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DESULPHURIZATION AND USAGE OF MEDIUM-METAMORPHIZED BLACK COAL. 1. DETERMINATION OF THE OPTIMAL CONDITIONS FOR OXIDATIVE DESULPHURIZATION

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Abstract. The conditions providing proceeding of the reactions between pyrite sulphur of medium-metamorphized coal and air-steam mixture in the kinetic area have been found. Experimental-statistical mathematical model has been designed. The optimal factors of medium-coalificated coal oxidative desulphurization have been determined on its basis. Under optimal conditions two samples of coking coal have been desulphurized. These samples will be used as components of the coal charge in the production of special types of coke.

Keywords: coal, sulphur, oxidative desulphurization, optimal conditions, charge, coke.

1. Introduction

One of the main requirements for the coking coal quality is the sulphur content in it, because over 50 % of total sulphur in the crude pass into the product coke. The growth of sulphur content in blast coke leads to increase of its consumption, reduction of blast furnaces productivity, worsening of the products quality and increase of SO_2 emissions into the environment. If the sulphur content in coke is high it is necessary to increase the amount of fluxes to bind sulphur so that it does not get into cast iron. The reduction of sulphur content by 0.1 mas % decreases coke consumption by 0.3 mas % and increases the blast furnaces productivity by the same value [1]. The same problems arise while using coke in other branches. Therefore, the sulphur content in the blast and foundry cokes should be not more than 1.0 mas %, in the coke for electrothermal productions – up to 3 mas %, in the coke for sintering ore – not more than 2–3 mas %., in the coke for shaft furnaces – less than 1.3 mas %, and in the coke for chemical production – up to 1.2 mas % [2, 3].

To date the deposits of high-quality low-sulphuric coking coal are constantly reducing. For example, in Ukraine the currently explored coal reserves are 33.9–56.7 billion tons, including 13.0–13.5 billion tons of medium-metamorphized coal, the main deposits of which are concentrated in the Donetsk basin (nearly 13 billion tons) [4-7]. However, 113 (47.5 %) from 238 coal bed mined in the Donetsk basin are classified as sulphuric ones (sulphur content is 2.5–4.0 mas %) [8] and only 4 mines out of 74, where medium-metamorphized coal is mined, exploit low-sulphuric coal beds.

Preventive removal of sulphur is one of the ways to solve the problem of high-sulphuric medium-metamorphized coal use in the coke production.

The possibility of coal desulphurization via oxidative method aimed at its further application in the energy field was studied in the previous works [9-14]. The process is carried out due to the selective conversion of pyrite sulphur into gaseous products in the presence of oxidant (air or air-steam mixture). The pyrite sulphur is the basis of total sulphur in the high-sulphuric coal. FeS_2 sufficiently selectively converts into Fe_2O_3 and SO_2 (during desulphurization of black coal) or H_2S (if the brown coal is used). As a result of the process low-sulphuric solid fuel and desulphurized gases with a relatively high content of sulphur-containing components are obtained, so SO_2 or H_2S may be effectively removed or converted by known methods [15].

The researches of oxidative desulphurization of coal, which is further intended for coke production, have no logical completion, because during the process the ability of coal to sintering reduces significantly [16].

On the other hand it is known that coke reactivity substantially depends on the composition and quality of inorganic matter of raw material, primarily on the content of iron (III) oxide [17]. During the production of special types of coke various additives similar in their characteristics to desulphurized coal, for example by high Fe_2O_3 content, are used [18, 19]. I. Sorokin [18] used red mud (mineral additive) as additive to the charge. Iron oxide is the basic active component of this additive; its content in red mud is approximately 40 mas %. The addition of red mud increases coke yield, mechanical strength, and its reactivity. A. Lazarenko *et al.* [19] used magnetite (a component with high content of Fe_3O_4 used in the coal beneficiation) as an additive to the coking crude. The most effective influence of magnetite is observed when its content in the charge is about 0.25–1.0 mas %. The increase of coke yield, reactivity, and porosity is observed as well. The increase of coke reactivity is a positive aspect in the case of non-metallurgical coke production, *e.g.* for electrothermal enterprises.

Taking into account the average content of Fe_2O_3 in the oxidative desulphurized coal within 4.0–18.0 mas %, the main purpose of this research was to establish the possibility of desulphurized coal used as a component of coal charge to produce special types of coke. The primary task of the research was to establish the optimum conditions for oxidative desulphurisation (OD) of high-sulphuric coking coal. Under such conditions it will be possible to remove most of the sulphur from the raw material and obtain the desulphurization gases with high content of SO_2.

2. Experimental

Fat coal F1 (Lisova mine of Lviv-Volyn coal basin), fat coal F2 (Samsonovska concentrating mill of Donetsk coal basin), coking coal C (Shcheglovka Glyboka mine of Donetsk coal basin) and lean-coking coal LC (Kalinina mine of Donetsk coal basin) were used as the raw materials of OD process study.

Characteristics of the initial coals are shown in Table 1.

One can see from Table 1 that all samples are high-sulphuric coals because the content of sulphur in them is more than 2.5 mas %. The basis of the total sulphur is its pyrite form. The desulphurization was carried out in a perfect-mixing reactor (fluidized bed) under the conditions close to the isothermal ones. Block diagram of OD process is shown in Fig. 1. The detailed procedure is described in [20]. The content of total sulphur and its different forms, ash content, moisture and volatile yield were determined according to the standard methods [21-25].

The desulphurization gases produced during the process are analyzed by chromatographic method. Qualitative and quantitative composition of desulphurization gases were determined using LHM (N 479) chromatograph with a thermal conductivity detector. Helium was a carrier-gas.

The temperature, the oxidant flow rate and composition (content of water vapour in the air-steam mixture), and the process time [26] are the main factors that affect the nature of sulphur conversion, primarily pyrite, and organic matter of coal. To characterize the oxidant consumption the term "repetition factor of oxidant flow rate" (RFO) was used. RFO was calculated as the ratio between volumetric flow air-steam mixture (m^3/h) and coal mass (kg).

Efficiency and selectivity of sulphur compounds removal were determined in the following way:

the degree of total or pyrite sulphur conversion (DTSC or DPSC, respectively, %) – by formula (1); DTSC or DPSC characterizes the amount of sulphur converted into gaseous sulphuric products that will not get into the environment during further use of desulphurized coal;

the degree of total or pyrite sulphur removal (DTSR or DPSR, respectively, %) – by formula (2); DTSR or DPSR characterize the ratio between the rates of sulphur conversion with the production of gaseous products and conversion of coal organic mass (COM).

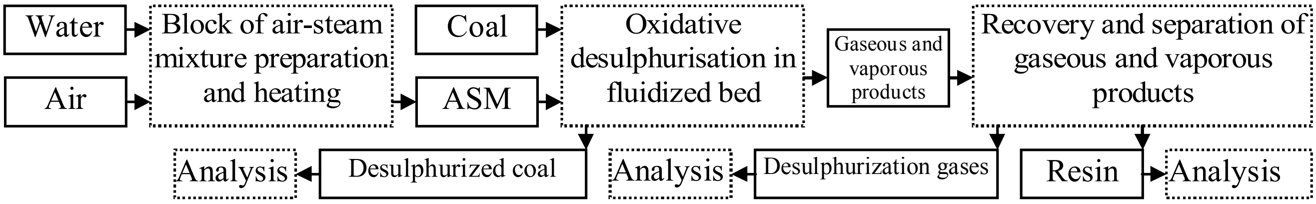

Fig. 1. Flowchart of the laboratory plant for coal oxidative desulphurization

$$D(T,P)SC=\frac{S^{a}_{X0}\cdot 100-S^{a}_{x}\cdot x_{c}}{S^{a}_{X0}} \qquad (1)$$

$$D(T,P)SC=\frac{S^{d}_{X0}\cdot 100-S^{d}_{x}\cdot x_{c}}{S^{d}_{X0}} \qquad (2)$$

where S^{a}_{X0} and S^{d}_{X0} – the content of total or pyritic sulphur in the initial coal relative to the analytical and dry sample, respectively, mas %; S^{a}_{X} and S^{d}_{X} – the content of total or pyritic sulphur in the desulphurized coal relative to the analytical and dry sample, respectively, mas %; x_c is the desulphurizated coal yield, mas %.

3. Results and Discussion

The rate of reactions between gaseous (the air-steam mixture) and solid porous bodies (coal, for which the most of the reaction centres (pyrite) is located in the bulk of grains) in the external diffusion area is defined by linear rate of the oxidant (LRO) and size of coal grain. The rate of the above-mentioned reactions, which occur in the internal diffusion area, is determined by the size of the crude particles only [27-29]. To achieve the highest possible conversion rates of sulphur (primarily pyrite) during OD process, it is necessary to find such factors of the process that will support the pyrite oxidation reactions in the kinetic area at the maximum possible temperature. In other words, if we achieve the conditions under which LRO and coal grain size will not affect the degree of sulphur conversion we may assert that the sulphur conversion occurs in the kinetic area.

LRO was calculated as the ratio between volumetric flow rate of oxidant (m^3/s) and the cross-sectional area of the reactor (m^2). To simplify the model description LRO was determined under normal conditions. The average size of coal particles was calculated as the geometric mean of two adjacent sieves.

The investigation results of LRO and medium coal grain size effect on selectivity and efficiency of sulphur removal from F1 coal are shown in Figs. 2 and 3. The study of LRO influence on F1 coal desulphurization process was carried out using the fraction 0.1–0.25 mm (average diameter is 0.158 mm), the coal grain size of 0.052 m/s and optimum temperature of 425 ºC (698 K), established in the Ref. [26]. These researches have shown that if the value of LRO is over 0.04–0.05 m/s and the size of coal grain is smaller than 0.5 mm, the mentioned factors do not affect the rate of conversion reactions, *i.e.* the pyrite conversion takes place in the kinetic area.

On the basis of LRO values and coal grain sizes, which were determined based on Figs. 2 and 3, and under which the areas of sulphur conversion reactions change from external diffusion into kinetic one and from kinetic into internal diffusion area, the parameters of the fluidized bed and the mass transfer coefficient per unit of the contact phase external surface were calculated. The calculations are represented in Table 2.

The mass transfer coefficient per unit of the contact phase external surface (β, m/s), was calculated according to Ref. [27]:

$$b = Sh\cdot D/d \qquad (3)$$

where *Sh* is Sherwood number (diffusion Nusselt number); *D* is the diffusion coefficient of the gas phase, m^2/s; *d* is the average size of coal grain, m.

$$Sh=0.01\cdot Sc^{1/3}\cdot \mathrm{Re}/e \qquad (4)$$

where *Sc* is Schmidt number (diffusion Prandtl number); Re is Reynolds number, ε is the porosity of fluidized bed.

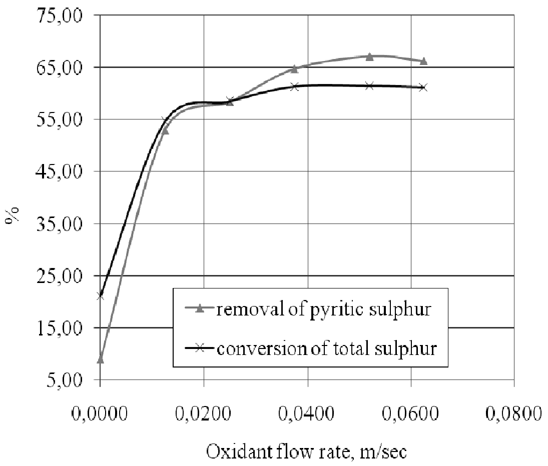

Fig. 2. Effect of oxidant flow rate on the oxidative desulphurization of fat (F1) coal

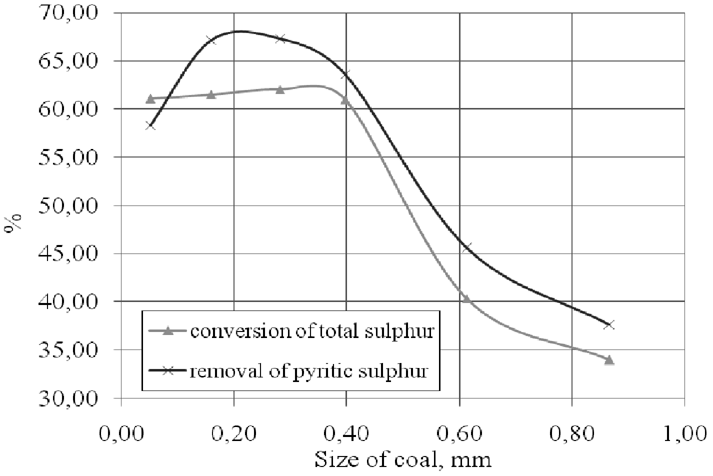

Fig. 3. Effect of coal size on the oxidative desulphurization of fat (F1) coal

Table 1

Characteristics of the initial coals

Size of coal, mm	Moisture content, W^a, mas %	Ash, A^d, mas %	Volatiles yield, V^{daf}, mas%	Sulphur content relative to the dry mass, 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	$S_{SO_4}^d / S_t^d$
Fat (F1)										
0.1–0.25	1.87	21.97	36.71	6.97	4.50	1.17	1.30	64.56	16.79	18.65
0.25–0.315	1.97	20.98	35.39	7.73	4.93	1.61	1.19	63.78	20.83	15.39
Fat (F2)										
0.1–0.25	3.82	9.32	33.94	2.98	1.29	0.34	1.35	43.29	11.41	45.30
0.25–0.5	3.87	9.30	34.16	3.10	1.33	0.34	1.43	42.90	11.29	45.81
Coking (C)										
0.1–0.25	1.35	27.71	31.86	2.74	1.13	0.75	0.86	41.24	27.37	31.39
Lean-coking (LC)										
0.1–0.25	1.72	27.23	21.20	3.41	1.37	0.96	1.08	40.18	28.15	31.67

Table 2

The dependence of the process stages on the fluidized bed parameters and mass transfer criteria (coal F1)

Stage	LRO, u, m/s	Average diameter of grain, d, m	Real LRO, u^r, m/s	Porosity, ε	Reynolds number, Re	Sherwood number, Sh	β, m/s
Transition area of sulphur conversion reactions[1] (external diffusion-kinetic)	0.0400	0.000158	0.1023	0.7068	0.2324	0.00273	0.00210
Transition area of sulphur conversion reactions[1] (kinetic - internal diffusion)	0.0520	0.000397	0.1330	0.5081	0.7584	0.01239	0.00380

[1] Reactions with gaseous reactant

$$\mathrm{Re} = u^r \cdot d / v \tag{5}$$

$$Sc = v / D \tag{6}$$

where u^r is the real LRO, m/s; v is the kinematic viscosity of the gaseous reactant, m^2/s.

The porosity of fluidized bed was calculated by the following formula:

$$e = \left(\frac{18\,\mathrm{Re} + 0.36\,\mathrm{Re}^2}{Ar} \right)^{0.21} \tag{7}$$

where Ar is Archimedes number.

$$Ar = \frac{d^3 \cdot g \cdot (r_{app} - r)}{r \cdot v^2} \tag{8}$$

where ρ is the density of air-steam mixture, kg/m^3; g is the acceleration of gravity, m/s^2; ρ_{app} is the apparent density of coal, kg/m^3.

All parameters of gaseous reactant in formulas (3-8) were assumed and calculated under the operating conditions [27, 30-32]. Taking into account that the pressure in the reaction system was close to the atmospheric one, the calculation of the real LRO per empty cross section of reactor was carried out according to the formula:

$$u^r = u \cdot (273 + t) / 273 \tag{9}$$

where u is the LRO under normal conditions, m/s; t is the process temperature, ^{o}C.

According to the data from Table 2, when using the coking coal, Sherwood number should not be less than 0.0027 and mass transfer coefficient should be higher than 0.0021 m/s so that the sulphur transformation reactions (where gas reagent is involved) occur in the kinetic area.

The increase of the intensity of gaseous reactant external transfer due to the increase of coal grain size results in the transition into the internal diffusion area (in the case of the kinetic area existence). The transition occurs if values of porosity correspond to the beginning of the fluidized bed formation (0.4–0.5).

The desulphurization of four coal samples under different process factors was carried out using the established parameters of fluidized bed and intensity of external mass transfer, which provide the proceeding of coking coal sulphur conversion in the kinetic area. The factors were changed within the optimal range, established in the works [11-14, 26].

The degree of pyrite sulphur conversion and SO_2 content in the desulphurization gases were the key factors of the process efficiency (response functions) during the development of experimental and statistical mathematical model (ESM) of the medium-metamorphized coal desulphurization. Moreover, we used the response function which partially describes the coal ability to cake (the degree of volatile matter reduction). While describing ESM the following notation of response functions and the process factors were used: Y_1 – DPSC, %; Y_2 – the content of sulphur dioxide in the desulphurization gases, vol %; Y_3 – the degree of volatile matter reduction, %.; X_1 – temperature, °C; X_2 – the process time, min; X_3 – the content of water steam in the oxidant, vol %; and X_4 – the repetition factor of the oxidant flow rate (RFO), m^3/h/kg of coal). It was found in [26] that the impact of certain factors on the coal desulphurization partly depends on sulphur content in coal. The sulphur content in the crude, primarily pyrite sulphur, also affects the concentration of sulphur dioxide in gases. Therefore the pyrite sulphur content in the original coal (X_5, S_p^d, mas %) is another factor which describes the impact of the raw material quality on the process. The factor values and results of studies according to which a mathematical model was created are represented in Table 3.

For the response functions we developed the following types of dependencies that showed the best conformity to the experimental data: for Y_1 – quadratic model (Eq. (10)), for Y_2 – quadratic model without considering X_5^2 (Eq. (11)), and for Y_3 – quadratic model without X_5 (Eq. (12)).

$$\begin{aligned}Y_1 = {} & -39689.50 - 0.004578\cdot X_1^2 - 0.007040\cdot X_2^2 - 0.003987\cdot X_3^2 - 0.819929\cdot X_4^2 + 5.236872\cdot X_5^2 - \\ & - 0.008412\cdot X_1\cdot X_2 + 0.005048\cdot X_1\cdot X_3 - 0.045962\cdot X_1\cdot X_4 - 21.7667\cdot X_1\cdot X_5 + 0.009846\cdot X_2\cdot X_3 - 0.093123\cdot X_2\cdot X_4 + \\ & + 2.172856\cdot X_2\cdot X_5 + 0.005444\cdot X_3\cdot X_4 + 20.03125\cdot X_3\cdot X_5 - 2.72014\cdot X_4\cdot X_5 + 102.2889\cdot X_1 - 5.19801\cdot X_2 - \\ & - 92.4872\cdot X_3 + 45.59695\cdot X_4 + 8578.043\cdot X_5\end{aligned} \tag{10}$$

$$\begin{aligned}Y_2 = {} & 5270.985 + 0.000397\cdot X_1^2 - 0.000055\cdot X_2^2 - 0.000482\cdot X_3^2 + 0.197470\cdot X_4^2 - 0.001507\cdot X_1\cdot X_2 + \\ & + 0.001033\cdot X_1\cdot X_3 + 0.002877\cdot X_1\cdot X_4 + 2.921787\cdot X_1\cdot X_5 - 0.000688\cdot X_2\cdot X_3 + 0.006095\cdot X_2\cdot X_4 - 0.034453\cdot X_2\cdot X_5 \\ & - 0.000256\cdot X_3\cdot X_4 - 2.73384\cdot X_3\cdot X_5 - 0.595158\cdot X_4\cdot X_5 - 13.4622\cdot X_1 + 0.712237\cdot X_2 + 11.97826\cdot X_3 - \\ & - 1.20949\cdot X_4 - 1155.34\cdot X_5\end{aligned} \tag{11}$$

$$\begin{aligned}Y_3 = {} & -1.95206 + 0.000000\cdot X_1^2 + 0.000060\cdot X_2^2 + 0.000031\cdot X_3^2 - 0.008077\cdot X_4^2 + 0.000091\cdot X_1\cdot X_2 + \\ & + 0.000071\cdot X_1\cdot X_3 - 0.001936\cdot X_1\cdot X_4 + 0.000009\cdot X_2\cdot X_3 - 0.000270\cdot X_2\cdot X_4 - 0.000049\cdot X_3\cdot X_4 + 0.005190\cdot X_1 - \\ & - 0.048557\cdot X_2 - 0.032802\cdot X_3 + 0.921093\cdot X_4\end{aligned} \tag{12}$$

To estimate the adequacy of the obtained regression equations, we substituted the given experimental parameters (X_1–X_5) and found the expected (regressive) values of response functions (Y_{ij}^{reg}), which are represented in Table 3.

The estimation of model adequacy is conducted using the following parameters: the mean relative error of approximation (ε_i); the coefficient of determination (R_i^2); Fisher criterion (F_i), and criterion of statistics (F_{r_i}).

The value of mean relative error of approximation was calculated by the formula (13):

$$e_i = \frac{1}{n}\sum_{j=1}^{n}\left|\frac{Y_{ij} - Y_{ij}^{reg}}{Y_{ij}}\right| \tag{13}$$

where n is the amount of sampling (number of experiments), Y_{ij} – values observed during the experiments, Y_{ij}^{reg} – values of response functions calculated using the regression equations, i is response function number, and j is experiment number.

To check the adequacy of multiple-factor regressive model we used Fisher criterion. It was calculated by the formula:

$$F = \frac{S_{reg_i}^2}{S_{res_i}^2} \tag{14}$$

where $S_{reg_i}^2$ is dispersion of experimental response functions relative to their mean values and $S_{res_i}^2$ is residual dispersion of response functions.

$$S_{res_i}^2 = \frac{1}{n-1}\sum_{j=1}^{n}(Y_{ij} - \overline{Y}_i)^2 \tag{15}$$

where $\overline{Y}_i$ is average experimental value of response function.

$$S^2_{res_i} = \frac{1}{n-m_i}\sum_{j=1}^{n}(Y^{reg}_{ij} - Y_{ij})^2 \qquad (16)$$

where m_i is number of coefficients in the regression equation.

In accordance with the mentioned calculations Fisher criterion should be greater than the table value at the significance level α and numbers of freeness (n-1) and ($n - m_i$). In such a case it means the quantitative change of results scattering relative to the line of obtained regression equation compared with scattering relative to the mean value [33].

The coefficient of determination R_i characterizing the significance of response functions dependence on the process parameters ranges from 0 to 1. It was determined using the standard procedures [34].

The criterion of statistics (F_{r_i}), which is a measure of statistic significance R_i^2, was calculated by the following formula [35]:

$$F_{r_i} = \frac{n-k_i-1}{k_i}\cdot\frac{R_i^2}{1-R_i^2}. \qquad (17)$$

where k_i is the number of regression equation coefficients without free term.

The calculated value F_{r_i} was compared with the critical value $F_{r_{cri}}$ determined according to the tables at the level of significance α and numbers of freeness k_i and ($n - k_i - 1$). If $F_{r_i} > F_{r_{cri}}$, then the regression is statistically significant.

The mean relative approximation error is lower than 10 % (ε_1 = 0.0275 (2.75 %), ε_2= 0.0971 (9.71 %), ε_3 = 0.0805 (8.05 %)). Therefore, according to [36] we may certify the high compliance with the experimental data.

The calculated values of Fisher criterion are: F_1 = 12.46; F_2 =16.91; and F_3=6.80. In accordance with the table of Fisher criterion values [37] at the level of significance α = 0.05 the critical values are: F_{1cr} = =F(0.05; 30; 10) = 2.70; F_{2cr} = F(0.05; 30; 11) =2.51 and F_{3cr} = F(0.05; 28; 14) = 2.13. They are lower then the calculated values and this fact also confirms the adequacy of the model.

The values of the coefficient of determination are: R_1^2 = 0.9742, R_2^2 = 0.9781, and R_3^2 = 0.7396. Therefore, 97.42 %, 97.81 %, and 73.96 % changes in response functions (Y_1, Y_2, and Y_3, respectively) are determined by the selected factors of the process control (X_1–X_5). The fact that R_1 = 0.9870, R_2 = 0.9890, and R_3 = 0.860 are close to 1, indicates the presence of "strong" bond between Y_1, Y_2, and Y_3 and process parameters (X_1–X_5).

The calculated values of the criterion of statistics are: F_{r_1} = 18.86, F_{r2} =25.88, and F_{r3}= 2.84. In accordance with the table of Fisher criterion values at the level of significance α = 0.05 the critical values are: F_{rcr_1} = = F(0.05; 20; 10) = 2.77; F_{rcr2} = F(0.05; 19; 11) = 2.69, and F_{rcr3} = F(0.05; 14; 14) = 2.50. This indicates the statistical significance of the determination coefficients R_i^2 ($F_{rcr_i} < F_{r_i}$).

All above-mentioned data indicate the ESM adequacy for medium-coalificated coal desulphurization process, the statistical significance of the results and the presence of link between response functions and selected factors of process control.

The process optimal conditions supporting the maximum degree of sulphur conversion, the maximum SO_2 content in the desulphurization gases, and the minimal volatile reduction were found on the basis of regression equations by the method of uniform search of the values of response functions.

Under determined optimal conditions, which are presented in Table 4, oxidative desulphurization of F1 and F2 coal was carried out. In the researches with F1 coal the fractions 0.1–0.25 mm (denoted $F1_1$) and 0.25–0.315 mm (denoted $F1_2$) were used. In case of F2 coal the fraction 0.25–0.50 mm was used.

The technical analysis of desulphurized coal is given in Table 5. The sulphur content in the resulting coal and its degree of conversion and removal are represented in Table 6. The compositions of desulphurization gases are given in Table 7.

The obtained data show that due to the realization of the process the total sulphur content in the coal was reduced noticeably. The degree of total sulphur conversion is 76–79 % for F1 coal and 67 % for F2 coal. In case of the process realization at the coke plant after removal of sulphur dioxide by known method (for example by cyclic ammonia [15]) the gases (that have heating value about 1.4 MJ/m^3) can be used as fuel in coking furnaces.

The desulphurized coal F2 has relatively low ash content because the original coal was taken from the beneficiation plant. Desulphurized coal F1 contains a rather large number of inorganic matters, therefore one of the samples of desulphurizated coal ($F1_2$) undergoes the flotation concentration. The characteristics of desulphurized and enriched coal are presented in Table 8.

The desulphurized coal samples $F1_2$ and F2 were used as the components of the charge for the production of special types of coke, which will be discussed in the next article.

Table 3

Experimental data, calculated values of response functions, and relative errors

No.	X_1*, °C (K)	X_2, min	X_3, vol %	X_4, m^3/h·kg	X_5, mas %	Y_1, %	Y_1^{reg}, %	Y_2, vol %	Y_2^{reg}, vol %	Y_3, %	Y_3^{reg}, %	Coal type	Relative errors		
													ε_1	ε_2	ε_3
1	400 (673)	15	30	2.40	4.50	54.89	57.06	5.09	5.54	0.20	0.21	F1	0.0396	0.0877	0.0607
2	425 (698)	15	30	2.40	4.50	72.61	68.57	7.14	6.35	0.31	0.31	F1	0.0556	0.1104	0.0156
3	450 (723)	15	30	2.40	4.50	68.44	74.05	7.05	7.84	0.43	0.42	F1	0.0820	0.1118	0.0246
4	425 (698)	15	30	7.21	4.50	89.94	91.30	3.38	3.71	0.41	0.38	F1	0.0151	0.0983	0.0639
5	425 (698)	30	30	7.21	4.50	94.75	96.38	1.51	1.76	0.26	0.26	F1	0.0172	0.1638	0.0178
6	425 (698)	45	30	7.21	4.50	95.86	97.93	0.89	0.82	0.14	0.16	F1	0.0216	0.0817	0.1261
7	425 (698)	60	30	7.21	4.50	96.45	95.95	0.72	0.89	0.07	0.06	F1	0.0052	0.2387	0.1013
8	425 (698)	30	30	2.40	4.50	83.38	80.49	3.78	3.40	0.19	0.21	F1	0.0346	0.0570	0.1240
9	425 (698)	45	30	2.40	4.50	85.29	88.88	2.50	2.65	0.13	0.12	F1	0.0421	0.0615	0.0423
10	425 (698)	60	30	2.40	4.50	93.10	93.74	2.23	2.33	0.05	0.05	F1	0.0069	0.0434	0.0466
11	425 (698)	15	4	2.40	4.50	69.24	72.48	3.61	4.39	0.34	0.36	F1	0.0468	0.2168	0.0537
12	425 (698)	15	15	2.40	4.50	71.22	71.48	5.71	5.28	0.27	0.33	F1	0.0037	0.0754	0.2394
13	425 (698)	15	50	2.40	4.50	69.20	61.91	7.98	7.53	0.36	0.31	F1	0.1054	0.0559	0.1370
14	425 (698)	15	70	2.40	4.50	46.78	52.06	7.75	8.43	0.37	0.33	F1	0.1129	0.0882	0.1027
15	425 (698)	15	30	4.81	4.50	83.86	84.82	3.71	3.83	0.39	0.44	F1	0.0114	0.0326	0.1301
16	425 (698)	15	30	3.61	4.50	79.20	77.95	4.94	4.79	0.37	0.40	F1	0.0158	0.0313	0.0838
17	425 (698)	15	30	2.40	4.50	72.15	68.57	7.32	6.35	-	-	F1	0.0496	0.1323	-
18	425 (698)	15	30	7.21	4.93	84.86	87.17	2.95	3.17	0.36	0.38	F1	0.0272	0.0811	0.0661
19	425 (698)	15	30	7.21	5.02	88.74	86.83	3.17	3.05	0.40	0.38	F1	0.0215	0.0604	0.0405
20	425 (698)	15	30	2.40	4.93	59.80	60.54	7.42	7.54	0.31	0.31	F1	0.0124	0.0163	0.0156
21	425 (698)	15	30	2.40	5.02	60.00	59.39	7.89	7.79	0.34	0.31	F1	0.0102	0.0127	0.0740
22	425 (698)	25	30	4.81	1.29	91.75	92.21	0.63	0.80	0.44	0.37	F2	0.0050	0.2768	0.1684
23	425 (698)	25	30	4.81	1.37	89.82	89.35	1.02	0.84	-	-	LC	0.0052	0.1753	-
24	400 (673)	10	4	2.40	1.13	73.23	73.23	2.14	2.14	0.40	0.35	C	0.0000	2.1818	0.1255
25	450 (723)	10	4	7.21	4.50	94.08	92.47	2.54	2.33	0.32	0.31	F1	0.0171	0.0834	0.0265
26	400 (673)	45	4	7.21	4.50	98.58	97.09	0.67	0.43	0.28	0.29	F1	0.0151	0.3525	0.0461
27	450 (723)	45	4	2.40	4.50	83.27	81.31	1.68	1.45	0.30	0.28	F1	0.0235	0.1379	0.0502
28	400 (673)	10	70	2.40	4.50	27.48	27.87	7.59	7.51	0.17	0.20	F1	0.0140	0.0101	0.2023
29	450 (723)	10	70	7.21	4.50	78.49	77.54	8.87	8.71	0.37	0.38	F1	0.0121	0.0178	0.0328
30	400 (673)	45	70	7.21	4.50	88.55	87.48	1.91	1.78	0.16	0.15	F1	0.0121	0.0698	0.0578
31	450 (723)	45	70	2.40	4.50	88.85	87.76	6.53	6.34	0.37	0.39	F1	0.0123	0.0286	0.0594
Mean relative error of approximation (ε)													0.0275	0.0971	0.0805

*To develop experimental-statistic mathemical model of the process we used X_1 in Celcius degree

Table 4

Optimal conditions for the medium-metamorphized coal desulphurization

Parameter	Fat ($F1_1$)	Fat ($F1_2$)	Fat (F2)
Temperature, ^0C (K)	445 (718)	425 (698)	425 (698)
Time, min.	21.5	60	25
RFO, m^3/h/kg	7.10	2.40	4.81
Content of water steam in the oxidant, vol %	51.0	30.0	30.0

Table 5

Technical analysis of the coal after desulphurization

Moisture content, W^a, mas %	Ash, A^d, mas %	Volatiles yield, V^{daf}, mas %
$F1_1$		
1.37	28.66	25.53
$F1_2$		
1.11	24.92	24.19
F2		
2.07	12.60	19.14

Table 6

Content of sulphur in the coal after desulphurization. Removal and conversion degree of sulphur

Sulphur content relative to the dry mass, mas %				DTSR, %	DPSR, %	DTSC, %	DPSC, %
total, S_t^d	pyritic, S_p^d	organic, S_o^d	sulphate, $S_{SO_4}^d$				
$F1_1$							
2.04	0.81	0.76	0.47	70.77	81.99	76.44	85.48
$F1_2$							
2.23	0.50	0.78	0.95	71.10	89.94	79.49	92.86
F2							
1.49	0.26	0.44	0.79	51.91	80.83	67.19	86.92

Table 7

Average characteristics of desulphurization gases composition

Content in desulphurization gases, vol %										
CH_4	C_2H_4	C_2H_6	C_3	SO_2	H_2S	CO_2	CO	N_2	O_2	Ar
$F1_1$										
1.45	0.21	0.43	0.18	2.58	0.05	9.84	1.81	78.64	3.89	0.92
$F1_2$										
0.67	0.05	0.15	0.10	2.16	0.00	14.08	2.93	75.78	3.20	0.88
F2										
0.26	0.05	0.03	0.03	0.72	0.00	4.73	0.98	81.36	10.89	0.95

Table 8

Technical analysis of the coal ($F1_2$) after desulphurization and benefication

Moisture content, W^a, mas %	Ash, A^d, mas %	Volatiles yield, V^{daf}, mas %	Sulphur content relative to the dry mass, mas %			
			total, S_t^d	pyritic, S_p^d	organic, S_o^d	sulphate, $S_{SO_4}^d$
1.17	19.86	26.59	2.10	0.47	0.84	0.79

4. Conclusions

The obtained results allow to assert that the oxidant linear rate should be greater than 0.04–0.05 m/s and the size of raw grains – less than 0.50 mm to achieve the proceeding of the pyrite sulphur conversion reactions (with gaseous reactant) in the kinetic area. Moreover, Sherwood number should be not less than 0.0027 and the coefficient of external mass transfer should be greater than 0.0021 m/s. The grain size of coal and LRO must provide porosity of fluidized bed at the level of more than 0.6. The intensity of the gaseous reactant external transfer increases due to the increase of grain size. The result is the transition into the internal diffusion area. This transition occurs if values of porosity correspond to the beginning of the fluidized bed formation (about 0.4–0.5).

Under the conditions supporting the reaction proceeding between oxidants and pyrite sulphur in the kinetic area, thirty one experiments with different types of medium-metamorphized coal were held. They gave the possibility to create a base for the development of adequate empirical mathematical model. Based on this model the optimal conditions for the coking coal desulphurization process were determined.

Under optimal conditions the oxidative desulphurization of two samples of medium-metamorphized coal was carried out. As a result 67–79 % of total sulphur were converted. Further use of such coal allows to reduce SO_2 emissions into the environment by 3–5 times.

Due to the oxidative desulphurization of F2 coal, as well as oxidative desulphurisation and enrichment of F1 coal we obtained a solid fuel with total sulphur content of 1.49 and 2.10 mas %, respectively. The obtained desulphurized coal samples were used as the components of coal charge for the production of special types of coke.

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ЗНЕСІРЧЕННЯ ТА ЗАСТОСУВАННЯ СЕРЕДНЬОМЕТАМОРФІЗОВАНОГО КАМ'ЯНОГО ВУГІЛЛЯ. 1. ВСТАНОВЛЕННЯ ОПТИМАЛЬНИХ УМОВ ОКСИДАЦІЙНОГО ЗНЕСІРЧЕННЯ

Анотація. *Знайдено умови, які забезпечують перебіг реакцій у кінетичній області між піритною сіркою середньометаморфізованого вугілля і паро-повітряною сумішшю. Розроблено експериментально-статистичну математичну модель та на її основі встановлено оптимальні значення чинників процесу оксидаційного знесірчення кам'яного вугілля середнього ступеня вуглефікації. У знайдених оптимальних умовах здійснено знесірчення двох зразків коксівного вугілля, які будуть використані як компоненти вугільної шихти у виробництві спеціальних видів коксу.*

Ключові слова: *вугілля, сірка, оксидацій знесірчування, оптимальні умови, шихта, кокс.*