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CHARACTERISTICS AND ASSESSMENT OF THE SUITABILITY OF COAL-RICH MINING WASTE IN THE PRODUCTION OF CERAMIC BUILDING MATERIALS

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ABSTRACT

Hard coal mining involves the generation of large quantities of waste materials. For every 1000 kg of hard coal produced in Poland an average of approx. 400 kg of different kinds of waste material is generated. Environmental regulations and new approaches based on the Clean Coal Technologies require manufacturers to recover or neutralize the generated wastes. Technological progress and the development of clean coal technologies have led to the wastes being treated as products for other industries. The ability to use the waste material depends on their chemical and mineral composition. Mining wastes are characterized by different properties depending on the stage of the coal-enrichment process in which they are formed. In spite of ever more efficient coal-enrichment technologies, in addition to mineral material, there is still a significant amount of carbon in the wastes that can be recovered in various ways. After the coal recovery process, the waste material is wet (20-30%), has a thick pasty consistency and is deposited in landfills, thus representing a hazard and nuisance to the environment.

This study focuses on the characteristics of the raw waste material and the possibility of using it in the production of building materials. Mineral compositions were tested with XRD and STA methods and the characteristics of thermal properties of waste material were investigated using STA and heating microscopy. Gases released during thermal processing of the waste material were analysed by the EGA / MS method. Particle size distribution was measured and the specific surface area of the waste mud samples was calculated. Preliminary analysis was carried out to assess the feasibility of using this waste as a raw material in the production of fired ceramic building materials.

1. INTRODUCTION

Hard coal mining is associated with the generation of significant quantities of wastes. The mining industry is one of the highest generators of wastes in Poland, where for every 1000 kg of hard coal produced approximately 400 kg of different kinds of wastes are generated. In the years 1998-2008, the majority of mining waste in Poland was generated by the exploitation of hard coal and accounted for 47% to 52% of total produced extractive wastes. Over the period analysed the amount of coal mining waste ranged from approx. 30 million Mg to 40 ml Mg per year. According to the Polish Central Statistical Office (2009) (GUS), at the end of 2008 approx. 600 million Mg of waste from hard coal mining was deposited in Poland (accumulated in landfills, dumps, sediment ponds), as the result of several hundred years of operation of this industry in Upper and Lower Silesia. In the past, due to limited possibilities of reuse, the vast majority of mining wastes were deposited on the ground in different kinds of mining waste landfills. The situation changed in the second half of the 1990s following economic changes and new regulations that resulted in the waste quantities used economically exceeding the amount of wastes directed to landfill.

Currently, in the formal and legal sense, approximately as little as 5% of waste generated in the mining sector is deposited in landfill on the ground surface. This does not mean, however, that the amount of waste disposed on the ground has decreased proportionately, as the waste subjected to so-called recovery processes is usually located in the form of various types of earthworks, as well as used for land levelling and reclamation. Accordingly, regardless of whether the wastes are stored on landfill or used economically (to build embankments, earthworks, levelling of land), they are in fact placed in the environment on the surface

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of the earth and affect the environment. The distinction between recovery and landfilling of waste is a technical rather than a legal issue, and is related to regulations governing waste management. In one instance the placement of material in the ground (for example road foundations) will be viewed as recycling, whilst in another, placing the same material on the ground may be treated as landfilling, which is comprised in a completely different legal category. The characteristic feature of hard coal mining wastes is that they are largely not inert wastes as intended by Article 3(3) of Directive 2006/21/EC. According to this article, the term "inert waste" refers to waste that does not undergo any significant physical, chemical or biological transformations. Inert waste will not dissolve, burn or otherwise physically or chemically react, biodegrade or adversely affect other matter with which it comes into contact, likely to give rise to environmental pollution or harm human health. The total leachability and pollutant content of the waste, and ecotoxicity of the leachate, should be insignificant, and in particular not endanger the quality of surface water and/or groundwater. From a technical point of view, the management of actual mining wastes should consist in processing of the latter to render them either inert wastes that are harmless to the environment, or conversion into a product compliant with relevant standards.

Based on this definition, the majority of waste generated from the extraction of hard coal is non-inert waste, especially those containing carbon residues and sulfur compounds. According to the applicable regulations, i.e. "Ustawa z dnia 10 lipca 2008 r. o odpadach wydobywczych, Dz. U. Nr 138, poz. 865 z późn. zm." (the act on mining waste), these wastes should be disposed of in the so-called Waste Neutralization Facility. Wastes of this type may also be processed using appropriate technology in products of standard value that conforming to relevant standards. The latter represents an optimum system of waste management as it contributes towards protecting the environment and safeguarding natural raw material resources, which can be replaced by the waste material. Wastes from hard coal mining are generated in millions of tonnes and should be utilized in industries equipped to manage such large quantities of material; the construction material industry is perfect for this purpose, once the technical properties have been appropriately verified. A good example of an appropriate industry is represented in the production of building ceramics, where clay raw materials are traditionally used, having a mineral and chemical composition similar to that of wastes from hard coal mining. An average-sized factory in this industry produces hundreds of thousands of tonnes of products, using the same quantity of raw materials.

2. MATERIALS AND METHODS

2.1 Materials

Waste mud originating from the hard coal mining industry in Poland was used in this study. The basic characteristics of the material were assessed using the methods described below in terms of the possibility of using this waste as a raw material in the production of fired ceramic building materials. The material is produced in large quantities and requires the use of large-scale management methods. The potential utilisation site for this type of waste may be the ceramic industry that uses a large amount of raw materials. The material initially has a high humidity of more than 30%, with a thick pasty consistency depending on storage conditions, which may, over time, dry and harden. Hardened material may need to be crushed for further use with the use of appropriate machinery and equipment, although due to the consistency of the material, the process should not require a lot of energy.

2.2 Methods

Raw waste material was subjected to chemical composition analysis by means of Wavelength Dispersive X-ray Fluorescence method, using WDXRF Axios maX PANalytical analyser, with 4 kW Rh lamp.

Analysis of the mineral composition of the raw material was carried out by XRD method (Phillips PW-1040 analyser, in the 2θ measuring range 5-70°).

Thermal characteristics of the raw material were characterized by means of simultaneous thermal analysis using NETZSCH STA 449 F3 Jupiter®; analysis of gaseous products was conducted using coupled mass spectrometer QMS 403 Aëolos (heating rate 10°C/min, atmosphere: synthetic air, dynamic flow 40 ml/min).

Thermal behaviour of waste sample with recording of area changes on heating was carried out using the Hesse Instruments heating microscope (heating rate 10°C/min to 1400°C in static air atmosphere).

Particle size distribution was measured by means of the Mastersizer 2000 device by Malvern Instruments. The device measures particle size in the range of 0.2 - 2000 µm. Measurements were made in liquid dispersion (isopropanol) on a 5 gram sample.

The specific surface area of the waste mud sample was measured using the Blaine method according to PN-EN 196-6 standard.

3. RESULTS AND DISSCUSSION

The analysis illustrated below shows basic properties of the raw material in view of the potential of use in production of building materials obtained by means of technologies including thermal treatment of materials. Characterization comprised chemical analysis of the material, and evaluation of thermal properties, mineral composition and particle characterization.

3.1 T Raw materials characteristics

3.1.1 Chemical analysis of the sample

Chemical analysis of the sample is shown in Table 1 and relates to 11 items. The dominant component in the tested sample was silicon dioxide, accounting for more than 53% of total sample content. Aluminium oxide was also present in the sample (26% of total content), thus underlining the possibility of using this waste in the production of building materials. The third largest content was iron oxide, with a value of approx. 10%. The oxides described above represent 90% of the total sample. Chemical analysis also showed the presence of approx. 4% alkaline ox-

TABLE 1: Semiquantitive chemical analysis (XRF) of raw materials.

Oxides	Content [%, wt]
SiO_2	52.4
Al_2O_3	25.6
Fe_2O_3	9.6
TiO_2	1.3
CaO	2.4
MgO	1.8
K_2O	3.6
Na_2O	0.5
SO_3	2.3
P_2O_5	0.3
Cl	0.2
Sum	100

ides ($Na_2O + K_2O$). Sodium and potassium oxides were not a predominant component of waste, but should not be underestimated. With regard to the process of storing these wastes, alkalis may represent an ecological hazard, while processing at high temperatures may exert a positive influence by reducing the temperature of eutectic points in the formation of desired phases. The presence of 2% calcium oxide (CaO) and also 2% SO_2^{2-} suggests that oxides may be present in the form of calcium sulphate compounds as well as in the form of sulphides (pyrite).

3.1.2 STA-EGA analysis of raw materials

Figure 1 illustrates thermal DTA/TG/DTG curves of the waste mud sample on heating to 1000°C. The initial loss of t sample mass, just over 2% wt, visible on the TG curve with a peak at about 70°C in the temperature range 30÷200°C, is related to adsorbed water evaporation and possibility dehydration of clay minerals. This effect is observed on the DTA curve as a slight endothermic deflection. The second, much larger, mass loss observed between 200÷745°C is mainly due to oxidation of organic matter and is equal to approx. 31%. On the DTA curve this effect is marked as wide exothermic deflection between 200÷745°C with low endothermic effect peaking at about 514 °C, likely due to dehydroxylation of clay minerals. No effects were registered above the temperature of 745°C on DTA and TG curves, implying that no exo and endothermal processes took place in the material during further heating.

The EGA curves of waste mud samples are shown in Figure 2 in form of ionic current curves in function of the temperature for CO_2 (m/z =44), H_2O (m/z = 18) and SO_2 (m/z = 64). The EGA curves are confirmative and complementary to DTA TG results and facilitate interpretation

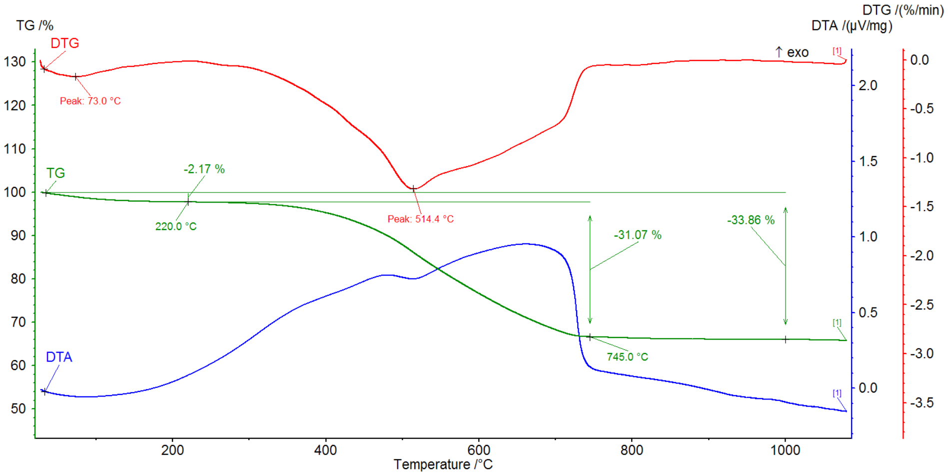

FIGURE 1: DTA/TG/DTG curves of waste mud.

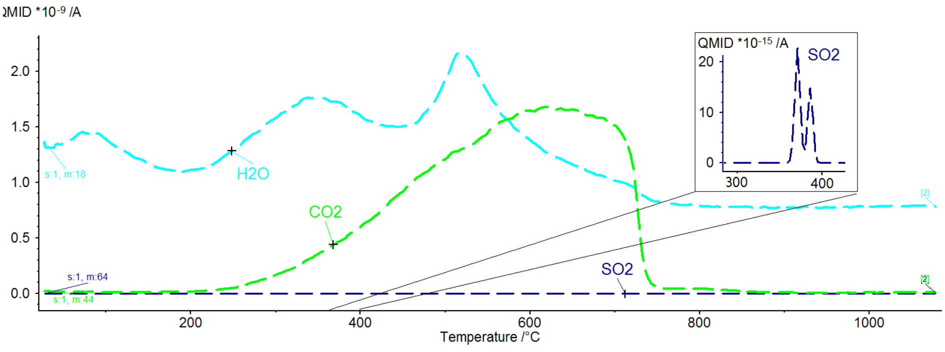

FIGURE 2: EGA curves of waste mud.

of the results of thermal analysis allowing for the separation of processes in temperature coincidence with others. The curves show that water is released in three steps between 20 and 745°C. First release is due to dehydration of clay minerals, second release to firing of organic matter (convergence with release of CO_2) and third release to dehydroxylation of clay minerals. CO_2 is released between 220°C and 745°C in one step visible as a large and wide convexity. This release is connected with burning of organic matter present in the sample mainly in the form of residual carbon released into the atmosphere as CO_2. The CO_2 curve illustrates gas release kinetics and the asymmetrical shape of the convexity. This demonstrates that gas release rate is variable with temperature. From a temperature of 220°C the quantity of evolved CO_2 increases uniformly up to about 600°C. The maximum level of gas release is reached between 600°C and 700°C and then suddenly ceases. SO_2 emission is very low (3 orders of magnitude lower) in comparison to other gases and is placed in the middle of the temperature range between 370°C and 400°C. The temperature range of sulphur dioxide emissions suggests the presence of sulphide (pyrite) residues in the sample. No gas emissions are detected above a temperature 7of 45°C, and no changes are observed on TG curve. This information may facilitate set up of the firing program of products the properties of which are obtained though high temperature treatment.

3.1.3 High-temperature characteristics of raw material observed by a heating microscope

Figure 3 shows the thermal behaviour of raw material as observed through a heating microscope. The results of measurements are shown in the form of a curve reflecting changes in the sample profile area as a function of temperature; a set of images (Figure 4) showing the changes in shape of the sample profile while heating at temperatures ranging between room temperature to 1400°C is also provided. From the start of measurements up to a temperature of 830 °C, the sample displays a small, regular thermal expansion corresponding to approximately 3% in comparison with the area manifested at 22°C. At a temperature of 830°C, the sample begins to shrink as the sintering process starts and continues up to a temperature of 1260°C. At this temperature, the sample profile reaches a minimum area corresponding to 61% the initial value and is referred to as the temperature of maximum sintering of the material. On reaching maximum sintering, as a result of a further rise in temperature, the sample profile begins immediately to swell and increases to approx. 76% once measurements stop at 1400°C.

The results obtained show how the material has a desirable sintering characteristic, placing it as a potential raw material for use in the production of fired ceramic building materials. By means of this technology, the thermal properties of the material are particularly advantageous, consisting in a wide sintering interval that starts at a relatively low temperature of approx. 830°C and peaks at 1260°C. This behaviour of the raw material on heating may result in a wide range of materials, from highly porous materials fired at low temperatures to highly sintered products with low porosity fired at higher temperatures with use of fluxes. Such a wide sintering temperature interval promotes the safe firing of ceramic products without the risk of deformation caused by reaching of the softening point.

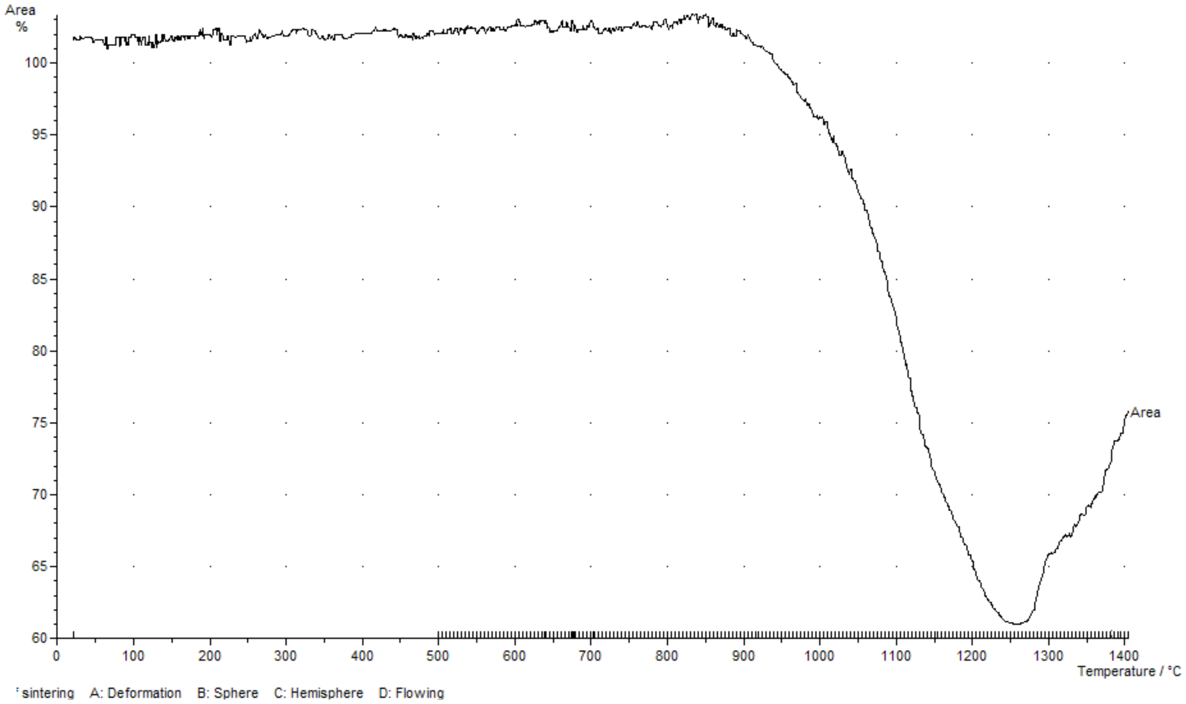

FIGURE 3: Curve showing the changes in sample profile area [in %] in line with measurements taken under the heating microscope.

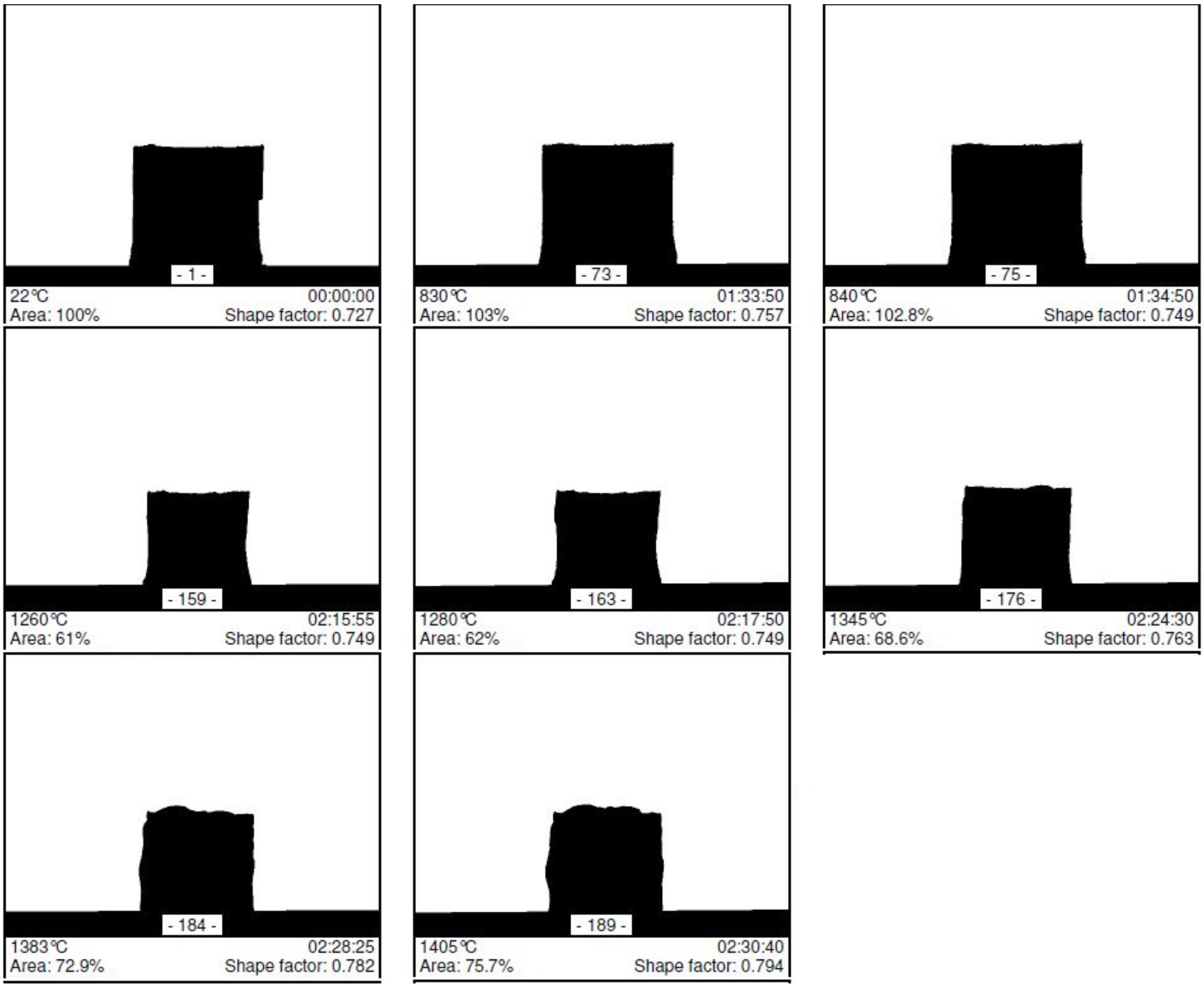

FIGURE 4: Images of changes in sample profile shape in line with measurements taken under the heating microscope.

3.1.4 XRD analysis of sample material

XRD analysis (Figure 5) revealed the presence of three crystalline phases visible in the diffraction pattern. In the range of low angles of 2 theta, i.e. the range from 0 to 10 degrees, there is a clearly visible reflect [dhkl = 10.000] coming from the crystalline phase of illite [ICDD 26-911]. Characteristic next peaks with lower intensity coefficients coming from the illite phase are assumed to correspond to the following values dhkl = 5.025; 3.344; 2.004. In the angular range of 10-15 2 theta, the most intense visible reflection comes from the kaolinite phase [ICDD 29-1488] with values of the strongest reflection corresponding to dhkl = 7.194. The marked phase of the hydrated aluminosilicate and its successive peaks assume the following values dhkl = 3.584; 2,342; 1,488.

The dominant phase in X-ray diffraction pattern is the SiO_2 phase with ICDD 33-1161, the highest reflection of which occurs in the angular range of 25-30 2theta (dhkl = 3.344). Further peaks occur throughout the course of the diffractogram and the values of the most intense peaks are shown in dhkl = 1.818; 1.541; 4.255.

It should be noted that the accuracy of diffractometric analysis reaches a value of crystalline phase content corresponding to approx. 5%. All crystalline phases present in the tested waste material below this value are outside the detection limit of XRD method.

3.1.5 Analysis of particle size distribution and specific surface area of the waste mud sample

The results of Blaine method air permeability analysis showed that the test material had a high surface area exceeding 10 000 cm^2/g at a specific density of 2.19 g/cm^3.

The surface area development analysis was supplemented by a detailed particle size analysis, the results of which are illustrated in the Figures 6 and 7. The particle size analysis showed how the material tested was very fine. The maximum grain size did not exceed a diameter of 0.5 mm. Detailed analysis of particle size ranges showed that the dominant fraction in the sample was 2.8 to 10 µm particles with a content of 31% v / v of the total sample. Significant contents in the sample were represented by 18% content of particles in the range of 10-19 µm and 16% particles in the range 19-40 µm Grains sized from 1.2 to 2.8 µm corresponded to 14% content and 40-100 µm 10%. The

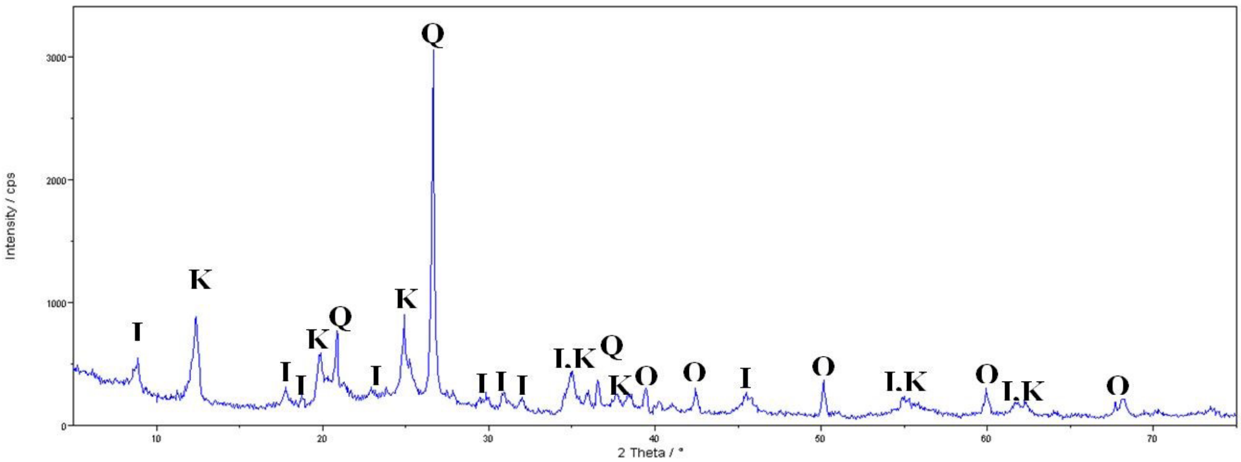

FIGURE 5: XRD curve of the waste mud sample; I - illite, K - kaolinite, Q - quartz.

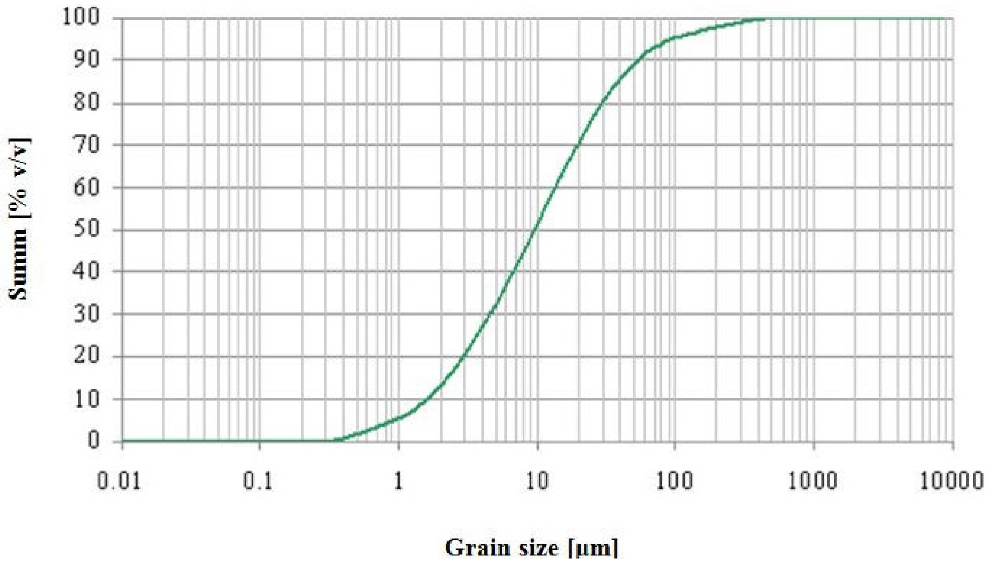

FIGURE 6: Cumulative curve of particle size distribution of the waste sample.

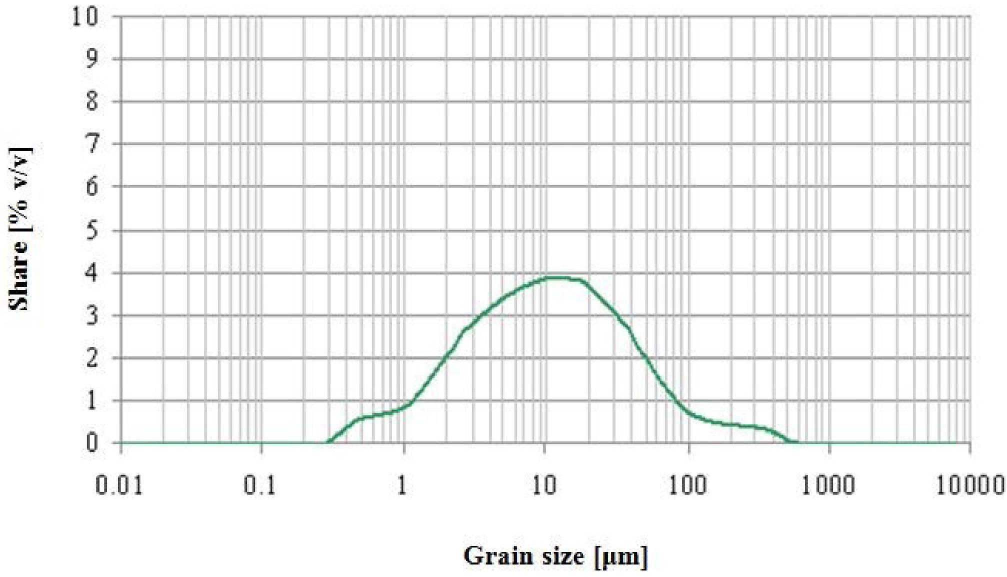

FIGURE 7: Histogram curve of particle size distribution of the waste sample.

sample was also characterized by particles sized between 0.5-1.2 and 100-300 µm in the range of 4% and 0.3-0.5 and in the range of 300-600 µm in the amount of about 1.5%.

4. CONCLUSIONS

The present study was focused on the preliminary characterization of waste from coal mines in the context of evaluation of its usefulness in the production of ceramic building materials. The results obtained in terms of thermal properties, mineral composition and granulometric analysis of the examined waste showed that these wastes could potentially constitute a component of ceramic masses in these technologies. In agreement with other studies, XRD analysis showed the presence of three main crystalline phases at varying contents in the material studied. The most prevalent component was SiO_2 quartz, as confirmed by chemical analysis, with approx. 54% of silica content. The second and third crystalline phases present in the sample were illite and kaolinite, both hydrated layer aluminosilicates. The content of these crystalline phases was confirmed by chemical analysis, which revealed an approx. 25% alumina content and approx. 3.5% potassium oxide. It should be noted that small amounts of other cations, such as Fe^{3+} or Na^{2+}, may be incorporated into the structure of clay minerals. Due to their crystallographic structure, with these silicates (mostly illite), the possibility of isomorphic substitution in the elemental cell and the ionic radii of the cations listed may serve as a matrix in which these cations can be incorporated. The suggested phenomenon may be explained by a small drift of peaks in the kaolinite diffractometric image in which Al^{3+} cations may incorporate Fe^{3+} cations. The same mechanism applies to illite mineral and sodium cations. It should also be noted that in the XRD image no reflections from hydrated calcium sulphates are visible, likewise failing to show STA thermal analysis, although the findings of chemical analysis suggest that this compound may be present. It is likely that content of the latter is below the detection threshold of these methods. The low sulfur content in form of sulphates and sulphides is advantageous for building ceramics, as it reduces the risk of corrosion of burnt products. The results of thermal analysis showed a significant amount of organic matter (carbon residue) in the waste to be treated, which may be problematic during firing, although at times may also prove advantageous. The organics present in the ceramic mass (in this case carbon) reduces consumption of the main fuel during firing due to an exothermic combustion effect, but only in the presence of a suitable firing process that ensures oxidation conditions in the kiln.

The results of thermal behaviour characterisation demonstrates that the material has a desirable sintering characteristic, placing it as a potential raw material for use in the production of fired ceramic building materials. In using this technology, similar thermal properties for the material, consisting in a wide sintering interval starting at a relatively low temperature (840 °C) and reaching approx. 1260 °C is an advantage. These properties of the raw material, when used during firing in the production of ceramics, facilitates the obtaining of a wide range of materials, from highly porous products fired at low temperatures to highly sintered with low porosity fired at higher temperatures with use of special fluxes. Such a wide sintering temperature interval likewise promotes the safe firing of ceramic products, without the risk of deformation caused by reaching of the softening point

The preliminary results obtained, confirming the presence of clay minerals, fine graining and thermal properties of the waste, suggest potential possibilities of using these wastes as a raw material to correct the rheological properties of the ceramic mass and porosity of the fired material in the technology of building ceramics.

The use of the waste material as a ceramic mass component in combination with a specific basic clay raw material should always be confirmed by initial laboratory tests. Subsequent tests should be performed on an industrial scale to determine the appropriate content of the additive and appropriate parameters for the manufacturing process.

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