

GEOPOLIMERS BASED ON TECHNOLOGICAL WASTE MATERIALS FROM B&H

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Abstract

The biggest global problem today is environmental pollution. The environment is polluted by the release of various gases and small particles into the atmosphere, which are the result of the production of various materials. During the production of 1 ton of cement, approximately 1 ton of CO₂ is emitted into the atmosphere. If we consider that the world production of cement is about 4.18 billion tons, then it can be seen that during the production of cement, the same amount of CO₂ is released into the atmosphere. Due to the increase in the consumption of concrete, there is also an increase in the production of cement, which results in an increase in environmental pollution and global warming. In addition to all greenhouse gases, carbon dioxide causes 65% of global warming.

Because of the above, solutions are being sought in the production of new materials that would at least partially replace cement. One of such materials is geopolymer.

In this paper, geopolymer samples based on fly ash from the Stanari thermal power plant were tested. Fly ash from the Stanari thermal power plant, 12M NaOH solution and commercial water glass were used as materials. The samples were made with an alkali to fly ash ratio of 1,2. The Na₂SiO₃/NaOH ratio ranged from 2; 2.5 and 3. The samples were thermally treated at geopolymerization temperatures of 60, 70 and 80 °C. After that, the compressive strengths of the samples were tested after 2, 7 and 28 days.

Key words: geopolymers, fly ash, environmental pollution, compressive strength

INTRODUCTION

After water, concrete is the second most consumed material in the world. The world consumption of concrete is 30 billion tons per year. In the field of construction, cement is the main ingredient for the production of concrete. However, cement production requires large amounts of raw material. During the production of cement, the burning of limestone causes the emission of carbon dioxide into the atmosphere. There are two sources of carbon dioxide emissions from cement production: the burning of fossil fuels to run the rotary kiln is the largest source, and the other is the chemical process of burning limestone. During the production of 1 ton of cement, approximately 1 ton of CO₂ is emitted into the atmosphere. If we consider that the world production of cement is about 4.18 billion tons, then it can be seen that during the production of cement, the same amount of CO₂ is released into the atmosphere. Of the total global annual CO₂ emissions, 5% is accounted for by cement production. [1,5,7]

Due to the increase in the consumption of concrete, there is also an increase in the production of cement, which results in an increase in environmental pollution and global warming. In addition to all greenhouse gases, carbon dioxide causes 65% of global warming.

Because of the above, solutions are being sought in the production of new materials that would at least partially replace cement. One of such materials is geopolymer. The name of geopolymer was proposed by Joseph Davidovits in 1978. According to Davidovits, geopolymers are inorganic, solid stable polymeric materials which are transform, polymerize and hardening at low temperatures, in the presence of acidic or alkaline activators.

During the last 20 years, geopolymers, which are also known as mineral polymers or inorganic polymers, have attracted a lot of attention as a promising new form of inorganic polymer

material that could be used as a substitute for conventional or ordinary Portland cement (OPC), for plastics, and many other mineral-based products. The development of geopolymer cement is an important step towards the production of environmentally friendly cements.

Geopolymers are members of a family of inorganic polymers with a chemical composition similar to natural zeolite materials (hydrated microporous aluminosilicates with a crystalline structure), but their structure is amorphous. The composition of zeolite is based on aluminosilicate frames and a three-dimensional network of inorganic polymers made of SiO_4 and AlO_4 tetrahedra, which are connected by oxygen atoms, and which they share with each other in rings.

Geopolymerization implies a heterogeneous chemical reaction between aluminosilicate oxides and solutions of alkali metal silicates and hydroxides at high-alkaline conditions and moderate temperatures, giving amorphous to polycrystalline polymer structures, consisting of Si-O-Al and Si-O-Si bonds. Geopolymerization is a geosynthesis (reaction that chemically integrates minerals) that depend on the ability of the aluminium ion (6-fold or 4-fold coordination) to induce crystallographical and chemical changes in a silica backbone [3,7].

The raw materials for the preparation of geopolymer

The raw materials for preparation of geopolymer can be any natural or unnatural (waste) materials with high content of silicon and aluminum. As natural raw materials most commonly used are different types of clay, and from unnatural raw materials are used fly ash, blast furnace slag and their combinations.

When milled coal burning in thermal power plants, particles of ash are collected together with flue gases, which are collected in bags and electro filters. These particles are called fly ash. From the total amount of ash generated in thermal power plants, about 85% is fly ash. [1]

World production of fly ash is about 400 million tons a year, while only 10-30 % of this waste material is again used in the production of cement, concrete and fillers. [1]

Since fly ash particles are very small, they quickly cool down and their structure is mostly amorphous (60 - 90%). Very small content of particles have a crystalline structure. The chemical composition of fly ash depends on the content of the impurities present in the coal used, and the combustion regime of that coal in the furnace of the thermal power plants.

According to EN 197-1 Fly ash V class has a lower content of CaO and contains several compounds combined between oxides of aluminum, silicon and iron. Fly ash class W contains a high percentage of CaO.

An important role in the geopolymerization process has a raw component that is an activator of the process. Such a raw material component has been called the "alkaline activator" since the reaction takes place in a highly alkaline medium. Various combinations of alkaline solutions can be used, and all alkaline activators, as Glukovsky systematized them, can be divided into six groups:

- Hydroxides: MOH ,
- Salts of weak acids: M_2CO_3 , M_2SO_3 , M_3PO_4 ,
- Silicates: $\text{M}_2\text{O} \cdot n\text{SiO}_2$,
- Aluminates: $\text{M}_2\text{O} \cdot n\text{Al}_2\text{O}_3$,
- Alumosilicates: $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (2-6)\text{SiO}_2$,
- Salts of strong acids: M_2SO_4 ,

where the letter M represents an alkali cation.

Palomo et al. (1999) concluded that the type of activator plays an important role in the polymerization process. The reactions take place at a high speed when the alkaline activator

contains soluble silicates, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. [3]

A study by Xu and Van Deventer (2000) showed that the addition of a sodium silicate solution to sodium hydroxide solution as an alkaline activator improved the reaction between the source material and the solution. [3]

Tempest et al. (2009) state that the sodium silicate activator dissolves rapidly and begins to bond particles of fly ash. Pores are quickly filled with gel as soon as the liquid phase succeeds in reaching ash particles. The liquid phase is important as a fluid transport medium that allows the activator to reach the fly ash particles and reacts with them. [3]

The geopolymerization mechanism is not yet completely clear, but it is assumed that Si and Al atoms in the original raw material begin to dissolve during the action of hydroxyl ions. After that, the dissolved ions Si and Al are transported, orientated and condensed into monomers. The resulting monomers bind to polymeric structures at mildly elevated temperatures by polycondensation / polymerization.

EXPERIMENTAL

In this paper, geopolymer samples based on fly ash from the Stanari thermal power plant were tested. Fly ash from the Stanari thermal power plant, 12M NaOH solution and commercial water glass were used as materials. The samples were made with an alkali to fly ash ratio of 1,2. The $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio ranged from 2; 2.5 and 3. The samples were thermally treated at geopolymerization temperatures of 60, 70 and 80 °C. After that, the compressive strengths of the samples were tested after 2, 7 and 28 days.

The chemical analysis of the fly ash TPP Stanari is shown in Table 1, and its granulometric composition is shown in Figure 1.

Table 1 - Chemical composition of fly ash from TPP Stanari, B&H[5,7]

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	Na ₂ O	K ₂ O	CO ₂	SO ₃	LOI
Content(%)	48,38	23,49	7,51	11,48	2,76	0,117	0,69	1,79	0,09	2,15	1,543

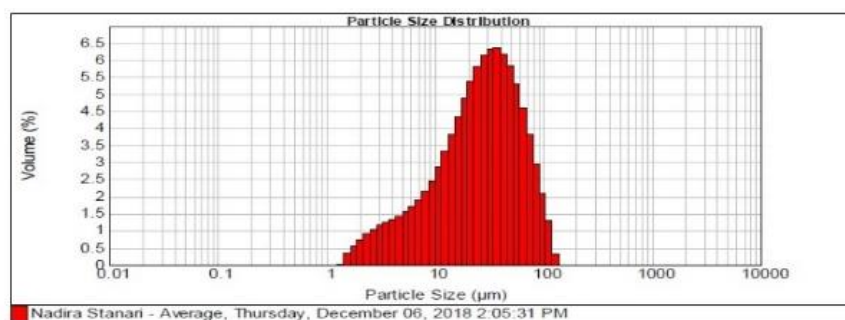


Figure 1 - Granulometric composition of fly ash[5,7]

From Figure 1 it can be seen that particles of fly ash range from 1 to 100 microns. The most of particles is about 50 microns in size. [5,7]

12 M NaOH solution was made in the Laboratory for Analytical Chemistry of the Metallurgical and Technology Faculty in Zenica.

Commercially water glass are used in the examination whose characteristics are shown in Table 2.

Table 2 - Characteristics of commercially water glass

Characteristics	SiO ₂ (%)	Na ₂ O(%)	Al ₂ O ₃ + Fe ₂ O ₃ (%)	Fe (%)	Density (g/cm ³)	Insoluble substances in water	Module (SiO ₂ / Na ₂ O)
Values	25,0– 27,5	11,5– 12,5	Max 0,3	Max 0,02	1,40– 1,45	Max 0,15	2,0–2,4

For the preparation of the samples, the ratio AA / FA = 1,2 was used, while the Na₂SiO₃/NaOH ratio was 2; 2,5 and 3. Mixing ratios and designations of fly ash-based geopolymer samples are shown in the table 3. The samples were manually blended and vibrated on a vibrating table for 10 minutes. The binding process is exothermic so the samples must be hermetically closed. After 24 h, the samples were taken out of the mold and wrapped in nylon bags, as shown in Figure 2. The wrapped samples were kept in the oven for 24 hours at activation temperatures of 60, 70 and 80 °C.

Table 3 - Mixing ratios and designations of fly ash-based geopolymer samples

Uzorak	A/FA	VS/NaOH
A	1,2	2.0
B		2.5
C		3.0



Figure 2 - Prepared of samples[5,7]

RESULTS AND DISCUSSION

After temperature activation, the samples were taken out from the bags and kept at room temperature. The compressive strength of the samples was tested after 2, 7 and 28 days after thermally treated. The results of the compressive strength are shown in Table 4, and in Figure 3.

Table 4. Compressive strength of the tested samples

Samples	Compressive strength (MPa)		
	2 days	7 days	28 days
A60	19.55	28	34.45
A70	23.05	27.3	39.95
A80	32	32.2	37.45
B60	15.26	23.8	25.8
B70	26.1	27.62	30
B80	29.95	33	39.5
C60	26.8	30.05	39.2
C70	28.15	33	46.9
C80	27.35	29.3	38.4

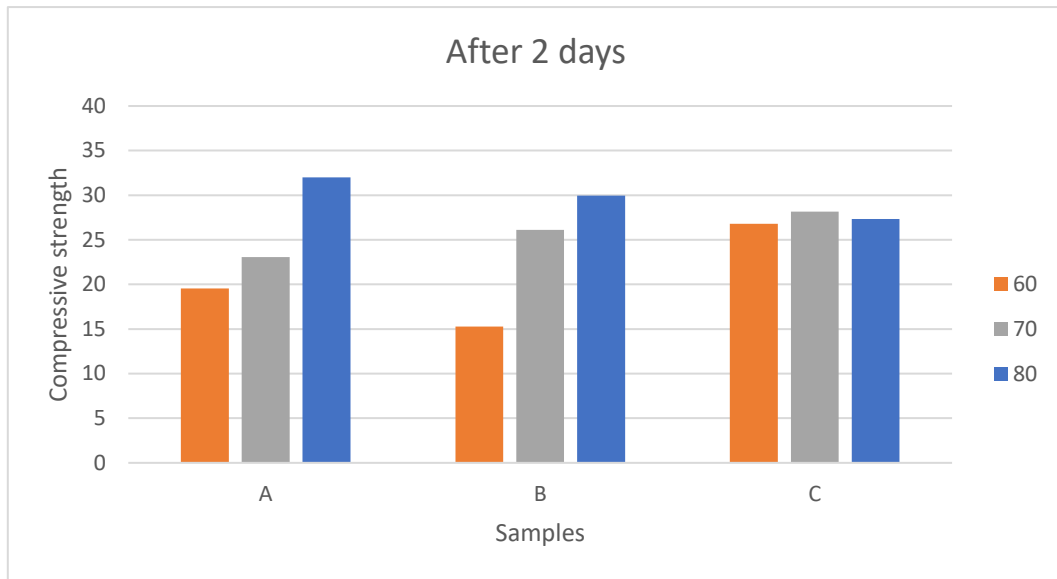


Figure 3 - Dependence of compressive strength after 2 days on temperature and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio

Figure 3 shows the dependence of the compressive strength after 2 days on the heat treatment temperature and the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. It can be seen from the figure that the compressive strength of the samples treated at a temperature of 70°C decreases slightly with an increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. The compressive strength value after 2 days of 32 MPa has a sample treated at a temperature of 80 °C with a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2$.

According to the EN 197-1 standard, the compressive strength of cement after 2 days must be greater than or equal to 10 MPa for cement classes 32.5R and 42.5N, greater than or equal to 20 MPa for cement classes 42.5R and 52.5N and greater or equal to 30 MPa for cement class 52.5R.

Figure 4 shows the dependence of compressive strength after 7 days on temperature and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio.

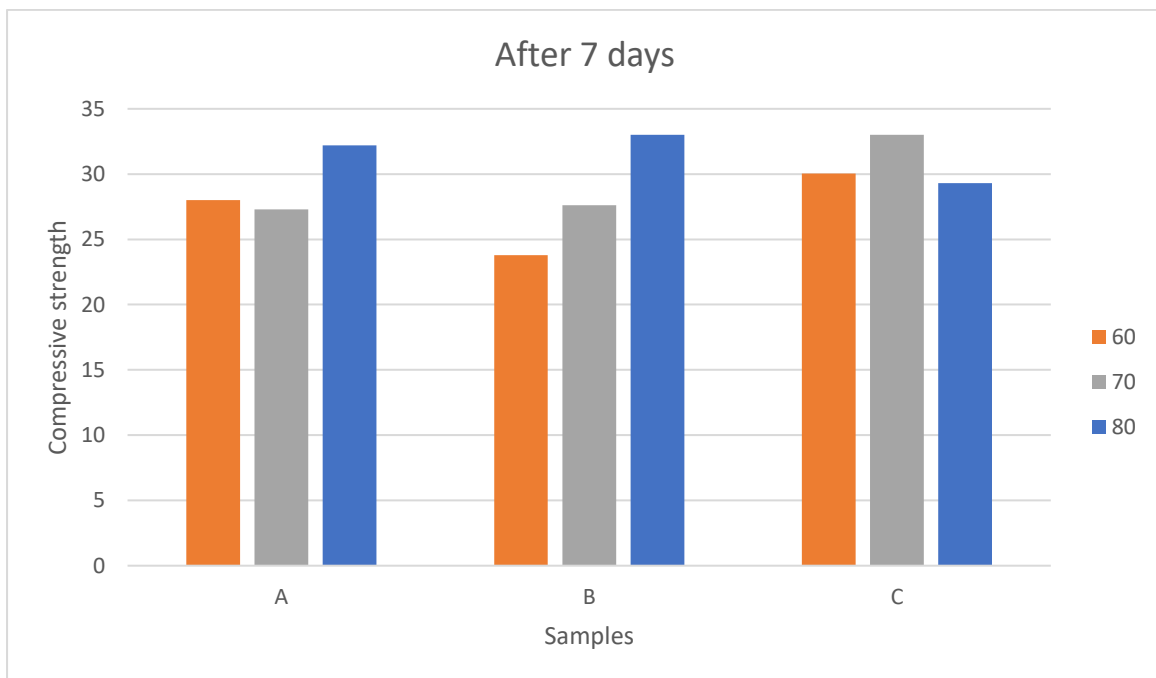


Figure 4 - Dependence of compressive strength after 7 days on temperature and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio

From Figure 4, it can be seen that the compressive strength after 7 days is the highest in samples with a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2.5$ at temperatures of 70°C , kao i uzorak with a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 3$ at temperatures of 80°C . With an increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, the compressive strength of the samples also increases.

Figure 5 shows the dependence of compressive strength after 28 days on temperature and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio.

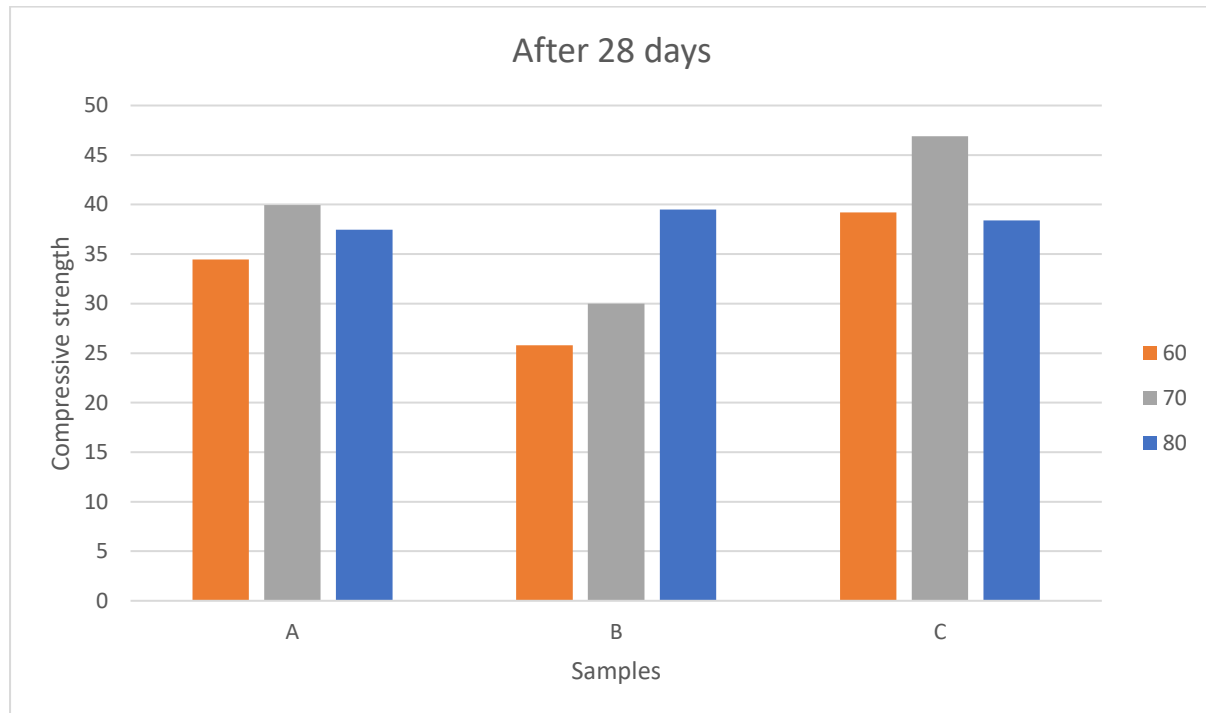


Figure 5 - Dependence of compressive strength after 28 days on temperature and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio

Figure 5 shows that the compressive strength after 28 days of samples treated at a temperature of 80°C and at a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 3$ increases to 46,9 MPa. The samples thermally treated at a temperature of 80°C have the most uniform compressive strength.

If we compare the compressive strength of the obtained geopolymers and the compressive strength of cement according to EN 197-1, geopolymers prepared with fly ash of the Stanari thermal power plant with a ratio of alkali and fly ash of 1.2, treated at a temperature of 80°C with ratios of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 3$ would correspond to cement class 42.5N and 42.5R.

CONCLUSION

The following can be concluded from all of the above:

- Materials similar to cement, so-called geopolymers, can be obtained from the fly ash of the Stanari Thermal Power Plant, Bosnia and Herzegovina with the addition of alkali.
- The compressive strength of the samples treated at a temperature of 70°C decreases slightly with an increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. The compressive strength value after 2 days of 32 MPa has a sample treated at a temperature of 80°C with a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2$.
- The compressive strength after 7 days is the highest in samples with a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2.5$ at temperatures of 70°C , kao i uzorak with a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 3$ at temperatures of 80°C . With an increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, the compressive strength of the samples also increases.

- The compressive strength after 28 days of samples treated at a temperature of 80 °C and at a ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH} = 3$ increases to 46,9 MPa. The samples thermally treated at a temperature of 80 °C have the most uniform compressive strength.
- If we compare the compressive strength of the obtained geopolymers and the compressive strength of cement according to EN 197-1, geopolymers prepared with fly ash of the Stanari thermal power plant with a ratio of alkali and fly ash of 1.2, treated at a temperature of 80 °C with ratios of $\text{Na}_2\text{SiO}_3/\text{NaOH}$ 3 would correspond to cement class 42.5N and 42.5R.

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