Yuri Prysiazhnyi[1], Serhiy Pyshyev[1], Viktoria Kochubey[1] and Denis Miroshnichenko[2]

DESULPHURIZATION AND USAGE OF MEDIUM-METAMORPHIZED BLACK COAL. 2. DESULPHURIZED COAL USED AS AN ADDITIVE FOR THE PRODUCTION OF SPECIAL TYPES OF COKE

[1]Institute of Chemistry and Chemical Technology, Lviv Polytecnic National University,
12, S. Bandery str., 79013 Lviv, Ukraine
[2]Ukrainian State Research Institute for Carbochemistry (UKHIN),
7, Vesnina str., 61023 Kharkiv, Ukraine

Abstract. Plastometric investigations of the coking basic charge and charge with desulphurized coal of various quality and quantity have been carried out. Non-volatile residues have been investigated using technical analysis and derivatographic investigations. Their mechanical strength, abrasive strength and reactivity have been examined. In spite of some worsening of medium-metamorphized coal capability to turn into plastic state and cake it may be used as a coking raw material additive (5 mas % relative to the finished mixture) during production of special types of coke. The obtained coke properties were found to be constant or even better compared with those of the basic charge or charge with sulphuric or high-sulphuric additives

Keywords: sulphur, desulphurized coal, charge, coke.

1. Introduction

Nowadays the reduction of costs necessary for power production is one of the most important problems throughout the world and in Ukraine, in particular. The possible solving of this problem is the increase in coal production and consumption (Figs. 1-4). Coal is the main part of fossil fuel and it is cheaper than oil or gas (Figs. 5 and 6).

However the main part of coal world resources is characterized by sulphur high content that is undesirable for its further application in any branch of industry. Some countries, including Ukraine, have at their disposal only sulphuric and high-sulphuric coal. The sulphur content in the coal from Donetsk Basin (the resource of which is 92 % of all Ukrainian resources [2]) varies from 0.5 to 9.3 mas %. In Donetsk Basin the amount of coal with sulphur content of 2.5 mas % and more is about 70 % [3].

The coal of Lviv-Volyn Basin (Ukraine) belongs to sulhuric and high-sulphuric ones: sulphur content is within the range of 2.5-7.7 mas % [4, 5]. The Ukrainian brown coal contains 3-7 mas % of sulphur [4].

The high sulphur content results in the atmosphere pollution by sulphur(IV) oxide while using such coal for electric power production and in the degradation of coke quality while using such coal in the coke industry [6-8].

The process of oxidative desulphurizaton as a method of sulphur removal from coal before its using is one of the possible way to solve the above-mentioned problem. The essence of the process is the treatment of coal by oxidizers (air-steam mixture or air) at 698–723 K, that is lower than temperature of coal burning. The pyrite sulphur which is the main part of all sulphur in the high-sulphuric coal is selectively converted into gaseous products [9-14].

Previously [15] we established the optimal conditions of oxidative desulphurization of medium-metamorphized black coal, under which the desulphurized samples were obtained, namely:

– desulphurized coal with the total sulphur content $S_t^d = 1.49$ mas % ($S_p^d = 0.26$ mas %, $S_o^d = 0.44$ mas %, $S_{SO_4}^d = 0.79$ mas %) was obtained from F2 initial coal with $S_t^d = 3.10$ mas % ($S_p^d = 1.33$ mas %, $S_o^d = 0.34$ mas %, $S_{SO_4}^d = 1.43$ mas %);

– desulphurized coal with the total sulphur content $S_t^d = 2.23$ mas % ($S_p^d = 0.50$ mas %, $S_o^d = 0.78$ mas %, $S_{SO_4}^d = 0.95$ mas %) was obtained from F1 initial coal with $S_t^d = 7.73$ mas % ($S_p^d = 4.93$ mas %, $S_o^d = 1.61$ mas %, $S_{SO_4}^d = 1.19$ mas %).
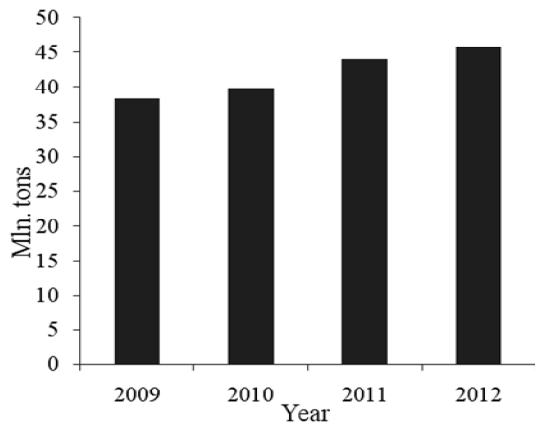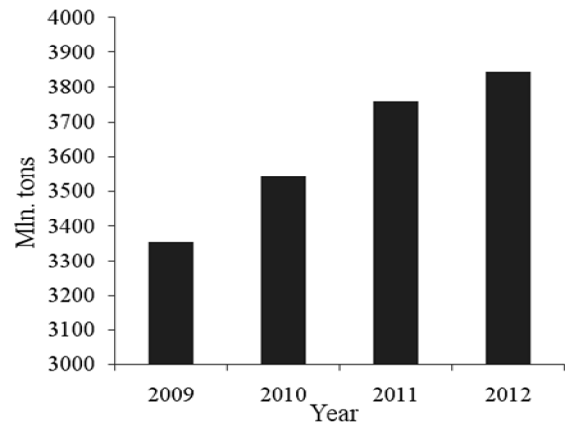
Fig. 1. Pattern of coal production in Ukraine [1]

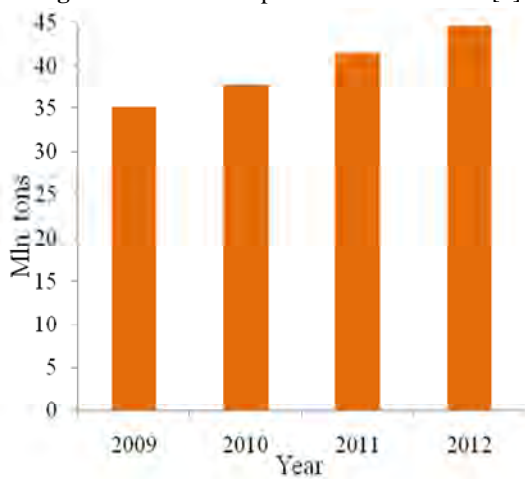**Fig. 2**. Pattern of coal production in the world [1]

Fig. 3. Pattern of coal consumption in Ukraine [1]
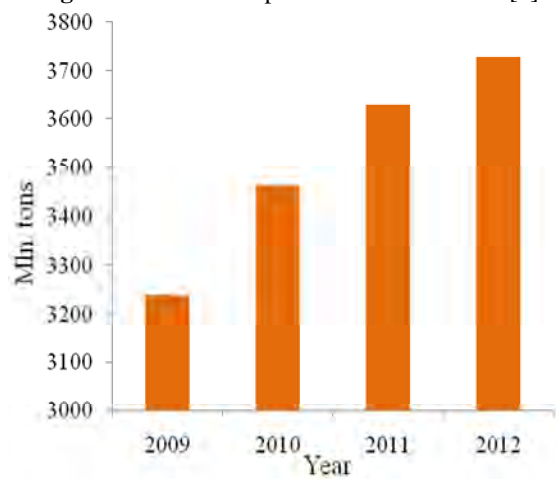

Fig. 4. Pattern of coal consumption in the world [1]
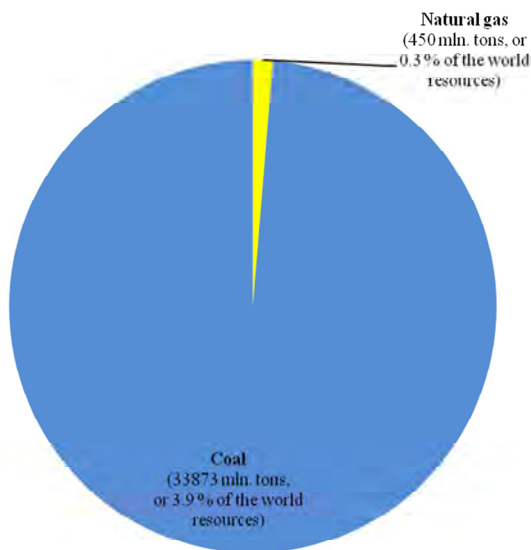

Fig. 5. Prospected resources of fossil fuel in Ukraine[1, 2] at the end of 2012 [1]
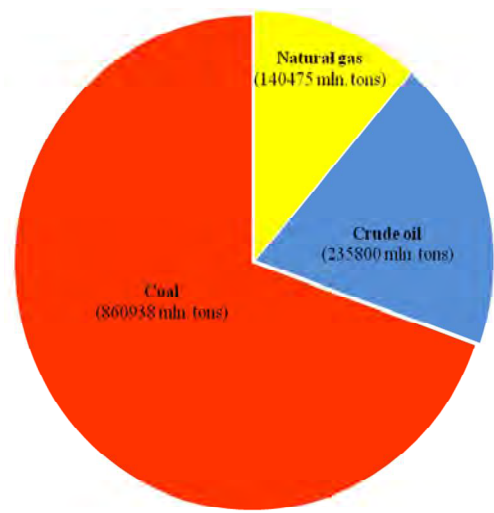

Fig. 6. Prospected resources of fossil fuel in the world[1] at the end of 2012 [1]

[1]Natural gas density is 0.75 kg/m^3

[2]Data about oil resources are absent because its amount is less than 0.05 % of the world one

At the same time we did not determine the possibility of desulphurized coal using as an additive to the crude material while producing special types of coke [15]. The aim of this work is to establish the mentioned possibility.

2. Experimental

2.1. Initial Materials

To determine the possibility of desulphurized coal using as an additive to the raw material while producing special types of coke we carried out the plastometry of basic charge (BC) and BC with additives of the initial and desulphurized coal according to [16].

The composition and characteristics of BC are represented in Tables 1 and 2.

The investigated charge was prepared using the basic charge with the additives of 2–10 mas % of the desulphurized coal F2 [15], as well as desulphurized and cleaned coal $F1_2$ [15]. One of the samples was prepared with the addition of F2 coal and decomposition resin formed during desulphurization due to the destruction of coal organic part. The characteristics of obtained charges are represented in Table 3. One can see that prepared samples do not practically differ from the initial charge. The samples obtained with using desulphurized coal (No. 2-4, 6 and 7) are characterized by lower sulphur content and volatile matter yield compared with the charge with addition of the initial coal (No. 1 and 5) that is logically explained by the characteristics of the initial components.

2.2. Quality Indexes of Plastometry Non-Volatile Residues

The following indexes were determined using the technical analysis of plastometry non-volatile residues (NVR): moisture content in the charge and charge + +desulphurized coal; moisture content in NVR; ash content; volatile matter yield and total sulphur content. NVR mechanical strength was determined according to the procedure similar to the determination of Rog (caking) index. The reactivity of NVR was estimated relative to the rate constants of the reaction between them and oxygen-containing gases.

All above-mentioned indexes were determined in accordance with Ukrainian standards. NVR abrasive hardness was determined according to the procedure described in [16].

Table 1

Quantitative and qualitative composition of the basic charge

Coal origin	Coal type	Content in charge, mas %
Ukraine, concentration plant "Samsonovskaya"	G	30
Ukraine, concentration plant "Belorechenskaya"	F	20
Ukraine, concentration plant "Mykhailovskaya"	F	30
Ukraine, concentration plant "Uzlovskaya"	LS	20

Table 2

Technical analysis of the basic charge

Moisture content, W^a, mas %	Ash content, A^d, mas %	Volatile matter yield, V^{daf}, mas %	Sulphur content, mas %			
			total	pyrite	organic	sulphate
			S_t^d	S_p^d	S_o^d	$S_{SO_4}^d$
1.76	9.63	33.38	2.37	1.02	0.24	1.11

Table 3

Characteristic of the initial charges

Sample	Charge composition	Moisture content, W^a, mas %	Ash content, A^d, mas %	Volatile matter yield, V^{daf}, mas %	Sulphur content, mas %			
					total	pyrite	sulphate	organic
					S_t^d	S_p^d	$S_{SO_4}^d$	S_o^d
1	95 % BC + 5 % initial F2	1.92	9.01	33.41	2.42	1.05	1.16	0.21
2	98 % BC + 2 % desulph. F2	1.82	9.63	33.09	2.38	1.01	1.13	0.24
3	95 % BC + 5 % desulph. F2	1.88	9.58	32.67	2.29	0.98	1.07	0.24
4	90 % BC + 10 % desulph. F2	1.88	9.86	31.95	2.25	0.95	1.03	0.27
5	95 % BC + 5 % initial $F1_2$	1.74	10.41	33.49	2.66	1.17	1.23	0.26
6	95 % BC + 5 % desulph. $F1_2$	1.71	9.77	32.83	2.30	0.98	1.12	0.20
7	95 % BC + 4.5 % desulph. F2 + 0.5 % resin	1.82	9.72	32.10	2.35	1.00	1.11	0.24

2.3. Derivatographic Investigations

Thermolysis of the basic charge, BC with addition of desulphurized coal, NVR and coke was carried out using Q-1500 D derivatograph of Paulik-Paulik-Erdey system recording the analytical signals of mass loss and heat effects. The samples were analyzed under dynamic mode with the heat rate of 10 K/min in the argon medium (for BC and BC with desulphurized coal) and in CO_2 medium (for NVR and coke). The sample mass was 50 mg.

2.4. Calculations of Fe_2O_3 Content in the Desulphurized Coal

As a result of pyrite sulphur oxidation ferrum converts into the oxides, Fe_2O_3, first of all, the content of which in the desulphurized coal is calculated according to the formula:

$$ X_{Fe_2O_3} = \left(\frac{\left(S^a_{p(in)} - \frac{S^a_{p(des.coal)} \cdot x_{des.coal}}{100} \right) \cdot M_{Fe_2O_3}}{2 \cdot M_S \cdot x_{des.coal}} \right) \cdot 100 \quad (1) $$

where $S^a_{p(in)}$ – pyrite sulphur content for analytical sample in the initial coal, mas %; $S^a_{p(des.coal)}$ – pyrite sulphur content for analytical sample in the desulphurized coal, mas %; $x_{des.coal}$ – desulphurized coal yield, mas %; $M_{Fe_2O_3}$ – Fe_2O_3 molecular mass, g/mol; M_S – sulphur molecular mass, g/mol.

3. Results and Discussion

3.1. Plastometry

We analyzed the capability of samples 1–8 to turn into plastic state and to be caked. The results of these plastometric investigations are represented in Table 4. One can see that addition of desulphurized and initial coal, as well as desulphurized coal together with decomposition resin (2–5 mas %) does not actually affect the thickness of plastic layer and plastometric subsidence. The content of

10 mas % of desulphurized coal F2 negatively affects the capability of the raw materials to turn into plastic state – the plastic layer thickness decreases by 25 % (compared with BC), though the plastometric subsidence of NVR increases. The latter fact allows to predict the improvement of coke column unloading from coking boxes while using desulphurized coal as an additive to the charge.

3.2. Investigations of Plastometry Products

The investigation results concerning the effect of additives type and amount on the technical analysis values, content of total sulphur and its variations, abrasive hardness, reactivity and mechanical strength of NVR are represented in Table 5.

One can see from Table 5 that NVR yields of the samples 1–7 and BC are the same. The ash and sulphur contents are also unchanging. It should be noted that the latter values of the samples 1 and 5 (with addition of the initial coal) are slightly higher than those of the samples 2–4, 7 and 6 (with addition of desulphurized coal). The volatile matter yield of the samples with addition of desulphurized coal F2 increase: the slight increase we observe while adding 2–5 mas % of the coal and considerable increase – adding 10 mas %. Apparently, during oxidative desulphurization the coal organic matrix is converted and forms more thermostable compounds. Part of them turns into volatile matter at the temperatures higher than maximum temperature of the plastometric investigations.

The addition of the initial and desulphurized coal to BC does not practically affect its caking ability (Table 4), hence its mechanical strength and abrasive hardness of non-volatile residue (Table 5). Some improvement in NVR mechanical properties is observed while adding the initial and desulphurized coal F2 in the amount of 5 mas % to BC.

The addition of desulphurized coal (compared with BC and BC+initial coal) inconsiderably increases the reactivity of the residue that is in good agreement with the changes of volatile matter yield (Table 5).

Table 4

Plastometric indexes of the initial charges

Raw materials	Plastometric subsidence X, mm	Thickness of plastic layer Y, mm
Basic charge	33	12
Sample 1	36	13
Sample 2	33	13
Sample 3	35	12
Sample 4	40	9
Sample 5	35	13
Sample 6	35	12
Sample 7	33	13

Characteristics of the non-volatile residues

Non-volatile residue	Yield, mas %	Ash content A^d, mas %	Volatile matter content V^{daf}, mas %	Total sulphur content S_t^d, mas %	Abrasive hardness AH, mg	Reactivity K_m, cm^3/g·s	Mechanical strength according to Rog method RI, units
Basic charge	79.91	10.94	9.27	1.95	20	1.54	93.63
Sample 1	81.36	10.81	8.94	2.19	22	1.62	95.44
Sample 2	80.77	10.73	9.63	1.99	19	1.62	95.62
Sample 3	79.90	11.08	9.84	2.09	21	1.70	95.94
Sample 4	80.92	10.92	12.11	2.05	19	1.81	94.62
Sample 5	80.79	10.91	8.22	2.02	19	1.47	94.95
Sample 6	81.08	10.50	9.65	1.94	19	1.78	95.07
Sample 7	79.02	9.85	7.61	1.86	17	1.46	92.03

While using even small amount of thermal decomposition resin as an additive, we observe the worsening of coke properties: mechanical characteristics of the sample 7 are worse and reactivity is less compared with other samples.

3.3. Derivatographic Investigations

To examine the indentity of coke obtained from the same raw material and NVR quality indexes, reactivity first of all, we carried out the following investigations:

1) according to the procedure described in [16] we obtained coke with BC and BC+5 mas % of desulphurized coal F1$_2$ (sample 6, Table 3)

2) we analyzed the following samples using DTA:

– BC and sample 6 in the argon medium;

– NVR+BC and NVR of the sample 6 in CO$_2$ medium;

– coke with BC and coke of the sample 6 in CO$_2$ medium.

DTA results are represented in Table 6 and Figs. 7–12.

The values of mass loss and thermal effects of thermodestructive processes for BC and sample 6 are almost the same (Figs. 7 and 8). The difference in the final mass loss is 3 mas % (Table 6). Taking into account that the amount of organic mass introduced into BC+coal F2 is approximately 4 mas % during the sample 6 preparation, the above-mentioned difference in mass loss may be explained by the change in BC reactivity while adding desulphurized coal with 12 mas % of Fe$_2$O$_3$ (Eq. (1)). It is known [17, 18] that while heating ferrum(III) oxide is an active component and intensifies destruction during coking. The mass losses of both samples are accompanied by exoeffects which are actually equal. However, destruction processes are more intensive for the sample 6, therefore its total thermal effect is lower (Fig. 7).

The analysis of TG and DTA thermolysis curves in CO$_2$ medium of NVR and coke obtained from BC and the sample 6 allows to assert that NVR and coke reactivity is higher for the sample 6 than that for BC (Figs. 9-12). According to TG curves the difference between total mass losses of BC and the sample 6 after plastometry is 17 mas % for NVR and 14 mas % for coke (Table 6). NVR and coke masses decrease due to the reaction between the coal organic matrix and carbon(IV) oxide followed by thermal destruction. The above-mentioned difference between the yields of thermolysis residues may be explained by the increase in residues reactivity obtained during coking and/or plastometry because the difference between total mass losses (due to the destruction of BC organic matrix and the sample 6) is only 3 mas %.

The character of thermal conversions in CO$_2$ medium is confirmed by DTA curves. They show the total exothermal effect of the reactions proceeding during residues thermal conversion in CO$_2$ medium. The reason is predominance of the synthesis reactions with heat release over cracking reactions with heat absorption. At the temperatures about 823 K and higher the increase of DTA curve becomes slower, *i.e.* intensity ratio between SR (synthesis reactions) and CR (coking reactions) equalizes.

It is known that the reactions between carbon and CO$_2$ characterize the coke reactivity and proceed with appreciable endoeffect (ΔH = 189.1 kJ/mol). CO$_2$ conversion above 50 % is achieved at the temperatures higher than 1073 K [19-23]. That is why we observe the decrease of DTA curve at the temperatures higher than 1213–1233 K (Fig. 9). While using coke within the range of 1143 (1188)–1273 K we observe clear endothermic effects caused by stimulation of the reaction between coal organic matrix and CO$_2$. Moreover, while using the residues of the sample 6 the stimulation of endothermic reactions proceeds more intensively compared with the thermolysis reactions of residues with BC.

Table 6

Derivatographic analysis results

Stage	Temperature range, K	Mass loss at the stage, mas %	Total mass loss, mas %
BC*			
I	273–399	1	1
II	399–601	–	1
III	601–776	9	10
IV	776–1029	16	26
V	1029–1223	12	38
VI	1223–1273	7	45
Sample No.6*			
I	273–393	1	1
II	393–607	–	1
III	607–776	9	10
IV	776–1028	16	26
V	1028–1163	9	35
VI	1163–1273	13	48
NVR of BC**			
I	273–408	3	
II	408–593	1	4
III	593–948	16	20
IV	948–1078	7	27
V	1078–1158	5	32
VI	1158–1273	23	55
NVR of the sample No.6**			
I	273–443	3	3
II	443–603	–	3
III	603–893	21	24
IV	893–1063	13	37
V	1063–1173	9	46
VI	1173–1273	26	72
Coke from BC**			
I	273–708	0,4	0.4
II	708–883	11	12
III	883–943	6	18
IV	943–1013	6	24
V	1013–1093	6	30
VI	1093–1143	3	33
VII	1143–1273	15	48
Coke from the sample No.6**			
I	273–713	1	1
II	713–868	11	12
III	868–973	10	22
IV	973–1033	6	28
V	1033–1118	8	36
VI	1118–1188	9	45
VII	1188–1273	17	62

* Derivatographic analysis was carried out in argon medium

** Derivatographic analysis was carried out in CO_2 medium
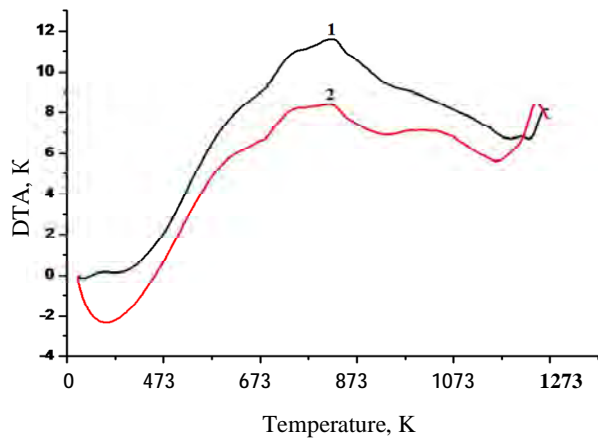
Fig. 7. DTA in argon medium: BC (1) and the mixture of 95 mas % BC + 5 mas % desulphurized coal Fl_2 (2)
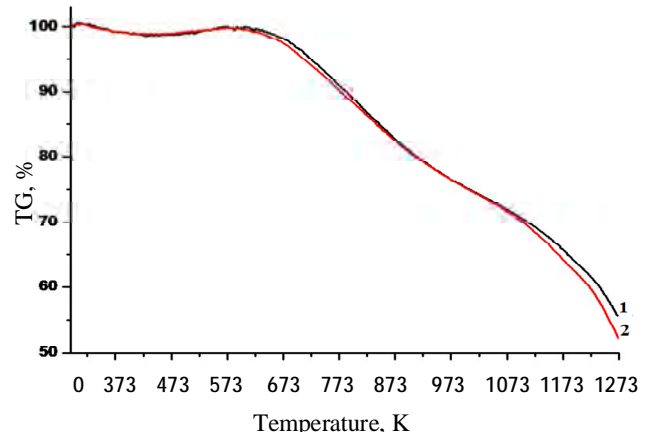

Fig. 8. Dependence of mass loss on the temperature in argon medium: BC (1) and the mixture of 95 mas % BC + 5 mas % desulphurized coal Fl_2 (2)
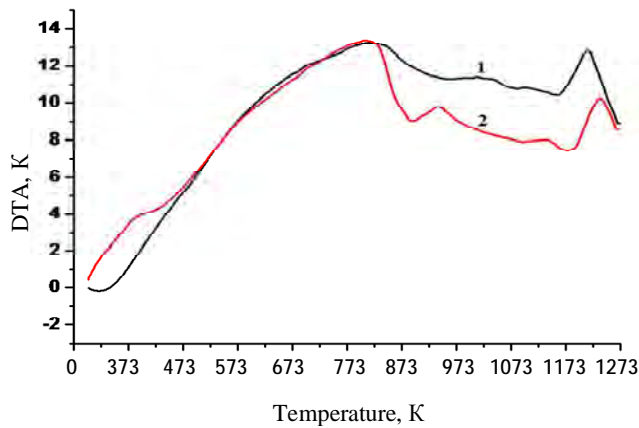

Fig. 9. DTA in CO_2 medium: NVR of BC after plastometry (1) and NVR of the mixture 95 mas % BC + 5 mas % desulphurized coal $F1_2$ after plastometry (2)
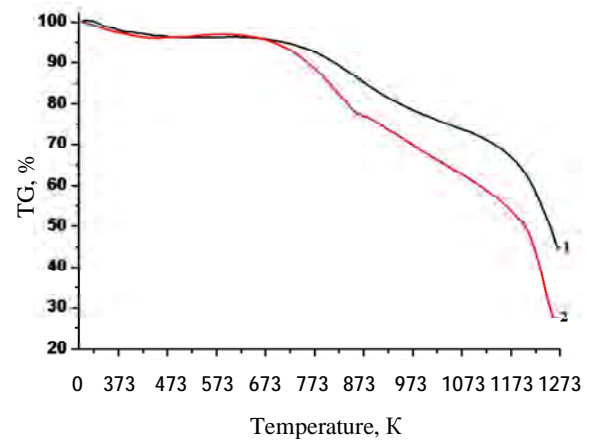

Fig. 10. Dependence of mass loss on the temperature in CO_2 medium: NVR of BC after plastometry (1) and NVR of the mixture 95 mas % BC + 5 mas % desulphurized coal $F1_2$ after plastometry (2)
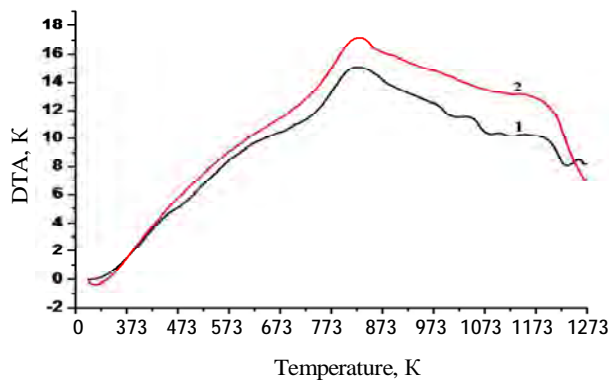

Fig. 11. DTA in CO_2 medium: coke of BC (1) and coke of the mixture 95 mas % BC + 5 mas % desulphurized coal $F1_2$
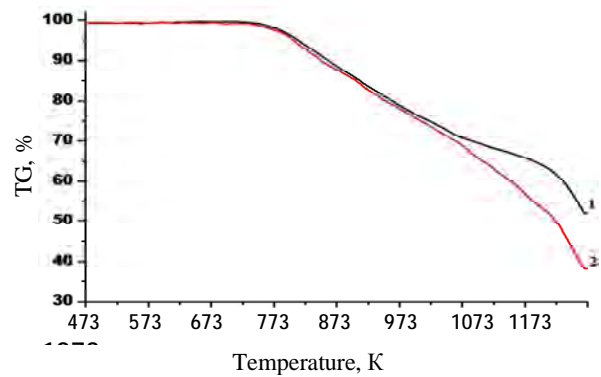

Fig. 12. Dependence of mass loss on the temperature in CO_2 medium: coke of BC (1) and coke of the mixture 95 mas % BC + 5 mas % desulphurized coal $F1_2$

All above-mentioned allows to assert that addition of desulphurized coal to BC enhances its capability of thermal destruction during coal carbonization. Due to these deep conversions and first of all, due to the presence of Fe_2O_3 great amount in the desulphurized coal, the reactivity of coke produced from BC and desulphurized coal increases.

The similar character of DTA and TG curves obtained in CO_2 medium during thermolysis of plastometry NVR and coke indicates that we can predict the reactivity of coke itself based on the reactivity of non-volatile residues.

4. Conclusions

Pyrite sulphur, which is the main part of total sulphur in high-sulphuric coal, converts first of all into Fe_2O_3 oxide as a result of oxidative desulphurization of medium-metamorphized black coal. Fe_2O_3 content in the desulphurized coal is 10–15 mas %. Such content worsens the capability of medium-metamorphized coal to turn into plastic state and be caked but allows to use the desulphurized coal as an additive (under 5 mas % relative to the finished mixture) to the raw material for the production of special types of coke. Moreover, the quality indexes of obtained coke are constant or improved compared with those of BC or BC + additives of the initial sulphuric or high-sulphuric coal.

We do not recommend to use the resin obtained as a result of thermal decomposition of coal organic matrix during oxidative desulphurization as additives to the raw material.

References

[1] BP statistical review of world energy 2013. Report breakdown by energy type. – Rezhym dostupu: http://www.bp.com/en/global/corporate/about-bp/statistical-review-of-world-energy-2013/statistical-review-downloads.html.
[2] Varlamov G., Liubchyk G. and Maliarenko V.: Teploenergetychni Ustanovky ta Ecologichni Aspecty Vyrobnyctva Energii. Vydavnyctvo "Politehnika", Kyiv 2003.
[3] Olijnyk T., Iegurnov O. and Panchenko V.: Visnyk Kyiv. Techn. Univ., 2010, **25**, 25.
[4] Dolgij V., Kaplanec H., Shvedyk P. and Shamalo M.: Kadastr Ugolnykh Shahtoplastov. DonUgI, Donetsk 2001.
[5] Kochetkov V.: Spravochnik po Obogatimosti Kamennykh Uglei i Antracytov Deistvuyushchih Shakht Ukrainy. IPP Kontrast, Kharkov 2004.
[6] Domennyie Pechi. Normativy rashoda koksa. Rukovodiashchij dokyment MCHM SSSR, ICHM, Dnepripetrovsk 1987.
[7] Zubilin I., Rudyka V. and Pinchuk S.: Poluchenie iz Uglei Energovosstanovitelei dlia Bazovykh Otraslei Promyshlennosti: Teoriya, Technologiya, Metodologiya. Kharkov. Nats. Univ., Kharkov 2004.

[8] Makarov G. and Harlampovich G.: Khimicheskaya Technologiya Tverdykh Goriuchyh Iskopaemykh. Khimiya, Moskwa 1986.
[9] Pysh'yev S., Gunka V., Astakhova O. et al.: Chem. & Chem. Techn., 2012, **6**, 443.
[10] Pysh'yev S., Gunka V., Bratychak M. and Grytsenko Y.: .: Chem. & Chem. Techn., 2011, **5**, 107.
[11] Pysh'yev S., Gayvanovych V., Pattek-Janczyk A. and Stanek J.: Fuel, 2004, **83**, 1117.
[12] Pysh'yev S., Bilushchak H. and Gunka V.: .: Chem. & Chem. Techn., 2012, **6**, 105.
[13] Pysh'yev S., Shevchuk K., Chmielarz L. et al.: Energy & Fuels, 2007, **21**, 216.
[14] Bratychak M., Gajvanovych V., Pyshiev S. and Brzozowski Z.: Chemia i Inz. Ekol., 2004, **11**, 59.
[15] Pyshyev S., Prysiazhnyi Y., Miroshnichenko D., et al.: .: Chem. & Chem. Techn., 2014, **8**, 225.
[16] Skliar M. and Tiutiunnikov Iu.: Khimiya Tverdych Goriuchih Iskopaemykh. Vyshcha shkola, Kyiv 1985.
[17] Sorokin Ie.: PhD thesis, Ukr. Derg. Vuglekhim. Inst. (UKhIN), Kharkiv 2006.
[18] Lazarenko A., Chuishchev V. and Kaufman S.: Koks i Khimiya, 2004, **1**, 24.
[19] Guliaev V.: D.Sc. thesis, Ukr. Derg. Vuglekhim. Inst. (UKhIN), Kharkiv 2012.
[20] Barsky V., Vlasov G, Rudnitsky A.: Chem. & Chem. Techn., 2009, **3**, 315.
[21] Barsky V., Vlasov G, Rudnitsky A.: Chem. & Chem. Techn., 2011, **5**, 139.
[22] Barsky V., Vlasov G, Rudnitsky A.: Chem. & Chem. Techn., 2011, **5**, 285.
[23] Barsky V., Vlasov G, Rudnitsky A.: Chem. & Chem. Techn., 2011, **5**, 439.

ЗНЕСІРЧЕННЯ ТА ЗАСТОСУВАННЯ СЕРЕДНЬОМЕТАМОРФІЗОВАНОГО КАМ'ЯНОГО ВУГІЛЛЯ. 2. ВИКОРИСТАННЯ ЗНЕСІРЧЕНОГО ВУГІЛЛЯ ЯК ДОДАТКІВ ДО СИРОВИНИ У ВИРОБНИЦТВІ СПЕЦІАЛЬНИХ ВИДІВ КОКСУ

Анотація. Здійснено пластометричні дослідження базової шихти коксування та шихт приготовлених з додаванням знесірченого вугілля різної якості та в різній кількості. Досліджено нелеткі залишки пластометрії, а саме: проведено їх технічний аналіз, визначено механічну міцність, абразивну твердість, реакційну здатність, а також проведено дериватографічні дослідження. Встановлено, що незважаючи на деяке погіршення здатності середньометаморфізованого вугілля після процесу оксидаційного знесірчення переходити у пластичний стан і спікатися, його можна використовувати як додаток до сировини коксування у кількостях до 5 % мас. (у розрахунку на готову суміш) у виробництві спеціальних видів коксу. При цьому, порівняно з базовою шихтою чи з базовою шихтою із добавками вихідного сірчистого і високосірчистого вугілля, показники якості отримуваного коксу будуть, в основному, незмінними, а подекуди й покращуватимуться.

Ключові слова: сірка, знесірчене вугілля, шихта, кокс.