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Proceeding Paper

Characterization of a Coal Shale from Marcel Mining as Raw Material for Geopolymer Manufacturing [†]

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Abstract: Implementing the idea of a circular economy is one way to reduce carbon emissions and, at the same time, the consumption of natural resources. The use of mining waste as a raw material helps meet the growing demand for construction materials with a smaller carbon footprint. The article shows the possibility of using a coal shale from Marcel mining to create new eco-friendly materials, geopolymers. The main aim of the presented research includes characteristics of raw material and synthesis of geopolymers based on mining waste (coal shale from Marcel mining) and next, investigations of the obtained materials. Geopolymer was prepared using a sodium activator plus milled and calcinated precursor materials. In this study, the following research methods were used: particle size analysis, XRD analysis, mechanical properties tests (compressive and bonding strength), and microstructure analysis—scanning electron microscopy. The results show potential for the extraction of waste from the Marcel company to obtain material for advanced applications in the geopolymerization process. The material had a compressive strength of 12.7 MPa and a bending strength of 3.4 MPa, which makes it possible for use in construction applications such as various types of foundations, walls, columns, lintels, terraces, stairs, ceilings, small building elements, and small architecture. The proposed process could be a promising alternative to current methods of managing waste rock, in particular hard coal mining.

Keywords: geopolymer; coal shale; mining waste; industrial by-products; circular economy

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1. Introduction

The concept of circular economy is expected to bring many benefits to both economic development and the environment. The potential environmental factors are those such as decreasing the use of natural resources, limitation of emissions, recycling, fewer material losses through recycling, etc. [1,2]. The circular economy can also be seen as the next possible step in the evolution of waste management systems, including the development of sustainable materials that will allow closed loops. It could be possible through the introduction of manufacturing processes by being able to reuse materials at the end of their useful life [2,3]. This issue is important in the context of a realistic introduction of the circular economy into existing systems [4,5]. Materials corresponding to the needs of this model are, among others, geopolymers.

Geopolymers are a class of synthetic inorganic aluminosilicate materials, usually formed as a result of the reaction of aluminosilicates (e.g., fly ash or metakaolin) with a solution of silicates under usually strongly alkaline or sometimes acidic conditions [5,6]. Their synthesis has been estimated to emit about five–six times less carbon dioxide than the production of Portland cement and needs significantly less energy for the manufacturing process [7,8], but it is not only the advantages of geopolymer materials that take into account the circular economy approach. One of the most important benefits is the possibility of using waste for production [5,7]. One of the most promising opportunities is mine tailings [7,9]. These types of wastes are reachable in aluminosilicate, which is a main component of the geopolymerization process [9,10].

In recent years, there has been a visible increase in interest in the use of mine tailings for the production of geopolymer materials in the literature [9,11,12]. Previous investigations were related to different kinds of waste, including coal shales [10], gold mining [13], tungsten mining waste mud [14], copper tailing [15], zinc mining [16], garnet tailings from molybdenum mines [17], and others [7,18]. From the point of view of Poland and neighboring countries, the promising materials are coal shales. Coal mine tailings represent a significant waste stream that is used for geopolymer manufacturing. The current work shows the possibility of using a coal shale from Marcel mining for this purpose. This mine tailing has not been previously analyzed as a raw material for geopolymerization. The main aim of the presented research is to characterize the raw material, design geopolymers based on mining waste from Marcel mining, and determine potential applications for them.

2. Materials and Methods

2.1. Materials

Geopolymer samples were produced based on mine tailings for coal production from a PGG Sp. z o.o. Branch KWK 'ROW' Ruch 'MARCEL' coal mine in the Silesia region (Radlin, Poland) and quartz sand as a fine aggregate. This mine was founded in 1949 and is still operating today. Currently, the mine employs 3,168 people, and its net daily output is 11,000 tons.

The main tailings were delivered in the form of rocks with dimensions ca. 20 cm. Firstly, they were fragmented into smaller particles by using a crushing machine. In the second step, they were ground using an ultra-centrifugal mill. The size reduction takes place by impact and shearing effects between the rotor and the fixed ring sieve. As a result of this operation, the fine powder (fraction < 40 μm) was obtained. In the next step, the obtained material was calcinated using a laboratory furnace. The calcinations were performed for 24 h at a temperature of 700 °C. The materials were heated and cooled together in a furnace. The main aim of this process was to increase the material reactivity by obtaining the appropriate microstructure. Additionally, the process made it possible to remove volatile substances, oxidize a portion of the mass of the material, and decrease the carbon content.

2.2. Samples Preparation

The calcined waste was mixed, in a ratio of 1:1, with quartz sand. The dry components were mixed in a slow-speed mixer (Geolab, Warsaw, Poland) cement mortar mixer for about 5 min. The prepared mix was activated with an activator solution consisting of a 10 M NaOH solution (technical sodium hydroxide flakes) and an aqueous sodium silicate solution—density 1.45 g/cm^3 (water glass solution, R-145)—in which the ratio of the sodium base solution to water glass solution was 1: 2.5. Tap water was used to prepare the solution. After the addition of liquid components, the process of mixing was continued for about 15 min, up to obtaining a homogeneous paste. The prepared geopolymer masses were poured into a set of molds with dimensions 50 mm × 50 mm × 200 mm (prismatic forms). Then, in order to remove air bubbles, the molds with the materials were placed on a vibrating table for 15 min. Subsequently, to prevent too-quick water evaporation, each mold was wrapped in a polyethylene film. For the acceleration of the curing process, the samples were placed at 75 °C for 24 h. After this time, they were cooled to room temperature, unmolded, and stored in laboratory conditions for 28 days at ambient temperature (ca. 23 °C). After this time, the mechanical properties were investigated—Figure 1.

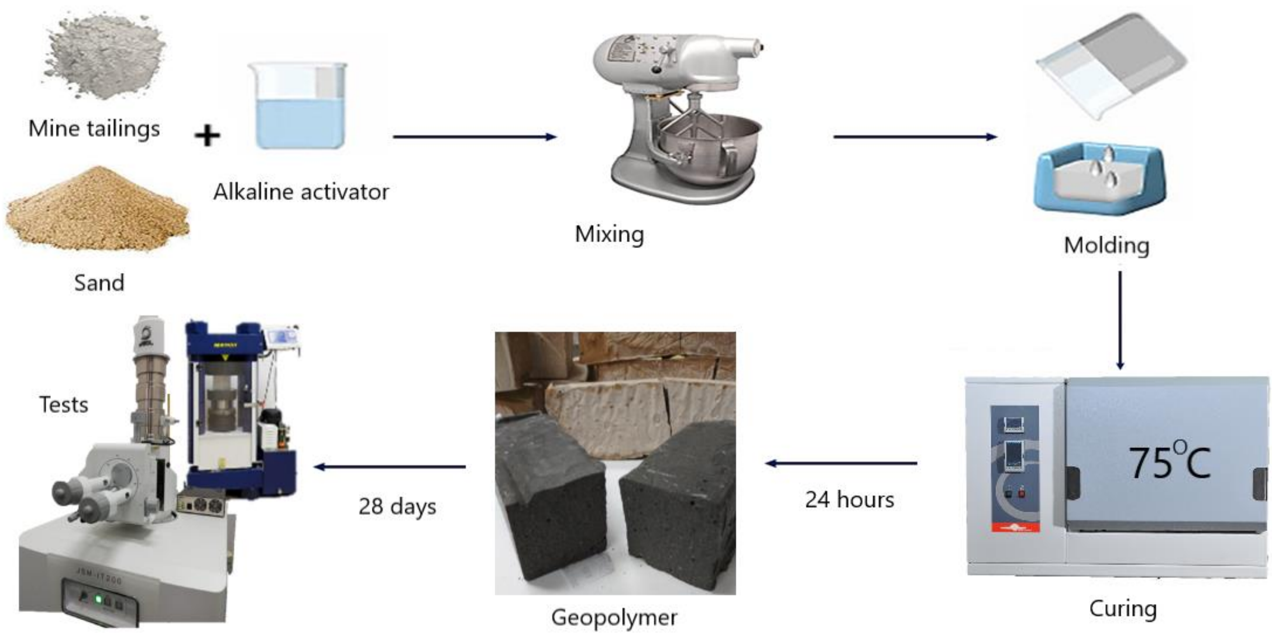

Figure 1. Scheme for sample preparation.

2.3. Methods

The particle size analysis was performed using a Particle Size Analyzer (AntonPaar GmbH, Graz, Austria) for the milled mine tailings after the calcination process to confirm the size of obtained grain and its distribution.

The mechanical properties of the samples were investigated using the MATEST 3000 kN test machine (Matest, Treviolo, Italy), according to the following regulations.

- PN-EN 12390-3:2019-07—Testing Hardened Concrete—Part 3: Compressive Strength of Test Specimens.
- PN-EN 12390-5:2019-08—Testing Hardened Concrete—Part 5: Flexural Strength of Test Specimens.

The applied speed in both cases was 0.05 MPa/s. The flexural strength was investigated in prismatic samples having dimensions: 50 mm × 50 mm × 200 mm and the distance between the supports was 150 mm (three-point bending test). The compressive strength was investigated in the samples after the flexural strength test with the use of a metal plate with dimensions: 50 mm × 50 mm.

The mineralogical composition was determined using X-ray diffraction XRD analysis. This investigation was carried out on powdered mine tailing before calcination using PANalytical AERIS (PANalytical, Almelo, The Netherlands). This device applies the X-ray method (Debye–Scherrer) for phase analysis. It was carried out using Cu-Kα radiation and components such as a nickel filter on the lamp, mask 13, and Szlot 1°. The following parameters were applied to this research—angle range: 9999–100°2Θ, measurement step: 0,0027166°2Θ, time of counts: 340,425 s, and total measurement time: 13 h 2 min 32 s. Next, the results were analyzed using HighScore Plus software, based on PDF4 + crystallographic database.

Microstructure investigation was performed on a JEOL JSM-IT200 scanning electron microscope (JEOL, Tokyo, Japan). This type of scanning electron microscope (SEM) has an energy-dispersive X-ray spectroscopy system (EDS), which allows for analyzing the chemical and oxygen composition of the investigated material. The research was provided on the material after mechanical properties tests. The samples were covered by gold plating for good conductivity. The cover layer was applied by a DII-29030SCTR Smart Coater (JEOL, Tokyo, Japan).

3. Results and Discussion

3.1. Physical Properties

The results of the particle size analysis, after grinding and milling, are presented in Figure 2 and Table 1.

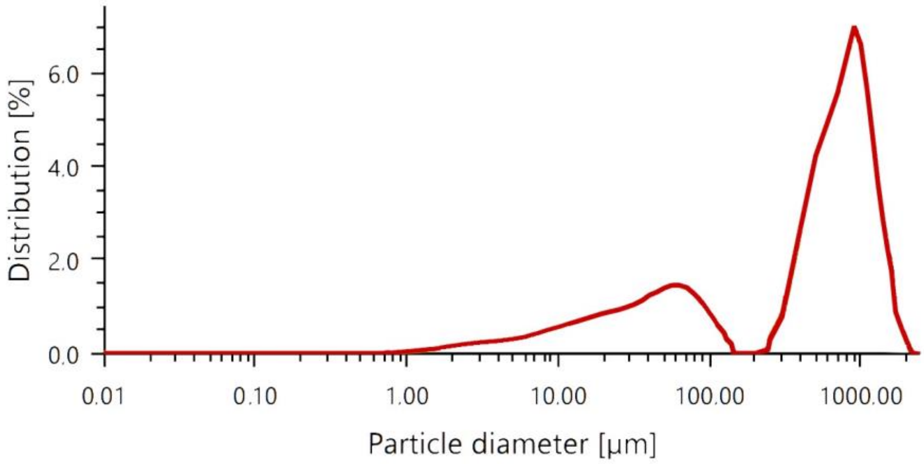

Figure 2. Particle size distribution.

Table 1. Basic parameters for the particle size distribution.

D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	Mean Size (µm)	Mean Size (µm)
19.697	548.445	1150.324	600.729	2.062

The mean size of the particle is about 600 µm. In comparison to the other raw materials used in the geopolymerization process, such as metakaolin or fly ash, this particle size is quite large [2]. It should be noted that research shows that decreasing the particle size can positively influence the material reactivity [2], but at the same time increase the energy consumption for the whole process.

3.2. Mechanical Properties

The results for compressive and flexural strength are presented in Table 2.

Table 2. Mechanical properties.

Sample	Compressive Strength (MPa)	Flexural Strength (MPa)
50% mine tailings + 50% sand	12.7 (±3.3)	3.4 (±0.2)

The obtained values for mechanical properties are quite reasonable. The obtained results are not as good as for fly-ash-based geopolymers [5]. However, the values allow for planning some possible applications for this material, especially as a material for construction purposes, such as pavements onsite at the mining place [19].

3.3. Microstructure Investigation

The obtained diffractogram is presented in Figure 3. Based on this investigation a quantitative analysis was performed and the mineralogical composition was determined—Table 3.

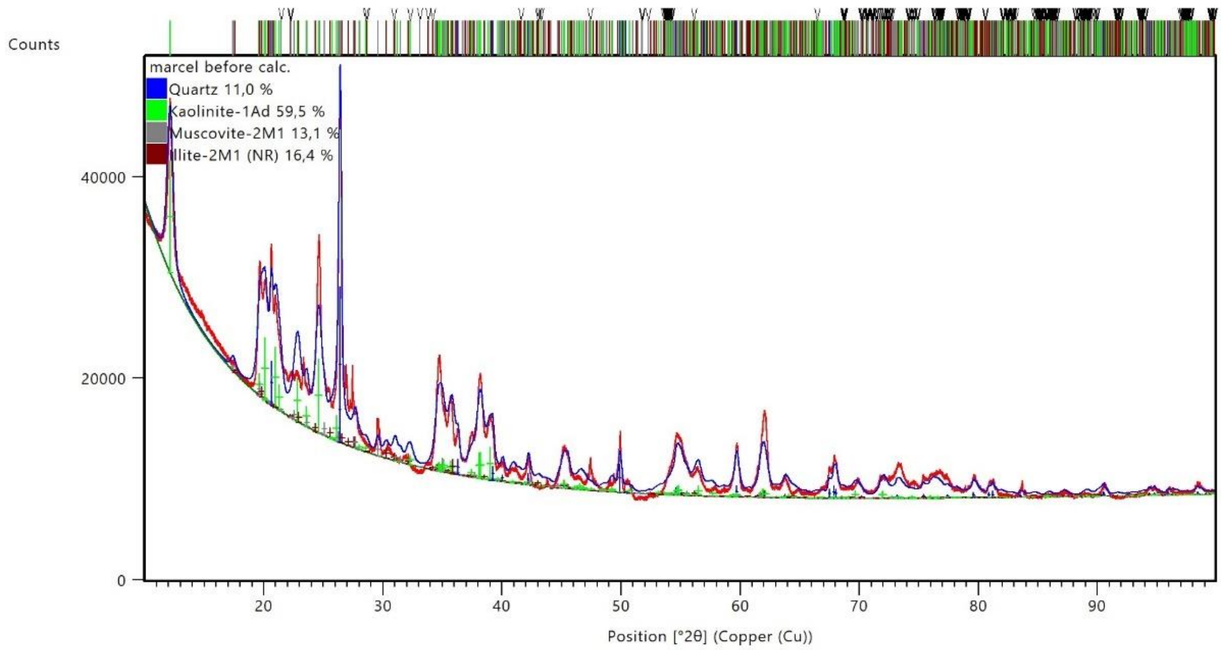

Figure 3. XRD analysis for coal shale from Marcel mining (before calcination).

Table 3. Phases identified along with their percentage share in the sample.

Identified Phases		Percentage (%)	Chart No.
Name	**Chemical Formula**		
Quartz	SiO_2	11.0	01-070-3755
Muscovite-2M1	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	13.1	00-006-0263
Kaolinite-1Ad	$Al_2Si_2O_5(OH)_4$	59.5	00-058-2006
Illite-2M1	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$	16.4	00-026-0911

The results show a relatively small amount of quartz, a high amount of kaolinite, and a slightly increased amount of illite and typical for coal shales amount of muscovite [20]. The relatively low mechanical properties of the designed geopolymers can be associated with a small amount of quartz that affects the mechanical properties [21]. At the same time, illite could also decrease the mechanical properties of geopolymer [21]. The common influence of a small amount of quartz and an elevated amount of illite probably decides the relatively low mechanical properties of the investigated material. The high amount of kaolinite, that under temperature is transformed into metakaolinite, should be a factor that makes the geopolymerization process possible. It is an advantage taking into consideration the geopolymerization process [22].

Moreover, SEM observation was provided for the investigated samples—Figure 4.

The visible microstructure of the material is typical for geopolymers [2,5]. In Figure 4a,c there is visible cracking which is an effect of previous mechanical strength tests. Additionally, an EDS analysis was performed for the selected points. Exemplary results are presented in Figure 5.

The oxide composition obtained as a result of EDS measurements is typical for a geopolymer material. It is characterized by a large amount of SiO_2, about 60%, and Al_2O_3 of more than 21% [2,5]. Another important compound, Na_2O at 17%, probably comes from the alkali activation process. There are also small amounts of MgO and K_2O (less than 1%), in the structure.

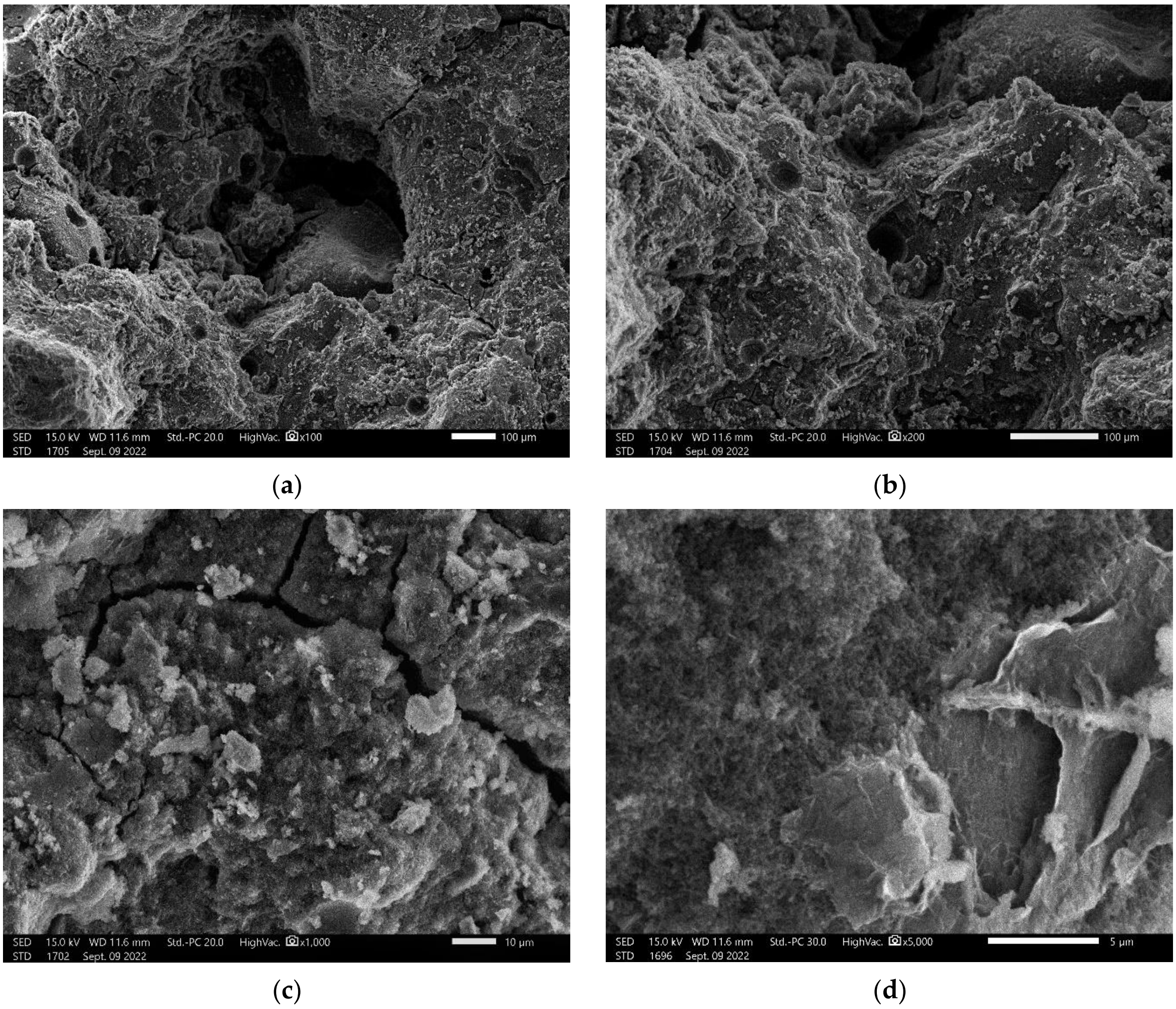

Figure 4. SEM images of geopolymer: (**a**) at 100× magnification; (**b**) at 200× magnification; (**c**) at 1000× magnification; and (**d**) at 2000× magnification.

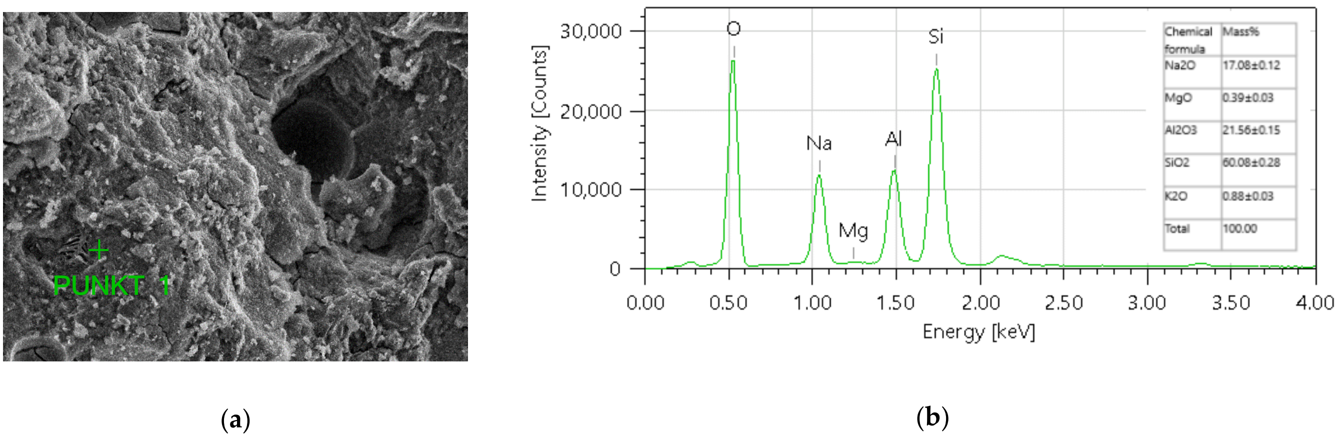

Figure 5. Geopolymer sample: (**a**) SEM image with the point of measurements; and (**b**) results of the EDS analysis.

4. Conclusions

The obtained results show the possibility of using a coal shale from Marcel mining to create new eco-friendly materials, geopolymers. The geopolymer was prepared using a sodium activator. The obtained material has a structure, chemical and mineralogical composition for geopolymer. The material had a compressive strength of 12.7 MPa and a bending strength of 3.4 MPa. These kinds of mechanical properties are relevant for construction applications such as various types of foundations, walls, columns, lintels, terraces, stairs, ceilings, small building elements, and small architecture. However, further applications required additional research, including durability studies. According to an environmental point of view, the most promising seems to be an application onsite for the mining industry to minimalize the cost of transportation.

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