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PROPERTIES OF DONETSK BASIN HARD COALS AND THE PRODUCTS OF THEIR HEAT TREATMENT REVEALED VIA MOSSBAUER SPECTROSCOPY

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Abstract

In this article, the authors present the results of the researches carried out on the properties of the Donetsk basin coals when they were in the original state, after pyrolysis and after combustion of the pyrolysed residue. The studies have been conducted via the Mossbauer spectroscopy. The changes in the structural and the magnetic properties of the iron-containing components of the hard coals after their heat treatment have been revealed and described. We assume that the obtained results can serve the theoretical needs and be of practical value for deeper understanding the processes occurring when hard coal processing under industrial conditions and their prediction, which can open the new approaches to the application both the coal products and the wastes of coal processing.

Keywords: *Mossbauer spectroscopy; Pyrolysis; Combustion; Hard coals; Iron-containing components; Ash.*

1. Introduction

Coal is the main raw material for the production of heat, electricity, chemicals, fuels and reducing agents for metallurgy, etc. Despite the increasing usage of renewable sources, the world demand for coals is predicted to remain at a steadily high level, at least until 2035, due to the growing demand for energy [1].

In Ukraine, as well as in many other countries of the world, coal is the main source of energy carrier for thermal power engineering and metallurgy while coal mining is of great economic importance thereof. Within the territory of Ukraine, the main coal reservoirs are found in the Donetsk and the Lviv-Volhynia coal basins, plus the Dnipro brown coal basin. Additionally, there are revealed low sulphur salt coals in the Western and the Northern Donbass and high-sulphur brown coal in Novo-Dmytrivske deposits. The main reservoirs of oil shale are located in the Baltic Depression (the boundary between the Kirovohrad Region and Cherkasy Region).

Coal as a product of different degrees of carbonisation, which the green plant remains underwent in the course of time, has a complicated and variable organic nature, it is chemically bounded to an inorganic substance dispersed randomly in the form of mineral inclusions, dissolved salts and inorganic substances.

The industrial coalfield of the Donetsk basin represents sandy-carbonate coaly rocks of carbon while the Lviv-Volhynia coalfield basin is sandy-clay rocks of lower and middle carbon. The coal deposits of the Donetsk basin belong to the Carbonic period (carbon) and are represented by all three stages, namely, lower, middle and upper. The share of the lower carbon is 11 % of all basin reservoirs, the middle one is 88 %, and the upper one is up to 1 % [2].

The coals of the Donetsk basin are characterized by the presence of all types of coals plus anthracite; they are considered to be petrographically homogeneous. Its coal layers have a complex structure, the mines are predominantly of low coal capacity, and most of the mines are dangerous with their emissions of gas and coal. The average mining depth of the coal layers is approximately 650-700 m. The dirt bands are predominantly in argillaceous states. Due to the different amounts of the dirt bands and low thickness of the coal beds, the run-of-mine coals are characterized by high ash content (up to 40 %) and therefore require beneficiation operations for further usage in energy generation or metallurgical coke production.

The mineral substances within coal represent a mixture of various components. Predominantly, they are several silicates (silicates of aluminium, iron, calcium, sodium, potassium and magnesium in the form of clay minerals), iron disulphides (in the forms of pyrite and marcasite), several carbonates (carbonates of calcium, iron (in the form of siderite) and magnesium), several sulphates (sulphates of calcium, aluminium and iron), iron oxides and calcium oxides, several chlorides and finally compounds of rare elements. Moreover, there are organomineral compounds of coal, for instance, salts of humic acids and humates within coal content.

In general, the mineral substances within coal can be divided into the groups of internal (mineral impurities inherent from the initial material since they have been accumulated in the process of coal formation) and external (penetrated into the coal mixture in the process of extraction). The composition of the coal ash is quite diverse and differs not only with the coal type and its field features, but the differences are also found within one coal field, however, the content of internal mineral substances is more or less constant within the coal belonging to one and the same deposit and, as a rule, is up to 7 wt % . Determining the content of the component within the coal mineral part is a complex task and, therefore, as a rule, the concerned enterprises are actually satisfied with determining the total number of mineral components using the ash content index.

Further, the prominent feature of the Donetsk basin coals is that the iron oxides can reach up to 88.5 % in the mineral part of the coal content [3]. The principle iron compounds within coal are iron disulphides (in the form of pyrite, marcasite), sulphates, carbonates, oxides and hydroxides, mica-like clay minerals that contain iron (ileth) and complex humates. The iron organically bounded with the coal structure can occur in the form of iron acetate-$Fe(C_2H_3O_2)_2$ [4], along with a carboxyl group [5], as well as in the protein-like structures and porphyrins [6]. The type of iron compounds and their amounts are surely in dependence with the coal basin, the coal seam and the coal type.

The most common iron compound found in coal is pyrite, which is in the form of concretions of various structures and sizes. In most cases, they are finely dispersed pyrite (<100 or <40 microns), closely linked with the organic matter. Since the iron content in aluminosilicate minerals is usually less than 3 % (based on Fe_2O_3), the alumosilicate form is to prevail over other forms of iron compounds only when Fe_2O_3 content in the ash is less than 2 %.

Furthermore, though coal is applied in various secondary processes, namely pyrolysis, combustion, gasification, and hydrogenation, only the primary processes, namely mining and beneficiation, play the crucial role in the amount and the composition of the mineral components present in coal.

The ash composition within coal is the really important issue for combustion since the ash melting temperature depends on this process as well as its ability to form fusible slags. In metallurgy, the composition of fuel ash determines the technological parameters of the processes. Thus, in the blast furnace practice, the ash composition within coke obtained from coals determines both the quality and the number of fluxes required for the cinder scorifying. In the basic oxygen furnace process, the slag viscosities and the slag heat capacities are important for calculating the thermal effect of fuel oxidation. The ash composition also determines the ways of recycling coal wastes after such processes as coal mining, beneficiation, and combustion. The search for the additional recycling opportunities for coal waste remained after coal treatment is an urgent task, both environmentally and economically, especially when taking into account the multi-tonnage of these wastes. In this aspect, the coal compositions

and properties are the determining factors for making the engineering solution on the suitability of the wastes for recycling. The most attractive ways to use them are in the secondary raw materials forms as those applied instead of the primary constituents and also in the further extraction of the useful components.

Eventually, there are the most valuable components of the coal mineral part, and it remains in its processing wastes – it is iron. In order to evaluate the possibility of using iron-containing wastes as raw materials and having the purpose of iron extraction, it is necessary to evaluate the peculiarities of the mineral composition and the structure of the iron-bearing components. The most effective method for determining and studying iron-containing components within substances is known to be Mossbauer spectroscopy.

Based on the developed background, the current publication aims at determining the iron-containing components of the mineral part of the coals belonging to the Donetsk coal basin and at studying their changes resulting from the pyrolysis and the subsequent combustion of the remained residue.

As the research method, the Mossbauer spectroscopy has been used since it is reported as a unique analytical tool for identifying iron ore minerals [7]. The application of this method for the Fe^{57} isotope is possible due to the iron content of up to 2.7 % or more within the research material. In this application, the Mossbauer spectroscopy has been widely used for almost 60 years, including the cases when the characterization of iron-containing components of the coal mineral part was required. Since the atomic weight of carbon in coal is low, the Mossbauer spectroscopy allows identifying iron-containing components within coal even in cases where the iron content does not exceed 1 %.

Moreover, the most widely spread studies conducted via the Mossbauer spectroscopy application are the studies of the magnetic microstructures, the changes in electron-nuclear interactions and the atomic media in solids, also the studies wherein it is necessary to identify the phase compositions and the structural properties of materials [8 9]. In particular, the method is actively used to investigate the catalyst reactivities in the production of synthetic fuels by the Fischer-Tropsch process [10-11], plus the Mossbauer spectroscopy actively serves for the coal gasification process [12]. Understanding the regularities in the phase state changes within the iron-containing components of coal both during coal gasification and during coals combustion allows ensuring the efficiency of these processes regarding their completeness. Further, the presence of certain iron-containing substances in the products of coal mining, beneficiation, and processing is significant for solving the issues of the environmental impact of the wastes generated from coal and the rational ways of their recycling [13].

Eventually, the Mossbauer spectroscopy can be applied for solving seismic geochemistry issues, practical and search geology. Another important problem to be solved with the Mossbauer spectroscopy is in monitoring the useful ore components during their extraction, in particular, when the presence of Fe^{2+} and Fe^{3+} and their dedicated ratios. This method is also used for defining the content of minerals for mining and the effective use of the mining equipment, as well as for increasing the equipment wear resistance when the further processing of the ores [1]. The study of the coal Mossbauer spectra allowed Alekseev *et al.* [14] to assume that the presence of explosive zones with high levels of methane is associated with the presence of double-valence iron in the coal, which acts as a catalyst. The optimal ratio of Fe^{2+} and Fe^{3+} if achieved can act as an efficiency indicator of the recovery process carried out by electric furnaces and to provide the best conditions for their operation [15].

Since the influence of heat treatment on coal mineral part is an interesting problem for the studies, it is suggested to make the research on the processes of pyrolysis and combustion processes with the special focuses on their features.

1.1. Coal pyrolysis

Coal pyrolysis is a complex process that occurs when coal is being heated to a certain temperature without oxygen access. Taking into account the absence of any oxidants during

the process, there mainly occurs the transformation of the organic matter during coal pyrolysis. Thus, the changes in the elemental composition are observed in this process along with the increase in the carbon content while the decrease in the oxygen, hydrogen, nitrogen and sulphur contents. The mineral part of the coal during pyrolysis loses its hydrated water, also there occur the decomposition reactions (commonly, with pyrite and carbonates) in coal. In general, the mineral part of coal is almost unchanged, and practically all the mineral components are converted into solids. At the same time, due to the release of the volatile organic compounds of coal, the ash content of the residue is to be higher than that in the initial coal since there is the increase of the concentrations of the mineral components.

1.2. Coal combustion

In the combustion process, all organic components of coal are removed (in the form of CO_2 and H_2O) while the mineral components are subjected to a number of transformations resulting in the formation of the ash residue only. It is known that when burning coal in a muffle furnace, the mineral components undergo the following transformations:

1) Loss of moisture (dehydration) of aluminosilicates (clays), oxides and iron hydroxides and also gypsum is added to this list at the temperature above 500°C. Moreover, the formation of Al_2O_3, SiO_2, Fe_2O_3, $CaSO_4$ and water occur.

2) Oxidation of Fe^{2+} to Fe^{3+} (converted into the dedicated oxide):

$$4FeO + O_2 = 2Fe_2O_3. \tag{1}$$

3) Decomposition of carbonates with carbon dioxide emissions at the temperatures of 500-900°C:

$$CaCO_3 = CaO + CO_2. \tag{2}$$
$$MgCO_3 = MgO + CO_2. \tag{3}$$
$$FeCO_3 = FeO + CO_2. \tag{4}$$

4) Formation of iron oxide, as described by Eq. 4. $FeCO_3$ is subsequently converted into oxide, and therefore the reaction takes place as shown by Eq. 5:

$$4FeCO_3 + O_2 = 2Fe_2O_3 + 4CO_2. \tag{5}$$

5) Oxidation of iron disulphides (pyrite, marcasite) at temperatures of 450-600 °C (refer to Eq. 6):

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2. \tag{6}$$
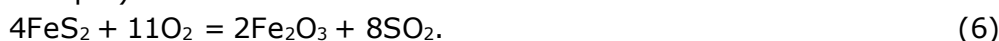
6) Sulphuric anhydride, which is formed by the oxidation of pyrite and the combustion of organic sulphur, reacts with calcium carbonate and oxygen (refer to Eq. 7):

$$2CaCO_3 + 2SO_2 + O_2 = 2CaSO_4 + 2CO_2. \tag{7}$$

7) The formation of calcium sulphate occurs in the temperature range of 700-1100°C (refer to Eq. 8):

$$2CaO + 2SO_2 + O_2 = 2CaSO_4. \tag{8}$$

The reaction takes place as SO_2 being released when organic sulphur burns while the oxidation of iron disulphide and the decomposition of carbonates occur.

8) Decomposition of iron sulphate at 850-950 °C (refer to Eq. 9):

$$2FeSO_4 = 2FeO + 2SO_2 + O_2. \tag{9}$$

Calcium sulphate at 1100°C starts its reaction with silica and aluminosilicates with the release of SO_2 while $CaSO_4$ decomposes at 1300°C.

9) The conversion of chlorides and the compounds of alkali metals at the temperatures above 500°C.

Due to the changes in the chemical composition of the coal mineral component during the process of combustion, the ash composition and the ash mass are not equal to the mass and the composition of the mineral substances within the coal. As a result, the ash value after coal combustion has to be slightly less than that in the content of the initial mineral part.

2. Experimental

2.1. Materials

With the purpose to study the iron-containing components of the coal mineral part, the coal from the Donetsk basin of Almazna Mine (Dobropillia city of Donetsk Region, Ukraine) was used for the research. The research samples were prepared from one coal rank, according to the current classification of Ukrainian coals it refers to GZhO rank [16].

The Almazna Mine is characterized by a high content of methane, the l_1 and m_5', which are being worked out and has the capacity of 1.1-2.2 m and the slope of 9-11°. Table 1 shows the parameters of the coal proximate analysis and Table 2 represents its petrographic characteristics.

Table 1. Proximate analysis of the hard coal

Sample	Parameters of proximate analysis, %						Fixed carbon, %
	W^a	A^d	V^d	V^{daf}	S_t^d	P^d	FC^d
Rank of GZhO, Almazna Mine (Dobropillia city, Ukraine)	1.5	6.55	33.9	36.3	2.55	0.006	59.5

Table 2. Petrographical analysis of the hard coal

Petrographical components, %				Sum fusainised components	Average reflection of vitrinite
Vitrinite (Vt)	Semivitrinite (Sv)	Inertinite (I)	Liptinite (L)	ΣOK, %	R_o, %
84	0	11	5	11	0.86

The chemical compositions of the principle mineral components of coal, presented in Table 3, show a high content of silica (SiO_2) - 37.97 %, hematite (Fe_2O_3) - 32.42 %, and aluminum oxide (Al_2O_3) - 22.2 %. Thus, with the ash content of coal A^d = 6.55 %, the above mentioned components are 2.49 %, 2.12 % and 1.45 % by weight of coal, respectively.

Table 3. Chemical composition of the coal ash

Content, % Dry state								Index of ash basicity
SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	I_o
37.97	22.2	32.42	1.26	1.75	0.92	1.17	0.74	0.624

The index of ash basicity, calculated via Eq. 10 is 0.624.

$$I_o = (Fe_2O_3 + CaO + MgO + Na_2O + K_2O)/(SiO_2 + Al_2O_3) \qquad (10)$$

If the index of coal basicity is calculated by means of Eq. 11, I_o has a rather high rate of 6.46 due to the high content of Fe_2O_3.

$$I_o = A^d \cdot 100 \cdot (Fe_2O_3 + CaO + MgO + Na_2O + K_2O)/(100 - V^{daf}) \cdot (SiO_2 + Al_2O_3). \quad (11)$$

2.2. Methodology

The Mossbauer spectra allow identifying the chemical composition and the structure of the tested substance, as this method of analysis is based on the phenomenon of resonant radiation and absorption of γ-quanta while different chemical compounds used as radiation sources (radionuclides) or as sinks (nuclides) have their own characteristic spectrum of radiation or absorption.

The currently reported analysis has been performed on powdered samples via using MS-1104EM spectrometer, which was operated in a constant acceleration mode for the experiment and its operational parameters were as follows: ^{57}Co (Rh) source activity - about 50 mCi, the metallic α-Fe line width - 0.29 mm/s, the calibration of isomeric shifts with respect to α-Fe. Additionally, the spectrum analysis has been carried out with the Univem software package.

The samples with the particle size less than 0.1 mm for the experiment were prepared in accordance with the standard procedures. The pyrolysis of the coal and the combustion of its

residue have been carried out under laboratory conditions in a muffle furnace, and the final temperature parameter has been 800ºC.

3. Results and discussion

The research has been conducted on the materials as follows: the coal, the residue after coal pyrolysis at the temperature up to 800°C and the ash remaining after the residue combustion at up to 800°C.

Schematically, the research procedure can be presented as shown in Fig. 1. The spectra characteristics revealed are given in Table 4 and their images - in Fig. 2-4.
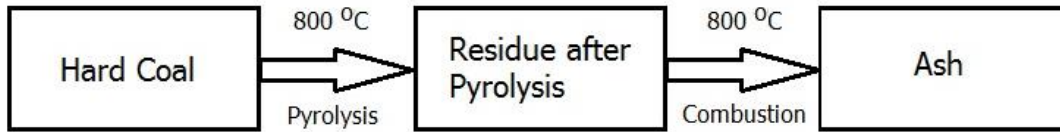

Figure 1. Scheme of the conducted research

The obtained Mossbauer spectra results have been further analysed, and the summarized data are presented in Table 4.

Table 4. Parameters of the components in Mossbauer spectra (Results obtained with different heat treatments)

Sample	Component	IS, mms^{-1}	QS, mms^{-1}	H Tesla	Relative intensity (%)	Interpretation
Hard coal	D1 (Fe^{2+})	0.28	0.55	0	25.12	Marcasite (FeS_2)
	D2 (Fe^{2+})	0.32	0.64	0	74.88	Pyrite (FeS_2)
After pyrolysis at 800ºC	S1 (Fe^{3+})	0.37	-0.17	515	89.49	Hematite (α-Fe_2O_3)
	D1 (Fe^{3+})	0.33	0.42	0	6.36	Fe^{3+}
	D2 (Fe^{2+})	0.82	1.69	0	4.15	Fe^{2+}
After combustion at 800ºC	S1 (Fe^{3+})	0.37	-0.19	51.5	87.47	Hematite (α-Fe_2O_3)
	D1 (Fe^{3+})	0.22	0.85	0	12.53	Fe^{3+} glass

3.1. Hard coal

Figure 2. Mossbauer spectra of the hard coal
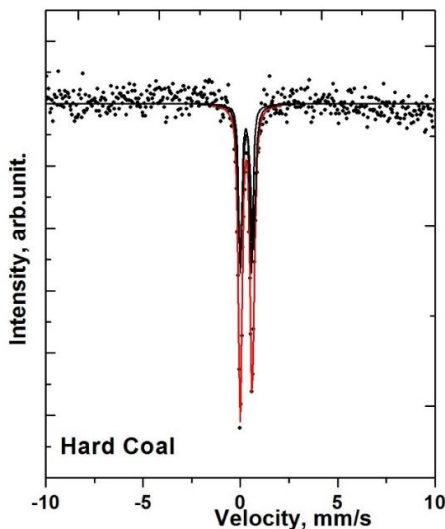
The Mossbauer spectrum of the original coal was approximated by the superposition of two doublet components with the close values of the isomer shifts and excellent quadrupole splitting. According to the obtained parameters, the coal under analysis was represented by iron disulphides – pyrite and marcasite [17], they differed in the types of crystal lattices. The share of pyrite was almost 75 %. The iron was in the bivalent state, and the bivalent iron is commonly known as the substance to concentrate in the clusters of evenly distributed volumes.

3.2. The residue after pyrolysis at the temperatures of up to 800°C

After pyrolysis at the temperatures of up to 800°C, the sample was analysed for the spectrum. The obtained results have shown that its composition consisted of a superposition of one sextet and two duplets. The iron valence varied with trivalent, but bivalency was also found with the sample. Thus, a doublet with a higher integral intensity had the velocity of 1.69 mm/s, indicating rather strongly distorted areas of iron and/or a relatively weak crystallinity of this component. The sextet with the isomer shift and quadrupole splitting and the magnetic field on the Fe^{57} nuclei corresponds to the antiferromagnetic hematite. In this case, Fe_2O_3 contained relatively large crystallites, as it was evidenced by the presence of a well-exposed sextet. The hematite share in the sample has been revealed as almost 90 %.

Pyrolysis is known as a process able to decompose iron disulphide. The beginning of the decomposition starts at about 450°C and almost completely finishes at 600°C, reaching the maximum intensity within the range of 550-600°C. Thus, at the temperature of 800°C, the pyrite and the marcasite are to be completely decomposed.
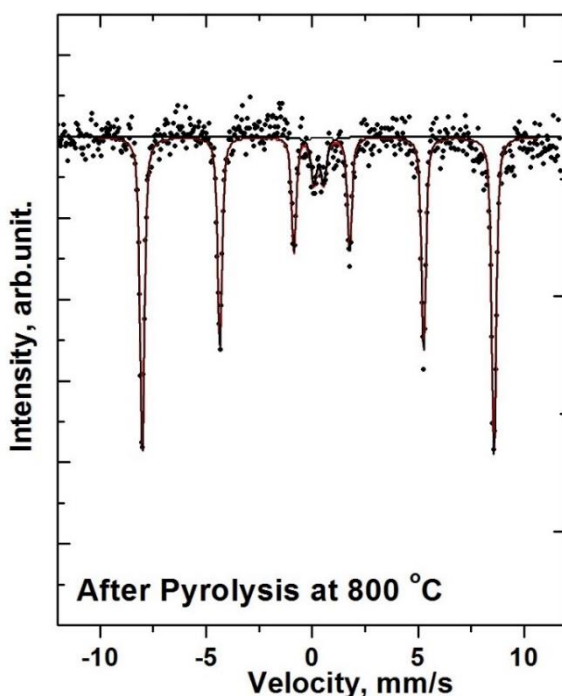

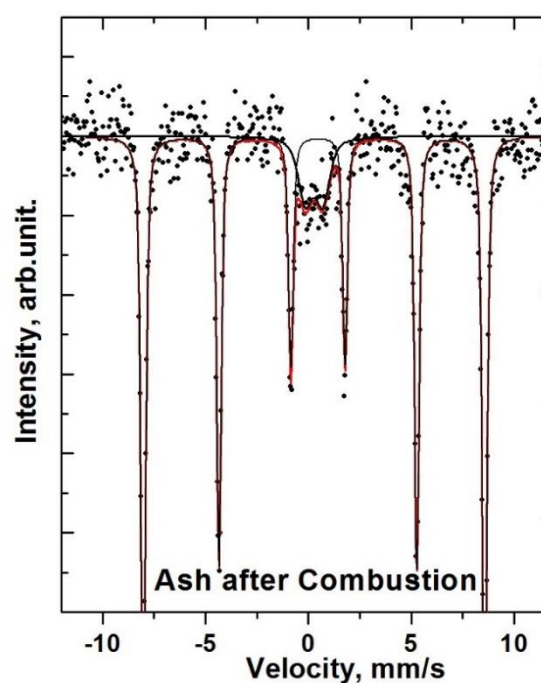Figure 3. Mossbauer spectra of the residue after pyrolysis

Figure 4. Mossbauer spectra of the ash after combustion

The analysis of the spectrum showed that another major component within it is the trivalent Fe^{3+}. The comparison of the results allows us to assume that the finely divided iron oxides are formed when decomposing pyrite [18].

3.3. Ash after combustion

The ash spectrum has shown that the dedicated sample consisted of a combination of one sextet and one duplet (refer to Fig. 4.). The sextet possessed the hematite parameters. Therefore it draws the conclusion that the final type of iron after combustion is hematite. Additionally to hematite, there occured the finely divided iron oxides, and silicates along with the ferritic glass had been formed due to Fe^{3+}. In the middle of these glass spherulites, the magnetite is assumed to occur.

4. Conclusions

The Mossbauer spectroscopy is a convenient tool for the differentiation of various types of coals and the products of coal heat treatment by the properties of their iron-containing components. With regard to the heterogeneity of coals and the products of their processing, this method has considerable potential for studying the structural and magnetic properties of iron-containing components. In Ukraine, which is rich in coal of varying metamorphism degrees, the Mossbauer spectroscopy has not yet been widely used due to the lack of spectrometers in sufficient quantities.

The results of the Mossbauer spectroscopy with the typical coal of the Donetsk basin has provided the information on the properties of iron-containing components of the dedicated coals and the mineral changes within them after pyrolysis and combustion of the pyrolysed residue. The difference in the properties and forms of iron has been detected. Thus, the original hard coal is represented by pyrite and marcasite, but the hard coal residue after pyrolysis contains weak magnetic iron-containing phases (hematite, finely divided ferric oxide). After combustion of the pyrolysed residue, the final type of iron is hematite and the iron-containing glass is also formed.

The obtained results have theoretical and practical value for better understanding and predicting processes occurring under industrial conditions, and they approach the coal products and the coal processing wastes to the recycling route. The presence of magnetic iron-containing phases grants the possibility of iron extraction by magnetic beneficiation. In this case, the presence of glass spherulites within the combustion products plays an adverse effect on the extraction effectiveness of that iron which is inside the coal products. In this case, it is necessary to apply to ground for the destruction of the spherulites.

Acknowledgments

Symbols

W^a	Moisture (air dried basis);	L	Liptinite;
A^d	Ash (dry basis);	ΣOK	The sum of the fusainised components;
V^d	Volatile Matter (dry basis);	R_o	The average reflection of vitrinite;
V^{daf}	Volatile Matter (dry, ash free basis);	I_o	Index of ash basicity;
$S_t{}^d$	Total Sulphur (dry basis);	D	Duplet;
P^d	Phosphor (dry basis);	S	Sextet;
FC^d	Fixed Carbon (dry basis);	IS	Isomer shift relative to α-Fe;
Vt	Vitrinite;	QS	Quadrupole splitting;
Sv	Semivitrinite;	H	Hyperfine magnetic field.
I	Inertinite;		

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