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EFFECT OF COAL QUALITY ON ITS DESULPHURIZATION
1. INFLUENCE OF THE ORGANIC MATTER

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Abstract. The desulphurization process of different coal types has been studied. The coal was treated by air-steam mixture in the fluidized-bed reactor under the conditions similar to isothermal ones. The influence of temperature and oxidant composition affecting the pyrite (which is the coal component) chemical conversion on the desulphurization efficiency has been investigated for coal with different metamorphism degree. The dry and wet samples of anthracite and brown coal were compared in order to propose the direction of brown coal pyrite conversion followed by the hydrogen sulphide production.

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

1. Introduction

Coal is one of the main energy carriers because its deposits exceed oil and gas deposits not only in Ukraine but all over the world too (Fig. 1) [1].

The direction of coal usage depends upon its metamorphism degree. In accordance with the scheme represented in Fig. 2 brown and black coal with low and high metamorphism degree may be considered as a power station coal used at heat power plants (HPP).

Black coal with medium metamorphism degree is generally used for coke production but sometimes it may be used as a fuel at HPP (for example if its deposits are far away from the by-product coke plants, or have high ash or sulphur content).

It should be noted that coal is not clearly divided into low-, medium- and high-metamorphized groups. For example, fiery (or gas) (G) and lean-baking (LB) coal sometimes are ascribed to the medium-metamorphized coal, though they are referred to the low- and high-metamorphized coal, respectively.

On the other hand, the considerable amount of coal is characterized by high sulphur content. Hence its burning leads to SO_2 emissions. Coal is the main source of atmosphere pollution by sulphur dioxide (Table 1). Therefore, the usage of some types of high-sulphuric coal is complicated or even impossible, in spite of its favourable bedding conditions.

Nowadays SO_2 is removed by means of its sorption from HPP smoke fumes by calcium compounds followed by gypsum production. However, except dividends for the environment, all desulphurization methods applied during coal burning or smoke fumes treating are unprofitable, even if we sale by-products (gypsum, dry ash, *etc*.). Therefore we may assert that the effective and profitable industrial method of SO_2 reduction during the burning of high-sulphuric coal has not existed till today.

The coal desulphurization *via* oxidation [7-10] is one of the purification methods. The essence of the process is the treatment of raw material by air-steam mixture. Pyritic sulphur (which is the main part of all sulphur in coal) converts selectively in this case. The process products are: solid low-sulphuric fuel; decomposition resin produced during thermal cracking of the organic matter; desulphurization gases with high (compared with HPP gases) content of sulphur-containing components, that allows to process or utilize them by the known methods [11-13] with further production of sulphur, liquefied sulphur dioxide, *etc*.

For some samples of black coal the temperature and water steam are factors affecting the chemism of oxidative desulphurization [7, 8]:

– at 698 K and higher temperatures the process is intensified due to the pyrite decomposition for pyrotite (FeS_x) and sulphur followed by their oxidation;

– if water steam is added to air, the rate and degree of pyrite oxidation increase; the reason is a steam-pyrite complex formation that increases reactivity.

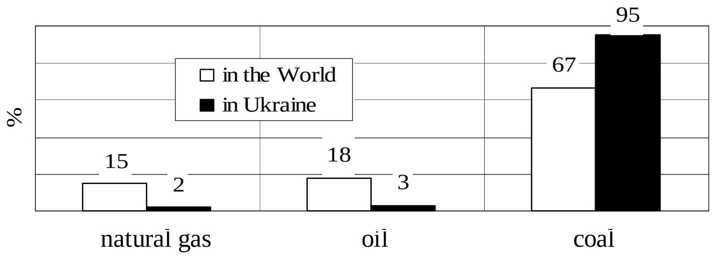

Fig. 1. Structure of organic fuel deposits in Ukraine and in the world (calculated for standard fuel)

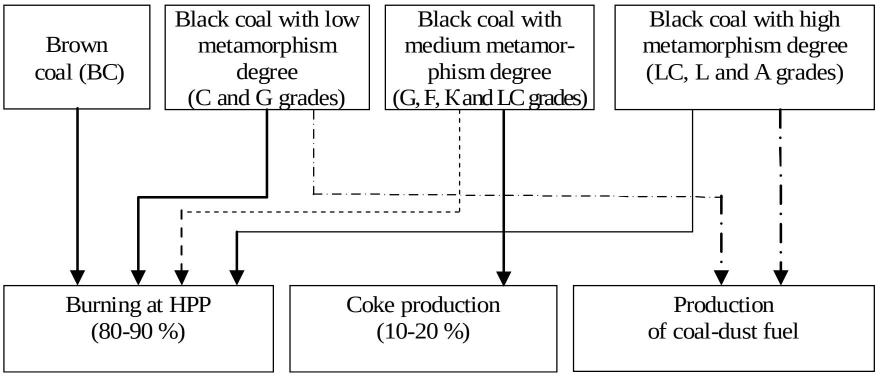

Fig. 2. Main directions of coal application

Table 1

Structure of sulphur(IV) oxide emissions into atmosphere

Emissions source	Year		
	2008	2009	2010
In Ukraine [2-4]			
1. Stationary sources	97.7	97.8	97.9
2. Mobile sources (motor-cars; railway, aircraft and water transport; industrial equipment)	2.3	2.2	2.1
In the world [5, 6]			
1. Stationary sources,	95.8	97.1	-
including production of electric power and heat	68.6	70.2	-
2. Transport,	4.0	2.5	-
including motor transport	0.7	0.2	-
3. Others	0.2	0.4	-

Table 2 presents possible reactions of pyrite conversion during oxidative desulphurization which are divided into pyrite reactions with oxygen (including previous thermal decomposition), water steam, coal organic matter (COM) and possible products of the process. The thermodynamic analysis was carried out for the mentioned reaction (Table 2). Since the reactions proceed under the pressure close to the atmospheric one, and with a small change of moles number, it was assumed that at negative value of Gibbs energy ($\leq$ -50 kJ/mol) the reaction is not limited by achievement of thermodynamic equilibrium, *i.e.* equilibrium conversion degrees of the initial components are $\geq$ 99 %. At the positive value of Gibbs energy ($\geq$ +50 kJ/mol) the reaction is thermodynamically impossible, *i.e.* equilibrium conversion degrees of the initial components are < 1 %. Within the range of values from -50 to +50 kJ/mol the reaction proceeds with thermodynamic limits.

Data from Table 2 allow to assert that pyrite oxidation is thermodynamically the most possible reaction within the temperature range of 623–723 K. The great positive values of Gibbs energy for the reactions of pyrite thermal decomposition may be caused by a non-stoichiometric compound with high reactivity – pyrotite – which is formed during the decomposition. The formation of pyrotite, not iron sulphide, the characteristics of which were taken into consideration during calculations, is the most probable explanation of such great values.

Table 2

Calculated values of Gibbs energies of the possible reactions at 623 and 723 K

No.	Equation	ΔG^0_c, kJ/mol		Temperature interval of the reaction proceeding, K; Ref.
		623 K	723 K	
Thermal decomposition and reactions of pyrite and its decomposition products with oxygen				
1	$4FeS_{2(s)}+11O_{2(g)}\rightarrow 2Fe_2O_{3(s)}+8SO_{2(g)}$	-3298.45	-3354.50	> 623–673; [14, 15]
2	$4FeS_{(s)}+5O_{2(g)}\rightarrow 2Fe_2O_{3(s.)}+2SO_{2(g)}$	-2167,97	-2154.70	[16, 17]
3	$FeS_{2(s)} + 3O_{2(g)} \rightarrow FeSO_{4(s)} + SO_{2(g)}$	-876.85	-848.26	[18]
4	$S_{(s)}+ O_{2(g)}\rightarrow SO_{2(g)}$	-317.76	-328.60	[16, 17]
5	$FeS_{2(s)}\rightarrow FeS\ (Fe_{1-x}S)_{(s)}+S_{(s)}$	35.14	–	–
6	$FeS_{2(s)}\rightarrow FeS\ (Fe_{1-x}S)_{(s)}+S_{(g)}$	–	204.28	> 773–873; [15, 16]
Reactions of pyrotite with water steam				
7	$FeS(Fe_{1-x}S)_{(s)}+H_2O_{(g)}\rightarrow FeO_{(s)}+H_2S_{(g)}$	54.09	55.00	[18]
8	$2FeS(Fe_{1-x}S)_{(s)}+3H_2O_{(g)}\rightarrow Fe_2O_{3(s.)}+2H_2S_{(g)}+H_{2(g)}$	115.94	126.04	[18]
Reactions of pyrite, pyrotite and iron sulfide with COM and its conversion products				
9	$3FeS_{2(s)}+c\text{-}C_6H_{12(g)}\rightarrow 3FeS_{(s)}+3H_2S_{(g)}+C_6H_{6(g)}$	-32.35	-94.55	–
10	$FeS_{2(s)}+H_{2(g)}\rightarrow FeS_{(s)}+H_2S_{(g)}$	-2.19	-9.98	> 773; [15, 18]
11	$FeS_{2(s)}+CO_{(g)}\rightarrow FeS_{(s)}+COS_{(g)}$	4.01	-1.72	> 1073; [15, 18]
12	$FeS_{2(s)}+C_6H_{14(g)}\rightarrow FeS_{(s)}+H_2S_{(g)}+\text{ц-}C_6H_{12(g)}$	16.92	4.66	–
13	$FeS_{2(s)}+1\text{-}C_4H_{8(g)}\rightarrow FeS_{(s)}+H_2S_{(g)}+1,3\text{-}C_4H_{6(g)}$	41.33	22.02	–
14	$FeS_{2(s)}+C_4H_{10(g)}\rightarrow FeS_{(s)}+H_2S_{(g)}+1\text{-}C_4H_{8(g)}$	43.14	21.59	–
15	$FeS_{2(s)}+C_2H_{6(g)}\rightarrow FeS_{(s)}+H_2S_{(g)}+C_2H_{4(g)}$	57.81	36.78	–
16	$FeS(Fe_{1-x}S)_{(s)}+H_{2(g)}\rightarrow Fe_{(s)}+H_2S_{(g)}$	65.48	65.49	> 1073; [15, 18]
17	$FeS_{2(s)}+C_2H_{4(g)}\rightarrow FeS_{(s)}+H_2S_{(g)}+C_2H_{2(g)}$	98.25	77.47	–
18	$FeS_{2(s)}+C_{(s)}\rightarrow Fe_{(s)}+CS_{2(g)}$	165.82	145.22	> 1273; [15, 18]
19	$2FeS\ (Fe_{1-x}S)_{(s)}+C_{(s)}\rightarrow 2Fe_{(s)}+CS_{2(g)}$	233.48	220.68	> 1273; [15]
Reactions of pyrite and iron sulfide with COM and water steam				
20	$C_{(s)}+FeS_{2(s)}+H_2O_{(g)}\rightarrow H_2S_{(g)}+FeS_{(s)}+CO_{(g)}$	58.76	36.46	[18]
Reactions of COM with pyrite conversion products				
21	$C_{(s)}+ 2S_{(g)}\rightarrow CS_{2(g)}$	–	-338.82	[15]
22	$H_{2(g)} + S_{(g)} \rightarrow H_2S_{(g)}$	–	-214.26	[19]
23	$C_{(s)} + SO_{2(g)} \rightarrow S_{(s)}+CO_{2(g)}$	-63.21	–	[12]
24	$S_{(s)}+H_{2(g)}\rightarrow H_2S_{(g)}$	-37.33	–	[19]
25	$C_{(s)}+ 2S_{(s)}\rightarrow CS_{2(g)}$	27.88	–	[15]
26	$SO_{2(g)}+C_{(s)}\rightarrow S_{(g)}+CO_{2(g)}$	–	122.78	[12]
Reactions of gaseous products				
27	$2SO_{2(g)}+CH_{4(g)}\rightarrow 2S_{(s)}+CO_{2(g)}+2H_2O_{(g)}$	-165.20	–	[12]
28	$2CO_{(g)}+ SO_{2(g)}\rightarrow S_{(s)} + 2CO_{2(g)}$	-140.02	–	[12, 19]
29	$CS_{2(g)} + H_2O_{(g)} \rightarrow H_2S_{(g)}+COS_{(g)}$	-35.38	-35.01	[20-22]
30	$SO_{2(g)} + 2H_2S_{(g)}\rightarrow 3S_{(s)} + 2H_2O_{(g)}$	-33.64	–	[12, 19]
31	$COS_{(g)}+H_2O_{(g)}\rightarrow H_2S_{(g)}+CO_{2(g)}$	-22.06	-20.53	[20-22]
32	$2CO_{(g)}+ SO_{2(g)}\rightarrow S_{(g)}+ 2CO_{2(g)}$	–	64.07	[12, 19]
33	$2SO_{2(g)}+CH_{4(g)}\rightarrow 2S_{(g)}+CO_{2(g)}+2H_2O_{(g)}$	–	207.76	[12]
34	$SO_{2(g)} + 2H_2S_{(g)}\rightarrow 3S_{(g)} + 2H_2O_{(g)}$	–	517.12	[12, 19]

The hydrogen sulphide formation is improbable because of the reactions of pyrite or pyrotite with water steam, but it is possible due to their interaction with hydrogen or coal organic matter. The analysis of the reactions between pyrite and hydrocarbons shows that the increase of hydrocarbon molecular mass increases the probability of the mentioned conversions proceeding. The reactions leading to the formation of cyclic unsaturated compounds are more probable than aliphatic unsaturated compounds formation.

Hydrogen sulphide may be formed owing to the reactions of coal with sulphur and its dioxide. At 623 K the sulphur formation due to the pyrite decomposition is impossible [7, 8], but it is possible due to the proceeding of the reactions 27 and 28 (Table 2).

Hydrogen sulphide formation is also possible due to the interactions between gaseous products (reactions 29 and 31).

The reactivity of coal organic matrix (COM) differs depending upon the degree of chemical maturity (metamorphism, coalification) of coal. Black high-metamorphized coal (*e.g.* L and A grade) has the inert organic matter and brown coal, on the contrary, has the high reactivity.

From the literature data it is impossible to understand if the reactions between COM and FeS_2 will proceed under the conditions of oxidative desulphurization and if the reaction intensity will depend on the COM coalification degree. Therefore the aim of the present work is to establish the effect of coal organic matter on the proceeding of oxidative desulphurization process.

2. Experimental

The following samples of Ukrainian coal were selected for investigations: anthracite (A) from Rovenkovska concentrating mill of Donetsk coal basin; lean coal (L) from Shidna mine of Donetsk coal basin; fat coal (F1) from Samsonovska concentrating mill of Donetsk coal basin; fat coal (F2) 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; candle coal (C) from Buzhanska mine of Lviv-Volyn coal basin; brown coal (B) from Morozivskyy deposit of Dnieper brown-coal basin and run-of-mine coal (R) from Dobrotvir HPP. The fraction of 0.1–0.25 mm was used for researches, because it is the optimal size for coal burning at HPPs.

A model mixture of pyrite (mixed with inert material in such a way that the content of pyritic sulphur in the mixture was comparable with that in the original coal) was prepared.

The results of initial coal and model mixture analyses are shown in Table 3.

All samples are high-sulphur coal ones with the pyritic sulphur amount of 50–90 %. Anomalous high content of sulphate sulphur in some coal samples can be explained by the fact that in some places there was an access for air.

To determine the effect of COM and its quality on the process, the comparative investigations of pyrite desulphurization and different types of coal were carried out. The effect of water steam and temperature on desulphurization of different coal was compared.

Table 3

Characteristics of the initial samples and model mixture

Coal type (symbol)	Moisture content, W^a, mas %	Ash, A^d, mas %	Volatiles yield, V^{daf}, mas %	Sulphur content for dry matter, mas %				Relative content of sulphur different types, %		
				total, S_t^d	pyritic, S_p^d	organic, S_o^d	sulphate, $S_{SO_4}^d$	S_p^d/S_t^d	S_o^d/S_t^d	$S_{SO_4}^d/S_t^d$
Anthracite (A)	3.50	6.22	2.00	2.85	1.41	1.21	0.23	49.47	42.46	8.07
Lean (L)	1.00	43.10	16.53	4.48	3.81	0.54	0.13	85.04	12.05	2.90
Fat (F1)	2.33	10.14	34.32	3.68	2.35	1.31	0.02	63.86	35.60	0.54
Fat (F2)	1.61	21.42	35.56	6.97	4.50	1.17	1.30	64.56	16.79	18.65
Gas (G1)	1.21	16.80	40.91	7.95	7.20	0.52	0.23	90.57	6.54	2.89
Gas (G2)	1.17	20.82	41.11	7.18	6.05	0.60	0.54	84.23	8.31	7.46
Candle (C)	4.85	11.36	37.67	3.98	2.34	0.54	1.1	58.79	13.57	27.64
Brown (B)	13.96*	9.42	63.78	4.28	2.10	2.07	0.11	49.07	48.36	2.57
Run-of-mine (R)	2.83	24.42	35.80	1.92	1.52	0.3	0.10	79.14	15.51	5.35
Model mixture (FeS_2 and SiO_2)	1.54	—	—	3.86	3.72	0.13**	0.01	96.37	3.37	0.26

Notes: * for wet ash-free sample (W^{af}); ** unidentified form of sulphur.

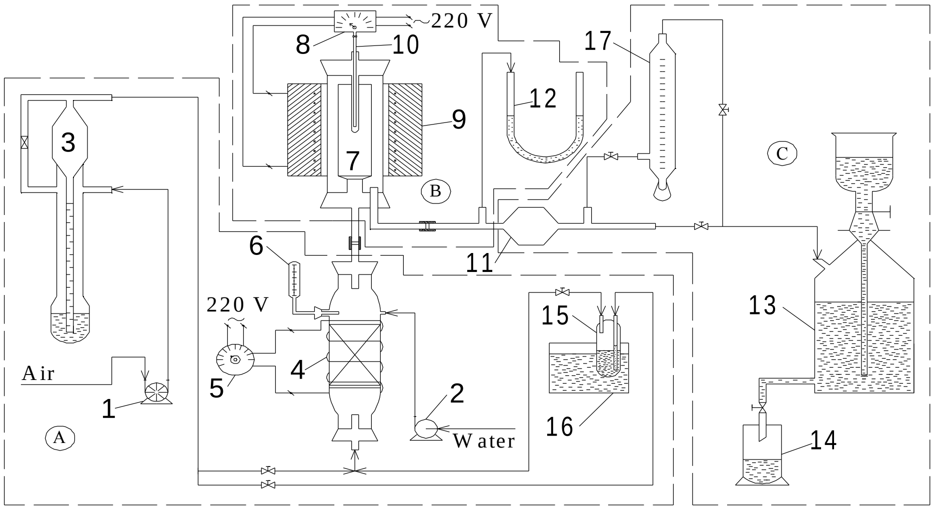

Fig. 3. Scheme of the laboratory plant for coal oxidative desulphurization: block of air-steam treatment and feed (A); reactor block (B) and block of volatile products elimination (C). The plant consists of: compressor (1); pump (2); rheometer (3); heater (4); electric transformer (5); thermometer (6); reactor (7); potentiometer (8); furnace (9); thermocouple (10); trap for decomposition resin (11); manometer (12); gasometer (13); beaker (14); vessel (15); thermostat (16) and flowmeter (17).

For the investigations we used the laboratory plant, the scheme of which is represented in Fig. 3. The detailed description of the laboratory plant is given in [23].

On the basis of obtained results the sulphur conversion and removal degree were calculated. Pyritic sulphur conversion was calculated by the following formula (%):

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

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

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

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

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

The sulphur conversion degree indicates the amount of sulphur converted into gaseous sulphur-containing products which will not eliminate into the environment during burning of desulphurized coal. In other words, it is a level of reduction of environment pollution.

The removal degree indicates the ratio between rates of the reaction of sulphur conversion with gaseous products obtaining and the reaction of COM gasification, *i.e.* the possibility of sulphur reduction in coal as a result of the process proceeding.

The desulphurization gases were analyzed by means of gas-adsorptive chromatography, using chromatograph "LHM". The analyzed gas (10.0 ml) is introduced by metering device into the flow of carrier gas (helium). Gas is fed into the first column (diameter of 2.0 mm and length of 3.0 m) filled with non-polar sorbent Polysorb-1 and then – to the second column (diameter of 2.0 mm and length of 4.5 m) filled with polar adsorbent – zeolite of CaX type. The hydrogen content was analyzed using a chromatograph "Tsvet". The analyzed gas (1.5 ml) is introduced into nitrogen (carrier gas). The column diameter is 2.0 mm and its length is 2.0 m; adsorbent – zeolite of NaX type. In both cases the detector of heat conduction is used as a sensor.

3. Results and Discussion

To determine the effect of COM presence and its quality on the process, we compared the desulphurization processes of pyrite and different types of coal. We compared the effect of factors upon which the chemism of pyrite conversion depends (temperature and water steam content in the air-steam mixture), on the desulphurization process of coal with different metamorphism degree. The degree increases in the row B → C → G → F → L →A (Table 3). The experimental results are represented in Tables 4-6 and Figs. 4 and 5.

Table 4

Characteristics of pyrite and desulphurized coal samples

Desulphurized samples of pyrite and different types of coal	Content of pyritic sulphur for analytical sample (S_p^a), mas %	Coal yield, mas %	Conversion of pyritic sulphur, %	Difference between conversion degrees of coal pyritic sulphur and model mixture $FeS_2 + SiO_2$, %
B	0.61	50.37	83.21	11.97
C	0.23	82.27	91.51	20.27
G1	2.19	75.33	76.80	5.56
F2	1.46	83.11	72.61	1.37
L	0.88	94.05	80.01	8.77
Model mixture (FeS_2 + SiO_2)	1.07	–	71.24	–

Table 5

Dependence of pyritic sulphur removal degree upon the temperature

Temperature, K	Removal degree of pyrite sulphur, %						
	B	C	G1	G2	F1	F2	L
623	44.96	13.28	18.42	25.32	2.89	28.76	12.85
673	55.04	52.12	46.97	63.57	24.04	47.97	41.95
698	70.31	89.84	68.93	86.47	81.70	67.12	76.70
723	75.73	96.04	74.04	92.99	73.48	58.20	79.35

Table 6

Dependence of pyritic sulphur removal degree upon the oxidant composition

Content in the oxidant, vol %		Removal degree of pyrite sulphur, %						
oxygen	water steam	B	C	G1	F1	F2	L	A
20.95	0	-	90.22	75.70	-	56.00	-	-
20.06	4	70.30	93.71	87.06	80.01	57.99	70.62	53.05
17.85	15	-	94.53	91.00	81.00	61.55	72.07	57.97
14.71	30	73.60	92.41	69.18	81.70	67.12	76.64	65.00
10.5	50	79.31	84.29	54.59	86.81	58.81	67.98	80.49
6.31	70	81.65	65.32	32.12	84.83	32.65	66.93	76.43

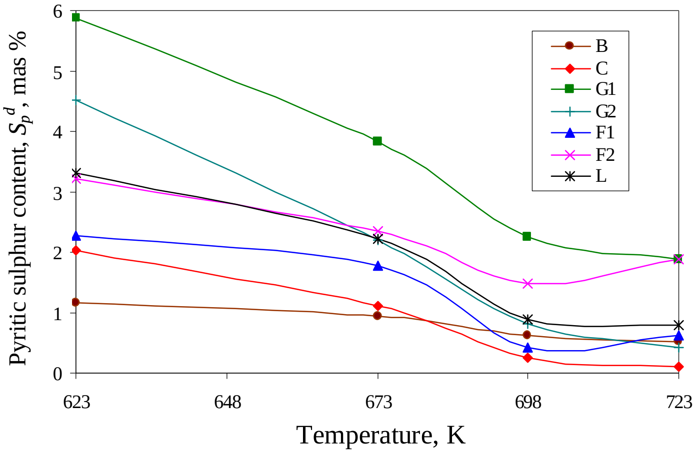

Fig. 4. Dependence of pyritic sulphur content upon the temperature for coal with different metamorphism degrees

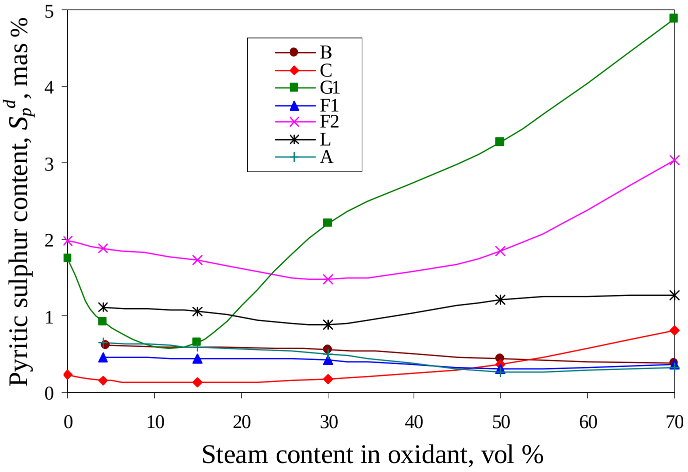

Fig. 5. Dependence of pyritic sulphur content upon the oxidant composition for coal with different metamorphism degrees

Table 7

Gases average composition at brown coal desulphurization under optimal conditions

Content in desulphurization gases, vol %								
H_2S	CH_4	C_2-C_3	CO	CO_2	O_2	N_2	Ar	H_2
8.0–12.5	2.6–3.3	2.8–4.6	5.5–6.5	23.5–25.0	0.6–1.2	45.7–54.8	0.5–0.7	0.7–1.4

Table 8

Gases average composition at desulphurization of C, F2, L and R coal types under optimal conditions

Content in desulphurization gases, vol %									
SO_2	H_2S	CH_4	C_2-C_3	CO	CO_2	O_2	N_2	Ar	H_2
2.5–7.0	till 0.4	0.5–3.9	0.4–2.6	1.1–3.8	5.0–9.9	1.6–11.1	71.6–78.7	0.8–0.9	till 0.4

Table 9

The characteristics of gases obtaining at desulphurization of wet and dry samples of coal

Content in desulphurization gases, vol %									
SO_2	H_2S	CH_4	C_2-C_3	CO	CO_2	O_2	N_2	Ar	H_2
The analytical sample of brown coal (W^{af} = 13.96 mas %)									
-	7.01	1.68	1.42	3.77	23.21	1.18	60.57	0.71	0.45
The sample of dry brown coal (W^{af} = 0.44 mas %)									
-	5.89	1.37	0.98	3.24	19.85	6.31	61.26	0.71	0.39
The analytical sample of anthracite (W^a = 3.55 mas %)									
0.88	-	0.78	0.35	traces	2.98	14.92	79.17	0.92	-
The sample of wet anthracite (W^a = 14.54 mas %)									
1.28	-	0.87	0.60	traces	3.59	14.43	78.32	0.91	traces

The presence of organic matter in the reaction zone affects the process in different ways. COM increases the removal degree of pyritic sulphur by 8.77–20.27 % for B, C and L coal; by 5.56 % – for G1 coal and only by 1.5 % – for F2. The less values of pyrite conversion for G1 and especially for F2 are caused by the fact that organic matter converts into plastic state in the investigated temperature range (623–723 K) and further may be baked leading to difficulties with oxidant access to pyrite particles.

The analysis of data from Table 5 and Fig. 4 shows that the temperature effect is the same for all types of coal. The sulphur content in coal decreases and removal degree of pyritic sulphur increases with the temperature growth to 698 K. The greatest increase is observed within the temperature range of 673–698 K. At the temperatures higher than 698 K the decrease of pyritic sulphur removal degree for F1 and F2 coal is observed. The reason is the above-mentioned ability of such type of coal to convert into plastic state and to bake at 723–823 K.

With the increase of water steam content in the oxidant the sulphur content in coal passes through the minimum and removal degree – through the maximum for all types of coal. The exclusion is brown coal the desulphurization of which does not depend on water steam amount in its mixture with coal (Table 6 and Fig. 5). It should be noted that there is not clear dependence between pyritic sulphur removal degree and metamorphism degree that changes in the row B → C → G → F → L → A.

Regularities occurred during the desulphurization of brown coal differ from those observed during black coal desulphurization. For example, the temperature increase is the least influential factor for all investigated samples (Table 5 and Fig. 4); sulphur converts into hydrogen sulphide (Table 7), not in SO_2, as for black coal (Table 8). During desulphurization of black coal hydrogen sulphide is observed in negligible amounts. All these facts indicate the change of desulphurization chemism while using brown coal compared with black one.

Brown coal essentially differs from black coal by the reactivity of organic matter and moisture content. In order to establish the factor (high moisture or COM reactivity) having the decisive influence on chemism during brown coal desulphurization we compared dry brown coal and wet anthracite. The anthracite was investigated as coal with the most inert COM. One can see from Table 9 that water adsorbed in coal may affect H_2S formation only in the presence of organic matter with high reactivity: the content of hydrogen sulphide in the gases is less for dry brown coal. At the desulphurization of dry and wet anthracite samples the hydrogen sulphide is absent in the gases. This fact indicates the dominant role of organic matter, as well as its gasification and cracking products, for the reactions of hydrogen sulphide obtaining.

4. Conclusions

It is possible to desulphurize any type of black coal at 698–723 K due to the treatment in fluidized bed formed by air-steam mixture. Such coal may be used in power engineering because the quality of organic matter does not have an essential influence on the efficiency of sulphur removing.

Under the same conditions the sulphur removal degree is less for medium-metamorphized black coal compared with other types of black coal. The reason is coal ability to convert into plastic state and to bake.

The effect of temperature (to 698 K) and water steam content on the pyritic sulphur conversion is the same for all types of coal.

At oxidative desulphurization of brown coal (compared with the black one) the main amount of sulphur converts into H_2S. It is obtained due to the reactions of pyrite with coal organic matter or its conversion products.

References

[1] Minyaev O., Kostenko V. and Shaforostova M.: Problemy Ecologii., 2008, **1-2**, 3.

[2] http://ukrstat.gov.ua/operativ/operativ2009/ns_rik/ns_u/vosr_u2008.html

[3] http://ukrstat.gov.ua/operativ/operativ2010/ns_rik/ns_u/vosr_u2009.html

[4] http://ukrstat.gov.ua/operativ/operativ2011/ns_rik/ns_u/vosr_u2010.html

[5] http://www.eea.europa.eu/data-and-maps/indicators/eea-32-sulphur-dioxide-so2-emissions-1/assessment-1

[6] http://www.eea.europa.eu/data-and-maps/indicators/eea-32-sulphur-dioxide-so2-emissions-1/assessment

[7] Pysh'yev S., Gayvanovych V., Pattek-Janczyk A. *et al.*: Fuel, 2004, **83**, 1117.

[8] Pysh'yev S., Shevchuk K., Cmielarz L. *et al.*: Energy & Fuel, 2007, **21**, 216.

[9] Pysh'yev S., Gunka V., Bratychak M. and Grytsenko Y.: Chem. & Chem. Techn., 2011, **5**, 107.

[10] Pysh'yev S., Bilushchak H. and Gunka V.: Chem. & Chem. Techn., 2012, **6**, 105.

[11] Yavorsky V.: Technologiya Sirky i Sulphatnoi Kysloty. Lvivska Politechnika, Lviv 2010.

[12] Rozenknop Z. Izvlechenie Dvuokisi Sery iz Gazov. GHI, Moskwa 1952.

[13] Grunvald V.: Technologia Gazovoi Sery. Khimiya, Moskwa 1992.

[14] Yurovsky A.: Sera Kamennykh Ugley. Akademia nauk SSSR, Moskwa 1960.

[15] Amir Attar: Fuel., 1978, **57**, 201.

[16] Ternovska A.: Obzhyg Sernogo Kolchedanu v Kipyashchem Sloe. Khimiya, Moskwa 1971.

[17] Smirnov V.: Obzhyg Mednykh Rud i Koncentratov. Metalurgia, Moskwa 1966.

[18] Jasienko S.: Chemia i Fizyka Wegla. Wroclaw Polytechnica, Wroclaw 1995.

[19] Nekrasov B.: Osnovy Obzchei Khimii. Khimiya, Moskwa 1973.

[20] Pelix A., Aranovych, Petrov E. and Kotomkina R.: Khimia i Tekhnologia Serougleroda. Khimiya, Moskwa 1986.

[21] http://ru.wikipedia.org/wiki/Сероуглерод

[22] Huang H., Young N., Williams B. *et al.*: Catal. Lett, 2006, **110**, 243.

[23] Pysh'yev S. and Gayvanovych V.: Visnyk Derzhavnogo Universytetu "Lvivska Politekhnika", 1996, **298**, 96.

ВПЛИВ ЯКОСТІ ВУГІЛЛЯ НА ПРОЦЕС ЙОГО ЗНЕСІРЧУВАННЯ

1. ВПЛИВ ОРГАНІЧНОЇ ЧАСТИНИ

Анотація. *Вивчено процес знесірчування різних типів вугілля внаслідок оброблення їх паро-повітряною сумішшю у реакторі з киплячим шаром за умов, що близькі до ізотермічних. Здійснено порівняння впливу чинників (температури і складу оксиданту), від яких залежить хімізм перетворення піриту, що міститься у вугіллі, на ефективність процесу знесірчування вугілля різних ступенів метаморфізму. Проведено порівняння знесірчування сухих і вологих зразків антрациту та бурого вугілля, що дало можливість запропонувати напрямки перетворення* FeS_2 *бурого вугілля з одержанням сірководню*

Ключові слова: *оксидаційне знесірчування, вугілля, сірка, пірит, сірководень, діоксин сірки, пароповітряна суміш.*