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Determination of properties of clean coal technology post-process residue

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ABSTRACT

This article presents the possibilities of using modern measuring devices to determine the properties of process residues (Polish acronym: UPP). UPP was taken from the combustion process from a power plant in Silesia. Determining the properties of UPP is the basis for making decisions about its practical application, for example, as a raw material to obtain useful products such as: pozzolan, cenosphere or zeolite, for which there is demand. The development of advanced technology and science has given rise to modern and precise research tools that contribute to the development of appropriate methods to assess the properties of post-process residue. For this study the following were used: scanning electron microscope with EDS microanalysis and an analyzer for particle size-, shape- and number- analysis. The study conducted confirms the effectiveness of SEM analysis to determine the properties of post-process residue from Clean Coal Technologies (CCT). The results obtained are an introduction to further research on the determination of properties of CCT post-process residue. Research to determine the properties of CCT post-process residue only began relatively recently.

1. Introduction

Natural solid fuels are now considered, in many countries in the world (China, India, the USA, Australia, Japan and South Africa), as a raw material of strategic importance for the protection of local energy security. The Polish energy sector is based on the thermal processing of fossil fuels, particularly coal and lignite, which leads to the production of large quantities of post-process residue, which need to be re-utilized. According to Central Statistical Office data (GUS, 2015), Poland in 2014 produced a total of 21,942.3 thousand tonnes of waste energy, of this, 3835.8 thousand tonnes were coal fly ash, and 11,950.9 thousand tonnes were ash and slag from wet waste disposal furnaces. The combustion of conventional fuels leads to the formation of UPP such as fly ash, slag, ash from fluidised bed boilers, microspheres etc. (Galos & Uliasz-Bocheńczyk, 2005). Ash grains exhibit a variety of physical, chemical and mineralogical properties which affect their disposal as well as their economic use. So far, to determine the properties of post-process residue, traditional research methods were used which include: the determination of chemical components with analytical methods, the determination of particle size by means of sieve analysis, the measurement of specific surface area, etc. The development of advanced technology and science has given rise to modern and precise research tools that contribute to the development of appropriate methods for assessing the properties of post-process residue. Among modern measuring methods the following can be distinguished: scanning electron microscopy and EDS microanalysis which allows the identification of the elemental composition of the analysed material, analysis of the size, shape and particle number and their chemical identification using a microscope optical system.

New methods and directions of economic utilization of CCT post-process residue, primarily enforce the need to improve the methods and research tools to formalize and optimize processes of this type (Łączny, 2011).

Conditions for the formation and properties of CCT "post-process residue" determine the direction of its development. However, the problem faced is both the number and high variability of parameters. It seems reasonable to approach this issue in the form of a phenomenological model, in which different types of anticipated needs are assigned to the physicochemical properties of raw materials – mainly coal (Łączny, 2011). Technologies of thermal coal use bring about the formation of solid by-products, the source of which is a mineral substance contained in the coal rock. This

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substance is subjected to vitrification processes, consisting of a controlled supply of energy to the substance being vitrified which in high temperatures undergoes thermal decomposition with the separation of gaseous products, and then it is incinerated. When the ash resulting from this incineration is rapidly cooled, it obtains the structure of glass (Łączny, 1983). The main part of the mineral substance accompanying coal deposits that undergoes vitrification processes is mudstone which is dominated by minerals from the groups of kaolinite and illite; sandstones, carbonicerous shales. Others such as grit-stone, limestone and tuffite occur sporadically (Góralczyk, 2011). The chemical composition of coal-associated substance is important because of the resulting by-products from the processes of thermal coal processing.

The mineralogical and chemical composition of mineral substances contained in coal and the parameters of the process and, above all, the temperature have a significant effect on the properties of the post-process waste obtained which in turn dictate their use. The particle size of ash is very important and this affects their pozzolanic properties. A large amount of ash grains creates "bubbles" filled with a mixture of gases, so-called cenospheres. From a chemical point of view, the most important components of ash are SiO_2 and Al_2O_3. An increase in their content increases the pozzolanic properties of the material. Carbon is a harmful component, which accumulates mainly in larger ash fractions of >100 μm. In terms of phase composition, the primary phase is glass, which amounts for up to 80% of (Kurdowski, 2010). Other crystalline phases are quartz, mullite, hematite and magnetite.

The pozzolanic properties of ashes are associated with a glassy phase. Good quality ash is distinguished by: low carbon content, large content of glass, low alkali content and high fragmentation. Such properties of fly ash are the result of mineral matter and high combustion temperature, which is well above the melting temperature of ash and make it a product sought after in the market as it finds uses in many areas of the economy. Post-process waste in CCT can be used, among others, in cement, adhesives, lightweight aggregates and insulating materials as well as construction aggregates, backfilling materials and filtration. It is also used in agriculture as fertilizers (Olszewski, Świnder, Klupa, & Ciszek, 2012, pp. 123–136).

Post-process waste is a good material for the production of zeolite. Zeolite is spatial aluminosilicate with unusual properties. A characteristic of zeolite is the presence, in its composition, of particles of so-called zeolitic water, which during heating are removed from the structure whilst leaving the open skeletal structure of the crystal unchanged. Such mineral construction provides a unique molecular-sieve, adsorption and ion exchange properties, which have found application in many areas of life. The amount of ions that can be absorbed by a zeolite structure is enormous. As absorbents and molecular sieves, zeolites are used in many branches of industry. Zeolite is obtained in two ways: it can be extracted from natural deposits or synthesized in a laboratory (Wiśniowska, Karwowska, & Sperczyńska, 2015). The substrate for the crystallization of zeolite is aluminosilicate which is unstable in these environments, this is often in the form of volcanic minerals or clay minerals. Natural zeolites have limited application. Therefore, research is focused on the search for cheap and available substrates for the production of zeolites (e.g. kaolinite), while striving to reduce the costs of the reaction itself (Kołodyńska & Franus, 2016). Fly ash seems to be a very promising material for the production of zeolite (Derkowski, Michalik, Franus, Kutrzuba, & Piasecki, 2003; Suchecki, 2005). The synthesis of zeolites from ashes lasts from a few to several hours. The most important aspect, in fly ash used in the synthesis of zeolites, is the ratio of SiO_2 to Al_2O_3, which should be from 1:2 (Tanaka, Matsumura, & Hino, 2004; Tanaka, Furusawa, & Hino, 2002). The mineralogical composition of the starting material is of high significance for the formation of zeolite phases (Derkowski & Franus, 2004; Majchrzak-Kucęba, 2001). The formation of zeolites is influenced by a non-crystalline phase and a high content of mullite during the crystalline phase. In the fluidal ash, due to the low temperature of the process, there is no mullite phase; however, these ashes demonstrate usefulness for the production of certain types of zeolites: Na-A, sodalite and zeolite X.

Its use in so many diverse fields makes zeolite a universal material in the 21st century. Its synthesis from fly ash has an environmental dimension. As, instead of storing waste (fly ash), it is neutralized by being used in the production of full value products.

Fly ash resulting from coal combustion predominantly takes the form of solid spherical particles and also of spherical particles that are hollow inside, called microspheres or cenospheres. By modifying the combustion process parameters and the adjusting the conditions of carbon particles' presence in the high temperature zone of a power boiler and through the use of additives to coal, the process can be guided so that cenospheres become the dominant component of the fly ash. The development and implementation of the production technology for cenospheres during coal combustion can lead to a significant reduction in the resulting stream of solid waste and a useful product, applicable in many industries, to be obtained.

The most important properties of microspheres include:

- high temperature resistance,
- neutral impact on the environment – natural product,
- good thermal insulation,
- good sound insulation,
- low specific gravity.

The aim of the research presented in this paper is to confirm the possibility of using modern measuring instruments to determine the properties of post-process residue, which acts as the basis for making decisions regarding its practical use, for example as a raw material to obtain useful products such as: pozzolan, cenosphere or zeolite, for which there is demand in the market. The paper presents the results of two samples:

- fly ash code 10 01 02 – sample A,
- slag grate code 10 01 01 – sample S (Regulation of the Minister of the Environment, 2014).

2. Methods

A scanning electron microscope with variable vacuum SEM SU3500 by Hitachi, which cooperates with an X-ray spectrometer with EDS energy dispersion UltraDry Thermo Scientific Noran System 7, was used in the study. The UltraDry detector in conjunction with the X-ray microanalysis system enables the collection of high-resolution data at high capacity without the use of liquid nitrogen.

A Scanning Electron Microscope (SEM) with an EDS attachment enables the observation of the surface structure of matter at a microscopic level, with magnification of 5–300,000 times. An SEM is used for the observation and characterization of organic and non-organic materials on a scale ranging from nanometer to micrometer in size. The microscope has a low vacuum of observation which enables the observation of non-conductive samples and objects containing water without the need to prepare formulation.

The SEM was equipped with an EDS detector, which allows for the identification of the elemental composition of the tested material for all elements with an atomic number greater than boron. Most of the elements are detected at concentrations in the range of

0.1%. SEM-EDS enabled the analysis of each grain and grain distribution in a specimen.

Grain-size analysis (particle size) was determined using an analyzer to determine the size, shape and number of particles and a Raman attachment was used for chemical identification – Morphologi G3S-ID by Malvern.

The study involved samples from power plants located in Silesia, which use energy production technology based on conventional coal combustion.

2.1. Preparation of samples for observation under an electron microscope

Metallographic specimens were made for the observation of ash under a microscope. A sample (approx. 0.5 g of powder) was mixed with iodinated epoxy resin, hardened and then poured into plastic moulds where it was allowed to solidify for about 24 h.

Iodized epoxy resin was prepared as follows:

a) 7 g of iodoform (CHI_3) were dissolved in 50 g of epoxy resin,
b) the mixture was heated in a water bath to about 60–80 °C.
c) cooled iodinated epoxy resin was ready to be used for the preparation of a microsection.

Iodinated epoxy resin was used to increase the contrast between the ash grains and the matrix in the BSE image on the electron microscope. Microsections were polished using abrasive paper (SiC), and then polished using a diamond slurry (final particle size of 1 μm).

The test samples were not coated with a conductive layer.

2.2. Preparation of the samples for the morphologi G3S-ID analyzer by malvern

From a representative sample, 4 mm^3 was taken using a spatula. The sample was put into a sample cartridge, then placed in a dispersion chamber. After inserting a cartridge into the dispersion chamber, the chamber is locked to form a hermetic seal. Then the chamber is inserted into the dispersion clamp and a hose is fastened to it that supplies air from the top of the chamber. A sample prepared in this way is ready to be dispersed.

The parameters of the dispersion:

- dispersing pressure – 0.8 bar,
- dispersing time – 20.0 ms,
- settling time – 60 s.

3. Results

The results of particle size analysis of the test samples A and S are summarized in Table 1, and particle size distribution is shown in Figs. 1–4.

The range of particle size in the tested samples was from 0 to 156.13 μm. The content of coarse grains in sample A was 0.24% and the maximum particle diameter was 156.13 μm. In sample S, the content of coarse grains was insignificant and amounted to 0.00038%, and their maximum diameter was 124.43 μm. The samples contained a greater number of smaller grains (1-10 μm) 69.38% (sample A) and 82.17% (sample S), but also a large population of particles of 1.0 μm grain size of (0.1-1.0 μm) 11.25% (sample S) and 20.15% (sample A). The samples were characterized by finer particle size distribution. Coarse grain content was negligible and amounted to approximately 0.24% of the sample of fly ash.

The test samples can be used for the production of adhesives, cements, concretes, fillings, ceramic materials and plastics.

To determine the properties of the samples tested using a scanning electron microscope, a total of about 100 microscopic morphology images of the samples were taken, along with a map of element distribution in microregions (mapping). Typically, several hundred particles were tested at several magnifications. Images were enlarged 500, 1300, 1500 times (due to different grain size), at an accelerating voltage of 20 keV. Due to the large number of pictures, this article only contains a selection of images, but conclusions are drawn on the basis of all the results of the research. The procedure for registering sample images consisted of point by point analysis (forming a grid) over the entire surface of the formulation. In order to demonstrate the possibility of SEM analysis in the study of the properties of post-process residue, exemplary images of morphology (shown in Figs. 5a and 6a) and the element distribution maps of micro-regions (in Figs. 5b and 6b) are presented. Maps shown in Figs. 5 and 6 show the distribution of elements in the analysed areas of the samples. Characteristic elements are shown in the form of bright (colourful) dots. In cases when there is an increased concentration of a given element in a specific area of the sample, the density of the points increases. Quantitative and qualitative parameters of the samples are determined using a scanning electron microscope with an EDS detector. EDS detector operation is based on the phenomenon of the production of X-rays by photons (interpretation of the spectrum of the characteristic X-ray radiation that is formed as a result of irradiation of analysed samples by high energy radiation).

Table 2
The average content of chemical composition.

Designation	Sample A Mean [%weight.]	Sample S Mean [%weight.]
SiO_2	13.07	52.42
Al_2O_3	10.28	20.50
Fe_2O_3	22.42	7.59
CaO	20.60	3.84
MgO	10.12	3.08
Na_2O	2.23	0.52
K_2O	0.24	2.63
SO_3	18.99	2.60
TiO_2	0.54	0.86
BaO	0.44	0.77
Total:	**99.61**	**94.82**

Table 1
Systematic parameters of size composition.

Sample symbol		Sample A	Sample S
Characteristic grain d (μm)	d^{10}	0.73	0.93
	d^{50}	2.08	3.09
	d^{90}	10.30	8.56
Average diameter	(μm)	4.85	4.21
Standard deviation		9.67	3.80

Key: d^{10}, d^{50}, d^{90} – characteristic grain diameters below which there is respectively: 10, 50, 90% of the material analysed.

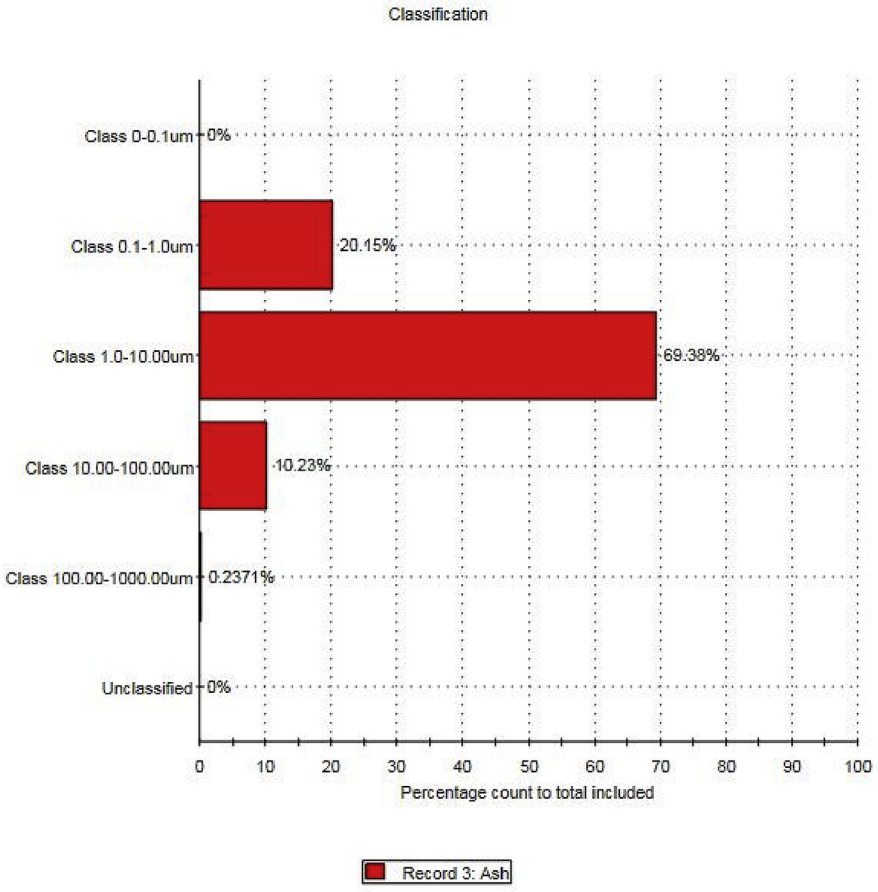

Fig. 1. Particle grain size of ash sample A, a histogram of the selected size grade.

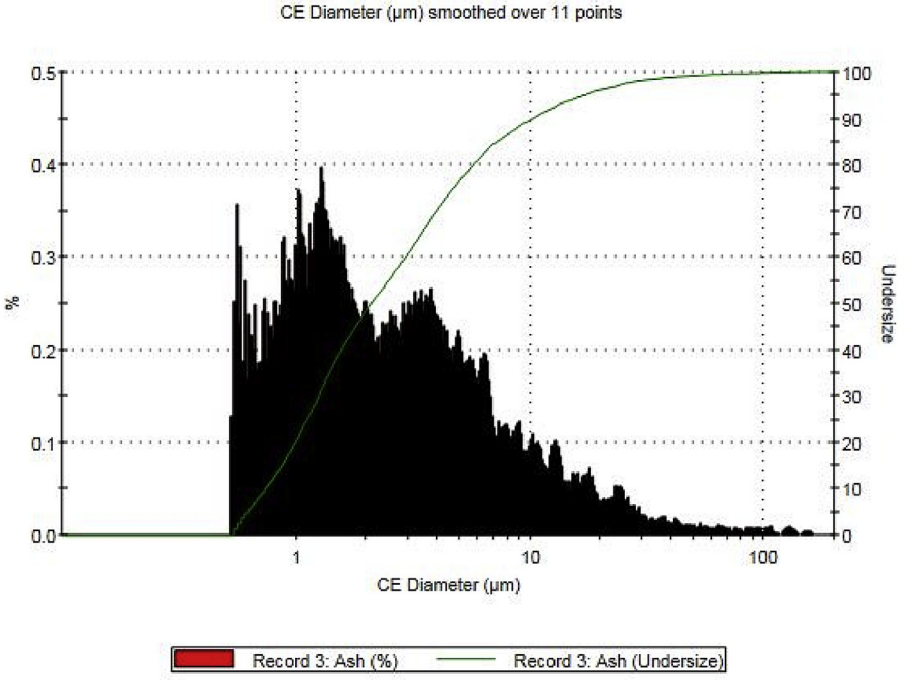

Fig. 2. Particle grain size of ash sample A, density grain size of slag and its cumulative distribution.

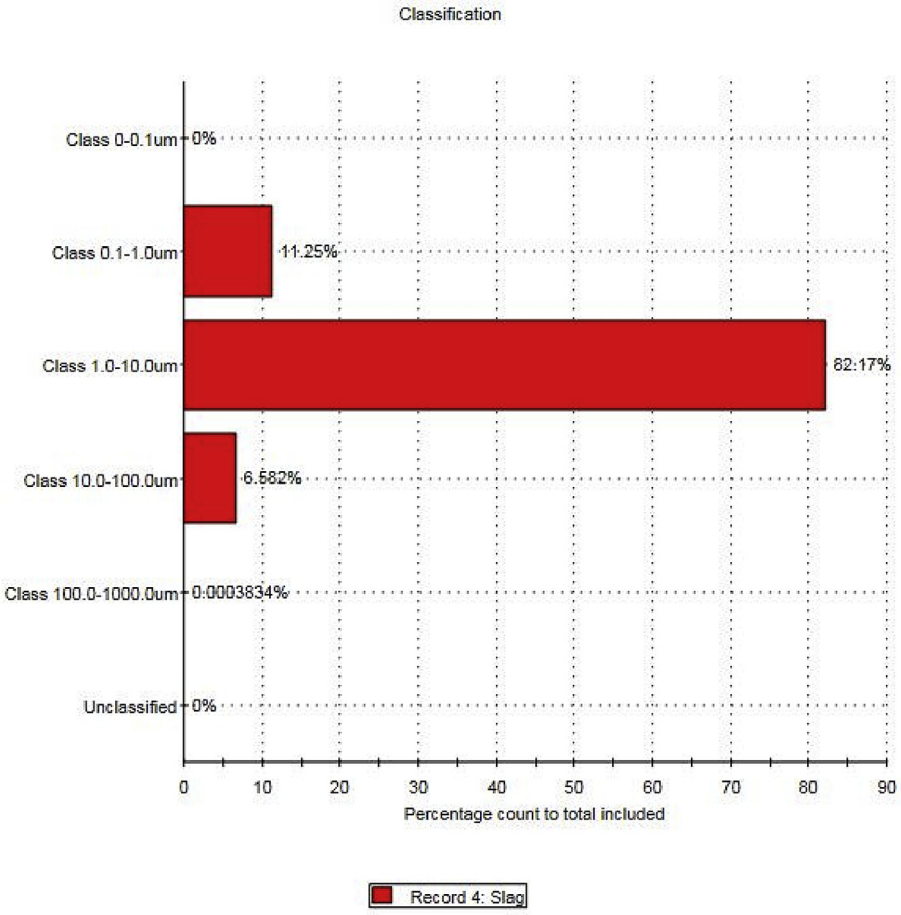

Fig. 3. Particle grain size of slag sample S, a histogram of the selected size grade.

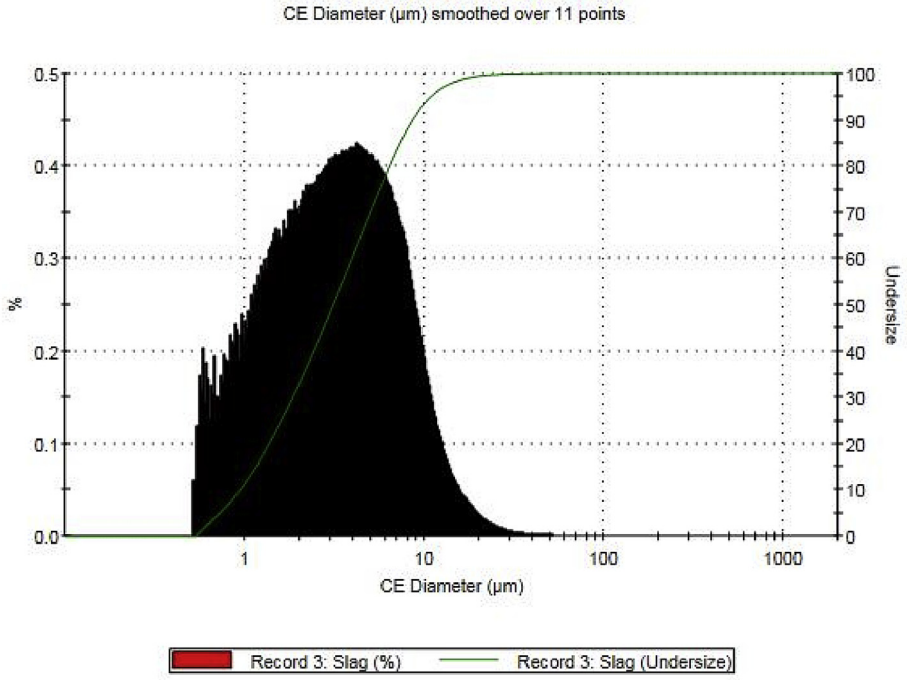

Fig. 4. Particle grain size of slag sample S, density grain size of slag and its cumulative distribution.

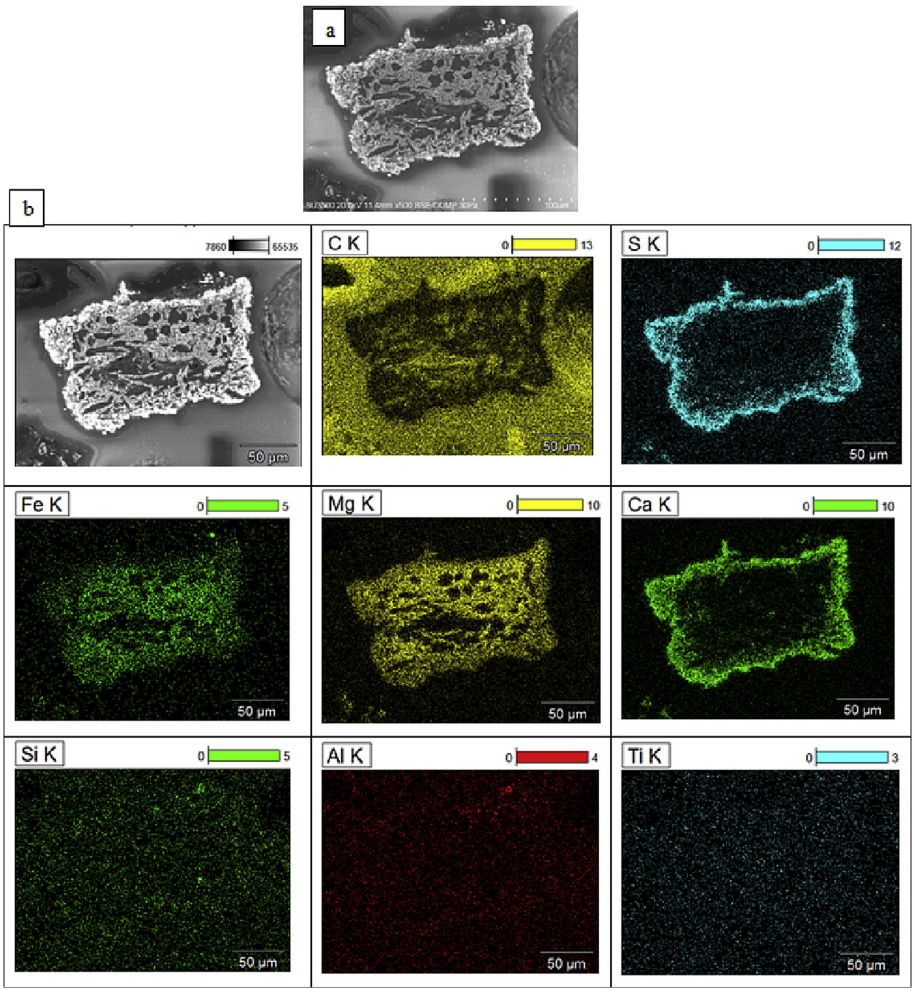

Fig. 5. Sample A exemplary grain, a) an SEM image of the selected area with a magnification of 500×; b) mapping of elements in these micro-regions.

The average content of the chemical composition of samples A and S is shown in Table 2.

Characteristics of the samples, based on the interpretation of photographs taken using a scanning electron microscope with X-ray microanalysis, includes the determination of: the shape of grains, approximate particle size (based on the attached scale) and elemental composition.

In ash sample A, there are Al and Si elements which is characteristic for the amorphous phase and minerals such as quartz and mullite. In smaller quantities there are Na, Mg and K elements which are also components of the amorphous and mineral phase, such as: periclase, mica and feldspar. In the sample, there are large amounts of Fe-O and Ca-O elements confirming the presence of pyrite, kaolinite and carbonates. Moreover, the ash contains insignificant amounts of Ti, which is present in iron-bearing minerals.

In sample S, there are Al, Si, Ca and Mg elements which are characteristic for melilite minerals, which consists of calcium silicates (larnite) and Fe sulfides. In addition, sample S contains small amounts of sulphur, in the case of slags that are low in sulphur, minerals such as magnetite, olivines and enamel with variable chemical composition are present.

Grains examined in the above test samples are characterized by irregular shapes; there are elongated grains, square-shaped grains and grains in the shape of plates or bands. Round grains do not occur.

Post-process residue (ash, slag) consist of a crystalline phase (e.g. anorthite, mullite, spinel), amorphous aluminosilicates of different elemental compositions and particles from underburnt coal.

Tested ashes and slags can be used in the production of construction materials in road construction, agriculture and mining for the production of fillings.

4. Conclusions

Post-process residue, formed in the energy industry, is a valuable secondary raw material that can be used in many ways. It is important to recognize the exact properties of by-products, as they may significantly vary in chemical composition and physical properties. Detailed determination of the properties will enable the selection of optimal directions for their use. SEM analysis can be successfully applied to determine the properties of post-process waste. Interpretation of the results of the research conducted allows relevant information on the physical properties and chemical composition in micro-regions' samples to be obtained, which is important in determining appropriate methods of disposal. The described methods of research show the image properties of the tested samples in micro-regions, but do not provide a full description. To undertake further research using modern methods of measurement (e.g. XRD, DTG, or analysis of the density by pycnometry) will comprehensively define the properties of UPP, which is the basis for making decisions regarding its practical use.

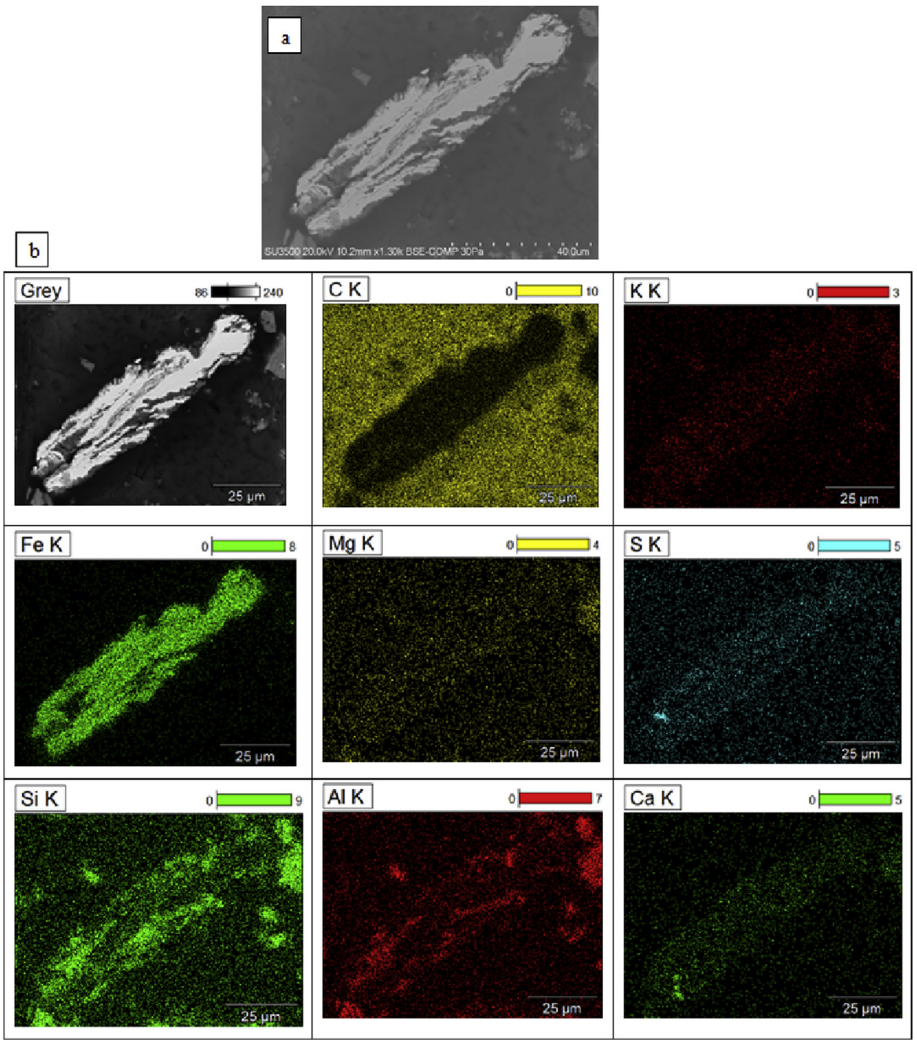

Fig. 6. Sample S exemplary grain, a) an SEM image of the selected area with a magnification of 1300×; b) mapping of elements in these micro-regions.

Currently, post-process residue (ash, slag) is used primarily in construction, ceramics, mining and road construction.

At the same time an important element of the optimal use of post-process residue, is to look for new forms of its disposal. The following represent a very promising direction of development of these products: recovery technologies of chemical elements, the preparation of zeolites, production of cenospheres and puzzolan, and agricultural use as fertilizer. Thanks to a fuller and better use of post-process residue, its storage and environmental impact is reduced. The use of post-process waste, especially as a secondary raw material allows the demands of sustainable development in the energy technology and industry to be met.

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