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KINETIC REGULARITIES OF HIGH-SULPHURIC BROWN COAL OXIDATIVE DESULPHURIZATION

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Abstract. The process of high-sulphuric brown coal oxidative desulphurization has been studied. The effect of grain size and oxidant linear rate on the process parameters has been determined. During the process the main part of pyritic sulphur is converted into hydrogen sulphide resulting in forming the gases with H_2S high content which may be utilized or processed by the known methods.

Keywords: brown coal, sulphur, pyrite, oxidation, hydrogen sulphide.

1. Introduction

Today the world output of heat and electric energy from coal is 23 and 55 % correspondingly [1]. In the energy balance of Ukraine coal is also of great importance. The comparative pattern of energy resources consumption in Ukraine, EU countries, USA and in the whole world is represented in Table 1 [2].

Table 1

Structure of primary energy resources consumption [2]

Primary energy resource	World	Ukraine	EU	USA
Gas	21	41	22	24
Oil	35	19	41	38
Coal	23	19	16	23
Uranium	7	17	15	8
Renewable energy sources	14	4	6	7

Among unrenewable energy resources a share of coal will continuously grow because in 2008 world deposits of coal were 67 %, oil – 18 % and gas – 15 % to calculate for equivalent fuel [3]. Therefore, as predicted, till 2020 coal will be number one among energy carriers and its share in the world balance of energy primary resources consumption will be above 30 % [1]. In our country the situation with organic deposits is sharply set toward coal [3]. The amount of coal deposits in 2008 in Ukraine was 95 % to calculate for equivalent fuel (oil and gas – 3 and 2 % correspondingly).

The main ways of produced coal application in Ukraine are: burning at heat power plants (HPP) – 40.0 %; metallurgy – 37.9 %; municipal and residential use – 11.1 % [4].

Medium-metamorphized black coal is used, as a rule, for coke production and coal with low and high metamorphism degree, as well as brown coal are used at HPP.

Concerning the brown coal use it should be noted that approximately 4 % of energy in the world is produced from it. In some countries this value increases to 70 % [5]. One of the directions of coal industry development in Ukraine is the increase of brown coal volume for heat-and-power engineering, because coal price is lower in 2.5 times than the price of oil volume equivalent by heat capacity and in 1.3 times than that of gas [5].

The explored reserves of brown coal in Ukraine are estimated in 6–8 billions tons. They are placed mainly in Dnieper lignite basin. The average characteristic of Ukrainian brown coal is given in Table 2 [5].

Table 2

Characteristics of Ukraine's brown coal [5]

The explored reserves, billion tones	6–8
Average ash, mas %	20
Moisture, W^r, mas %	42–62
Average sulphur content, mas %	3–4
Energy values, kJ/kg	7332–9637

The data from Table 2 allow to assert that while burning the brown coal the environment is polluted by sulphuric anhydride because of the high sulphur content in coal. The same situation is with burning the black coal mined in Ukraine: 59.2 % belong to sulphuric coal (sulphur content is 1.6–4 mas %); 14.4 % belong to high-sulphuric (sulphur content is above 4 mas %) and only 26.4 % belong to the low-sulphuric coal (sulphur content is less than 1.0–1.5 mas %) [6].

Today the coal desulphurization industrial technology before coal burning is absent. The problem is solved by the removal of sulphur dioxide from smoke fumes mainly with the production of plaster. Such method is unprofitable and demands additional capital outlays for HHP reequipment and state subsidy. Therefore only high-developed states use it [7]. In most cases thermal plants do not go beyond paying a fine for pollutant emissions and do not refuse from sulphuric or high-sulphuric coal mining.

Desulphurization by the oxidative method is one of the alternatives of sulphur removal from coal [8, 9]. During the process the raw material is treated by air-steam mixture. Pyritic sulphur which is the main part of total sulphur in coal is converted selectively. The process products are as follows: solid low-sulphuric fuel; resin which is formed during organic part thermal decomposition; desulphurization gases with sufficiently high sulphur-containing components (compared with HPP gases) which may be processed or utilized by the known methods with the following production of liquefied sulphur dioxide, sulphuric acid, *etc*.

Our previous investigations [8, 9] showed the possibility of black coal desulphurization by the mentioned method. Brown coal (compared with black coal) is characterized by high moisture; its organic part contains many oxygenated compounds with low thermal stability and high reactivity. The aim of this work was desulphurization of brown coal by the oxidative method and so the reduction of sulphur dioxide emissions at brown coal burning. Since the process is a heterophase one, the primary task was to establish conditions (oxidant rate and coal grains size) which ensure pyritic sulphur conversion in the kinetic area.

2. Experimental

The sample of brown coal for investigation was withdrawn at Morozivske coal-field of Dnieper lignite basin. The coal sample was grinded and sifted by grains size. For all coal fractions the technical analysis was carried out and sulphur different forms such as organic sulphur (S_o^d), pyritic sulphur (S_p^d) and sulphate sulphur (S_{SO4}^d) were determined. The results are given in Table 3.

The oxidation desulphurization process was investigated using the procedure described in [10] at the laboratory plant, block diagram of which is represented in Fig. 1.

Table 3

Characteristics of brown coal fractions

Fraction, mm	Moisture (W^{af}), mas %	Ash (A^d), mas %	Volatiles (V^{daf}), mas %	Sulphur content, mas %			
				Total, S_t^d	Pyritic, S_p^d	Organic, S_o^d	Sulphate, $S_{SO_4}^d$
< 0.1	12.64	9.89	63.02	4.34	1.88	2.36	0.10
0.1-0.25	13.96	9.42	63.78	4.28	2.10	2.06	0.11
0.25-0.315	14.03	9.16	64.34	4.31	1.97	2.20	0.13
0.315-0.5	14.02	9.25	64.83	4.25	1.80	2.23	0.22
0.5-0.75	13.49	9.16	66.77	4.25	1.71	2.36	0.17
0.75-1.00	13.51	9.44	66.90	4.36	1.81	2.37	0.17
1.00-1.60	13.44	9.25	67.34	4.38	1.92	2.27	0.19
1.60-2.00	13.43	8.62	66.60	4.53	1.64	2.64	0.25

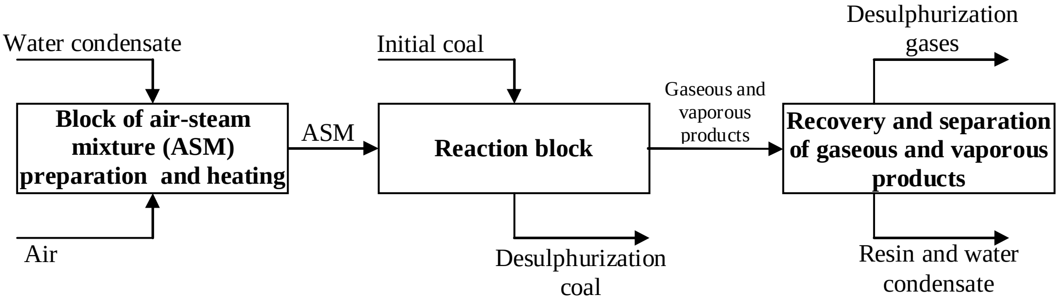

Fig. 1. Block diagram of the laboratory plant for coal oxidative desulphurization

Conversion of total or pyritic sulphur is calculated without taking into consideration its loss with the resin by the following formula (mas %):

$$\Delta S_x^a = \frac{S_{x\,0}^a \cdot 100 - S_x^a \cdot x_C}{S_{x\,0}^a}$$

where $S_{x\,0}^a$ – content of total or pyritic sulphur in the initial coal to calculate for analytical sample, mas %; S_x^a – content of total or pyritic sulphur in desulphurized coal to calculate for analytical sample, mas %; x_C – desulphurizated coal yield, mas %.

Removal degree of pyritic sulphur (mas %) is calculated by the formula:

$$\Delta S_p^d = \frac{S_{p\,0}^d - S_p^d}{S_{p\,0}^d} \cdot 100$$

where $S_{p\,0}^d$ – content of pyritic sulphur in the initial coal to calculate for dry sample, mas %; S_p^d – content of pyritic sulphur in desulphurized coal to calculate for dry sample, mas %.

To denote the ratio of oxidant flow rate (m^3/s under normal conditions) to coal volume (m^3) the term “volumetric feed rate” (VFR) is used.

The oxidant linear rate (OLR) is calculated as a ratio of oxidant volumetric flow rate (m^3/s under normal conditions) to sectional area of an empty reactor (m^2).

3. Results and Discussion

The investigations of process parameters, namely grains size and OLR were carried out at 698 K. Such temperature was chosen because it is the optimum temperature for black coal desulphurization [8, 9]. Brown coal contained 13–14 mas % of water (see Table 3), therefore the process was studied without water steam addition to the oxidant. The experimental results are given in Tables 4-6 and Figs. 2-4.

The increase of oxidant flow rate at low VFR (0.162 s^{-1} at possible deficit of oxygen) decreases the yield of desulphurized coal (Table 4). The possible reasons are the intensification of oxidation reactions of coal organic matrix (COM) increasing the content of CO_2 and CO in oxidation gases (Table 5) and acceleration of thermal destruction reactions increasing the yield of resin and hydrocarbon gases (Tables 4 and 5). At higher values of VFR the increase of OLR strongly accelerates COM oxidation. The content of CO_2 and CO increases and resin amount decreases (Tables 4 and 5).

Table 4

Effect of OLR on desulphurizated products yield at different VFR

VFR, s^{-1}	OLR, m/s	Yield, mas %		
		Desulphurized coal	Resin	Desulphurized coal and resin
0	0	54.14	18.12	72.26
0.162	0.00625	53.12	16.01	69.13
	0.01250	52.27	16.27	68.54
	0.01875	51.30	17.87	69.17
	0.02500	50.13	19.53	69.66
	0.03750	47.86	20.31	68.17
	0.05000	47.48	20.05	67.53
0.324	0.00625	54.14	18.12	72.26
	0.01250	52.82	23.01	75.83
	0.01875	52.45	22.44	74.89
	0.02500	51.66	20.71	72.37
	0.03750	50.37	18.47	68.84
	0.05000	47.94	18.21	66.15
0.648	0.00625	54.14	18.12	72.26
	0.01250	52.76	27.81	80.57
	0.01875	52.69	26.60	79.29
	0.02500	51.04	25.44	76.48
	0.03750	49.63	23.66	73.29
	0.05000	46.89	22.69	69.58

Table 5

Effect of OLR on desulphurization gas composition at different VFR

VFR, s^{-1}	OLR, m/s	Content, vol %									
		CH_4	C_2H_4	C_2H_6	C_3	H_2S	CO_2	CO	N_2	O_2	Ar
0	0	5.07	1.06	1.88	1.72	15.68	62.07	9.86	0.00	2.66	0.00
0.162	0.00625	0.73	0.00	0.25	0.12	3.60	13.15	1.57	75.93	3.86	0.78
	0.01250	0.89	0.19	0.33	0.29	3.62	18.35	2.65	71.43	1.71	0.54
	0.01875	1.01	0.16	0.39	0.45	3.53	20.33	3.71	68.09	1.68	0.66
	0.02500	1.46	0.25	0.63	0.40	3.33	22.45	3.59	65.00	2.08	0.80
	0.03750	1.42	0.29	0.53	0.40	3.14	26.92	3.45	61.80	1.23	0.83
	0.05000	1.16	0.28	0.47	0.36	2.97	31.10	2.82	59.05	1.02	0.77
0.324	0.00625	0.60	0.11	0.09	0.72	1.61	10.19	1.25	76.98	7.16	1.29
	0.01250	0.77	0.13	0.11	0.17	1.72	12.76	2.05	76.05	5.00	1.25
	0.01875	0.74	0.13	0.13	0.18	1.84	14.09	2.52	75.89	3.37	1.13
	0.02500	0.65	0.12	0.13	0.09	1.90	16.51	2.54	75.27	1.88	0.93
	0.03750	0.74	0.15	0.19	0.51	1.76	21.26	3.27	69.07	2.11	0.93
	0.05000	0.69	0.14	0.26	1.01	1.68	23.49	3.40	66.68	1.91	0.74
0.648	0.00625	0.42	0.06	0.08	0.08	0.73	10.25	0.90	77.78	8.54	1.17
	0.01250	0.49	0.08	0.10	0.09	0.78	12.57	1.37	76.03	7.39	1.12
	0.01875	0.46	0.08	0.09	0.09	0.83	14.37	2.21	75.67	5.22	0.98
	0.02500	0.66	0.13	0.13	0.10	0.85	16.04	2.52	74.74	3.90	0.93
	0.03750	0.61	0.13	0.15	0.13	0.84	19.61	3.13	71.42	3.11	0.86
	0.05000	0.58	0.13	0.16	0.13	0.82	18.48	3.57	73.07	2.36	0.70

Table 6

Effect of OLR on sulphur content in desulphurized coal at different VFR

VFR, s^{-1}	OLR, m/s	Sulphur content, mas %			
		Total, S_t^d	Pyritic, S_p^d	Sulphate, $S_{SO_4}^d$	Organic, S_o^d
0	0	3.90	0.89	2.57	0.45
0.162	0.00625	3.50	0.63	2.33	0.53
	0.01250	3.32	0.53	2.39	0.41
	0.01875	3.25	0.52	2.25	0.48
	0.02500	3.31	0.57	2.06	0.67
	0.03750	3.46	0.63	2.13	0.69
	0.05000	3.54	0.64	2.19	0.71
0.324	0.00625	3.59	0.68	2.39	0.53
	0.01250	3.42	0.59	2.25	0.58
	0.01875	3.34	0.58	2.19	0.57
	0.02500	3.39	0.62	2.20	0.57
	0.03750	3.53	0.63	2.24	0.66
	0.05000	3.61	0.73	2.05	0.83
0.648	0.00625	3.69	0.73	2.64	0.32
	0.01250	3.51	0.66	2.44	0.42
	0.01875	3.46	0.65	2.36	0.46
	0.02500	3.51	0.69	2.34	0.48
	0.03750	3.66	0.78	2.32	0.56
	0.05000	3.79	0.76	2.43	0.59

The dependence of pyrite oxidation reaction rates upon OLR (Table 6 and Figs. 2-4) shows that this value slightly affects the sulphur removal degree and conversion (compared with black coal desulphurization [8, 9]). Evidently the reason is that the majority of pyritic sulphur in brown coal is converted owing to its interaction with water and/or COM but not with air oxygen. The high values of sulphur removal degree and conversion at air rate equal to zero confirm this fact. Moreover, hydrogen sulphide is present in desulphurized gases (Table 5). Its forming may be described by Eqs. (1)–(3):

$$FeS_2 + C + H_2O \rightarrow H_2S + FeS\ (FeS_x) + CO \qquad (1)$$

$$2FeS\ (FeS_x) + 3H_2O \rightarrow Fe_2O_3 + 2H_2S + H_2 \qquad (2)$$

$$3FeS\ (FeS_x) + 4H_2O \rightarrow Fe_3O_4 + 3\ H_2S + H_2 \qquad (3)$$

At the same time it should be noted that pyritic sulphur of black coal is converted due to its oxidation with SO_2 forming.

The removal degree of pyritic sulphur indicating the rate ratio between pyrite and COM conversions slightly increases to the linear rate value of 0.01250-0.01875 m/s and then decreases (Fig. 2). Conversion of total and pyritic sulphur increases to the similar values (Figs. 3 and 4). All these facts indicate that at oxidant rates of 0.01250–0.02500 m/s the pyrite oxidation with air oxygen proceeds in the kinetic area.

The amount of hydrogen sulphide in desulphurization gases does not change or decreases with the increase of OLR (Table 5). The reason is the increase of carbon oxides amount in the gases.

Coal burned at HPP is not homogeneous by fractions and may contain grains of different size. Therefore we studied the effect of fineness of coal grinding on the products quality and composition. It was necessary to establish the range of grains sizes at which pyritic sulphur conversion takes place in pore-diffusion area (temperature is 698 K, OLR is 0.02500 m/s). The experimental results are represented in Tables 7-9 and Fig. 5.

The process proceeding incidentally depends upon grains size. The yield of desulphurized coal and decomposition resin is commensurable with the content of volatile components in the initial fractions. At grain size less than 1.00 mm the coal yield decreases and resin yield increases at the increase of volatile components yield of initial coal (Table 7). At further increase of grain size (1.00–1.60 and 1.60–2.00 mm) the opposite tendency takes place, that is explained by the partial condensation of volatile compounds in coal pores and strengthening of pore-diffusion processes effect (concerning oxidation and decomposition reactions of organic part). The confirmation is a slight decrease of CO_2 content in desulphurization gases at grain size enlargement (more than 1.00 mm, Table 8).

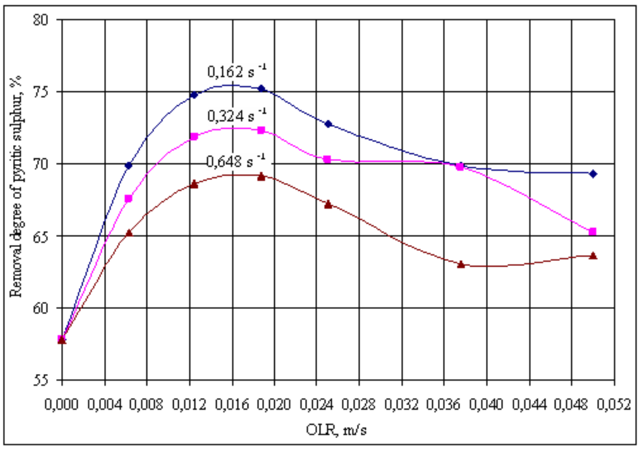

Fig. 2. Effect of OLR on removal degree of pyritic sulphur at different VFR

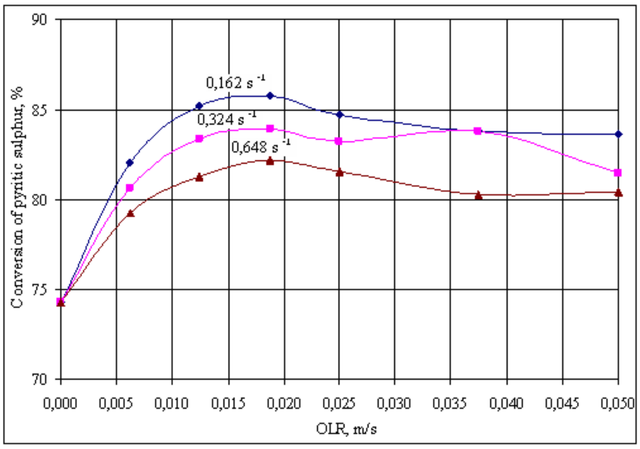

Fig. 3. Effect of OLR on conversion of pyritic sulphur at different VFR

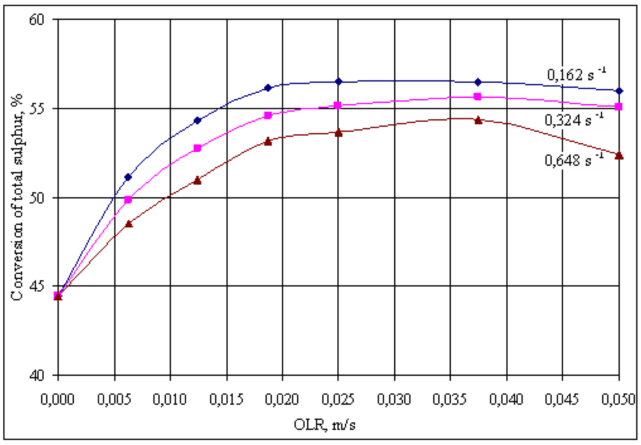

Fig. 4. Effect of OLR on total sulphur conversion at different VFR

The increase of grain size to 0.75 mm increases the sulphur conversion and the increase of size to 0.315 mm increases a removal degree (Fig. 5). Such tendency confirms the previous assumption that pyrite reactions with organic mass and coal moisture (Eqs. (1)–(3)) play the main role during brown coal desulphurization. Since the moister content increases till 0.315 mm size of initial coal grains and volatile compounds yield (content of thermally instable and low-molecular compounds with high reactivity) – till 0.75 mm, the increase of pyrite conversion rate till the same values is logical. It means the increase of sulphur removal degree and conversion (Fig. 5).

Table 7

Effect of grain size on desulphurizated products yield

Fraction, mm	Yield, mas %		
	Desulphurized coal	Resin	Desulphurized coal and resin
< 0.10	50.91	18.92	69.83
0.10-0.25	50.13	19.53	69.66
0.25-0.315	49.14	19.87	69.00
0.315-0.50	47.70	19.32	67.01
0.50-0.75	46.19	19.94	66.13
0.75-1.00	46.17	20.21	66.38
1.00-1.60	47.20	18.89	66.09
1.60-2.00	47.44	19.01	66.45

Table 8

Effect of fractional decomposition on desulphurization gas composition

Fraction, mm	Content, vol %.									
	CH_4	C_2H_4	C_2H_6	C_3	H_2S	CO_2	CO	N_2	O_2	Ar
< 0.10	0.89	0.34	0.40	0.32	3.24	20.39	3.22	67.05	3.33	0.82
0.10-0.25	1.46	0.25	0.63	0.40	3.33	22.45	3.59	65.00	2.08	0.80
0.25-0.315	1.66	0.39	0.62	0.42	3.38	23.20	4.01	63.32	2.13	0.87
0.315-0.50	1.87	0.54	0.87	0.42	3.44	25.20	4.46	60.22	2.26	0.72
0.50-0.75	1.81	0.53	0.76	0.43	3.33	28.66	5.02	56.63	2.07	0.75
0.75-1.00	1.43	0.57	0.67	0.41	3.29	28.06	5.38	57.42	2.02	0.76
1.00-1.60	1.48	0.33	0.52	0.26	3.17	26.71	6.26	58.65	1.85	0.78
1.60-2.00	1.32	0.50	0.67	0.38	3.04	24.94	6.21	60.44	1.76	0.73

Table 9

Effect of grain size on sulphur content in the desulphurized coal

Fraction, mm	Sulphur content, mass %			
	Total, S_t^d	Pyritic, S_p^d	Sulphate, $S_{SO_4}^d$	Organic, S_o^d
< 0.10	3.48	0.63	0.58	2.26
0.10-0.25	3.31	0.57	0.67	2.06
0.25-0.315	3.21	0.47	0.50	2.24
0.315-0.50	3.09	0.43	0.43	2.22
0.50-0.75	3.04	0.42	0.39	2.23
0.75-1.00	3.14	0.63	0.38	2.13
1.00-1.60	3.36	0.78	0.40	2.18
1.60-2.00	3.55	0.74	0.39	2.42

Unsatisfactory results of powdered coal (fraction less than 0.10 mm) desulphurization may also be explained by the removal of the lightest coal particles (with less pyrite content) with reaction volatile products.

At desulphurization of the fraction with grains size more than 0.75 mm the sulphur content slightly increases, the removal degree of pyritic and the total sulphur decreases (Table 9 and Fig. 5), *i.e.* the oxidation rate decreases, because some of sulphur conversion reactions proceed in the pore-diffusive area.

The obtained results show the principal possibility of essential decrease of sulphur emissions while applying the oxidative method for brown coal desulphurization. If we assume that all hydrogen sulphide in the desulphurization gases will be removed or converted into sulphur by known methods [11-13], the total sulphur conversion (TSC) is practically equal to the degree of environment pollution decrease. Therefore we may assert that the suggested method gives the possibility to decrease the sulphur emissions more than twice (TSC in some cases exceeds 60 %).

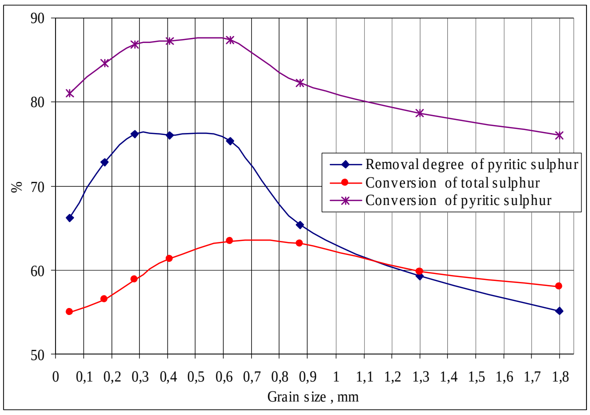

Fig. 5. Effect of grain size on removal degree of pyritic sulphur and conversion of total and pyritic sulphur

4. Conclusions

1. It has been established that the total sulphur conversion is 55–65 % and the pyritic sulphur conversion is 85–87 % at the oxidative desulphurization of thebrown coal. Taking into consideration that the brown coal is usually used for heat production at heat power plants the application of the suggested process before burning will allow to decrease sulphur emissions at least by 55–65 %.

2. The pyritic and partially organic sulphur, is converted mainly owing to its interaction with moisture of the initial brown coal and coal organic part. The removed sulphur is converted into the hydrogen sulphide.

3. The oxidant linear rate insignificantly affects the process. The range of 0.01250–0.02500 m/s is optimum.

4. At rates of 0.02500 m/s the grains size must not exceed 0.75 mm. In such a case sulphur conversion reactions proceed in the kinetic area. Also it is undesirable to grind the coal grains to the size less than 0.1 mm because it leads to the additional energy consumption and does not favor the process intensification.

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ДОСЛІДЖЕННЯ КІНЕТИЧНИХ ЗАКОНОМІРНОСТЕЙ ПРОЦЕСУ ОКСИДАЦІЙНОГО ЗНЕСІРЧУВАННЯ ВИСОКОСІРЧИСТОГО БУРОГО ВУГІЛЛЯ

Анотація. *Вивчено процес оксидаційного знесірчування високосірчистого бурого вугілля. Встановлено вплив крупності зерна і лінійної швидкості руху оксиданту на процес. Показано, що основна кількість піритної сірки в ході процесу перетворюється у сірководень, внаслідок чого отримуються гази з порівняно високим вмістом* H_2S*, які можна утилізувати або переробляти відомими методами.*

Ключові слова: *буре вугілля, сірка, пірит, окиснення, сірководень.*