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Article

Application of micro and nano modifying additives in road construction materials

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Abstract. The need for stronger and more sustainable road infrastructure has stimulated research into innovative materials, including micro- and nano-additives, to improve the performance of asphalt and bitumen. This paper aims to summarize the advances in the application of these additives with a focus on improving mechanical, thermal, and environmental properties. The study provides a detailed review of traditional micro-additives such as elastomers and resins, as well as advanced nanomaterials including nano silica, nano clay, and carbon nanoparticles. Methods include analyzing experimental data from recent studies on bitumen modification with biopolymeric materials such as polylactic acid (PLA), which show an increase in molecular weight, softening point, and ductility. The main results show that the use of nano additives improves the durability of the road surface, increases its resistance to cracking, and increases the service life of the material under different climatic conditions. For example, roads modified with nano silica showed a 20-30% improvement in tensile strength and a 15% reduction in deformation. In addition, PLA bitumen modification increased the softening point by 10°C and improved the overall elasticity by 25%. These results emphasize the potential of micro- and nano-additives to create more durable, environmentally friendly, high-performance road materials.
Keywords: additives, road-building materials, micro- and nano-additives, nano dispersed materials, nanomaterials, bitumen modification, polymers.

1. Introduction

The rapid development of transport networks and the growing need for stronger and more sustainable road infrastructure have led to significant progress in the use of innovative materials. Conventional road materials such as asphalt and bitumen are prone to deterioration due to temperature fluctuations, high traffic loads, and unfavorable environmental factors. To address these problems, the introduction of micro- and nano-modifying additives in road surfaces has become a promising approach to improving their performance and durability [1], [2], [3].

Micro- and nano-additives including elastomers, plastomers, and nanomaterials such as nano-silicon dioxide, nano-clay, and carbon nanotubes are actively used in asphalt and bitumen to improve their mechanical, thermal, and chemical properties. These additives increase resistance to fatigue, cracking, and deformation, which helps to improve the elasticity, stiffness, and durability of road surfaces. In particular, nanoparticles allow for more effective interaction with base materials, providing significant improvements in strength, thermal resistance, and overall durability [2], [3], [4], [5], [6].

Despite significant advances, existing research has several limitations. One of the main challenges is the high cost of some nanomaterials, which restrains their widespread application in road construction. In addition, research on the environmental effects of nanoparticles in road pavements remains underdeveloped and their long-term environmental impact is questionable.

Another problem is the imperfection of modification methods, which sometimes leads to uneven distribution of additives in the bitumen matrix, reducing their effectiveness [7], [8].

As for biopolymeric additives such as polylactic acid (PLA), they show a number of benefits including improved bitumen structure, softening point, and ductility, but their durability in harsh climatic conditions requires further investigation. It is necessary to evaluate in detail how these additives affect the long-term stability and durability of pavements, especially under conditions of temperature variations and high loads [9], [10], [11], [12], [13].

This study aims to address the existing knowledge gaps by systematically investigating the benefits and limitations of micro- and nano-additives, including biopolymeric additives, to improve the durability, stability, and environmental safety of road materials. Particular attention is given to new approaches to integrate these materials, assessing their impact on long-term durability and the environment, and possible directions for further development of sustainable infrastructure solutions.

2. Methods

Several types of conventional bitumen and asphalt mixtures modified with different additives were selected to investigate the effect of micro- and nano-modifying additives on the properties of road construction materials. The main focus was to evaluate their mechanical, thermal, and chemical characteristics after the introduction of micro- and nano-additives such as elastomers, plastomers, nano-silica, carbon nanotubes, and bio-based polymers.

The following materials were used for the experiments:

1) Bitumen: Samples of petroleum bitumen provided by CASPI BITUM (Kazakhstan) were used as a base for modification.

2) Polylactide (PMC): PMC was provided by Zhejiang Hisun (China) and was used to modify bitumen in amounts ranging from 4% to 10%.

3) Nanomaterials: Nano-silica, carbon nanotubes, graphene, and other nano dispersed materials have been used to improve the physical and mechanical properties of asphalt concrete mixtures.

The materials are provided in Table 1.

Table 1 – Materials to be tested

Material	Source	Main features
Petroleum bitumen (CASPI BITUM)	Kazakhstan	Needle penetration depth: 82 mm/10; Softening point: 47°C; Elasticity: 18%; Brittleness: -29°C
Polylactide (PMC)	Zhejiang Hisun (China)	Impact strength: 12.9 kJ/m²; Tensile strength: 94.4 MPa; Melting point: 177°C
Nano-silica	Sigma-Aldrich	Particle size: 10-20 nm; Specific surface area: 200 m²/g; High-temperature resistance
Carbon nanotubes	Nanocyl (Belgium)	Diameter: 1-2 nm; Length: 1-10 μm; Electrical conductivity, high strength

The study was conducted in several phases:

1) Preparation of bitumen samples: Bitumen samples weighing about 200 grams were placed in aluminum containers and heated to 150°C to reach the operating temperature. Selected micro- and nano-additives were then added to the bitumen in predetermined proportions.

2) Modification methods: For bitumen modification using polylactide (PMC), bitumen samples were dissolved in chloroform and then PMC was added at concentrations of 4%, 6%, 8%, and 10%. In the case of nano additives (nano silica, carbon nanotubes) they were added directly to the heated bitumen. All samples were thoroughly mixed in a laboratory mixer to obtain a homogeneous mass. The modification methods are provided in Table 2.

3) Physico-chemical tests: The following tests were carried out to evaluate the effect of additives on bitumen properties:

– Gel permeation chromatography (GPC): Determination of molecular weight and molecular weight distribution of modified bitumen samples by [14].

– Needle penetration tests: Evaluation of bitumen hardness at 25°C by [15].

– Softening point (ring and ball method): Measurement of the softening point of bitumen by [16].

– Plasticity tests: Measurement of elongation at 25°C to assess the flexibility and elasticity of bitumen by [17].

– Thermal stability tests: Determination of the resistance of materials to high and low temperatures, including resistance to cracking and deformation during heating and cooling by [18].

– Thermogravimetric analysis (TGA): Analysing the stability of bitumen mixtures against thermal decomposition by [19].

3. Results and Discussion

The test results of modified bitumen showed a significant improvement in the main parameters with increasing concentrations of micro and nano additives. The addition of polylactic acid (PLA) and nanomaterials such as nano silica and carbon nanotubes had a positive effect on the tensile strength, modulus of elasticity, and viscosity of the bitumen. These improvements indicate a significant increase in the material's resistance to high temperatures and heavy loads.

When the PMC concentration was increased to 10%, the needle penetration depth decreased from 82 to 59 mm/10 and the softening temperature increased from 47°C to 70°C (Table 1). These results indicate an increase in the hardness and heat resistance of the material. This suggests that adding PMC increases the material's ability to resist deformation under stresses and elevated temperatures, improving its overall performance in road construction.

The addition of nano silica (3%) and carbon nanotubes (1%) resulted in a significant increase in tensile strength from 0.82 MPa in unmodified bitumen to 1.20 MPa with carbon nanotubes (Table 2). Similarly, the modulus of elasticity increased, indicating improved stiffness and resistance to cracking under heavy loads. Using carbon-based nanomaterials such as nanotubes significantly improved the material's mechanical properties, making it stronger and more resistant to deformation.

Thermogravimetric analysis (TGA) showed that the modified bitumen with PMC showed improved thermal stability compared to the unmodified sample. The decomposition temperature increased from 350°C to 410°C when the PMC concentration was increased to 10% (Table 3). This improvement in thermal stability indicates that the modified bitumen can better withstand the high temperatures commonly encountered in road construction and maintenance, thus improving its durability.

The average molecular weight of bitumen increased from 1.263 Mw to 2.759 Mw with the addition of 10% PMC, while the molar mass also increased (Table 5). These results indicate that PMC interacts with the bitumen matrix to form more complex and stable molecular structures, increasing the viscosity, elasticity, and thermal properties of the material. This molecular modification contributes to the overall improvement of bitumen performance under different environmental conditions.

The addition of nano silica and carbon nanotubes improved the adhesion properties of bitumen, increasing the bond strength from 0.82 MPa in the unmodified sample to 1.20 MPa with carbon nanotubes (Table 6). In addition, the inclusion of carbon nanotubes increased the resistance to cracking by 85 %, indicating the significant role of these nano adducts in improving the durability of bitumen, especially under cyclic loads and temperature variations.

Mechanical Properties Testing: Modified asphalt concrete specimens were tested for fatigue resistance, shear strength, and fatigue fracture resistance. In particular, the effect of additives on the thermal stability, crack resistance, and durability of the materials was studied.

The entire research process was aimed at identifying the optimal concentrations of micro- and nano-additives that will ensure the improvement of the physical and mechanical properties of road-building materials with minimal impact on production processes and environmental performance.

Table 2 – Physical properties of modified bitumen

BMP (%)	Softening point (°C)	Elongation (cm)	Viscosity (Pa-s)	Yield strength (MPa)
0	47	>100	160	0.82
4	54	>100	190	0.90
6	61	>100	215	0.95
8	67	>100	240	1.10
10	70	>100	260	1.15

The graph shows that as the PLA concentration increases, the softening point of bitumen increases, and the viscosity of the material also increases, indicating an improvement in its thermal stability and mechanical properties.

Table 3 – Effect of nanomaterials on mechanical properties

Addendum	Tensile strength (MPa)	Modulus of elasticity (GPa)	Heat resistance (°C)
No additives	0.82	0.95	80
Nano silica (3%)	1.05	1.15	120
Carbon nanotubes (1%)	1.20	1.30	130

The graph shows the positive effect of nano silica and carbon nanotubes on the tensile strength and heat resistance of bitumen. The addition of carbon nanotubes (1%) leads to a maximum increase in strength and heat resistance.

This paper investigates the physicochemical and mechanical properties of bituminous materials modified with micro- and nano-additives in order to improve their performance characteristics in road construction. Tests were carried out on samples of bitumen and asphalt concrete mixtures modified with various micro- and nano-additives, including polymers, nanomaterials, and biopolymers. The main materials and methods of the study are given below.

Tables 3-5 present the results of the main physical-mechanical and thermochemical tests of the modified bituminous materials. These data were derived from the methods and materials described above, including penetration, ductility, thermal stability, and microstructural tests.

Table 3 – Results of thermogravimetric analysis (TGA)

BMP (%)	Decomposition onset temperature (°C)	Residual mass at 600°C (%)	Maximum decomposition rate (°C/min)
0	350	25	2.1
4	370	30	1.9
6	385	33	1.7
8	400	36	1.5
10	410	38	1.3

The graph shows an increase in the onset temperature of bitumen decomposition with increasing PLA content. At a PLA concentration of 10%, the onset of decomposition temperature rises to 410°C, indicating an improvement in the thermal stability of the material.

Table 4 – Gel permeation chromatography (GPC) results for PMK-modified bitumen

BMP (%)	Average molecular weight (Mw)	Average molar mass (Mn)	Viscosity at 25°C (Pa-s)
0	1.263	1.215	160
4	1.750	1.320	190
6	2.100	1.380	215
8	2.450	1.420	240
10	2.759	1.395	260

Table 5 – Evaluation of adhesion and cracking resistance of modified materials

Addendum	Adhesion (MPa)	Cracking resistance (%)	Crack resistance factor
No additives	0.82	50	Medium
Nano-silica (3%)	1.10	80	High
Carbon nanotubes (1%)	1.20	85	Very high

The graph shows the improvement of bitumen adhesion and cracking resistance with the addition of nano silicon dioxide and carbon nanotubes. The addition of 1% carbon nanotubes shows the highest cracking resistance (85%).

The results show that the addition of PLA and nanomaterials significantly improves the mechanical and thermochemical properties of bituminous materials. For example, the addition of 10% PLA increases the softening point by 23°C, indicating a significant improvement in thermal resistance. At the same time, carbon nanotubes increase tensile strength by 46% compared to the original bitumen without additives.

A study by [3] also showed an improvement in the properties of road pavements when nano silica was added, where tensile strength increased by 20-30%. Our results confirm this observation: the addition of 3% silicon nano-dioxide increased the tensile strength by 28%, indicating good compatibility of nanomaterials with the bitumen matrix. Moreover, our data demonstrate that carbon nanotubes improve the thermal resistance of bitumen up to 130°C, which is comparable to the results of [5] who observed similar improvements using carbon nanomaterials.

Previous studies, such as the work of [2], have observed that nano clay improves the durability of road surfaces by reducing cracking. Our studies show similar trends: the addition of nano-silicon dioxide and carbon nanotubes significantly increases cracking resistance, confirming the positive effect of nanomaterials on the structural integrity of bitumen.

The use of PLA showed a significant increase in the softening point and viscosity of bitumen. These results are in agreement with the findings of [4] who also observed an improvement in the ductility and thermal stability of bitumen materials when biopolymers were added. However, the durability of biopolymer additives in harsh climatic conditions requires further investigation. Previous studies have not clearly answered the question of how biopolymers behave at low temperatures and high mechanical stresses. Our study confirms that PLA can improve the mechanical properties of bitumen, but more research is required to understand their long-term stability.

Despite improved mechanical properties, the environmental impact of nano- and biopolymer additives remains unresolved. [3] emphasized the importance of further research in this area. Our results suggest that the use of PLA may be an environmentally friendly alternative, but long-term studies on the degradation and stability of biopolymers under real-world conditions are needed to confirm their environmental benefits.

The results clearly show that the addition of both micro- and nano modifying additives significantly improves the performance of bitumen in road construction. The combination of PMC and nanomaterials results in increased hardness, improved thermal resistance, and improved mechanical properties such as tensile strength and elasticity. The modified bitumen has demonstrated improved adhesion, resistance to deformation, and greater thermal stability, which is essential for its application in modern road construction where durability and long-term performance are important.

The use of carbon-based nanomaterials, particularly carbon nanotubes, has shown exceptional results in terms of mechanical strength and crack resistance. These materials, although relatively expensive, offer significant benefits in improving the structural integrity of roads, especially in regions with extreme temperature variations and high traffic loads.

The microstructural analysis confirmed that the uniform distribution of nano adducts in the bitumen matrix plays a crucial role in achieving the observed performance improvements. The low agglomeration of nano silica and good dispersion of carbon nanotubes contributed to the improvement of the mechanical and thermal properties of the material.

4. Conclusions

The present study showed that the incorporation of micro- and nano-modifying additives such as polylactic acid (PLA), nano silicon dioxide, and carbon nanotubes into bituminous materials significantly improves their mechanical, thermal, and chemical properties. The main findings include the following:

Improved thermal resistance and ductility: The addition of PLA resulted in a significant increase in the softening point and viscosity of bitumen, indicating its resistance to high temperatures. This makes the modified bitumen more suitable for use in regions with extreme climatic conditions. Improved mechanical strength: The addition of nano silica and carbon nanotubes has significantly increased the tensile strength and modulus of elasticity of bitumen, indicating its improved resistance to deformation and cracking under load.

Resistance to cracking: Modification of bitumen with nanomaterials also significantly increased its resistance to cracking, which is particularly important for pavements subjected to cyclic temperature fluctuations and traffic loads.

Environmental aspect: The use of biopolymers such as PLA may offer environmentally friendly alternatives to conventional modifying additives. However, further research is required on their durability and environmental impact, especially under conditions of prolonged use and exposure to environmental factors.

Thus, the results of this study highlight the potential of using micro- and nano-additives to improve the durability and sustainability of road surfaces. It is important to note that further research should focus on evaluating the long-term effects of these additives under real-life conditions as well as on their environmental effects.

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Article

Complex additive for improving the strength properties of heavy concrete based on industrial waste

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Abstract. The article presents the results of using a complex modified additive to improve concrete's physical and mechanical properties. The complex additive includes industrial production wastes: metallurgical slag and alcohol production wastes (post-alcohol bard). To stabilize the hydrogen index the alkali KON is included in the composition of the additive. A set of laboratory studies was carried out to measure the strength, absorption, and frost resistance of test specimens to assess the effect of the additive on the properties of concrete. A comparison of physical and mechanical properties was made for samples of different concentrations of slag. The ratio of slag components to cement was from 5 to 25% by the total mass of the binder, a multiple of 5%. The optimal composition of the mixture, with maximum strength values, corresponds to the percentage of slag 15%, post-alcohol bard 22.5 liters, and alkali 150 grams. In general, the results obtained from data points of the compared parameters showed consistent results with minimal variation in the data. The results obtained are of practical value related to the reduction of the cost of production of structural concrete with an increase in its strength indicators.
Keywords: concrete, production waste, slag, post-alcohol bard, strength, frost resistance, water absorption.

1. Introduction

Modern construction requires the development of materials that are strong, durable, and cost-effective. The use of additives in concrete mixtures made from industrial wastes such as metallurgical slag and chemical by-products is a successful trend to improve the performance of concrete. Studies show that such additives can significantly increase the strength properties of concrete, as well as improve its frost resistance and reduce water absorption. For example, metallurgical slag not only increases strength but also helps to improve the durability of concrete, as well as solving environmental problems related to waste disposal. Nevertheless, the effectiveness of different types of industrial additives in concrete mixtures continues to raise questions. Different admixtures may have different effects on the physical and mechanical properties of concrete, including strength, frost resistance, and water absorption. The aim of further research should be to develop a comprehensive admixture that best combines the benefits of different industrial wastes and allows for improved concrete performance, which will contribute to more sustainable construction.

The incorporation of additives to enhance the physical and mechanical properties of concrete is a prevalent practice in contemporary urban development [1]. Currently, there is significant market demand for specialized concrete additives utilized in both large-scale industrial production of concrete mixtures and individual construction projects [2]. A wide array of additives exists, ranging from those with complex effects to those that specifically target certain concrete properties [3].

Additives are used as follows depending on the construction conditions:

Antifreeze additives are used when the hydration temperature of concrete is between 5 and 250 °C to prevent the natural crystallization of water at sub-zero temperatures and to maintain the necessary hydration conditions [4], [5].

Additives to improve water permeability are used in hydraulic engineering and other types of construction to produce high-density concrete with a minimum number of micro and macro pores. [6]. Additives to improve water absorption are based on hydrophobizing concrete by reducing its wettability [7].

Additives to improve strength properties may include the addition of durable inert aggregates, fibrous materials, chemicals, plasticizers, and superplasticizers which together improve the properties of concrete [8].

The purpose of the research work was to develop a complex modifying additive based on the waste products of industrial production to improve the physical and mechanical properties of concrete. The additive based on metallurgical plant slags, and alcohol production wastes (post-alcoholic bard) with the addition of alkali is aimed at improving the strength properties, frost resistance, and water absorption capacity of concrete.

2. Methods

Tests were performed on samples with varying concentrations of slag (Table 1). Sample 1 represents the reference concrete composition, with no additives included. When selecting the composition, a superposition by mass was maintained: the cement content decreases directly proportional to the increase in slag, and water directly proportional to the content of after-alcohol bard with alkali (the density of after-alcohol bard is close to 1 g/ml).

Table 1 – Composition of the samples compared

Specimen type	Cement, kg	Slag, kg	Post-alcohol bard, l	KOH, g	Water, l
Type 1 (0%)	300	0	0	0	90.00
Type 2 (5%)	285	15	7.425	75	82.50
Type 3 (10%)	270	30	14.900	100	75.00
Type 4 (15%)	255	45	22.350	150	67.50
Type 5 (20%)	240	60	29.800	200	60.00
Type 6 (25%)	225	75	37.250	250	52.50

The mineralogical composition of blast furnace slag was obtained by X-ray diffractometric and X-ray phase analysis, presented in Table 2. The analysis was carried out on an automated diffractometer DRON-3 with CuKa-radiation, β-filter.

Table 2 – Mineralogical composition of slag

Akermanite	Fluorophosphate	Hematite	Spessartin	Jococuit	Quartz	Hollandite
$Ca_2Mg(Si_2O_7)$	$Ca_{9.3}Mn_{0.7}F_2(PO_4)_6$	Fe_2O_3	$Mn_3Al_2(SiO_4)_3$	$Mn(SO_4)(H_2O)_5$	SiO_2	$Mn_{6.95}Fe_{0.64}Al_{0.26}Si_{0.02}Ba_{0.47}K_{0.33}Pb_{0.11}Na_{0.11}O_{16}H_{1.41}$
36.0%	22.6%	11.7%	9.6%	8.4%	6.3%	5.4%

Laboratory tests to assess the physical and mechanical characteristics of the compared sample types include:

- Determination of cubic strength by destructive method in compression;
- Determination of water absorption capacity;
- Assessment of frost resistance by loss of strength and mass of samples after cyclic freezing.

Determination of cube strength was performed on automated press Pilot, controls. A total of 30 samples were made, 5 samples of each type. The use of five samples was accepted from the condition of the minimum number of samples in the case of mutually exclusive erroneous measurements (exceeding the coefficient of variation - 15%). Measurements of the samples were carried out after reaching the design age of 28 days.

Water absorption was determined by the standard method of specimen soaking followed by their weighing, after full water saturation and full drying. The criterion of complete water saturation was taken as the mass change of not more than 0.1% during the last hour of observation. Water absorption measurements were made for 30 samples, 5 samples of each type.

Assessment of frost resistance was performed on automated heat and cold equipment. Before the test, the samples were kept in water until completely soaked for 96 hours. The maximum number of freezing and thawing cycles was 350. Control measurements of the strength and mass of the samples were made in the following sequence of cycles: 100, 150, 200, 250, 300, 350. Each control measurement was matched with at least 3 specimens (for mutual exclusion in case of large deviation). Since the test method itself has a high variation, a total of 24 samples of each type were made, a network with a margin of 25% for random error. In any case, the remainder of the samples (in the case of the minimum number of errors) will give the best statistical values of the private values of the last cycle.

All tests were performed for 10x10x10 cm cube-shaped specimens.

3. Results and Discussion

Figure 1 shows the compared sample types of the results of cubic strength tests. According to the comparison results, the maximum strength value corresponds to samples of 15% slag concentration. Samples with a slag percentage of 25% showed very low strength values, 15% lower than the samples of traditional composition, without the inclusion of additives. The latter indicates that the use of slag over 20%, in order to improve the strength of concrete, is not recommended. In terms of saving the cost of concrete production, it is possible to use 25% concentration of slag, taking into account the reduction of strength characteristics.

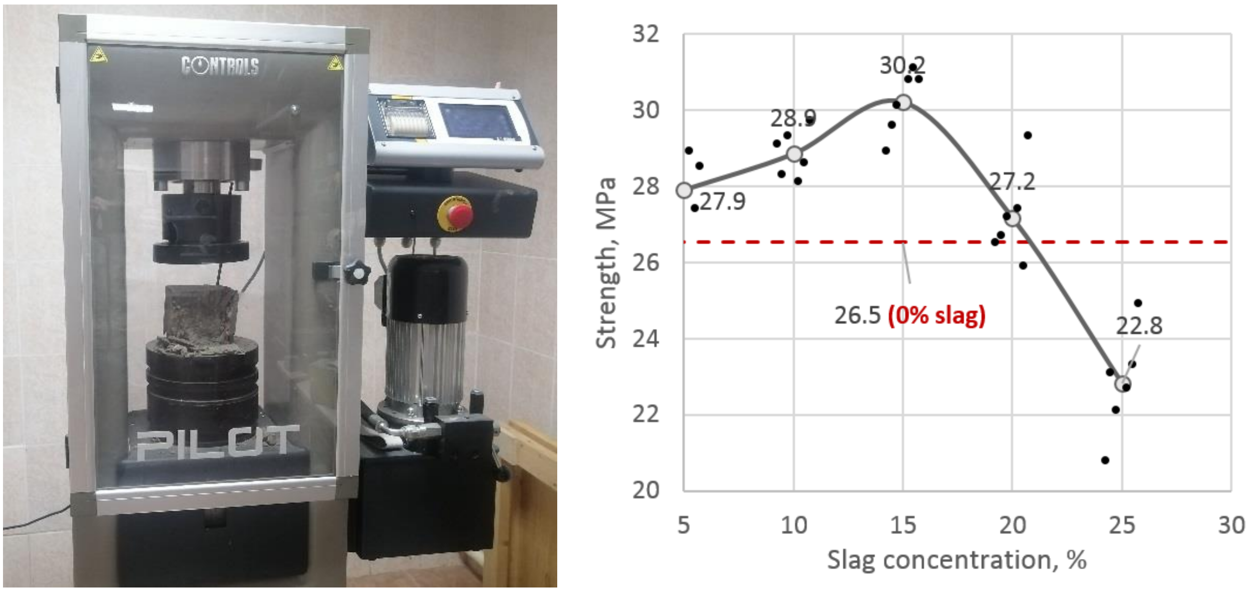

Figure 1 – Results of cube strength tests of specimens

The statistical data indicates that all measurements exhibit a high degree of consistency and strong correlation. Specifically:

For type 1, the standard deviation is no greater than 0.74, with an average value of 26.5 MPa and a coefficient of variation of 2.79%.

Type 2 has a standard deviation not exceeding 0.71, an average value of 27.9 MPa, and a coefficient of variation of 2.53%.

In type 3, the standard deviation reaches up to 0.62, the average value is 28.8 MPa, and the coefficient of variation is 2.14%.

Type 4 shows a standard deviation of no more than 0.84, an average value of 30.2 MPa, and a coefficient of variation of 2.80%.

For type 5, the standard deviation does not surpass 1.17, with an average value of 27.16 MPa and a coefficient of variation of 4.31%.

Lastly, type 6 exhibits a standard deviation of up to 1.36, an average value of 22.8 MPa, and a coefficient of variation of 5.96%. It will be noted that samples with a higher slag concentration have a greater scatter of individual values (higher coefficient of variation), which indicates the instability of strength indicators at high concentrations of slag. The correlation coefficient for the increase of strength characteristics as the percentage of additive increases has a direct proportional regularity in the range from 0 to 15% and is 0.997. The same coefficient in the range from 0 to 25% decreases to -0.408, indicating a violation of the pattern and the optimality of 15% concentration.

The results of water absorption tests are shown in Figure 2. According to the results, the minimum value of water absorption is observed in samples with maximum slag content, and the minimum in samples without additives. The obvious pattern can be explained by the presence of post-alcohol bard in the concrete composition, and the higher the concentration, the greater the hydrophobization of the material.

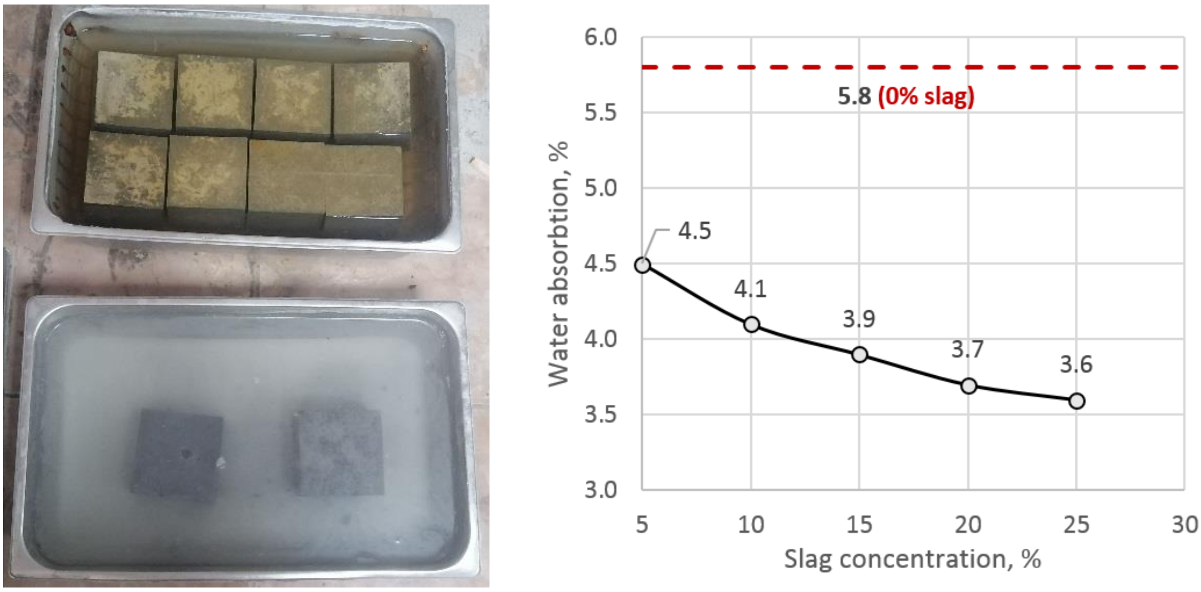

Figure 2 – Test results of cubic strength of specimens

According to statistical analysis, all particular values have a high degree of convergence, as evidenced by statistical indicators: coefficients of variation of all particular values lie in the range from 4.42 to 9.5%, for the average values shown in Figure 2 the standard deviations lie in the range from 0.108 to 0.336. The percentage decrease in water absorption with 5% of slag and 8.3% of post-alcohol bard with alkali is 22.4%; with 10% of slag and 16.7% of bard with alkali, the decrease in water absorption is - 29.3%; with 15% of slag and 25.0% of bard with alkali - 32.7%; with 20% of slag and 33.3% of bard with alkali - 36.2%; with 25% of slag and 41.7% of bard with alkali - 37.9%. Frost-resistance test results are shown in Figure 3 and Table 3. Figure 3 shows the dependences of the decrease in strength characteristics according to the increase in the cycles of freezing and thawing of the samples. Table 3 shows partial values of percentage strength reduction by control tests. According to the test results, the maximum resistance to cyclic icing is in type 4 specimens, with the percentage of slag - 15% and post-alcoholic bard with alkali - 25%.

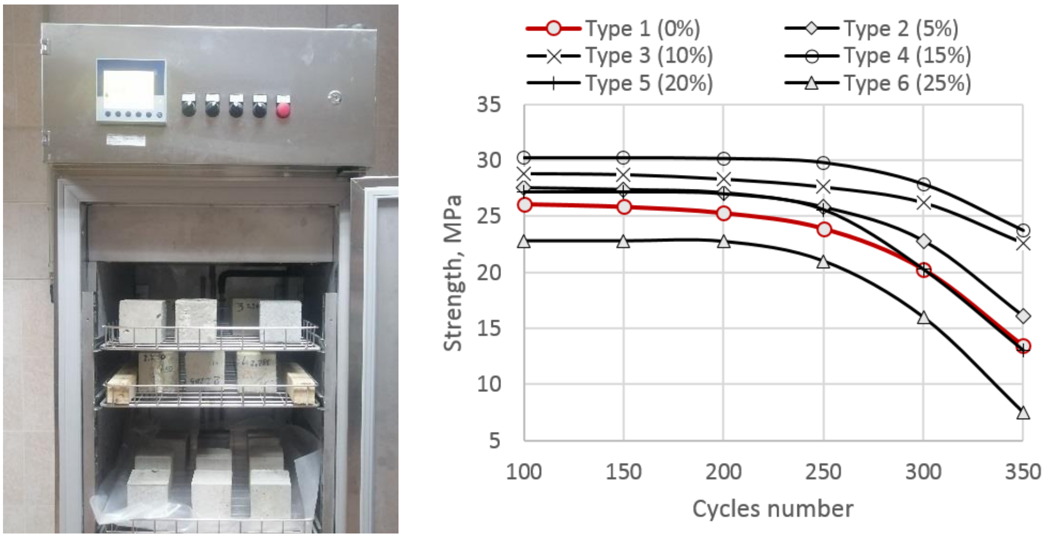

Figure 3 – Results of frost resistance of specimens

Table 3 – Results of the strength of control measurements

Type	Number of cycles					
	100	150	200	250	300	350
Type 1 (0%)	1.5	2.4	4.5	9.7	23.4	49.2
Type 2 (5%)	1.2	1.8	2.8	7.4	18.2	42.4
Type 3 (10%)	0	0.3	1.7	4.2	9.1	21.8
Type 4 (15%)	0	0	0.2	1.4	7.7	21.3
Type 5 (20%)	0	0	0.6	5.8	25.4	52.1
Type 6 (25%)	0	0	0.2	7.9	29.9	67.3

The statistical indices of the partial values of strength characteristics showed a medium to a high degree of convergence: the standard deviations are from 0.48 to 2.01 (at the average values presented in Table 3), which correspond to the coefficients of variation lying in the range from 1.87 to 13.32%. It should be noted that a greater scatter of particular strength values is observed for samples with a higher concentration of slag component (type 5 and 6), and the lowest for samples with a lower concentration (type 1 and 2). The latter characterizes the instability of samples with high slag content. The maximum reduction of strength characteristics was observed in specimens of types 1, 5, and 6, at 350 cycles a twofold reduction of strength was recorded. The obvious decrease in strength of specimens of type 1 is explained by the lower hydrophobicity of concrete in relation to specimens of another type. The decrease in type 5 and 6 specimens indicates the negative effect of less active slag in its excess in relation to cement content. Type 3 and 4 specimens showed relatively similar resistance to cyclic freezing. From the point of view of economic efficiency, the best option would be type 4 specimens with 15% slag component

4. Conclusions

– The research was carried out for concrete samples with different concentrations of slag components from 5 to 25%. Used as a substitute binder, slag from metallurgical production includes in its composition active elements, which in the process of electrolytic dissociation and hydrolysis take part in the process of concrete hydration.

– The optimal composition according to the results of laboratory research, which corresponds to the best values of comparable physical and mechanical parameters of concrete: slag content of 15%, content of post-alcohol bard, and alkali of 25%. The resulting composition can improve the design strength properties of concrete by 12-14%, reduce the water absorption of the material to 32%, as well as increase the frost resistance of concrete from grade F250 to grade F300.

– In the case of reducing the cost of concrete, it is possible to use a 20% concentration of slag with 32.7% of bard and alkali. In this case, the economic effect of the use of the additive will be achieved without compromising the design indicators of strength, water absorption, and frost resistance.

– Compared to other complex admixtures, metallurgical slag shows similar results in concrete strength and water resistance, while contributing to lower production costs. The use of metallurgical slag can achieve strength properties comparable to concrete containing traditional modifiers, making it a more cost-effective choice. This confirms its effectiveness in improving concrete properties without significantly increasing costs.

– In general, slag reduces water absorption but improves the frost resistance of concrete compared to mineral admixtures. Comparative studies show that concrete with slag addition exhibits stable strength properties under repeated freeze-thaw cycling, thus extending the service life of the material.

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Article

Heat-resistant concretes based on cement binders and waste from the metallurgical industry

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Abstract. The main direction of the development of heat-resistant concrete production is the use of new materials, ensuring mechanization and industrialization of construction, increasing the performance characteristics of refractory compositions, reducing material consumption, introducing waste-free technologies in the production of concrete with increased physical and mechanical characteristics under prolonged exposure to high temperatures on cement binders and waste from the metallurgical industry and reducing environmental pollution. A significant environmental impact on the environment is exerted by large-tonnage technogenic waste produced by JSC «Aluminum of Kazakhstan» – bauxite sludge obtained by processing bauxite into alumina containing 42.7% Fe_2O_3. The prospects of its application as a filler in heat-resistant concretes are considered, which makes it possible to increase the physico-mechanical and thermal characteristics. The composition and properties of this waste and the change in the properties of heat-resistant concrete during the introduction of filler have been studied. Reactive alumina has been studied, which is 99.9% submicron alumina with a very low content of Na_2O oxide. It is shown that the properties of concrete change after the introduction of iron-containing waste in the amount of 5% and reactive alumina – 37.5% and 38.8%. Their volumetric weight, control strength, and other properties are increased. The improvement of physical, mechanical, and thermal characteristics depends on the structure and neoplasms in the obtained samples. Samples of heat-resistant concrete were analyzed using electron probe X-ray spectral qualitative and quantitative microanalysis and X-ray fluorescence spectrometry and it was shown that the iron-alumina waste contributes to the compaction of the structure due to its resistance to delamination and has increased fluidity at low humidity in the cementing mass. For further investigation of the physical-thermal characteristics, depending on the structure and neoplasms in the obtained samples, a petrographic method using a polarization microscope in transmitted and reflected light is required.

Keywords: waste, heat-resistant concrete, metallurgical industry, bauxite sludge, reactive alumina, perlite.

1. Introduction

One of the most acute environmental problems currently is the pollution of the environment by the production and consumption of waste and, first of all, hazardous waste. One of the solutions to the urgent problem related to the environmental situation is the effective disposal of large-scale industrial waste. As practice shows, the formation of high-tonnage waste occurs in industrial areas, and the nomenclature of substandard raw materials has a wide range. However, the widespread use of waste is difficult due to high transport and other costs, so it is advisable to use them in the regions where they are concentrated. To solve this problem, first of all, waste-generating enterprises must change their approaches to the status of these entities, that is, treat waste as promising and inexpensive raw materials and apply various innovative technologies involving the use of man-made resources. For example, slags, enrichment sludge, etc. are formed at ferrous and non-ferrous metallurgy enterprises, and various thermal installations are used to produce metals that require continuous repair and maintenance of furnaces with special heat-resistant, refractory, and thermal insulation materials made of concrete or others. The proximity of most industrial waste in chemical composition to classical binders opens up a wide range of opportunities for scientists in this field to develop and design new effective heat-resistant concrete compositions with the required physical and thermal properties [1].

According to [2], the authors have established a connection between the phase processes of formation during heating and the thermomechanical properties of heat-resistant concrete from metallurgical slags. Methods of X-ray phase analysis (XFA) and differential thermal analysis (DTA) were used to study the physico-chemical changes occurring in samples of slag products. Based on these methods, methods for predicting high thermomechanical properties of heat-resistant concrete based on metallurgical slags are proposed. To produce heat-resistant concrete, ash-containing wastes were widely used, which are formed in large quantities as a result of the operation of thermal power plants (CHP). Today, many foreign countries have experience in developing effective ecological and economic systems of waste-free technology. For Kazakhstan, this experience can be useful in terms of using innovative solutions in the field of processing and disposal of sludge and ash and slag waste in domestic practice. Thus, ash and slag are a complex system, the properties of which depend on the type of fuel and its combustion mode, boiler design, and many other factors. This determines the relevance of researching the possibilities of using solid man-made waste from the Pavlodar region in the production of building materials. The continuous growth of metallurgical production leads to an increase in man-made environmental impacts in the form of accumulated production waste. This makes the problem of waste disposal by recycling them with additional recovery of the contained useful components urgent. In the Pavlodar region, one of the types of such waste is sludge from alumina production. In the production of aluminum, bauxite is used as the main raw material, as a result of which large quantities of waste are formed in the form of aqueous suspensions of dispersed particles – sludge. About four tons of sludge are produced per ton of alumina. A characteristic feature of bauxite slurries is the high content of iron and aluminum oxides. Nepheline, bauxite, sulfate, white, and monocalcium slurries are of industrial importance for the production of building materials. The aluminum plant uses bauxite, respectively, the waste is red bauxite sludge.

One of the main ways to recycle red sludge in the field of construction production is to use it as an iron-alumina component of the raw material mixture in the manufacture of Portland cement clinker. According to research [1], raw mixtures containing red sludge are characterized by high reactivity during firing, especially in the temperature range corresponding to the passage of reactions in the solid phase. The iron oxide and alkalis contained in the sludge lower the temperature of the appearance of the liquid phase by 343-323 ° C, which favorably affects the absorption of calcium oxide during clinker firing. Raw sludge containing red sludge is not prone to delamination and has increased fluidity at low humidity. Also, the possibility of using bauxite sludge as an additive in the grinding of cement clinker has been obtained. Thus, the addition of 5% sludge significantly increases the grinding capacity and grade strength of cement. In Japan, concrete has been developed in which red sludge is used as a substitute for some cement, sand, and pigment. Studies have shown that dry red sludge is a good substitute for sand as a fine aggregate in concrete. At the same time, the resistance to variable freezing and thawing is higher than that of conventional concretes. In Germany, studies have been conducted on the possibility of manufacturing brick products from a mixture of waste such as red bauxite sludge, bleaching clay used in the purification of edible oils, as well as household garbage. Pressed bricks are fired for 40 hours at a temperature of 1060 ° C. During their sintering, the alkalis of the red sludge react with $C0_2$ from household waste and are neutralized as a result of the formation of clay materials [1].

German specialists have developed methods for manufacturing building materials based on red sludge and silica materials. In the first method, the red sludge is mixed with sand activated in a vibrating mill, burnt lime, and a 50% solution of sodium alkali. The resulting mixture is fired for 30 minutes at a temperature of 350 ° C. The compressive strength of the resulting material is 36-45 MPa. According to the second method, the red sludge is mixed with activated silicon dioxide and alkaline earth metal compounds, then the products are molded and fired. According to research [3], sufficient plasticity of red sludge is noted in the works.

Based on the generalization of the voluminous literary and scientific material, it can be concluded that the red sludge of individual plants was studied as an additive that increases the mechanical strength of concrete. However, comprehensive studies of bauxite sludge in carbonate concrete have not been conducted. At the same time, the landfill sludge of the Pavlodar aluminum plant is specific in composition and properties, cheap raw materials in Kazakhstan, which have not been studied in this direction. Its high content of iron oxides and a limited amount of calcium oxides do not allow it to be considered as a base for a binder. This bauxite (red) sludge can be used as a modifying component of the latter, taking into account the complex nature of its effect on the properties of concretes. Also, the use of sludge contributes to a significant reduction in the cost of concrete by 2-3 times and additionally allows you to solve the environmental problem of freeing land plots of JSC «Aluminum of Kazakhstan» from production waste. The analysis of literature sources on the subject of the study revealed the main directions of application of industrial waste, in particular, fuel ashes and slags, as well as dump bauxite sludge in the production of construction products. Mainly as binders, as an active additive (modifier) in the production of Portland cement, and as large and small aggregates for both heat-resistant, heavy, and light concrete, for the construction of upper and lower layers of road foundations.

Heat-resistant concretes are characterized by the ability to maintain physical and mechanical properties within certain limits under prolonged exposure to high temperatures. The main field of application of heat–resistant concrete is the lining of thermal units and structures, where heat-resistant properties allow for safety and proper operating conditions, as well as heat-resistant concrete, which is used as a thermal insulator. For the manufacture of heat-resistant concretes, Portland cement grades M400-M500 and FHC (fast-hardening cement), slag Portland cement according to [4], and liquid glass according to [5] alumina cement is used as binders. These types of cement have good water retention properties due to the acceptable granulometry of the grain composition and fineness of grinding. It should be noted that heat-resistant concretes based on alumina cement are more widely used, since they have high values: a) fire resistance (up to 1700 °C); b) compressive and bending strength even at temperatures of 1150-1200 °C; c) abrasion resistance; d) heat resistance, as well as low wettability with molten metals [6].

Setting the task. Taking into account the pollution of large areas with man-made raw materials and a significant decrease in natural raw materials, new methods and methods should be found to replace them with industrial waste of a man-made nature for the production of heat-resistant concrete.

Purpose: taking into account the increasing requirements for heat-resistant materials of the construction direction, to create concrete with increased physical and mechanical characteristics (indicators) based on a binder – alumina cement, filler – perlite, an iron-containing component – bauxite sludge (waste from the metallurgical industry), an additive - technical (reactive) alumina.

2. Methods

2.1 Raw materials

According to the set goal, the following raw materials were used to create heat–resistant concrete: alumina cement grade 400 as a binder, contains perlite as a filler, technical (reactive) alumina as an additive, and bauxite sludge (red) and water as an iron-containing component.

The chemical oxide composition of raw materials and the element-by-element chemical composition of bauxite sludge was performed using an EDX9000B X-ray fluorescence spectrometer and is presented in Table 1.

Table 1 – Oxide chemical composition of raw materials, %

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	TiO_2	Na_2O	K_2O	Cl
Alumina cement	7.11	40.2	8.22	37.2	-	-	-	-	-	-
Bauxite sludge	17.09	4.07	42.7	40.1	0.61	0.59	1.15	0.03	0.13	0.0037
Perlite	125.3	13.9	0.62	5.13	0.02	0.51	0.24	0.02	1.71	0.0038
Reactive alumina	0.08	99.2	0.05	0.10	-	-	-	0.37	-	-

Alumina cement M400, manufactured by «Kislotoupor Kazakhstan» LLP, was used as a binder, designed to work in an aggressive hydrogen environment, while the content of iron oxide should not exceed 0.05% and silica oxide 0.1% according to [7]. The true density of alumina cement is 3200 kg/m^3, the bulk density is 1100 kg/m^3. The normal density is 24-28% [7]. The raw materials for the production of alumina cement clinker are pure limestones ($CaCO_3$) and rocks containing alumina, for example, bauxite ($Al_2O_3 \cdot nH_2O$). Alumina cement contains mainly two minerals: calcium mono aluminate (CA) and helenite (C_2AS) and related minerals: dicalcium silicate (C_2S), calcium aluminum ferrites (C_6A_2F), and some other minerals [8].

Perlite, manufactured by «Argo» LLC, was used as a filler, with a volume weight of 150-200 kg/m^3, fractions of 5-15 mm according to [9].

Water – according to [10].

Waste from the metallurgical industry of JSC «Aluminum of Kazakhstan» – bauxite sludge was used as an iron-containing filler for the production of heat-resistant concretes. It is a by-product of the processing of bauxite into alumina. The studied sludge is obtained after complete scattering with slow cooling, while its color turns red, and is a wet loose sand-like material having a size of 0-5 mm. The size modulus is 1.6-2.2, the density of the sludge is in the range of 2.86-2.98 g/cm^3, and the bulk mass in the dry state is 1000-1200 kg/cm^3 [11].

The element-by-element chemical composition of bauxite sludge is presented in Table 2.

Table 2 – Element-by-element chemical composition of bauxite sludge, %

Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	Sr
0.40	0.85	8.48	24.62	8.85	0.49	32.73	1.83	0.15	21.57	0.01

The oxide and element–by-element chemical compositions of the studied sludge showed a high content of oxide Fe_2O_3 and elemental iron Fe – 42.7%, respectively (see Table. 1) and 21.57%.

Mineralogical composition of bauxite sludge: sodalite ($3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot Na_2SO_4$) 4-40 %; aluminogetite (iron oxide with an admixture of aluminum) 10-30 %; hematite (iron oxide) 10-30 %; silica (silicon dioxide), crystalline and amorphous 5-20%; tricalcium aluminate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$) 2-20 %; boehmite (AlO(OH)) 0-20%; titanium dioxide 2-15%; muscovite ($K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$) 0-15 %; calcium carbonate 2-10%; gibbsite ($Al(OH)_3$) 0-5%; kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) 0-5% [12].

Reactive alumina [13], produced by LLC «Shiber» is a synthetic product of corundum composition with a low content of impurities. LISAL 07RA reactive alumina is made from high-purity technical alumina and is a ready-to-use fine powder.

Thanks to the special technology for the production of reactive alumina LISAL 07RA, it is possible to obtain heat-resistant concrete with the necessary parameters of particle size, Na_2O content, specific surface area, and modality (mono, two, and multimodal) powders.

The technological process of heat-resistant concrete production includes preparation of the molding mass, molding of products, and heat treatment. It should be noted that heat-resistant concretes require special heat treatment for their solidification and a set of vintage strength. The heat treatment takes place up to 1200 °C. An increase in temperature to 200 °C takes place at a speed of 60 °C/h, and up to 1200 °C – already at a speed of 150 °C/h. Then it is kept for 2 hours and cooled together with the oven. Compositions for the production and physical and mechanical properties of heat-resistant concretes are presented in Tables 3 and 4.

Table 3 – Components of heat-resistant concrete, mass. %

Composition No.	Alumina cement	Perlite	Bauxite sludge	Reactive alumina	Water
1	16.25	37.50	5.0	37.50	other
2	20.00	38.20	5.0	38.80	other

Table 4 – Physical and mechanical properties of heat-resistant concrete

Volume weight, kg/m^3	Control strength of Rc, MPa	Thermal conductivity, λ_{600}, W/(m·°C)	Thermal stability in the water heat exchange of the theater Tw, the number of cycles	Note
Composition 1				
850	35.6	2.4	20	Racks in a gaseous environment of carbon monoxide and hydrogen
Composition 2				
950	36.6	2.4	20	Racks in a gaseous environment of carbon monoxide and hydrogen

As can be seen from Table 3, due to the use of bauxite sludge and reactive alumina as an iron-containing component and additive, contributes to the production of heat-resistant concretes with high physical and mechanical properties.

2.2 The principle of X-ray fluorescence spectrometry

X-ray fluorescence spectroscopy is a modern instrumental method of analysis. Incident X-rays (primary X-rays) are generated through an X-ray tube to excite the measured sample; each element in the excited sample emits characteristic X-ray radiation (secondary X-ray radiation). X-rays - this characteristic of X-ray radiation has certain characteristics of energy and wavelength (Mosley's law). The energy and number of secondary X-rays emitted are measured by the detection system, and these radiation signals are converted into the specific content of the various constituent elements in the sample.

Equipment: one X-ray fluorescence spectrometer EDX9000B; electronic scales (accuracy 0.01 g); one mechanical tablet press (pressure not less than 40T); one jet drying oven; one ball mill; non-metallic sample sieve (200 mesh).

Reagents: boric acid powder; national building reference material; sample of raw materials [14].

Air drying or drying of samples is carried out following the [14]. After grinding, the samples are passed through a 200-mesh sieve and dried at 105 °C for use.

Electronic scales are used to weigh 3.00 g of sifted (200 mesh) bauxite standard substance or sample and 14.00 g of boric acid powder (edge material), weighing error ± 0.05 g. Then it is placed in a tablet press to form a tablet, the pressure is 30T (pressure range 20-30T), and the pressure holding time takes 30 seconds.

Construction of the working curve and analysis of the sample

Appropriate measurement conditions are established using the EDX9000B to scan national standard materials (called standard samples) and establish a linear working curve of the content and intensity of the corresponding elements in standard samples of the material under study.

Measurement of the limits of detection of chemical elements and oxides in a sample of the test material

The EDX9000B is equipped with three sets of filters to create the best test conditions according to the characteristics of the studied sample elements. The national standard sample of the material (cement and refractory material) is used to calibrate the device and build the working curve of the material. According to the working curve of the sample, high-purity SiO_2 is used as a blank substrate and continuously tested 5 times according to the detection limit formula: 3 times the standard deviation of the blank substrate divided by the sensitivity of the device [15].

2.3 The method of electron probe X-ray spectral qualitative and quantitative microanalysis of the composition of samples

The Hitachi TM 4000 Plus desktop scanning electron microscope is characterized by its compact size and wide capabilities. The device normally has a low vacuum mode, which allows you to do without sample preparation and examine non-conductive samples without pre-spraying metal. An ordinary laboratory table is sufficient to use a microscope. The microscope is controlled through a simple and intuitive interface, in which the functions of automatic adjustment of focus, contrast, and brightness are available. The device is ready for operation within 3 minutes after switching on, and the sample change time does not exceed 2 minutes. The microscope is equipped with two detectors – secondary and reflected electrons, so it can provide comprehensive information on the surface of the objects under study. The new TM4000Plus optimizes the operation of the detector, thereby significantly improving the image quality when working at low accelerating voltages.

The study was carried out under native conditions in a low vacuum mode without spraying a conductive layer at an accelerating voltage of 15 kV and on a working interval from 7.5 to 10.5 mm. The samples were mounted on a table with a diameter of 80 mm using conductive double-sided tape. The only requirement for the samples is that they must be «dry». The maximum size is 80 mm while moving around the field of the object is available within 35x35 mm.

The built-in energy dispersion spectrometer allows for obtaining elemental composition data ranging from light elements (B – boron, atomic number 5) to heavy actinoids (Cf – californium, atomic number 98).

Among the advantages of the equipment used, can be noted: the possibility of large magnification with scaling and measuring the size of the details of interest in the image; the choice of a place on the sample and the area of the analyzed area for elemental analysis and control; the expressiveness of obtaining information; non-destructive research method; large size of the sample under study; the equipment compact dimensions and the absence of special requirements for the room [16].

3. Results and Discussion

The conducted studies have shown that bauxites are a rock consisting mainly of aluminum hydroxide, iron oxide, and oxide of mineral components (Table 1). The main components of bauxite are gibbsite (hydrargillite), boehmite, and diaspore. In addition, bauxites contain iron minerals (hematite, hydrohematite, siderite); and silica in the form of quartz, hydroxide (opal, etc.). In smaller quantities, bauxite contains calcium and magnesium carbonates, as well as impurities of organic substances. The quality of bauxite is characterized by two factors: the content of $A1_20_3$ and the flint module (weight ratio $Al_20_3/Si0_2$). The content of impurities is also essential for the characterization of bauxites, which complicates the processing of raw materials (in particular, carbonates, sulfates, iron oxides, chlorides, and organics), as well as the mineralogical features of bauxites, and the content of the clay component.

The oxide and element–by-element chemical compositions of the studied sludge showed a high content of oxide Fe_2O_3 and elemental iron Fe – 42.7%, respectively (Table. 1) and 21.57%.

Energy dispersion spectral analysis showed that the bauxite particle contains a large amount of aluminum Al and oxide O, which allows it to be attributed to a rock consisting mainly of aluminum hydroxide, iron oxide, and oxide of mineral components.

Figure 1 below shows the spectra of a bauxite sludge sample and the results of its semi-quantitative analysis.

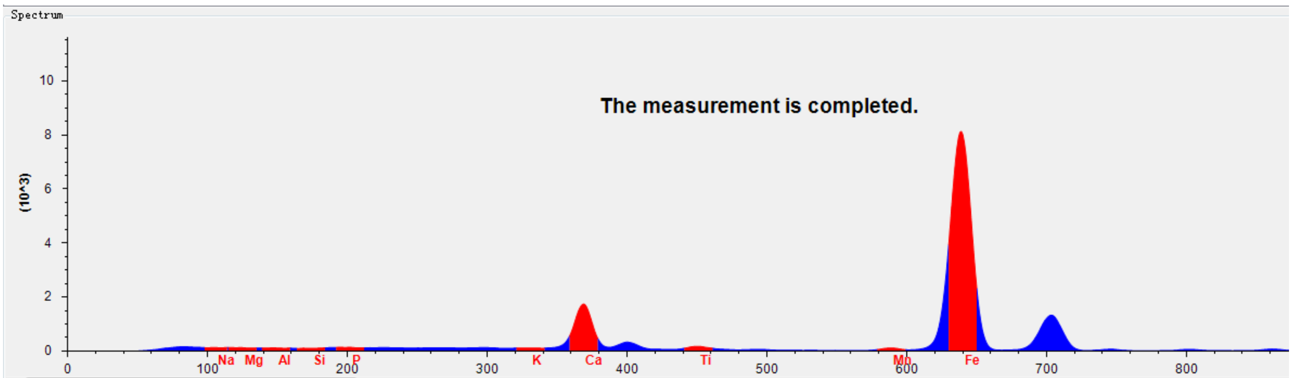


Figure 1 – Spectra of bauxite sludge in comparison with refractory material

As shown in Figure 1, matrix effects have a significant effect on the linearity of the calibration curve. The EDX spectrometer software easily eliminates all matrix effects occurring in an iron-based matrix and contains four of the most widely recognized algorithms for automatic matrix correction. In addition, each element can have several calibration curves, and depending on the concentration range (low or high), a specific curve is accessed. The specific curves in the sludge are determined by the high content of calcium, iron, and silicon. The improvement of the physical-thermal characteristics largely depends on the element-by-element chemical composition and structure in the obtained samples.

A preliminary analysis of the chemical composition of the sludge allows us to assume the expediency of their processing with the extraction of iron oxides contained in them. As scientific studies have shown [1], [11], [17], the use of bauxite sludge is possible as additives in agglomeration, pelletizing, blast furnace smelting of iron ores, raw materials for iron production, a slag-forming agent for refining cast iron and steel, a partial clay substitute in the manufacture of molds, additives in the production of cement and ceramics, filler in production of heat-resistant concrete, building bricks and refractories.

In [17], the structure of the sample is amorphous fine-grained, and unevenly porous. Small white inclusions in the amorphous silicate mass are clearly distinguished. Inclusions along the contour are fused and consist of mineral growths. The grain size ranges from 0.01 to 0.5 mm, 0.1 mm is predominant. The pores are irregularly shaped, more often fractured, isolated, and not evenly distributed in an amorphous granular mass. The pore size ranges from 0.1 to 1.0 mm, with 0.5 mm predominate.

An effective tool is the function of mapping the elemental composition by the field of view of the microscope (Figure 2).

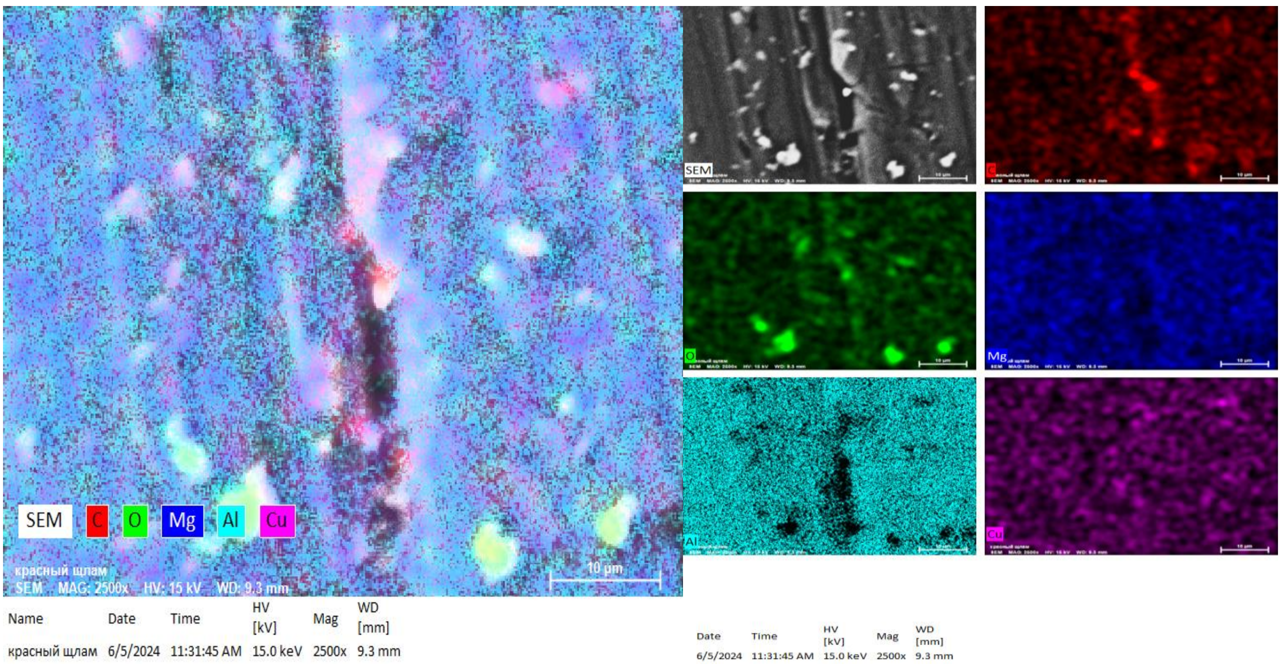
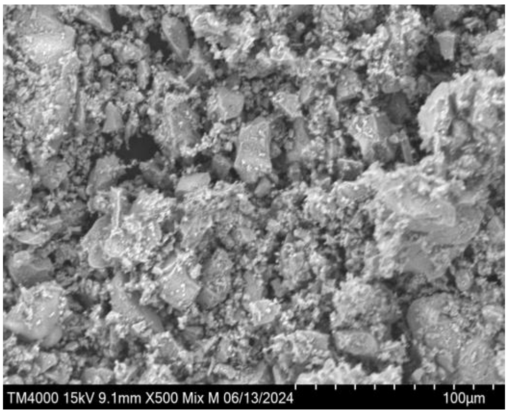


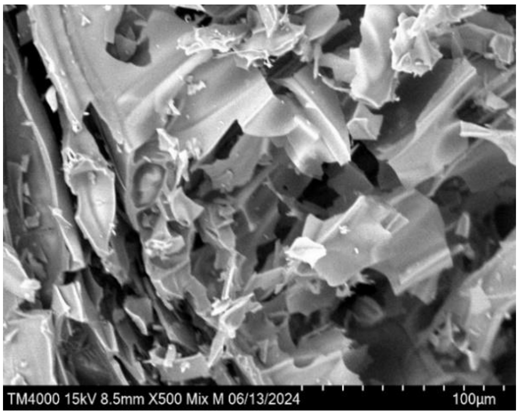
Figure 2 – Mapping the surface of the bauxite (red) sludge

The color graphical distribution of elements by area, depending on the atomic number, presents the results of the research in the most visual form, the black-and-white image of the topography provides information about the morphology of the sample surface. This largely objectifies the selection of analyzed sites with introduced elements and controls.

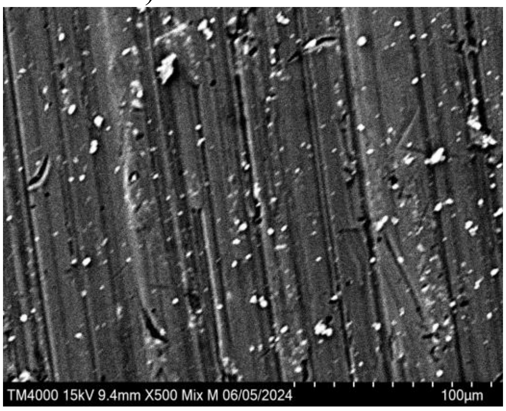
The micrograph shown in Figure 3 contains detailed information about the microstructure of materials, as well as the behavior of the material under various conditions, phases detected in the system, failure analysis, grain size estimation, and elemental analysis.



a) Alumina cement



b) Perlite



c) Bauxite sludge

d) Reactive alumina

Figure 3 – Electronic micrography of materials

Detailed analysis with large magnifications made it possible to detect, measure and analyze individual particles.

The microstructure of materials, as shown in Figure 2: a) Fine-grained unevenly porous. The particle size ranges from 0.1 to 9.1 mm, the more predominant size is 1 mm; b) Thin-porous with pore formations in the form of curved cracks. The size of the cracks ranges from 0.5 to 8.5 mm; c) Thinly porous in the form of slit-like straight lines. The size of the gap ranges from 0.05 to 9.4 mm; d) Fine-grained porous with formations in the form of uneven small pores. Non-finely ground alumina powders of the R and C series with a low content of Na_2O oxide are available. The particle size of D50 is from 70 to 90 microns, the crystal size of D50 is from 0.5 to 3 microns, and the content of Na_2O oxide is 0.06-0.07%. The structures were tightly connected and compacted by filling the pore space with an alumina mass, which acts as a reinforcing material. Sealing the structure and strengthening the amorphous component with newly formed crystals increases strength, wear resistance, fire resistance, chemical resistance, the ability to strengthen the contact zone with the main fillers, and also reduces water absorption.

4. Conclusions

1) The content of belite in bauxite sludge reaches 45-55 % by weight. The ticket in the sludge is partially hydrated. Iron oxides are represented by magnetite and hematite. A small amount of sodium sulfoaluminate and calcium carbonate of secondary origin. The main components of the sludge are calcium, silica, aluminum, and iron oxides. The sludge has a high content of elements and oxides, in the amount of CaO – 41.181; Fe_2O_3 – 44.201; Ca – 62.172. Elements P, S, Fe, Cl, Ca, Mn, Ni, Cr, Fe, Co, Na, Mg, Al, Si, K, Ti and Sr, as well as oxides Na_2O, MgO, Al_2O_3, SiO_2, SO_3, K_2O, CaO, TiO_2, Fe_2O_3, Na_2O, P_2O_5, Cr_2O_3 and MnO comply with the national standard. Also, the

following elements and oxides were found in samples of bauxite sludge in comparison with refractory material (Refractory material): Ca – 32.726; Iron – 21.572 and Si – 24.621;

2) The effect of iron-containing bauxite sludge and the addition of reactive alumina on the physical and mechanical properties of heat-resistant concrete based on alumina cement has been studied. The resulting heat-resistant concretes had high mechanical strength and heat resistance.

3) The control strength of heat-resistant concrete can be increased to 40.0 MPa and higher if man-made waste production is introduced into alumina cement (see Table 4).

4) The use of alumina cement as a binder in heat-resistant concretes makes it possible to create concrete with increased physical and mechanical characteristics (fire resistance up to 1700 °C, abrasion resistance, heat resistance, as well as low wettability of molten metals).

5) The use of a synthetic product of corundum composition with a low content of impurities – reactive alumina in heat-resistant concretes allows: a) due to the high reactivity, reduce the sintering temperature and synthesis of phases during firing; b) reduce the amount of water for sealing refractory concretes without deteriorating their rheological characteristics; c) in the manufacture of refractory low- and ultra-low-cement concretes, denser packing of particles and the structure of the material can be obtained; d) improve the physical and operational characteristics of heat-resistant concrete; e) to increase the «cold» and high-temperature strength of products and their abrasive resistance; f) to obtain heat-resistant concrete with the necessary parameters of particle size, Na_2O content, specific surface area, and modality (mono, two, and multimodal) powders.

6) The use of man-made raw materials (waste from the metallurgical industry) in heat-resistant concretes allows: a) disposal of industrial waste; b) protect ecological systems and the natural environment and additionally solves the environmental problem of freeing land plots of JSC Aluminum of Kazakhstan from production waste; c) solve the issue of raw materials through the use of man-made raw materials; d) significantly reduce the cost of concrete by 2-3 times.

Acknowledgments

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Article

Development of composition of fine-grained concrete based on ash-and-slag wastes for additive technology of manufacturing small architectural forms

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Abstract. Developing a fine-grained concrete composition for additive technologies is an important scientific and practical task, since traditional building mixtures are unsuitable for 3D printers, and special solutions are practically absent in mass production. This study aims to develop a composition of fine-grained concrete for additive technologies using local resources and ash and slag waste of the Ust-Kamenogorsk thermal power plant, which contributes to the expansion of the raw material base used in this area. The work was carried out taking into account the analysis of the literature review, which made it possible to identify key aspects and directions in the development of concrete mixtures for additive technologies. This article discusses the possibility of using ash and slag waste in concrete as a filler. Ash has a grain size comparable to river sand, so it can be used as a new material to replace fine filler. To obtain the mixture, 5 experimental mixtures and one reference sample were prepared. The optimal composition is considered to include 30% of M500 Portland cement, 40% of sand, and 30% of ash and slag. The physical and mechanical characteristics of this composition are as follows: the mobility of the mixture is 5.81 cm, and the setting completion time is 4 hours 19 minutes. The results of the sample tests confirmed that the created fine-grained concrete compositions are suitable for extrusion on construction 3D printers. The possibility of creating a composition based on local ash and slag waste for additive technologies used in producing small architectural forms was experimentally confirmed.
Keywords: additive technologies, 3D-printer, ash and slag waste, fine-grained concrete, mixture mobility, extrusion, water retention capacity, adhesion strength of layers, frost resistance.

1. Introduction

The use of additive technologies in the construction industry allows the implementation of architectural projects of any complexity and reduces the amount of industrial waste, the housing shortage, materials, energy, and labor costs for construction. Currently, a wide range of materials is used for additive technologies: various polymers and rubbers, powders of steel, titanium alloys, nickel, aluminum, and copper, as well as tool and structural ceramics, biocompatible and nano-reinforced composites [1].

Cement-based materials that take a long time to harden cannot meet the performance requirements of 3D printing. The composition must have thixotropic properties: reduce viscosity under mechanical impact and restore it at rest [2].

A pressing issue in the design of concrete mixtures is to ensure a set of required material properties using available man-made raw materials. The economic efficiency of using ash and slag waste from coal-fired thermal power plants to produce fine-grained concrete was confirmed by science and practice. In addition, ash and slag waste from thermal power plants is one of the most common man-made wastes in the country and therefore represents a virtually unlimited and inexpensive local resource. When assessing the suitability and possibility of using ash, special attention should be paid to compliance with the requirements of the interstate standard [3].

In the work [4] it was found that the molding of the studied sand-cement mortar by the extrusion method (3D printing) [5] leads to an increase in the total pore volume by 10%, the volume of open capillary pores by 22%, the volume of conditionally closed pores by 9%, microporosity by 8%, a decrease in the open non-capillary volume by 65% compared to traditional casting samples of similar composition with further compaction. This leads to a decrease in compressive strength by two times compared to the injection molding method with further compaction, and an increase in water absorption by 22%. Based on the results obtained, directions for improving raw mixtures for 3D printing were determined.

Ash and slag are more susceptible to the effects of cyclic wetting and drying than standard aggregates, therefore fine-grained concrete prepared using ash and slag materials exhibits more active water-absorbing properties. For this reason, finished building structures made of fine-grained concrete are coated with special protective solutions that prevent moisture from penetrating into the product and protect it from the effects of external environmental factors [6]. Without special coatings, structures made of ash and slag fine-grained concrete cannot be durable. However, the application of such coatings requires significant labor costs and financial resources.

Control of the properties of concrete mix and hardened concrete is an integral part of the construction process. However, with the use of 3D printing technology in construction, some methods for assessing the properties of concrete mix and concrete will have their characteristics associated with the formation of the structure and properties of concrete mix and concrete under conditions of laying and strength gain in thin layers. The composition of the construction mixture was selected based on the technological requirements of 3D printing equipment and ensuring the required characteristics of the mixture [7]. The paper substantiates the main problems of quality control of concrete when using additive technology, and proposes methods for determining strength characteristics taking into account the features of 3D printing.

This paper [8] presents the results of experiments that allow us to continue developments in the field of optimization of construction mixture compositions in experimental construction using 3D printing. As a result of testing the concrete mixture, it was found that the density is 1940.3 kg/m^3, setting time: start - 3 hours 20 minutes, end - 4 hours, mobility by cone immersion, 3.40 mm, strength (28 days): under compression - 30.4 MPa, under bending - 4.7 MPa. The data indicate that the resulting mixture has the necessary rheological properties and optimal setting time and can be used for the construction of buildings and structures using 3D printing.

The research work [9] recommends using standard sand concrete M300 based on Portland cement grade 500 for printing. In the laboratory of the V.S. Gryzlov State University, studies were conducted on the main characteristics of sand concrete M300 (B22.5). Based on these studies, minimum requirements for the properties and characteristics of mixtures for the manufacture of building structures using the additive technology method were determined.

The grain size of fly ash is comparable to river sand, which allows its use as an alternative material to replace fine aggregate. Studies have shown that ash has a porous structure, which can help reduce concrete shrinkage [10], [11]. However, to our knowledge, the use of significant amounts of fly ash and slag as a replacement for both fine and coarse aggregate to produce fine-grained concrete has not been the subject of research. Therefore, this study focuses on the mechanical and physical-technical properties of concrete. Ash and slag waste from the Ust-Kamenogorsk thermal power plant was selected as the material under study.

2. Methods

Development of compositions of construction mixtures for additive technology, research of their properties, and testing were carried out based on recommendations of the relevant standards.

The ash and slag waste of the Ust-Kamenogorsk thermal power plant was used in the study. Ash-and-slag mixture (ASM) for preparation of fine-grained concrete (FGC) should meet the requirements of [3], [12], which were used to study their following properties: grain composition, specific surface area of fine-grained ASM mixture, bulk density, grain density, humidity. The chemical composition of ash and slag was determined according to [13], and the content of free calcium oxide - by [14]. The total specific activity of natural radionuclides in ash and slag was determined by gamma-spectrometric method according to [15].

For the study, the following characteristics of the construction mix and cured fine-grained concrete to be tested were identified:

1. The mobility of the mix;
2. Timing of the beginning and end of the setting of the mix;
3. Compressive strength of the hardened mortar (concrete);
4. Water retention capacity of the mixture;
5. Water absorption.
6. Bond strength of the cured mortar layers;
7. Average density of the hardened concrete;
8. Frost resistance.

Tests of the construction mixture and hardened samples of fine-grained concrete were carried out following [16], [17]. The mobility of the mixture was determined by the slump of the cone molded from the concrete mixture following [18], [19]. The water retention capacity of the mixture was determined by the water content in the sample after testing following the recommendations of [20].

Compressive strength and adhesion strength of hardened samples were determined according to [21], [22]. Compressive strength on standard consistency prism samples of size 160x40x40 mm was determined on a machine to determine the strength according to [23]. The adhesion strength of hardened concrete was assessed by the force of separation of the sample from the base - a concrete slab, applied to the sample through a metal disk with an anchor.

Frost resistance of hardened concrete was determined according to [24], [25]: the number of freeze-thaw cycles - up to 400; samples of 100x100x100 mm were frozen for 2.5 hours at a temperature of minus (18±2) and thawed at a temperature of (20±2). The average density of hardened concrete was determined according to [26] by the accelerated method using a Le Chatelier device.

3. Results and Discussion

The chemical composition of ash and slag wastes from Ust-Kamenogorsk Thermal Power Plant according to the test results is given in Table 1.

Table 1 – Chemical composition of ash and slag

Test	Chemical composition, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	$Na_2O·K_2O$	Impurities
Ash and slag	51.27	22.49	9.32	2.95	1.69	0.95	0.93	4.67	5.63

The specific effective activity of radionuclides (Aeff) was 287.74 Bq/kg (less than 370 Bq/kg), i.e., ash and slag waste according to this indicator can be used to manufacture building structures for any purpose. The fraction of ash and slag particles was 0.63 mm, the bulk density was 1107 kg/m^3, i.e., less than the limit of 1200 kg/m^3 [3].

Manufacturers of 3D printers [5] and the study [4] recommend using standard sand concrete M300 (B22.5) based on Portland cement M500 for building mixtures. Therefore, for the experiment, a reference sample recommended by manufacturers, and five experimental samples, with part of the sand composition replaced with ash and slag from 10 to 100% were developed (Table 2). The adopted water-cement ratio for sand concrete M300 was 0.37, which is also recommended by [5].

Table 2 – Composition of samples

Sample	Components of the mixture, %		
	Cement	Sand	Ash and slag
Reference	30	70	0
No.1	30	60	10
No.2	30	40	30
No.3	30	20	50
No.4	30	10	70
No.5	30	0	100

The physical and mechanical characteristics of the samples obtained as a result of the tests are given in Table 3.

Table 3 – Physical and mechanical characteristics

Indicators	Unit	Sample					
		Reference	No.1	No.2	No.3	No.4	No.5
Mixture mobility	cm	5.75	5.77	5.81	5.84	5.91	5.94
Beginning of setting	h, min	3.15	3.18	3.18	3.21	3.25	3.27
End of setting	h, min	4.20	4.18	4.19	4.25	4.28	4.32
Normal density	mm	17	17	19	22	23	23
Water retention capacity	%	91.5	91.5	91.7	91.8	92.1	92.3
Compressive strength after 28 days	MPa	31.2	31.2	31.1	30.8	29.4	28.3
Adhesion strength	MPa	3.89	3.87	3.78	3.44	3.12	3.05
Frost resistance	cycles	75	75	76	76	77	77
Average density	kg/m^3	1980	1993	2027	2085	2150	2194
Water absorption	%	4.8	4.82	4.87	4.95	5.01	5.12

The analysis of the data presented in Table 3 allows us to formulate several main conclusions about the influence of ash and slag particles on the physical and mechanical properties of mortar for 3D printing.

The addition of ash and slag increases the mobility of the mixture (Figure 1). This is because ash and slag particles have glazed surfaces, reducing their friction against each other. The glazing of particles explains the reduction in the total viscosity of the mixture containing ash and slag, compared to standard sandcrete, and the increase, although insignificant, of the setting period of concrete (Figure 2).

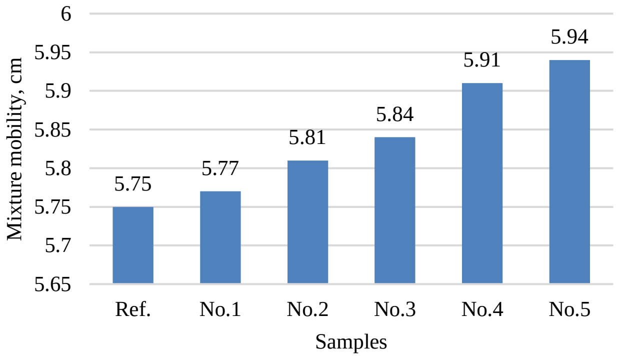

Figure 1 – Mixture mobility

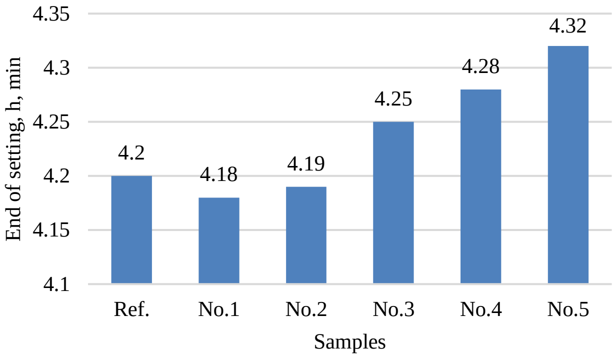

Figure 2 – End of setting time

The normal density of the mixture grows as the share of ash and slag in its composition increases (Figure 3). This phenomenon is probably because ash and slag particles have a small specific surface area and finer grinding than sand, and therefore more effectively fill the cement pores.

The introduction of ash and slag into the composition of the mixture increases its water retention capacity (Figure 4), while the setting time increases insignificantly. The increase in water retention capacity is due to the fact that water is absorbed on the surface of ash particles. Absorption prevents the movement of water and its escape to the surface, which, in turn, leads to a decrease in water separation and delamination of concrete prepared with the addition of ash and slag, compared to the standard solution [18]. (10) For the same reason the water absorption of concrete increases (Figure 5).

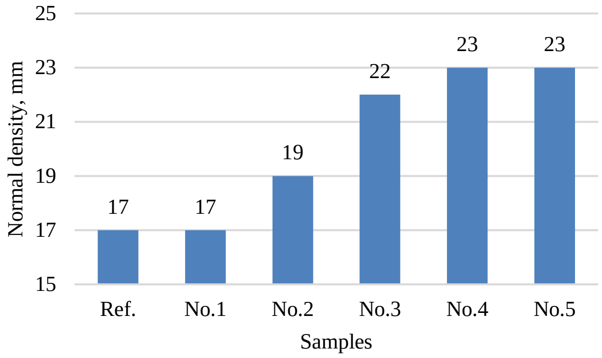

Figure 3 – Normal density

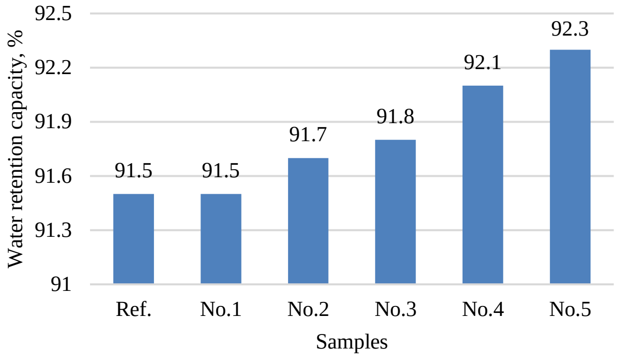

Figure 4 – Water retention capacity

Concerning the strength of modified samples, it can be noted that the addition of ash and slag to the mixture reduces the compressive strength values after 28 days (Figure 6), which is associated with an increase in the volume of water for mixing compared to the standard composition. Thus, in our experiment the water-cement ratio for sandcrete M300 is 0.37, and for ash-and-slag mixtures - in the range from 0.38 to 0.55.

The adhesion strength of layers also decreases with increasing ash-and-slag content in the compositions of experimental samples (Figure 6). Note that for small architectural forms, the reduction of strength values to the obtained values is not critical.

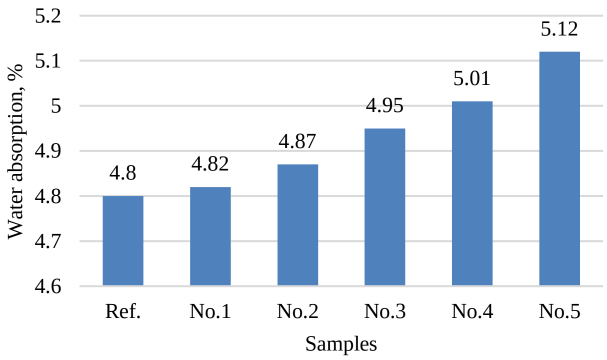

Figure 5 – Water absorption

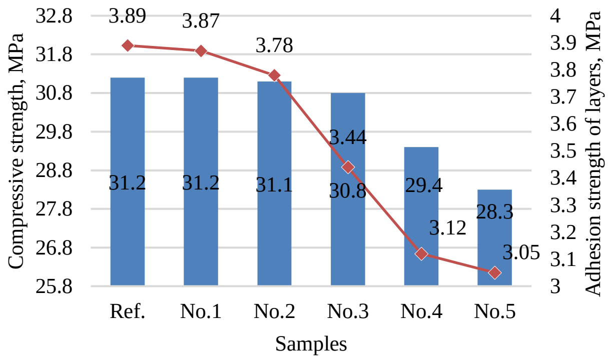

Figure 6 – Strength parameters of samples

Frost resistance of samples at an increase of ash and slag share in their compositions does not undergo significant changes (Figure 7).

The study showed that the introduction of ash and slag into the mixture increases the average density of samples (Figure 8). This phenomenon is due to the smaller specific surface area of ash microspheres compared to sand. The filling of voids between cement particles is denser, which leads to an increase in the average density of hardened concrete. Therefore, the surface of such a product does not contain large pores and will be smoother than a structure made of standard sandcrete.

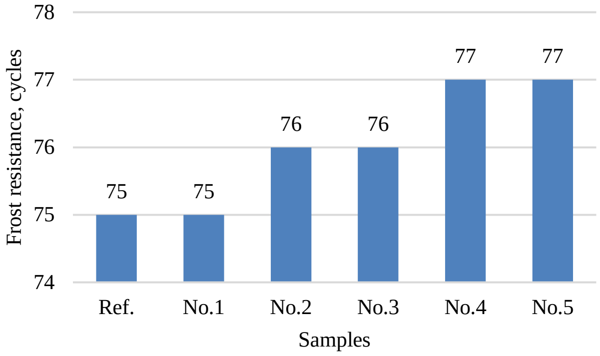

Figure 7 – Frost resistance

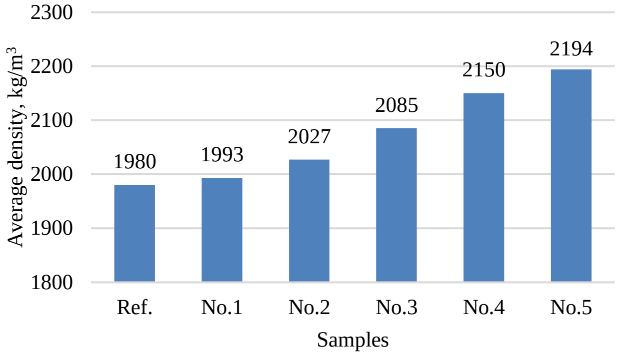

Figure 8 – Average sample density

Comparing the data in Table 3 and Figures 1-8 with the recommended values, we can draw several conclusions about the compliance of the experimental ash-and-slag fine-grained concrete compositions with them:

In terms of compressive strength, all compositions correspond to the recommended value. The highest compressive strength was obtained in the sample with the replacement of 10% of sand with ash and slag. Frost resistance of all samples corresponds to the normative. The highest index of frost resistance (77 cycles) was obtained in the samples in which the replacement of sand with ash and slag was 70% and 100. The water retention capacity of experimental samples corresponds to the recommended values.

Density corresponds to the normative value in samples with sand replacement with ash and slag more than 30%. Normal density is within the recommended values, but, as it seems, the optimal value is close to the value of the reference sample; it is obtained in samples with replacement of sand with ash and slag not more than 30%.

The setting time of experimental samples does not exceed 5 hours and is close to the indicator of the reference sample. Obviously, the shorter the setting time, the more preferable will be the composition of ash-and-slag concrete. The mobility of the mixture does not exceed the limit values, i.e., all compositions are suitable for extrusion.

In the course of the research, considerable attention was paid to the search for the recommended values of the indicators of construction mixtures for additive technology. Analysis of the data available in the special literature [7], [8], etc. allowed us to formulate the requirements to the compositions used for 3D printing of small architectural forms, in particular:

1. Compressive strength - not less than 22.5 MPa;
2. Frost resistance - not less than 70 cycles;
3. Water retention capacity - not less than 90%;
4. Average density - not less than 2000 kg/m^3.

With regard to other characteristics (normal density, setting time, mobility of the mixture) it can be noted that in laboratory conditions it is difficult to determine their lower limit. The data of [9], [25], indicate that the normal density should be in the range of 10-25 mm, and mobility by cone immersion should be 5-8 cm. If the indicators do not meet these values, the concrete mixture is not suitable for extrusion.

According to [27], the optimum setting time is 2.5 hours. The termination of the setting should be no more than 5 hours [28], as too long curing will not allow the production of a building structure layer by layer.

Thus, replacing a portion of the sand with ash and slag provides a mixture suitable for use in additive technology for making small architectural shapes. The optimal composition of fine-grained concrete for 3D printing of small architectural forms is a composition containing 30% Portland cement M500, 40% sand, and 30% ash and slag. It should also be noted the high-performance characteristics of fine-grained concrete made with the addition of ash and slag: water resistance, fire resistance, and frost resistance.

4. Conclusions

Based on the results of the study, it is worthwhile to formulate several main conclusions:

Experimentally confirmed the possibility of developing a composition based on ash and slag waste of the Ust-Kamenogorsk Thermal Power Plant for additive technology for the manufacture of small architectural forms;

Tests of prototypes showed that fine-grained concrete compositions suitable for extrusion in a 3D construction printer were obtained;

The optimal composition is 30% Portland cement M500, 40% sand, and 30% ash slag. Physical and mechanical indicators of this composition: mixture mobility - 5.81 cm; setting end time - 4 hours 19 minutes; normal density - 19 mm; water retention capacity (9)- 91.7%; compression strength after 28 days - 31.1 MPa; adhesion strength - 3.78 MPa; frost resistance - 76 cycles; average density - 2027 kg/m^3; water absorption - 4.87%.

The disadvantage of ash-slag concretes is their high water-absorbing capacity, therefore, finished building structures made of fine-grained concrete must be covered with special protective solutions that prevent moisture from penetrating inside and thereby increase the durability of the structure.

The main effects of modifying the composition of fine-grained concrete with ash and slag are economic (reducing its cost through the use of affordable and cheap technogenic waste) and environmental (reducing coal ash dumps Thermal Power Plant, which reduces their dangerous and harmful impact on the environment and human health).

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Article

Dependence of biopolymer activity on pH and their influence on soil moisture behavior

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Abstract. The study presents the treatment of soil with chitosan and xanthan gum, examines the influence of the pH of base solutions on the solubility and activity of these biopolymers, and investigates the changes in soil properties resulting from their application. The first stage of the study is devoted to the peculiarities of preparing soil reinforcement with biopolymers and their mixing process. The obtained samples were analyzed for their texture, which allowed identifying the optimal conditions for maximum solubility. The second stage of the study is devoted to evaluating the modified soil's behavior under wetting conditions. The moisture level of the soil directly affects its physical and mechanical properties. Understanding these changes makes it possible to predict the behavior of the soil under different service conditions. The study considered 10 soil samples prepared with base solutions of different acidity (pH 4, pH 7, pH 9), among which one sample serves as a control sample without modification with biopolymers. This makes it possible to evaluate the effect of modification on soil properties and to identify optimal conditions for its use. The analysis showed that the solutions' moisture level and acidity significantly affect the samples' structural characteristics. At the same time modified soils show improved performance compared to the control sample, the sample reinforced with chitosan increased density by 16 %. These data are important for the development of effective solutions in geotechnical and construction engineering.
Keywords: soil properties, biopolymer, pH, moisture, mixing process, soaking time.

1. Introduction

Using new biopolymers for soil improvement is a significant step in sustainable construction practices [1]. Biopolymers are increasingly applied in geotechnical engineering due to their unique properties and environmental safety. Biopolymers are natural polymers formed in living organisms and are categorized into three main groups: polynucleotides, polypeptides, and polysaccharides. They are sustainable, low-carbon, and renewable resources because they originate in nature. Polysaccharides such as xanthan, gellan, guar gum, alginate, and agar are known for their properties that contribute to soil quality. The constant discovery of different biopolymers provides engineers with a wide range of options, allowing them to find more customized solutions to meet specific project requirements. Thus, in the study [2], the modification efficiency of xanthan gum increases when combined with utilizing alkaline Class-F fly ash (FA). Improvement of mechanical strength and compressibility of acidic soils containing xanthan gum (XG) can be caused by crosslinking of XG molecular filaments and weakening of XG hydrogels hydrolysis under the action of FA. Based on the results obtained, it was proposed to use FA in combination with XG for the treatment of acidic soils and to use only XG for the treatment of neutral soils. In [3] the silty sand from Waynad, Kerala was treated with agar biopolymer, providing significant liquefaction resistance as a noteworthy reduction in excess pore pressure was observed. A series of cyclic triaxial tests showed that shear modulus increased with an increase in biopolymer content, curing period, and over-consolidation ratio.

Chitosan is a biopolymer derived from chitin, which is found in the exoskeletons of crustaceans and the cell walls of fungi [4]. It has high strength and biocompatibility, which makes it a promising material in geotechnical engineering. Chitosan has antimicrobial properties, which can reduce the risk of pathogens in the soil. Due to its adhesive properties, it binds soil particles, preventing soil leaching and erosion. Xanthan gum is a polysaccharide derived from the fermentation of sugars involving bacteria such as Xanthomonas campestris. It is known for its gel-forming properties and high viscosity. This biopolymer forms gels that help bind soil particles, due to its biocompatible properties, it is safe for the environment and non-toxic to plants and microorganisms [5]. The authors [6] in the paper note that stable strength parameters under all curing conditions in unconfined compressive strength (UCS) tests were demonstrated by specimens treated with Stabilized soil composites incorporating Cr3+-crosslinked xanthan gum (CrXG) with a clay-sand mixture (CSM) containing 15% fines. CSM15 also retains a 90% durability index after eight dry-to-wet cycles and a dry UCS of 300 kPa after 130 days of atmospheric weathering. The microscopic analysis confirmed the stable agglomeration of the CrXG-clay matrix between sand grains. The results of this study indicate that these composites can be applied as a sustainable surface protection strategy for earth structures such as dams and road slopes. The study of the effect of gum stabilization has been presented in many research [7], [8]. The investigation into the characteristics of soil stabilized with biopolymeric materials—specifically xanthan gum and guar gum—conducted by [6], [7], [8], [9], confirms their effectiveness, demonstrating that the strength of the soil increases with the addition of these biopolymers.

In another study [10], different concentrations of biopolymer were used and tested before and after soil curing. At the same time, mixing parameters were measured in both wet and dry soil conditions. Thus, a relationship between the way biopolymers are mixed with soil and their further utilization has been established.

The importance of soil pH in biopolymer activity is noted in a study [11]. The effect of pH on the activity of biopolymers is due to changes in the structure and function of these molecules depending on the acidity or alkalinity of the medium. For example, at low pH, biopolymers can denature, that is lose their spatial structure and functionality due to disruption of hydrogen bonds and ionic interactions between amino acids or other elements of the molecule. Moreover, at high pH, changes in the structure of biopolymers may also occur, which affects their ability to interact with other molecules and participate in biological processes in the soil [12]. Thus, optimal soil pH can help to maintain the activity of biopolymers and their role in soil fertility and plant growth. Liming techniques or the addition of organic fertilizers are often used to maintain appropriate soil pH levels to compensate for changes caused by anthropogenic influences or natural soil processes [13].

The interaction of chitosan and xanthan gum with soil depends on their properties and the pH of the medium [14]. Chitosan is a positively charged biopolymer that has good adhesion to soil particles due to electrostatic attractions. At a low pH value, chitosan has a high solubility in water, which favors its interaction with soil. However, at higher pH values, chitosan can deprotonate, lose its positive charge, and become less adhesive to soil particles. Xanthan gum has a high viscosity and good stability in solution. Its interaction with soil depends on the pH of the medium. At low pH values, xanthan gum can form gels with soil particles and improve their adhesion. However, at high pH values, it is possible to form gravitational suspensions, which may result in reduced adhesion to the soil. Thus, it is important to consider the pH of the medium when chitosan and xanthan gum interact with soil to optimize their solubility and adhesion to soil particles. Also, the physical properties of biopolymers can vary significantly depending on their type and composition [15]. The main objective of this study is to investigate the effect of different pH values on the interaction of biopolymers (xanthan gum and chitosan) with soil, which may influence their solubility and interaction with soil particles, and to evaluate the behaviour of modified soils under moisture conditions. Humidity is a critical factor affecting soil behaviour as it can significantly alter the soil structure. When moistened, the soil begins to absorb water, which can lead to a change in its volume and a reduction in strength, especially if insufficiently resistant materials are used. Moisture resistance also affects the durability of structures, so such assessments are key to evaluating the risk of failure.

2. Methods

The investigations were conducted in the "ENU-Lab" laboratory of L.N. Gumilyov Eurasian National University, Astana, Republic of Kazakhstan. The experiment's technical process consisted of the following main procedures:

1. Test setup and equipment calibration.
2. Determination of physical and mechanical properties of soil.
3. Preparing solutions with different pH.
4. Preparing modified soil.
4. Measurement of the pH level of soil and the biopolymer soil.
5. Evaluation of the behavior of modified soil samples under humid conditions.
6. Scanning electron microscopy analyses of soil and the biopolymer soil.
7. Analysis exploring the interrelationship between received results.

Sand with fine friction (Astana, Kazakhstan) was employed for the experiment. Sieve, hydrometer, liquid, and plastic limit analyses were conducted to classify the soil. The liquid and plastic limit analyses assessed the soil's consistency and plasticity characteristics [16]. These tests allowed for a comprehensive understanding of the soil's texture and behavior, essential for evaluating its suitability for reinforcement.

The study used pre-dissolution of chitosan and xanthan gum, which were pre-dissolved in water before their application to the soil. One of the main advantages of this procedure is the improved interaction of the components, which promotes a more homogeneous distribution in the soil. This procedure also reduces the likelihood of clumping, which is important for achieving a homogeneous mixture texture, and allows easier control of the moisture level in the soil, which is particularly useful when preparing samples for experiments. It also avoids the loss of active ingredients that can occur with mixing [10]. The preparation of base solutions included the preparation of solutions with different pH values tested with litmus paper. The pH values were 4, 7, and 9 (Figure 1). The choice of pH levels 4, 7, and 9 is because they represent three different values on the pH scale, reflecting acidic, neutral, and alkaline conditions respectively.

A pH level of 4 corresponds to acidic conditions, which may be caused, for example, by the presence of acidic precipitation in the environment or the use of acidic solutions in construction. Acidic conditions can lead to corrosion of metal structures and damage to concrete surfaces. A pH level of 7 corresponds to neutral conditions, which are the most favorable for most building materials and structures. A neutral pH provides stability and preservation of materials over long periods. A pH level of 9 corresponds to alkaline conditions, which can be caused by the use of alkaline solutions or highly alkaline soil conditions. Alkaline conditions can also lead to corrosion of metal structures and changes in the properties of building materials.

Thus, selecting pH levels of 4, 7, and 9 allows the effects of different conditions on building materials and structures to be assessed and precautions to be taken for their protection and durability.

a) pH 4 b) pH 7 c) pH 9

Figure 1 – Preparation of solution with different pH

The ratio of biopolymer to soil was 2g:100g respectively. Soil samples were prepared with the addition of different concentrations of chitosan and xanthan gum at different pH levels, and one control sample without the addition of biopolymer. Mixing of the soil was carried out gradually to avoid the formation of lumps and to obtain a homogeneous consistency (Figure 2). An important step after mixing the biopolymer with the soil is to ensure its stabilization. This process allows the biopolymers to interact with the soil particles, forming stronger bonds, which in turn increases resistance to external loads and moisture. The finished modified soil was evaluated for pH levels.

a) mixing with chitosan at the beginning of the process

b) mixing with chitosan at the end of the process

c) mixing with xanthan gum at the beginning of the process

d) mixing with xanthan gum at the end of the process

Figure 2 – Process of soil mixing with biopolymers

When chitosan is mixed with water, the homogeneity of the mixture is quickly achieved. Chitosan dissolves easily, does not stick to gloves, and is then effectively combined with the soil. In the case of mixing the soil with gum, it is necessary to mix the gum with water thoroughly beforehand to obtain a homogeneous mass. When gum comes into contact with water, a thick gel is formed, which requires additional thorough mixing when adding the soil to ensure homogeneity of the entire mixture. Gum, in turn, being a complex polysaccharide upon initial reaction with water leads to the formation of heterogeneous areas in the mixture. The evaluation of the behavior of the modified specimens under moisture conditions involved the preparation of specimens of the same size and weight to ensure comparability (Figure 3).

Figure 3 – Modified samples

After the samples were subjected to humidification. Instrumental and visual inspection were used during the testing process. The initial dimensions of the specimens were recorded and the dimensions after wetting were measured at fixed intervals using a caliper. The control interval was every 20 minutes for the first hour and 3, 5, 9, 13, 17, 21, and 24 hours thereafter. One of the parameters monitored was also the change in weight of the samples.

Changes in color, texture, and cracking were recorded during visual inspection. A rating scale from 1 to 5 was applied to assess the shape preservation, in which: 1 - destruction: the specimen is destroyed, and has lost structural integrity; 2 - significant destruction: the specimen has severe cracks, deformations, or destroyed areas; 3 - moderate failure: the specimen shows some signs of failure, such as minor cracks or deformations; 4 - minor degradation: the specimen is generally intact, with minor surface damage or cracks; 5 - perfect condition: the specimen is in perfect condition, with no visible damage or changes.

The water absorption coefficient and soil density were calculated by equation 1,2 [17]:

$$W = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100\%, \tag{1}$$

where: m_{wet} – mass of moistened soil sample, g.; m_{dry}– mass of dry soil sample, g.

$$\rho = \frac{m}{V}, \tag{2}$$

where: m – soil weight, g.; V– the volume of the wet sample, cm^3.

3. Results and Discussion

Table 1 presents the soil's physical characteristics obtained in laboratory tests. The soil composition contains 60.794 % sand, 19.193 % silt and 15.609 % clay. The particle size distribution curve for soil is shown in Figure 4.

Table 1 – Physical characteristics of the soil

Soil characteristic	Value
Specific gravity, g/cm3	2.538
Maximum dry density, g/cm3	2.031
Optimum water content, %	10.194
Sand-sized fraction (75 µm–2 mm), %	60.794
Silt-sized fraction (5–75 µm), %	19.193
Clay sized fraction (<5 µm), %	15.607
Liquid limit, LL, %	23.251
Plastic limit, PL, %	1.190
Plasticity Index, PI, %	22.061

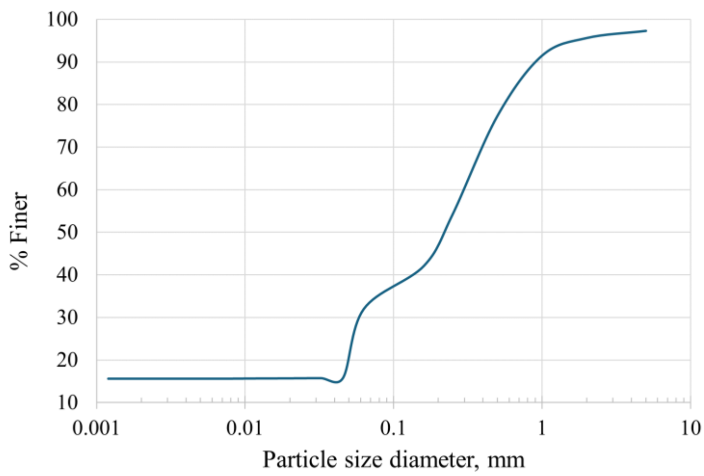


Figure 4 – Particle size distribution curve

The modified soils' pH results corresponded to the prepared solutions' pH values. Table 2 presents the changes in parameters for chitosan – and xanthan gum-modified soil samples.

Table 2 – Weight of moistened samples

Time, hour	Soil sample without modification	Soil sample modified by chitosan			Soil sample modified by xanthan gum		
	Weight of moistened sample, g.						
		pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
0	105	105	105	105	105	105	105
0.3	110	111	112.3	115.5	111.5	111	112
0.7	111	114	117.6	121	111.9	111.3	112.2
1	114	116.3	120.5	128.3	114	116	116.3
3	115	124.2	131.4	136.2	117	119	120.8
5	123	128.6	135	140.1	124	127.3	128
9	126	131.4	139.1	144.3	126.2	128.1	129.8
13	114	135.5	142.3	147.7	129	130.1	131.5
17	110	137	144.1	150.1	129.1	131	133
21	107	134.3	144.1	145.2	128.5	129.6	131
24	103	131.2	140.2	145	127.2	128.4	130.6

According to the data obtained, the weight of the control soil sample changed from 105 grams to 103 grams when moistened. Moistening caused a change in the soil's structure, leading to its loosening. This factor affects the bearing capacity of the soil. The chitosan-modified soil sample showed significant performance when alkaline base solution was used, the weight increase was from 105 grams to 145 grams, indicating an increase in moisture-holding capacity caused by the biopolymer. This may be because chitosan improves the soil structure by increasing porosity and water retention capacity.

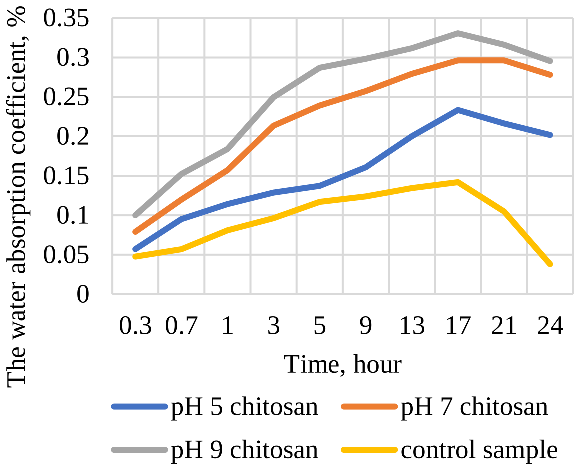
A significant performance improvement was observed in experiments with chitosan-modified soil, especially when an alkaline base solution was used, as previously stated in the study [14].

The modification with xanthan gum increased the weight from 105 grams to 130.6 grams, indicating that the soil increased its moisture retention capacity and improved its structural characteristics. This weight increase indicates that xanthan gum promotes the formation of gels that fill the pores and improve the soil's water retention properties.

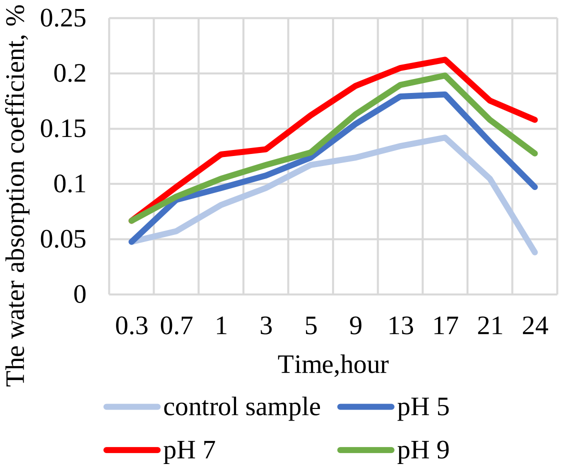
Samples of soil modified with biopolymers in the process of moistening are presented in Figure 5.

Figure 5 – Samples during the process of moistening

Figures 6-7 present the values of the modified specimens' water absorption coefficient and soil density.



a) W, soil modified by chitosan



b) W, soil modified by xanthan gum

Figure 6 – Graphs of water absorption coefficient

The error of each measurement was reduced by using weight instruments and accurately accounting for the biopolymers added. The total error consists of measurement error and test error and ranges from 0.01-0.1%.

The results showed that with increasing soil acidity, the use of xanthan gum leads to an improvement in the geotechnical performance of soils which is also established in the study [2]. This improvement can be attributed to cross-linking of the biopolymer molecular strands and attenuation of hydrolysis of soil particles under acid exposure. It is suggested to use xanthan gum in combination with acids for the treatment of acidic soils or separately for neutral soils. Along with this, when the studied soil was modified with xanthan gum, the soil behavior showed a stable result in terms of establishing the dependence of water absorption on the amount of biopolymer used, the results of which are presented in Table 2.

The water absorption coefficient shows how much water the soil absorbs about its original mass. The data presented in Figure 6 show that soil modified with chitosan absorbs more water than soil modified with gum. However, when modified with gum, the behavior of the soil is more stable, and there are no large variations in the data. The results of determining soil density as a characteristic that determines the mass of soil per unit volume showed variation depending on the biopolymer used for modification. Figure 7 shows the density values for each soil modification. The maximum density value was demonstrated by the soil modified with chitosan under an alkaline environment in relation to the density of the control soil sample.

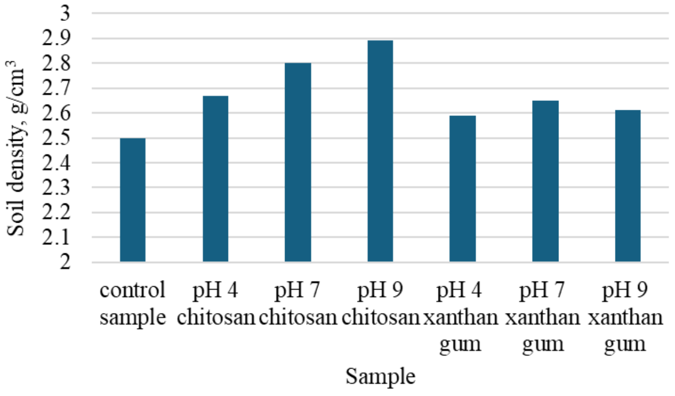


Figure 7 – Soil density values

Many studies [2], [3] do not provide information on the density of biopolymer-modified soil, which is an important aspect of evaluating its physical and mechanical characteristics. However, this study considered the density of biopolymer-modified soil at different pH values, which allows a more accurate assessment of the effect of changing the acidity of the medium on its structure and properties. Consideration of density in such studies is important because it directly affects characteristics such as water absorption and strength properties of soils.

After modifying the soil with chitosan, there was a 16 percent increase in density and a 6 percent increase in gum density. Visual observation of the behavior of the soil samples modified with biopolymers under different media of the base solution showed that the soil with chitosan retained its original shape, did not collapse, and absorbed moisture well. In contrast, the soil with gum under alkaline and acidic environments was quickly susceptible to drying out, and small cracks formed on the top surface of the molds, first small cracks and then larger cracks. However, the gum-modified soil samples were less susceptible to cracking and failure than the control soil sample.

According to the five-point scale evaluation of the behavior of the modified soil during wetting, presented in Figure 8, it is revealed that over time the soil samples lose their shape.

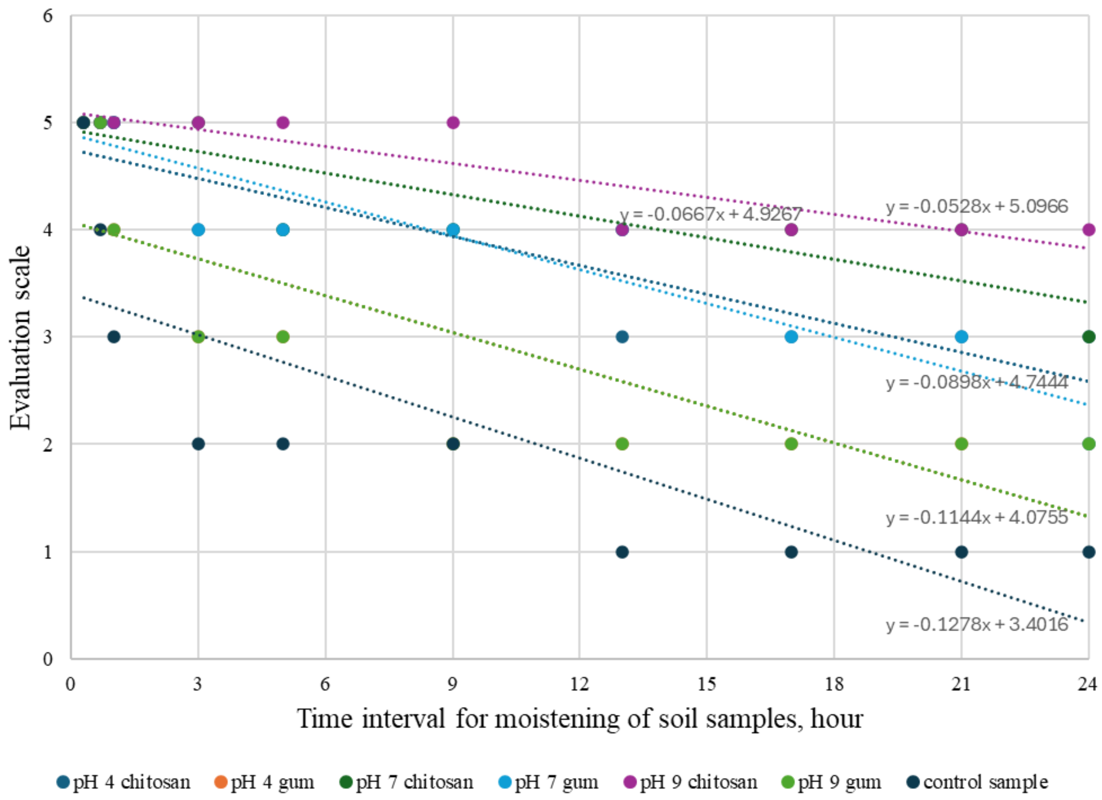


Figure 8 – Correlation of visual assessment data

However, a comparative analysis of the control sample with the biopolymer-modified samples shows that the modification favors soil strengthening. In particular, the biopolymer-treated samples show significantly less susceptibility to deformation and failure, indicating improved resistance to moisture. This is due to improved soil structure, increased cohesion, and soil density.

4. Conclusions

The applications of biopolymers for soil stabilization are extensive and each can be used according to their properties. Some biopolymers can improve the properties of drainage systems by promoting more efficient water drainage, while others are used to stabilize slopes and prevent slumping. The conducted study showed that:

1. The biopolymers showed good compatibility with the soil, and the wet mixing method allowed for a homogeneous structure.

2. The treated soil showed the best water absorption results in the following sequence using biopolymers: chitosan with alkaline medium base solution, chitosan with neutral medium, chitosan with acidic medium, gum with neutral medium, gum with alkaline medium, and gum with acidic. medium.

3. The density of the soil increased in the following ratio compared to the control soil sample: chitosan with alkaline medium 16 %, chitosan with neutral medium 12 %, chitosan with acidic medium 7 %, gum with neutral medium 6 %, gum with alkaline medium 4 % and gum with acidic medium 3 %.

4. Visual inspection showed that the soil sample reinforced with xanthan gum in solution with pH 4 is most susceptible to shape change and destruction.

To improve the physicochemical properties of soil in engineering practices, it is recommended to carry out preliminary site-specific tests to determine the optimum dose and type of biopolymer, and for this purpose, it is necessary to investigate the required composition of the base solution to dissolve with the biopolymer.

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