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The basic mechanical properties of the fluidised bed combustion fly ash-based geopolymer

Podstawowe cechy mechaniczne geopolimeru na bazie fluidalnego popiołu lotnego

Abstract

The main goal of the research was to check the influence of different factors on the mechanical behaviour of the fluidised bed combustion (FBC) fly ash-based geopolymer. Tests have shown that the increasing the proportion of sodium silicate to sodium hydroxide causes a decrease of compressive strength and an increase of flexural strength. The addition of aggregate significantly increased flexural strength but decreases compressive strength. Samples cured at higher temperatures obtained higher strength. Finally, it was concluded that taking into account the mechanical behaviour, FBC fly ash-based geopolymer can be treated as an alternative building material; however, its strength is lower than a metakaolin-based geopolymer made of the same mixture composition.

Keywords: FBC fly ash, geopolymer, curing conditions, compressive strength, flexural strength

Streszczenie

Głównym celem badania było wyznaczenie wpływu wybranych czynników na wytrzymałość geopolimeru bazującego na fluidalnym popiele lotnym. Badanie wykazało, że wzrost stosunku masowego szkła wodnego do wodorotlenku sodu powoduje spadek wytrzymałości na ściskanie i wzrost wytrzymałości na rozciąganie geopolimeru. Dodatek kruszywa (piasku) powoduje natomiast wzrost wytrzymałości na rozciąganie i spadek wytrzymałości na ściskanie. Odnotowano, że próbki dojrzewające w wyższych temperaturach uzyskują wyższą wytrzymałość. Na podstawie wykonanych badań stwierdzono, że biorąc pod uwagę wytrzymałość badanego geopolimeru, można uważać go za alternatywny materiał budowlany. Wytrzymałość badanego geopolimeru jest jednak niższa od wytrzymałości geopolimeru na bazie metakaolinu.

Słowa kluczowe: popiół fluidalny, geopolimer, warunki dojrzewania, wytrzymałość na rozciąganie i na ściskanie

1. Introduction

Fluidised-bed combustion (FBC) fly ash is a by-product of the combustion process in a fluidised-bed boiler furnace. Fluidised-bed combustion occurs at relatively low temperatures (around 800–900°C). For this reason, obtained fly ash has a low glassy phase and consists mainly of irregular dehydrated grains and dehydroxylated gangue minerals of significant pozzolanic activity [3, 11]. The characteristics of FBC fly ash differ from the characteristics of fly ash from conventional combustion process. As a result of its properties, the possibility of using FBC fly ashes as an addition to concrete is limited [2]. In Poland, FBC fly ashes are used mainly for the stabilisation of soils, in mining technologies, for geotechnical filling during earthworks, as an addition in the ceramic industry and sometimes in building binders [11]. Since fluidised-bed combustion is becoming more popular nowadays, scientists are trying to find new uses for FBC fly ash. For example, Brzozowski [2] presents research on the application of FBC fly ash in underwater concrete. He reports that it is possible to use FBC fly ash in underwater concrete; however, both compressive and tensile strength decreases with the increase of the FBC fly ash content. He places particular emphasis on the problem of the workability of the concrete mixture with the addition of FBC fly ash. The number of works devoted to FBC fly ash-based geopolymer is small, but this subject has been raised in the past. Chindaprasirt et al. [3] presents tests performed on aFBC fly ash-based geopolymer. Tests showed that there is the possibility to make a durable FBC fly ash-based geopolymer; however, the compressive strength can be significantly enhanced (from 10 MPa to around 25 MPa) through the addition of pulverised coal combustion high calcium fly ash.

The main goal of works presented in this paper was to examine the possibility of using particular FBC fly ash coming from the Polish company TAURON Polska Energia S.A. The authors also wanted to check the influence of different factors on the geopolymer's strength.

1.1. The influence of the activator ratio on geopolymers strength

Experiments concerning the issue of the influence of the ratio of sodium silicate to sodium hydroxide on geopolymers strength give diverse results. Hardjito et al. [7] claims that the increase of sodium silicate to the sodium hydroxide mass ratio causes significant growth of the compressive strength of a fly ash-based geopolymer. Similarly, research shown in [9] proves that the strength of *a* metakaolin-based geopolymer increases with the increase of sodium silicate to the NaOH molar ratio. Heah et al. [8] did not notice any direct dependence between the ratio of sodium silicate to NaOH and the compressive strength of a kaolin-based geopolymer after seven days, but reports the general increase of strength with the increase of the above-mentioned ratio after one-hundred-eighty days. Poowancum et al. [10] came to different conclusions. According to [10], the strength of a clay-based geopolymer decreases rapidly with the increase of the volume ratio of sodium silicate to sodium hydroxide from 0.5 to 1.0. It is also reported that strength increases for the ratio of 1.5. On the contrary,

Fernandez-Jimenez [6] reports that the compressive strength of *a* fly ash-based geopolymer decreases constantly with the increase of the sodium silicate content in the mixture.

1.2. The influence of the curing conditions on the strength of geopolymers

Many scientific papers are concerned with the influence of curing conditions, especially the influence of curing temperature on the mechanical behaviour of different kinds of geopolymer. Bing-hui et al. [1] found that compressive strength tested after seven days increases monotonically with the increase of the curing temperature of metakaolin-based geopolymer samples. However, the growth of the strength was registered only to a temperature of 60°C; for higher curing temperatures, a significant decrease in strength was noticed. Ekaputri et al. [4] came to different conclusions. Scientists did not notice any significant difference after seven days in either the flexural or the compressive strength of metakaolin-based geopolymer samples cured at different temperatures. No significant influence of curing temperature on geopolymer density was noticed during this experiment. But it was registered that after fourteen days, the compressive strength of samples cured at higher temperatures is greater. The decrease of density of a metakaolin-based geopolymer with the increase of the curing temperature was described in [12]. According to [12], both the flexural and compressive strength of a geopolymer after one day increases with the increase of the curing temperature but with time, the strength of samples cured at lower temperatures (20°C and 40°C) is higher than the strength of samples cured at 60°C or 80°C. Swanepoel et al. [13] identified a decrease in the density of a fly ash-based geopolymer with increases to the curing temperature. In their paper, it can be found that after seven and twenty-eight days, the strength of samples cured at 40°C and 50°C is higher than the strength of samples cured at 60°C or 70°C. By contrast, Hardjito et al. [7] describe the almost monotonic growth of the strength of a fly ash-based geopolymer with the increase of the curing temperature. Zhang et al. [14] performed testing on a red mud-fly ash-based geopolymer and came to the conclusions that both short- and long-term strength is higher for samples cured at higher temperatures.

As can be concluded, both the influence of the curing conditions and the ratio of sodium silicate to sodium hydroxide on geopolymers strength depends not only on the type of precursor but also on the specific mixture composition and can differ even within one general type of geopolymer. This, as well as the fact that there are not many reports from experiments performed on the fluidised bed combustion ashes, are the main reasons why authors decided to check the influence of curing conditions and the ratio of sodium silicate to NaOH on the strength of the geopolymer made of the new mixture.

2. Laboratory tests

The main goal of the laboratory tests was to establish the flexural and compressive strength and the density of FBC fly ash-based geopolymer samples. In the first part of testing, the influence of the ratio of sodium silicate to sodium hydroxide on the strength of the FBC

fly ash-based geopolymer was investigated. In the second part of testing, the strength of FBC fly ash-based geopolymer samples containing different amounts of aggregate (sand) was compared with the strength of metakaolin-based geopolymer samples. In the last part of the experiment, the influence of the curing temperature on the strength of geopolymer samples made from one chosen mixture was investigated. A flexural strength test was performed on prismatic samples with dimensions of 40x40x160 mm. Broken halves of the samples were subjected to compressive strength testing in accordance with standard EN 196-1:2016 [5].

2.1. Mixtures compositions

Several different mixtures containing different amounts of FBC fly ash, sand, sodium silicate and sodium hydroxide were prepared. Three control mixtures containing metakaolin instead of FBC fly ash were also prepared. The water solution of sodium hydroxide was prepared a minimum twenty-four hours before the mixture preparation. In all mixtures, the concentration of sodium hydroxide was equal to 10 mol/L. The used sodium silicate solution had a ratio of SiO_2 to Na_2O of between 2.4 and 2.6. The minimum content of oxides (SiO_2 and Na_2O) in the sodium hydroxide solution was 39%. The particle size distribution of sand used as an aggregate is presented in Fig. 1.

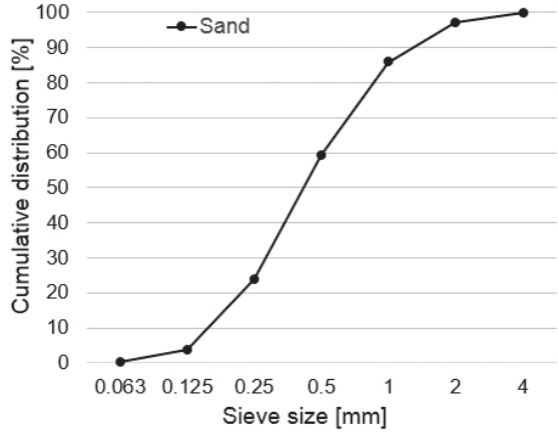

Fig. 1. Particle size distribution of the sand

The compositions of all mixtures are presented in Table 1. Mixtures are identified with codes which represent the main characteristics of their composition. In the first four geopolymer mixtures, either FBC fly ash (FA) or metakaolin (M) were used as the precursors. Numbers 2, 2.5 and 3 represent the ratio of sodium silicate to sodium hydroxide. The next four mixtures (5, 6, 7 and 8) contain the precursor (FA – fly ash or M – metakaolin) and aggregate (sand). The numbers following the letters in the name of the mixtures represent the percentage mass ratio of the precursor to the aggregate. There is a small difference in the amount of activator added to the mixtures containing metakaolin and the FBC fly ash.

Table 1. Composition of geopolymer mixtures

No	Mixture	FBC Fly ash		Metakaolin		Sand		Sodium silicate		NaOH	
		[kg/m³]	[%]	[kg/m³]	[%]	[kg/m³]	[%]	[kg/m³]	[%]	[kg/m³]	[%]
1	**FA 2**	1083	51.7	–	–	–	–	674	32.2	337	16.1
2	**FA 2.5**	1083	51.7	–	–	–	–	723	34.5	289	13.8
3	**FA 3**	1083	51.7	–	–	–	–	762	36.3	253	12.0
4	**M 2**	–	–	1083	51.7	–	–	674	32.2	337	16.1
5	**FA 33/67**	657	24.9	–	–	1335	50.6	430	16.3	215	8.1
6	**FA 50/50**	898	33.7	–	–	898	33.7	581	21.8	285	10.7
7	**M 33/67**	–	–	657	25.9	1335	52.6	365	14.4	182	7.2
8	**M 50/50**	–	–	898	36.4	898	36.4	449	18.2	225	9.1

The difference is caused by the greater water absorption of the FBC fly ash. The FBC fly ash-based geopolymer mixtures need more liquid to obtain proper workability.

2.2. Preparation of the samples

All samples were prepared in the same manner. In the case of samples containing the precursor and aggregate, these two dry components were first mixed together. The activators were then mixed together for 5 minutes. The activators were then poured into the vessel with the dry components and all ingredients were mixed together. At the end of the process, the mixture was placed in the moulds and covered. All mixtures were cured for the first twenty-four hours in the climatic chamber at a temperature of 60°C and humidity 40%. After this time, the samples were demoulded and cured at room temperature and with a humidity level of around 25–30% in the laboratory for the remaining six days. Strength tests were conducted seven days after the samples were prepared.

In addition to the above, mixture no 3 FA 3 was chosen for the determination of the influence of curing temperature on the strength and density of the FBC fly ash-based geopolymer. The next three batches of this mixture were prepared. One batch was cured for the first 24 hours in the climatic chamber at a temperature of 40°C and a humidity of 40%. After this time, the samples were demoulded and cured at room temperature for the next six days. Two other batches were cured for the whole seven days at room temperature. One of these was demoulded after twenty-four hours and the second was demoulded after seven days (immediately prior to the strength test).

2.3. The tests results

The test results are presented in bar graphs. The bars represent the average value of flexural and compressive strength. The numbers written above the bars are the exact value of the average strength. On each bar, there are shown the minimum and maximum strength values obtained in each set of samples in the form of small black line segments. The upper line segment is the maximum and the lower line segment is the minimum value of strength.

In addition to the flexural and compressive strengths, the densities of samples were also measured. Each sample was weighed before the strength test. The mass of each sample was divided by its volume to obtain the density. The tables presented below present the average value of densities of samples from each set.

2.3.1. The influence of sodium silicate to sodium hydroxide ratio

Figure 2 presents the results of flexural and compressive strength tests performed on FBC fly ash-based geopolymer samples activated with the addition of different proportions of activators.

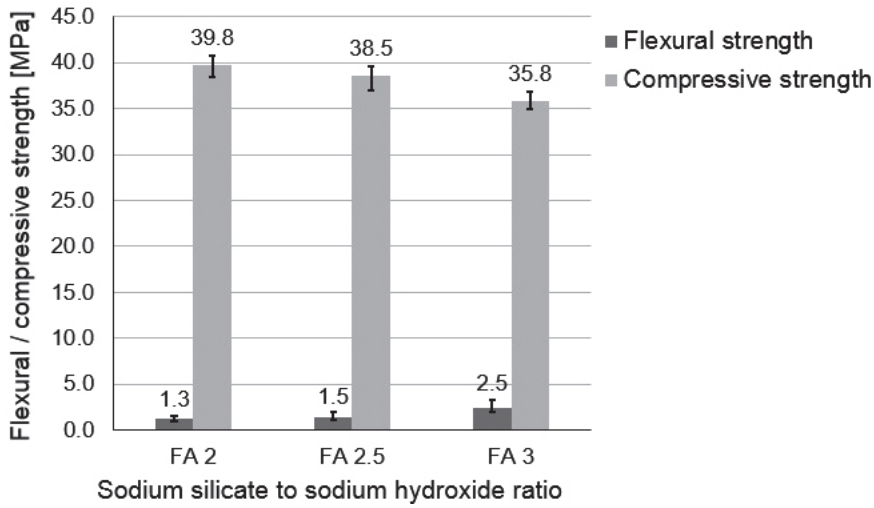

Fig. 2. Flexural and compressive strength of geopolymer samples containing different sodium silicate to sodium hydroxide ratios, after 7 days

As shown in the graph, flexural strength slightly increases with increases in the ratio of sodium silicate to sodium hydroxide while the compressive strength decreases.

Table 2 presents the average densities of FBC fly ash-based geopolymer samples made from mixtures containing different ratios of sodium silicate to sodium hydroxide. No strict dependence between activator ratio and density was observed. The differences in densities between geopolymers made of different mixtures are small.

Table 2. Density of geopolymer made of different mixtures

	FA 2	FA 2.5	FA 3
Density [kg/m^3]	1570	1520	1530

2.3.2. The comparison of strength of FBC fly ash-based geopolymer with metakaolin-based geopolymer

Figures 3 and 4 present a comparison of the flexural and compressive strength test results obtained from FBC fly ash-based geopolymer samples with results obtained from metakaolin--based geopolymer samples. The graphs show results of samples containing 33, 50 and 100% of precursor (FBC fly ash or metakaolin). The abbreviation P/A refers to precursor/aggregate. The numbers following the letters represent the percentage mass ratio of the precursor to the aggregate. All of the compared samples contain sodium silicate to sodium hydroxide at the ratio 2.0.

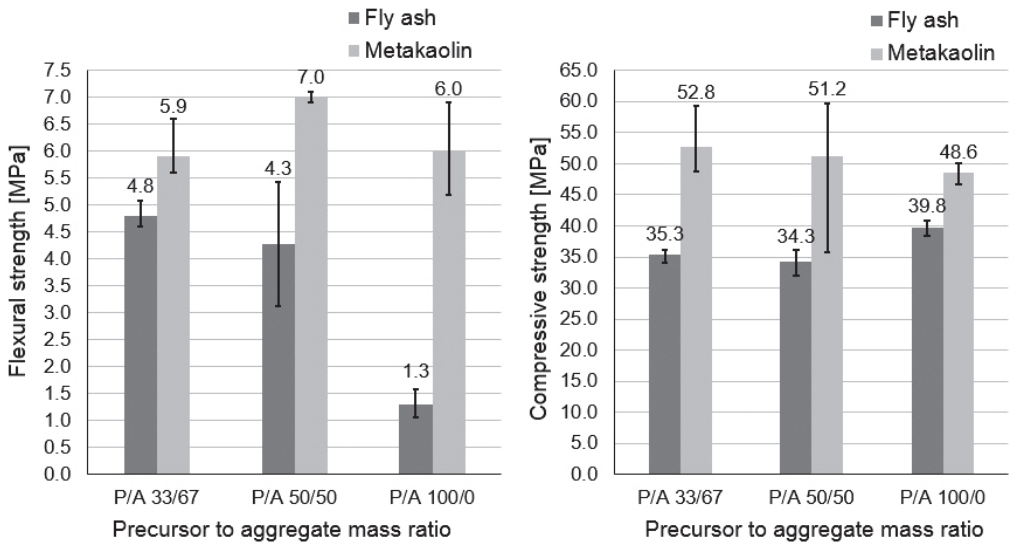

Fig. 3. Flexural and compressive strength of geopolymer samples based on different precursors and having different precursor to aggregate ratios; after 7 days

Figure 3 shows that the FBC fly ash-based geopolymers have lower flexural strength than the metakaolin-based geopolymers. The biggest difference is between the samples containing only the precursor without any aggregate. The metakaolin-based geopolymer without aggregate addition has over 4.5 times the flexural strength of the fly-ash based geopolymer. According to the diagram, the flexural strength of the FBC fly ash-based geopolymers decreases with the decrease of the aggregate content. In the case of the metakaolin-based geopolymers, there is no monotonic dependence between the aggregate content and flexural strength.

The compressive strength of the FBC fly ash-based geopolymers is lower than that of the metakaolin-based geopolymers. There is no clear dependence between the aggregate content

and the compressive strength in either the case of the FBC fly ash-based geopolymers or in the case of the metakaolin-based geopolymers. Contrary to the results of flexural strength, the FBC fly ash-based samples containing only the precursor obtained the highest compressive strength. The standard deviation of the compressive strength results obtained by the FBC fly ash-based geopolymer was much smaller than that of the metakaolin-based geopolymer.

Table 3 presents the average densities of FBC fly ash-based and metakaolin-based geopolymer samples containing different amounts of aggregate. The density of the FBC fly ash-based geopolymer is smaller than that of the metakaolin-based geopolymer. In both cases, the density increases with the increase of the aggregate (sand) content.

Table 3. The density of samples made with different ratios of precursor to aggregate (P/A)

Density [kg/m^3]		**P/A 33/67**	**P/A 50/50**	**P/A 100/0**
	FBC fly ash	1850	1780	1570
	metakaolin	2080	1950	1590

2.3.3. The influence of curing temperature on FBC fly ash-based geopolymer strength

During this part of the experiment, it was observed that samples cured for the whole time at room temperature and demoulded after twenty-four hours got cracked. The system of cracks appeared on the upper surface of samples and in the upper parts of the side surface (see Fig. 4). Furthermore, these samples were affected by apparent shrinkage. After seven days, the samples lost around 3 mm of length and 1 mm of width. The cracks and shrinkage were probably caused by the fact that samples were demoulded and as a consequence, all the surfaces were exposed to air before the reactions inside the geopolymer's structure were finished. The strength of cracked samples was not included in the graphs. No apparent shrinkage nor cracks were registered in the case of other samples. For comparison, Fig. 5 presents uncracked surfaces of samples cured for the first twenty-four hours at elevated temperatures of 40°C and 60°C.

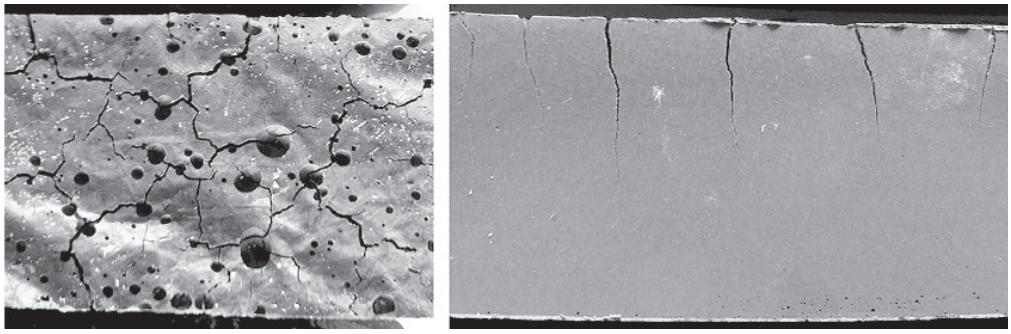

Fig. 4. Cracked upper and side surfaces of the sample cured at 20°C and demoulded after 24 hours

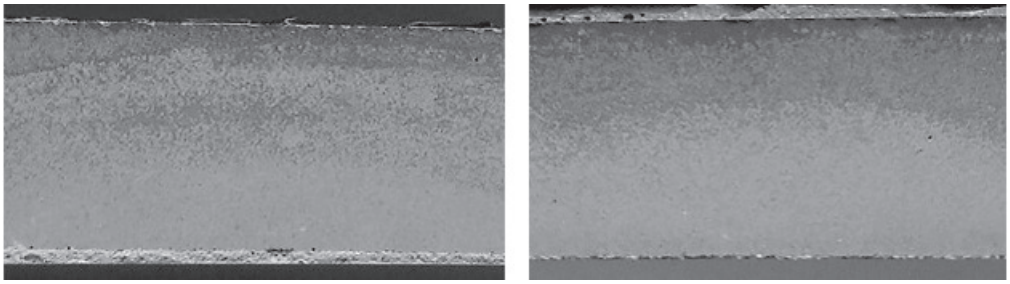

Fig. 5. Uncracked surface of the sample cured at 40°C and 60°C for the first 24 hours

Figure 6 presents the results of flexural and compressive strength tests performed on FBC fly ash-based geopolymer samples cured under different conditions. The curing conditions are described on the X-axis. Samples cured at room temperature for the entire time and demoulded after seven days (immediately prior to the test) are marked as 20°C. Samples cured for the first twenty-four hours at temperatures of 40°C and 60°C are marked accordingly. These two groups of samples were demoulded after twenty-four hours and cured at room temperature for the rest of the time. This test was conducted on samples made of the mixture named as FA 3.

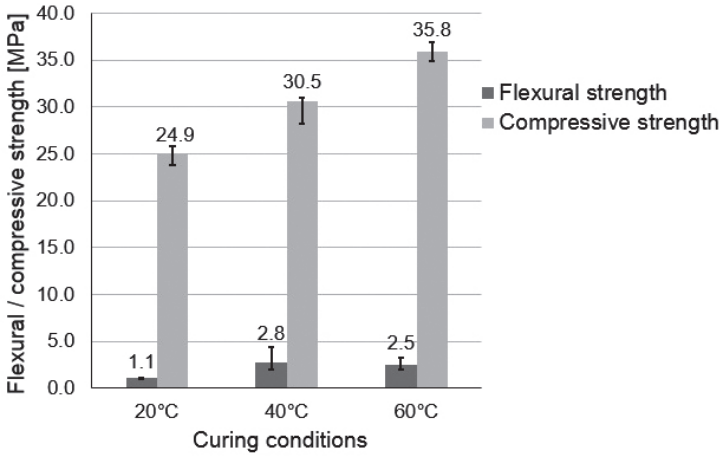

Fig. 6. Flexural and compressive strength of geopolymer samples after 7 days and cured in different conditions

The graph shows that compressive strength increases with the increase of the curing temperature. The growth of compressive strength is almost monotonic. In the case of flexural strength, it can be seen that the strength of samples cured in the climatic chamber at increased temperature for the first 24 hours is higher than of samples cured all the time at room temperature. However, the flexural strength of samples cured at 40°C is slightly higher than the strength of samples cured at 60°C. The test has also shown that FBC fly ash-based geopolymers should not be demoulded after 24 hours while cured at room temperature because cracks and significant shrinkage are unwanted and dangerous features.

Table 4 presents the average densities of the FBC fly ash-based geopolymer cured under different conditions. It was noticed that density decreases with the increase of the curing temperature; however, the difference between the density of the samples cured at 40°C and at 60°C is small. The higher density of samples cured at room temperature is probably caused by a greater amount of unevaporated water inside the structure. However, it could also be caused by differences in the structure formed during the curing process.

Table 4. Density of the geopolymer cured under different conditions

	20°C	**40°C**	**60°C**
Density [kg/m^3]	1750	1580	1530

3. Summary

The above paper presents tests performed on the fluidised bed combustion fly ash-based geopolymer. The main goal of the tests was to verify the influence of different factors on the mechanical behaviour of the FBC fly ash-based geopolymer and to assess whether it is possible to treat it as a building material.

Three different ratios of sodium silicate to sodium hydroxide were used in the mixtures: 2.0, 2.5 and 3.0. It was observed that compressive strength decreases and flexural strength increases slightly with the increases to the ratio of sodium silicate to sodium hydroxide. No influence of the activator ratio on the density of the geopolymer was observed.

The influence of the curing temperature on mechanical behaviour was checked on one chosen mixture. Two batches were cured for the whole duration at room temperature and two were cured at higher temperature (40°C and 60°C) for the first twenty-four hours. The experiment showed that the compressive strength increases slightly while the density decreases with the increase of the curing temperature. It was also registered that geopolymer samples cured at room temperature and demoulded after twenty-four hours are cracked while the surface of samples demoulded after seven days is plain.

Two mixtures were prepared with the addition of aggregate (sand) to the precursor at different mass proportions. The strength results were compared with results obtained from metakaolin-based geopolymer samples of almost the same composition. It occurred that the addition of sand significantly increases flexural strength but decreases compressive strength. All FBC fly ash-based samples achieved lower strength results than metakaolin-based samples. In the case of both precursors, the addition of sand increases the density of the samples.

The highest compressive strength (39.5 MPa) was obtained by samples containing the precursor and activators mixed at a ratio of 2 and cured at 60°C. The highest flexural strength (4.8 MPa) was obtained by samples containing 33% of precursor and 67% of aggregate with activators mixed at a ratio of 2 and cured at 60°C.

To sum up, taking into account the mechanical behaviour of FBC fly ash-based geopolymer, this material can be treated as an alternative building material.

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