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Geopolymers Based on Fly Ash from the Bełchatów Power Plant †

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Abstract: Geopolymer materials are attracting increasing interest from scientists due to their specific properties and the possibility of using waste materials from the power industry for their production. The most common raw material for their production is fly ash from the combustion of hard coal in pulverized coal boilers, but it is also possible to use ash from the combustion of lignite for this purpose. This article presents the results of a study of geopolymers produced with the use of ashes from lignite combustion at the Bełchatów Power Plant. It includes characterization of the ashes (laser particle size analysis, SEM/EDS morphology, XRD phase composition) and the strength properties of geopolymers made from these ashes and activated with 10 M and 14 M aqueous sodium hydroxide solution with water glass. As a result of this study, it was found that it is possible to obtain geopolymers characterized by flexural strength of almost 3 MPa and compressive strength of 30 MPa. A comparison of activators with concentrations of 10 M and 14 M made it possible to conclude that, due to the lack of significant differences in the properties of the obtained geopolymers, from an economic point of view, it is more advantageous in this case to use activators with a lower concentration.

Keywords: geopolymers; fly ash; fly ash from lignite; Belchatów; alkaline activation; flexural strength; compressive strength

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1. Introduction

Fly ash is a waste material that settles in electrostatic precipitators as a residual after the combustion of coal dust in the furnaces of a power plant or thermal power plant. Fly ashes vary in chemical and phase composition. The best-known fly ashes are those with a high silica or calcium content. In this paper, the latter will be presented. Fly ash from the Bełchatów mine is ash with a high calcium oxide content. This material is a by-product of lignite coal combustion. This ash can come from conventional furnaces or be generated by dry flue gas desulfurization (from conventional or fluidized bed furnaces). The concentration of reactive calcium oxide required as a pozzolan and hydraulic component in the whole mixture is more than 10% for lignite fly ash [1–3]. According to EN 197-1 [4], only the fly ash from boiler furnaces can be used. However, EN 206 [5] states that lignite fly ash cannot be used as a Type II active additive.

In Poland, lignite fly ash is a by-product of combustion mainly in the boilers of the Bełchatów Power Plant and Combined Heat and Power Plant, as well as Pątnów, Adamowa and Konin (the PAK region). Table 1 shows the chemical composition of the lignite fly ash from the Bełchatów Power Plant and, for comparison, Table 2 shows the coal fly ash from the Skawina Power Plant. Tables 3 and 4 show the phase composition of the fly ash from the Bełchatów Power Plant and, for comparison, the phase composition of fly ash from hard coal. The data presented in Tables 1–4 highlight the great diversity in domestic fly ashes. The fly ash from the Bełchatów Power Plant has the characteristic of calcium aluminosilicates and is characterized by a high content of silicon, aluminum and calcium oxide and a small amount of other oxides [6,7].

Table 1. Oxide composition of the Belchatów lignite fly ash.

Precursor	Oxide Composition (wt%)									
	LOI *	**SiO_2**	**CaO**	**Al_2O_3**	**Fe_2O_3**	**SO_3**	**CaO Free**	**MgO**	**K_2O**	**Na_2O**
F.A. Bełchatów **	2.1	42.8	22.5	20.5	4.4	4.3	4.1	0.9	0.2	0.1

* LOI—Loss on ignition; ** F.A. Bełchatów—Fly ash from Bełchatów.

Table 2. Oxide composition of the Skawina charcoal fly ash.

Precursor	Oxide Composition (wt%)							
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**K_2O**	**CaO**	**MgO**	**TiO_2**	**Na_2O**
F.A. Skawina ***	55.9	23.49	5.92	3.55	2.72	2.61	1.09	0.59

*** **F.A. Skawina**—Fly ash from Skawina.

Table 3. Phase composition of the Belchatów lignite fly ash.

Fly Ash from Bełchatów
Mineral components listed in the decreasing order of content
Quartz Gehlenite Anhydrite Hematite AnorthiteLarnite Ye'elemit $C_4A_3\hat{S}$ $C_{12}A_7$ C_3A Free lime Mullite
Amorphous phase
Calcium aluminosilicate glass

Table 4. Phase composition of the Skawina charcoal fly ash.

Fly Ash from Skawina
Mineral components listed in the decreasing order of content
Mullite Quartz Hematite Magnetite
Amorphous phase
Aluminosilicate glass

Fly ash from Bełchatów lignite is characterized by a more complex mineral composition compared to fly ash from Skawina coal. As shown in Tables 3 and 4, this observation applies to both the glass phase and minerals. The main minerals in lignite fly ash are quartz, gelenite, anorthite, anhydrite and calcium oxide. Typical cement clinker phases, i.e., $C_{12}A_7$, C_3A and $C_4A_3\hat{S}$, have also been identified [6]. These phases determine the hydraulic properties of fly ash. The pozzolanic and hydraulic properties of lignite fly ash are also related to the concentration of the amorphous phase. In the case of lignite fly ash, aluminosilicate glass is identified as the amorphous phase [8]. Fly ash from lignite Bełchatów is characterized by a relatively high variability in chemical and phase composition. This is also true for other characteristics that affect their functional properties [9].

The purpose of this paper is to study lignite fly ash from the Bełchatów Power Plant and Combined Heat and Power Plant as a replacement for hard coal fly ash from the Skawina Power Plant and Combined Heat and Power Plant. In this paper, the base material was tested and then specimens were made for bending and compression tests, so the mechanical strength of the finished structural material was shown. For the alkaline activation of the raw material, the same activator with different molar concentrations of 10 and 14 M NaOH was used.

2. Materials and Methods

The test samples were made from lignite fly ash, which came from the Bełchatów Power Plant (Bełchatów, Poland), with waste code 10 01 02, and river sand from a sand plant in Świetochłowice (Świetochłowice, Poland). The test material was made in a 50/50 wt.% ratio. The base material used for the study, fly ash, was tested for phase analysis and particle size distribution. Table 5 show the XRD phase analysis, while Table 6 shows the particle size distribution analysis. The reaction activator was a 10 M and 14 M NaOH solution. Technical sodium hydroxide flakes and an aqueous solution of sodium silicate R-145 with a molar modulus of 2.5 and a density of about 1.45 g/cm^3 were used. The ratio of the two components was 1:2.5. Distilled water was not used—the supplementary water added was "mains" water. To prepare the alkaline solution, solid sodium hydroxide was poured over an aqueous solution of sodium silicate and water. The solution was mixed thoroughly and allowed to equilibrate until it reached a constant concentration and temperature. The compositions of the geopolymer mixture are shown in Table 7. The samples were cured in an SLW 750 laboratory dryer (POLEKO, Wodzisław Śląski, Poland), at 60 °C for 24 h. After 28 days of sample preparations, the geopolymers were tested for flexural and compressive strength.

Table 5. Phase analysis of the Belchatów lignite fly ash.

Fly Ash from Bełchatów			
Identified Phase	**Chemical Formula**	**Percentage Share [wt.%]**	**Data Sheet Number**
Quartz	SiO_2	1.7	01-074-1811
Gehlenite	$Ca_2Al_2SiO_7$	31.3	04-015-3030
Anhydrite	$CaSO_4$	15.9	00-006-0226
Hematite	Fe_2O_3	9.8	04-006-2616
Anorthite	$CaAl_2Si_2O_8$	15.1	00-041-1486
Ye'elimite	$Ca_4Al_6(SO_4)$	5.9	04-009-7268
Chlormayenite ($C_{12}A_7$)	$C_{12}A_{14}O_{33}$	3.4	00-048-1882
Lime	CaO	3.2	04-005-4757
Mullite	$Al_6Si_2O_{13}$	13.7	00-015-0776

Table 6. Particle size analysis of the Belchatów lignite fly ash.

Material	D_{10} [µm]	D_{50} [µm]	D_{90} [µm]	Mean Size [µm]
Fly ash from Bełchatów	3.29	20.74	37.24	21.46
	3.35	20.80	37.06	21.45
	3.46	20.83	36.81	21.43
	3.87	21.88	37.30	22.21
	3.88	21.42	37.23	21.91

Table 7. Compositions of geopolymer mixture of the Belchatów lignite fly ash.

Index	Base Materials (S) [Weight Ratio]		Alkaline Activator (L)	Liquid/Solid Ratio [Weight Ratio]
	Fly Ash	Sand		
R10	1	1	10 M NaOH + sodium water glass (weight ratio: 1:2.5)	1:0.30
R14	1	1	14 M NaOH + sodium water glass (weight ratio: 1:2.5)	1:0.30

3. Results

3.1. Tests of Mechanical Properties—Flexural Strength Tests

Flexural strength tests were carried out on an MTS Criterion 43 testing machine with TestSuites 1.0 software (MTS System Corp., Eden Prairie, MN, USA) with a measuring range of up to 30 kN. The method for determining the flexural strength of cement mortar specimens is specified by EN 196-1:2016-07 (Cement test methods—Part 1: Determination of strength—Section 9.1) [10]. Test specimens in the form of cuboids are subjected to a bending moment by applying a uniform load, induced by the lower and upper rollers of the testing machine. The test continues until the maximum load is reached, which causes the failure of the component, and the bending strength is calculated based on this parameter. The bending strength is determined by the formula for the three-point method:

$$\mathrm{R}_f = \frac{1.5 * \mathrm{F}_f * \mathrm{l}}{b^3}\ [\mathrm{MPa}] \quad (1)$$

where:

R_f—flexural strength (MPa)
b—lateral length of the section (mm)
F_f—maximum load (N)
l—length between supports (mm).

For the tests, six specimens activated with 10 M NaOH and six specimens activated with 14 M NaOH with dimensions of 40 × 40 × 160 mm were prepared. Based on the results obtained, a graph (Figure 1) was made showing the results of flexural strength tests.

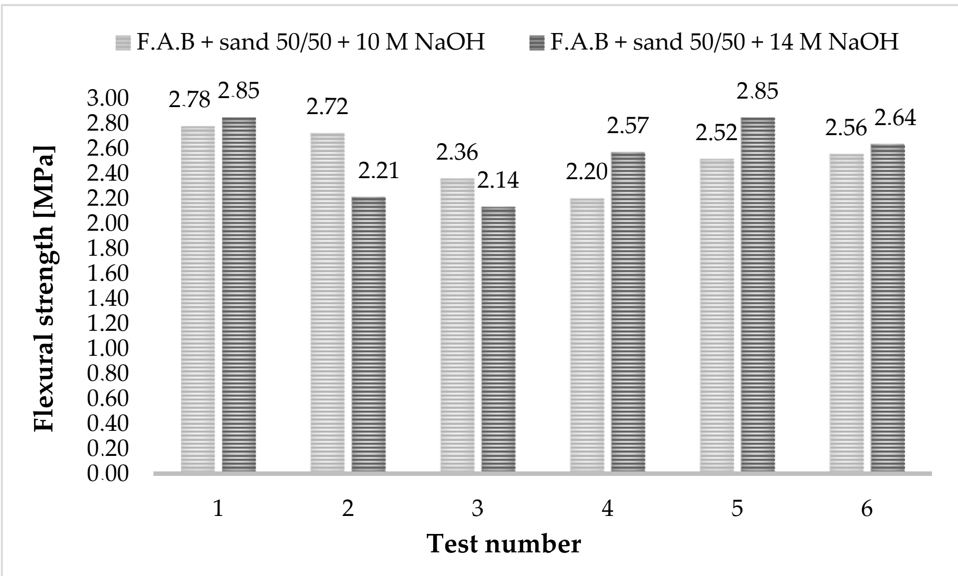


Figure 1. Flexural strength of the Belchatów lignite fly ash samples.

The above image shows that the test results for samples activated with 10 M solution and 14 M solution are comparable. The values for all samples are in a range of 2–3 MPa. The average strength value for both activators is 2.5 MPa. However, for economic reasons, a better choice would be solutions with a lower molar concentration.

3.2. Tests of Mechanical Properties—Compressive Strength Tests

Compressive strength tests were carried out on an MATEST 3000 kN testing machine (Matest, Treviolo, Italy). In the building and construction sector, the document that regulates the method for determining the compressive strength of cement mortar specimens is PN-EN 196-1:2016-07 (Methods for testing cement—Part 1: Determination of strength—Section 9.2) [10]. Compression testing involves loading specimens until a critical value is reached that will cause the material to fail. The maximum load is the basis for calculating the compressive strength of the concrete material according to the following formula:

$$R_c = \frac{F_c}{1600}\ [\text{MPa}] \tag{2}$$

where:

R_c—compressive strength (MPa)
1600—surface of tiles (or auxiliary tiles) (mm^2)
F_c—maximum load (N).

Specimens formed after flexural strength tests—12 specimens activated with 10 M NaOH and 12 specimens activated with 14 M NaOH with dimensions of 40 × 40 × 40 mm—were used for the tests. Based on the results obtained, a graph (Figure 2) was made showing the results of compressive strength tests.

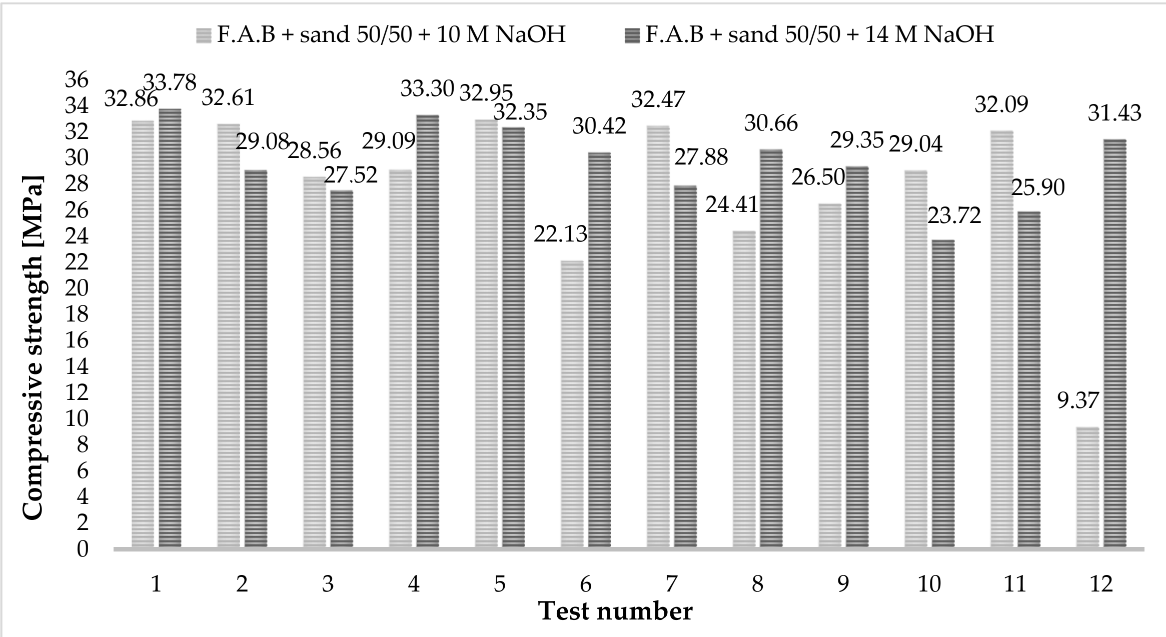
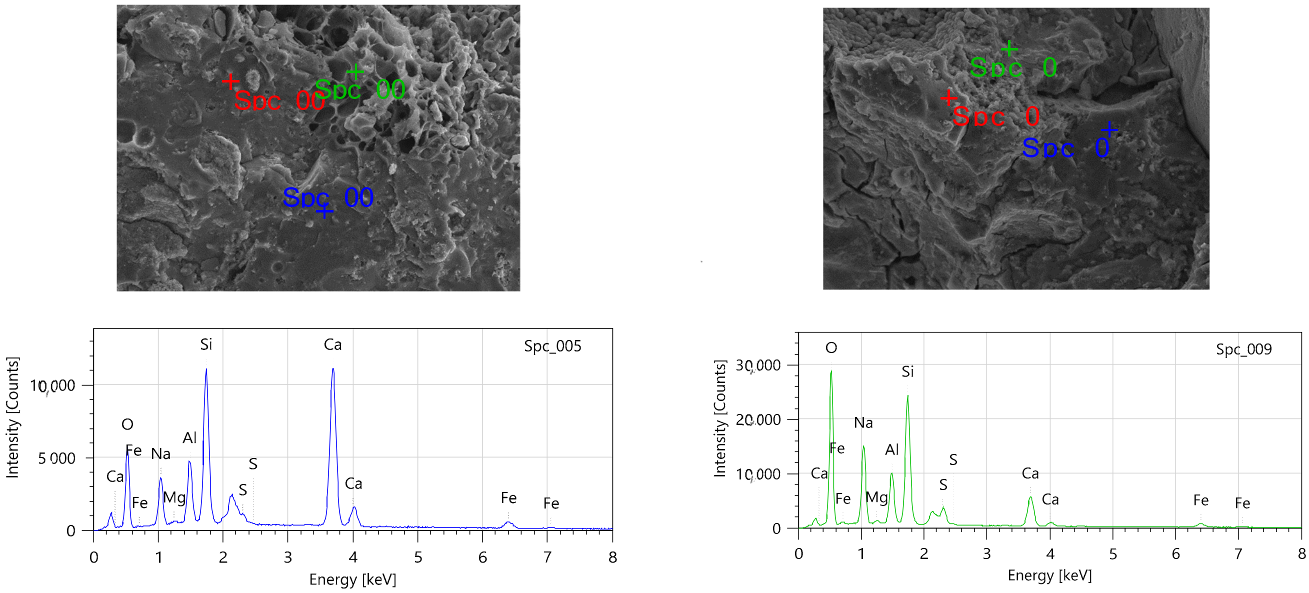


Figure 2. Compressive strength of the Belchatów lignite fly ash samples.

The above picture shows that the test results for samples activated with 10 M solution and 14 M solution are comparable, as is the case for the testing of crushing strength. The values for all samples are in a range of 20–35 MPa (the last result for the 10 M activator is only a deviation from this norm). The average strength value for both activators is 28 MPa. Again, for economic reasons, a solution with a lower molar concentration would be a better choice.

3.3. Evaluation of the Microstructure and Analysis of the Oxide Chemical Composition of the Resulting Geopolymers

A JEOL IT200 SEM scanning microscope (JEOL, Warszawa, Poland) was used to perform oxide analysis of the resulting samples, as shown in Figure 3.



Chemical formula	Line	Mass%	Mol%	Cations
O	K			
Na2O	K	10.29±0.13	10.28±0.13	3.29
MgO	K	0.51±0.04	0.78±0.06	0.12
Al2O3	K	11.69±0.14	7.10±0.08	2.27
SiO2	K	33.69±0.24	34.72±0.25	5.55
SO3	K	0.77±0.05	0.60±0.04	0.10
CaO	K	38.91±0.22	42.96±0.25	6.87
FeO	K	4.13±0.11	3.56±0.09	0.57
Total		100.00	100.00	
Spc_005				Fitting ratio 0.0501

(**a**)

Chemical formula	Line	Mass%	Mol%	Cations
O	K			
Na2O	K	21.85±0.13	22.88±0.14	6.29
MgO	K	0.90±0.03	1.45±0.06	0.20
Al2O3	K	14.27±0.11	9.09±0.07	2.50
SiO2	K	42.43±0.20	45.83±0.22	6.30
SO3	K	6.47±0.09	5.24±0.07	0.72
CaO	K	11.02±0.09	12.75±0.10	1.75
FeO	K	3.06±0.07	2.76±0.06	0.38
Total		100.00	100.00	
Spc_009				Fitting ratio 0.0327

(**b**)

Figure 3. Analysis of the oxide composition of the Belchatów lignite fly ash—(**a**) 10 M NaOH, (**b**) 14 M NaOH.

The above photo shows the structure of a geopolymer based on limestone fly ash Belchatów, activated with solutions of different molar concentrations. There are no visible differences in the structure and the oxide analysis performed as well [11,12].

4. Short Discussion

The analysis of the phase composition performed within the scope of the article is consistent and comparable with the analysis presented in the literature [6]. Only larnite and one phase of C_3A cement clinker were not identified during the study.

Oxide chemical composition analysis was carried out using a scanning microscope with an EDS system. A comparison of the literature condition with the test results (Figure 3) showed that the same oxides are mostly present in the base material [6].

The presented tests of mechanical properties, i.e., bending and compressive strength, showed that there is no major difference between the activator 10 M and 14 M. The obtained results are comparable with the results of other researchers [13]. Fly ash from lignite combustion has a less amorphous phase (glassy particles), so it is less reactive compared to hard coal ash from pulverized coal boilers. The use of an activator with a higher concentration does not bring results, because the phases that can be solubilized and activated become active at a concentration of 10 M. For economic reasons, i.e., ever-increasing inflation and current fuel prices, a better activator is one with a lower concentration.

5. Conclusions

Based on the above discussion of the research results, several conclusions can be drawn to summarize the research work:

- Limestone fly ash contains quartz, gelenite, anorthite, hematite, anhydrite, mullite and calcium oxide, as well as typical cement clinker phases, i.e., $C_{12}A_7$, C_3A and $C_4A_3\hat{S}$.
- The following oxides can be identified in the base material: SiO_2, CaO, Al_2O_3, Fe_2O_3, SO_3, CaO free, MgO, K_2O and Na_2O.
- The flexural strength for samples activated with the two solutions is at a similar level and is no more than 3 MPa. Compressive strength for both activators is similar, with results not exceeding 35 MPa.

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