural and human-made materials containing an aluminosilicate phase were used as components of the binding system. In particular, opoka was studied—a sedimentary rock with high reactivity after heat treatment. In its natural state, even after mechanical activation, when mixed with an alkaline solution, the system did not show signs of setting. To increase the activity, the opoka was fired in a muffle furnace at a maximum temperature of 700 °C for 4 h, after which it was studied using microstructural analysis methods. The chemical composition and morphology of the heated sample were studied using a Quanta 3D 200i scanning electron microscope (FEI Company, Hillsboro, OR, USA) equipped with a dispersive energy spectrometer (DES) (Shimadzu, Japan) and a Genesis Apex 2 EDS (EDAX) (EDAX Corporate, Pleasanton, CA, USA) microanalysis system. The obtained spectra were processed using EDAX TEAM 2.0 software, and the results of microanalysis are presented in Figures 1–3. The study of the microstructure of the thermally activated opoka particles showed that the material particles are heterogeneous, with aggregates and small clusters with clearly expressed closed porosity (Figure 1). The EDX spectra of the phases of the bulk of the opoka heat-treated at 700 °C confirmed the predominance of calcium and silicon oxides, and the presence of aluminates and alkali oxides in the material was also established (Figure 2).

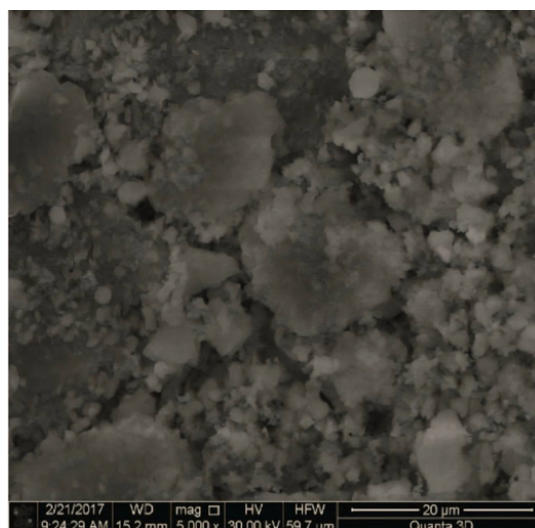


**Figure 1.** SEM images of the seeds of the porcupine mergel (700 °C) (5000×).

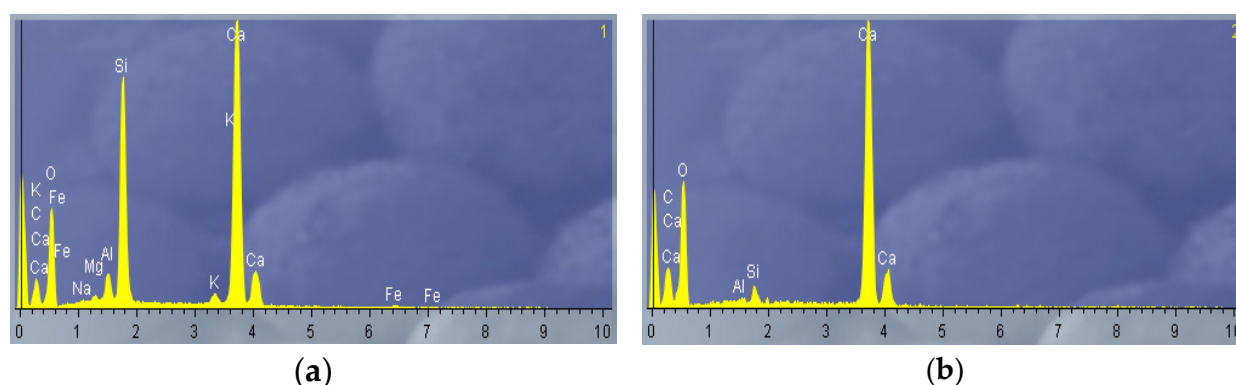


**Figure 2.** EDX spectra phase of the porcupine mergel (700 °C). (a) sample 1; (b) sample 2.

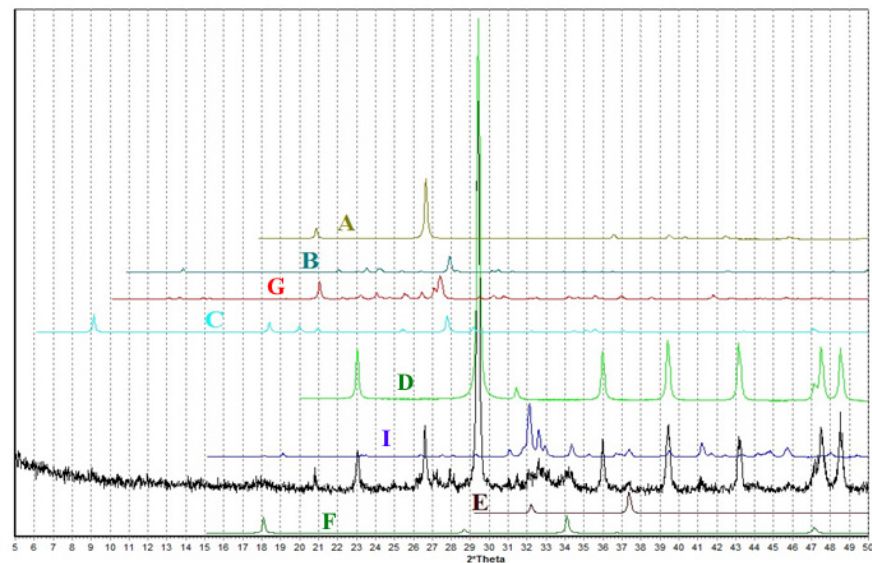


**Figure 3.** Diffractogram of the sample of the porcupine mergel 700 °C: A—quartz; D—calcite; B—albite; C—paragonite; F—portlandite; E—calcium oxide; I—larnite; G—microcline/orthoclase.

The results of X-ray qualitative phase analysis indicate the presence of calcite, quartz, plagioclase, and mica-hydromica phases in the sample of heat-treated opoka. The presence of calcium silicate reflexes, such as larnite and portlandite, was observed (Figure 3).

After thermal activation, the opoka was further ground in a laboratory roller mill for 10 min, the specific surface was determined on a PSKh-12 device (Saint-Peterburg, Russia) and was  $S_{\text{specific}} = 526 \text{ m}^2/\text{kg}$ .

The second powder component of the geopolymer binder was studied as waste from the cement industry in the form of aspiration and clinker dust, which is formed in tons after one cycle of clinker firing and is extracted from the dust precipitation system of the clinker kiln. A significant advantage of dust is the lack of a need for mechanical activation and the possibility of using it in its natural form. Clinker dust is reused in the technological process—clinker grinding—and in studies, it was used in small quantities (5%). Aspiration dust is completely removed from production and has not found proper application, therefore confirming the disposal of this full-fledged man-made product for the proposed purposes.

Aspiration dust has the following indicators: true specific gravity,  $2.58 \text{ g}/\text{cm}^3$ ; bulk density,  $1.13 \text{ g}/\text{cm}^3$ ; and specific surface area,  $280 \text{ m}^2/\text{kg}$ . Clinker dust is characterized by the following indicators: true specific gravity,  $3.12 \text{ g}/\text{cm}^3$ ; bulk density,  $1.24 \text{ g}/\text{cm}^3$ ; and specific surface area,  $220 \text{ m}^2/\text{kg}$ . The energy dispersive analysis of the powders under study confirms the presence of an aluminosilicate phase and the similarity with the specified characteristics of clinker (Figure 4a,b); micrographs were taken on a Quanta 3D 200i scanning electron microscope (Figure 5a,b).

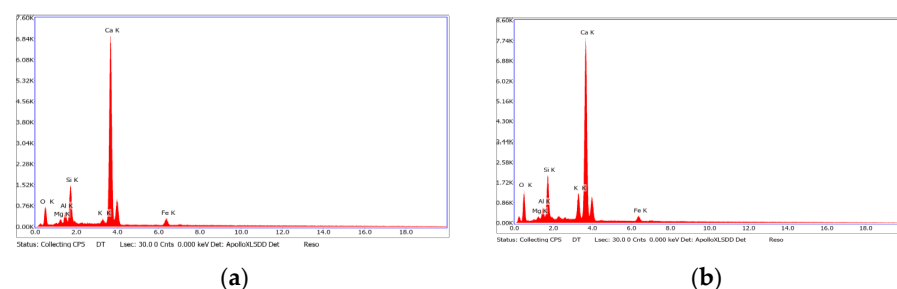


**Figure 4.** EDX spectra of the bulk phases of clinker (a) aspiration and (b) dust.

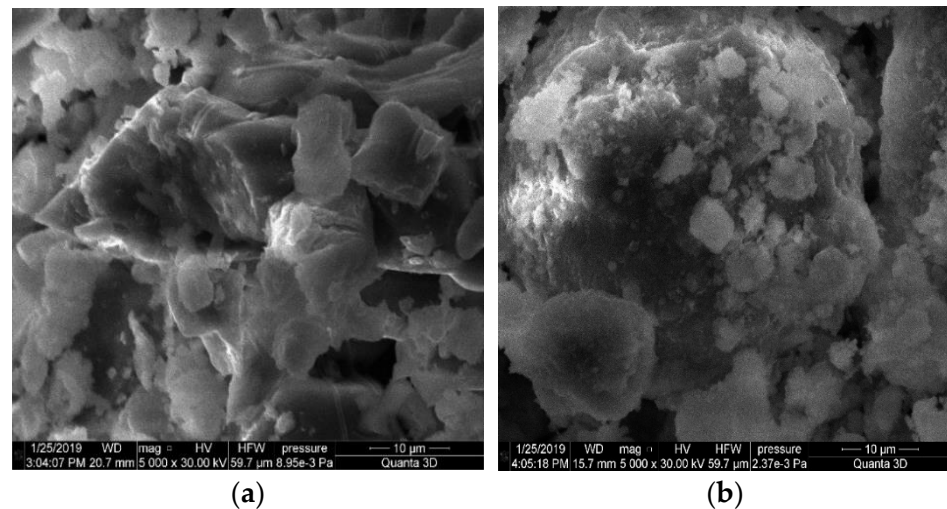


**Figure 5.** Micrographs of clinker grains (a) and aspiration dust (b); magnification 5000 $\times$ .

The study of the microstructure of cement dust particles showed that the bulk of heterogeneous dust systems consist of volumetric aggregates and intergrowths and small clusters on their surface with clearly expressed cleavage. The features of the microstructure indicate mineral formation processes (Figure 5).

Mechanically and thermally activated opoka, aspiration, and clinker dust exhibit weak hydraulic activity when mixed with water. The color range of the powders studied gives us a superficial understanding of the degree of material crystallinity (Figure 6). However, the reaction activity is increased sharply by the alkaline activation of these powders, especially in the presence of sodium silicium (6%) from the mass of  $\text{Na}_2\text{SiO}_3$ . We used an aqueous solution of sodium metasilicate from the LLC «Tantal 4» as an alkaline activator blocker in the study (silico-carbonate module 2.8 and density 1420 kg/m<sup>3</sup>).

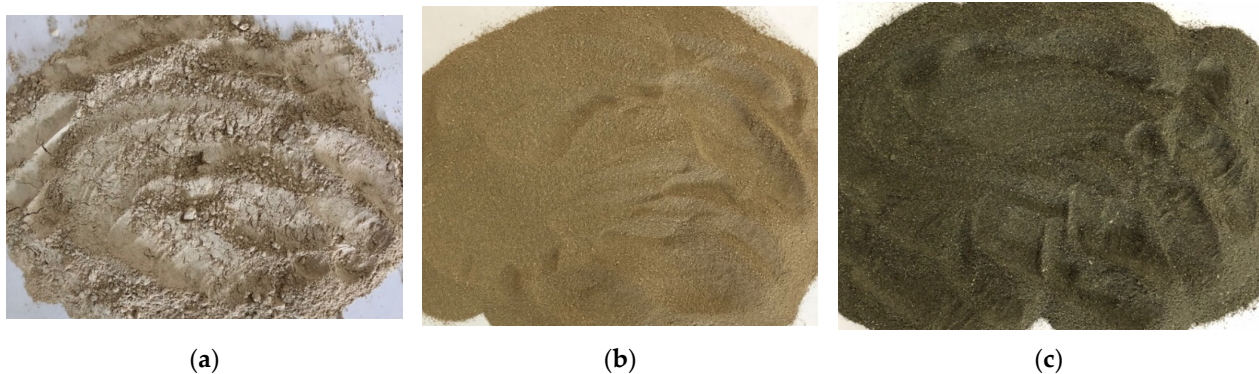


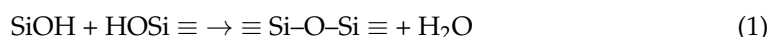
**Figure 6.** Photos of reactive mineral powders: (a) heat-activated porcupine mergel; (b) aspirating dust; (c) clinker dust.

For an in-depth study of this topic, it is necessary to analyze in detail all the information concerning the alkaline activator, which plays a key role in the formation of the binding structure. Commercial liquid glass, an aqueous solution of alkali metal silicates, is widely used as such an activator. Depending on the type of cation, it is divided into sodium, potassium, lithium, and ammonium. In this work, sodium liquid glass became the object of study. The unique properties of this material are beyond doubt, which is confirmed by the experimental results obtained [10,11].

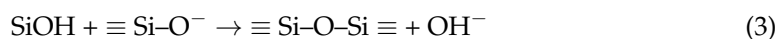
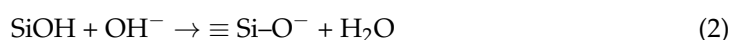
The anhydrous  $\text{Na}_2\text{O SiO}_2$  system has three binary compounds depending on the melting point:  $2\text{Na}_2\text{O SiO}_2$  orthosilicate;  $\text{Na}_2\text{O SiO}_2$  metasilicate, and  $\text{Na}_2\text{O 2SiO}_2$  sodium

disilicate. The phase transitions of the anhydrous  $\text{Na}_2\text{O-SiO}_2$  system, depending on the temperature and proportion of silica, can be represented by the following description: the melting of sodium orthosilicate,  $2\text{Na}_2\text{O-SiO}_2$ , occurs incongruently at a temperature of  $1118^\circ\text{C}$ ; the melting of the other two compounds occurs congruently at temperatures of  $1086^\circ\text{C}$  and  $874^\circ\text{C}$ , respectively. The  $\text{Na}_2\text{O-SiO}_2$  system is characterized by three eutectic points at  $1022^\circ\text{C}$ ,  $846^\circ\text{C}$ , and  $793^\circ\text{C}$  [18].

In the aqueous system of sodium hydrosilicates,  $\text{Na}_2\text{O-SiO}_2\text{-H}_2\text{O}$ , there is a large number of different crystal hydrates, which are the modifications of orthosilicic acid  $\text{Si(OH)}_4$  and are capable of forming polysilicic acids as a result of the polycondensation reaction:



Chemical reactions of the interaction in the  $\text{Na}_2\text{O-SiO}_2\text{-H}_2\text{O}$  system proceed according to the acid–base mechanism:



The protolytic reaction (Equation (2)) proceeds in the forward direction when interacting with the base, resulting in the formation of an ionized form of silica. This process is typical for polysilicates and colloidal systems. In the reverse direction (Equation (3)), the reaction occurs through the hydrolysis of ionized silica, which leads to an increase in the pH of the liquid glass medium [18].

The polymerization–depolymerization process promotes the dispersion of silica. The compounds formed during the reverse reaction are characterized by spherical morphology and, upon crystallization, form colloidal particles with a negative charge in the solution. These particles do not interact with each other without creating certain conditions for coagulation [18].

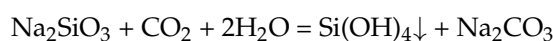
An aqueous solution of sodium metasilicate from the Russian manufacturer LLC “Tantal 4” (silicate module 2.8 and density  $1420 \text{ kg/m}^3$ ) was used as an alkaline activator solvent in the studies. To accelerate the crystallization processes, sodium fluorosilicate was introduced into the binder system at a dosage of 6% of the  $\text{Na}_2\text{SiO}_3$  mass.

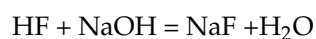
The preparation and testing of binder samples were carried out in accordance with the following regulatory documents: GOST 30744-2001 Cements [26], for test methods using polyfractional sand; GOST 310.4-81 Cements [27], for methods for determining the ultimate strength in bending and compression; and GOST 310.3-76 Cements [28], for methods for determining the normal density, setting time, and uniformity of volume change.

### 3. Results and Discussion

To determine the optimal formulation of the geopolymer binder, the first stage involved studying the “reaction powder–grouting fluid” systems. The results of the experiment are shown in Table 2.

The analysis of the obtained data makes it possible to judge the behavior of alkaline systems in the state of cement paste and stone after hardening. It is necessary to note the formation of a dense crust on the surface of the sample during the determination of the normal density and setting time of the cement paste. This is due to the carbonization processes in the system:





All samples, regardless of the sealer type, are characterized by the high consumption of the liquid phase, and this can be explained by the high adsorption capacity of heat-treated powders because they are products of thermal action. In particular, aspiration dust is collected in the heating and dehydration zone of the furnace at a temperature of 400–500 °C, which is comparatively less than that of clinker dust and flask, at 700 °C.

**Table 2.** Properties of geopolymer compositions “reaction powder–grouting fluid”.

| № | Quality Indicators                                | Heat-Activated<br>Porcupine Merge 700 °C                               |                  | Clinker Dust                                                           |                  | Aspiration Dust                                                        |                  |
|---|---------------------------------------------------|------------------------------------------------------------------------|------------------|------------------------------------------------------------------------|------------------|------------------------------------------------------------------------|------------------|
|   |                                                   | Type of Grouting Fluid                                                 |                  |                                                                        |                  |                                                                        |                  |
|   |                                                   | Na <sub>2</sub> SiO <sub>3</sub> +<br>Na <sub>2</sub> SiF <sub>6</sub> | H <sub>2</sub> O | Na <sub>2</sub> SiO <sub>3</sub> +<br>Na <sub>2</sub> SiF <sub>6</sub> | H <sub>2</sub> O | Na <sub>2</sub> SiO <sub>3</sub> +<br>Na <sub>2</sub> SiF <sub>6</sub> | H <sub>2</sub> O |
| 1 | Normal density of alkaline cement paste (NGCT), % | 56.5                                                                   | 40.0             | 50.0                                                                   | 30.0             | 70.0                                                                   | 42.0             |
| 2 | Setting time, start/end, hours–min.               | 00–26<br>00–32                                                         | 01–37<br>06–29   | 00–40<br>01–20                                                         | 00–54<br>01–56   | 00–24<br>00–36                                                         | 06–08<br>07–16   |
| 3 | Activity, 28 days, MPa                            | 32.1                                                                   | 9.2              | 24.0                                                                   | 6.3              | 32.6                                                                   | 5.3              |

Therefore, the maximum NGCT indicator, with short setting times, start at 24 min and end at 36 min. The activity of the binders corresponds to the M300 cement grade. This property is desirable for carrying out some emergency repair work, but in traditional concrete technology, sufficient time is needed for the high-quality molding of concrete and reinforced concrete products.

Therefore, after a preliminary assessment of the qualities of geopolymer binders, the goal was set to improve the performance of both the alkaline cement paste and the stone as a whole. Clinker dust, as mentioned earlier, is subject to return to the technological cycle and, after collection from the dust settling chamber, is characterized by a low specific surface area of 180–210 m<sup>2</sup>/kg.

When designing the binder formulations, this material was used as a catalyst additive in the amount of 5%, and sodium fluorosilicate, Na<sub>2</sub>SiF<sub>6</sub>, was also introduced into all compositions; the dosage was 6% of the mass of liquid glass and was the most advantageous. Volcanic tuff and substandard fine dune sands were used to regulate the setting time and increase the aluminosilicate component in the binder composition, in the hope of improving the properties of the cement paste. Before being introduced into the binder, these rocks were finely ground in a laboratory roller mill for 20 min to activate the surface and reveal hidden crystallization centers. During the experimental studies, the optimal degree of filling the binder with the additive was identified, which was 10%. The results of modeling the binders, the “reaction powder–mineral powder–Na<sub>2</sub>SiO<sub>3</sub>”, the specific surface of the filler powders, the properties of the alkaline dough, and the kinetics of strength gain are all given in Table 3.

The obtained data confirm the positive concept of filling the binder with a more dispersed additive containing an aluminosilicate phase. The properties of the cement paste improved, the NGCT decreased by 8–10%, and the setting time increased slightly, but by 10–40 min depending on the active component. The introduction of powders in the amount of 10% contributed to the creation of a denser and more impermeable structure, as shown by the water absorption by weight decreasing by 5%. The strength gain of the samples was studied for longer periods; the effect of heat and moisture treatment had a positive effect

on the properties of the stone, causing the strength to increase by 10–12%. It should be noted that the mineral powder from the volcanic additive, in comparison with dune sand, contributed to the higher strength gain; the numerical indicator of activity increased by 10–13%. The explanation for this is the nature of volcanic rocks (a product of natural heat treatment) and the presence of an amorphous substance in the mineral composition, which was proven by previously conducted studies [4,6].

**Table 3.** Formulations and properties of geopolymer binders.

| Mix ID                                                                                        | Mineral Powder | S <sub>specific</sub> ,<br>m <sup>2</sup> /kg | Normal Density of<br>alkaline Cement<br>Paste (NGCT), % | Setting Time,<br>Hours–<br>Minutes | Compressive Strength, MPa |         |         |                                    |
|-----------------------------------------------------------------------------------------------|----------------|-----------------------------------------------|---------------------------------------------------------|------------------------------------|---------------------------|---------|---------|------------------------------------|
|                                                                                               |                |                                               |                                                         |                                    | 7 Days                    | 28 Days | 60 Days | Heat Generating<br>Waste + 27 Days |
| aspiration (85%) + clinker dust (5%) + min. powder + Na <sub>2</sub> SiO <sub>3</sub>         |                |                                               |                                                         |                                    |                           |         |         |                                    |
| 1                                                                                             | Velvat sand    | 80                                            | 61.2                                                    | 00–45<br>01–35                     | 9.8                       | 8.4     | 8.9     | 1.5                                |
| 2                                                                                             | Velvet tuff    | 76                                            | 62.0                                                    | 00–32<br>01–21                     | 2.8                       | 2.6     | 7.8     | 9.3                                |
| opoka 700 °C (85%) + clinker dust (5%) + min. powder (10%) + Na <sub>2</sub> SiO <sub>3</sub> |                |                                               |                                                         |                                    |                           |         |         |                                    |
| 3                                                                                             | Velvat sand    | 80                                            | 50.1                                                    | 00–56<br>01–50                     | 8.6                       | 8.0     | 0.5     | 2.1                                |
| 4                                                                                             | Velvet tuff    | 76                                            | 50.4                                                    | 00–33<br>01–35                     | 2.4                       | 2.1     | 6.2     | 0.0                                |

The problem with early setting times was not resolved by introducing a filler additive into the binder composition at an amount of 10% by weight, so it was necessary to resort to methods of binder chemical modification. To conduct a comparative analysis, additives of different compositions were studied. The setting retarder sodium tetraborate decahydrate (borax), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, is a weak salt of boric acid and sulfanilic acid, C<sub>6</sub>H<sub>7</sub>NO<sub>3</sub>S, is a water-insoluble internal salt in which the amino group is neutralized by a sulfonic acid residue. The dosage of modifiers was determined experimentally; both additives in the required amount were mixed with an aqueous solution of sodium metasilicate, and the test results are shown in Figure 7a,b. The results of the studies show that sulfanilic acid and borax at appropriate dosages coped well with the task. But, if we compare the data, we can note that sodium tetraborate decahydrate is significantly more effective than sulfanilic acid, even at lower dosages, evidenced by the fact that the setting time increased by 2–3 h.

The optimum dosage of sulfanilic acid was 1% of the alkali activator weight and that of sodium tetraborate decahydrate was 0.45%. When preparing batches of alkaline cement paste, a decrease in the need for an alkaline solution by approximately 35–46% was noted; the ratio of the alkaline solution to the reactive component (AS/RC) changed depending on the binder composition. In the binder compositions “aspiration dust (85%) + clinker dust (5%) + volcanic tuff 10% + borax”, the ratio of AS/RC was 0.64; “aspiration dust (85%) + clinker dust (5%) + volcanic tuff 10% + sulfanilic acid”—0.71; “opoka 700 °C (85%) + clinker dust (5%) + volcanic tuff 10% + borax”—0.61; and “opoka 700 °C (85%) + clinker dust (5%) + volcanic tuff 10% + sulfanilic acid”—0.67. After stripping, the samples were placed in a drying oven for 3 h at a temperature of 65–70 °C for a week. During the specified time intervals, the binder samples were tested; the results are presented in Table 4.

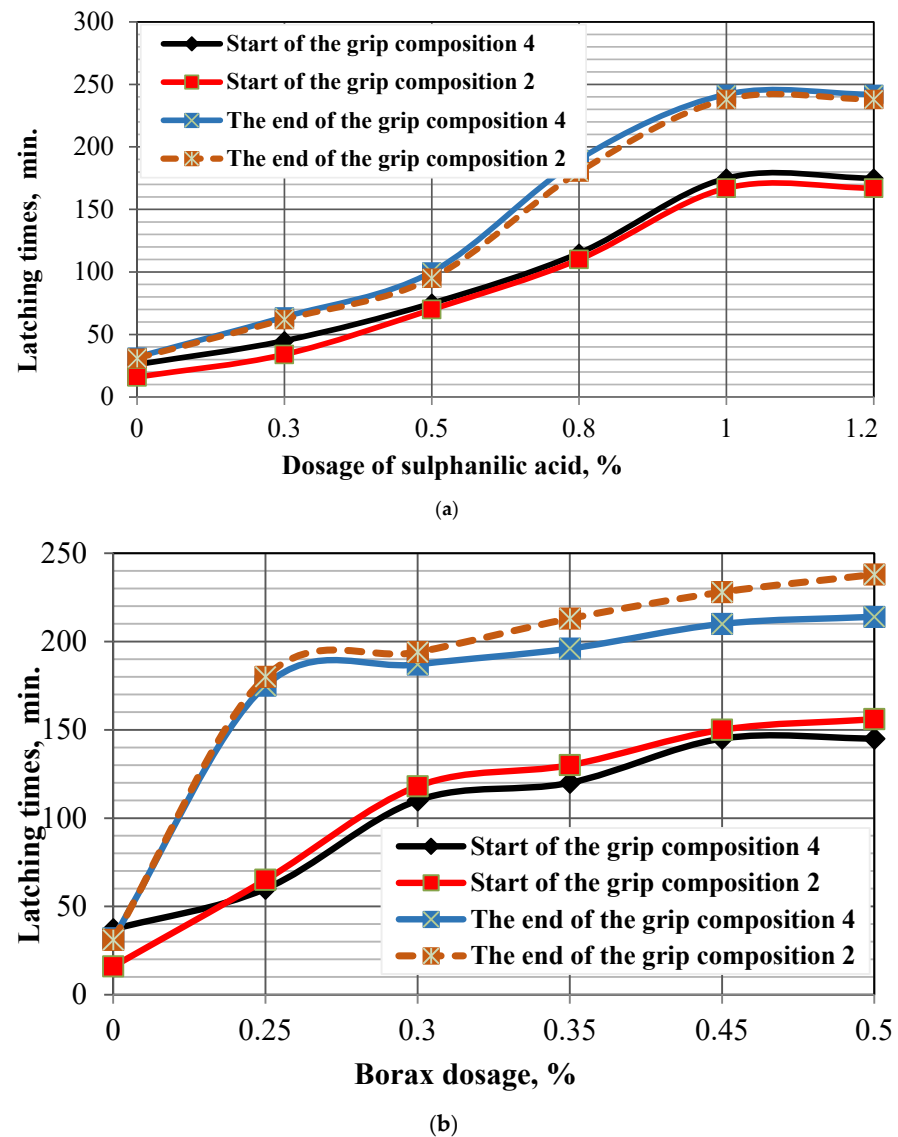


Figure 7. Effect of additives on setting time: (a) dosage of sulfanilic acid; (b) borax dosage.

Table 4. Properties of modified geopolymer binders.

| Compositions                                                                                              | Mineral Powder                                                     | Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10N <sub>2</sub> O, % | C <sub>6</sub> H <sub>7</sub> NO <sub>3</sub> S, % | Destiny, kg/m <sup>3</sup> | Water Absorption, % | Compressive Streght, MPa |         |         |
|-----------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------------|----------------------------|---------------------|--------------------------|---------|---------|
|                                                                                                           |                                                                    |                                                                      |                                                    |                            |                     | 7 Days                   | 28 Days | 60 Days |
| aspiration dust (85%) + clinker dust (5%) + min. powder 10% + Na <sub>2</sub> SiO <sub>3</sub> + additive |                                                                    |                                                                      |                                                    |                            |                     |                          |         |         |
| 1                                                                                                         | Volcanic tuff<br>S <sub>specific</sub> =<br>476 m <sup>2</sup> /kg | 0.45                                                                 | -                                                  | 2162                       | 4.1                 | 27.3                     | 38.9    | 45      |
| 2                                                                                                         |                                                                    | 0.35                                                                 | -                                                  | 2151                       | 4.3                 | 25.4                     | 36.5    | 9.343.8 |
| 3                                                                                                         |                                                                    | -                                                                    | 0.8                                                | 2130                       | 4.9                 | 15.8                     | 20.7    | 21.4    |
| 4                                                                                                         |                                                                    | -                                                                    | 1.0                                                | 2119                       | 4.8                 | 14.6                     | 18.9    | 20.1    |
| 700 °C opoka (85%) + clinker dust (5%) + min. powder 10% + Na <sub>2</sub> SiO <sub>3</sub> + additive    |                                                                    |                                                                      |                                                    |                            |                     |                          |         |         |
| 5                                                                                                         | Volcanic tuff<br>S <sub>specific</sub> =<br>476 m <sup>2</sup> /kg | 0.45                                                                 | -                                                  | 2135                       | 4.4                 | 24.9                     | 36.1    | 41.1    |
| 6                                                                                                         |                                                                    | 0.35                                                                 | -                                                  | 2140                       | 4.6                 | 22.7                     | 33.5    | 41.9    |
| 7                                                                                                         |                                                                    | -                                                                    | 0.8                                                | 2120                       | 5.1                 | 11.6                     | 17.0    | 18.3    |
| 8                                                                                                         |                                                                    | -                                                                    | 1.0                                                | 2114                       | 5.0                 | 10.8                     | 15.3    | 16.1    |

The research data revealed the dependence of the chemical modifier influence on the cement stone's structure and properties. In modifying the system with sodium tetraborate decahydrate in dosages of 0.35–0.45% of the mass of the alkaline activator, the structure was compacted and the porosity of the stone decreased, which had a positive effect on the activity of the binder. The activity of the geopolymer binder “aspiration dust (85%) + clinker dust (5%) + mineral powder 10% +  $\text{Na}_2\text{SiO}_3$  + borax” is 38.9 MPa and corresponds to the cement grade M400; over time, the strength increased by 14–15%. The results of the studies of the samples of the binder “reaction powder (85%) + clinker dust (5%) + mineral powder 10% +  $\text{Na}_2\text{SiO}_3$  + sulfanilic acid” in all cases are inferior in strength by about 46–50% to the samples using borax. This fact can be substantiated by the nature of sulfanilic acid, because the processes of hydration and geotransformations occur only in the presence of an alkaline environment, and by introducing a certain amount of sulfonic acid into the system, neutralization and a decrease in the pH of the internal background occur. The concentration of the dispersed colloidal system decreases, which complicates the dispersion of the  $-\text{Si}-\text{O}-\text{Si}$  and  $\text{Al}-\text{O}-\text{Si}$  groups, and the process of the formation of three-dimensional aluminosilicate structures  $\text{M} \cdot [-(\text{Si}-\text{O})_z-\text{Al}-\text{O}]_n \cdot n\text{H}_2\text{O}$  slows down and will not occur at all. It should be noted that the obtained dependencies and results do not contradict known literary sources [3,7–11].

#### 4. Conclusions

The alkaline mixing of mineral powders of aluminosilicate nature are similar to natural mineral formation in the mechanism of reactions of interaction and hardening. The development of the proposed model of geopolymer binders will allow the transition to new environmentally friendly technologies. The study of the microstructure of the samples showed that the bulk of heterogeneous systems consist of volumetric aggregates and intergrowths, small clusters on their surface with pronounced cleavage; the features of the microstructure indicate mineral formation processes.

The research data revealed the dependence of the influence of the chemical modifier on the structure and properties of the cement stone. In modifying the decahydrate system with sodium tetraborate in dosages of 0.35–0.45% of the mass of the alkaline activator, the structure was compacted and the porosity of the stone decreased, which had a positive effect on the activity of the binder.

A positive concept of filling the binder with a more dispersed volcanic additive containing an aluminosilicate phase at an amount of 10% was established. The properties of the cement paste improved; the need for an alkaline solution decreased by 8–10%; the setting time was insignificant but increased by 10–40 min depending on the active component; water absorption by weight decreased by 5%; and strength increased by 10–12%.

Thus, the research results presented in this work allow us to evaluate the effectiveness of the geopolymer direction; it is especially valuable that possible ways of recycling cement production waste are proposed, since fine aspiration dust is dispersed to nearby agricultural lands, polluting nature, water bodies, and all living things.

The transition to geopolymers based on aluminosilicate alkali-activated raw materials will allow us to abandon the method of the high-temperature firing of Portland cement clinker and will lead to saving expensive energy resources and natural potential. In addition, the negative impact of carbonate technology on the surrounding atmosphere and climate change is known.

**Author Contributions:** Conceptualization, B.S. and A.A.; methodology, B.S.; software, B.S. and G.S.; validation, S.-A.M. and G.S.; formal analysis, S.-A.M.; investigation, M.S. (Madina Salamanova) and N.S.; resources, M.S. (Magomed Saidumov) and N.S.; data curation, S.A.; writing—original draft

preparation, S.-A.M.; writing—review and editing, E.K.; visualization, E.K.; supervision, M.S. (Madina Salamanova); project administration, M.S. (Magomed Saidumov) and S.A.; funding acquisition, A.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan, grant number BR21882292.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data used to support the findings of the present study will be provided upon request by the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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