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The forms of occurrence and chemical composition of sulfides in the LW Bogdanka bituminous coal deposits of the Lublin Coal Basin

Introduction

Minerals present in coal can be divided into three groups on the basis of their origin: minerals from the original plants (Stach et al. 1982; Ward 2002) formed in the initial stage of the coalification process or introduced into the peat by water and wind (Zarębska and Pernak-Miśko 2007) or deposited in the second phase of the coalification, after the consolidation of coal, by ascending or descending solutions in cracks, fissures, and cavities or as a result of the alteration of primarily deposited minerals (Ward 2016). Usually, the carrier of these components is the inorganic matter. The inorganic matter present in coal includes: dissolved salts and other inorganic substances in the coal's pore water; inorganic elements incorporated within the organic compounds of the coal macerals; and discrete inorganic particles (crystalline or non-crystalline) representing true mineral components. In coal, inorganic matter is most commonly found in the form of minerals, aggregations (veins), macroscopically visible layers, or dispersed throughout the coal macerals (Ward 2002). The size of individual mineral grains is highly variable, ranging between less than one micrometer to tens or hundreds of micrometers (Taylor and Glick 1998).

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The most commonly found minerals in coal are: quartz, clay minerals, carbonates, and sulphide minerals. Sulphides can be categorized as either of syngenetic (primary), early-diagenetic, or epigenetic (secondary) origin (Stach et al. 1982) which are mainly represented by: pyrite (FeS₂), marcasite (FeS₂), pyrrhotite ($Fe_{(1-x)}S$), sphalerite (ZnS), galena (PbS), and chalcopyrite (FeCuS₂). It should be noted that pyrite is a common mineral in many coal seams (Demchuk 1992). A number of studies (Adams Frankie and Hower 1987; Balme 1956; Chou 2012; Dai et al. 2006, 2010; Elswick et al. 2007; Renton and Scott Bird 1991; Widodo et al. 2010) have described the characteristics, type, morphology, genesis, and distribution of pyrite in coal seams from different deposits. In Poland, this topic has been discussed by (Bielowicz and Misiak 2016, 2017; Kucha and Lipiarski 1998; Matl and Wagner 1995; Sawłowicz 2000; Wagner 2001). However, is to determining the effect of a given component on the natural environment and human health more important.

This study is aimed at investigating the quality of bituminous coal in the Bogdanka coal mine seams with a special emphasis placed on the sulphur content and critical raw materials content, the forms of occurrence of sulphides on both macroscopic and microscopic scale, and on the chemical analysis in the micro area.

1. Location

The Bogdanka coal mine is located in the Bogdanka syncline which belongs to the platform part of the Lublin Coal Basin. The geological formations that are found in the area include Quaternary, Paleogene, Cretaceous, Jurassic, and Carboniferous formations. The Westphalian coal-bearing formations of the Lublin Basin are also being exploited. The thickness of this series is between 43.30 and 408.10 m, while the bottom is in the range between 750–1115 m. The layers (indexed from 369 to 399) and the coal seams (numbered 2–49) occur among claystone-sandstone formations. The profile of the component discussed above is well formed in the area of the Bogdanka syncline, where the layers thickness reaches up to about 400 m. The coal seams of the Lublin formation are highly variable; while their maximum thickness is 4.10 m, they locally disappear due to sedimentation and erosion processes (Dembowski and Porzycki 1988).

2. Sampling and analytical methods

Coal samples for this study were collected from boreholes and outcrops in the Bogdanka coal mine. One channel sample and 15 spot samples were collected from each coal seam; seven spot samples were selected for further, more detailed analysis. A petrographic analysis of samples from the No. 385/2 and No. 391 seams was performed. Petrographic examination was performed in both reflected white and blue light using a Zeiss Opton microscope according to the PN-ISO 7404-3:2001 standard. Two coal seams with the most diverse forms of sulphides were selected for the wavelength dispersive X-ray spectrometer (WDS) analysis. The coal samples were tested using a JEOL JXA-8230 superprobe electron microprobe to analyze the chemical composition of mineral in the micro area (<1 μ m). The elemental composition analysis in the micro area was performed using an energy dispersive spectrometer (WDS) X-ray microprobe analysis for all elements from boron to uranium. The quantitative analysis of the elemental composition using the secondary wavelength-dispersive X-ray spectroscopy (WDS) was performed using five spectrometers. The WDS analysis was performed with a 20 nA current and an accelerating voltage of 20 kV. Counting times of 20 seconds on peak and 10 seconds on both (+) and (-) backgrounds were used. The following standards and lines were used: HgTe, PbS, CdS, FeS₂, Au, Co, Sb₂S₃, Ag, Ni, ZnS and GaAs.

The pictures in the micro area and the EDS analysis were taken using a FEI Quanta 200 FEG field emission scanning electron microscope.

3. Results and discussion

3.1. Petrographic analysis

When it comes to the petrographic composition of coal from the No. 385/2 seam, the mineral matter content is 1.4%; the share of macerals from the vitrinite group is 61.0%, while in the case of the liptinite and inertinite groups amounts to 17.4% and 20.2%, respectively. Compared to the above mentioned seam, the mineral matter content in the No. 391 seam (3.4%) is slightly higher, the content of macerals from the vitrinite group (66.3%) is higher, while the content of macerals from the liptinite and inertinite groups is lower.

Based on the macroscopic observation, it was found that iron sulphides (pyrite, marcasite) in the currently exploited coal seams of the Lublin Coal Basin are relatively rare. The average sulphur content for the No. 385/2 seam is 0.98%, and for the No. 391 seam is higher and amounts to 1.15%. They usually occur in the dispersed form in dull coal (durain) layers with a thickness ranging from several millimeters to several centimeters. Massive forms of iron sulphides, typically of irregular or lenticular shape and with maximum dimensions of up to several centimeters, are less commonly found. Vein forms are considered to be rare. Other common forms of iron sulphides associated with coal cracks are finely crystalline pyrite and marcasite.

A standard microscopic examination, using a reflected light optical microscope, allows for several forms of the occurrence of iron sulphides in the examined coal seams to be distinguished. The presence or absence of bireflection is an undisputed determinant used to differentiate pyrite from marcasite (Uytenbogaardt and Burke 1985). The varying proportions of pyrite and marcasite depend on the form of their occurrence. When it comes to macroscopically isolated massive forms, the microscopic examination has shown massive

aggregations of iron sulphides (Fig. 1A, B) including euhedral crystals with dimensions of up to 100 μ m (Fig. 2) and framboids with a maximum diameter of up to 40 μ m (Fig. 1B). Massive sulphide forms are often accompanied by a halo of dispersed veins and framboids (Fig. 1C). In the examined coal, vein forms and dispersed framboidal forms are often isolated and not associated with massive aggregations. Such forms of iron sulphides, occurring in fractures and cleats in coal, are referred to as "infiltrational pyrite" by (Kortenski and Kostova 1996). Pyrite and marcasite commonly fill the fusinite cells (Fig. 1D). Such forms of iron sulphides, that shape cell lumens and pores filled with plant debris (dead plant material), are referred to as "anhedralpyrite" (Kortenski and Kostova 1996). The most common form of the occurrence of iron sulphides in the examined coal seams are dispersed framboidal forms (Fig. 1 E–H). Framboidal pyrite is an early diagenetic form of pyrite (Diehl et al. 2005; Wilkins et al. 1995) that is categorized as syngenetic (Dai et al. 2007) and originates from the pyritization of sulphur bacteria (Casagrande et al. 1977; Kortenski and Kostova 1996; Querol et al. 1989; Renton and Cecil 1979). The dimensions of individual framboids vary between less than 1 up to 50 µm. Occasionally, framboids are accompanied by iron sulphide coat (Fig. 1E). In the case of high concentrations of framboids, polyframboids with sizes of up to 900 µm (Fig. 1E-H) are being formed. As shown in Figure 1G, the density of polyframboids is variable; in the upper part of the image, a polyframboid with a diameter of 300 microns is characterized by a low density, while in the bottom side polyframboid with a diameter of 700 µm is characterized by a substantial (solid-like) density.

Finel crystalline pyrite occurring in the coal cracks were examined using a SEM microscope. These are octahedral crystals with sizes of up to 100 μ m (Fig. 2), which were formed in the later stage of coal formation (epigenetic). They are typical euhedral forms with well-developed crystals in the dispersed form, as described by (Kortenski and Kostova 1996; Querol et al. 1989).

<sup>Fig. 1. (A) Pyrite and marcasite in massive forms containing euhedral crystals (reflected light).
(B) Pyrite and marcasite in massive forms containing framboids. (C) Massive sulphide forms, often accompanied by a halo of dispersed veins and framboids. (D) Pyrites and marcasites filling fusinite cells.
(E) Framboids accompanied by iron sulphide coat. (F) Framboidal and polyframboidal iron sulphides.
(G) Polyframboids with variable density. (H) Variable density of framboids within a single polyframboid</sup>

^{Rys. 1. (A) Piryt i markasyt masywny zawierające euhedralne kryształy (światło odbite). (B) Piryt i markasyt masywny zawierające framboidy. (C) Masywne formy siarczków, którym często towarzyszy aureola żył i framboidów. (D) Piryty i markasyt wypełniające komórki fuzynitu. (E) Framboidy z otoczką z siarczków żelaza. (F)) Framboidyi poliframboidy siarczków żelaza. (G) Poliframboidy o zmiennej gęstości. (H) Zmienna gęstość framboidów w obrębie pojedynczego poliframboidu}



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Fig. 2. Octahedral crystals of pyrite occurring in coal cracks (SEM) Rys. 2. Oktaedryczne kryształy pirytu występujące w szczelinach węgla (SEM)

3.2. The chemical analysis of sulphides in the micro area

The WDS in-situ analysis revealed the chemical composition of sulphides, showing that the examined seams mainly contain iron sulphides. The scanning proton microprobe can observe and quantify trace metals that are below the detection limit of an electron microprobe. In addition, small amounts of galena and sphalerite were also found. The iron sulphides also contained admixtures of Pb, Hg, Cu, Au, Ag, As, Co, and Ni. The contents of the listed elements are above the detection limits of the electron microprobe (Table 1). Minor differences in the chemical composition were manifested with the change of the image color.

Pure pyrite and marcasite contained 46.55% Fe and 53.45% S. The sulphides in the tested samples ranged from 45.42 to 46.44% Fe and between 52.82 and 53.70% S, with mean values of 46.14% Fe and 53.18% S (Table 1). Both iron and sulphur content in the tested minerals were poorly variable. Similar results for Fe and S content in iron sulphides from coal were obtained by (Finkelman et al. 2002; Kucha and Lipiarski 1998).

No.	1	2	3	4	5	6	7
	Seam No. 385/2				Seam No. 391		
Hg	0.000	0.029	0.000	0.000	0.000	0.000	0.000
Pb	0.056	0.251	0.207	0.155	0.017	0.050	0.129
Cd	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	46.220	46.169	46.437	46.300	46.271	45.425	46.123
S	53.005	53.705	53.103	53.172	52.939	52.823	53.495
Au	0.007	0.087	0.000	0.123	0.046	0.007	0.105
Со	0.070	0.069	0.049	0.075	0.056	0.056	0.069
Sb	0.000	0.002	0.000	0.000	0.000	0.000	0.009
Cu	0.006	0.017	0.000	0.000	0.000	0.000	0.028
Ag	0.007	0.003	0.003	0.003	0.000	0.000	0.006
Ni	0.000	0.008	0.003	0.010	0.001	0.000	0.005
Zn	0.000	0.000	0.000	0.000	0.000	0.016	0.000
As	0.068	0.000	0.000	0.447	0.000	0.000	0.000
Ge	0.000	0.000	0.000	0.005	0.025	0.000	0.000
Total	99.439	100.340	99.802	100.290	99.355	98.377	99.969
Comment	Fig. 7A	Fig. 7B	Fig. 7C	Fig. 7D	Fig. 7E p.1	Fig. 7E p.2	Fig. 7F

 Table 1.
 The chemical composition (%) of iron sulphides determined by WDS analysis

Lead reaches up to 0.05% in massive pyrite and marcasite forms (Table 1, Fig. 3B). The Clarke value of this element in the Earth's crust is 15 ppm (Kabata-Pendias and Mukherjee 2007).

The sulphides with high lead content are characterized by a lighter color. Generally, framboidal pyrites contain less lead; its maximum value in the examined sulphides is up to 0.15%. In the study by (Hower et al. 2008), the lead content in pyrites also did not exceed 0.2%. The study by Diehl et al. (2004) on Alabama coals has confirmed up to 18 ppm Pb in pyrites while has found no relationship between pyrite development and the Pb content.

Mercury abundance in the Earth's crust is very low, ranging between 0.02–0.06 ppm (Kabata-Pendias 2011; Mastalerz et al. 2004) assumed a correlation between Hg and pyrite, suggesting that mercury is only partially associated with pyrite. Similar observations, indicating that elevated mercury content has been determined in only a few sulphides, have been reported by (Hower et al. 2008).



In the analyzed sulphides, Hg has been found in only one sample (Fig. 3B), while its content amounted to 0.03%. Significant differences in mercury content, depending on the pyrite and marcasite morphological type, have not been shown.

The Clarke value of zinc in the Earth's crust is 52–80 ppm (Kabata-Pendias and Mukherjee 2007). The zinc content in the tested coal sulphides is very variable, with a maximum of 0.02% in framboid binder. Locally, in some deposits, Zn content in pyrites can reach up to 0.05% (Belkin and Luo 2008).

Copper occurs in the Earth's crust at concentrations between 25-75 ppm. Copper has a high affinity for sulphur. It is commonly associated with chalcopyrite, FeCuS₂; sphalerite, ZnS; pyrite, FeS; and galena, PbS. In the case of sulphides in the tested coal, higher Cu values, reaching up to 0.03% (Fig. 8F), are observed in massive forms. In Lower Cambrian black shale (stone coal), Guizhou Province, China, the content of Cu in pyrites amounts up to 0.79% (Belkin and Luo 2008).

BDL

In the earth's crust, the mean Ni abundance has been estimated at about 20 ppm (Kabata-Pendias and Mukherjee 2007). Nickel reveals both chalcophilic and siderophilic affinity. Nickel occurred only in some of the tested sulphides, regardless of their morphological type. The highest measured content was 0.01% in framboidal pyrite. Locally, at individual deposits, the nickel content can reach 1.37% (Belkin and Luo 2008). In the study by (Hower et al. 2008), Ni, Cu, and Zn were found in some of the samples, while their concentrations ranged from low values to more than 0.01%.

Cobalt is a relatively rare element; its average content in the Earth's crust amounts to 200 ppm (Kabata-Pendias and Mukherjee 2007). The cobalt content in the tested sulphides

Fig. 3. The WDS (wavelength-dispersive X-ray spectroscopy) image of sulphides with the measurement points (A). Iron sulphides (pyrite, marcasite) with a local Ag and Co enrichment (Seam No. 385/2),

- (B) Iron sulphides (pyrite, marcasite) with a local Hgand Pbenrichment (Seam No. 385/2),
- (C) Iron sulphides (pyrite, marcasite) with a local Pb enrichment (Seam No. 385/2),
- (D) Massive ironsulphides (pyrite, marcasite) with a local Au enrichment (Seam No. 385/2),
 - (E) Polyframboids with a local Ge enrichment (Seam No. 391, point 1),
 - (F) Iron sulphides (framboids) with a local Cu enrichment (Seam No. 391),

(G) Iron sulphides (pyrite, marcasite) with galena (Seam No. 391),(H) Siderite (Seam No. 385/2)

Rys. 3 Obraz WDS (spektroskopia rentgenowska z rozpraszaniem długości fal) siarczków z punktami pomiarowymi (A). Siarczki żelaza (piryt, markasyt) z miejscowym wzbogacaniem Ag i Co (pokład 385/2), (B) Siarczki żelaza (piryt, markasyt) z miejscowym wzbogaceniem Hg i Pb (pokład 385/2), (C) Siarczki żelaza (piryt, markasyt) z miejscowym wzbogaceniem Pb (pokład 385/2), (D) Masywne siarczki żelaza (piryt, markasyt) z miejscowym wzbogaceniem Au (pokład 385/2),

(E) Poliframboidy z miejscowym wzbogaceniem w Ge (pokład 391, punkt 1),

(F) Siarczki żelaza (framboidy) z lokalnym wzbogaceniem Cu (pokład 391),

(G) Siarczki żelaza (piryt, markasyt) z galeną (pokład 391), (H) syderyt (pokład 385/2)

ranged from 0.05 to 0.7% (Fig. 3A). The analysis has not confirmed significant differences in the cobalt content of different types of sulphides.

The geochemical characteristics of Ag are similar to those of Cu. Silver was measured only in some of the sulphides and the maximum content amounted to 0.01%.

The abundance of Au in the Earth's crust is about 3 ppb; in the case of coal, this value amounts to 4 ppb. In the analyzed minerals, the Au content amounts up to 0.12%. The average Au content in the tested crystals is 0.05%. Such Au contents are often found in natural pyrites (Fleet and Mumin 1997).

Antimony (Sb) is a rare element; its average content in the Earth's crust ranges from 0.2 to 0.5 ppm (Kabata-Pendias and Mukherjee 2007). The study has shown that antimony is present only in massive sulphides, where its content reaches up to 0.01%.

Arsenic has the highest concentration of all admixtures in pyrite and marcasite. Arsenic is widely distributed in the environment. It occurs in the Earth's crust in the range from 0.5 to 2.5 ppm (Kabata-Pendias and Mukherjee 2007). In the massive pyrites, its content reaches up to 0.45% (Fig. 3D). The measured content is relatively low. Meanwhile, higher content can be observed in other deposits, including the Lost Creek deposit, where the arsenic content in pyrites is 0.65 % (Diehl et al. 2004). What is more, the study (Diehl et al. 2004) suggests the dependence of pyrite concentration on the morphology of sulphides, while the highest concentrations can be observed in massive forms. However, the question of enrichment in arsenic in impregnation forms is not clear. The element distribution map of As demonstrates at least two episodes of opening and sealing of the veins by As-poor and As-rich pyrite (Diehl et al. 2004). An electron microprobe study of a 0.04% Aslithotype from the Fire Clay coal bed, eastern Kentucky, by (Hower and Eble 2005) has found wide variations in the concentration of As in different Fe-sulphide morphologies. In the examined bituminous coal from the Bogdanka coal mine only some of framboidal pyrites, believed to be syngenetic framboids, were enriched in As. Drobniak and Mastalerz (2007) have examined pyrite-As associations in the Springfield and Danville coals, Indiana. It has been suggested that arsenic is mainly associated with pyrite, both syngenetic and epigenetic. Similar observations have been presented by (Hower et al. 2008; Yudovich and Ketris 2005).

Germanium is not considered to be an extremely rare element. Its crustal average is estimated to be about 1.6 ppm (Taylor and McLennan 1995). In the examined sulphides, germanium was found only in framboids, while its content reached up to 0.02% (Fig. 3E).

In addition to pyrite and marcasite, other sulphides and siderite can also be found (Fig. 3H). Sparsely occurring sphalerite and galena (Fig. 3G) are in the form of inclusions within pyrite and marcasite.

Conclusions

Iron sulphides (pyrite and marcasite) usually occur in the dispersed form. Massive forms are generally less common. Vein forms occur very rarely. Finely crystalline pyrite and marcasite were found in coal cracks.

When it comes to macroscopically isolated massive forms, microscopic examination has shown massive aggregations of iron sulphides including euhedral crystals and framboids. In the examined coal, vein forms are usually isolated or are associated with massive aggregations. Pyrite and marcasite often fill the fusinite cells. The most common iron sulphides in the studied coal seams are dispersed framboidal forms. In the case of high concentration of framboids, polyframboids of variable density are being formed. Both framboids and polyframboids in coal are of early-diagenetic and syngenetic origin.

The fine-crystalline pyrite occurring in coal cracks is in the form of octaedrite crystals (scattered or forming clusters with variable density). This form of sulphides is indicative of an epigenetic (secondary) origin.

The analysis has also confirmed that the sulphides occurring in the examined coal are mainly pyrite or marcasite. Their composition is similar regardless of morphological formation. However, no significant admixtures other than iron and sulphur have been observed in both pyrite and marcasite. In addition to the iron sulphides, individual inclusions of galena and sphalerite within the pyrite and marcasite have been identified. In addition to sulphides, siderite has also been observed. The amounts of critical elements in the examined samples do not allow for their economically justified exploitation. Higher concentrations of these elements can be found in the ashes resulting from the combustion process. Their recovery can be profitable under favorable economic and technological conditions.

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THE FORMS OF OCCURRENCE AND CHEMICAL COMPOSITION OF SULFIDES IN THE LW BOGDANKA BITUMINOUS COAL DEPOSITS OF THE LUBLIN COAL BASIN

Abstract

The Bogdanka coal mine, the only currently operating mine in the Lublin Coal Basin (LCB), extracts coal from the Upper Carboniferous formations of the LCB. The average sulfur content in the No. 385/2 seam is 0.98%, while in the case of the No. 391 seam it is slightly higher and amounts to 1.15%. The iron sulfides (pyrite and marcasite) in bituminous coal seams form macroscopically visible massive, vein, and dispersed forms. A microscopic examination has confirmed their complex structure. Massive forms contain euhedral crystals and framboids. The sulfide aggregations are often associated with a halo of dispersed veins and framboids. Pyrite and marcasite often fill the fusinite cells. Framboids are highly variable when it comes to their size and the degree of compaction within the carbonaceous matter. Their large aggregations form polyframboids. The cracks are often filled with crystalline accumulations of iron sulfides (octaedric crystals). The Wavelenth Dispersive Spectrometry (WDS) microanalysis allowed the chemical composition of sulfides in coal samples from the examined depoists to be analyzed. It has been shown that they are dominated by iron sulfides FeS_2 – pyrite and marcasite. The examined sulfides contain small admixtures of Pb, Hg, Zn, Cu, Ag, Sb, Co, Ni, As, and Cd. When it comes to the examined admixtures, the highest concentration of up to 0.24%, is observed for As. In addition, small amounts of galena, siderite, and barite have also been found in the examined coal samples. The amounts of the critical elements in the examined samples do not allow for their economically justified exploitation. Higher concentrations of these elements can be found in the ashes resulting from the combustion process.

Keywords: coal, sulfides, petrology, WDS analysis

FORMY WYSTĘPOWANIA I SKŁAD CHEMICZNY SIARCZKÓW W POKŁADACH WĘGLA KAMIENNEGO LW BOGDANKA W LUBELSKIM ZAGŁĘBIU WĘGLOWYM

Streszczenie

Kopalnia Bogdanka jest jedyną obecnie czynną kopalnią na terenie Lubelskiego Zagłębia Węglowego – eksploatuje węgiel kamienny z formacji lubelskiej karbonu górnego. Średnia zawartość siarki dla pokładu 385/2 wynosi 0,98%, a dla pokładu 391 jest nieco wyższa i wynosi 1,15%. Siarczki żelaza (piryt i markasyt) w pokładach węgla kamiennego tworzą widoczne makroskopowo formy masywne, żyłowe i rozproszone. Pod mikroskopem widoczna jest złożoność budowy tych wystąpień. Formy masywne zawierają euhedralne kryształy bądź framboidy. Nagromadzenia tych siarczków często połączone są z aureolą rozproszonych żył i framboidów. Piryt i markasyt często wypełniają komórki w fuzynicie. Framboidy wykazują duże zróżnicowanie wielkości i stopnia zagęszczenia w obrębie substancji węglowej. W przypadku dużego zagęszczenia tworzą się poliframboidy. W szczelinach często występują krystaliczne nagromadzenia siarczków żelaza (oktaedryczne kryształy). Analiza Wavelenth Disspersive Spectrometry (WDS) w mikroobszarze pozwoliła na zbadanie składu chemicznego siarczków w próbkach węgla z badanych pokładów. Potwierdzono, że badane wystąpienia są zdominowane przez siarczki żelaza FeS_2 – piryt i markasyt. W ich obrębie można zaobserwować niewielkie domieszki Pb, Hg, Zn, Cu, Ag, Sb, Co, Ni, As i Cd. Największą koncentrację wśród domieszek ma As dochodzącą do 0,24% w analizowanych punktach. W badanych próbkach węgla znaleziono również niewielkie ilości galeny, syderytu i barytu. Ilości pierwiastków krytycznych stwierdzone w badanych próbkach nie pozwalają na ich ekonomicznie uzasadnione pozyskiwanie. Większe stężenia tych pierwiastków można znaleźć w popiołach powstałych w wyniku procesu spalania węgla.

Słowa kluczowe: węgiel, siarczki, petrologia, analiza WDS