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EFFECT OF COAL QUALITY ON ITS DESULPHURIZATION 2. INFLUENCE OF THE INORGANIC MATTER

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Abstract. The effect of pyrite size and distribution character, as well as the amount of inorganic matter on the removal degree of sulphur from coal during its oxidative desulphurization and beneficiation has been studied. The efficiencies of oxidative desulphurization processes for different types of the initial and concentrated black coal have been compared.

Keywords: oxidative desulphurization, coal, sulphur, pyrite, sulphur dioxide, air-steam mixture.

1. Introduction

The part of the heat and electric power produced from coal increases every year throughout the world and in Ukraine as well (Table 1). In spite of the rapid growth of electric power production from the renewed sources, it is forecasted that coal will become the main energy carrier till 2035 [1].

On the other hand, coal is a raw material, the usage of which in any branches of industry results in the greater or lesser negative ecological and technological consequences. The reason is the presence of great amount of sulphuric compounds in it. Due to the coal burning the power engineering pollutes the environment by toxic and greenhouse compounds: SO₂, H₂S, CO₂, CO, NO₂, NO,

dust, soot, and ash. The share of all sulphur(IV) oxides emitted by stationary sources of power and heat production [3] reaches 69–70 % in the world and 73–79 % in Ukraine.

Existing methods of sulphur(IV) oxide emissions reduction are unprofitable and low-effective.

The prospective direction is coal desulphurization before its usage *via* oxidation method developed at the Department of Oil and Gas Processing of Lviv Polytechnic National University. The essence of the process is coal treatment by the oxidant. Sulphur in coal (first of all pyritic sulphur) converts into gaseous sulphur-containing components, the concentration of which in the desulphurization gases allow to extract the components using known methods [4, 5]. The raw material quality is one of the factors affecting the yield and properties of the obtained products. The influence of organic matter on the coal oxidative desulphurization is described in [8].

The quantity and quality of coal inorganic matter also influence the process proceeding. On the one hand, mineral components may have catalytic properties, and on the other hand, they may block oxidant access to the pyrite grains. To date beneficiation is the only one industrial method which allows to remove sulphur from coal before its usage. However, the sulphur content significantly decreases during beneficiation only in the

Table 1

Year, information source →	2005, [2]	2006, [1]	2009, [2]		2010, [2]	
Power supply ↓	Ukraine	World	Ukraine	World	Ukraine	World
Natural gas	41.0	23.7	37.7	23.4	39.7	23.8
Petroleum	19.0	35.8	11.9	34.4	9.8	33.6
Coal	19.0	28.4	31.2	29.1	30.8	29.6
Nuclear raw material	17.0	5.8	16.8	5.4	17.1	5.2
Hydro-resources and other renewed sources	4.0	6.3	2.4	7.7	2.5	7.8
Total	100.0	100.0	100.0	100.0	100.0	100.0

case, when pyrite (the main sulphur-containing component of coal) is in the form of large pieces. If the pieces are small, only negligible amount of sulphur is removed from coal [6, 7].

On the basis of all mentioned above the aim of our investigations was to determine the inorganic matter effect on the coal oxidative desulphurization and to compare the desulphurization efficiency of different types of coal *via* beneficiation and oxidative method.

2. Experimental

The following samples of Ukrainian coal were selected for investigations: lean coal (L) from Shidna mine of Donetsk coal basin; fat coal (F3) from Lisova mine of Lviv-Volyn coal basin; gas coal (G1) from Chervonograd mine of Lviv-Volyn coal basin; gas coal (G2) from Zarichna mine of Lviv-Volyn coal basin and candle coal (C) from Buzhanska mine of Lviv-Volyn coal basin. The fraction of 0.1–0.25 mm was used for investigations, because it is the optimal size for coal burning at heat power plants (HPPs).

The content of total (S_t^a) and pyritic (S_p^a) sulphur in the samples was respectively (mas %): lean (L) – 4.48 and 3.81; fat (F3) – 7.09 and 4.09; gas (G1) – 7.95 and 7.20; gas (G2) – 7.18 and 6.05; candle (C) – 3.98 and 2.34.

The investigations were carried out at the laboratory plant the main part of which was an ideal mixing reactor (with a boiling bed) working in the regime close to isothermal one.

The detailed characteristics of the raw material, scheme and description of the laboratory plant are given in [8, 9].

To estimate the desulphurization efficiency the removal degree of pyritic sulphur (%) is calculated in accordance with the formula:

$$\Delta S_p^a = \frac{S_{p0}^a - S_p^a}{S_{p0}^a} \cdot 100,$$

where S_{p0}^a – the content of pyritic sulphur in the initial coal calculated for the analytical sample, mas %; S_p^a – the content of pyritic sulphur in desulphurized coal calculated for the analytical sample, mas %.

The coal beneficiation was carried out *via* flotation. For this purpose the laboratory model of FL-1.5 impeller flotator was used. One flotation cycle was as follows: pulp preparation from coal and water (ratio 1:25); addition of flotation reagent to the pulp (montanol – 30 vol % and kerosene – 70 vol %) in the amount of 0.1 % regarding the raw material; pulp pouring into the flotator; air supply for 10 min, flow rate of which was 4 m³/h for 1 kg of coal.

Electron-microscopic investigations were carried out using a scanning electronic microscope ZEISS EVO 40XVP with the system of X-ray microanalysis INCA Energy. Silicon-lithium energodispersive detector was used for microanalysis [10].

3. Results and Discussion

The analysis of oxidation desulphurization and flotation of different types coal (Table 2) allows to assert that coal of C, G1, G2 and L types is well desulphurized during flotation (removal degree of the total sulphur is 43.54, 61.27, 56.20 and 50.23 %, respectively) and coal of F3 type is badly desulphurized (removal degree of the total sulphur is 25.07 %). It is assumed that coal of F3 type has pyrite fine-grained agglomeration and coal of other types – the coarse-grained one.

Table 2

The flotation results of different types coal

Black coal type	C	G1	G2	F3	L
Flotation reagent, mas %	65.23	77.33	72.00	64.03	61.97
Sulphur content, mas %					
total, S_t^a	2.14	3.04	3.11	5.23	2.21
pyritic, S_p^a	0.88	1.65	1.77	3.36	1.24
sulphate, $S_{SO_4}^a$	0.38	0.45	0.38	0.85	0.10
organic, S_o^a	0.88	0.94	0.96	1.02	0.87
Ash content, A^a , mas %	6.88	9.86	9.41	13.43	16.14

This assumption was confirmed by photomicrographs and elemental analysis of the initial and concentrated F3 and G2 samples using SEM with the system of X-ray emission analysis (XEA). Photomicrographs and elements content in the certain points are given in Figs. 1-12 and Tables 3-14. The point of sample composition determination is situated in the left upper corner of the marker indicating the spectrum number.

In the samples depicted in Fig. 1 the main part of inorganic matter is in the form of plates; Figs. 2-4 – large agglomerates.

The character of the photos where G2 floto-concentrate is depicted (Figs. 5 and 6) allows to assert that the form, location and sizes of FeS₂ are changed after flotation compared with the initial coal. After flotation pyrite is in the form of extremely small impregnations in the organic matter (Fig. 5) and in the structure of fine mineral particles (Fig. 6).

The appearance of F3 coal inorganic matter confirms the previous assumption concerning its fine-grained character (Figs. 7-9). XEA results show that:

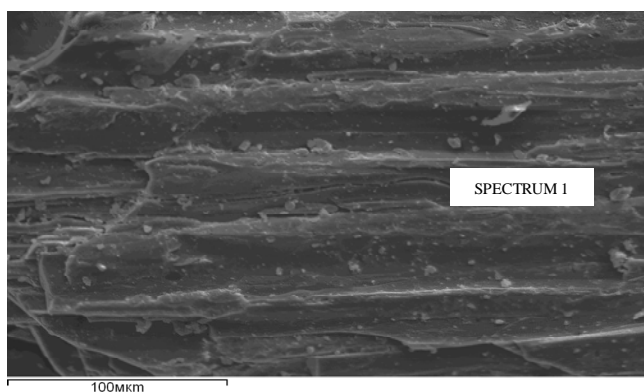


Fig. 1. Photomicrograph of G2 initial coal

XEA results for the spectrum 1

Element	Relative content	
	mass, mas %	atomic, at. %
C	84.98	93.81
S	15.02	6.19
Total	100.00	100.00

Table 3

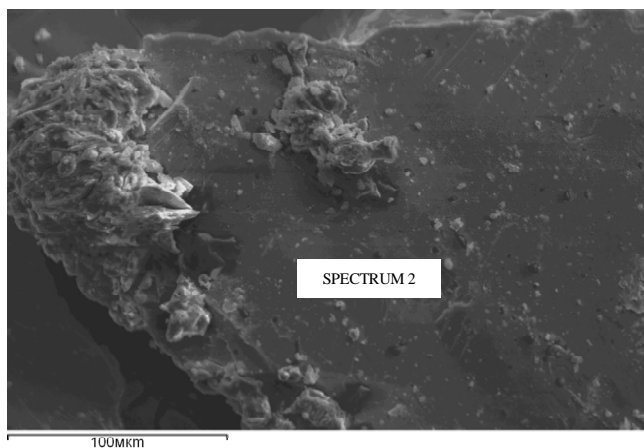


Fig. 2. Photomicrograph of G2 initial coal

XEA results for the spectrum 2

Element	Relative content	
	mass, mas %	atomic, at. %
C	78.59	92.00
S	13.85	6.09
Fe	7.55	1.91
Total	100.00	100.00

Table 4

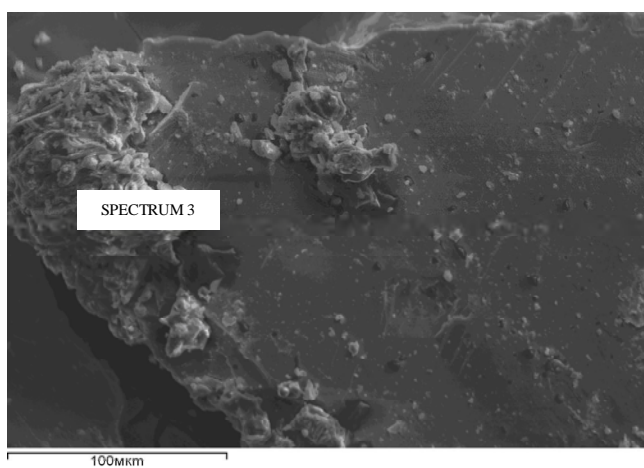


Fig. 3. Photomicrograph of G2 initial coal

XEA results for the spectrum 3

Element	Relative content	
	mass, mas %	atomic, at. %
C	16.84	41.74
Al	1.24	1.37
Si	1.50	1.60
S	31.42	29.17
Fe	48.39	25.81
Co	0.60	0.31
Total	100.00	100.00

Table 5

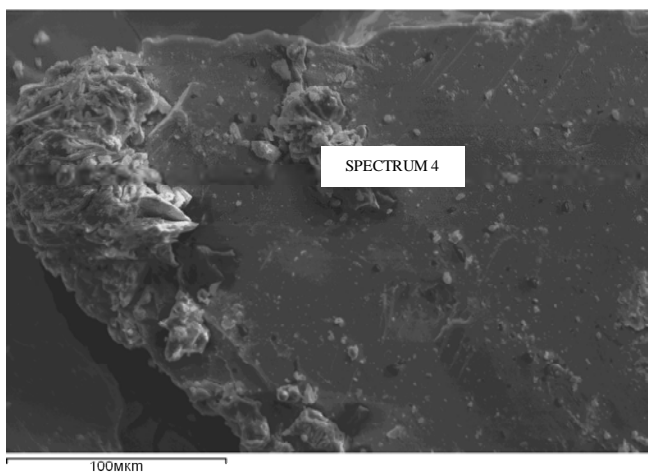


Fig. 4. Photomicrograph of G2 initial coal

Table 6

XEA results for the spectrum 4

Element	Relative content	
	mass, mas %	atomic, at. %
C	16.62	41.25
Al	1.34	1.48
Si	1.29	1.38
S	33.88	31.53
Fe	38.26	20.44
Co	0.18	0.07
Zn	8.42	3.84
Total	100.00	100.00

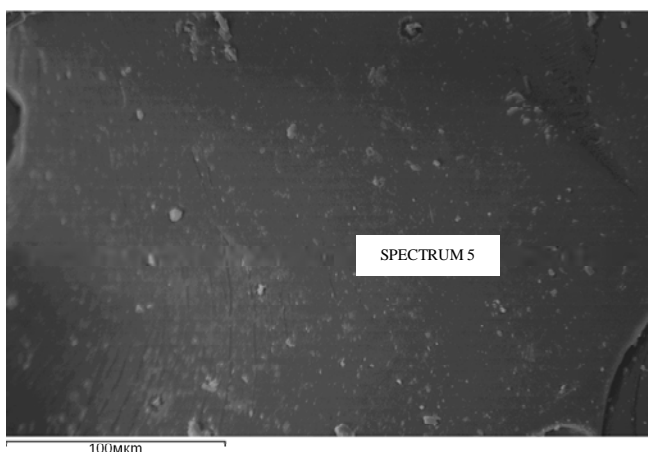


Fig. 5. Photomicrograph of G2 coal flocculate

Table 7

XEA results for the spectrum 5

Element	Relative content	
	mass, mas %	atomic, at. %
C	73.97	92.43
S	2.88	1.36
Fe	23.15	6.21
Total	100.00	100.00

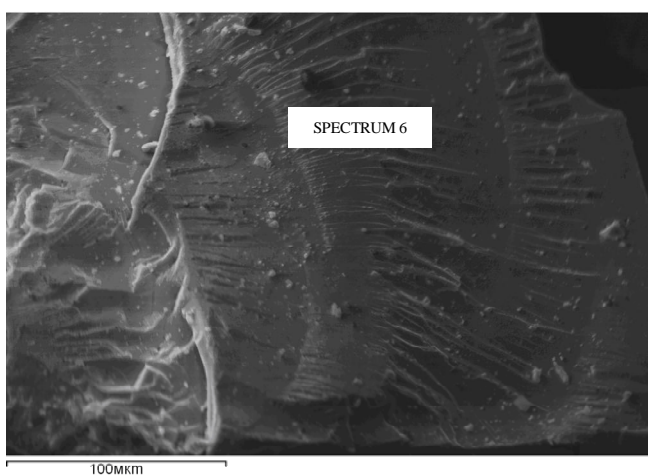


Fig. 6. Photomicrograph of G2 coal flocculate

Table 8

XEA results for the spectrum 6

Element	Relative content	
	mass, mas %	atomic, at. %
C	13.74	27.99
Al	36.33	32.95
Si	34.00	29.60
S	7.55	5.79
Fe	8.39	3.67
Total	100.00	100.00

Table 9

XEA results for the spectrum 7

Element	Relative content	
	mass, mas %	atomic, at. %
C	84.25	93.77
Si	1.18	0.55
S	12.24	5.11
Fe	2.33	0.58
Total	100.00	100.00

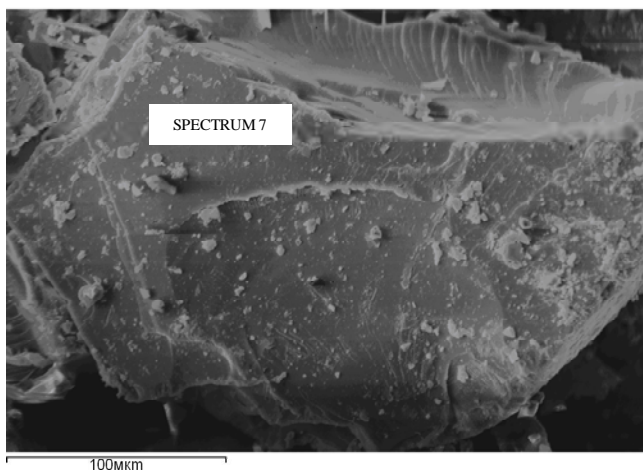
**Fig. 7.** Photomicrograph of F3 initial coal

Table 10

XEA results for the spectrum 8

Element	Relative content	
	mass, mas %	atomic, at. %
C	62.63	82.60
Al	5.71	3.36
Si	8.65	4.88
P	0.06	0.03
S	12.49	6.17
Fe	10.46	2.97
Total	100.00	100.00

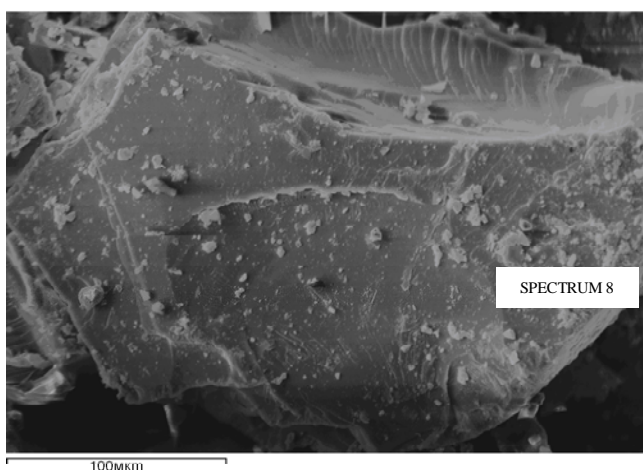
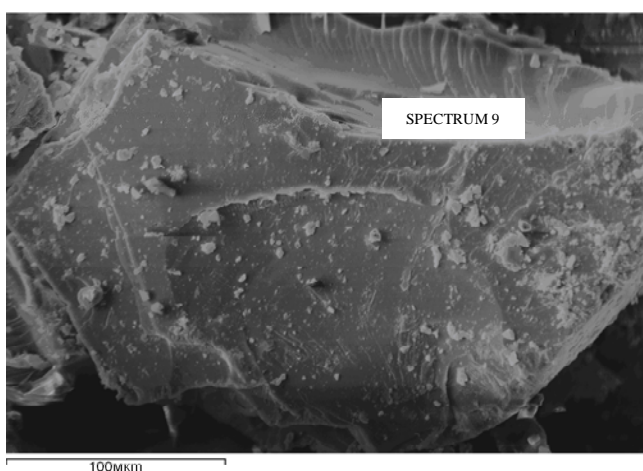
**Fig. 8.** Photomicrograph of F3 initial coal

Table 11

XEA results for the spectrum 9

Element	Relative content	
	mass, mas %	atomic, at. %
C	32.11	65.20
Al	1.29	1.16
Si	3.27	2.84
P	0.21	0.17
S	9.46	7.19
Fe	53.66	23.44
Total	100.00	100.00

**Fig. 9.** Photomicrograph of F3 initial coal

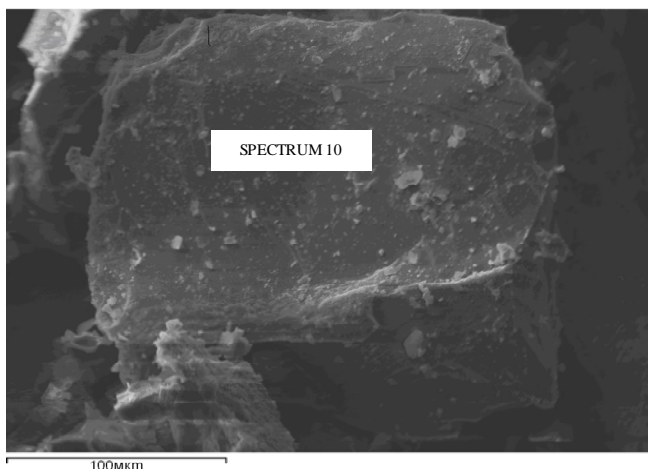


Fig. 10. Photomicrograph of F3 coal flotation concentrate

Table 12

XEA results for the spectrum 10

Element	Relative content	
	mass, mas %	atomic, at. %
C	62.21	82.88
S	29.52	14.77
Fe	8.28	2.36
Total	100.00	100.00

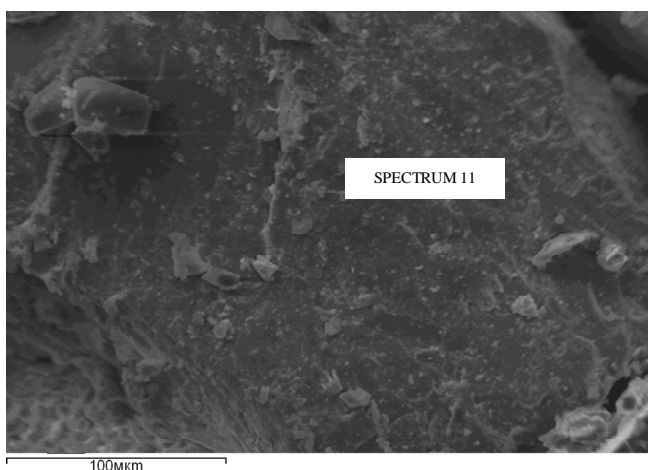


Fig. 11. Photomicrograph of F3 coal flotation concentrate

Table 13

XEA results for the spectrum 11

Element	Relative content	
	mass, mas %	atomic, at. %
C	60.34	80.86
Al	6.53	3.89
Si	9.86	5.66
S	13.48	6.76
Fe	9.80	2.83
Total	100.00	100.00

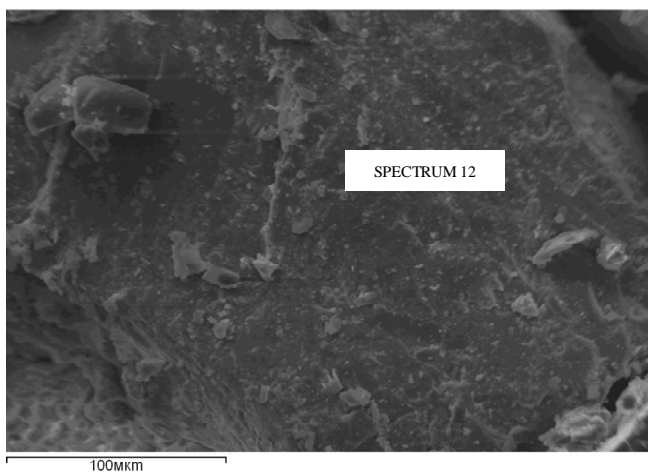


Fig. 12. Photomicrograph of F3 coal flotation concentrate

Table 14

XEA results for the spectrum 12

Element	Relative content	
	mass, mas %	atomic, at. %
C	61.96	81.24
Al	8.45	4.93
Si	10.79	6.04
S	11.88	5.84
Fe	6.91	1.95
Total	100.00	100.00

Table 15

Comparison of sulphur removal degree during oxidative desulphurization of the initial and concentrated samples of black coal

Black coal type	C	G1	G2	F3	L
Initial coal					
Sulphur removal degree, %					
pyritic	88.79	69.20	46.66	67.41	76.66
total	49.08	60.51	36.62	51.58	65.54
Concentrated coal (flotoconcentrate)					
Sulphur removal degree, %					
pyritic	84.09	87.27	55.37	67.86	85.48
total	55.61	35.20	32.48	39.20	59.28

Table 16

Results of beneficiation and oxidative desulphurization of different types black coal

Black coal type	C	G1	G2	F3	L
Results of beneficiation of the initial black coal					
Sulphur content, mas %					
total, S_t^a	2.14	3.04	3.11	5.23	2.21
pyritic, S_p^a	0.88	1.65	1.77	3.36	1.24
Sulphur removal degree, %	43.54	61.27	56.20	25.07	50.23
Results of oxidative desulphurization of the initial black coal					
Sulphur content, mas %					
total, S_t^a	1.92	1.78	1.97	1.53	1.16
pyritic, S_p^a	0.09	0.73	0.34	0.81	0.72
Sulphur removal degree, %	49.34	77.32	72.25	78.08	73.87

- spectrum 7 is made in the points related to the coal organic matter;

- spectrum 8 – in the points which are the organic matter with a relatively high content of pyrite;

- spectrum 9 – mixture of organic-inorganic matter, including pyrite.

In F3 coal inorganic matter is in the form of relatively small particles and associates with organic matter.

The distribution character of inorganic matter, including pyrite, is slightly changed in the case of concentrated F3 coal (Figs. 10-12). The photos show finer inorganic particles (compared with the initial coal).

For F3 coal XEA results show that dark surface (except spectrum 10) is organic matter with relatively high content of inorganic matter, including pyrite.

Thus, photomicrographs and XEA results confirm the assumption that in the initial G2 coal the inorganic matter, including pyrite, is in the form of large plates which are removed during flotation. The result is sulphur essential removal from coal.

In the case of F3 coal the inorganic part, including pyrite is in the form of fine particles associated with

organic matter. Therefore sulphur content slightly decreases during flotation.

To study the effect of inorganic matter amount on the process the initial coal and flotoconcentrate were desulphurized (Table 15). The results show that the concentrated coal is desulphurized with the same efficiency as the initial coal. It means that the amount of inorganic matter does not affect the desulphurization process, *i.e.* the coal may be desulphurized before and after its beneficiation.

Table 16 represents the efficiency of sulphur removal from different types of the initial black coal *via* beneficiation (flotation) and oxidative desulphurization under the optimum condition. The analysis of the data from Tables 16 show that desulphurization using oxidative method is more effective than sulphur removal using beneficiation, because higher values of sulphur removal degree are achieved. Moreover, using the investigated method we may remove pyrite of both (fine-grained and coarse-grained) forms. It means that inorganic matter sizes (pyrite first of all) do not influence the character of coal desulphurization *via* oxidative method.

4. Conclusions

The desulphurization efficiency *via* oxidation method does not depend on sizes and amount of inorganic impregnations in the coal matrix. Therefore the desulphurization process may be realized before and after coal beneficiation. The developed oxidation method allows to remove sulphur from different types of coal more efficiently than coal beneficiation.

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ВПЛИВ ЯКОСТІ ВУГІЛЛЯ НА ПРОЦЕС ЙОГО ЗНЕСІРЧУВАННЯ 2. ВПЛИВ НЕОРГАНІЧНОЇ ЧАСТИНИ

Анотація. Вивчено вплив розмірів і характеру розподілу піриту та кількості неорганічної частини на ступені вилучення сірки з вугілля під час його оксидаційного знесірчення та збагачення. Порівняно ефективність процесів оксидаційного знесірчення різних зразків вихідного та збагаченого кам'яного вугілля.

Ключові слова: оксидаційне знесірчення, вугілля, сірка, пірит, оксид сірки (IV), паро-повітряна суміш.