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Microsilica and steel dust as nano- and micro-particles addition for increasing the mechanical strength of fly ash and blast furnace slag-geopolymer concrete

Microsilica și praf de oțel ca adaos de nano și microparticule pentru creșterea rezistenței mecanice a betonului geopolimeric pe bază de cenușă zburătoare și zgură de furnal

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Abstract. *The paper is a contribution to developing the manufacturing technique of fly ash and blast furnace slag-geopolymer concrete with compressive strength increased up to 73 MPa and flexural strength reaching 12.1 MPa (after 180 days of curing) by adding low amounts of nanosilica (20-50 nm) and steel dust (1-5 µm) captured from electric arc furnace exhaust gases. The originality of the work consists in combining the concrete production technique by using alumino-silicate industrial by-products (ash and slag) with the addition of nano or micro-particles in order to significantly increase the mechanical strength of geopolymer concrete.*

Key words: geopolymer concrete, fly ash, blast furnace slag, steel dust, mechanical strength.

Rezumat. *Lucrarea constituie o contribuție la dezvoltarea tehnicii fabricării unui beton geopolimeric pe bază de cenușă zburătoare și zgură de furnal cu rezistență la compresiune crescută până la 73 MPa și rezistența la încovoiere atingând 12,1 MPa* *(după 180 zile de întărire) prin adaosul unor mici cantități de nanosilica (20-50 nm) și praf de oțel (1-5 μm) captat din gazele evacuate din cuptorul electric cu arc. Originalitatea lucrării constă în combinarea tehnicii producerii betonului prin utilizarea produselor secundare industriale aluminosilicatice (cenușă si zgură) cu adaosul unor nano sau microparticule în scopul creșterii semnificative a rezistenței mecanice a betonului geopolimeric.*

Cuvinte cheie: beton geopolimeric, cenușă zburătoare, zgură de furnal, nanosilica, praf de oțel, rezistență mecanică.

1. Introduction

As a result of the serious ecological problems faced by the planet in the last decades, environmentally friendly technologies have become appropriate solutions that need to be implemented in economic activities. The construction materials industry is one of the most affected production activities, the usual concrete binder (i.e. Portland cement) largely contributing to the global emission of greenhouse gases (mainly carbon dioxide CO_2). The cement industry is responsible for about 10 % of the global CO_2 emissions. In 2021, the CO_2 emission in the world was 2.9 billion tons representing 0.93 kg CO_2/kg concrete. In addition, the industrial manufacture of cement is characterized by very high consumption of fossil fuel, in the current conditions of the world energy crisis [1, 2]. Under these conditions, geopolymer concrete is an excellent alternative building material for the cement [3], according to the invention of French researcher J. Davidovits [4].

Geopolymer is based on alumino-silicate natural materials (metakaolin, kaolin, rice husk ask, volcanic rock powder, etc.) or representing industrial by-products (coal fly ash, granulated blast furnace slag, red mud, mining tailing, etc.). These materials are dissolved in alkaline activating aqueous solution that facilitates the geopolymerization reaction forming molecular chains with the role of binder [3].

Several manufacturing techniques of geopolymer concrete were tested according to the literature in the first two decades of the new millennium. The best-known method of making the geopolymer is that of using coal fly ash as the basic raw material, sodium hydroxide (NaOH) solution with a concentration between 8M-16M together with sodium silicate ($Na_2 SiO_3$) solution as an alkaline activator. The mixture of these components leads to the formation of a gel, which is poured into a metal tray, covered with thin plastic film, and placed in an oven for curing treatment at a relatively low temperature (60-90 ºC) followed by curing at room temperature. The determination of geopolymer concrete characteristics is carried out after 7, 28 or even 90 days. The results showed the increase of the mechanical strength of the concrete as follows: compressive strength by 1.5 times, split tensile strength by 1.45 times, and flexural strength by 1.6 times [3].

According to [5], geopolymer concrete made with fly ash and blast furnace slag had higher strength compared to geopolymer made with fly ash due to higher bulk density (2055-2100 kg·m^{-3}) and lower apparent porosity (about 17 %) and water absorption (about 7 vol. %).

Natural fibers in the form of pineapple leaf fibers soaked in NaOH solution and cut to lengths between 10-30 mm were used for increasing the mechanical strength of geopolymer concrete composed of fly ash (27.5 %), fine aggregate (55 %), NaOH 14-16M (5.7 %), Na_2SiO_3 (11.4 %), and pineapple fibers (between 0.25-0.5 %). Under the conditions of using the NaOH concentration of 16M and the maximum proportion of natural fibers (0.5 %) with the length of 30 mm, the highest values of compressive strength (41.5 MPa) and flexural strength (9.2 MPa) were reached after the curing process of 28 days [6].

In another paper [7], the mechanical characteristics (compressive strength and flexural strength) of fly ash-geopolymer reinforced with short natural fibers such as: cotton, sisal, raffia, and coconut are analyzed. The experimental results indicated that the appropriate addition of natural fibers in low proportions improves the mechanical properties of these geopolymer composites, reaching 39 MPa for compressive strength, and 8 MPa for flexural strength.

Very high performances of the mechanical strength of geopolymer concrete have been achieved by using steel fibers and microsilica [8]. The solid raw materials with very low average grain sizes were fly ash (38 μm), blast furnace slag (17 μm) and microsilica (0.18 μm), to which silica sand (900 kg·m^{-3}) was added. After mixing these materials, the alkaline activator composed of NaOH dissolved in water, and aqueous solution of Na_2SiO_3 (including 28 % SiO_2, 6 % Na_2O, and 64 % water) was added as well as the steel fibers (length 15 mm). Mixing these components generated slurry, that was poured into a mold. The curing process was carried out in the steam curing room at 85 ºC for 24 hours. Next, 28 days of curing process at room temperature were used before determining the product characteristics. Depending on the weight proportion of steel fibers between 1-3 %, compressive strength had values between 110-156 MPa, the highest value corresponding to the 3 % proportion, and the elasticity modulus increased from 28 to 32 GPa.

Some nanoparticles (nanosilica, nanotitania, nanoalumina, nanoclay, etc.) added to the material mixture favour the improvement of the structural properties of geopolymers. According to the literature [9, 10], their durability and mechanical characteristics are significantly increased.

The preparation of fly ash-geopolymer concrete quite frequently uses nanosilica leading to a maximum compressive strength of 51.8 MPa for the addition of 2 % nanosilica [11]. Also, in the case of manufacturing fly ash/slag-geopolymer concrete, the partial replacement of slag with nanosilica allowed obtaining a compressive strength of 54 MPa for the addition of 2 % nanosilica [12]. Testing under the conditions of increasing its proportion above 2 % showed a decrease of compressive strength value [13]. The use of nanoalumina in the manufacturing process of fly ash-geopolymer allows intensifying the geopolymerization reaction and has important effects on the mechanical properties of geopolymer [14]. Also, nanotitania added in proportion of 1-5 % contributes to the increase of compressive strength [15]. The investigation of the influence of SiO_2, TiO_2, and Fe_2O_3 nanoparticles on the properties of fly ash blended cement mortars was carried out by [16]. Workability was influenced in a limited way by low proportions of nanoparticles (1-5 % of cement). Also, in low quantities, these nanoparticles contributed to increasing the compressive strength and tensile strength, instead higher proportions negatively influenced the mechanical strength.

A new construction material similar to concrete, but even stronger, was proposed in a doctoral thesis [17]. The manufacture of this material (called Ferrock) is based on 95 % recycled residual materials: steel dust captured in the gas filtration installations released from steelmaking furnaces in steel industry [18] as well as silica from recycled ground glass waste. The product is more strength (five times) than the traditional concrete, but it can erode over time in contact with salt water or with chemicals used to treat water in sewer pipes.

Considering the tested techniques and the performances obtained in the manufacturing process of high-strength geopolymer concrete presented above, the solution adopted by the authors is based on the use of granulated blast furnace slag and coal fly ash as geopolymer type raw materials and the addition of low amounts of nanosilica and steel dust as nano- and micro-particles. The alkaline activation method of geopolymers is the one commonly used including NaOH dissolved in water and Na_2SiO_3 aqueous solution, which favours the development of the geopolymerization reaction forming geopolymer concretes.

2. Methods and materials

The geopolymerization process that is the basis of the transformation of alumino-silicate materials into geopolymeric concrete involves a rapid chemical reaction in a highly alkaline environment of Si and Al rich-materials, which leads to the formation of a three-dimensional polymer chain and ring structure including Si-O-Al-O bonds [2]. According to [19], the geopolymerization is a particularly complex process, which develop in three stages, that can intersect and influence each other. Deep knowledge of the process mechanism is still difficult and its understanding requires additional research.

The preparation of geopolymer concrete is carried out in the following way. The alumino-silicate materials with the role of concrete binder (slag and fly ash) in ground state are mixed in a container together with fine aggregate (quartz sand) and coarse aggregate (gravel) for 5 min. The preparation of the alkaline activator takes place in a separate vessel, mixing NaOH and Na_2SiO_3 in water by stirring for 5 min. The liquid mixture is then poured over the solid materials and also nano-particles of silica and micro-particles of steel dust are added and the mixing of all components is carried out for another 5 min until a gel is formed. The gel is poured into a metal mold protected with a thin plastic film and placed in a thermally insulated room for the curing treatment by blowing steam at 85 ºC for 24 hours. The hot curing process is followed by room temperature curing for 48 hours. Next, the geopolymer concrete is kept for free curing removed from the mold before making the measurements to determine the characteristics of specimens at 28, 90, and 180 days.

The following materials were used in the experiment of this work: coal fly ash, granulated blast furnace, river sand, gravel, NaOH, Na_2SiO_3, nanosilica, and EAF steel dust. The chemical composition of materials mentioned above is presented in Table 1.

Table 1

Chemical composition of materials (wt. %)

Composition	Coal fly ash	Blast furnace slag	River sand	Gravel	Nanosilica	EAF steel dust [20]
SiO_2	45.18	37.4	98.8	87.50	99.8	
Al_2O_3	33.59	6.4	0.77	6.10	-	1.1
CaO	9.36	39.9	0.01	0.28	-	6.0
MgO	0.83	3.5		0.03	-	2.5
Fe_2O_3	4.54	6.9	0.05	1.62	-	-
K_2O	1.13	0.2	0.22	-	-	-
Na_2O	1.07	0.1		2.08	-	-
SO_3	0.74	-	-	0.06	-	-
TiO_2	1.26	-	-	-	-	-
MnO	0.11	2.3	-	-	-	-
Fe_3O_4	-	-	-	-	-	34.4
ZnO	-	-	-	-	-	15.0
PbO	-	-	-	-	-	2.3
Mn_2O_3	-	-	-	-	-	3.2
Cr_2O_3	-	-	-	-	-	0.3
LOI	1.72	-	-	-	0.2	-

Coal fly ash was provided 5 years ago by the Paroseni (Romania) thermal power plant. The material as an industrial by-product of the energy industry had a grain size below 200 μm and was processed by grinding in a ball mill and sieved to sizes below 25 μm.

Granulated blast furnace slag was provided about 7 years ago by ArcelorMittal Galati (Romania). This material with the grain size below 3 mm was also subjected to grinding in the ball mill, its granulation being reduced below 36 μm.

River sand was commercially purchased having the grain size below 2 mm, while gravel provided by a Romanian building company had dimensions between 4-8 mm.

Nanosilica (99.8 % SiO_2) IOTA HL 4200 type with the granulation in the range of 50-200 nm was commercially purchased. EAF steel dust with grain size within the limits of 1-5 μm was provided by ArcelorMittal Galati.

In general, the methods for investigating the characteristics of geopolymer concrete samples were those commonly used. The density was measured as the ratio between the sample mass obtained by weighing with an electronic balance and the volume with a regular shape that is easy to calculate [21]. Using the ASTM C642-97 standard, the apparent porosity was determined by dividing the difference between wet weight and dry weight by the difference between wet weight and suspended weight of the sample [5]. Thermal conductivity was measured at room temperature using the heat-flow-meter HFM448 Lambda (SR EN 1946-3:2004). The 100 kN-compression fixture Wyoming Test Fixture [22] was used to determine the compressive strength. The flexural strength determination method was based on SR EN ISO 1412:2000 [23]. Immersion of the sample under water for 24 hours (ASTM D570) allowed the measurement of water absorption. The microstructural aspect of the specimens could be identified using the Biological Microscope MT5000 model with captured image, 1000 x magnification.

3. Results and discussion

Four experimental variants were adopted, in which the main variable parameters were nanosilica and EAF steel dust. Component values of mixtures are presented in Table 2.

Table 2

Composition of experimental variants

Composition ($kg·m^{-3}$)	Variant			
	1	2	3	4
Blast furnace slag	300	300	290	290
Fly ash	170	170	175	175
River sand	650	650	650	650
Gravel	600	600	600	600
NaOH 8M	120	120	120	120
Na_2SiO_3	250	250	250	250
Water	60	60	60	60
Nanosilica	3.8	4.7	5.6	6.5
EAF steel dust	3.5	4.3	5.2	6.0

According to the data in Table 2, the ratio of the two alumino-silicate components (slag and fly ash) had values between 1.66-1.76, the ratio between the components of the alkaline activator (Na_2SiO_3 and NaOH) was 2.08, and the ratio between the solid and liquid components of the mixture was around 4.02. Nanosilica was used in a weight ratio between 0.8-1.4 % of the amount of alumino-silicate binder (blast furnace slag and fly ash), while EAF steel dust represented between 0.7-1.3 % of the same amount of binder.

The manufacturing recipes corresponding to the four experimental variants together with the curing process mentioned above in this paper led to the production of very dense and high hardness geopolymer concrete specimens. Appearance images of experimentally making concrete specimens are shown in Fig. 1.

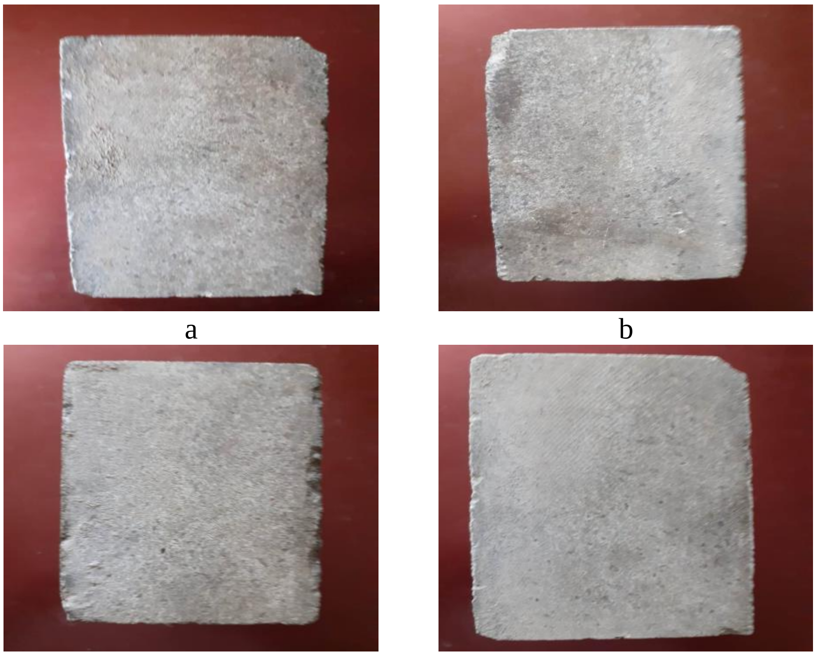

Fig. 1. Appearance images of geopolymer concrete specimens
a – variant 1; b – variant 2; c – variant 3; d – variant 4.

To identify the physical, mechanical, thermal, and microstructural characteristics, geopolymer concrete specimens were tested by the mentioned methods, results being centrally presented in Table 3.

Table 3

Characteristics of geopolymer concrete specimens

Characteristic	Variant			
	1	2	3	4
Density ($kg \cdot m^{-3}$)	2054	2070	2086	2102
Apparent porosity (%)	19.9	20.1	20.4	20.6
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	0.415	0.423	0.428	0.435
Compressive strength (MPa)	42.5	50.1	61.2	73.0
Flexural strength (MPa)	8.9	9.5	10.8	12.1
Water absorption (vol. %)	10.8	11.0	11.2	11.5

Data in Table 3 show the significance influence of addition of nano and micro-particles representing by nanosilica and EAF steel dust on mechanical properties of geopolymer concrete as well as on its thermal insulation properties (density, thermal conductivity, and apparent porosity). Compressive strength after 180 days of curing reached high values (42.5-73.0 MPa) increasing with the increase of nanosilica and steel dust proportions. Also, flexural strength registered the same increasing evolution (8.9-12.1 MPa). The density of material as well as the thermal conductivity had high values of over 2000 $kg \cdot m^{-3}$ and respectively, over 0.41 $W \cdot m^{-1} \cdot K^{-1}$, suggesting a dense material with very few pores. By default, the concrete porosity was low, around 20 %. Water absorption was within normal limits by comparison with other geopolymer concretes made and presented in the literature.

Microstructural appearance of geopolymer concrete specimens is shown in Fig. 2.

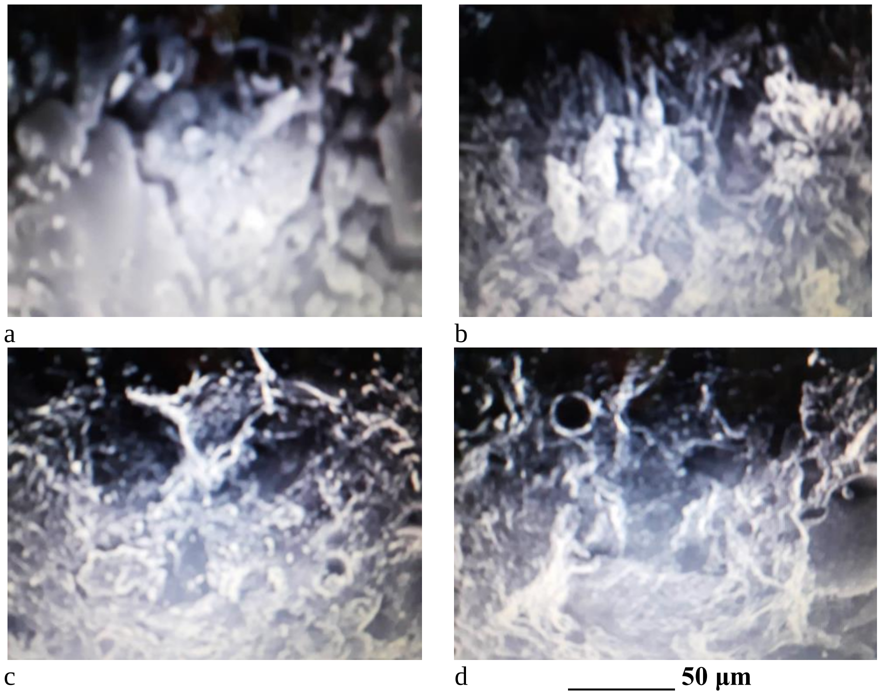

Fig. 2. Microstructural appearance of geopolymer concrete specimens
a – variant 1; b – variant 2; c – variant 3; d – variant 4.

According to Fig. 3, the compactness degree of geopolymer concrete specimens is quite high and it is accentuated towards position (d) corresponding to variant 4. This explains the high mechanical strength of samples and their very low thermal insulation properties.

The experimental results confirmed that residual alumino-silicate materials can completely replace cement in the manufacture of geopolymer concrete and the addition of nanoparticles significantly contributes to increasing its mechanical strength.

4. Conclusions

Adopting the same modern trend of protecting the planet's ozone layer against the emission of greenhouse gases (CO_2), the objective of the work was to manufacture a high-strength geopolymer concrete using fly ash and blast furnace slag, i.e. industrial by-products completely replacing cement as well as nanosilica and EAF steel dust in order to increase the mechanical strength of concrete up to 73 MPa for the compressive strength and 12.1 MPa for the flexural strength. The combined use of alumino-silicate waste and nano and micro-particles represents the originality of this paper.

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