

# NONCONVENTIONAL GEOPOLYMERIZATION AND DENSIFICATION METHOD OF ALUMINA-SILICATE WASTE SOLIDS FOR PRODUCING EXTREMELY HIGH-STRENGTH GEOPOLYMERS

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**ABSTRACT:** Simultaneous geopolymerization and densification of geopolymeric products is a viable process by cold sintering of residual alumina-silicate. The procedure peculiarity is the axial pressing of the powder previously produced by the usual geopolymerization. Sodium metasilicate nonahydrate is the type of alkaline activator used in the experiment, which does not require the addition of water and does not lead to the formation of a suspension. The geopolymer manufacturing process involved a mixture composed of coal ash, ground metallurgical slag, nano-silica, and sodium metasilicate nonahydrate, the pressing force of the powder being between 60-90 MPa. The compression resistance of the geopolymer reached a maximum of 51.75 MPa.

**KEYWORDS:** cold sintering, geopolymerization, densification, fly ash, slag, strength.

## 1. INTRODUCTION

Very large amounts of gases that affect the protective ozone layer of the atmosphere (mainly CO<sub>2</sub>) have been counted in the last decades and the consequences of this excess due to the exaggerated consumption of fossil fuel, especially in industry and transport, have been the global warming of the planet [1]. Obviously, this situation of major ecological crisis imposed extreme measures on the international level, being reduced or closed some large industrial technological flows consuming fossil fuel and by default, supplying huge amounts of CO<sub>2</sub> emitted into the atmosphere.

Optimal solutions adopted by international organizations to overcome this situation were the search and finding substitute materials with low carbon footprint largely based on recycling wastes and industrial by-products existing in excess in the environment [2]. Except for the production of basic materials with low energy consumption as substitutes for traditional raw materials, waste recycling can contribute significantly to improving the environment quality (air, surface or underground water, etc.) [3].

Recycling wastes or industrial by-products is a typical activity for recovering valuable components that are re-found in low quantities in many final products and this concern of manufacturers has existed a long time ago. However, the recycling

initiated in the last decades aims at the possibility of obtaining products with newly created value capable of replacing existing materials unacceptable in ecological or energetic terms. Most products with newly created value are intended for the construction sector, manufactured by recycling and turning numerous types of alumina-silicate waste through chemical activation. The method designed by the French scientist J. Davidovits starting in the 1990s and continued at the beginning of the 21<sup>st</sup> century [4-6] proposed the use of a liquid alkaline activator composed of Na- or KOH and Na<sub>2</sub> or K<sub>2</sub>SiO<sub>3</sub>, having the ability to generate the so-called geopolymerization reaction by activating waste rich in alumina and silica. Forming geopolymers through this general method has allowed the production of materials with remarkable mechanical, chemical, and physical properties, offering the optimal solution for replacing the traditional Portland cement at a very good quality level, considered for over 150 years as the ideal binder for the manufacture of construction concrete.

A special role of the curing process of fresh geopolymer by its activating with an alkaline solution for the production of a high strength-geopolymeric material was highlighted in the paper [7].

A cold sintering process, unused in the first decades of the 21<sup>st</sup> century, aiming at geopolymer densification by using a transitory transport phase

(usually liquid) and a pressing force uniaxially applied on the powder was presented in the paper [8]. In this way, ceramic powders can be turned into ultra-dense materials at relatively low temperatures.

An innovative technique exhibited by Nishikawa in 2022 [9] showed a version of producing ultra-dense geopolymeric materials through the method called cold reaction sintering. Unlike the alkaline activation method of alumina-silicate solids adopted by Davidovits-research team, the new technique gave up on the liquid alkaline activation, choosing sodium metasilicate hydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ). The method included two hardening stages of the geopolymer. The first stage, according to the conventional method, meant mixing the alumina-silicate solids with the alkaline aqueous solution until the suspension was formed, which was subjected to hardening the fresh material at temperatures below  $85\text{ }^\circ\text{C}$ . Preparing the second stage was performed by crushing and grinding the previously hardened material, adding sodium metasilicate hydrate, and axial pressing into a matrix at 100 MPa, developed by a press machine, and  $130\text{ }^\circ\text{C}$  for 10 min [9].

The same Nishikawa's research team carried out scientific investigations for the application of the cold reaction sintering method in a medical environment for the sintering of boron carbide ( $\text{B}_4\text{C}$ ) by hardening with an inorganic polymer binder [10]. The raw materials were residual coal ash,  $\text{Na}_2\text{SiO}_3$ , and sodium metasilicate nonahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ), the carbide material being heated to  $130\text{ }^\circ\text{C}$  and pressed in an axial press-machine. The result was simultaneous geopolymerization and densification. The compressive strength had high values (over 50 MPa) corresponding to  $\text{B}_4\text{C}$  material weight proportion of 30 % and the polymer binder proportion was 20 %.

The new cold sintering system mentioned above has experimentally proven to offer a viable method of geopolymerization and densification of geopolymers, the two processes taking place simultaneously and leading to excellent results in terms of strength with low energy consumption.

The writers' team of this article has been already interested in this new technique and has carried out preliminary tests, the results being included in an article completed in 2024, which is being analyzed for publication in the Romanian journal edited in Iasi [11]. The principle of the pressing method of geopolymer powder mix hardened and crushed in a previous preparation stage using sodium metasilicate nonahydrate was tested under conditions where the axial pressure applied to the powder material was  $400\text{ daN}\cdot\text{cm}^{-2}$  at ambient temperature. The

compression strength of specimens after 28 days was high in the range of 48.33-51.02 MPa and flexural resistance had values between 6.35-6.44 MPa.

The paper further presented aimed at improving the technical conditions to achieve a higher degree of pressing the geopolymer powder obtained in the first stage of the process. Implicitly, the expected effect of this technical improvement would be the important growing of the geopolymer strength.

## 2. METHODS AND MATERIALS

### 2.1 Methods

The production of geopolymers through the method patented by Davidovits involves the reaction between residual alumina-silicate and the alkaline activator representing Na- or KOH dissolved in deionized water and Na- or  $\text{K}_2\text{SiO}_3$  aqueous solution. This dissolution reaction, called geopolymerization reaction, contributes to breaking the siloxo (Si-O-Si) and sialate (Al-O-Si) connections by the hydroxyl groups  $\text{OH}^-$  from the alkaline activation solution. The geopolymerization reaction is followed by coagulation and condensation processes through the reaction between dissolved ionic groups and alkaline metal cations ( $\text{Na}^+$  or  $\text{K}^+$ ) as well as the reaction between silica monomers and other monomers. In this way, these chemical processes favour the formation of three-dimensional polymer networks [12].

The new method of preparing ultra-dense geopolymer differs from Davidovits' method in that the geopolymerization and densification process takes place without passing through the suspension stage of the fresh mixture. Pressing the raw material in a powder state and the use of sodium metasilicate nonahydrate allowed the chemical activation of alumina-silicate materials through developing the geopolymerization reaction and at the same time, acted as a densifier of the geopolymeric material [9].

The main alumina-silicate materials (coal ash and ground metallurgical slag) were processed in a ball mill so that their particle size was under  $20\text{ }\mu\text{m}$ . Their mixing with NaOH pellets dissolved in deionized water and aqueous solution of sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) produced a suspension, which was hardened by heating at  $80\text{ }^\circ\text{C}$  for 8 hours. The hardened material was then crushed and ground and mixed with sodium metasilicate nonahydrate. The powder material loaded in a stainless steel mould was subjected to pressing at  $100\text{-}110\text{ }^\circ\text{C}$  and different axial pressures between 60-90 MPa for 10 min in a 5 ton-force press in the Romanian Metallurgical Research Society (ICEM SA).

As in the case of manufacturing the geopolymeric material by the usual method recommended by Davidovits, the product hardened by the cold sintering method is stored at ambient temperature to complete the free hardening process before carrying out the investigations regarding the physio-mechanical characteristics after 7 and respectively, 28 days of storage.

## 2.2 Materials

Materials utilized in the experiment presented in this work were: fine ash recovered in thermal power plant, ground metallurgical slag, nano-silica, as solid components as well as sodium metasilicate nonahydrate.

Fine ash particles carried in flight by waste gases are secondary products of the energy generating industry. These fine particles are recovered in electro-filters before releasing gases into the atmosphere. The size of fly ash particles is generally below 250  $\mu\text{m}$ . The supply of this by-product was made by Paroseni-Thermal power plant (Romania) eight years ago. The reduction of the particle size under 20  $\mu\text{m}$  was necessary for the ash application in this experiment and was achieved by grinding the material in an electric grinder. The fly ash type falls into class F (with low content of calcium oxide) [13].

The slag resulted together with the pig iron in the blast furnace is a secondary product of the iron and steel industry. It was procured eight years ago from ArcelorMittal Galati (Romania) [14]. Following the process of wet granulation of slag, relatively spherical granules with the size between 2-6 mm result. In order to be used in manufacturing process of geopolymers, the slag granules were ground in successive stages in a ball mill until a powder with particle size under 20  $\mu\text{m}$  was obtained.

Oxidic components of the two alumina-silicate residues are presented in Table 1.

**Table 1.** Oxide composition of ash and slag

Composition	Ash (%)	Slag (%)
SiO <sub>2</sub>	52.0	38.0
Al <sub>2</sub> O <sub>3</sub>	23.8	15.5
CaO	3.6	40.8
MgO	3.3	0.2
Na <sub>2</sub> O	5.2	0.3
K <sub>2</sub> O	3.8	0.9
Fe <sub>2</sub> O <sub>3</sub>	7.3	1.1
SO <sub>3</sub>	1.0	0.1

Nano-silica as a by-product of the ferroalloy industry was introduced into the composition of the solids mixture of solid materials due to its capacity

to favour the polymerization reaction and to improve the mechanical properties of the geopolymeric material [15]. Having very small dimensions (around 100 nm), the nano-silica purchased from the market (97 % SiO<sub>2</sub>) did not require additional mechanical processing.

Due to the chemically bound water in the sodium metasilicate nonahydrate (Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O) alkaline activator [16], the cold sintering process takes place without the addition of water and therefore without forming the typical suspension in the geopolymerization process designed by Davidovits.

## 2.3 Methods used for investigation the geopolymer specimen features

Analyzing the geopolymer specimen features was carried out using traditional procedures. The denseness was identified through Archimedes' method based on the water-intrusion method (ASTM D792-20). The compression resistance was investigated according to EN 12390-3: 2001 standard on cubic specimens, while the flexural resistance was measured on rectangular prism shape of specimens by applying the three-point bend test (SR EN ISO 14125: 2000). The water uptake was determined through the immersing method of samples under water (ASTM D570). The structural appearance of samples was identified with Biological Microscope model MT5000, 1000 x magnification.

## 3. RESULTS AND DISCUSSION

### 3.1 Results

Four experimental versions were chosen in this experiment. As mentioned above, the axial pressure applied to the powder mixture in the mould was increased from version 1 to version 4 between 60 and 90 MPa. Alumina-silicate waste (coal ash and metallurgical slag) followed decreasing slopes: ash from 48 to 42 wt. % and the slag from 17 to 14 wt. %. Nano-silica added to the solid powder had uniformly growing values from 2 to 5 wt. %. Also, Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O was introduced in uniformly increasing proportions from 33 to 39 wt. %. Table 2 presents in a centralized way the input data of the experiment.

**Table 2.** Adopted variants for experimentation

Material	Variant 1	Variant 2	Variant 3	Variant 4
Coal fly ash	48	46	44	42
Granulated blast furnace slag	17	16	15	14
Nano-silica	2	3	4	5

Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	33	35	37	39
Axial pressure (MPa)	60	70	80	90

The duration of pressing the powder was a maximum of 10 min.

The geopolymer specimens produced by the cold sintering technique are very dense materials according to the images exposed in Figure 1.

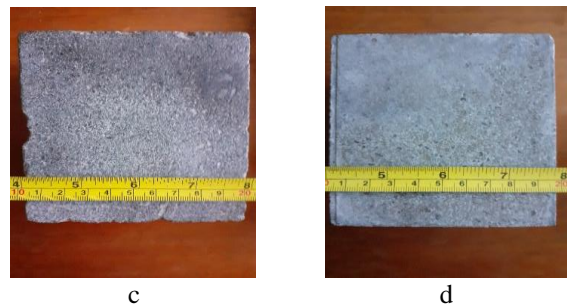
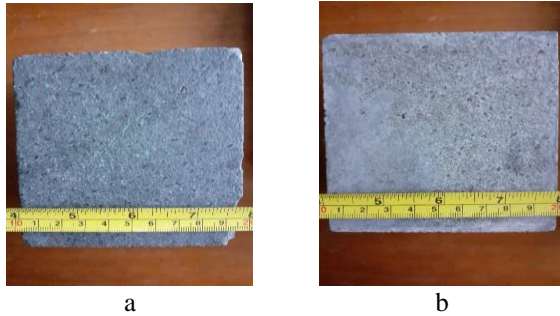


Figure 1. Images of the geopolymer specimen surfaces a – variant 1; b – variant 2; c – variant 3; d – variant 4.



Determining physico-mechanical characteristics of samples through the methods specified above led to the results shown in Table 3. The denseness values of specimens, compression resistance obtained in 7 curing days and 28 days, respectively, bending resistance obtained in 7 and 28 days as well as water uptake are presented.

Table 3. Geopolymer characteristics obtained by applying the cold sintering preparation technique

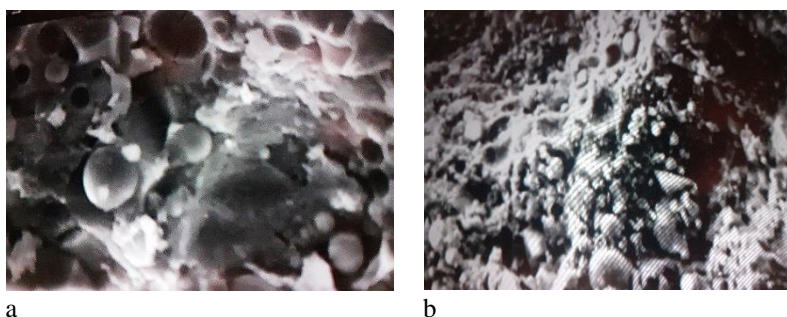
Experimental version	Denseness (g·cm <sup>-3</sup> )	Compression resistance (MPa)		Flexural resistance (MPa)		Water uptake (%)
		In 7 days	In 28 days	In 7 days	In 28 days	
1	2.22	31.06	48.12	6.19	7.42	5.2
2	2.29	36.10	50.14	6.48	7.62	5.3
3	2.38	36.31	51.36	6.77	7.65	5.7
4	2.46	36.58	51.75	6.85	7.74	5.5

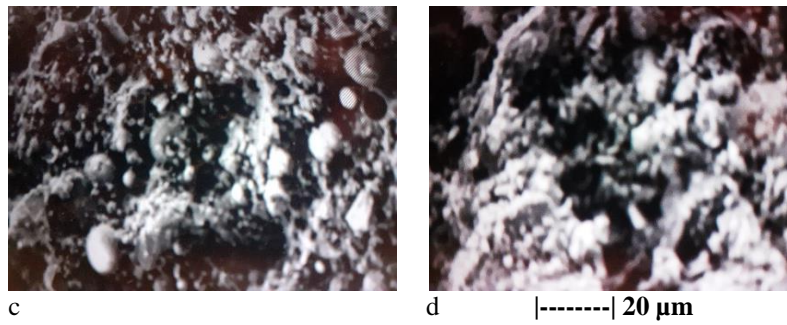
The experimental results confirmed the important role of pressing degree of the geopolymeric powder in the cold sintering procedure. The increase of pressing force applied to the powder from 60 to 90 MPa influenced in all experimental versions the values of the compression and flexural resistance both at the early age (after 7 hardening days) and at the end of the hardening process (after 28 days) as well as the denseness values, which were increasing.

Thus, it could be deduced that the strength improvement and obtaining of a very dense material depend to a great extent on the increase of the nano-silica ratio in the solid mixture and the sodium metasilicate nonahydrate proportion as well as the

pressing degree of the geopolymeric powder. The decrease in the amount of ash and slag also influences the strength characteristics and densification of the geopolymer, but probably to a lesser extent.

Investigations on the characteristics of geopolymer specimens also aimed at their microstructural appearance, interesting the particularities related to the densification degree of samples. Pictures of the microscopic appearance of specimens made in the four experimental versions are shown in Figure 2.





**Figure 2.** Structural aspect of geopolymer samples  
a – version 1; b – version 2; c – version 3; d – version 4.

The images in Figure 2 show increasing tendency of the sample densification starting from version 1 to version 4, corresponding to the increase of pressing force of geopolymeric powders starting from 60 to 90 MPa.

### 3.2 Discussion

Alumina-silicate wastes were used as cementitious materials with pozzolanic properties substituting the ordinary Portland cement and sodium metasilicate hydrate was utilized as an alkaline activator replacing the usual alkaline solution of NaOH and  $\text{Na}_2\text{SiO}_3$ . Water addition for hardening the geopolymer is substituted by hydrate, that provides it in this case.

The principal feature of the cold sintering procedure is the simultaneous development of hardening and the geopolymerization reaction, according to Nishikawa [9].

The experimental variation of the mechanical (pressing pressure of the powder specimens) and chemical (the composition of the materials used in the experiment) parameters offered the possibility of determining their optimal values for obtaining the best performing geopolymeric material in terms of resistance and densification degree.

Thus, in mechanical terms, the optimal pressing pressure of the geopolymeric powder was 90 MPa, i.e. the maximum value of the range of values tested between 60-90 MPa. It contributed in the highest extent to the product densification.

In terms of the weight proportion of mix components, it has been found that the maximum tested values of sodium metasilicate nonahydrate (39 wt. %) and nano-silica (5 wt. %) contributed to the increase of strength and denseness of the specimen. Instead, reducing the proportion of metallurgical slag and especially, ash had the opposite effect on these physico-mechanical characteristics.

Therefore, the optimal specimen of geopolymer prepared and hardened by the cold sintering process was the one obtained in version 4. The compression resistance reached at early age (7 days) was 36.58 MPa, while its maximum value at the end of the hardening process (28 days) was 51.75 MPa, i.e. values at a high level by comparison with ordinary geopolymers.

Also, denseness reached a high value ( $2.46 \text{ g}\cdot\text{cm}^{-3}$ ) in the case of the specimen made in the experimental version 4.

### 4. CONCLUSION

An innovative geopolymer curing technique called "cold sintering" has contributed to obtaining superior results in terms of mechanical resistance and degree of densification of this type of material. Recently designed by the Japanese researcher Nishikawa, the cold sintering method is based on the high pressure pressing of the geopolymer powder made in a previous stage and the use of sodium metasilicate hydrate replacing the usual alkaline solution. Applying this procedure creates the conditions for obtaining geopolymeric products with very high mechanical resistance and a high degree of densification. The principle of the cold sintering method was adopted by the authors of this work, the used alumina-silicate waste being coal fly ash (between 42-48 wt. %) and granulated blast furnace slag (within the limits of 14-17 wt. %). Nano-silica (in the range of 2-5 wt. %) was also chosen as a component of the mixture and  $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$  was adopted as an alkali-activator. The experimental outcomes showed the viability of the new procedure. Under the conditions of applying the powder pressing pressure of 90 MPa, the consumption of sodium metasilicate hydrate of 39 wt. %, nano-silica of 5 wt. %, coal fly ash of 42 wt. %, and blast furnace slag of 14 wt. %, the compression resistance values reached 36.58 MPa (in 7 days) and 51.75 MPa (in 28 days).

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