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Influence of the Size of Milled Coal Gangue Particles on the Mechanical Properties of Geopolymers †

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Abstract: Geopolymers are inorganic materials resulting from the synthesis of silicon and aluminum in a polycondensation reaction. In this study, coal mine waste material from the Wieczorek mine in the Śląskie Voivodeship was used to produce geopolymers. The material was prepared, crushed and milled beforehand due to its large dimensions. The material was subjected to sieve analysis, which allowed to distinguish three fractions. The next step was thermal activation of the obtained powder grain sizes. After thermal activation, the material was combined with an alkaline solution to prepare geopolymers. Photographs of the microstructure were taken in order to determine the chemical composition of the geopolymer and to study the phase composition. The best compressive and bending strengths were exhibited by geopolymer samples with particle sizes ranging below 200 µm—19 MPa and 5.7 MPa, respectively.

Keywords: geopolymer; coal gangue; particle size; circular economy

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1. Introduction

Geopolymers are called alkaline-activated materials (due to the first phase of geopolymer formation), and are created by combining aluminosilicate materials with alkaline compounds—strongly basic sodium, potassium [1,2] or acid phosphates [3,4]. Aluminum and silicon are obtained from minerals (most often metakaolin [5], volcanic tuffs and waste materials, such as fly ash or slags) [6–8]. Geopolymerization takes place at temperatures not exceeding 100 °C [9,10]. Geopolymers are characterized by good mechanical properties [11], including compressive strength, fire resistance, corrosion resistance, binding of heavy metal elements, [12,13] these properties predispose geopolymeric materials to construction applications, immobilization of hazardous materials or securing waste landfills [14]. Geopolymer materials are generally expected to replace Portland cement, the long-term use of which has led to a high carbon footprint and environmental problems [15,16]. Geopolymers are environmentally friendly compared to conventional cement, and their production results in approximately six times lower CO_2 emissions to the atmosphere than the manufacturing of cement [17,18].

Coal shales are materials produced during coal mining [19]. Their amount increases year by year alongside energy consumption. One of the largest coal mining countries is China, where the annual production is over 70 million tons, resulting in the creation of huge amounts of deposited coal shales [20]. So far, they are not used in large quantities, hence the need to find an appropriate application for this waste [21]. The main components of gangue include quartz, kaolinite and illite, all three of which contain silicon and

aluminum compounds [22]. One of the possible applications for coal shales is to use them in geopolymerization [23].

This study aimed to observe the effects of different particle sizes of milled coal gangue on the mechanical properties of geopolymers. In order to better understand the potential of coal gangue in the geopolymerization process, various components of the process were examined, e.g., the influence of thermal activation on the reactivity of the raw material, the influence of particle size [24] especially on fly ash-based geopolymers [25,26] or the influence of the type of alkaline activator on the strength properties [27].

2. Materials and Methods

The base raw material for the production of geopolymers was obtained from the Wieczorek mine (Poland). The first stage of work with this material required crushing it in a jaw crusher and grinding, as the coal shales were rather large. The obtained sample of the material was subjected to a quantitative analysis of the phase composition using the company's X-ray diffractometer PANanalitycal Almelo. The study showed the presence the following minerals in the material: quartz—42.5%, muscovite—12.5%, kaolinite—36.5%, and illite—9.0% (see: Table 1). The quantitative analysis of the phase composition given in Table 1 shows approximate values. The amorphous phase was not determined in the material.

Table 1. Percentage of the minerals in the material.

Identified Phase	Quartz	Kaolinite	Illite	Muscovite
Chemical Formula	SiO_2	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	$Al_2Si_2O_5(OH)_4$	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$
Percentage (%)	42.5%	35.6%	9.0%	12.6%

The crushing stage was followed by sieve analysis of the obtained material and divided the material into specific fractions; below 200 µm, in the range of 200 µm to 900 µm and from 900 µm to 1.25 mm. The raw material was heated in a chamotte furnace at 700 °C for 24 h. Calcination is a thermal method of activating a material to remove the carbon content and create the appropriate microstructure. The loss of ignition was 5.2% (LOI).

After grinding and calcination of the material, an analysis of the particle size of the obtained material was carried out. Figure 1 shows the results obtained with this method. The main particle size under 200 µm for the material obtained by sieve analysis was 21 µm, the overall particle size did not exceed 70 µm. For the material in the size range of 200–900 µm, the average particle size was 409 µm, whereas less than 2% of the particles were of the size within the range of 2.2 µm to 125 µm. In the highest size range of 900 µm–1.25 mm, the average grain size of the raw material was 924 µm. The wide distribution of particles for W 200–900 µm was caused by the error of sieve analysis. Some of the undersized particles were not able to pass through the sieve due to the agglomeration of larger particles, while some of them became stuck in the mesh of the sieve.

The finished material with a different range of grain fractions was mixed with a prepared 10 M alkaline solution.

An alkaline solution of 10 M sodium hydroxide with aqueous sodium silicate was prepared. For this purpose, a weighed amount of technical sodium hydroxide flakes was mixed with tap water and stirred until the component dissolved. Then, aqueous sodium silicate was added to the mixture at a ratio of 1:2.5. The resulting solution was allowed to stand for 24 h to stabilize the concentration under laboratory conditions. After this time, the solution and material from the mine were placed in the bowl of a low-speed mixer for approximately 10 min. In this way, three geopolymer mixes were produced (Table 2). The resulting mass was poured into a set of rectangular molds, then to remove air bubbles, the molds were placed on a vibrating table. The last stage of preparing the samples entailed placing them in a laboratory dryer at the temperature of 75 °C for 24 h. On the second day,

after taking the molds out of the dryer, the samples were demolded and then seasoned under laboratory conditions for 28 days.

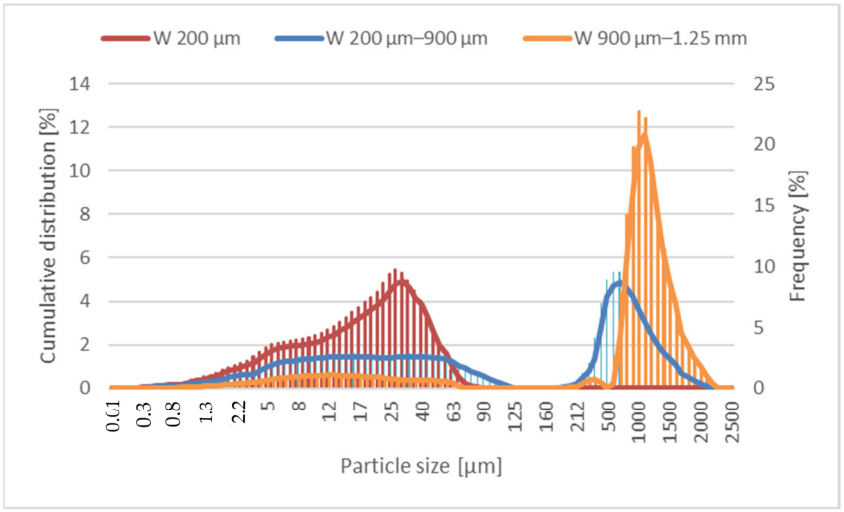


Figure 1. Diagram of particle distribution of W 200 µm, W 200–900 µm and W 900 µm–1.25 mm.

Table 2. Composition of the prepared geopolymers.

Sample	Alkaline Solution 10 M	Mining Raw Material Particle Size
G 900 µm–1.25 mm	Technical sodium flakes, tap water, sodium silicate	900 µm–1.25 mm
G 200 µm–900 µm	Technical sodium flakes, tap water, sodium silicate	200 µm–900 µm
G 200 µm	Technical sodium flakes, tap water, sodium silicate	200 µm

The mineral phase was identified using X-ray diffraction on a PANanalitycal Almelo. The test was carried out on powdered material using a Cu lamp. Analysis of the identified phases was performed with the use of High Score Plus software.

The particle size analyses were performed with using a Particle Size Analyzer AntonPaar GmbH (Graz, Austria). Compressive strength tests were carried out on a testing machine MATEST 3000 kN with a speed of 0.05 MPa/s, according to PN-EN 196-1:2016-07 standard "Cement test methods—Part 1: Strength determination ". The tests were carried out on cubic samples with dimensions of 50 mm × 50 mm × 50 mm. The flexural strength tests were carried out similarly to the compressive strength tests, according to the PN-EN 196-1:2016-07 on the MATEST 3000 kN testing machine with a speed of 0.05 MPa/s. These tests were carried out on 50 mm × 50 mm × 200 mm. The distance between the support points was 150 mm. The observation of the microstructure of the geopolymers was made using scanning electron microscope (SEM) of the JEOL JSM 820 type with EDS on the breakthroughs of the samples after the compressive strength tests. The preparation of samples for observation entailed sputtering a thin layer of gold by a vacuum sprayer JEOL—JEE-4X.

3. Results

3.1. Compressive Strength

The results for compressive strength are shown in Figure 2. The test was carried out on four samples for each variant. The graph shows the average value obtained from these measurements.

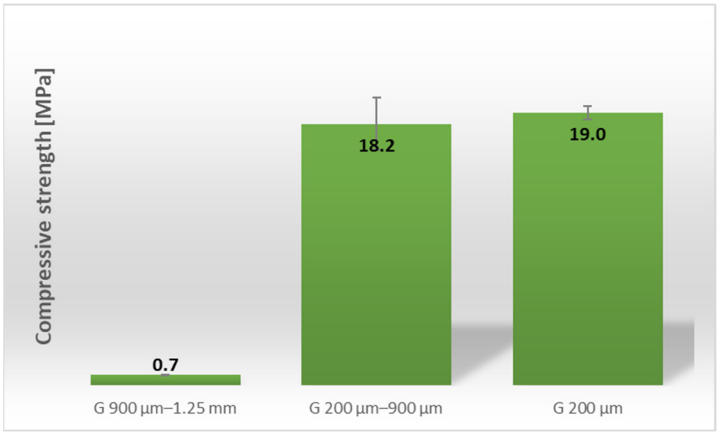


Figure 2. Results from the compressive strength test.

The best compressive strength was achieved by geopolymers with particle sizes of less than 200 µm—19 MPa. A slightly lower compressive strength was obtained by geopolymers from the base material fraction of 200 µm to 900 µm—18.2 MPa. A significant decrease in strength was noted for geopolymers whose particle sizes of the raw material were in the range of 900 µm to 1.25 mm—0.7 MPa.

3.2. Flexural Strength

The results for flexural strength are shown in Figure 3. The test was carried out on three samples for each variant. The graph shows the mean value obtained from these measurements.

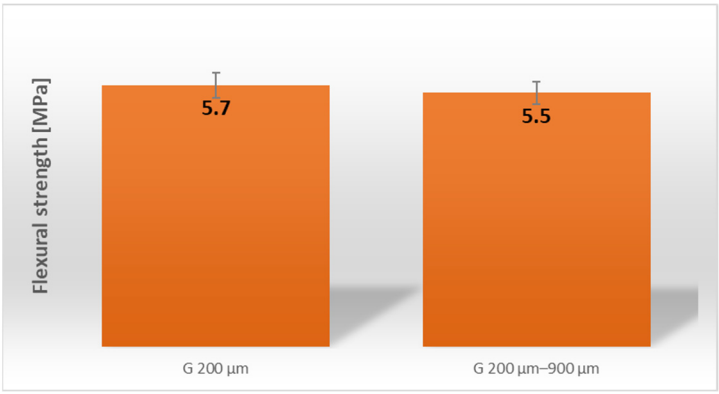


Figure 3. Results from the flexural strength test.

In the case of bending strength, samples with particle sizes of the raw material above 900 µm obtained a result below the reading sensitivity of the testing machine, hence no value was recorded for this type of sample. Again, the best strength was achieved with geopolymers with particle sizes below 200 µm, while this value was comparable to the result for geopolymers with grain sizes of 200–900 µm.

3.3. SEM Observation

Figure 4 shows a SEM image for sample G 200–900 µm.

The observed microstructure is typical for geopolymers. A significant number of pores ranging from 2 to 3 µm were observed. The EDS analysis identified compounds of silicon, aluminum, sodium, calcium, potassium, chlorine and iron in the selected areas 1–3 (Figure 5).

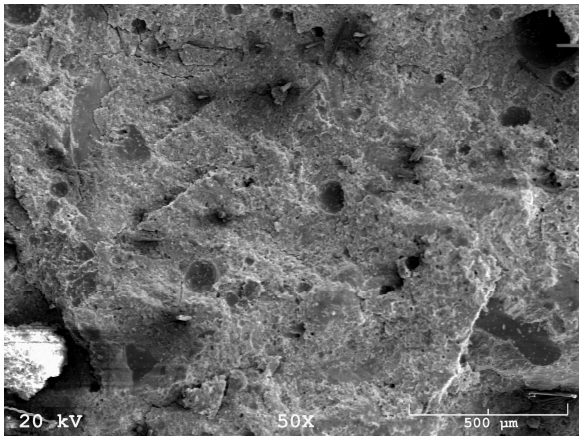
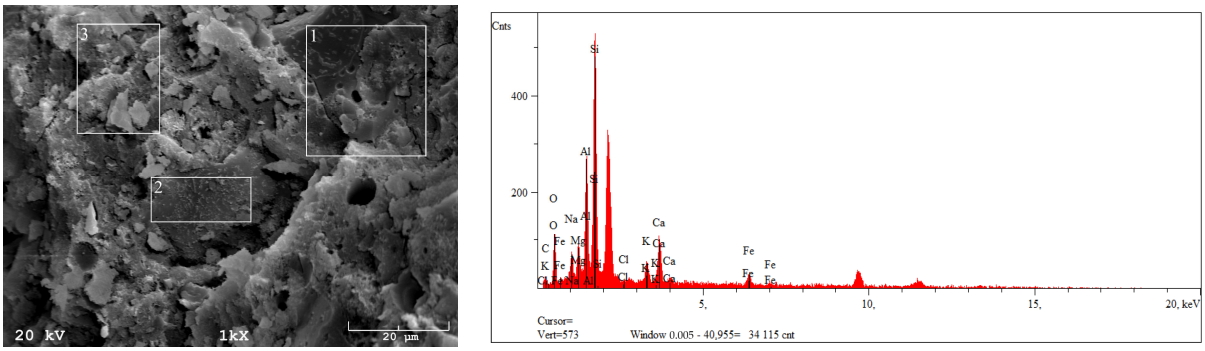


Figure 4. SEM image of geopolymer G 200–900 µm at 50× magnification.



(**a**) (**b**)

Figure 5. Sample G 200–900 (**a**) with marked areas of measurements, (**b**) results of the EDS analysis.

4. Conclusions

The obtained results show the influence of precursor particle size for geopolymerization using a sodium activator on mechanical properties. The best result for mechanical strength, both for compression and flexural strength, was obtained for geopolymers where particle sizes were below 200 µm—19 MPa and 5.7 MPa, respectively. A slightly worse result, about 4% lower, was obtained for samples with particle sizes in the range of 200–900 µm. The worst results were obtained from samples with the largest particle sizes from 900 µm to 1.25 mm. A large amount of fine-fraction particles in the geopolymer G 200–900 µm, below 100 µm, can affect the high strength of the geopolymer, giving the effect of a filler. The high mechanical strength of G 200 µm resulted from the presence of very small particles below 90 µm, which facilitate the solubility of SiO_2 and Al_2O_3 in the NaOH solution [24,28]. Grinding precursor particles to sizes below 900 µm allows improved strength properties to be achieved, and at the same time saving energy, without the need to further grind particles to smaller than 200 µm.

Coal gangue from the mining industry, for example Wieczorek, is a material that is still being researched and has the potential to be used in geopolymerization.

It is an environmentally friendly solution, especially if the method for its preparation as a raw material to produce geopolymers is energy-saving.

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