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INFLUENCE OF Na_2SiO_3/NaOH RATIOS ON THE COMPRESSIVE STRENGTH OF FLY ASH BASED GEOPOLYMERS FROM THERMAL POWER PLANT STANARI IN BIH

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ABSTRACT

In this paper, the influence of Na_2SiO_3 /NaOH ratio on the compressive strength of fly ash - based geopolymers was tested. The fly ash from thermal power plant Stanari near Doboj, BiH is used.The ratio of alkali activator to fly ash (AA / FA ratio) was constant in all samples and it was 0.8. A 12M NaOH solution was used. The heat treatment temperatures of the samples were 60, 70 and 80 ° C. The samples are made of fly ash and alkali activators, without the addition of aggregates, so they are geopolymer pastes. The compressive strengths after 1, 7 and 28 days from the thermal treatmentwere tested. The obtained values of compressive strengths, especially after 1 and 7 days, are far above the compressive strengths of cement.

1. INTRODUCTION

After water, concrete is the second most used material in the world, and cement is one of the components in concrete. However, cement production requires large amounts of raw material, mainly limestone and clay. During cement production, carbon dioxide is emitted into the atmosphere. During the production of 1 ton of cement, approximately 1 ton of CO_2 is emitted into the atmosphere. If we take 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 CO_2 is released into the atmosphere. From the world's total annual CO_2 emissions, 5% is accounted for by cement production.[1]

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

Over the past 20 years, geopolymers, also known as mineral polymers or inorganic polymers, have attracted much attention as a promising new form of inorganic polymer material that could be used as a replacement for conventional or ordinary Portland cement (OPC). The development of geopolymer cement is an important step towards the production of environmentally friendly cements.

Geopolymers are inorganic polymers with a chemical composition similar to natural zeolite materials, but their structure is amorphous.The name of geopolymer was proposed by Joseph Davidovitsin 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.

Geopolymerization involves a heterogeneous chemical reaction between aluminosilicate oxides and solutions of alkali metal silicates and hydroxides under highly alkaline conditions and moderate temperatures to give amorphous to polycrystalline polymer structures, consisting of Si-O-Al and Si-O-Si bonds.[2]

In this regard, as the technology of geopolymer synthesis is based on the alkalization of the source material containing mainly silicon (Si) and aluminum (Al) in amorphous form, the similarity of some fly ash to natural aluminosilicates (due to the presence of SiO_2 and Al_2O_3in the ash) has encouraged geopolymerization as a potential technology for cement production with specific characteristics.

Fly ash (LP) is a waste material generated in coal-fired thermal power plants, which is separated from waste gases by means of electrostatic and bag filter devices. The testing work of Thermal Power PlantStanari started at the beginning of 2016. This is the first TPP that combusts crushed coal, not pulverized coal. In this TPP, coal is burned in a fluidizing layer at a lower temperature (850 to 870 ° C), from the temperature of the furnace for pulverized coal. Fly ash is collected on a bag filter and then deposited in a fly ash silo.[5]

The most commonly used alkaline component in geopolymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate. The type and concentration of the alkaline solution affects the dissolution of the fly ash.

Studies conducted by Bakri, Kamarudin et al. (2011) found that 12 M NaOHsolution gives the highest compressive strength. This result is consistent with previous studies where 12 M NaOHsolution gave better results than NaOH solutions of higher concentration. According to the findings from such research, a lower polymerization rate is obtained due to the high concentration of NaOH, which results in a decrease in strength. In contrast, other studies have found that increasing the molarity of NaOH also increases the compressive strength of geopolymers.[3]

In alkalizing fly ash, an elevated temperature is necessary for a reaction to occur at all. Mixtures with fly ash (as raw material) have a high activation energy, so in order for the reaction to start at all, this energy needs to be brought to the system in the form of heat. The geopolymerization reaction itself is exothermic, which is why heat is released during bonding, which can cause water to evaporate from the system. Water loss during the early stages of the reaction will result in poor mechanical properties, and therefore samples must be stored in hermetically sealed containers / molds.

The geopolymerization process involves a significantly rapid chemical reaction under alkaline conditions on Si-Al minerals resulting in three-dimensional polymer chains and a ring structure consisting of Si-O-Al-O bonds.

According to J. Davidovits, the mechanism of geopolymerization consists of the following steps:

1. Alkalization of raw materials
2. Depolymerization of aluminosilicates
3. Formation of oligo-sialate in gel
4. Polycondensation (growth of molecules)

5. Reticulation (networking or networking)
6. Hardening of geopolymers.

These processes generally take place simultaneously. Aluminate and silicate products are formed by dissolving solid aluminosilicate material through the process of alkaline hydrolysis with the addition of water. After dissolution, aluminosilicate products are formed, and a mixture of silicates, aluminates and aluminosilicates is formed. At high pH, the aluminosilicate dissolves rapidly and a supersaturated aluminosilicate solution is formed, leading to the formation of a geopolymer gel. During this process, water is released. After the gelling process, the system is further rearranged and reorganized with the formation of aluminosilicate structures characteristic of geopolymers.

2. MATERIALS AND METHODS

In this paper, the influence of the Na_2SiO_3 / NaOH ratio on the compressive strength of fly ash - based geopolymers from thermal power plant Stanariwasinvestigated.The fly ash from TPP Stanari, BiH, 12M NaOH solution and commercially water glass are used as material.
The chemical analysis of the fly ash TPPStanari 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]

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	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

Mesh No	Aperture µm	Volume In %	Vol Below %
8	2000		100.00
10	1700	0.00	100.00
12	1400	0.00	100.00
14	1180	0.00	100.00
16	1000	0.00	100.00
18	850	0.00	100.00
22	710	0.00	100.00
25	600	0.00	100.00
30	500	0.00	100.00

Mesh No	Aperture µm	Volume In %	Vol Below %
30	500		100.00
36	425	0.00	100.00
44	355	0.00	100.00
52	300	0.00	100.00
60	250	0.00	100.00
72	212	0.00	100.00
85	180	0.00	100.00
100	150	0.00	100.00
120	125	0.11	99.89

Mesh No	Aperture µm	Volume In %	Vol Below %
120	125		99.89
150	105	1.38	98.51
170	90	2.49	96.02
200	75	4.21	91.81
240	63	5.37	86.44
300	53	6.46	79.98
350	45	6.91	73.07
400	38	7.63	65.45

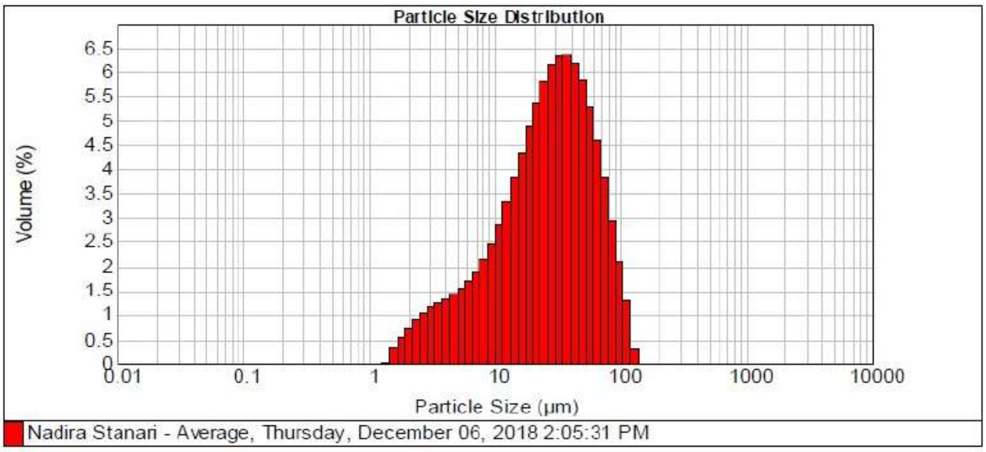


Figure 1.Granulometric composition of fly ash[5]

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.

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

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

Table 2. Characteristics of commercially water glass

Characteristics	Values
SiO_2(%)	25,0 – 27,5
Na_2O (%)	11,5 – 12,5
$Al_2O_3 + Fe_2O_3$(%)	Max 0,3
Fe (%)	Max 0,02
Density (g/cm^3)	1,40 – 1,45
Insoluble substances in water	Max 0,15
Module (SiO_2/ Na_2O)	2,0 – 2,4

For the preparation of the samples, the ratio AA / FA = 0.8 was used, while the Na_2SiO_3 / NaOH ratio was 2, 2,5 and 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 ^{0}C.

Figure 2. Prepared of samples

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 1, 7 and 28 days after thermally treated.

Figure 3.Geopolymer samples that have undergone heat treatment

3. RESULTS AND DISCUSSION

As already mentioned in the test, the ratio AA / FA = 0.8 was used, while the ratio Na_2SiO_3 / NaOH was 2, 2.5 and 3. The prepared samples were marked as shown in Table 3.

Table 3. Marks of prepared samples

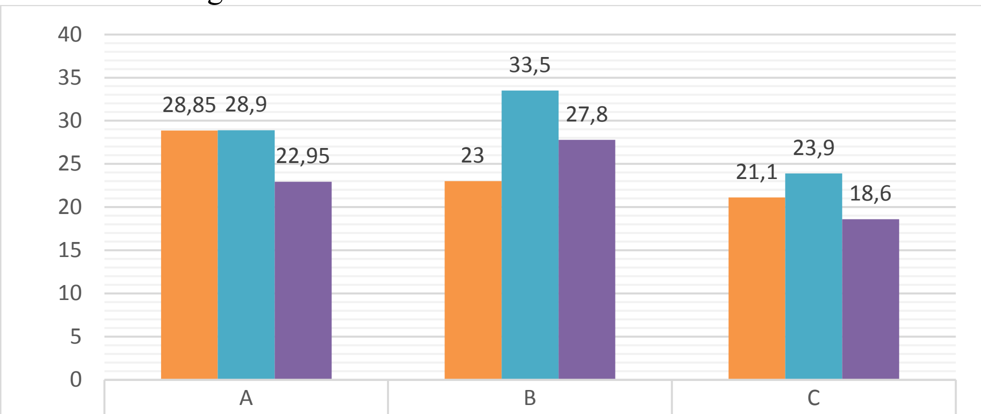
Sample mark	AA/FA ratio	Na_2SiO_3 / NaOH ratio	Treatment temperature
A60	0,8	2	60 °C
A70	0,8	2	70 °C
A80	0,8	2	80 °C
B60	0,8	2,5	60 °C
B70	0,8	2,5	70 °C
B80	0,8	2,5	80 °C
C60	0,8	3	60 °C
C70	0,8	3	70 °C
C80	0,8	3	80 °C

The compressive strength of the samples was tested after 1, 7 and 28 days, and the values of compressive strengths are shown in Table 4.

Table 4.Compressive strengths of samples tested after 1, 7 and 28 days prepared at ratio AA / FA = 0.8 and Na2SiO3 / NaOH ratio = 2, 2.5 and 3

Uzorak	Pritisna čvrstoća (MPa)		
	1 dan	7 dana	28 dana
A60	25.85	29.3	29.4
A70	28.9	31.45	32.4
A80	22.95	26.95	30.1
B60	23.0	31.4	34.55
B70	33.5	31.35	40.7
B80	27.8	27.25	38.25
C60	21.1	56.6	34.4
C70	23.9	49.65	51.6
C80	18.6	46.6	38.8

The dependence of compressive strength after 1 day on the test temperature and the Na_2SiO_3 / NaOH ratio is shown in Figure 4.

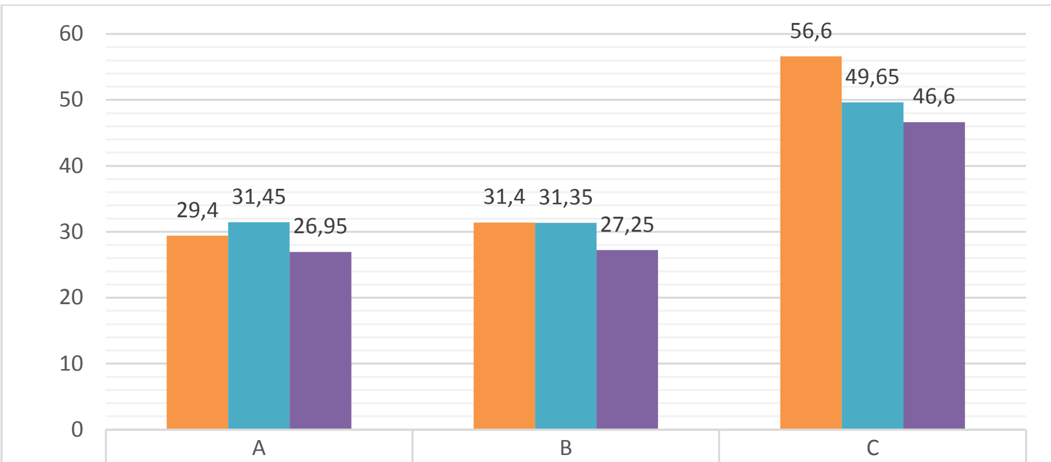


	A	B	C
60	28,85	23	21,1
70	28,9	33,5	23,9
80	22,95	27,8	18,6

Figure 4.Dependence of compressive strength after 1 day on test temperature and Na_2SiO_3 / NaOH ratio

It can be seen from Figure 4 that the compressive strength is highest in samples treated at a temperature of 70 ° C. The highest compressive strength after 1 day has a sample with a ratio of Na_2SiO_3 / NaOH= 2.5 which was thermally treated at a temperature of 70 ° C which is 33.5 MPa. In samples treated at 60 ° C, the compressive strength decreases after 1 day with increasing Na_2SiO_3 / NaOHratio. The compressive strength of samples treated at temperatures of 70 and 80 ° C show the highest compressive strength at the ratio Na_2SiO_3 / NaOH= 2.5. It can also be concluded that all tested samples have high compressive strengths after 1 day ranging from 18.6 to 33.5 MPa.

Figure 5 shows the compressive strengths of the samples tested after 7 days depending on theNa_2SiO_3 / NaOHratio and temperature.



	A	B	C
60	29,4	31,4	56,6
70	31,45	31,35	49,65
80	26,95	27,25	46,6

Figure 5. Dependence of compressive strength of samples after 7 days on test temperature and Na_2SiO_3 / NaOH ratio

From Figure 5 it can be seen that the compressive strengths of the samples tested after 7 days increase with increasing Na_2SiO_3 / NaOHratio. The highest value of compressive strength has a sample that was treated at a temperature of 80 ° C and whose ratio is Na_2SiO_3 / NaOH = 3 and is 56.6 MPa. If samples with the ratio Na_2SiO_3 / NaOH = 3 are observed, it can be noticed that with increasing temperature of thermal treatment, the compressive strength decreases. It can also be concluded that all tested samples have high compressive strengths ranging from 26.96 to 56.6 MPa.

Figure 6 shows the dependence of the compressive strength of the samples after 28 days on temperature andNa_2SiO_3 / NaOH ratio.

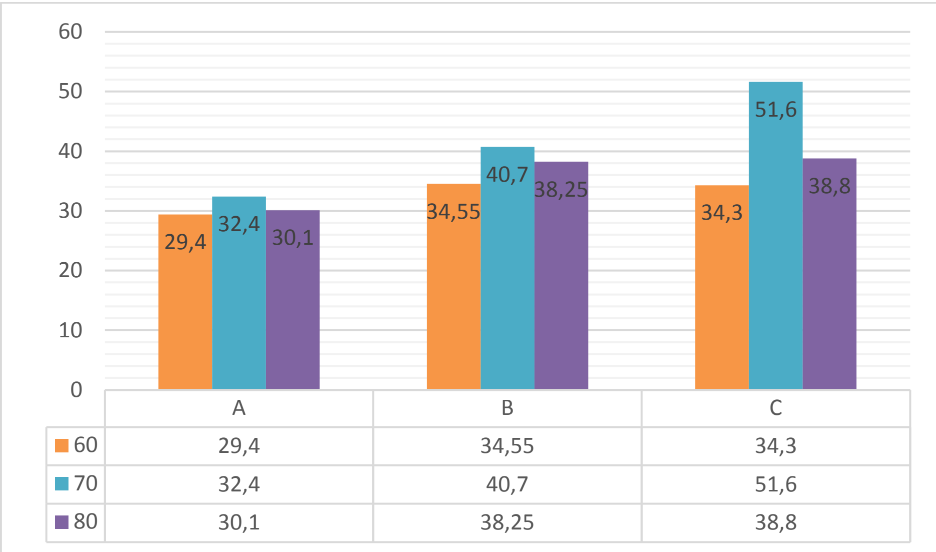


Figure 6. Dependence of compressive strength of samples after 28 days on temperature and Na_2SiO_3 / NaOHratio

It can be seen from Figure 6 that the compressive strength of the samples increase with increasing Na_2SiO_3 / NaOH ratio and at a temperature of 70 ° C. Samples treated at a temperature of 70 ° C have the highest value of compressive strength. A sample treated at 70 ° C and having a Na_2SiO_3 / NaOH = 3 ratio has a compressive strength after 28 days of 51.6 MPa. It can also be concluded that all tested samples have high compressive strengths ranging from 29.4 to 51.6 MPa.

4. CONCLUSIONS

Based on the obtained results, the following can be concluded:

• The highest compressive strength of the samples tested after 1 day has a sample with the ratio Na_2SiO_3 / NaOH= 2.5 which was thermally treated at a temperature of 70 ° C which is 33.5 MPa.

• The highest value of compressive strength of samples tested after 7 days has a sample that was treated at a temperature of 80 ° C and whose ratio is Na_2SiO_3 / NaOH = 3 and is 56.6 MPa.

• The highest value of compressive strength of samples tested after 28 days has a sample that was treated at a temperature of 70 ° C and whose ratio is Na_2SiO_3 / NaOH= 3 and is 51.6 MPa.

• The optimal temperature of thermal treatment of fly ash-based geopolymers from TPP Stanari is 70 ° C.
• The optimal ratio of Na_2SiO_3 / NaOH, with a ratio of AA / FA of 0.8, for geopolymers based on fly ash of TPP Stanari is 3.

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