

INVESTIGATION OF DURABILITY OF GEOPOLYMER MATERIALS OBTAINED USING THERMALLY MODIFIED CLAY ROCKS

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Abstract

World cement industry currently accounts for about 8% of the global carbon dioxide emissions from clinker production by firing the carbonate component of the raw mix. Geopolymer materials can be an alternative to ordinary Portland cement, as carbon dioxide emissions are reduced by about 80%. In addition, given that geopolymer concretes are generally stronger and more durable, they offer a longer service life, which reduces the need for raw materials in the future. Metakaolin, a product of heat treatment of kaolin clays at temperatures of 750 – 850°C, is usually used to obtain geopolymer materials, but limited world reserves of kaolin clays prevent their widespread use. Paper describes the production of geopolymer materials synthesized on the basis of thermally modified clay rocks and their study for durability. Studies have shown that geopolymer materials have good durability and higher resistance to aggressive solutions compared to ordinary Portland cement.

1. Introduction

The global cement industry currently accounts for about 8% of the world's carbon dioxide emissions from clinker production by firing the carbonate component of the raw mix. In addition, the cement industry is associated with high fuel and energy costs, as it requires high-temperature firing in the range of 1400 – 1450°C, which has a particularly negative impact on the environment against the background of global warming. Alkaline activation binders are one of the most promising technological platforms for the development of energy and resource-saving production of building materials, products and structures.

V. Glukhovskiy [1] was the first to discover the possibility of making binders from low-base calcium or calcium-free aluminosilicates (clays) and solutions of alkali metals. He named these binders “soil cements” and “soil silicates” to reflect their similarity to natural minerals. Fundamental research in this direction was carried out by V. Glukhovskiy and his collaborators

[2], as a result of which a new class of alkaline or AAC (Alkali-Activated Cements) appeared. Analysis and generalization of numerous works by various authors and his own research on alkaline activation binders allowed the French scientist J. Davidowitz to develop the concept of geopolymer binders [3, 4] – inorganic materials of polymer structure based on thermally treated aluminosilicate materials – kaolins and feldspar rocks, as well as ash, slags and other industrial wastes that exhibit binding properties upon alkaline activation. It is J. Davidowitz who owns the saying that: “Geopolymers are ceramic-like inorganic polymers”. 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 condition of high alkali concentration. Such interaction takes place with clay minerals, aluminosilicate glasses of natural and artificial origin, in which calcium is absent, as well as with calcium-based cementitious systems in ambient conditions with the formation of water-resistant alkaline or alkaline–alkaline earth aluminosilicate hydrates – analogues of natural zeolites and micas.

Geopolymer is a material obtained by alkaline activation of aluminosilicates at ambient or slightly elevated temperature, having an amorphous or semi-crystalline polymer structure with Si^{4+} and Al^{3+} cations, tetrahedrally coordinated and linked by oxygen bridges [7]. When hydrated, geopolymers give a product that is predominantly calcium silicate hydrate. 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. When heated, the dehydration of kaolinite occurs according to the scheme: $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$. Heat treatment increases the amount of the amorphous phase, which increases the reactivity of aluminosilicates. Alkaline activation of metakaolin makes it possible to obtain a geopolymer binder of high strength and network structure. In the presence of $\text{Ca}(\text{OH})_2$, the reaction proceeds according to a different scheme: the form of the gel and the form of the network change [8]. According to the research of A. Palomo, et al. [8, 9], there are two models of alkaline activation. The first applies to slag-alkaline binders, when blast-furnace slag (Si+Ca) is activated by a solution of alkalis of medium concentration. In this case, the main reaction products received are CHSs (Calcium HydroSilicates). According to the second model, a concentrated alkaline solution activates compounds of aluminosilicates such as metakaolin, the main oxides of which are Al_2O_3 and SiO_2 . In this case, a material with higher mechanical strength and polymer structure is obtained.

A. Palomo, 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. Under the leadership of V. Kalashnikov [12] a geopolymer binder was developed with a content of up to 40% clay and other dispersed rocks, the activation of which was carried out with small doses of alkali. R. Rakhimova, et al. [13, 14] carried out research on the structure formation of slag-alkaline cements, when blast-furnace slag was used in the form of the main component with the addition of various rocks and man-made materials: zeolites, burnt clays, ceramic brick breakage, etc. N. Eroshkina, et al. [15] developed a number of compositions of geopolymer binders based on thermally treated magmatic rocks (granite, dacite, basalt, etc.).

As is known, in ordinary concretes there is a problem of the interaction of reactive (amorphous) SiO_2 contained in the aggregate to cement alkalis, which can cause damage to the concrete structure and its complete destruction. The results of the study [16] showed that active

alumina (metakaolin and fly ash) in alkali-activated cements had a beneficial effect, making it possible to effectively control the formation of the structure in the interfacial transition zone “cement paste, alkali-sensitive aggregate” and reduce the expansion to an acceptable level or completely avoid it. Despite the fact that the processes of structure formation of geopolymer and other binders have not been studied well enough, these binders are considered as a promising resource-saving alternative to Portland cement. Studies have shown that a significant advantage of geopolymers is their high strength, density, water-, heat- and corrosion-resistances [15, 17, 18]. However, today, the advantage of using these materials is only the possibility of using a huge amount of accumulated industrial waste all over the world.

In the TSU's Caucasian Institute of Mineral Resources, has been conducting research for a number of years to study the possibility of obtaining geopolymer binders using local raw materials. Technologies have been developed for the production of geopolymer materials using thermally modified clay rocks of Georgia and geopolymer materials of different compositions have been synthesized [19 – 21]. The widespread Introduction of geopolymers in construction requires, along with other properties, to study their durability, as well as their behavior in aggressive environments. This paper describes the production of geopolymer materials synthesized on the basis of thermally modified clay rocks and their study for durability.

2. Experimental part

2.1. Materials

The clay rocks of Georgia were used for research: clay shales from Kvareli, argillite from Teleti, clay from Gardabani, as well as granulated blast furnace slag of the Rustavi Metallurgical Plant. An alkaline activator – NaOH, Na₂CO₃, and Na₂SiO₃ or their mixture was used as a mixing liquid.

2.2. Methods

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 -Al₂O₃. The X-ray phase analysis was carried out using a Dron-4.0 diffractometer (Burevestnik, Russia) with a Cu-anode and a Ni-filter, U = 35 kV, I = 20 mA, intensity 2°/min, λ = 1.54178 Å.

2.3. Geopolymers preparation

Temperature modification of clay rocks was carried out by heating the material in a muffle furnace to a temperature of 700°C with holding at a maximum temperature of 1 h. Geopolymer materials were prepared as follows: granulated blast-furnace slag and modified shale, argillite or clay in different ratios were ground together in a laboratory ball mill to a specific surface area of 8000 – 10000 g/cm². Dry substances were added to the resulting powder in a certain amount: NaOH or Na₂CO₃, or Na₂SiO₃, or their mixture, which were mixed well for 5 min. Water was added to the dry mixture to obtain a normal consistency dough. Samples were molded with a size of 2×2×2 cm. The molds, together with the samples, were wrapped in a plastic film to prevent the binder from drying out and were immediately placed in a heat treatment chamber. Heat treatment of geopolymer materials was carried out at 80°C for 24 h. The samples were randomly cooled in the chamber until they reached room temperature.

To determine the durability of geopolymers, the samples hardened after thermal heating, were stored in air for 30, 60, 180 and 360 days at temperature of 20°C and relative humidity of 60%. In order to test for corrosion resistance, geopolymer materials were immersed in aggressive solutions: H₂SO₄ (concentration 2 and 5%), HCl (2 and 5%) and Na₂SO₄ (5%).

3. Results and discussion

Table 1 shows the chemical compositions of clay rocks. Clay minerals (14.66 – 14.96, 7.14, 4.25, 3.66, 2.86, 2.327 Å) are noted on the XRD (X-Ray Diffraction) patterns (**Figure 1**); quartz (3.34 Å); feldspar (3.87 Å), calcium carbonate (3.03 Å).

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

Clay rock	LOI	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Mn ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
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
Argillite	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

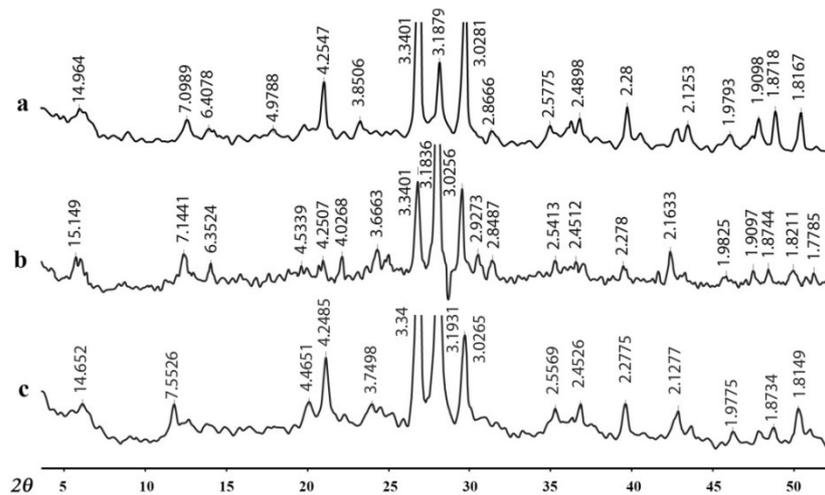


Figure 1. XRD patterns of clay rocks: (a) shale, (b) argillite and (c) clay.

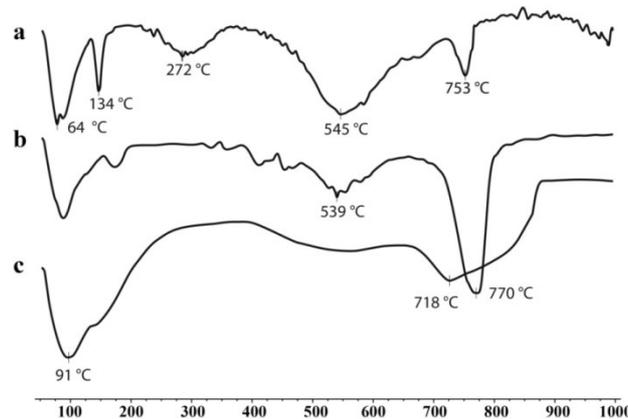


Figure 2. DTA curves of clay rocks: (a) shale, (b) argillite and (c) clay.

According to DTA (Differential Thermal Analysis) data (**Figure 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). On this basis, the temperature of 700°C was chosen for the thermal treatment of clay rocks.

The results of our research [20, 21] showed the possibility of obtaining high-strength geopolymer binders from 80 to 100 MPa based on thermally modified local clay rocks and granular blast-furnace slag using an alkaline activator of different compositions. **Figure 3** shows micrographs obtained using SEM (Scanning Electron Microscopy) measurements using reflected BEC (Backscattered Electron Composition) and SE (Secondary Electron) images for a GPM (GeoPolymer Material) synthesized from thermally modified argillite, granular slag and an alkaline activator NaOH+Na₂SiO₃, which had the best strength indicators [20, 21]. As can be seen in the micrographs, heat treatment contributes to the compaction of the material, which has a positive effect on its mechanical strength.

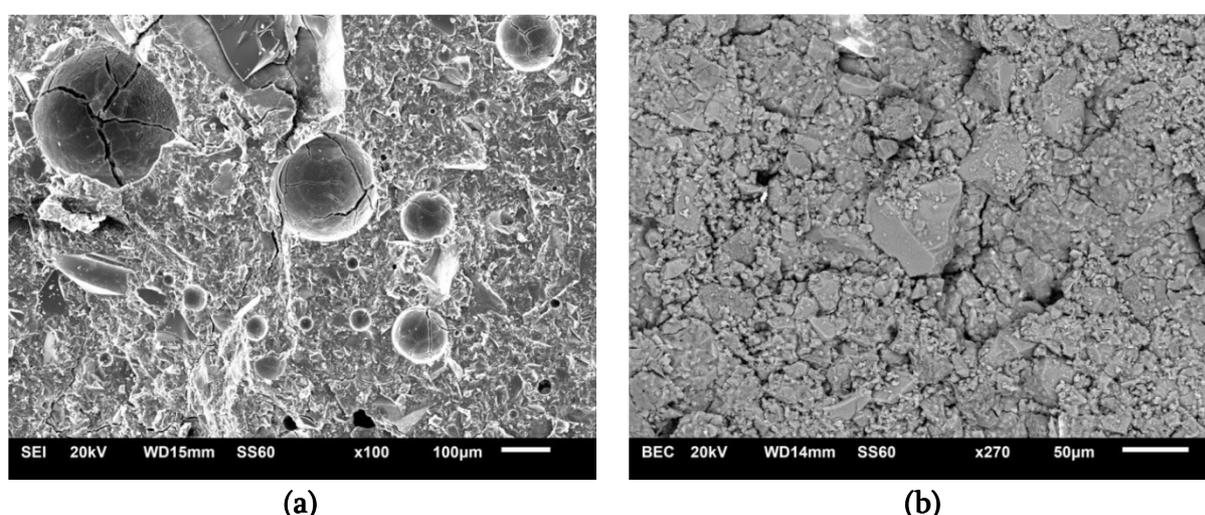


Figure 3. Micrographs of GPM: (a) after 28 days of curing under normal conditions (SE, ×100) and (b) after 2 days of heat treatment (BEC, ×270).

The durability of the geopolymer was determined using the composition: slag (80%) + argillite (20%). The composition of the alkaline activator is NaOH+Na₂SiO₃. The results of tests for strength during storage in air are given in **Table 2**. As the results show, the dynamics of changes in strength over time reveal stable indicators.

Table 2. Dynamics of changes in GPM compressive strength over time.

After days	Original	30	90	180	360
Strength, MPa	92.5	95.1	89.7	93.6	91.9

The assessment of the corrosion resistance of geopolymer materials was carried out according to the change in the mass and strength of the samples after 180 days their immersion in aggressive solutions, which were 2 and 5% solutions of H₂SO₄ and HCl, as well as 5% solution of Na₂SO₄. For the purpose of comparison, OPC (Ordinary Portland Cement) was tested, sealed with ordinary water, which was immersed in the same aggressive solutions.

As shown by the test results (**Table 3**), GPMs have higher acid resistance and sulfate resistance compared to OPC, which is in good agreement with other studies [22 – 24].

According to the authors of [25], the high corrosion resistance of geopolymer materials is explained by the absence of $\text{Ca}(\text{OH})_2$ in their composition, a compound that is the main cause of the destruction of Portland cement concrete.

Table 3. Corrosion resistance of GPM and OPC: weight and strength losses of samples after 180 days immersion in aggressive solutions.

Material	Strength before testing, MPa	Weight loss, %					Strength loss, %				
		H_2SO_4		HCl		Na_2SO_4	H_2SO_4		HCl		Na_2SO_4
		2%	5%	2%	5%	5%	2%	5%	2%	5%	5%
GPM	92.5	0.25	1.32	0.15	3.91	0.63	7	11	10	15	1.9
OPC	73.0	18.11	*	27.7	*	32.8	62	*	70	*	80

* Samples collapsed.

The XRD patterns of the GPM show a certain process. The main phases of the material before its immersion in an aggressive solution (**Figure 4a**) are: X-ray amorphous phase and diffraction lines of quartz (3.33 Å), feldspar (3.19 Å), calcite (3.03 Å) and slag (2.86 Å).

After 180 days immersing of the material in a 5% H_2SO_4 solution (**Figure 4b**), the phase composition remains the same, but the amount of the X-ray amorphous phase decreases, as does the intensity of the diffraction lines of calcite (3.03 Å). The same picture is observed after immersion of the material in 5% HCl solution: a decrease in the amount of the X-ray amorphous phase and calcite (**Figure 4c**).

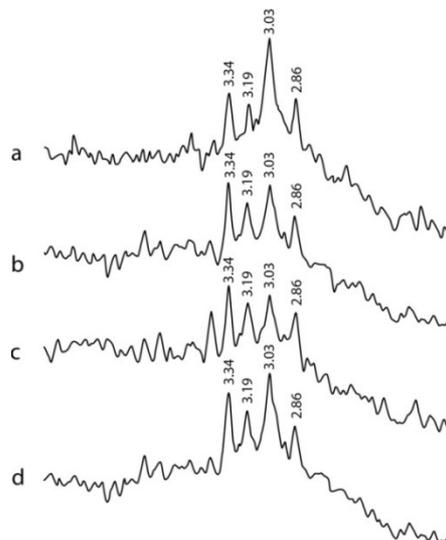


Figure 4. XRD patterns of GPM: (a) before immersion in an aggressive solution and after 180 days of immersion in 5% (b) H_2SO_4 , (c) HCl and (d) Na_2SO_4 solutions.

As the authors of [26] believe, the main reason for the loss of concrete strength in an acid solution is the degradation of the geopolymer matrix, which is reflected in a decrease in the intensity of the X-ray amorphous phase in XRD patterns (**Figures 4b** and **4c**). Another process is observed when the material is immersed in a 5% Na_2SO_4 solution (**Figure 4d**). Here, the phase composition and phase ratios remain almost on par with the initial material.

As our studies have shown, GPOs obtained from local raw materials have good durability and high resistance to aggressive solutions, which is in good agreement with the data of other researchers whom we have cited.

Geopolymers are an environmentally friendly materials, and the transition from conventional Portland cements (calcium silicate cements) to geopolymer cements (aluminosilicate cements) in the construction industry holds great promise for the environment around the world. Given the conservative nature of the global cement industry, the need for industry standards and the general dependence on ambient temperature curing, this transition will take time [27, 28].

4. Conclusions

1. GPMs synthesized on the basis of thermally modified clay rocks have good durability: the dynamics of changes in strength over time show stable indicators.
2. Corrosion resistance of GPM depends on the composition of the aggressive solution: (a) the higher the concentration of the aggressive solution, the greater the loss of mass and strength; and (b) they are less stable in HCl solutions than in H₂SO₄, and rather stable in Na₂SO₄ solution.
3. The indicators of corrosion resistance of GPM (change in mass and strength) after immersion in various aggressive solutions correspond to changes in their phase compositions.
4. Corrosion resistance of GPM is always higher than OPC under the same conditions of aggression.

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