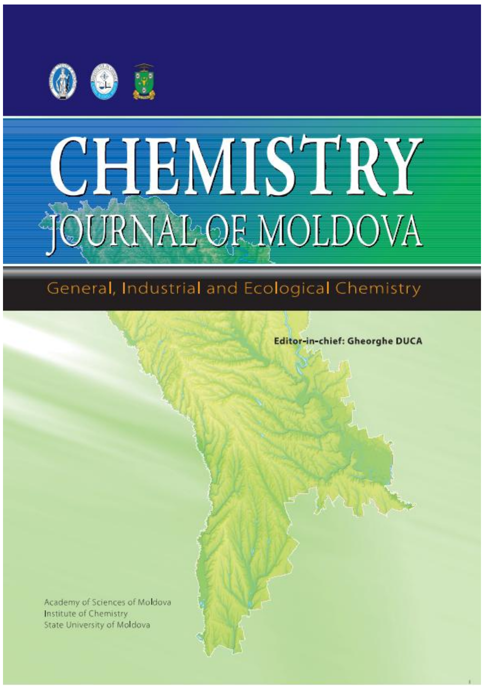

CHEMISTRY JOURNAL OF MOLDOVA.
General, Industrial and Ecological Chemistry

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Accepted version posted online: 29 November 2018

To cite this article: O. Zelenskii, Yu. Vasil'ev, A. Sytnik, N. Desna, E. Spirina, A. Grigorov. Metallurgical Cokemaking with the Improved Physicochemical Parameters at Avdeevka Coke Plant. *Chemistry Journal of Moldova, 2018*, DOI: dx.doi.org/10.19261/cjm.2018.516

CHEMISTRY JOURNAL OF MOLDOVA. General, Industrial and Ecological Chemistry
ISSN (p) 1857-1727 ISSN (e) 2345-1688
http://cjm.asm.md
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Abstract. The article presents the results of studies regarding the improvement of the qualitative characteristics of blast furnace coke obtained from modified coal blend in industrial conditions of Avdeevka Coke Plant. Inorganic corundum powders are applied to modify the coal blend, namely electrocorundum (α-Al_2O_3) and carborundum (α-SiC). It has been found that the introduction of non-caking corundum materials in small concentrations (0.25 wt %) affects the structure of the organic mass of coal as it is assumed that the corundum materials act as centers of crystallization. The influence of a certain type of modifying additive on the quality of coke is significantly dependent on the brand composition of the blend. The use of electrocorundum and carborundum is especially important for blends with reduced caking ability.

Keywords: coal, blend, coke, electrocorundum, carborundum.

Received: 27 September 2018/ Revised final: 15 November 2018/ Accepted: 16 November 2018

Introduction

Coke performs three main functions in a blast furnace: it is a heat source for chemical reactions and phase transformations of a blast furnace charge, a reducing agent in chemical reactions, and a physical support - of a column of charge materials [1]. The normal course of the blast-furnace process depends on the performance of these coke functions, which are determined by the physical-chemical properties of this product [2].

The operation of blast furnaces with high productivity, long service life and low coke consumption is achievable only with the use of high-quality charge materials - iron ore with high iron content and high quality coke produced from coking coals with the necessary mineral composition and low sulfur content. It should be noted that most of coking coals produced in Ukraine have high sulfur content,allowing to obtain, on average, coke with the coke reactivity index (CRI) and coke strength after reaction (CSR) values within 40% [3,4]. In the U.S.A., Germany, Poland, China, Japan metallurgical plants impose very high requirements regarding the quality of blast furnace coke for these parameters (CRI ≤ 30%; CSR ≥ 60%) [2].

Coke consumption for iron blast furnaces in the Ukraine is on average up to 450 kg/t [1] while leading ironmakers in other countries have reduced coke usage to 300 kg/t. The specific coke consumption in Ukraine is much higher, which reduces the economy of smelting cast iron, because coke is the most expensive component of the blast furnace charge. Therefore, leading manufactures substitute coke (up to 40%) with additional fuels, primarily pulverized coal. To get the blast-furnace coke with necessary quality indicators at the existing coal base, coke-makers develop and use techniques that improve quality parameters of coal. One of such methods is the targeted influence of the coke quality by adding non-coking additives into the coal blend: coke dust and fines, anthracite, semi-coke, as well as inorganic additives (finely dispersed oxides of titanium, iron and aluminum) [5].

The use of nanomaterials as additives is known to be effective in improving the wear resistance, strength, crack resistance and other characteristics of hard alloys [6]. For example, Al_2O_3, SiC, B_4C, TiN, TiCN and WC nanopowders have been used successfully as modifying additives [7-9]. In this paper, the task was set to use micropowders of electrocorundum (α-Al_2O_3) and carborundum (α-SiC) as additives in coal blends for the production of metallurgical coke with improved quality parameters.

Experimental

Cokemaking procedure

One of the coke plants in Ukraine, Avdeevka Coke Plant has been selected for research. Cokemaking trials were carried out using metal coke boxes. The box dimensions were as follows: length 200 mm; width 200 mm; height 280 mm. The total mass of the coal batch in the box was 8 kg.

The packing density of the coal blend in the box was 800 kg/m^3 and the moisture content was 8–10%. To attain this density, the appropriate mass of coal was charged in the box corresponding to the density achieved industrially.

Four coking ovens in a coke oven battery No. 1 were selected to study. Four boxes with experimental blend were placed in each coking chamber. The boxes were loaded through the middle charging hole in the coking chamber. The coking time was set to 21 h.

After the oven was pushed and the coke was quenched, the metal boxes were removed from the coke wharf and were water quenched, if necessary.

The additives that were selected for the use in this study, crystalline (α-modification) powders of aluminum oxide (electrocorundum) and silicon carbide (carborundum) with different particle size, were purchased from Private Joint Stock Company ZAPOROZHABRASIVE (Zaporozhe, Ukraine).

Characterization techniques of coal and coke

The technical analysis of coal and coke (volatility, sulphur and ash content) was performed using standard test methods [10-12]. The technical analysis was carried out on dried samples of coal and coke. Samples of coal and coke were dried in an oven for 1 hour at 105 °C and 150 °C respectively.

The mean vitrinite reflection coefficient (R_0) and *vitrinite content* (V_t) were performed using a Petrographic complex “OLYMPUS BX51M”. For the analyses, the samples were prepared by standard methods [13,14].

The chemical composition of the ash was determined by the standard method [15]. *The basicity index* (B_b) and *the base/acid ratio* (I_b) were calculated by the Eqs.(1,2) [16].

$$B_b = \frac{100A^d(Fe_2O_3+CaO+MgO+Na_2O+K_2O)}{(100-V^{daf})(SiO_2+Al_2O_3)} \quad (1)$$

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

$$I_b = \frac{Fe_2O_3+CaO+MgO+Na_2O+K_2O}{SiO_2+Al_2O_3} \quad (2)$$

The coke reactivity index (CRI) and *coke strength after reaction (CSR)* were determined by the standard methods [17].

The physicochemical properties of coke (*structural strength according to Gryaznov, abrasive hardness according to Ginzburg, reactivity, electrical resistivity* and *porosity)* were obtained by appropriate methods [18-20].

Results and discussion

The production blend of the plant from two coal preparation departments was used in this study. To determine the effect of additives on the coke quality, box coking was conducted on two different blends, Blend 1 - obtained from coal blend of ordinary quality and Blend 2 - obtained from coal blend with improved quality.

Table 1 presents the composition and characteristics of the coal used in the experiments and Table 2 presents the chemical composition of the ash, basicity index Eq.(1) and base/acid ratio Eq.(2).

Table 1

Characteristics of coal concentrate and coal blend.

Coal blend	*Supplier*	*Content, %*	*Ash A^d, %*	*Sulphur S^d_t, %*	*Volatility V^{daf}, %*	*Mean vitrinite reflection coefficient R_0, %*	*Vitrinite V_t, %*
1	Toldinskaya Yuzhnaya (Russia)	25.1	7.0	0.15	40.5	0.67	85
	Samsonovskaya Zapadnaya (Ukraine)	38.6	8.4	1.13	36.4	0.97	85
	Yunyaginskiy razrez (Russia)	22.7	8.1	0.68	25.4	0.98	82
	Suhodolskaya Vostochnaya (Ukraine)	3.6	8.1	0.99	24.9	1.30	96
	Kolosnikovskaya (Ukraine)	4	8.6	1.56	32.2	0.70	93
	Samsonovskaya (Ukraine)	3	8.7	2.67	27.0	1.12	92
	Uzlovskaya (Ukraine)	3	8.2	2.21	23.0	1.15	89
	Total	**100**	**8.2**	**1.34**	**29.9**	**0.98**	**89**

Continuation of Table 1

Coal blend	*Supplier*	*Content, %*	*Ash A^d, %*	*Sulphur S^d_t, %*	*Volatility V^{daf}, %*	*Mean vitrinite reflection coefficient R_0, %*	*Vitrinite V_t, %*
	Komsomolskaya (Ukraine)	4	6.1	1.09	37.0	0.88	70
	Prokopevskaya (Russia)	7	7.6	0.49	42.2	0.67	86
	Toldyinskiy razrez (Russia)	15	8.7	0.33	38.9	0.64	83
	Promugol (Russia)	4	9.8	0.72	33.2	1.01	90
	Duvanskaya (Ukraine)	7	8.5	2.04	33.2	0.99	92
	Kievskaya (Ukraine)	6	8.7	2.06	31.3	1.04	93
2	Samsonovskaya (Ukraine)	4	8.9	2.68	31.5	0.99	94
	Pokrovskaya (Ukraine)	15	7.8	0.62	28.3	1.09	86
	Kalininskaya (Ukraine)	4	8.5	1.09	25.0	1.23	90
	Uzlovskaya (Ukraine)	4	8.2	2.21	23.0	1.45	91
	Wellmore (U.S.A.)	6	8.5	0.91	34.1	0.93	70
	Carter Roag (U.S.A.)	14	8.5	0.69	31.8	1.02	92
	Pocahontas (U.S.A.)	10	8.9	0.94	18.0	1.54	73
	Total	**100**	**8.4**	**1.01**	**31.3**	**1.03**	**85**

A^d – ash content of coal in the dry state;
S^d_t – sulphur content of coal in the dry state;
V^{daf} – volatile matter in the dry ash-free state;
R_0 – mean vitrinite reflection coefficient of coal;
V_t – vitrinite content of coal.

Table 2

Chemical composition and basicity of coal blend.

Coal blend	*Chemical composition of ash, %*								*Basicity*	
	SiO_2	*Al_2O_3*	*Fe_2O_3*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*SO_3*	*B_b*	*I_b*
1	51.79	24.47	11.97	1.76	2.80	1.42	1.99	2.28	3.06	0.261
2	50.16	28.33	9.98	1.76	2.63	1.26	2.37	2.04	2.80	0.229

The additives added in the blend were crystalline (α-modification) powders of aluminum oxide (electrocorundum) and silicon carbide (carborundum) with different particle size. These powders were chosen as additives based on the fact that they are mass produced by abrasive companies and have a low cost. Additives were added to the coal blend in the amount of 0.25 wt % by mechanical stirring of the additive with a coal charge for box coking (8 kg). The choice of this range of additives was based on previous studies that showed an optimum level of additives in the blend of 0.25 wt % [21]. Table 3 presents sample compositions.

The technical analysis and CRI/CSR indicators of coke obtained by box coking is given in Table 4. The obtained results show that addition of additives into the coal blend in quantities up to 0.25 wt % has no effect on the ash content of the coke (Table 4).

The dynamics of the effect of additives on the qualitative indices of CRI and CSR of coke is shown in Figures 1 and 2, respectively. The CRI/CSR indexes for the reference coke samples No. 1 and No. 5 were considered as zero. Data showing improvement (decrease) in CRI index values is in the negative area with the sign "–" (Figure 1). The improvement (increase) in CSR index / parameter values (Figure 2) is shown in the positive area with the sign "+".

Table 3

Characteristics of bulk modifying additives.

Sample	*Additive*	*Amount of additive in the sample, wt %*	*Particle size, μm*
1	Standard coal blend – Variant 1	without additives	–
2	α-Al_2O_3	0.25	40-80
3	α-SiC v/g*	0.25	8-12
4	α-SiC	0.25	125-150
5	Standard coal blend – Variant 2	without additives	–
6	α-Al_2O_3	0.25	40-80
7	α-SiC v/g	0.25	8-12
8	α-SiC	0.25	125-150

** v/g – vibro-ground treatment.*

Figures 1 and 2 shows that the optimal results for improving coke quality from the Blend 1 were obtained while using the following additives:

- α-Al_2O_3 (0.25 wt %) with a registered 4.1% decrease in CRI and a 5.5% increase in CSR;
- α-SiC v/g (0.25 wt %) with a recorded 3.7% decrease in CRI and a 6.1% increase in CSR;
- α-SiC (0.25 wt %) with a registered 5.2% decrease in CRI and a 6.2% increase in CSR.

Other additives either slightly worsen the CRI and CSR values or maintain the level of the standard coke within the accuracy of measurement. The improvement in CRI/CSR indices of coke characteristics with additives No. 2, 3 and 4 was also confirmed by some other analyses of the physicochemical properties of coke (structural strength according to Gryaznov, reactivity), as follows from the data presented in Table 5.

Table 4

Technical analysis and values of CRI/CSR for coke produced.

Sample	*Ash* A^d, %	*Volatility* V^{daf}, %	*Sulphur* S^d_t, %	*Coke reactivity index CRI, %*	*Coke strength after reaction CSR, %*
1	11.2	0.3	0.81	37.3	39.5
2	11.6	0.2	0.84	33.2	45.0
3	11.5	0.6	0.82	33.6	45.6
4	11.4	0.4	0.81	32.1	45.7
5	10.6	0.2	0.72	34.2	46.7
6	10.6	0.2	0.71	33.4	47.1
7	11.1	0.3	0.74	34.8	47.4
8	10.6	0.2	0.72	32.2	49.3

A^d – ash content of coke in the dry state;
V^{daf} – volatile matter in the dry ash-free state;
S^d_t – sulphur content of coke in the dry state;
CRI – coke reactivity index;
CSR – coke strength after reaction with CO_2.

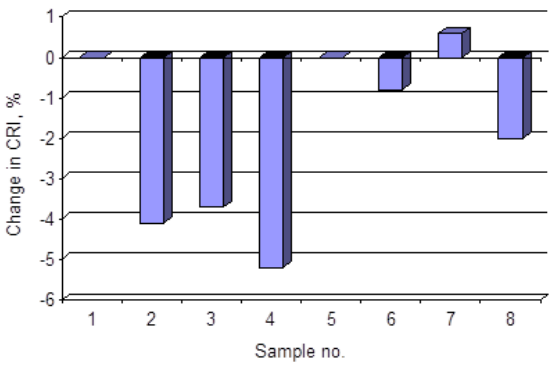

Figure 1. The dependence of various additives influences on CRI coke characteristics.

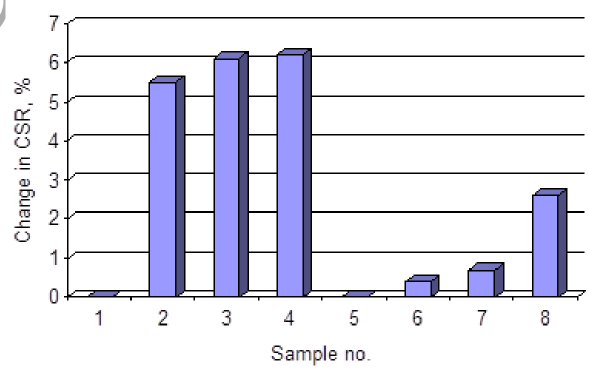

Figure 2. The dependence of various additives influences on CSR coke characteristics.

Table 5

Physicochemical parameters of experimental cokes.

Sample No.	*Structural strength according to Gryaznov, %*	*Abrasive hardness according to Ginzburg, mg*	*Electrical resistivity, Ω·cm*	*Reactivity, $cm^3/g·sec$*	*Porosity, %*
1	83.0	95.7	0.163	0.37	50.2
2	89.1	103.1	0.207	0.26	47.1
3	87.1	101.1	0.230	0.23	49.9
4	87.0	100.6	0.248	0.21	49.3
5	83.3	96.7	0.210	0.65	50.1
6	88.0	105.1	0.193	0.53	47.3
7	86.0	105.5	0.163	0.50	50.3
8	81.3	100.6	0.223	0.46	49.2

By action on the indicators of CSR and CRI, inorganic additives may be divided into two: those that improve these indicators and those that significantly reduce CSR [22]. The first group comprises aluminum oxide, compounds of silicon and minerals: apatite, muscovite and orthoclase. Additives that improve the properties of coke, i.e. increase CRI and decrease CSR include magnesium oxide, iron compounds (Fe_2O_3, $FeCO_3$, $FeO·Fe_2O_3$, FeS_2) and calcium oxides.

According to literature data, the addition of aluminum oxide and silicon compounds reduces the content of isotropic textures in the coke and increases the content of fine mosaic textures [22]. Thus, the introduction of inorganic additives in small concentrations affects the structure of the organic mass of coal, since it is assumed that the additives act as crystallization centers at the stage of plastic state of the coal blend.

Conclusions

The introduction of a specific quantity (0.25 wt %) of non-clinkering additives allows the modification of the processes that occur when the coal blend is plastic, with consequent improvement in coke strength.

The obtained results show that coke reactivity index (CRI) and coke strength after reaction (CSR) values of the coke are improved by introducing modifying additives in the coal blend in quantities of 0.25 wt %.

It was shown that positive results are obtained along with the additives 2 (α-Al_2O_3 0.25 wt %), 3 (α-SiC v/g 0.25 wt %) and 4 (α-SiC 0.25 wt %).

The influence of each specific additive on the coke properties depends significantly on the rank composition of the blend. Thus, the improvement in the coke quality with the addition of additives was obtained with Blend 1, and, accordingly, there was no improvement in the quality of the coke obtained from Blend 2 with the addition of additives. Therefore, it can be concluded that the use of these additives is relevant for batch materials with reduced caking index.

References

1. Downie, S.R.; Plunkett, G.M.; Watson, M.F.; Spalik, K.; Katz-Downie, D.S.; Valiejo-Roman, C.M.; Terentieva, E.I.; Troitsky, A.V.; Lee, B.-Y.; Lahham, J.; El-Oqlah, A. Tribes and clades within *Apiaceae* subfamily *Apioideae*: the contribution of molecular data. Edinburgh Journal of Botany, 2001, 58(2), pp. 301–330. Filatov, Y.V.; Kovalev, E.T.; Shulga, I.V.; Kaufman, S.I.; Kolomiychenko, A.I. Theory and practice of production and application of blast-furnace coke of improved quality. Naukova dumka: Kiev, 2011, 128 p. (in Russian). http://www.ndumka.kiev.ua/
2. Zolotukhin, Yu.A.; Andreichikov, N.S.; Kukolev, Ya.B. Quality requirements on coke for blast furnaces operating with coal-dust fuel. Coke and Chemistry, 2009, 52(3), pp. 110-115. DOI: https://doi.org/10.3103/S1068364X09030053
3. Ryshchenko, A.I.; Kovalev, E.T.; Shulga, I.V.; Miroshnichenko, D.V.; Shmalko, V.M. The influence of the properties of coals on the reactivity and the post-reactive strength of coke. Coal Chemistry Journal, 2009, 5-6, pp. 11-17. (in Russian). http://www.ukhin.org.ua
4. Gusak, V.G.; Rubchevskiy, V.N.; Tkalich, G.M.; Chernyshov, Yu.A.; Ovchinnikova, S.A.; Podlubnyy, A.V.; Kovalev, E.T.; Drozdnik, I.D.; Kaftan, Yu.S. Producing high-quality coke from blends of domestic and imported coal at PAO Zaporozhkoks. Coke and Chemistry, 2014, 57(4), pp. 141-146. DOI: https://doi.org/10.3103/S1068364X14040024
5. Zelenskii, O.I. Modern trends in the use of nonmetallurgical additives in the coke production. Coal Chemistry Journal, 2013, 3-4, pp. 21-28. (in Russian). http://www.ukhin.org.ua/
6. Ryzhonkov, D.I.; Levina, V.V.; Dzidziguri, E.L. Nanomaterials: Manual, BINOM: Moscow, 2008, 365 p. (in Russian). http://www.lbz.ru/
7. Tsikarev, D.A. Effect of mineral additives in coal blends on the properties of blast furnace coke. Coke and Chemistry, 1993, 4, pp. 30-32. (in Russian). http://vlib.ustuarchive.urfu.ru/cox_chem/index.html
8. Semchenko, G.D.; Panasenko, M.A.; Zelenskii, O.I.; Baklan, V.Yu. Carbon precursors for synthesizing oxygen-free refractory new formations in carbon-graphite materials. Refractories and Industrial Ceramic, 2010, 51(3), pp. 193-196. DOI: https://doi.org/10.1007/s11148-010-9287-4.
9. Fuping, T.; Xiaoyang, L.; Xu, W.; Xibo, M. Coal blending coking technology. China Patent, 2010, No. 102559230A.
10. ISO 1171:2010. Solid mineral fuels. Determination of ash. https://www.iso.org/standard/55944.html
11. ISO 334:2013. Solid mineral fuels. Determination of total sulphur. Eschka method. https://www.iso.org/standard/63441.html
12. ISO 562:2010. Hard coal and coke. Determination of volatile matter. https://www.iso.org/standard/55943.html
13. ISO 7404-5:2009. Methods for the petrographic analysis of coals. Part 5: Method of determining microscopically the reflectance of vitrinite. https://www.iso.org/standard/42832.html
14. ISO 7404-3:2009. Methods for the petrographic analysis of coals. Part 3: Method of determining maceral group composition. https://www.iso.org/standard/42831.html
15. GOST 10538-87. Solid fuel. Methods for determination of chemical composition of ash. (in Russian).

16. Lyalyuk, V.P.; Sokolova, V.P.; Shmeltser, E.O.; Timofeeva, D.Yu.; Beryeza V.V. Predicting the reactivity and hot strength of coke on the basis of ash basicity. Coke and Chemistry, 2014, 57(6), pp. 238-244.
DOI: https://doi.org/10.3103/S1068364X14060052
17. ISO 18894:2018. Coke. Determination of coke reactivity index (CRI) and coke strength after reaction (CSR). https://www.iso.org/standard/72266.html
18. Sklyar, M.G.; Tutunnikov, Yu.B. Chemistry of solid fossil fuels. Laboratory practical work. Vischa shkola: Kiev, 1985, 247 p. (in Russian).
19. SSU 7664:2014. Coke. Method for determination of reactivity. (in Ukrainian).
20. ISO 1014:1985. Coke. Determination of true relative density, apparent relative density and porosity. https://www.iso.org/standard/5483.html
21. Zelenskii, O.I.; Gaidaenko, A.S.; Tkalich, G.M. Coking of batch with modifying additives at ChAO Zaporozhkoks. Coke and Chemistry, 2017, 60(5), pp. 189-192.
DOI: https://doi.org/10.3103/S1068364X17050088
22. Price, J.T.; Gransden, J.F.; Khan, M.A.; Ryan, B.D. Effect of selected minerals on high temperature properties of coke. 2-nd International Cokemaking Congress; The Institute of Materials: London, 1992, vol. 2, pp. 286-292.