

## THE INFLUENCE OF ORGANIC AND INORGANIC ADDITIVES ON THE SPECIFIC ELECTRICAL RESISTANCE OF COKE

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<https://doi.org/10.23939/chcht18.01.109>

**Abstract.** This study aimed to evaluate the effect of both inorganic (boron carbide nanopowders and silicon carbide (carborundum) and organic lean (petroleum coke) additives on the quality of coke produced in a laboratory furnace, as well as on its electrical properties. Analyzing the results of the quality assessment of the obtained coke, it can be argued that the addition of a fixed amount (0.25-0.5 wt.%) of non-caking nanoadditives allows to regulate the process in the plastic state in order to increase the coke strength. This modification affects the coke quality and has a significant dependence on the grade composition of the coal charge. The use of nanoadditives is especially important for coal charges with poor coking properties. Adding 5% of petroleum coke to the coal charge leads to an increase in the gross coke yield by 1.2-1.3%; a decrease in coke ash content by 0.2-0.3%; an increase in the total sulfur content in coke by 0.15-0.23%; deterioration in both mechanical (P25 – by 0.1-0.6%; I10 – by 0.1-0.2%) and coke strength after the reaction (CSR – by 0.6-1.0%), coke reactivity (CRI – by 0.2-0.3%), as well as structural strength (SS by 0.3-0.4%), abrasive hardness (AH by 0.7-1.0 mg) and specific electrical resistance ( $\rho$  by 0.002-0.007  $\text{Om}\times\text{cm}$ ). The obtained data may indicate an increase in the order degree of the coke structure and the appearance of a larger number of nanostructures. In addition, it should be noted that a sharper deterioration in blast furnace coke quality is observed when using a coal charge characterized by a lower coal content of the Concentrating Factory Svyato-Varvarynska LLC.

**Keywords:** petroleum coke, coal blends, coking, blast furnace coke quality, electrical resistivity, nanopores, modification, nanoadditives, boron carbide, silicon carbide.

### 1. Introduction

It is known that blast furnace coke plays a very important role in iron production. Therefore, the quality of blast furnace coke is constantly monitored to ensure its high strength and resistance to  $\text{CO}_2$ . On the other hand, standard test results cannot adequately predict the behavior of coke in blast furnaces, as they do not accurately reflect the actual operating conditions. In the blast furnace, coke is exposed to temperatures above 1600 °C and gases/vapors, mainly  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which change its strength and structure, while industrial coke testing is limited to lower temperatures. For example, ISO 18894:2018 specifies the equipment and methods used to determine the reactivity of lump coke (nominal lump size >20 mm) in carbon dioxide at elevated temperatures (1100 °C) and its strength after reaction in carbon dioxide by tumbling in a cylindrical chamber.

The nanotexture of coke has been described in several studies using transmission electron microscopy (TEM),<sup>1</sup> or determined by small-angle neutron scattering technique (SANS).<sup>2</sup> According to TEM data, the coke nanotexture is characterized by molecular orientation domains, the size of which varies from 5 nm to several micrometers. Molecular orientation domains (MOD) consist of polyaromatic basic structural units arranged in parallel planes of aromatic layers that are either mis-oriented or locally oriented. The size of polyaromatic basic structural unit is about 1 nm; it is formed by polyaromatic layers (4 to 10 rings) isolated or superimposed on each other in two or three layers. Optical microscopy classifies MODs smaller than 300 nm as isotropic texture, while those with a size >300 nm are part of an anisotropic texture. These molecular orientation domains increase continuously in size with increasing temperature, even above 2000°C. Changes in the pore carbon distribution have been widely studied by petrographic methods by

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Suarez-Ruiz and Crelling.<sup>3</sup> Such studies have shown that at temperatures below or around 1300°C, the porosity of coke hardly changes, but increases significantly at higher temperatures. This explains the behavior of coke as an inert material in coke production; thus, its addition to coke charges has an important impact on the properties of metallurgical coke.

The porosity changes significantly only at higher temperatures. The oxidation of coke by its minerals, although occurring at lower temperatures, becomes much more intense at about 1300°C according to Sakurovs.<sup>2</sup> An alternative explanation has been proposed. It states that at temperatures below 1400 °C, any increase in coke porosity caused by carbon rearrangement is canceled out by the melting and flowing of some mineral material that blocks the pores. At higher temperatures, the increased ordering of the carbon according to Zhu, Zhan, He,<sup>4</sup> creates pores. Petrographic methods have a maximum resolution of about 1 micron. However, Sakurovs *et al.*,<sup>1</sup> smaller pores, nanopores, are known to exist in coke and can be expected to change during annealing as well. However, the decreasing availability of primary coking coals and problems with their supply force coke companies to look for alternative raw materials and process mixtures with deteriorated properties by Flores *et al.*<sup>5</sup> Therefore, petroleum coke (PC) has become an interesting component of coke production in this context.

Over the years, petroleum coke has been used in various proportions for the production of metallurgical coke, from 5 to 40 wt.%. However, in many cases it is unclear how and why the addition of petroleum coke affects the properties of metallurgical coke. There are conflicting reports in the literature about the positive Zhang *et al.*<sup>6</sup> or negative by Malaquias, Flores, Bagatini<sup>7</sup> impact of PC on coke quality.

Currently, in Ukraine, most coking coals have high sulfur content and produce coke with CRI and CSR values averaging 40% according to Larionov *et al.*<sup>8</sup>

In addition, many of the coals used for coking are oxidized, which also worsens the CRI and CSR of the blast furnace coke produced. Similar conclusions can be found in Shmeltser *et al.*,<sup>9</sup> Gunka *et al.*,<sup>10</sup> Shved *et al.*<sup>11</sup> and Zelenskii.<sup>12</sup>

Therefore, there is a growing interest in modifying coal, which is in a plastic state during coking, in order to improve the coke quality and expand the resource base of coke production in the current shortage of coking coal. One of the ways is to introduce various modifying additives into the coke charge according to Nag *et al.*<sup>13</sup>

Summarizing the long-term practice of many researchers and producers of coking coal charges with various additives, it is possible to propose a conditional classification of these additives into three main groups depending on their technological origin. (Table 1).

**Table 1.** Classification of coal charge additives

Coal charge additives		
Inorganic and non-sticky	Organic (caking)	Mesogenic

The group of inorganic additives includes oxides, carbonates, carbides, etc., and the sintering ones include anthracite, semi-coke, coke fines, and soot.

Organic additives are mainly solid and liquid wastes of petrochemical (acidic tars, oil sludge, used oils, lubricating and cooling fluids) and coke-chemical industries (acidic tar, carbon blacks).

It should be noted that the introduction of sintering and organic additives into the charge is not generally driven by the trend towards high quality coke. Most often, this is due to the need to dispose the production waste without reducing the quality of coke and coking chemicals or by reducing the need for coke fines and dust (in the case of sintering additives).

Mesogenic additives, for example, petroleum and coal pitches, are of particular interest. They reduce thermoreactivity and under certain conditions pass into the mobile mesophase according to Zelenskii.<sup>14</sup> This mesophase also plays a special role in the sintering process of the coal composition and the formation of a strong coke structure with certain properties. This is important because the main properties of coke, such as strength, micro- and macro-crack development, and reactivity, are related to its anisotropic structure. The use of nanomaterials as additives is also effective. Their addition improves the wear resistance, strength, crack resistance, and other characteristics of hard alloys. Al<sub>2</sub>O<sub>3</sub>, SiC, TiN, TiCN, WC nanopowders for example, were used as modifying additives Wu, Sun, Zhu, Wang and Zhang.<sup>15</sup>

The effect of B<sub>4</sub>C and SiC micro- and nanopowders on coke quality was studied by Kumar, Jayakumari, Tomas with co-authors.<sup>16-18</sup> It was found that the reaction between these additives and active oxygen obtained from oxygen-containing compounds during coal carbonization leads to a decrease in condensation and crosslinking reactions and an increase in secondary cracking reactions. This leads to an increase in the size of the aromatic layer and the degree of anisotropy in the modified coke structure, which is responsible for a significant improvement in coke quality.

This study investigates the effect of adding both inorganic (boron carbide and silicon carbide nanopowders) and organic (petroleum coke) additives on the quality of the coke produced, including the specific electrical resistance of blast furnace coke, which is characterized by the degree of orderliness of its structure according to Miroshnichenko *et al.*<sup>19</sup>

## 2. Experimental

### 2.1. Methods

To determine the quality indicators of coals, coal mixtures and obtained blast furnace coke, the following standard methods were used:

ISO 17246:2010 Coal – Proximate analysis;

ISO 18283:2022 Coal and coke – Manual sampling;

ISO 17247:2020 Coal and coke – Ultimate analysis;

ISO 334:2020 Coal and coke – Determination of total sulfur;

ISO 1170:2020 Coal and coke – Calculation of analyses to different bases;

ISO 7404-5:2009 Methods for the petrographic analysis of coals – Part 5: Method of determining microscopically the reflectance of vitrinite;

ISO 7404-3:2009 Methods for the petrographic analysis of coals – Part 3: Method of determining maceral group composition;

ISO 18894:2018 Coke – Determination of coke reactivity index (CRI) and coke strength after reaction (CSR);

ISO 1953:2015 Hard coal – Size analysis by sieving;

ISO 5074:2015 Hard coal – Determination of Hardgrove grindability index;

DSTU 7722:2015 Hard Coal. Method for determination of plastometric indexes.

The chemical composition of ash was determined according to DSTU 9045:2020 Solid fuel. A method of determining the chemical composition of ash. The basicity index ( $B_b$ ) and the base/acid ratio ( $I_b$ ) were calculated by Miroshnichenko *et al.*<sup>20</sup> according to the equations:

$$B_b = \frac{100A^d (Fe_2O_3 + CaO + MgO + Na_2O + K_2O)}{(100 - V^{daf})(SiO_2 + Al_2O_3)}$$

where  $A^d$  is an ash content of coal in the dry state, %;  $V^{daf}$  is a volatile matter in the dry ash-free state, %.

Index of abrasive hardness according to Ginzburg and Index of structural strength according to Gryaznov were determined by authored methods.

To determine the specific electrical resistance of coal coke, we used DSTU 8831:2019. The essence of this method is to measure the voltage drop when a direct current passes through a compressed column of coke with a particle size of less than 0.2 mm, enclosed in a matrix between two punches (Fig. 1).

The coking of coal mixtures was carried out in a laboratory 5-kilogram electric coking furnace (Fig. 2).

The essence of the method is as follows. A metal chamber with the width of 150 mm, length of 270 mm,

and height of 300 mm was inserted into an electric furnace preheated to 1100 °C. The chamber was loaded with 4.5-5.0 kg of the tested coal mixture of a given grinding class of less than 3 mm with a mass fraction of total moisture of  $8 \pm 0.5\%$ ; the loading density was  $\sim 800 \text{ kg/m}^3$ . After reaching a temperature of  $950 \pm 10 \text{ }^\circ\text{C}$  in the center of the loading center, the experiment was stopped.



Fig. 1. Testing unit for determining the coke powder SER



Fig. 2. Laboratory 5-kg electric coking furnace

Test duration was 2 hours 50 minutes – 3 hours. Coke quenching was dry. The coke was weighed and the yield of dry gross coke was determined per loading of dry coal.

## 2.2. Materials

### 2.2.1. Charges with an Organic Lean (Petroleum Coke) Additive

Coal concentrates (Pavlogradska CPP, Dobropilska CPP, grade “G (G1)”); Dobropilska CPP, grade “G(G2)”); Svyato-Varvarynska CPP, grade “K”) were studied by the

methods of proximate ( $W^r$ ,  $A^d$ ,  $S_t^d$ ,  $V^{daf}$ ), plastometric ( $x$ ,  $y$ ) and petrographic ( $R_0$ , petrographic composition) analyses. The experimental results are shown in Tables 2 and 3.

Analyzing the above data, it can be concluded that the studied coal is characterized by the inherent values of quality indicators. However, it is necessary to note the reduced ash content of the “G (G1)” coal (4.6%), which can positively affect the ash content of the coke obtained from it.

Technological indices of the petroleum coke quality are given in Table 1. The ultimate and granulometric compositions are in Tables 4 and 5.

It should be noted that petroleum coke has low ash content (0.5%) and fairly high total sulfur content (4.08%). The values of volatile matter (13.2%) and carbon content (89.87%) correspond to the “P” grade coal.

Hardgrove's grindability coefficient (HGI) of the studied petroleum coke is 94 units, and the Rog's index (RI), which characterizes its cohesiveness, is 14 units.

The values of HGI and RI also correspond to the “P” grade coal. Given the above, it can be expected that petroleum coke in the coal charge will function as a lean component.

The results of the granulometric composition of petroleum coke indicate that it is characterized by the 0-3 mm class content of 54.1%. Taking into account the value of its Hardgrove grindability coefficient (94 units), we can conclude that in the process of its simultaneous grinding with coal components, it will be thoroughly crushed.

Four variants of coal blends were investigated (Table 6). Variants 1 and 2 are typical variants for coal charges of Ukrainian coke-chemical plants, which differ in the content of “K” coal (52 and 58 %).

In variants 1+PC and 2+PC, 5% of petroleum coke was introduced instead of Dobropilska CPP grade “G(G1)” coal. The results of proximal, plastometric, and petrographic analyses are shown in Tables 7 and 8.

**Table 2.** Technological properties

Component	Grade	Proximate analysis, %				Plastometric indexes, mm	
		$W^a$	$A^d$	$S_t^d$	$V^{daf}$	$x$	$y$
Pavlogradska CPP	DG	2.1	6.4	1.38	42.3	48	9
Dobropilska CPP	G (G1)	1.3	4.6	1.11	39.3	44	16
Dobropilska CPP	G (G2)	1.1	6.2	1.33	38.7	38	16
Svyato-Varvarynska CPP	K	1.1	9.1	0.69	27.3	25	15
Petroleum coke		0.6	0.5	4.08	13.2	Not defined	

**Table 3.** Petrographic characteristics

Componen	Grade	Petrographic composition (without mineral impurities), %					Index of reflection vitrinite, %
		$V_t$	$S_v$	$I$	$L$	$\sum FC$	$R_0$
Pavlogradska CPP	DG	69	0	24	7	24	0.62
Dobropilska CPP	G (G1)	63	0	26	11	26	0.78
Dobropilska CPP	G (G2)	71	0	23	6	23	0.78
Svyato-Varvarynska CPP	K	87	0	12	1	12	1.17
Petroleum coke		Not defined					

**Table 4.** Ultimate composition of petroleum coke

Ultimate analysis (dry, ash-free state), %				
$C^{daf}$	$H^{daf}$	$N^{daf}$	$S_t^d$	$O_d^{daf}$
89.87	4.11	1.02	4.08	0.92

**Table 5.** Granulometric composition of petroleum coke

Granulometric composition (mm), %						Average particle diameter, mm
$>13$	$6-13$	$3-6$	$1-3$	$0.5-1$	$<0.5$	$d_s$
13.7	18.2	14.0	19.6	11.5	22.9	6.15

**Table 6.** Compositions of coal charges

Component	Grade	Variant, %			
		1	1+PC	2	2+PC
Pavlogradska CPP	DG	6	6	6	6
Dobropilska CPP	G (G1)	21	16	18	13
Dobropilska CPP	G (G2)	21	21	18	18
Svyato-Varvarynska CPP	K	52	52	58	58
Petroleum coke		0	5	0	5
Blend		100	100	100	100

**Table 7.** Technological properties of coal blends

Variant	Proximate analysis, %				Plastometric indexes, mm	
	$W^a$	$A^d$	$S_t^d$	$V^{daf}$	$x$	$y$
1	1.2	7.4	0.95	33.1	33	15
1+PC	1.2	7.2	1.10	31.8	31	14
2	1.2	7.6	0.92	32.4	32	15
2+PC	1.2	7.4	1.07	31.1	30	14

**Table 8.** Petrographic characteristics of coal blends

Variant	Petrographic composition (without mineral impurities), %					Index of reflection vitrinite, %
	$V_t$	$S_v$	$I$	$L$	$\Sigma FC$	$R_o$
1	78	0	18	4	18	0.97
1+PC	78	0	18	4	18	0.93
2	79	0	17	4	17	1.00
2+PC	79	0	17	4	17	0.96

**Table 9.** Characteristics of coke

Rank of coal	Content, %	$R_o$ , %	Proximate analysis, %			Y, mm	Basicity index
			$A^d$	$V^{daf}$	$S_t^d$		
Erunakovsk mine; G	25.0	0.632	8.0	38.5	0.41	9.5	2.00
Dobropol'skaya enrichment facility (EF); G	5.0	0.783	6.4	37.3	1.30	13.5	3.09
Abashevskaya EF; GZh + Zh	7.0	0.781	8.9	37.2	0.59	25.0	2.53
Abashevskaya (Esaul) EF; Zh	12.0	0.777	8.0	37.0	0.64	22.5	3.46
Duvanskaya EF, Zh	6.0	0.970	9.5	31.9	1.30	21.5	3.56
Wellmore EF, Zh	10.0	0.949	7.4	33.0	1.08	22.5	2.80
Donetskstal' EF; K	18.0	1.154	8.7	28.0	0.65	13.5	2.21
Severnaya EF; KO	13.0	1.119	9.3	25.3	0.70	16.0	2.80
Pocahontas EF; OS	4.0	1.492	8.0	18.5	0.75	12.0	1.34
Total	100	0.911	8.3	32.8	0.71	16.0	2.56



**Fig. 3.** Nanopowder of boron carbide



**Fig. 4.** Nanopowder of silicon carbide

Analyzing the results given in Table 6 and 7, it can be concluded that the addition of petroleum coke leads to a decrease in ash content (by 0.2%), the rate of volatile substances release (by 1.3%), the thickness of the plastic layer (by 1 mm) and the vitrinite reflection (by 0.04%).

### 2.2.2. Charges with an Inorganic Additive (Nanopowders of Boron Carbide and Silicon Carbide)

The additives are introduced into the production charge from the coal preparation shop of Zaporozhkoks PJSC. Table 9 shows the composition and characteristics of the charge used in the experiments.

The additives introduced into the charge are crystalline nanopowders of boron carbide and silicon carbide

(carborundum) produced by the Research Institute of Refractories. Their appearance is shown in Figs. 3 and 4, and their brief characteristics are given in Table 10.

## 3. Results and Discussion

### 3.1. Coke with an Organic Lean (Petroleum Coke) Additive

The gross coke yield, parameters of proximate analysis ( $A^d$ ,  $S_t^d$ ,  $V^{daf}$ ), mechanical strength ( $M_{25}$ ,  $M_{10}$ ), structural strength ( $SS$ ), abrasive hardness ( $AH$ ), and specific electrical resistance ( $SER$ ) of coke were determined after coking. The results of coke quality study are given in Table 11 and Table 12.

**Table 10.** Characteristics of modifying additives

Sample	Additive	Content in sample, wt.%	Particle size, nm
1	Standard charge (without additives)	–	–
2	B <sub>4</sub> C	0.25	< 100
3	B <sub>4</sub> C	0.50	< 100
4	SiC	0.25	< 100
5	SiC	0.50	< 100

**Table 11.** Quality indicators of the obtained coke

Variant	Proximate analysis, %			Coke yield, %	Mechanical strength		Expected mechanical strength of production coke, %	
	$A^d$	$S_t^d$	$V^{daf}$		$B_K$	$P_{25}$	$I_{10}$	$M_{25}$
1	10.4	0.86	0.8	70.8	93.2	6.1	90.2	7.6
1+PC	10.2	1.01	0.7	72.0	92.6	6.3	89.6	7.8
2	10.6	0.77	0.8	71.1	93.4	5.8	90.4	7.3
2+PC	10.3	1.00	0.7	72.4	93.3	5.9	90.3	7.4

**Table 12.** Quality indicators of the obtained coke

Variant	Index of abrasive hardness according to Ginzburg, mg	Index of structural strength according to Gryaznov, %	Reactivity and strength after reaction, %	
	$AH$	$SS$	$CRI$	$CSR$
1	59.4	83.3	41.7	40.2
1+PC	58.7	82.9	41.9	39.2
2	59.8	86.3	41.2	40.0
2+PC	58.8	86.0	41.5	39.4

Analyzing the results of determining the quality of the coke produced, it can be argued that the addition of 5% petroleum coke to coal charges leads to

- 1) increase in gross coke yield by 1.2-1.3%;
- 2) reduction of coke ash content by 0.2-0.3%;
- 3) increase of total sulfur content in coke by 0.15-0.23%;
- 4) deterioration of both mechanical ( $P_{25}$  – by 0.1-0.6%;  $I_{10}$  – by 0.1-0.2%) and post-reaction ( $CSR$  – by

0.6-1.0%) strength, coke reactivity ( $CRI$  – by 0.2-0.3%), as well as structural strength ( $SS$  – by 0.3-0.4%) and abrasive hardness ( $AH$  – by 0.7-1.0 mg).

The effect of the petroleum coke addition on the electrical resistance of blast furnace coke obtained with its participation is shown in Fig. 5.

The results shown in Fig. 5 indicate that the specific electrical resistance  $\rho$  increases by 0.002-0.007 Ohm×cm with the addition of petroleum coke. The

increase in the resistance may be caused by an increase in the porosity of coke obtained from coal and petroleum coke blends.

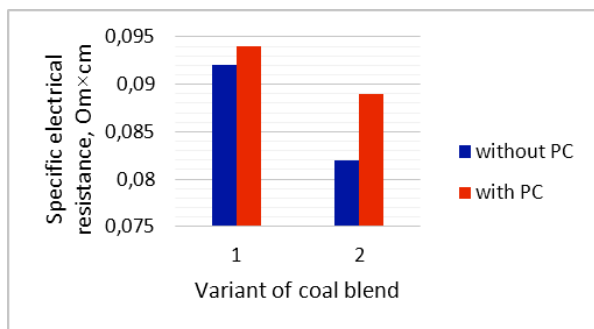


Fig. 5. Specific electrical resistance vs. variant of coal blend

In addition, it should be noted that a sharper deterioration in blast furnace coke quality is observed when using coal charge with lower coal content from Svyato-Varvarinskaya CPP. This is a consequence of the positive impact of this coal on the quality of blast furnace coke produced with its participation.

The results obtained by Barsky<sup>21</sup> and Pyshyev *et al.*<sup>22,23</sup> indicate that the quality indicators of coal and coal blends have a decisive influence on the quality indicators of blast furnace coke obtained from them.

Our results are consistent with the previous ones of Flores with co-authors,<sup>24</sup> where petroleum coke, as an inert material, greatly impairs the flowability of coal but some interaction with coal can occur due to the release of volatile substances from petroleum coke, which smooths out this negative effect. In addition, no significant effect of petroleum coke on the type of coke texture was found. All coke matrices (binder phase) were formed by ring texture

components, the proportion of which decreased with increasing participation of petroleum coke. In addition, it was found that coal inert substances are more reactive to CO<sub>2</sub> compared to petroleum coke, which is consumed first. The latter, together with the negative impact of petroleum coke on coke structure and cohesion, can be crucial for achieving CSR requirements for blast furnaces.

### 3.2. Coke with an Inorganic Additive (Nanopowders of Boron Carbide and Silicon Carbide)

The proximate analysis of coke obtained in box coking is summarized in Table 13.

It is evident from Table 13 that introducing additives in the charge in quantities up to 0.25 wt.% has no effect on the ash content of coke. The ash content slightly increases with 0.5 wt.% additives.

Table 13 shows that the introduction of additives into the charge in the amount of up to 0.25 wt.% does not affect the ash content of coke. The ash content slightly increases at the introduction of 0.5 wt.%.

Table 14 shows the effect of additives on CRI and CSR.

Analyzing the given indicators, it can be argued that the coke quality is improved with the additives:

- B<sub>4</sub>C (0.25 wt.%) with a registered 3.0 % decrease in CRI and a 7.6 % increase in CSR;
- B<sub>4</sub>C (0.50 wt.%) with a registered 2.8 % decrease in CRI and a 5.7 % increase in CSR;
- SiC (0.25 wt.%) with a registered 2.1 % decrease in CRI and a 5.5 % increase in CSR;
- SiC (0.50 wt.%) with a registered 2.6 % decrease in CRI and a 4.4 % increase in CSR.

Table 13. Proximate analysis of coke

Sample	$W_t^r, \%$	$A^d, \%$	$V^{daf}, \%$	$S_b^d, \%$
1	0.72	11.6	0.95	0.68
2	0.57	11.9	0.89	0.69
3	0.46	12.4	0.81	0.67
4	0.75	11.8	0.92	0.67
5	0.52	12.2	0.94	0.65

Table 14. Values of CRI and CSR for produced coke

Sample	Additive, content in the sample, wt.%	CRI, %	CSR, %
1	Standard charge (without additives)	41.6	35.8
2	B <sub>4</sub> C, 0.25	38.6	43.4
3	B <sub>4</sub> C, 0.50	38.8	41.5
4	SiC, 0.25	39.5	41.3
5	SiC, 0.50	39.0	40.2

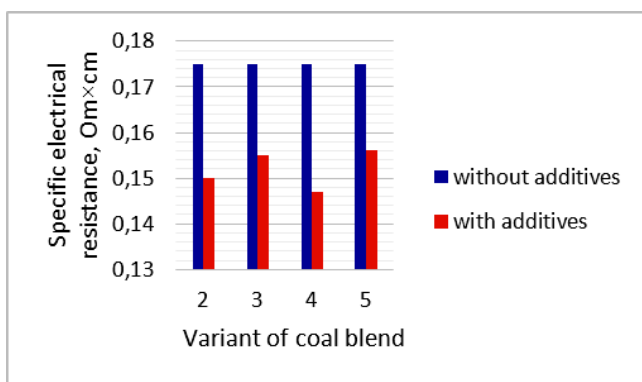
**Table 15.** Physico-chemical properties of coke

Sample	Gryaznov structural strength, %	Combustibility, s	Electrical resistivity, $\Omega$ cm	Porosity, %
1	80.1	23	0.175	45.6
2	85.3	28	0.150	42.9
3	84.5	27	0.155	43.5
4	84.1	25	0.147	44.4
5	83.6	27	0.156	42.3

The additives improve the hot strength index (CSR) and have a little effect on the reactivity index (CRI).

The improvement in CRI and CSR values of coke with nanoadditives  $B_4C$  and  $SiC$  is confirmed by analysis of other physico-chemical properties of coke: the Gryaznov structural strength, combustibility, and porosity (Table 15).

The effect of adding inorganic nanoadditives to the charge is illustrated in Fig. 6.



**Fig. 6.** Specific electrical resistance vs. variant of coal blend

## 4. Conclusions

Analyzing the results of determining the quality of the coke produced, it can be stated that the addition of 5% of petroleum coke to coal blends leads to an increase in the gross coke yield by 1.2-1.3%; a decrease in coke ash content by 0.2-0.3%; an increase in the total sulfur content in coke by 0.15-0.23%; deterioration of both mechanical (P25 – by 0.1-0.6%; I10 – by 0.1-0.2%) and post-reaction (CSR – by 0.6-1.0%) strength, reactivity of coke (CRI – by 0.2-0.3%), as well as structural strength (SS – by 0.3-0.4%), abrasive hardness (AH – by 0.7-1.0 mg), and resistivity ( $\rho$  – by 0.002-0.007 Ohm×cm). In addition, it should be noted that a sharper deterioration in blast

furnace coke quality is observed when using a coal charge with lower coal content from Svyato-Varvarinskaya CPP. This is a result of the positive impact of this coal on the quality of blast furnace coke produced with its participation. On the other hand, taking into account the slight deterioration in coke quality and certain technical and economic objectives of each individual coke plant, the introduction of up to 5% of petroleum coke into the coal charge as an additive can be used to utilize it and increase the gross coke yield.

At the same time, the introduction of a certain amount (0.25 wt.%) of non-caking  $B_4C$  and  $SiC$  nanoadditives allows modifying the processes occurring during the plasticization of the coal charge, with a subsequent increase in coke strength.

Thus, the CRI and CSR values of coke are improved when modifying nanoadditives are introduced into the coal charge in an amount not exceeding 0.25 wt.%. The effect of  $B_4C$  and  $SiC$  nanoadditives on coke properties significantly depends on the rank composition of the charge. The proposed additives are particularly effective in charge with poor coking properties. The additives can be introduced into the charge by means of a feeder (e.g., a screw feeder), which feeds a dosed amount of the additive (0.25 wt.%) to the belt conveyor together with the charge. The feeder should be preceded by a final crusher (for production of <3 mm class). The crusher acts then as a mixer. As we know, it is necessary to mix the additive evenly throughout the entire volume of the charge. Another option is to inject one component of the charge into the bottom of the silo with compressed air. This involves installing an additive hopper in the existing pneumatic system.

## References

- [1] Sakurovs, R.; Koval, L.; Grigor M.; Sokolova, A.; de Campo, L.; Rehm, K. Nanostructure of Cokes. *Int J Coal Geol* **2018**, *188*, 112–120. <http://dx.doi.org/10.1016/j.coal.2018.02.006>



- [2] Sakurovs, R.; Grigor, M.; Sokolova, A.; Mata, Ya. Effect of High Temperature on Nanopores in Coke. *Fuel* **2023**, *334*, 126821. <https://doi.org/10.1016/j.fuel.2022.126821>
- [3] Suarez-Ruiz, I.; Crelling, J.C. Coal-Derived Carbon Materials. In *Applied Coal Petrology. The Role of Petrology in Coal Utilization*; Suarez-Ruiz, I.; Crelling, J.C., Eds.; Burlington, 2008; pp 193–225. <https://doi.org/10.1016/B978-0-08-045051-3.X0001-2>
- [4] Zhu, H.-b.; Zhan, W.-l.; He, Z.-j.; Yu, Y.-c.; Pang, Q.-h.; Zhang, J.-h. Pore Structure Evolution During the Coke Graphitization Process in a Blast Furnace. *Int. J. Miner. Metall. Mater.* **2020**, *27*, 1226–1233. <https://doi.org/10.1007/s12613-019-1927-1>
- [5] Flores, B.D.; Flores, I.V.; Guerrero, A.; Orellana, D.R.; Pohlmann, J.G.; Díez, M.A.; Borrego, A.G.; Osório, E.; Vilela, A.C.F. Effect of Charcoal Blending with a Vitritinite Rich Coking Coal on Coke Reactivity. *Fuel Process. Technol.* **2017**, *155*, 97–105. <https://doi.org/10.1016/j.fuproc.2016.04.012>
- [6] Zhang, H.; Bai, J.; Li, W.; Cheng, F. Comprehensive Evaluation of Inherent Mineral Composition and Carbon Structure Parameters on CO<sub>2</sub> Reactivity of Metallurgical Coke. *Fuel* **2019**, *235*, 647–657. <https://doi.org/10.1016/j.fuel.2018.07.131>
- [7] Malaquias, B.; Flores, V.I.; Bagatini, M. Effect of High Petroleum Coke Additions on Metallurgical Coke Quality and Optical Texture. *REM – International Engineering Journal* **2020**, *73*. <https://doi.org/10.1590/0370-44672019730097>
- [8] Larionov, K.; Mishakov, I.; Slyusarskiy, K.; Vedyagin, A.A. Intensification of Bituminous Coal and Lignite Oxidation by Copper-Based Activating Additives. *Int J Coal Sci Technol.* **2021**, *8*, 141–153. <https://doi.org/10.1007/s40789-020-00350-z>
- [9] Shmeltser, E.O.; Lyalyuk, V.P.; Sokolova, V.P.; Miroshnichenko, D.V. The Using of Coal Blends with an Increased Content of Coals of the Middle Stage of Metamorphism for the Production of the Blast-Furnace Coke. Message 1. Preparation of Coal Blends. *Pet. Coal* **2018**, *60*, 605–611.
- [10] Gunka, V.; Shved, M.; Prysiashnyi, Y.; Pyshyev, S.; Miroshnichenko, D. Lignite Oxidative Desulphurization: Notice 3–Process Technological Aspects and Application of Products. *Int J Coal Sci Technol.* **2019**, *6*, 63–73. <https://doi.org/10.1007/s40789-018-0228-z>
- [11] Shved, M.; Pyshyev, S.; Prysiashnyi, Y. Effect of Oxidant Relative Flow Rate on Obtaining Raw Material for Pulverized Coal Production from High-Sulfuric Row Grade Coal. *Chem. Chem. Technol.* **2017**, *11*, 236–241. <https://doi.org/10.23939/chcht11.02.236>
- [12] Zelenskii, O.I. Modern Trends in the Use of Nonmetallurgical Additives in the Coke Production. *J. Coal Chem.* **2023**, *3*, 21–28.
- [13] Nag, D.; Karmakar, Sh.; Burgula, L.; Dash, J.; Dash P.S.; Ghorai S. Use of Organic Polymers for Improvement of Coking Potential of Poorcoking Coal. *Int. J. Coal Prep. Util.* **2020**, *40*, 427–437. <https://doi.org/10.1080/19392699.2019.1686365>
- [14] Zelenskii, O.; Vasil'ev, Y.; Sytnik, A.; Desna, N.; Spirina, E.; Grigorov, A. Metallurgical Cokemaking with the Improved Physicochemical Parameters at Avdeevka Coke Plant. *Chem. J. Mold.* **2018**, *13*, 32–37. <https://doi.org/10.19261/cjm.2018.516>
- [15] Wu, Q.; Sun, C.; Zhu, Z.-Z.; Wang, Y.-D.; Zhang, C.-Y. Effects of Boron Carbide on Coking Behavior and Chemical Structure of High Volatile Coking Coal during Carbonization. *Materials* **2021**, *14*, 302. <https://doi.org/10.3390/ma14020302>
- [16] Kumar, A.; Kaur, M.; Kumar, R.; Sengupta, P.R.; Raman V.; Bhatia, G. Effect of Incorporating Nano Silicon Carbide on the Properties of Green Coke Based Monolithic Carbon. *Indian J. Eng. Mater. Sci.* **2010**, *17*, 353–357.
- [17] Jayakumari, S.; Tangstad, M. Transformation of  $\beta$ -SiC from Charcoal, Coal, and Petroleum Coke to  $\alpha$ -SiC at Higher Temperatures. *Metall Mater Trans B* **2020**, *51*, 2673–2688. <https://doi.org/10.1007/s11663-020-01970-1>
- [18] Tomas, P.; Manoj, B. Dielectric Performance of Graphene Nanostructures Prepared from Naturally Sourced Material. *Mater. Today: Proc.* **2021**, *43*, 3424–3427. <https://doi.org/10.1016/j.matpr.2020.09.075>
- [19] Miroshnichenko, D.V.; Saienko, L.; Demidov, D.; Pyshyev, S.V. Predicting the Yield of Coke and its Byproducts on the Basis of Ultimate and Petrographic Analysis. *Pet. Coal* **2018**, *60*, 402–415.
- [20] Miroshnichenko, D.V.; Saienko, N.; Popov, Y.; Demidov, D.; Nikolaichuk, Y.V. Preparation of Oxidized Coal. *Pet. Coal* **2018**, *60*, 113–119.
- [21] Barsky, V.; Vlasov, G.; Rudnitsky, A. Composition and Structure of Coal Organic Mass. 3. Dynamics of Coal Chemical Structure During Metamorphism. *Chem. Chem. Technol.* **2011**, *5*, 285–290. <https://doi.org/10.23939/chcht05.03.285>
- [22] Pyshyev, S.; Zbykovskyy, Y.; Shvets, I.; Miroshnichenko, D.; Kravchenko, S.; Stelmachenko, S.; Demchuk, Y.; Vytrykush N. Modeling of Coke Distribution in a Dry Quenching Zon. *ACS Omega*. **2023**, *8*, 19464–19473. <https://doi.org/10.1021/acsomega.3c00747>
- [23] Pyshyev, S.; Prysiashnyi, Y.; Miroshnichenko, D.; Bilushchak, H.; Pyshyeva, R. Desulphurization and Usage of Medium-Metamorphized Black Coal. 1. Determination of the Optimal Conditions for Oxidative Desulphurization. *Chem. Chem. Technol.* **2014**, *8*, 225–234. <https://doi.org/10.23939/chcht08.02.225>
- [24] Flores, B.D.; Flores, I.V.; Guerrero, A.; Orellana, D.R.; Pohlmann, J.G.; Díez, M.A.; Borrego, A.G.; Osório, E.; Vilela, A.C.F. On the Reduction Behavior, Structural and Mechanical Features of Iron Ore-Carbon Briquettes. *Fuel Process. Technol.* **2017**, *155*, 238–245. <https://doi.org/10.1016/j.fuproc.2016.07.004>

Received: September 11, 2023 / Revised: October 11, 2023 / Accepted: January 11, 2024

## ВПЛИВ ОРГАНІЧНИХ І НЕОРГАНІЧНИХ ДОБАВОК НА ПИТОМІЙ ЕЛЕКТРИЧНИЙ ОПР КОКСУ

**Анотація.** Метою цього дослідження була оцінка впливу як неорганічних (нанопорошків карбиду бору та карбиду кремнію (карборунд)), так і органічної опісноїочої (нафтового коксу) добавок на якість коксу, виробленого в лабораторній печі, включаючи електричну структурність. Аналізуючи результати визначення якості отриманого коксу, можна констатувати, що введення фіксованої кількості (0,25–0,5 мас. %) неспікливих нанодобавок дає змогу регулювати процеси в пластичному стані з метою підвищення міцності коксу. Вплив такої

модифікації на якість коксу істотно залежить від сортового складу вугільної шихти. Використання нанодобавок особливо актуальне для вугільної шихти з поганими спікливими властивостями. Введення 5% нафтового коксу у вугільні шихти приводить до збільшення валового випуску коксу на 1,2-1,3%; зниження зольності коксу на 0,2-0,3%; збільшення загального вмісту сірки в коксі на 0,15-0,23%; погіршення стану як механічної міцності ( $P_{25}$  – на 0,1-0,6%;  $I_{10}$  – на 0,1-0,2%), так і міцності після реакції (CSR – на 0,6-1,0%), реакційної здатності (CRI – на 0,2-0,3%) коксу, а також структурної міцності (CM на 0,3-0,4%), абразивної твердості (AT на 0,7-1,0 мг) і питомого електричного опору ( $\rho$  на 0,002-

0,007 Ом $\times$ см). Отримані дані можуть свідчити про збільшення ступеня впорядкованості структури коксу і появу більшої кількості наноструктур. Крім того, слід зазначити, що різкіше погіршення якості доменного коксу спостерігається у разі використання вугільної шихти, що характеризується нижчим вмістом вугілля ЦЗФ “Свято-Варваринська”.

**Ключові слова:** нафтовий кокс, вугільні шихти, коксування, якість доменного коксу, екологічна структурність, нанопори, модифікація, нанодобавки, карбід бору, карбід кремнію.