Annals of Agrarian Science

Journal homepage: http://journals.org.ge/index.php

Study Of Corrosion Resistance of Geopolymers Obtained On The Basis Of Local Raw Materials

E. Shapakidze*, M. Nadirashvili*, V. Maisuradze*, I. Gejadze*, M. Avaliani, T. Petriashvili***

*Ivane Javakhishvili Tbilisi State University, A. Tvalchrelidze Caucasian Institute of Mineral Resources, 0186, Mindeli str.11, Tbilisi, Georgia/elena.shapakidze@tsu.ge

**Ivane Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry, 0186, Mindeli str.11, Tbilisi, Georgia

Received 21 December 2021, Accepted: 03 August 2022`

ABSTRACT

During the production of ordinary Portland cement (OPC), as a result of the decarbonization of limestone, a huge amount of greenhouse gases, mainly CO_2, are emitted into the atmosphere, which makes up about 8% of all world emissions. Consequently, any reduction in clinker use will have a serious impact on global warming. To achieve this goal, new technologies are being developed for producing clinker-free binders, one of which is geopolymers, which are considered an alternative to Portland cement.

For the widespread introduction of geopolymers into construction, it is necessary, along with other properties, to study their durability, as well as their behavior in aggressive environments, i.e., corrosion resistance.

The article is devoted to the study of the corrosion resistance of geopolymer materials obtained from local raw materials.

It was found that the indicators of corrosion resistance of geopolymer materials (changes in mass and strength) correspond to changes in their phase compositions after immersion in various aggressive solutions. In all cases, geopolymer materials showed higher resistance to aggressive solutions compared to OPC.

Key words: Geopolymers; OPC, aggressive solutions; corrosion resistance; thermally modifiedclayey rocks.

*Corresponding author: Elena Shapakidze, E.mail: elena.shapakidze@tsu.ge

INTRODUCTION

Population growth worldwide increases the demand for building materials, especially for Portland cement, which remains an energy-intensive and polluting production [1, 2]. Global production of Portland cement is 4.6 billion tons per year. During the production of 1 ton of cement, 0.78 tons of CO_2 are emitted into the atmosphere by flue gases [3]. This makes cement companies one of the main producers of greenhouse gases, which account for 8% of the world's CO_2. In order to cope with the environmental crisis associated with the production of Portland cement, the trend to search for new environmentally friendly building materials has significantly expanded over the past few decades, either by partially replacing cement with materials with pozzolan properties [4, 5], or by completely replacing cement, for example, with geopolymers [6, 7].

Geopolymers are considered environmentally friendly materials due to lower CO_2 emissions compared to analogues from Portland cement.

Using modern research methods, it has been proven that geopolymer concrete was an ancient form of concrete, which was rediscovered in the second half of the 20th century by Joseph Davidovich. He developed the concept of geopolymerization and gave a new insight into this class of inorganic polymers. Davidovich developed the concept of geopolymer (Si/Al inorganic polymer) to better explain these chemical processes and the resulting material properties.

But even earlier, in the late 50s of the twentieth century, V. D. Glukhovsky [8] was the first to discover the possibility of manufacturing binders from low-base calcium or calcium-free aluminosilicates (clays) and solutions of alkali metals. He called these binders “soil cements” and “soil silicates” to reflect their similarity to natural minerals.

Fundamental research in this direction was carried out by V. D. Glukhovsky and his collaborators [9], as a result of which a new class of alkaline or alkali-activated cements (AAC) appeared. Many large infrastructure projects have been built in Ukraine using “alkaline cements” [10, 11].

A geopolymer is a material obtained by alkaline activation of aluminosilicates at ambient temperature or slightly elevated temperature, having an amorphous or semi-crystalline polymer structure with Si^{4+} and Al^{3+} cations, tetrahedrally coordinated and linked oxygen bridges [1, 2]. During hydration, geopolymers give a product that is predominantly calcium silicate hydrate.

Geopolymers have a number of properties compared to Portland cement: high compressive and flexural strength, low shrinkage, low permeability; high resistance to fire and aggressive environments. Due to these properties, geopolymers can be used in many areas: ceramics [12], concrete [13], insulation [14], stabilization and sorption of hazardous waste [15], etc. They depend on many factors, including nature and chemical mineralogical composition of raw materials.

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 resistance, heat and heat resistance, and corrosion resistance [16-18]. 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.

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 resistance, heat resistance and corrosion resistance [16-18]. 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.

For the widespread introduction of geopolymers in construction, it is necessary, along with other properties, to study their durability, as well as their behavior in aggressive environments, i.e., corrosion resistance.

Sulfate and chloride corrosion of building materials is one of the most significant types of corrosion. It manifests itself when building structures are exposed to saline sea and ground waters, atmospheric air with an increased content of sulfur compounds, as well as acid rain [18].

Geopolymer concrete based on low-calcium fly ash has, according to [19], high sulfate resistance. Samples exposed to sodium sulfate solution for one year showed no visible signs of surface deterioration, cracking, or flaking. The compressive strength values remained the same as before the samples were immersed in an aggressive environment.

According to [20, 21], the leading cause of the destruction of reinforced concrete structures is the destruction under the action of carbonation and chloride ions that cause corrosion of reinforcement. They do not directly affect concrete and contribute to the corrosion of reinforcement in concrete. Atmospheric carbon dioxide reacts with calcium hydroxide, causing a decrease in pH in the pore space. As a result, the protective properties of concrete in relation to reinforcing steel are reduced. Chloride ions can penetrate into concrete through aggregate, mixing water or accelerating additives. However, in practice this rarely happens due to strict restrictions on the content of chlorides in concrete. As a rule, chlorides penetrate concrete from the outside, or from seawater, as well as due to the use of de-icing salts. Carbon dioxide and chlorine compounds, as well as other aggressive substances can cause the destruction of concrete only in the presence of water.

The mechanism of chloride penetration and diffusion of CO2 from the environment together with the movement of water in concrete plays an important role in the destruction of concrete. These phenomena are the key factors that determine the durability of concrete based on Portland cement and geopolymer concrete.

As many researchers note, geopolymers have less acid resistance than sulfate resistance: the maximum decrease in the characteristics of geopolymer materials after 1 year of holding samples in a 2% solution of sulfuric acid did not exceed 3%, which was quite insignificant compared to the complete destruction of control samples based on Portland cement [19]. The degree of damage associated with acid exposure is directly proportional to the concentration of acid in the immersion solution.

For a number of years, we have carried out research on the production of geopolymer materials using local raw materials. Technologies have been developed for obtaining geopolymer materials using thermally modified clay rocks of Georgia, on the basis of which geopolymer materials of various compositions have been synthesized [22, 23, 24].

This article presents the results of studies of the corrosion resistance of these materials.

EXPERIMENTAL PART

2.1. Materials

For the study, a geopolymer materials was used, made on the basis of clay rocks of Georgia (argillite and low-melting clay) modified at 700 °C and granulated blast-furnace slag of the Rustavi Metallurgical Plant.

An alkaline activator NaOH, Na_2CO_3, and Na_2SiO_3 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-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.

2.3. Geopolymers preparation

Temperature modification of argillite and clay was carried out by heating the material in a muffle furnace to a temperature of 700 ° C with exposure at a maximum temperature of 1 hour.

Geopolymer materials were prepared as follows: granulated blast-furnace slag and modified argillite or clay in a ratio of 80:20, were ground together in a laboratory ball mill to a specific surface area of 8000-10000 g/cm^2. Dry substances were added to the resulting powder in a certain amount: NaOH or Na_2CO_3, or Na_2SiO_3, or their mixture, which were mixed well for 5 minutes. Water was added to the dry mixture to obtain a dough of normal consistency. Samples were molded with a size of 2 x 2 x 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 hours. The samples were randomly cooled in the chamber until they reached room temperature.

In order to test for corrosion resistance, geopolymer materials were immersed in aggressive solutions: H_2SO4 (concentration 2% and 5%), HCl (concentration 2% and 5%) and Na_2SO_4 (concentration 5%).

RESULTS AND DISCUSSION

Table 1 shows the chemical compositions of clay rocks: argillite from the Teleti deposit (No.1) and clay from the Gardabani deposit (No.2).

Table 1. *The chemical composition of clay rocks, mass. %*

No.	LOI	SiO_2	Al_2O_3	Fe_2O_3	Mn_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
1	7.01	47.19	15.90	13.36	0.10	6.30	4.10	1.39	2.86	1.30
2	10.60	52.84	15.07	6.47	-	7.06	2.49	1.36	1.19	2.17

In Fig. 1 shows X-ray patterns of the studied clay rocks where the presence of clay minerals is recorded (14.66 - 14.96, 7.14, 4.25, 3.66, 2.86, 2.327 Å); quartz (3.34 Å); feldspar (3.87 Å), calcite (3.03 Å).

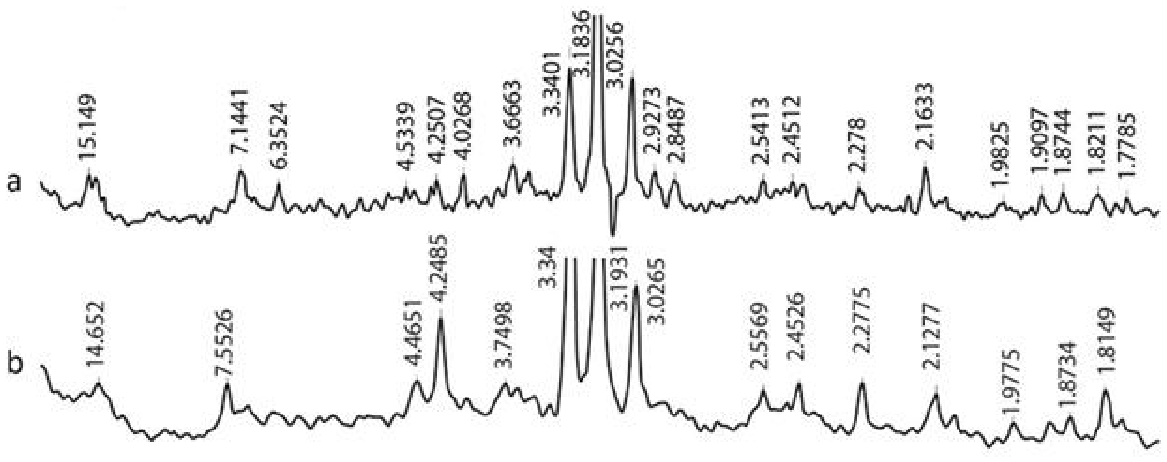

Fig. 1. X-ray patterns of clay rocks: a - argillite, b - clay

According to the data of differential thermal analysis (Fig. 2), the endo-effect at 100–150°C is present on all DTG curves, which corresponds to the removal of physically bound water. In the temperature range of 650–850°C, an endo-effect is observed, which is obviously connected with the destruction of the crystal lattice of clay minerals and their transition to the active amorphous form (metakaolin). On this basis, the temperature of 700°C was chosen for the thermal treatment of clayey rocks.

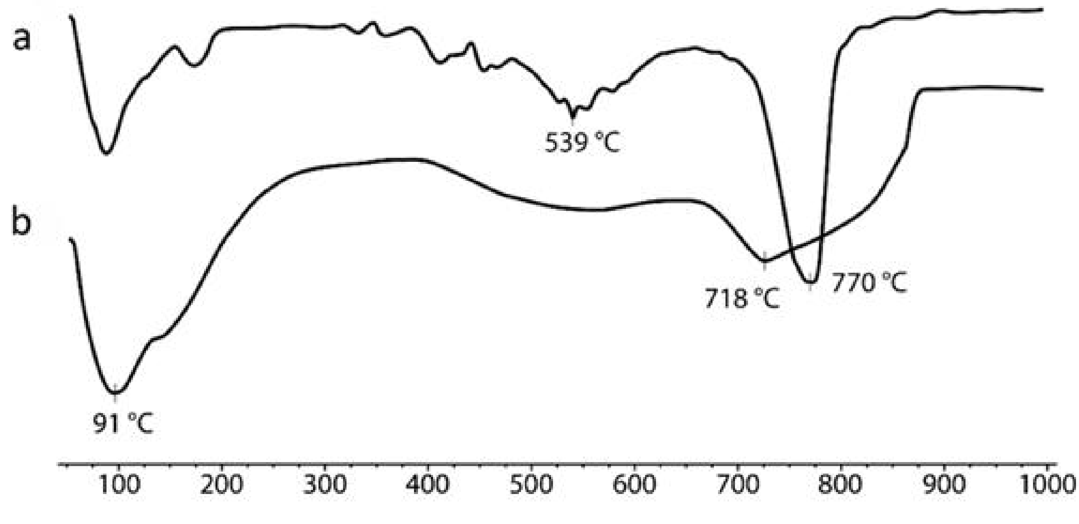

Fig. 2. DTG curves of clayey rocks: a- argillite, b - clay

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 H_2SO_4 and HCl, as well as a 5% solution of Na_2SO_4.

For the purpose of comparison, Ordinary Portland Cement (OPC) was tested, sealed with ordinary water, which was immersed in the same aggressive solutions.

As shown by the test results (Table 2), geopolymer materials have a higher acid resistance and sulfate resistance compared to OPC, which is in good agreement with the data of other studies [25, 26]. According to the authors of [27], the high corrosion resistance of geopolymer materials is explained by the absence of $Ca(OH)_2$ in their composition, a compound that is the main cause of the destruction of Portland cement concrete.

Composition No.**27 showed lower results in corrosion resistance, which is obviously due to the fact that this composition was not subjected to heat treatment. It is known that the heat treatment of geopolymers accelerates the processes of polymerization and pozzolanization [28, 29], which increases their resistance to aggressive solutions.

Compositions No.6 and No. 7 were also characterized by lower mechanical strength and corrosion resistance, since they do not include a clay component - a source of metakaolin, which provides the geopolymer structure with a high degree of polymerization.

Table 2. Compositions of geopolymer materials and the results of their corrosion resistance

No.	Composition of the geopolymer, (%)		Alkaline activator composition, (%)	Weight loss of samples (%) after 180 days immersion in solution					Strength before testing, MPa	Loss of strength of samples (%) after 180 days immersion in solution				
				H_2SO_4		HCl		Na_2SO_4		H_2SO_4		HCl		Na_2SO_4
				2%	5%	2%	5%	5%		2%	5%	2%	5%	5%
*11	Slag 80	Clay 20	NaOH (4) + Na_2SiO_3 (10)	1.49	2.17	2.67	4.77	0.62	97.5	6	8	9	11	1.8
*27	Slag (80)	Argillite (20)	NaOH (4) + Na_2SiO_3 (10)	0.25	1.32	0.15	3.91	0.63	92.5	7	11	10	15	1.9
**27	Slag (80)	Argillite (20)	NaOH (4) + Na_2SiO_3 (10)	7.34	9.50	4.53	12.9	0.64	65.0	12	25	17	29	2.6
*15	Slag (80)	Argillite (20)	Na_2CO_3 (15)	1.15	2.49	1.72	5.5	0.22	88.0	7	12	11	17	1.5
*25	Slag (80)	Argillite (20)	Na_2CO_3 (7)	1.38	2.92	0.75	5.88	0.87	82.0	8	11	10	17	2.1
*6	Slag (100)	-	Na_2SiO_3 (10)	4.53	6.97	5.34	9.94	2.29	77.0	15	26	24	37	3.3
*7	Slag (100)	-	NaOH (4) + Na_2SiO_3 (10)	5.81	9.18	3.22	9.06	2.53	75.0	19	23	22	31	4.2
Ordinary Portland Cement (OPC)				18.11	***	27.7	***	32.8	73.0	62	***	70	***	80

* Curing mode: heat treatment at 80 ° C for 24 hours.

** Curing mode: in air at 20 ° C for 28 days.

*** Samples collapsed.

According to the authors [27, 30], the corrosion resistance of geopolymer materials is also due to the fact that there are no high-base calcium hydroaluminates in their hardening products that cause sulfate corrosion, and there is also no free lime, leaching of which occurs in soft waters. Therefore, geopolymer concretes are superior in corrosion resistance even to sulphate-resistant concretes based on Portland cement.

According to [26], if metakaolin is mixed with a certain amount of NaOH solution or NaOH + Na_2SiO_3 solution, and then cured at temperatures below 100°C, it is possible to obtain a solid substance having a lattice structure of aluminosilicate resembling a zeolite material having high mechanical strength. This is what happens when geopolymers are hardened according to the curing mode: heat treatment at 80 °C for 24 hours (Table 2 - compositions №*11, *27, *15, *25).

For X-ray phase analysis composition No.*27 was chosen, which was synthesized from 80% slag and 20% argillite (Table 2) and activated with a solution of NaOH + Na_2SiO_3.

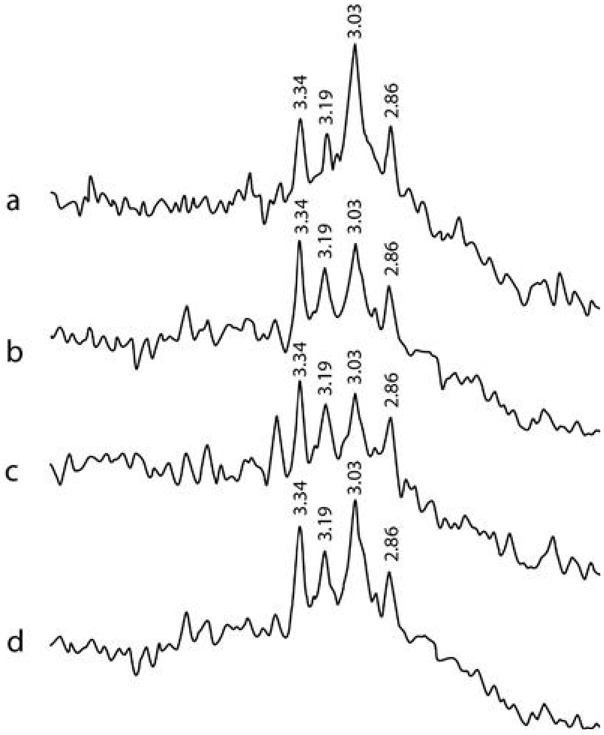

Fig. 3. *X-ray patterns of sample No. ∗27: a - before immersion in an aggressive solution; b - after 180 days of immersion in 5% H2SO4 solution; c - after 180 days of immersion in 5% HCl solution; d- after 180 days of immersion in 5% Na2SO4 solution*

The X-ray diffraction patterns of the geopolymer material show a certain process. The main phases of the material before its immersion in an aggressive solution (Fig. 3a) 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 (Fig. 3b), 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 a 5% HCl solution: a decrease in the amount of the X-ray amorphous phase and calcite (Fig. 3c).

As the authors of [31] 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 X-ray patterns 3b and 3c.

Another process is observed when the material is immersed in a 5% Na_2SO_4 solution (Fig. 3d). Here, the phase composition and phase ratios remain almost on par with the initial material.

So, as our studies have shown, geopolymers obtained from local raw materials have a high resistance to aggressive solutions, which is in good agreement with the data of other researchers whom we have cited.

Geopolymers are environmentally friendly materials, and the technology for their production belongs to green technologies.

If geopolymer materials displace, or at least reduce the production of OPC, this will allow to obtain resource-saving and environmental effects by replacing carbonate raw materials, which during firing loses almost half of its mass when emitting carbon dioxide polluting the environment.

CONCLUSIONS

Corrosion resistance of geopolymer materials obtained on the basis of local raw materials depends on the composition of the aggressive solution:

1. The higher the concentration of the aggressive solution, the greater the loss of weight and strength.
2. Geopolymer materials are less stable in HCl solutions than in H_2SO_4, and rather stable in Na_2SO_4 solution.

The indicators of corrosion resistance of geopolymer materials (change in mass and strength) after immersion in various aggressive solutions correspond to changes in their phase compositions.

The corrosion resistance of geopolymer materials is always higher than the OPC under equal conditions of aggression.

ACKNOWLEDGMENT

The authors are grateful to the Shota Rustaveli National Science Foundation of Georgia, with the financial support of which this work was carried out [grant number FR-18-783].

REFERENCES

[1] J. Davidovits. Carbon-Dioxide Greenhouse-Warming: What Future for Portland Cement. Proceedings, Emerging Technologies Symposium on Cement and Concretes in the Global Environment / Portland Cement Association, Chicago, Illinois, March 1993. 21 p.

[2] P. Duxon et al. 2007, Geopolymer technology: the current state of the art. Journal of Materials Science, Vol. 42, pp. 2917-2933.

[3] European Commission. Integrated Pollution Prevention and Control. Reference Document on Best Available Techniques (BAT) in the Cement and Magnesium Oxide Manufacturing industries. May 2010. http://eippecb.jrc.ec.europa.eu;

[4] Y. Jeong, S.-H. Kang, M.O. Kim, J. Moon. Acceleration of cement hydration from supplementary cementitious materials: performance comparison between silica fume and hydrophobic silica. Cement Concrete Compos., 112 (2020).

[5] E. Shapakidze, I. Gejadze, M. Nadirashvili, V. Maisuradze, T. Petriashvili, A. Skhvitaridze. Using Clay Rocks of Georgia to Obtain High-Active Pozzolanic Additives to Portland Cement. International Journal of Applied Engineering Research. V. 14, No. 18 (2019) pp. 3689-3695.

[6] B. Singh, G. Ishwarya, M. Gupta, S. Bhattacharyya. Geopolymer concrete: A review of some recent developments. Constr. Build. Mater. 2015, 85, 78–90.

[7] A. Ayoub et al. Effect of acidic volcanic perlite rock on physio-mechanical properties and microstructure of natural pozzolan based geopolymers. Published by Elsevier Ltd. 2021. https://doi.org/10.1016/j.cscm.2021.e00712

[8] V. D. Glukhovsky. Soil silicates, (in Russian), 1959, Publish. Gosstroyizdat, Kiev.

[9] V. D. Glukhovsky, P. V. Krivenko, P. V. Ryumi-

na, V. L. Gerasimchuk. Production of concrete and structures based on slag-alkali binders. Publish. Budivelnik, Kiev, 1988. 144p.

[10] P. Krivenko. Alkaline Cements., in Proceedings of the First International Conference on Alkaline Cements and Concrete, VIPOL Stock Company, Kiev, Ukraine, 1994, Vol. 1, pp 11-129.

[11] A. Palomo, P. Krivenko, I. Garcia-Lodeiro, E. Kavalerova, O. Maltseva, A. Fernández-Jiménez. A review on alkaline activation: new analytical perspectives. Materiales de Construcción, 2014, Vol 64, p.315,

[12] P.N. Lemougna, K. Wang, Q. Tang, X. Cui. Synthesis and characterization of low temperature (< 800° C) ceramics from red mud geopolymer precursor. Constr. Build. Mater., 131 (2017), p. 564-573.

[13] H.Y. Zhang, V. Kodur, B. Wu, J. Yan, Z.S. Yuan. Effect of temperature on bond characteristics of geopolymer concrete. Constr. Build. Mater., 163 (2018), pp. 277-285.

[14] F. Colangelo et.al. Mechanical and thermal properties of lightweight geopolymer composites. Cement Concrete Compos., 86 (2018), p. 266-272.

[15] M.R. El-Naggar, M. Amin. Impact of alkali cations on properties of metakaolin and metakaolin/slag geopolymers: microstructures in relation to sorption of 134Cs radionuclide. J. Hazard. Mater., 344 (2018), pp. 913-924.

[16] P. T. Fernando, J. Said. Resistance to acid attack, abrasion and leaching behavior of alkali-activated mine waste binders // Materials and Structures, 2011, Vol. 44. p. 487–498.

[17] T. Bakharev. Resistance of geopolymer materials to acid attack. // Cement and Concrete Research, vol. 35, 2005, pp. 658-670.

[18] N. A Eroshkina., M. O. Korovkin. Geopolymer building materials based on industrial waste. Publishing house of the Penza State University of Architecture and Construction (PGUAS). Penza. 2014. 128 p.

[19] J. Davidovits Geopolymer chemistry and applications. 3rd eddition. – France, Saint-Quentin: Institute Geopolymer, 2011. 614 p.

[20] K. S. Siddiqui. Strength and Durability of Low-Calcium Fly Ash-based Geopolymer Concrete. Final Year Honours Dissertation. – Perth: The University of Western Australia, 2007.

[21] F.U.A. Shaikh. Effects of alkali solutions on corrosion durability of geopolymer concrete // Advances in Concrete Construction, Vol. 2, No. 2 (2014). p.109-123.

[22] E. Shapakidze, M. Nadirashvili,, V. Maisuradze, I. Gejadze, T. Petriashvili, M. Avaliani, G. Todradze. Elaboration of Optimal Mode for Heat Treatment of Shales for Obtaining Metakaolin. Eur. Chem. Bull., 2019, 8(1), 31-33. DOI: 10.17628/ecb.2019.8.31-33.

[23] E. Shapakidze, M. Avaliani, M. Nadirashvili, V. Maisuradze, I. Gejadze, T. Petriashvili. Obtaining of Geopolymer Binders Based on Thermally Modified Clay Rocks of Georgia (in Georgian). Nano Studies. 2020, 20(1), 43-52. DOI: 10.13140/RG.2.2.18756.17281.

[24] E. Shapakidze, M. Avaliani, M. Nadirashvili, V. Maisuradze, I. Gejadze, T. Petriashvili. Geopolymers based on local rocks as a future alternative to Portland cement. In Advanced Materials, Polymers, and Composites: New Research on Properties, Techniques, and Applications, Apple Acad. Press, USA, 2020, 3(25). DOI: 10.13140/RG.2.2.28081.12644.

[25] T. Bakharev. Resistance of geopolymer materials to acid attack. Cement and Concrete Research, vol. 35, 2005, pp. 658-670.

[26] A. Palomo, M.T. Blanco-Varela, M.L. Granizo, F. Puertas, T. Vazquez, M.W. Grutzeck. Chemical stability of cementitious materials based on metakaolin. Cement and Concrete Research 29 (1999) 997–1004.

[27] Y. Y. Kim, B. J. Lee, V. Saraswathy, S. J. Kwon. Strength and Durability Performance of Alkali-Activated Rice Husk Ash Geopolymer Mortar. Sci. World. J. 2014. Vol. 2014. 1–11.

[28] Hewlett P., Liska, M. Lea's Chemistry of Cement Concrete (5th edition), Imprint: Butterworth-Heinemann. Elsevier. 2019, 896 p.

[29] T. Bankharev. Durability of geopolymer materials in sodium and magnesium sulfate solutions. Cement and Concrete Research, Vol. 35, No. 6, 2005, pp. 1233–1246.

[30] N. A. Eroshkina, M. O. Korovkin. Methods for assessing and increasing the durability of geopolymer building materials based on industrial waste. Tutorial. Publishing house of the Penza State University of Architecture and Construction (PSUAC), Penza. 2014, 115 p.

[31] T. Lingyu, H. Dongpo, Zh. Jianing, and W. Hongguang. Durability of geopolymers and geopolymer concretes: A review. Rev. Adv. Mater. Sci. 2021; 60:1–14. https://doi.org/10.1515/rams-2021-0002.