OBTAINING AND STUDYING THE PROPERTIES OF NEW GEOPOLYMER BINDERS BASED ON CALCINED CLAY ROCKS AND LOCAL INDUSTRIAL WASTE

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Abstract: The building materials industry in Georgia is entirely based on the production of Portland cement and concrete made from it, which is a particularly energy-intensive and environmentally harmful production. Considering the high prices for fuel and in the light of unfavorable environmental conditions in the country, the development of technologies for obtaining new alternative types of binders that do not require high-temperature firing is especially urgent. These materials can be geopolymer binders. The purpose of this work is to identify the possibility of obtaining and studying the properties of geopolymer binding materials of alkaline activation based on thermally modified clay rocks of Georgia, as well as geopolymers of acid activation using local industrial waste - dump blast furnace slags.

Keywords: geopolymer, alkali activation, acid activation, clay rock, dump blast furnace slag, magnetite.

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INTRODUCTION

The rapid growth of the world population has contributed to an increase in the consumption of cement / concrete as the main building material. Despite the unique properties of ordinary Portland cement (OPC), its production is characterized by a number of negative aspects: large consumption of energy resources and raw materials, as well as high carbon dioxide emissions (associated with limestone decarbonization). Based on the foregoing, scientists all over the world seek alternative sources of energy, raw materials and try to create new types of binders that would become an analogue of Portland cement with improved environmental performance. Geopolymers can be one of such materials. Geopolymers, which can be characterized as a stable and synthesized composite of aluminosilicate materials, has emerged as a potential substitute for Portland cement as it has similar initial strength and good mechanical properties, without producing high carbon dioxide (CO_2) emissions.

Alkali Activated Geopolymer Binders: Alkaline activated binders are one of the most promising technological platforms for the development of energy and resource-efficient production of building materials, products and constructions. V. Glukhovsky[1] was the first to discover the possibility of producing binding materials using low-basic-calcium or calcium-free aluminosilicates (clays) and solutions of alkali metals. Fundamental research in this field was carried out by V. Glukhovsky and his collaborators[2], as a result of which a new class of alkaline or alkali-activated cements (AAC) appeared.

Based on the overview and analysis of numerous works of various authors and the generalization of his own research on alkaline activation binders, the French scientist J. Davidovits[3] managed to develop the concept of geopolymer binders - inorganic materials of polymer structure based on thermally treated aluminosilicate materials - kaolin and feldspar rocks, as well as ash, slag, etc. - other industrial waste that exhibit astringent properties upon alkaline activation.

Geopolymer binders, unlike Portland cement, are environmentally friendly, they are characterized by durability and low CO_2 emissions into the atmosphere. Only 0.18 ton of CO_2 is released into the environment per 1 ton of geopolymer produced, which is 5 times less compared to Portland cement production[4].

P. Krivenko[5,6] further demonstrated that alkalis and alkali metal salts, similar to silicates, aluminates and aluminosilicates, enter into reaction in an alkaline aqueous medium under conditions of high alkali concentration.

At the initial stage of obtaining geopolymer binders, metakaolin was used as an aluminosilicate material - a product of heat treatment of kaolin clays at temperatures of 750-850 °C.

Alkaline activation of metakaolin makes it possible to obtain a geopolymer binder of high strength and network structure. In the presence of $Ca(OH)_2$, the reaction proceeds according to a different scheme: the shape of the gel and the shape of the network change[7-9].

P. Duxson et al.[10] compiled a brief history and overview of geopolymer technology and concluded that a lot of work has been done, but still a lot remains to be accomplished.

A. Attanasio et al.[11] developed certain recommendations for the design of cementless binders, taking into account the influence of each investigated aluminosilicate component.

A number of scientists have conducted research on obtaining geopolymer materials of different compositions using rocks and man-made materials[12-16].

In the Caucasian Institute of Mineral Resources (Tbilisi State University), study has been carried out for a number of years to identify the possibility of obtaining geopolymer binders using local raw materials: trachytes, clay shales, dump blast furnace slags, etc.[17,18]. A temperature regime has been developed for obtaining metakaolin during the calcination of local clay shales[19] and other clay rocks[20,21]. The conducted research formed the basis of the present work.

Acid Activated Geopolymer binders

J. Davidovits developed two directions for the synthesis of geopolymers[22]:

- in an alkaline medium (Na^+, K^+, Li^+, Ca^{++}, Cs^+, etc.);
- in an acidic medium with phosphoric acid and organic carboxylic acids.

From a commercial point of view, alkaline activation geopolymers are more important than acidic (mainly phosphoric acid), although the latter are also of some interest especially when it comes to waste disposal.

A group of scientists[23] has developed a technology for producing geopolymer foam, which is formed by the interaction of metakaolin and phosphoric acid and with the addition of natural calcite or dolomite in the form of a foaming agent.

A. Wagh[24] suggested that inorganic polymers containing $[PO_4]_3$ instead of $[SiO_4]_4$ should be considered as a new class of geopolymers. Having studied the reactions between metakaolin and phosphoric acid, A. Wagh came to the conclusion that the reaction between the phosphate tetrahedron and the Al-O interlayer in metakaolin proceeds with the formation of a wood-like network. In the author's opinion, the proposed model contains metakaolin particles, which are interconnected by oxygen bridges in tetrahedral coordination, which eliminates the need for a compensating charge outside the framework. Thus, the material acquires a new property and is characterized by low dielectric losses.

Geopolymer-phosphate cements are a two-component system that consists of a hardener liquid and a solid phase. After mixing them, a ceramic material with a three-dimensional structure is formed, which has high strength, durability and fire resistance. Due to the fact that phosphate cements do not create an alkaline environment, to which glass and basalt are unstable, excellent conditions are created for obtaining concretes with textile reinforcement based on phosphate cements.

A. Katsiki et al.[25] synthesized metakaolin-phosphate cements from metakaolin, phosphoric acid, and distilled water. The mechanical strength of the obtained materials reached 68 MPa.

D. Perera et al.[26] showed that phosphoric acid-bonding of metakaolinite could lead to high-strength materials (146 MPa as a paste), with superior strength to alkali activated ones (72 MPa as a paste). They performed a study on the polymerization conditions of the acidic activated inorganic polymer and obtained a phosphate cementitious paste with remarkable strength. They found that 6-fold coordinated aluminium and silicon in different environments probably coupled to Al and P over O-bridges.

The work of Y. Han et al.[27] is of great interest; the authors used waste products from the production of electrolytic manganese dioxide (EMDR) to obtain geopolymers.

By the various authors' suggestion[28,29] the products of reactions between magnetite and phosphoric acid are iron hydrophosphates.

Phosphoric acid geopolymers are usually obtained from aluminosilicate raw materials, and the production of geopolymers from magnetite can provide new means for treating iron-rich industrial solid waste, such as iron mine waste, dump blast furnace slags, and so on.

According to the famous scientist and inventor A. Wagh[24], chemically bonded phosphates are materials of the 21st century. But so far, they have not received due attention.

This work presents studies on the preparation of geopolymers of acid activation using dump blast furnace slags and phosphoric acid[30].

EXPERIMENTAL PART

Materials

Clay rocks of Georgia were used for the purpose of research: clay shale from Kvareli, mudstone from Teleti, clay from Gardabani, as well as granulated and dump blast furnace slags from the Rustavi Metallurgical Plant.

An alkaline activator, NaOH, Na_2CO_3, and $Na_2O(SiO_2)$ n, was used as a mixing liquid in one series of experiments; in another, phosphoric acid (H_3PO_4) of various concentrations was used.

Methods: The mineral composition of clays was determined using an Optika B-383POL polarization microscope (Italy).

A NETZSCH derivatograph with STA-2500 REGULUS thermogravimetric and differential thermal analyzer (TG / DTA) was used for thermogravimetric analysis. Samples were heated to 1000 ° C, in a ceramic crucible, heating rate 10 °C / min. Reference substance α-Al_2O_3.

The X-ray phase analysis was carried out using a Dron-4.0 diffractometer ("Burevestnik", St. Petersburg, Russia) with a Cu-anode and a Ni-filter. U=35kv. I=20mA. Intensity - 2 degrees / min. λ = 1.54178 Å.

Scanning electronic microscope (SEM) measurements were performed on a JEOL scanning electronic microscope JSM–6510LV (well-appointed by energy-disperse X–Max No.20 micro-X-ray spectral analyzer produced by Oxford Instruments). SEM measurements were carried out by means of reflected (BES) as well as secondary (SEI) electrons at an accelerating voltage (at 20 kV). The working distance was approximately 15 mm. Micrographs have been taken at the diverse enlargements.

Thermal conductivity was measured on ITP-MG4 "100" device ("Stroypribor", Chelyabinsk), in a stationary thermal mode in the temperature range 15 to 30 °C.

RESULTS AND DISCUSSIONS

Table 1 shows the chemical compositions of clay rock

Table 1. Chemical compositions of clay rocks, wt.%

Material	L.O.I.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	Mn_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
Shale	4.50	59.95	0.89	17.30	3.45	3.65	0.59	1.53	2.43	0.30	2.20	2.20
Mudstone	7.01	47.19	-	15.90	13.36	-	0.10	6.30	4.10	1.39	2.86	1.30

Clay	10.60	52.84	-	15.07	6.47	-	-	7.06	2.49	1.36	1.19	2.17

Clay minerals (14.66 - 14.96, 7.14, 4.25, 3.66, 2.86, 2.327 Å) are noted on the X-ray diffraction patterns (Fig. 1); quartz (3.34 Å); feldspar (3.87 Å), calcium carbonate (3.03 Å).

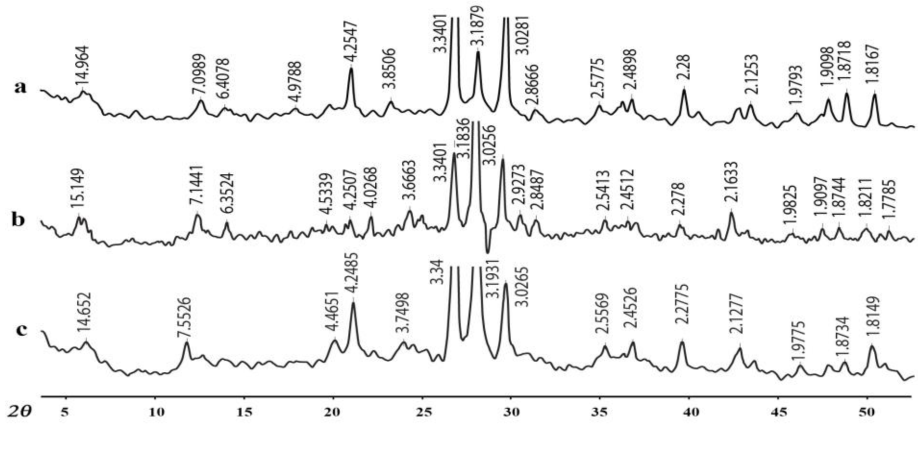

Figure 1. X-ray diffraction patterns of clay rocks: a) shale, b) mudstone, c) clay

Clay materials were thermally modified for synthesizing the geopolymer binder. In order to establish the temperature of the heat treatment, differential thermal analyzes were carried out.

According to DTA data (Fig. 2), endothermic regions within 100 - 150 °C associated with the loss of mechanically bound water are noted on all curves. In the temperature range 650-850 °C, endo-effects are noted, which are presumably associated with the destruction of the crystal lattice of clay minerals, their transformation into an amorphous reactive phase (formation of metakaolin).

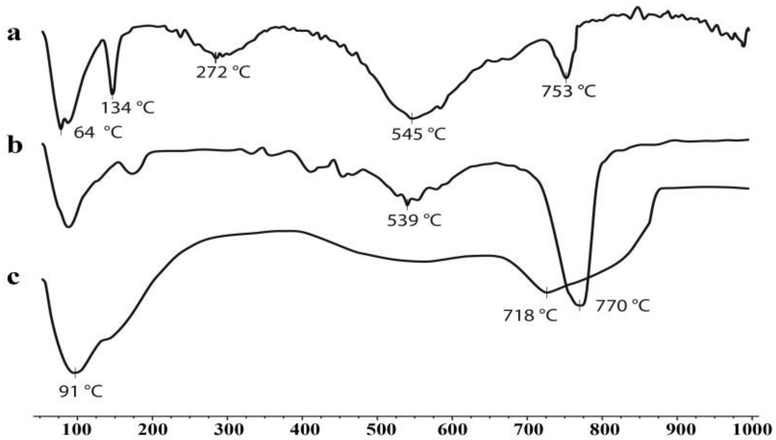

Figure 2. DTA curves of clay rocks: a) shale, b) mudstone, c) clay

According to the test results (Fig. 3a, 3b and 3c), it is obvious that clay rocks thermally modified at 700 °C have a rather high pozzolanic activity.

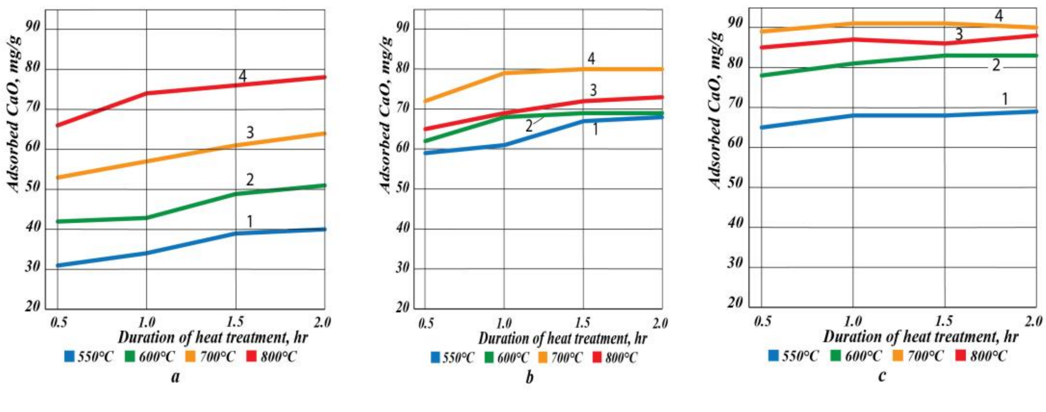

Figure 3. The kinetics of CaO absorption by heat-treated clay rocks from a saturated solution: a) shale, b) mudstone, c) clay

Heat treatment (modification) of clay materials was carried out in a muffle furnace at a heating rate of 250-300 °C per hour and at an exposure time of 1 hour at a maximum temperature of 700 °C. The samples were cooled naturally at room temperature.

For the preparation of geopolymer compositions, granulated blast furnace slag and modified clay rocks were used, which were ground in a laboratory ball mill to a specific surface area of 8,000-9,000 cm^2/g. As an alkaline activator, we used: sodium alkali - NaOH, sodium carbonate -Na_2CO_3, or liquid glass - $Na_2O(SiO_2)n$, or a combination of them. The alkaline activator was added in an amount that obtain the dough of normal density.

Samples of 20 x 20 x 20 mm were formed, which were removed from the mold 2 days after forming. Some samples were stored in air, some in water, and some in air-wet conditions. The curing temperature was 20°C for 28 days, after which the samples were tested for mechanical strength.

After being removed from the mold part of the samples was subjected to heat treatment according to the mode: 80 °C for 20 hours and after cooling, they were tested for mechanical strength.

As shown by the test results (Table 2), after heat treatment (80 °C for 20 hours), the strength of geopolymer binders significantly increases compared to binders that have hardened under normal conditions. Heat treatment accelerates the transition of gel - like products of hydration of geopolymers to the crystalline phase; with increasing temperature, the solubility of Si^{4+}, Al^{3+}, and Ca^{2+} ions increases and, accordingly, the rate of pozzolanic and geopolymer reactions increases[31].

Table 2. Compositions of geopolymer binders and the results of their physical and mechanical testing

No.	**Components, (%)**		**Alkaline component, (dry matter above 100%), %**	**Compressive strength after 28 days of curing depending on curing conditions, kg/cm^2**			**Compressive strength after heat treatment, kg/cm^2**
				Air	Water	Air-wet	
1	Slag (80)	* Shale (20)	NaOH (10)	410	452	440	690
2	Slag (80)	* Shale (20)	Na_2CO_3 (10)	210	245	240	537
3	Slag (80)	* Shale (20)	$Na_2O(SiO_2)n$ (10)	187	334	212	488
4	Slag (80)	* Mudstone (20)	NaOH (10)	469	480	418	695
5	Slag (80)	* Mudstone (20)	Na_2CO_3 (10)	335	420	390	685
6	Slag (80)	* Mudstone (20)	NaOH (2.5) + $Na_2O(SiO_2)n$ (7)	536	472	450	856
7	Slag (80)	* Clay (20)	NaOH (10)	460	510	478	630
8	Slag (80)	* Clay (20)	Na_2CO_3 (10)	175	223	217	575
9	Slag (80)	* Clay (20)	$Na_2O(SiO_2)n$ (10)	75	88	85	150
10	Slag (80)	* Clay (20)	NaOH (4) + Na_2CO_3 (6)	215	254	230	266
11	Slag (80)	* Clay (20)	NaOH (4) + $Na_2O(SiO_2)n$ (10)	850	940	935	1025
12	Slag (80)	* Clay (20)	Na_2CO_3 (4) + $Na_2O(SiO_2)n$ (10)	112	145	156	320

* Clay rocks modified at 700 °C

Fig. 4 and Fig. 5 show the micrographs obtained using SEM measurements by means of reflected (BEC) as well as secondary (SEI) electrons for geopolymer binders No.6 and No.11 (Table 2), which had the best strength indicators. As can be seen in the figures, heat treatment promotes compaction of the material, which has a positive effect on its mechanical strength.

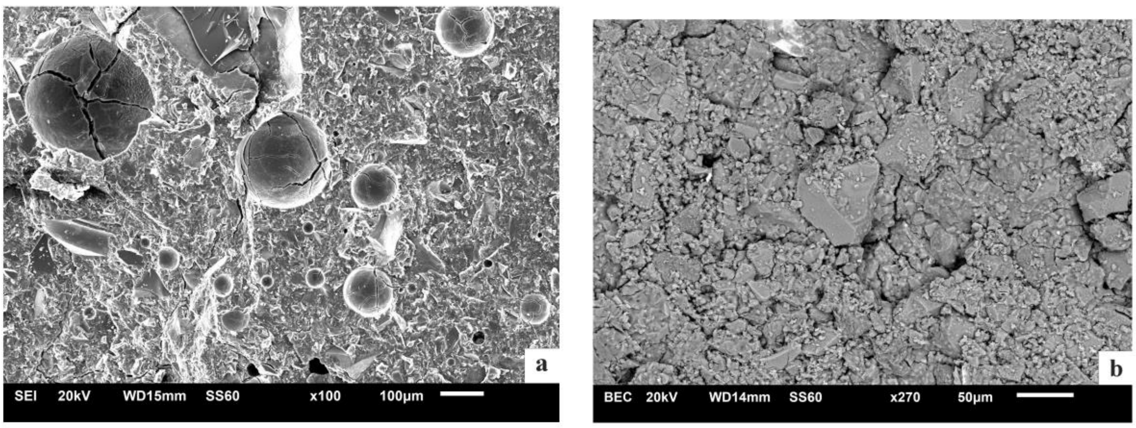

Figure 4. Micrographs of geopolymer binder No.6: a – after 28 days of curing under normal conditions (SEI, enlargement 100), b – after 2 days of curing and heat treatment (BEC, enlargement 270)

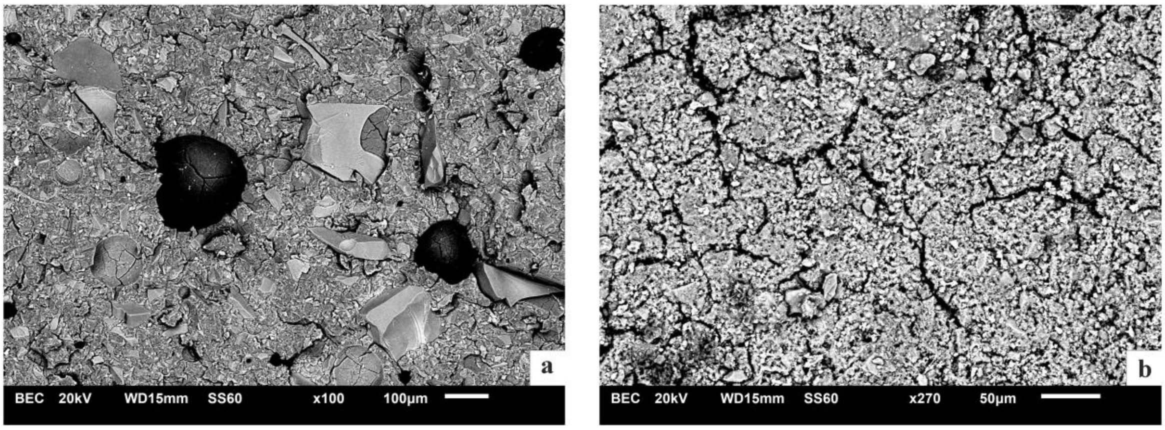

Figure 5. Micrographs of geopolymer binder No.11: a – after 28 days of curing under normal conditions (BEC, enlargement 100), b – after 2 days of curing and heat treatment (SEI, enlargement 270)

Thus, the possibility of obtaining geopolymer binders (with high physical and mechanical characteristics) based on thermally modified local clay rocks, granulated blast furnace slag and an alkaline grout of various compositions has been proved.

The next stage of this research is the production of geopolymer binders for acid hardening using dump blast furnace slag and phosphoric acid.

Dump slags are waste products of the metallurgical industry and, unlike granular slags, are not of interest for the production of building materials as a hydraulically active component. Although in many countries where the metallurgical industry is developed, there is a large amount of dump slag on the territories of factories, which create many problems from an environmental point of view. This problem also exists in Georgia, where several million tons of dump blast furnace slag have accumulated on the territory of the Rustavi Metallurgical Plant which further aggravates the rather difficult ecological situation in the country.

Previously, we conducted a number of studies to establish the possibility of obtaining geopolymer binders based on dump blast furnace slags and rocks using an alkaline missing agent[17]. Although the methods of mechanical and thermal activation of slags were used, it was not possible to obtain the binder with the required quality.

The high content of iron oxides in the dump slag from the Rustavi Metallurgical Plant (Table 3) was a prerequisite that phosphoric acid could activate their hydraulic properties.

Table 3. Chemical compositions of waste blast furnace slags, wt.%.

No.	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	SO_3	Na_2O	K_2O
1.	5.40	32.52	10.70	3.15	1.32	39.90	3.20	0.65	1.10	0.80	0.36
2.	4.30	33.15	9.96	4.27	1.07	42.20	2.70	0.86	0.35	0.56	0.20
3.	6.05	27.4	9.10	12.90	9.50	29.20	3.10	0.20	0.50	1.40	0.20

Slag No.3 was used for the experiments, and phosphoric acid with a concentration of 85% was used as an activator. Rocks served as additives. Table 4 shows the compositions of geopolymer binders and the results of their physical and mechanical testing.

Table 4. Compositions of geopolymer binders and the results of their physical and mechanical testing

No.	Composition of geopolymer binder				Compressive strength, kg/cm^2	Note
	*DBFS, %	Additive, %	Phosphoric acid conc., %	Water over 100%, ml		
1	100	-	85%	-	-	Samples did not form due to fast setting
2	80	Basalt-20	85%	-	-	
3	60	Basalt-40	85%	-	-	
4	100	-	65%	-		Samples did not form due to fast setting
5	100	-	65%	-		
6	100	-	65%	60		
7	80	Sand-20	65%	60	75	Porous samples
8	60	Sand-40	65%	60	96	Porous samples

*DBFS – dump blast furnace slag

As can be seen from Table 4, during the experiments, the interaction of magnetite (contained in the dump slag) and 85% phosphoric acid was accompanied by the release of a large amount of heat and there was a rapid setting of the material, which made molding impossible (compositions No.: 1, 2 and 3).

The next series was carried out on 65% phosphoric acid (compositions no.: 4, 5 and 6). The situation repeated itself.

It was possible to mold only compositions No. 7 and No. 8 with the addition of natural sand and an additional amount of water.

Samples of 20 x 20 x 20 mm were molded. In order to avoid rapid evaporation of water, the samples were stored in plastic bags. The samples were removed from the mold after 2 days, after which they were subjected to heat treatment according to the mode: 80 ° C for 20 hours and after cooling were tested for mechanical strength.

Porous samples were obtained (Fig. 6). The density of sample No. 7 was 0.68 g/cm^3 (680 kg/m^3), and for sample No. 8 it was 0.720 g/cm^3 (720 kg/m^3).

Figure: 6. Geopolymer binder based on waste slag, natural sand and phosphoric acid (sample No. 8)

A thermal conductivity test was carried out: the thermal conductivity coefficient (λ) was: for sample No. 7 - 0.098 W/(m·°C), and for No. 8 - 0.115 W/(m·°C). Then, as the coefficient of thermal conductivity of lightweight concrete ranges from 0.20 - 0.52 W/(m·°C).

Thus, a heat-insulating geopolymer material was obtained based on dump blast-furnace slag and sand with the addition of phosphoric acid. When changing the ratio: dump slag/sand, you can get a material with different indicators of strength and density.

The development of the technology for obtaining geopolymers based on magnetite opens up prospects for the production of heat-insulating materials using industrial waste rich in iron, for example, dump blast furnace slags, which will contribute to improving the environmental situation.

The production of new environmentally friendly and cost-effective materials from local industrial waste is essential. Further research is expected to identify new compositions and study their properties, structure formation and hardening processes of geopolymer binders, which will be done during the next experiments in the near future.

CONCLUSIONS

- Geopolymer binders of alkaline activation were obtained on the basis of clay rocks of Georgia thermally modified at 700°C.
- Sodium alkali and sodium carbonate, as well as liquid glass or a combination of them, can be used as an alkaline component.
- After 2 days of curing and heat treatment (80°C for 20 hours) the mechanical strength is significantly increased.
- A heat-insulating geopolymer material based on blast furnace slag and sand with the addition of phosphoric acid was obtained.
- When changing the ratio: dump slag/sand, you can get a material with different indicators of strength and density.

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