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GEOPOLYMER CONCRETE-A SUITABLE NONCONVENTIONAL ALTERNATIVE SOLUTION FOR THE GLOBAL REDUCTION OF CO_2 EMISSIONS IN MANUFACTURING THE CONCRETE

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ABSTRACT: The innovative method of geopolymer concrete making by completely replacing the cement with coal fly ash and granulated blast furnace slag (residual aluminosilicate materials) was experimentally applied and presented in the paper. Compared to other experiments described in literature, the work originality is the significant increasing of slag ratio (15-25 %) in the aluminosilicate binder, to increase the compressive strength despite the decrease in workability. Sodium silicate and aqueous solution of sodium hydroxide were used as activators. River sand (fine aggregate) and natural gravel (coarse aggregate) completed the concrete making recipe. The compressive strength had increasing values (above 51 MPa) with the increase of slag ratio, density decreased up to 2290 kg/m^3, fresh concrete workability according to standard for concrete slump test decreased from 70 mm up to 45 mm, while water absorption was relatively constant between 0.78-0.80 vol. %. The making variant adopted as optimal was that with 80 % fly ash and 20 % slag having the compressive strength of 53.3 MPa, density of 2298 kg/m^3 and fresh concrete workability of 58 mm (i.e. a medium workability).
KEYWORDS: geopolymer concrete, coal fly ash, granulated blast furnace slag, alkali activator, compressive strength.

1. INTRODUCTION

Worldwide, in the last decades there is a pronounced tendency to reduce greenhouse gas emissions (GHG) by searching for alternative solutions for environmentally friendly technologies and raw materials. An example of this is the building materials industry and especially the manufacture of Portland cement used on a large scale in the manufacture of concrete. The manufacturing process of Portland cement, a great consumer of fossil fuel, causes carbon dioxide (CO_2) emissions at a global level of up to 10 % [1]. Natural aluminosilicates or silica and alumina-rich residual materials have been highlighted to be adequate as raw materials in the manufacturing process of geopolymer concrete substituting the cement. According to [2], the cost of preparing this material mixture is comparable to that of ordinary Portland cement and in addition, the fuel consumption used in the production of the mixture is 40 % lower compared to the consumption required to manufacture ordinary Portland cement. The geopolymer concrete has the peculiarity of completely replacing the cement in its composition with amorphous aluminosilicate pozzolanic materials activated by liquid alkaline solutions to allow the polymerization reaction to take place [3]. The usable aluminosilicate materials can be natural materials (clay, kaolinite, and calcined kaolinite) or residual materials (coal fly ash, metallurgical slag, rice-husk ash, red mud, and silica fume) with a role in the synthesis of geopolymers. Alkaline compounds used as activators are usually: sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium silicate (Na_2SiO_3), sodium carbonate (Na_2CO_3), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), potassium sulfate (K_2SO_4) [3]. Concrete curing can be performed at room temperature or at high temperature. Increasing the temperature, the polymerization process intensifies and the mechanical strength highly increases in a much shorter time compared to the curing at room temperature [4].

Several variants were tested in [5] for making geopolymer concrete through room temperature curing, using the Taguchi method. Ground granulated blast furnace slag (450 kg/m^3) as aluminosilicate binder was chosen. The alkaline activator (NaOH)/binder ratio was 0.35, Na_2SiO_3/NaOH was 2.5, and NaOH concentration was 14 M. The highest value of the compressive strength after 7 days of 60.4 MPa was thus obtained. However, the setting time was not long enough. Partial replacements of blast furnace slag with different proportions of coal fly ash, metakaolin and,

respectively, silica fume were used to increase the setting time. In this way, the workability of the concrete increased, but the compressive strength decreased due to the lower calcium content.

Geopolymer concrete according to the paper [6] was making using coal fly ash and was cured at room temperature. A mixture of Na_2SiO_3 and NaOH solutions was used as activator, the activator/binder ratio being kept at 0.35. The ground granulated blast furnace slag was added in proportions up to 20 % of the total binder. The results were compared with concrete samples made with Portland cement cured at room temperature. The compressive strength of geopolymer concrete increased from the early age. By increasing the proportion of slag in the mixture, the strength also increased. The drying shrinkage, sorption, and void volume of geopolymer concrete were generally similar to the same properties of Portland cement concrete. The work conclusion was that the concrete obtained from coal fly ash and slag by curing at room temperature has durability properties at least similar with the conventional concrete.

Other experimental research [7] aimed at the total replacement of coal fly ash from the aluminosilicate binder with granulated blast furnace slag and rice husk ash, considering the possible reduction of ash reserves of thermal power stations. The results showed that the complete replacement of fly ash is not feasible, severely affecting the compressive strength of concrete due to the low alumina content of rice husk ash and blast furnace slag. However, up to 50 % slag and 5-10 % rice husk ash as separate substitutes for coal fly ash allow obtaining a compressive strength of about 13.8 MPa.

According to [8], the concentration of the NaOH solution has a significant influence on the mechanical properties (especially the bending strength) of geopolymer concrete based on coal fly ash. The optimal concentration of NaOH was identified at 12 M. Curing of the concrete was carried out at 60 ºC and the duration of the process was 1 day.

The paper [9] presents experimental work for identification the effect of various parameters affecting the compressive strength in order to enhance the performance of geopolymer concrete. The results show that compressive strength increases with increase of the curing time and temperature, and concentration of NaOH solution and decreases with increase of the ratio water/geopolymer ratio. The addition of naphthalene-based superplasticiser improves the workability of the fresh geopolymer concrete.

The influence of different curing types of geopolymer concrete (with steam, with hot air, and at room temperature) on its mechanical properties are presented in [10] based on the experimental results. The making recipe used by the authors contained: low calcium fly ash, granulated blast furnace slag, sand as fine aggregate, coarse aggregate (grain size below 20 mm), and alkaline liquid solution prepared by mixing Na_2SiO_3 and NaOH (as pellet). The Na_2SiO_3/NaOH ratio was 2.5. Three experimental variants were adopted, in which fly ash amount was 436, 414.2, and respectively, 392.4 kg/m^3 blast furnace slag amount was zero, 21.8 and 43.6 kg/m^3, the other material components being kept constant, i.e.: 17.94 kg/m^3 NaOH, 38.12 kg/m^3 water, 140.14 kg/m^3 Na_2SiO_3, 654 kg/m^3 sand, and 1308 kg/m^3 coarse aggregate. Density of geopolymer concrete samples after curing at room temperature between 3-12 days decreased up to 2320 kg/m^3 in the case of variant 1, 2294 kg/m^3 in variant 2 and 2285 kg/m^3 in variant 3. The average density of fly ash-based geopolymer is approximately similar to that of concrete with Portland cement. Hot air curing allowed reaching the highest values of compressive strength of 24.5 MPa corresponding to specimen 1, 25.75 MPa (specimen 2) and 28.34 MPa (specimen 3). Curing at room temperature registered the highest increasing of compressive strength in 12 days compared to its value after 3 days, even reaching 25.5 MPa in the case of sample 3. The slag role as component of fly ash-based binder was acceleration of the concrete setting time at ambient temperature. The conclusion of the paper [10] was that the geopolymer concrete based on low calcium-fly ash is suitable for structural applications (the manufacture of precast concrete products) due to its sufficiently high compressive strength.

The objective of the current work was the experimental manufacture of a geopolymer concrete based on coal fly ash and granulated blast furnace slag as well as Na_2SiO_3 and NaOH in aqueous solution as activators. In order to obtain a sufficiently high value of the compressive strength of concrete, it was chosen for curing the fresh concrete with hot air at 75-85 ºC for 7 days. The originality of the work is the adoption of a substantially higher mass proportion (up to 25 %) of blast furnace slag in the mixture with coal fly ash to increase the compressive strength.

2. METHODS AND MATERIALS

2.1 Methods

Geopolymer concrete experimental making was performed in laboratory. The method is based on the

complete replacement of the usual Portland cement with aluminosilicate waste (in this case fly ash and granulated furnace slag). The dry mixture of ground fly ash, ground granulated blast furnace slag, and fine sand (below 100 μm) as fine aggregate was firstly made in a mixer for 3-4 min. The coarse aggregate (natural gravel) was dried and sieved at a grain size below 7 mm. Na_2SiO_3 and NaOH in solution were used as activators. The mixture of the alkaline solution (Na_2SiO_3, NaOH and water) in liquid state was poured over the mixture of dry materials and their mixing was carried out for 5 min, obtaining the fresh concrete. The setting time of fresh concrete was evaluated at approx. 120 min, although the presence of blast furnace slag in the composition of the starting mixture slightly decreases this property. The geopolymer concrete specimens were poured into metal molds and placed in a refractory insulated enclosure heated with a recirculated stream of hot air at 75-85 ºC provided by an electric air preheater, to create the conditions for the polymerization reaction to take place. The time of maintaining the samples in the enclosure was 7 days.

Three variants of geopolymer concrete were adopted, in which the components of the aluminosilicate binder (coal fly ash and granulated blast furnace slag) were dosed in the following ratios: 85/15 (variant 1), 80/20 (variant 2), and 75/25 (variant 3). The total amount of the binder was kept constant at the value of 450 kg/m^3. Na_2SiO_3 and NaOH were used as activator and the activator/binder ratio was also kept constant at 0.362. The mass ratio between Na_2SiO_3 and the NaOH aqueous solution had a constant value of 2.51 in all three making variants. River sand as a fine aggregate was dosed so that it represented 1.5 of the total amount of the binder (i.e. 675 kg/m^3), while coarse aggregate (natural gravel) had a value three times higher than the aluminosilicate binder (i.e. 1350 kg/m^3). Table 1 shows the amounts of component materials used in the three experimental variants.

Table 1. Composition of geopolymer concrete making variants

Material	**Amount (kg/m^3)**		
	Variant 1	Variant 2	Variant 3
Fly ash	382.5	360.0	337.5
Granulated blast furnace slag	67.5	90.0	112.5
NaOH	18.4	18.4	18.4
Na_2SiO_3	144.7	144.7	144.7
Water	39.3	39.3	39.3
Fine sand aggregate	675.0	675.0	675.0
Coarse aggregate (natural gravel)	1350.0	1350.0	1350.0

2.2 Materials

The solid materials adopted for this experiment were: coal fly ash and granulated blast furnace slag as aluminosilicate materials binder, Na_2SiO_3 and NaOH as activators, sand as fine aggregate and gravel as coarse aggregate.

Coal fly ash, a by-product of the combustion process of coal in energy industry, captured in electrofilters, was purchased from the thermal power station Paroseni (Romania) at a grain size below 200 μm and it was ground in ball mill and sieved below 100 μm for using in this experiment [11]. The chemical composition of coal fly ash is shown in Table 1.

Granulated blast furnace slag supplied by ArcelorMittal Galati is a by-product of making pig iron in the blast furnace, granulated by pouring the molten slag into cold water. The grain size of granulated slag is in general below 3 mm. The current experiment required fine grinding of the slag in a ball mill, the final size of the particles being reduced below 100 μm. The chemical composition of the blast furnace slag is presented in Table 2 [12].

Table 2. Chemical composition of fly ash and granulated blast furnace slag

Chemical composition	**Coal fly ash (%)**	**Granulated blast furnace slag (%)**
SiO_2	46.5	36.44
Al_2O_3	23.7	11.60
CaO	7.9	41.81
MgO	3.2	5.80
MnO	-	0.55
Fe_2O_3	8.6	0.78
Na_2O	6.0	0.35
K_2O	4.1	0.43

Except for the most silicon-rich materials, sodium silicate (Na_2SiO_3) also called water glass or liquid glass is soluble in water forming an alkaline solution. It is the most important of the soluble silicates. Na_2SiO_3 is used as a binder and has remarkable contribution at increasing the mechanical strength of materials [13]. Na_2SiO_3 is available on the market in the form of a liquid solution with the concentration of 38 %, which was used in the experiment.

Sodium hydroxide (also called caustic soda) is in a solid state, hygroscopic, very soluble in water. NaOH with 98 % purity is commercially available in pellet form.

River sand as fine aggregate with the grain size below 0.15 mm was used in this experiment and

natural gravel with the grain size below 7 mm was used as coarse aggregate.

2.3 Geopolymer concrete characterization methods

Workability of the fresh geopolymer concrete was determined using the slump test apparatus according to Standard for concrete slump test (ASTM C 143-10). Water absorption was measured by the method of immersion of the sample under water for 24 hours (ASTM D570), after the 7 days of curing the concrete [14]. The concrete density was measured by the gravimetric method [15] at the end of the curing time. The compressive strength was determined with a 100 kN-hydraulic press with the axial application of the pressing force (EN 826-2013), existing in the Metallurgical Research Institute of Bucharest. The microstructural peculiarities of the geopolymer concrete samples were observed with the Biological Microscope model MT5000 with image captured with a Nikon Coolipix 3 mp Camera, 1000 x Magnification.

3. RESULTS AND DISCUSSION

3.1 Results

The appearance of the three geopolymer concrete specimens is shown in Figure 1.

Figure 1. Image of the three samples of geopolymer concrete

The characteristics of the geopolymer concrete samples influenced by the decreasing ratio between coal fly ash and granulated blast furnace slag in the composition of aluminosilicate binder are presented in Table 3.

Table 3. Characteristics of the geopolymer concrete specimens

Characteristic	Specimen 1	Specimen 2	Specimen 3
Workability (mm)	70 (medium)	58 (medium)	45 (low)
Water absorption (vol. %)	0.80	0.78	0.78
Density (kg/m^3)	2310	2298	2290
Compressive strength (MPa)	51.8	53.3	55.2

The workability of the concrete was influenced by the increase of the mass proportion of blast furnace slag in the binder composition from 15 to 25 %. According to the standard for concrete slump test, specimens 1 and 2 have medium workability (between 50-100 mm), while specimen 3 has a low workability (between 25-50 mm).

Water absorption in the mass of concrete specimens immersed in water has low values between 0.78-0.80 vol. %, practically unaffected by the ratio between fly ash and blast furnace slag.

The density of geopolymer concrete was slightly reduced by increasing the proportion of blast furnace slag from 2310 to 2290 kg/m^3. On the other hand, the compressive strength of concrete increased under the conditions of increasing the proportion of blast furnace slag from 51.8 to 55.2 MPa. Also, due to the application of fresh concrete curing with hot air at 75-85 ^{o}C, the compressive strength level is high.

The microstructural configuration of geopolymer concrete samples was identified with the microscope, the images being shown in Figure 2.

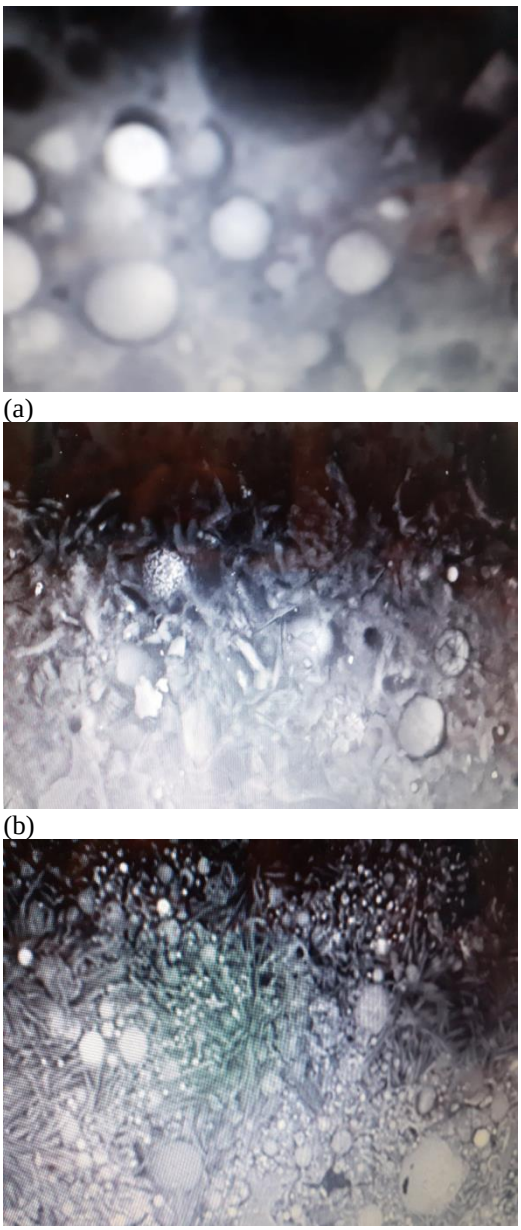

Figure 2. Microstructural appearance of geopolymer concrete samples
(a) – sample 1; (b) – sample 2; (c) – sample 3.

According to the pictures in Figure 2, the highest content of coal fly ash in the composition of the aluminosilicate binder is indicated by the predominant presence of fly ash cenospheres (a), while by decreasing the content of fly ash (b and c) the typical appearance of the slag microstructure significantly decreases.

3.2 Discussion

Two categories of materials are suitable and necessary for the manufacture of geopolymer concrete: materials containing silica and alumina and alkali aqueous solutions to facilitate the polymerization reaction. The aluminosilicate materials can be natural materials (clay, kaolinite, calcined kaolinite) or coming from residual materials that represent an environmental friendly and economical alternative solution adopted by the authors of this work, including fly ash, metallurgical slag, rice-husk ash, red mud, i.e. by-products of various industrial activities.

Geopolymer concrete represents a nonconventional material radically different from the conventional concrete by the complete replacement of Portland cement commonly used in the manufacture of building concrete. The total substitution of cement in the composition of concrete has a major role in the environmental protection taking into account that its industrial manufacture is a high energy consuming process that releases large amounts of carbon dioxide (CO_2) into the atmosphere.

The addition of aluminosilicate materials in the starting mixure of geopolymer concrete (especially coal fly ash and granulated blast furnace slag) has an already known role in improving the mechanical strength of cured concrete. A major effect on increasing its strength is the curing process of fresh concrete through different methods, of which the authors chose to introduce hot air stream at a temperature of around 80 ºC for 7 days into the room containing the molds with fresh concrete.

4. CONCLUSION

Making a geopolymer concrete as a nonconventional building material different from conventional concretes due to the total lack of ordinary cement (Portland) substituted with an aluminosilicate binder containing industrial by-products (coal fly ash and granulated blast furnace slag) was the objective of the current work. The making recipe also included an aqueous solution of Na_2SiO_3 and NaOH as activators for the polymerization reaction as well as a fine aggregate (fine sand) and a coarse aggregate (natural gravel). The work originality was the adoption of a substantially higher mass ratio (up to 25 %) of granulated blast furnace slag in the mixture with coal fly ash in order to increase the compressive strength value.

The fresh geopolymer concrete obtained in three variants by mixing the raw material and ingredients and pouring it into molds was subjected to the curing process in a stream of hot air at approx. 80 ºC for 7 days in a thermally insulated enclosure.

The caracteristics investigation of the three cured specimens showed that the compressive strength increased from 51.8 to 55.2 MPa with the increase of the slag mass ratio in the aluminosilicate binder from 15 to 25 %. The density decreased from 2310 to 2290 kg/m^3 and the workability of fresh concrete also decreased from 70 mm (i.e. medium workability) to 45 mm (i.e. low workability). The concrete variant adopted as optimal was that with 80 % fly ash and 20 % blast furnace slag, in which high

mechanical strength (53.3 MPa), relatively low density of 2298 kg/m^3 and medium workability (58 mm) were obtained.

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