BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 70 (74), Numărul 4, 2024
Secţia
CHIMIE şi INGINERIE CHIMICĂ
DOI: 10.5281/zenodo.14581968

MODERN MECHANO-CHEMICAL PROCEDURE FOR OBTAINING A HIGH-STRENGTH GEOPOLYMER COMPOSITE

BY

LUCIAN PĂUNESCU[1,*], ENIKÖ VOLCEANOV[2,3] and BOGDAN VALENTIN PĂUNESCU[4]

[1]Daily Sourcing & Research SRL, Bucharest, Romania
[2]National University of Science and Technology “Politehnica” Bucharest, Faculty of Engineering in Foreign Language, Bucharest, Romania
[3]Metallurgical Research Institute SA Bucharest, Romania
[4]Consitrans SA Bucharest, Romania

Received: October 10, 2024
Accepted for publication: November 20, 2024

Abstract. Replacing the usual alkaline solution with sodium metasilicate nonahydrate as an alkaline activator of alumina-silicate waste for the manufacture of geopolymers represents a recent technical solution for significantly increasing their mechanical resistance. The principle of this method was tested in an own version by the authors’ team of the current work. Coal fly ash, river sand, and silica fume (nano-silica) were solid precursors used in the starting material mixture. Under the conditions of pressing the geopolymer powder (made by the conventional method) at the axial pressure of 400 daN·cm^{-2}, compared to its value of 1000 daN·cm^{-2} used by (Nishikawa *et al*., 2022), the level of resistance to compression and flexure reached values very high, superior compared to that of usual geopolymers.

Keywords: geopolymer composite, alumina-silicate, sodium metasilicate nonahydrate, pressure, mechanical resistance.

*Corresponding author; *e-mail*: lucianpaunescu16@gmail.com

1. Introduction

The climate changes identified at a global level in the last decades, caused by excessively high emissions of greenhouse gases in the earth's atmosphere, have radically modified the humanity's attitude towards the activities responsible for CO_2 emissions, especially in industry and transport. Thus, it was opted, on the one hand, for the reduction or elimination of large industrial activities that consume fossil fuel and, on the other hand, the replacement of their products with new products with a low carbon footprint made by recycling and using the abundant existing waste in landfills from all over the world. By utilizing these wastes, a serious problem of environmental protection caused by them (soils, underground and surface waters, etc.) is simultaneously solved (Ćirović, 2018; Turk *et al*., 2023; Recycling, 2020).

The exceptional set of patents and scientific works made at the end of the 20^{th} century and the beginning of the new millennium, due to the team of the French researcher J. Davidovits, laid the foundations for the production of so-called geopolymers through the chemical activation of alumina-silicate waste (Davidovits, 1989; Davidovits *et al.*,1994; Davidovits, 2013; Davidovits, 2005). Numerous researchers from various countries of the world independently contributed during this period to the development of knowledge in the field of new geopolymeric materials.

Initially, the technique of activating alumina-silicate waste, as an excellent source of cementitious materials with pozzolanic properties largely similar to traditional Portland cement, included alkaline activators in liquid state (NaOH dissolved in deionized water and water glass) capable to initiate and to develop the geopolymerization reaction that turns alumina-silicate materials into geopolymers with outstanding physico-chemical properties (according to the inventor Davidovits). The alkaline activator is the basic component of the geopolymer. It contributes to improving the rheological properties of the new material type. Two roles of the activator are most often recognized: it dissolves the Si-O, Al-O, and Ca-O bonds (to be restored later) and balances the charge of alkali metal cations in the mix. According to (Nodehi *et al*., 2022), solutions with low concentrations lead to increasing the size and volume of the material pores and increasing the water absorption capacity. Also, the lower molarity of the activator solution requires the intensification of the thermal curing process of the geopolymer concrete to improve the reactivity of the mixture components.

Usually, geopolymers are made by the chemical reaction of a natural alumina-silicate precursor (e.g. metakaolin, volcanic ash, etc.) or in the form of an industrial by-product (coal fly ash, metallurgical slag, red mud, etc.) with alkaline solution as an activator. After mixing them until the sludge is formed, the fresh material is poured into a mould and hardened by heating in an oven at 60-80°C for a variable period between 8-24 hours. The time allocated for the

curing process by free storage at ambient temperature varies between 7-28 days or even more (Vakifahmetoglu and Karacusulu, 2020; Paunescu *et al.*, 2022).

Aiming at reducing primary energy consumption for a favourable effect on environmental protection, the cold binding process was applied in order to make fly ash-aggregates using this modern method (Their and Özakça, 2018). Several mixtures of geopolymer concrete containing fly ash cold-bonded aggregates, nano-silica, and steel fibers activated with 12M NaOH solution were designed. Hardening the fresh concrete was performed at room temperature. Geopolymer concrete properties were determined after 28 and 90 days. The optimal proportions of nano-silica and steel fiber volume were experimentally established at 2% and 1%, respectively. The compression resistance reached 28.2 MPa after 28 days and 36.6 MPa after 90 days.

Testing the application of a new procedure for choosing the starting mixture for the preparation of high-strength geopolymer based on Na_2O/SiO_2, SiO_2/Al_2O_3, and liquid/solid ratios using the alkaline activator consisting of NaOH and Na_2SiO_3 solution was performed and analyzed in the paper (Mahmoodi *et al.*, 2021). Fly ash classes C and F, metakaolin, and granulated blast furnace slag (as a substitute for 15-45% of the amount of recycled concrete after building demolition) were incorporated into these mixtures. Improving the mechanical resistance of geopolymer concrete was observed in the case of ratio values of SiO_2/Al_2O_3 of 12.9 and Na_2O/SiO_2 of 0.23 as well as by using fly ash with high calcium content (class C). The recycled concrete waste had a negative influence on the strength of the hardened material.

The utilization of cold bonded-geopolymer aggregate, as an artificial material made by agglomeration of hardened alumina-silicate powder industrial by-products, subjected to the alkaline activation, constituted the originality of the manufacturing method presented and tested in (Huang *et al*., 2023). The used precursor materials were metakaolin, fly ash, and silica fume. The results indicated an optimal composition of the mix containing 36-48 % metakaolin, 33-46% fly ash, and 15-24% silica fume. The features of the geopolymeric product were: bulk density of 1.2 $g \cdot cm^{-3}$, crushing resistance of above 21 MPa, and water uptake under 10%. The adequate amount of silica fume (Si/Al ratio below 1.7) led to the formation of C-A-S-H gels in the geopolymer aggregate, contributing to the increase in the strength and density of the material.

A new curing method of geopolymers, known as “cold reaction sintering” has been recently designed by Nishikawa *et al.* (2022) in order to obtain a high-strength material in a shorter time compared to the usual geopolymers. Unlike the already known alkaline solution, proposed by J. Davidovits in his scientific works and patents, the new method mentioned above uses sodium metasilicate ($Na_2SiO_3 \cdot nH_2O$) as a substitute for the alkaline solution. In this paper, the cured geopolymer was made utilizing the cold reaction sintering, which is a procedure that occurs in two stages. In the first stage, the geopolymer is obtained through conventional hardening method of creating the slurry. Then,

the hardened geopolymer is crushed. In the second stage, the production of extremely dense geopolymer is performed through pressing the crushed powder. During this stage, the hydroxyl ions (OH^-) existing in the geopolymer powder are used instead of water or alkaline aqueous solution. The densification of the material hardened in this way leads to obtaining the ultra-dense geopolymer with a significantly higher mechanical resistance than that produced by the known Davidovits method. The fine powders of materials that composed the starting mixture (cold-bonded coal fly ash, nano-silica, and steel fiber) were cold sintered at 130°C and axial pressure of 100 MPa for 10 min. Sodium metasilicate nonahydrate ($Na_2SiO_3{\cdot}9H_2O$) was the water supplier in the absence of the aqueous alkaline solution and the added water.

The current work adopted the principle of geopolymer composite preparation through the "cold reaction sintering". For this purpose, four experimental versions of material mixtures were chosen, including coal fly ash as the dominant alumina-silicate material, river sand as a fine aggregate, and low amounts of silica fume (also known as nano-silica) that strongly improves the geopolymerization process with the formation of a well refined and compact matrix (Bajpai *et al*., 2020; Khater, 2014). For the chemical activation of alumina-silicate solids, the version of using sodium metasilicate nonahydrate was adopted.

2. Methods and Materials

Geopolymers (Davidovits, 2005) are generated by the interaction of alumina-silicate materials with the adopted alkaline solution (sodium or potassium hydroxide and sodium or potassium silicate). The first step of the geopolymerization reaction (dissolution) is breaking of siloxo (Si-O-Si) and sialate (Al-O-Si) bonds by the hydroxyl groups (OH^-) of the alkaline solution. The second step of the reaction is constituted by coagulation-condensation, in which the dissolved ionic groups react with the alkali metal cations (Na^+ or K^+) and the silica monomers react with other monomers. At the end of the process, three-dimensional polymer networks are formed (Khale and Chaudhary, 2007).

The method adopted in this experiment was the use of mechanically processed solid raw materials (coal fly ash, river sand, silica fume) in the form of very fine powder. Sodium metasilicate nonahydrate ($H_{18}Na_2O_{12}Si$) (Sodium, 2024) was chosen as the liquid material required for the chemical activation of alumina-silicate solids, simultaneously providing the necessary water. By using sodium metasilicate nonahydrate as an activator, the practical conditions were created for the material densification and the geopolymerization reaction to take place without the need to produce a suspension (Nishikawa *et al*., 2022).

The method chosen for the production of the high-strength geopolymer is relatively close to the "cold reaction sintering" procedure mentioned above. As a first process stage, the method of slurry formation by mixing solid materials with sodium metasilicate (liquid) and then hardening it was preserved compared

to the conventional technique. The continuation of the technological process provided for the mechanical crushing of the hardened geopolymer in the first stage and then pressing in an improvised pressing device with the maximum capacity of 400 daN·cm^{-2} at room temperature. The pressing device containing the geopolymer powder into a metal tube provided with a piston was placed between the jaws of a vise and the required pressing force was obtained by extending the vise rod with a metal pipe of 2.5 m, thus ensuring the adequate length of the arm of the clamping force.

Materials used in this experiment were: coal fly ash, river sand, silica fume and sodium metasilicate nonahydrate.

Coal fly ash, as an industrial by-product of the coal burning process in the boilers of thermal power plants in the energy industry, was supplied approximately 8 years ago by Paroseni-Thermal power station (Romania). The waste having the initial size of granules below 200 μm required an additional repeated mechanical processing in a ball mill, its dimensions being reduced under 20 μm. The oxide composition of fly ash contained 49.7% SiO_2, 23.6% Al_2O_3, 5.9% Fe_2O_3, 3.8% CaO, 3.2% MgO, 3.9% K_2O, 1.7% Na_2O, and 1.0% TiO_2.

River sand is one of most important fine aggregates used in concrete making. Its bulk density falls within the limits of 1.4-1.6 g·cm^{-3}. Concretes made with this fine aggregate have a good durability according to Nudinho Abdias *et al*., 2023. River sand contains 97-98% SiO_2, 2-3% Al_2O_3 and its particle size is less than 25 μm (Mudinho Abdias *et al*., 2023).

Silica fume was added in low quantities (under 7 wt. %) in the solid starting mixture due to its ability for improving the geopolymerization reaction in geopolymer composite making process and increasing its mechanical features. It was avoided exceeding the maximum using limit of silica fume, beyond which the mechanical resistance tends to decrease. Silica fume (or nano-silica) as a by-product of ferroalloy industry was commercially purchased at very low grain size (below 1 μm).

The alkaline activator–sodium metasilicate nonahydrate ($Na_2SiO_3·9H_2O$) recommended in (Nashikawa *et al*., 2022) was chosen in this "cold reaction sintering" process, carried out without the addition of water, due to the nine water molecules chemically bound in the material's formula.

The material composition of adopted experimental versions is shown in Table 1.

The weight proportion of coal fly ash was adopted in the range of 44.1-47.7 wt. %), as well as the proportion of river sand within the limits of 18.9-20.5 wt.% (both decreasing), while the silica fume consumption varied with an increasing trend between 1.8-2.0 wt. % as well as $Na_2SiO_3·9H_2O$ whose proportions increased from 30 to 35 wt. %.

Table 1
Composition of experimental versions (wt. %)

Composition	Version 1	Version 2	Version 3	Version 4
Coal fly ash (under 20 μm)	47.7	46.3	45.2	44.1
River sand (under 25 μm)	20.5	19.8	19.4	18.9
Silica fume (under 1 μm)	1.8	1.9	1.9	2.0
$Na_2SiO_3 \cdot 9H_2O$	30.0	32.0	33.5	35.0

Examining the geopolymer composite features was carried out using well-known usual methods. The density was determined by Archimedes' method based on the water-intrusion method (ASTM D792-20). The compression strength was investigated through the method recommended by EN 12390-3: 2001 on cubic specimens, while the flexural resistance was measured on rectangular specimens by applying the three-point bend test (SR EN ISO 14125: 2000). The water uptake was measured through the immersing method of samples under water (ASTM D570). The microstructural aspect of specimens was identified with Biological Microscope model MT5000, 1000 x magnification.

3. Results and Discussion

The four material mixture versions (exposed above in Table 1) allowed to make the geopolymer composite through the "cold reaction sintering", whose images are shown in Fig. 1.

The investigation methods of physio-mechanical features led to experimental results presented in Table 2.

The physio-mechanical characteristics of geopolymeric composite samples shown in Table 2 indicate that the compositional changes of mixtures prepared in the four versions did not unequivocally lead to increasing the mechanical properties of specimens. Although their density followed an increasing trend from 1.83 to 2.11 $g \cdot cm^{-3}$ with the decrease in the weight proportion of coal fly ash, the improvement of the compression strength did not exhibit obvious increases except in the case of version 2 and very little in the case of version 3. The increase in compression strength values was much more evident after the first 7 days of curing (i.e. at the early age of the process) compared to the results obtained after 28 days of storage at ambient temperature. However, a high level of resistance values was found (between 30.15-36.23 MPa after 7 days and between 48.33-51.02 MPa after 28 days) compared to the usual level of compression strength of geopolymers made by usual procedures. This qualitative improvement suggests the effectiveness of the "cold reaction sintering" method experienced in this research. Flexural

strength values show also a higher level than the usual geopolymers. As in the case of compression resistance, flexural strength registered a continuous increase in the four versions after 7 days of curing from 5.10 to 5.88 MPa. Not the same evolution of its values was recorded at the end of the 28 days of hardening by storage. A slight increase in flexural strength was observed between the first two experimental versions (1 and 2) from 6.35 to 6.44 MPa, after which this type of mechanical strength began to slightly decrease to 6.38 MPa.

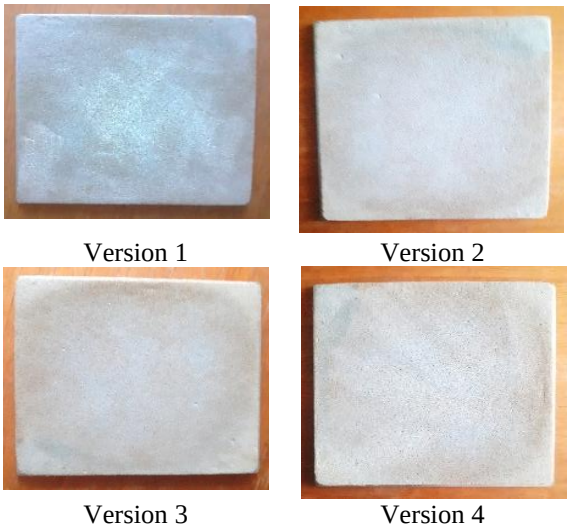

Fig. 1 – Images of the four versions of geopolymer composite prepared through the cold reaction sintering method

Table 2
Geopolymer composite features obtained by applying the new making method

Feature	Version 1	Version 2	Version 3	Version 4
Density ($g \cdot cm^{-3}$)	1.83	1.95	2.06	2.11
Compression strength (MPa) - after 7 days - after 28 days	 30.15 48.33	 35.90 50.16	 36.23 51.02	 36.08 50.87
Flexural strength (MPa) - after 7 days - after 28 days	 5.10 6.35	 5.43 6.44	 5.70 6.40	 5.88 6.38
Water uptake (%)	5.6	5.5	6.0	5.9

The pictures of the microstructural aspect of geopolymer composite in the four experimental versions (according to data in Table 1) are shown in Fig. 2.

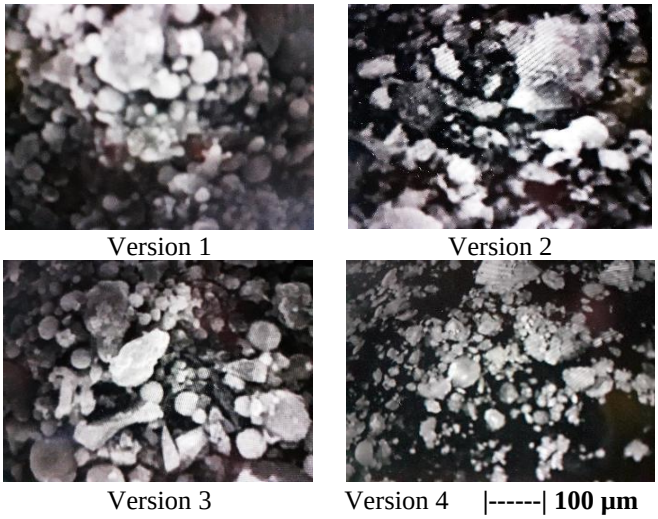

Fig. 2 – Microstructural aspect of geopolymer composite in the four experimental versions.

Specific elements of the fly ash microstructure (the existence of generally spherical particles with sizes between 10-100 nm) are visible especially in the picture representing version 1 (the weight proportion of fly ash being the highest at 47.7%). In the other pictures showing the microscopic image of versions 2-4, the presence of spherical particles is diminished due to reducing the amount of fly ash in the mixture.

Analyzing the results obtained in this experiment, experimental variant 3 offered the best performances, especially in terms of the mechanical resistance of the geopolymer. Thus, these features were: density of 2.06 $g \cdot cm^{-3}$, compression strength after 7 days of 36.23 MPa and after 28 days of 51.02 MPa, flexural strength after 7 days of 5.70 MPa and after 28 days of 6.40 MPa. The water uptake was 6%.

The manufacturing recipe included coal fly ash as alumina-silicate material, river sand as a fine aggregate containing predominantly silica and low amount of alumina as well as silica fume as a by-product of ferroalloy industry. Facilitating the development of the geopolymerization reaction was done with sodium metasilicate nonahydrate.

The peculiarity of the new procedure presented in this paper and adopted by the authors is the use of starting materials in solid state as powders (without the addition of water). By adopting sodium metasilicate nonahydrate, the conditions were created for geopolymerization and densification at the same time, without the need to form the usual suspension in known geopolymerization

processes. In this way, the final products had the characteristics of an extremely dense material with high compressive strength.

4. Conclusions

A new geopolymer curing technique called “cold reaction sintering” constitutes the latest project aiming at significantly increasing the mechanical resistance of the geopolymeric material in a shorter time. The difference compared to the usual method of manufacturing geopolymers consists in developing the process in two distinct stages: the first stage using the conventional hardening procedure through the intermediate production of a slurry, while the second stage was based on grinding thus hardened material and pressing it together with sodium metasilicate nonahydrate at relatively high pressure and low temperature.

The authors' team used coal fly ash (44.1-47.7%), river sand (18.9-20.5%) and silica fume (1.8-2.0%) as solid precursors as well as sodium metasilicate nonahydrate (30-35%) without water added. In the second stage of the geopolymer hardening process, an improvised processing device was used at 400 daN·cm^{-2} and room temperature. The optimal version was chosen experimental version 3 prepared from 45.2% fly ash, 19.4% sand, 1.9% silica fume, and 33.5% $Na_2SiO_3 \cdot 9H_2O$. The characteristics of the geopolymer composite were: density of 2.06 g·cm^{-3}, compression strength after 7 days of 36.23 MPa and after 28 days of 51.02 MPa, flexural strength after 7 days of 5.70 MPa and after 28 days of 6.40 MPa. The water uptake was 6%.

The new making procedure of geopolymers has the advantage of an environmentally friendly and more economical energy consumer procedure.

REFERENCES

Bajpai R., Choudhary K., Srivastava A., Sangwan K.S., *Environmental Impact Assessment of Fly Ash and Silica Fume Based Geopolymer Concrete*, J. Clean. Prod., Elsevier, **254**, https://doi.org/10.1016/j.jclepro.2020.120147 (2020).

Ćirović M.D., *Risk Analysis of the European Union 2030 Greenhouse Gas Emission Target Compliance*, Int. J. Global Warming, **16**, *1*, 64-85, https://doi.org/10.1504/IJGW.2018.10015566 (2018).

Davidovits J., *Geopolymers and Geopolymeric Materials*, J. Therm. Anal., Springer Link, **35**, 429-441 (1989).

Davidovits J., Davidovits M., Davidovits N., *Process for obtaining a geopolymeric alumino-silicate and products thus obtained*, US Patent no. *5342595* (1994).

Davidovits J., *Geopolymers: Inorganic Polymeric New Materials*, J. Therm. Anal. Calorim., **37**, *8*, 1633-1656, https://doi.org/10.1007/bf01912193 (2005).

Davidovits J., *Geopolymer Cement-A Review*, Geopolymer Sci. Technics., Geopolymer Institute Library, Saint-Quentin, France, 2-11 (2013).

Huang H., Zhang H., Lv Y., Chen Y., *Performance and Optimization Design of High-Strength Geopolymer Cold-Bonded Lightweight Aggregate: Effect of Silica Fume*, Case Stud. Constr. Mater., Elsevier, **18**, https://doi.org/10.1016/j.cscm.2023.e02047 (2023).

Khale D., Chaudhary R., *Mechanism of Geopolymerization and Factors Influencing its Development: A Review*, J. Mater. Sci., Springer Link, **42**, 729-746, https://link.springer.com/article/10.1007/s10853-006-0401-4 (2007).

Khater H.M., *Effect of Silica Fume on the Characterization of the Geopolymer Materials*, 2014 World Congress Adv. Civil, Environ. Mater. Res., Busan, South Korea, August 24-28 (2014).

Mahmoodi O., Siad H., Lachemi M., Dadsetan S., Sahmaran M., *Development of Normal and Very High Strength Geopolymer Binders Based on Concrete Waste at Ambient Environment*, J. Clean. Prod., Elsevier, **279**, https://doi.org/10.1016/j.jclepro.2020.123436 (2021).

Mudinho Abdias M.W., Manjia M.B., Pettang N.U.J., Abanda Fonbeyin H., Ngapgue F., Pettang C., *River Sand Characterization for its Use in Concrete: A Review*, Open J. Civil Eng., Scientific Research Publishing, **13**, 353-366, ISSN Online: 2164-3172, https://www.scip.org/journal/ojce (2023).

Nodehi M., Ozbakkaloglu T., Gholampour A., Mohammed T., Shi X., *The Effect of Curing Regimes on Physico-Mechanical Microstructure and Durability Properties of Alkali-Activated Materials: A Review*, in Constr. Build. Mater., Elsevier, **321**, https://doi.org/10.1016/j.conbuildmat.2022.126335 (2022).

Nishikawa K., Hashimoto S., Imai H., Rossignol S., *Cold Reaction Sintering for Preparation of Ultra-Dense Geopolymer Products*, Constr. Build. Mater.**,** Elsevier, **328**, https://doi.org/10.1016/j.conbuildmat.2022.127101 (2022).

Paunescu L., Volceanov E., Ioana A., Paunescu B.V., *High-Strength Geopolymer Building Material*, J. Eng. Stud. Res., Nedeff V. (Ed.), University of Bacău Publishing, **28**, *4*, 107-115 (2022).

Their J.M., Özakça M., *Developing Geopolymer Concrete by Using Cold-Bonded Fly Ash Aggregate, Nano-Silica, and Steel Fiber*, Constr. Build. Mater., Elsevier, **180**, 12-22 (2018).

Turk J., Obrecht T.P., Rebec K.M., Ostruh P., *Circular and low-carbon building materials. Practical guideline*, European Climate Initiative EUKI, 2-38, https://www.euki.de/wp-content/uploads/2024/03/WP3-Circular-low-carbon-materials_ENG_update1.pdf (2023).

Vakifahmetoglu C., Karacasulu L., *Cold Sintering of Ceramics and Glasses: A Review*, Curr. Opin. Solid State Mater. Sci., Elsevier, **24**, *1*, https://doi.org/10.1016/j.cossms.2020.100807 (2020).

** *Recycling of Secondary Raw Material for a Sustainable Optimization of Construction Processes in Civil Engineering: Internal Market, Industry, Entrepreneurship and SMEs, European Commission* (2020).

** *Sodium Metasilicate Nonahydrate*, National Library of Medicine, National Center for Biotechnology Information, (2024), https://pubchen.ncbi.nlm.nih.gov/compound/Sodium-metasilicate-nonahydrate.

PROCEDEU MODERN MECANO-CHIMIC PENTRU OBȚINEREA UNUI COMPOZIT GEOPOLIMERIC CU ÎNALTĂ REZISTENȚĂ

(Rezumat)

Înlocuirea soluției alcaline obișnuite cu metasilicat de sodiu nonahidrat ca activator alcalin al deșeurilor alumino-silicatice pentru fabricarea geopolimerilor reprezintă o soluție tehnică recentă pentru creșterea semnificativă a rezistenței lor mecanice. Principiul acestei metode a fost testat într-o versiune proprie de către echipa de autori a lucrării curente. Cenușa zburătoare de cărbune, nisipul de râu și fumul de silica (nano-silica) au fost precursori solizi utilizați în amestecul de material de start. În condițiile presării pulberii geopolimerice (realizată prin metoda convențională) la presiunea axială de 400 daN·cm^{-2}, față de valoarea sa de 1000 daN·cm^{-2} utilizată de (Nishikawa *et al*., 2022), nivelul rezistenței la compresiune și încovoiere a atins valori foarte mari, superioare față de cel al geopolimerilor uzuali.