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PREPARATION OF OXIDIZED COAL

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Abstract

The oxidation index is an important supplementary characteristic of coal and coal blends, indicating the change in coking properties during oxidation. The coke obtained from coal blend containing poorly coking oxidized coal has a higher content of isotropic carbon and a lower content of anisotropic carbon. That explains its increased reactivity and impaired mechanical and strength after reaction. The oxidation throughout storage is the greatest for small coal classes (<0.5 mm). Preliminary removal of <0.5 mm oxidized coal markedly improves the reactivity and also the mechanical and coke strength after reaction. A method of preparing oxidized coal for coking is proposed: finer grinding (until the content of the ≤1 mm class is 100%). That considerably reduces the influence of the oxidized coal on the quality of the blast-furnace coke produced.

Keywords: coal; oxidation; coal preparation; coke; isotropic carbon.

1. Introduction

The intensification of blast-furnace operation calls for stable high quality of the coke employed. Fluctuation in the coke quality disrupts blast-furnace operation, with loss of productivity and overconsumption of the coke. In such conditions, the composition and properties of the coal blends must be corrected so as to reduce these effects.

Accordingly, one of the best means of improving the stability of blast-furnace operation today is to ensure uniform coke quality [1]. We know that one of the main factors responsible for constant coke quality is constant quality of the coal from which it is produced [2-3].

Recently, marked decline in coke quality in particular, in mechanical and strength of after reaction the coke has been observed with unchanged composition of the coal blends. This may be attributed to the introduction of domestic and imported oxidized coal in the blends.

Accordingly, we need to correct the storage, preparation, and use of oxidized coal at coke plants. In the present work, we investigate means of preventing the impact of oxidized coal on the coke produced, by optimizing its preparation.

2. Experimental

The determination of oxidation and degree of oxidation was carried out accordingly DSTU 7611:2014 Method for determination of the oxidation and degree of the oxidation. The determination of proximate analysis was carried out accordingly ISO 17246:2010 Coal – Proximate analysis. The determination of ultimate analysis was carried out accordingly ISO 17247:2013 Coal – Ultimate analysis.

The determination of petrographic analysis was carried out accordingly ISO 7403–3:2009 Methods for the petrographic analysis of coals – Part 3: Method of determining maceral group composition; ISO 7404–5:2009 Methods for the petrographic analysis of coals – Part 5: Methods of Determining microscopically the reflectance of vitrinite.

The determination of coke reactivity index (CRI) and coke strength after reaction (CSR) was carried out accordingly ISO 18894:2006 Coke-Determination of coke reactivity index (CRI) and coke strength after reaction (CSR). The determination of expansion pressure was carried out accordingly DSTU 8724:2017 Coal and charge based on it. Method for determination of expansion pressure that occurs during coking.

The determination of size analysis of coals was carried out accordingly ISO 1953:2015 Hard coal. Size analysis by sieving. The determination of plastometric indices was carried out accordingly GOST 1186–2014 Hard Coals. Method for determination of plastometric indices.

Microstructure of laboratory coke was determined by optical microscopy. Previously prepared 10 mm coke sample was used for analysis. The sample preparation included grinding and polishing. The sample was ground and polished under top water using automatic sample preparation unit. The 600 grit size send paper was used for grinding and microcloth containing alumina aqueous suspension of 0,3 φm granulation was used in the polishing phase. After polishing, the sample was rinsed with water and alcohol and dried by hot air.

Microstructure was analyzed by the «Olympus GX S1» with digital camera DP 70. Microstructure was observed at different magnifications under polarized light.

The structural characteristics of the coal were calculated from formulas given in [12]. The aromatic content of the structure f_a is

$$f_a = 1.007 - 0.3857(H/C) - 0.3725(O/C) \qquad (1)$$

The degree of molecular association of the coal cA is

$$cA = 1 - \frac{H + 0.125(O + N + S)}{0.333C} \qquad (2)$$

3. Results and discussions

Table 1 presents the proximate analysis and oxidation characteristics of Pokrovskoe coal of different size classes after open storage for four months [4-5]. Coal of the <0.5 mm class is the most oxidized throughout storage, as we see in Table 1. This corresponds to elevated oxidation index Δt and degree of oxidation d_0, which are more than double those for coal of other size classes. In our view, the <0.5 mm class is effectively an additive to the blend.

Table 1. Proximate analysis and oxidation characteristics of Pokrovskoe coal of different size classes after open storage

Size analysis		Proximate analysis, %			Oxidation characteristics	
class, mm	yield, %	A^d	S^d_t	V^{daf}	Δt, °C	d_0, %
>25	8.1	8.0	0.75	29.5	3	6.7
25–13	10.8	8.8	0.77	29.8	3	6.8
13–6	18.0	8.1	0.85	29.6	3	7.3
6–3	14.5	8.0	0.80	29.4	3	6.7
3–1	17.1	8.2	0.79	29.0	3	6.8
1.0–0.5	6.3	8.2	0.81	28.8	3	7.2
<0.5	25.2	10.3	0.75	27.5	8	17.5

The ultimate composition and structural characteristics of the coal in Table 2 show that the oxidation of <0.5 mm coal sharply reduces the carbon and hydrogen content and leads to extreme increase in the oxygen content. Accordingly, the degree of aromatic structure and molecular association of the coal's organic mass are significantly less for the <0.5 mm class than for the other coal.

We now determine the change in coke quality when using both oxidized and unoxidized Pokrovskoe coal in the blend and assess the possibility of reducing the influence of the oxidized coal by removing the <0.5 mm class.

Table 3 presents the properties and petrographic characteristic of the coals in the experimental blends and the characteristics of Pokrovskoe coal in three states: (1) initial unoxidized coal; (2) partially oxidized coal; (3) partially oxidized coal after the removal of the <0.5 mm class.

Table 2. Ultimate composition and structural characteristics of the coal's organic mass

Size class, mm	Ultimate composition, %					Degree of aromatic structure f_a	Molecular association cA
	C^{daf}	H^{daf}	N^{daf}	S^d_t	O^{daf}_d		
>25	90.05	5.55	1.85	0.75	1.80	0.716	0.716
25–13	89.76	5.38	1.86	0.77	2.23	0.742	0.742
13–6	89.27	5.31	1.87	0.85	2.70	0.743	0.743
6–3	89.45	5.29	1.88	0.80	2.58	0.744	0.744
3–1	88.45	5.13	1.88	0.79	3.75	0.746	0.746
1.0–0.5	88.34	5.08	1.89	0.81	3.88	0.747	0.747
<0.5	78.04	4.65	1.85	0.75	14.71	0.698	0.698

Table 3. Properties and petrographic characteristics of coal blends

Supplier	Proximate analysis, %			Plastometric characteristics, mm		Mean vitrinite reflection coefficient R_0, %
	A^d	S^d_t	V^{daf}	x	y	
Sentyanovskaya mine	5.6	0.95	31.1	22	18	1.06
Kuzbassrazrezugol enrichment facility	7.4	0.41	25.1	38	10	1.05
Pokrovskoe facility, initial state	8.9	0.78	29.0	11	15	1.13
Pokrovskoe facility, partially oxidized	8.8	0.81	29.1	12	12	1.11
Pokrovskoe facility, partially oxidized, <0.5 mm class removed	8.2	0.80	29.4	12	14	1.12

Analysis of Table 3 indicates that partial oxidation markedly impairs the coking properties. Thus, the plastic-layer thickness *y* falls from 15 to12 mm. The other properties are unchanged. After removing the < 0.5 mm class, *y* is restored practically to its initial value. Some reduction in ash content is observed but is unrelated to oxidation.

Table 4 presents the composition of the experimental blends. The differ only in the degree of oxidation and blends size composition of the Pokrovskoe coal, with constant of the other components.

Table 4. Composition of experimental blends

Supplier	Content (%) in blend 1	2	3
Sentyanovskaya mine	5	5	5
Kuzbassrazrezugol' enrichment facility	15	15	15
Pokrovskoe facility, initial state	80	0	0
Pokrovskoe facility, partially oxidized	0	80	0
Pokrovskoe facility, partially oxidized, <0.5 mm class removed	0	0	80
Total	100	100	100

Table 5 summarizes the properties of the experimental blends, while Table 6 presents their vitrinite reflection coefficients. Analysis of these data indicates that the addition of partially oxidized Pokrovskoe coal to the blend mainly affects its coking power, with decrease in plastic-layer thickness *y* from 15 to 10 mm. Note that removing the <0.5 mm class reduces the oxidation characteristics Δt and d_0 somewhat.

The presence of the partially oxidized coal in the blend markedly affects the expansion pressure, which falls sharply from 16.8 to 2.7 kPa. Removal of the <0.5 mm class increases the expansion pressure to 15.6 kPa, which is close to its initial value. As we see in Table 6, the presence of partially oxidized coal considerably increases the oxygen content in the blend, while reducing the carbon and hydrogen content. Removal of the <0.5 mm class somewhat restores the initial ultimate composition.

Table 5. Properties of experimental blends

Blend	Proximate analysis, %			Plastometric characteristics, mm		Expansion pressure P^h_{max}, kPa
	A^d	S^d_t	V^{daf}	x	y	
1	8.5	0.73	28.5	11	15	16.8
2	8.4	0.76	28.6	19	10	2.7
3	8.0	0.75	28.8	16	13	15.6

Table 6. Vitrinite reflection coefficient and ultimate composition of experimental blends

Blend	Mean vitrinite reflection coefficient R_0,%	Ultimate composition, %				
		C^{daf}	H^{daf}	N^{daf}	S^d_t	O^{daf}_d
1	1.12	87.28	5.82	5.82	0.70	4.30
2	1.10	86.21	5.74	5.74	0.74	5.42
3	1.11	87.07	5.80	5.80	0.75	4.47

We conclude from the coking of the experimental blends in a 5-kg laboratory furnace (designed by the Ukrainian Coal-Research Institute) that the presence of partially oxidized coal reduces the mechanical strength of the coke by 1.7% in terms of the crushability M_{25}, with 1.0% increase in the wear index M_{10} (Table 7). The total content of anisotropic carbon in the coke is reduced from 80 to 73%, while the content of isotropic carbon rises from 4 to 12%. In other words, the coke becomes less ordered (Table 8). Note that our results confirm the simultaneous change in mechanical strength and expansion pressure of the experimental blends reported in [6-8].

Table 7. Quality of coke from experimental blends

Blend	Proximate analysis, %			Mechanical strength, %		Reactivity and strength after reaction, %	
	A^d	S^d_t	V^{daf}	M_{25}	M_{10}	CRI	CSR
1	11.1	0.65	0.7	90.0	8.1	38.6	49.1
2	11.2	0.62	0.8	88.3	9.1	40.5	44.9
3	10.4	0.63	0.7	89.8	8.3	34.4	53.6

Table 8. Microstructure of coke

Blend	Inertinite	Isotropic carbon (I)	Anisotropic carbon (A)			
			mosaic (M)	striated (S)	plate (P)	ΣA
1	16	4	78	2	0	80
2	15	12	73	0	0	73
3	17	6	75	2	0	77

Along with the loss of mechanical strength and decrease in the content of anisotropic carbon, we note deterioration in the reactivity *CRI* and strength after reaction *CSR* of the coke.

Specifically, *CRI* increases from 38.6 to 40.5%, while *CSR* decreases from 49.1 to 44.9%. For coke from blend 3, *CRI* and *CSR* are better than for the initial blend, thanks to the removal of the <0.5 mm Pokrovskoe coal.

After removal of the <0.5 mm class, the M_{25} and M_{10} values of the coke are practically the same as for coke from blend containing unoxidized Pokrovskoe coal. After removal of the <0.5 mm class, the *CRI* and *CSR* values are better than for blend 1.

Our results indicate that it is advisable to use oxidized coals separately from the other flotation concentrate for example, as a fuel in thermal power stations or as an additive to coal blend in the production of the special types of coke.

We now consider the influence of the degree of grinding of oxidized coal in coking blend on the coke quality.

Other researchers have reached a conclusion stated as follows by Gryaznov [9]: "Since the coking of coal grains is a surface process, the best coking will be observed when poorly coking components are ground more finely, while satisfactorily coking components are ground more coarsely. This will also reduce the internal stress in the coke."

Currently, Ukraine is importing large quantities of poorly coking coal and petrographically nonuniform coals, which is often oxidized. Accordingly, it is of interest to assess the prospects for reducing the negative influence of such coal on coke quality by grinding it more finely.

Tables 9 and 10 present the properties and petrographic characteristics of the coals in the experimental blend. As we see, the properties of the coal samples correspond to their rank assignments.

Table 9. Properties of coal in blends

Supplier	Proximate analysis, %			Plastometric characteristics, mm		Oxidation index Δt, °C
	A^d	S^d_t	V^{daf}	x	y	
Taldinskii mine	8.7	0.62	38.2	39	10	1.0
Shchedrukhinskaya enrichment facility, sample 1	8.0	0.63	38.9	33	11	4.0
Shchedrukhinskaya enrichment facility, sample 2	7.6	0.42	39.4	32	10	10.0
Duvanskaya enrichment facility	7.1	1.23	33.4	13	21	1.0
Wellmore	7.0	1.08	33.7	23	19	1.0
Pokrovskoe facility	8.6	0.75	27.7	13	13	1.0
Bochatskii mine, sample 1	8.0	0.31	24.8	32	10	2.0
Bochatskii mine, sample 2	8.0	0.36	26.3	33	9	11.4
Pocahontas	7.7	0.82	17.9	8	12	2.0

Table 10 Petrographic characteristics of coal in blend

Supplier	Petrographic composition, %					Mean vitrinite reflection coefficient R_0, %
	Vt	Sv	I	L	ΣFC	
Taldinskii mine	73	2	2	2	25	0.67
Shchedrukhinskaya enrichment facility, sample 1	81	0	0	2	17	0.66
Shchedrukhinskaya enrichment facility, sample 2	82	0	0	2	16	0.61
Duvanskaya enrichment facility	88	0	0	3	9	1.00
Wellmore	78	0	0	4	18	0.96
Pokrovskoe facility	87	1	1	2	10	1.19
Bochatskii mine, sample 1	48	1	1	1	51	1.08
Bochatskii mine, sample 2	55	1	1	1	44	1.07
Pocahontas	74	0	0	0	26	1.58

Supplier	Vitrinite reflection, %					
	0.50–0.64	0.65–0.89	0.90–1.19	1.20–1.39	1.40–1.69	1.70–2.59
Taldinskii mine	73	2	2	2	25	
Shchedrukhinskaya enrichment facility, sample 1	81	0	0	2	17	
Shchedrukhinskaya enrichment facility, sample 2	82	0	0	2	16	
Duvanskaya enrichment facility	88	0	0	3	9	
Wellmore	78	0	0	4	18	
Pokrovskoe facility	87	1	1	2	10	
Bochatskii mine, sample 1	48	1	1	1	51	
Bochatskii mine, sample 2	55	1	1	1	44	
Pocahontas	74	0	0	0	26	

Marked oxidation of the petrographically uniform coal from Shchedrukhinskaya mine and the petrographically nonuniform coal from Bochatskii mine changes many of their properties. For example, volatile matter is higher in the oxidized coal, while the plastic-layer thickness is less. That significantly affects the coking properties, as will be shown later. The petrographic characteristics are partially unchanged, as noted in [10].

Table 11 presents the composition of the experimental blends containing oxidized coal. Blend preparation is as follows. Blend 1 is average coking blend used at Zaporozhcoke, produced by grinding until the content of the ≤3 mm class is 80%. In blend 2, 10% of the unoxidized Shchedrukhinskaya coal (sample 1) is replaced by oxidized coal of the same type (sample 2). Otherwise, blend preparation is unchanged. In blend 3, the oxidized Shchedruk-hinskaya coal is ground until the content of the ≤1 mm class is 100%. As before, the remainder of the blend is ground until the content of the ≤3 mm class is 80%.

Table 11. Composition of experimental blends

Supplier	Content (%) in blend					
	1	2	3	4	5	6
Taldinskii mine	20	20	20	30	30	30
Shchedrukhinskaya enrichment facility, sample 1	10	0	0	0	0	0
Shchedrukhinskaya enrichment facility, sample 2	0	10	10	0	0	0
Duvanskaya enrichment facility	10	10	10	10	10	10
Wellmore	18	18	18	18	18	18
Pokrovskoe facility	35	35	35	25	25	25
Bochatskii mine, sample 1	0	0	0	10	0	0
Bochatskii mine, sample 2	0	0	0	0	10	10
Pocahontas	7	7	7	7	7	7

Blends 4–6 are produced analogously but with petrographically nonuniform Bochatskii coal (samples 1 and 2), instead of the Shchedrukhinskaya coal.

Analysis of Table 12 indicates that, in the experimental blends, which have a relatively low content of oxidized coal, the ash content, total sulfur content, volatile matter, plastic-layer thickness, and vitrinite reflection coefficient are practically the same. Consequently, we may assess the influence of the blend preparation on the coke quality.

Table 12. Properties of experimental blends

Blend	Proximate analysis, %			Plastometric characteristics, mm		Mean vitrinite reflection coefficient R_0, %
	A^d	S^d_t	V^{daf}	x	y	
1	8.1	0.82	31.9	22	14	1.00
2	8.0	0.80	31.9	22	14	0.99
3	8.0	0.80	31.9	21	14	0.99
4	8.1	0.78	31.5	24	14	0.99
5	8.1	0.78	31.7	24	13	0.99
6	8.1	0.78	31.7	24	13	0.99

We conclude from the coking of the experimental blends in a 5-kg laboratory furnace (designed by the Ukrainian Coal-Research Institute) that the presence of partially oxidized coal Shchedrukhinskaya enrichment facility, sample 2 and petrographically nonuniform coal impairs the crushability reactivity, and coke strength after reaction (Table 13).

As already noted, the introduction of oxidized coals has practically no influence on the blend-in particular, on the volatile matter and plastic-layer thickness, which are generally used to assess the blend properties. However, as is evident from the coking results, these characteristics are insufficient to assess the change in coking properties of the blend on introducing oxidized coal.

Table 13. Quality of coke from experimental blends

Blend	Proximate analysis, %			Mechanical strength, %		Reactivity and strength after reaction, %	
	A^d	S^d_t	V^{daf}	M_{25}	M_{10}	CRI	CSR
1	10.7	0.74	0.3	92.9	5.8	32.6	52.7
2	10.8	0.72	0.2	91.7	6.3	33.5	51.2
3	10.9	0.72	0.3	92.5	6.1	32.7	52.6
4	10.6	0.70	0.4	92.8	5.9	32.8	52.4
5	10.8	0.71	0.2	91.4	6.2	34.0	50.3
6	10.7	0.71	0.3	92.7	6.0	32.9	51.9

The volatile matter and plastic-layer thickness are also practically unchanged during oxidation (Table 9). Accordingly, we may suppose that the oxidation index Δt is an important supplementary characteristic of coal and coal blends, reflecting the change in coking properties on oxidation.

Finer crushing of poorly coking oxidized coal practically eliminates its effect on coal quality specifically on M_{25}, M_{10}, CRI, and *CSR.*

4. Conclusions

The oxidation index is an important supplementary characteristic of coal and coal blends, indicating the change in coking properties during oxidation. The coke obtained from coal blend containing poorly coking oxidized coal has a higher content of isotropic carbon and a lower content of anisotropic carbon. That explains its increased reactivity and impaired mechanical and strength after reaction.

The oxidation throughout storage is the most for small coal classes (<0.5 mm). Preliminary removal of <0.5 mm oxidized coal markedly improves the reactivity and also the mechanical and coke strength after reaction.

A method of preparing oxidized coal for coking is proposed: finer grinding (until the content of the ≤1 mm class is 100%). That considerably reduces the influence of the oxidized coal on the quality of the blast-furnace coke produced.

Symbols

A^d	*ash content of coal in the dry state, %;*
V^{daf}	*volatile matter in the dry ash-free state, %;*
S_t^d	*sulphur of coal in the dry state, %;*
cA	*the degree of molecular association;*
f_a	*the aromatic content of the structure;*
R_0	*mean vitrinite reflection coefficient, %;*
Vt	*vitrinite, %;*
Sv	*semivitrinite, %;*
I	*inertinite, %;*
L	*liptinite, %;*
ΣFC	*sum of fusinized components, %;*
ΣA	*sum of anisotropic texture of carbon in coke, %;*
Δt	*oxidation index, °C;*
d_0	*degree of oxidation, %;*
y	*thickness of the plastic layer, mm;*
$P^h{}_{max}$	*expansion pressure of coal (blend), kPa;*
CRI	*coke reactivity index, %;*
CSR	*coke strength after reaction, %;*
I	*isotropic texture of carbon in coke, %;*
M	*mosaic texture of carbon in coke, %;*
S	*striated texture of carbon in coke, %;*
P	*plate texture of carbon in coke, %;*
C^{daf}, H^{daf}, N^{daf}, $O^{daf}{}_d$	*carbon, hydrogen, nitrogen and oxygen in the dry, ash-free state, %;*
M_{10}, M_{25}	*indices of resistance of coke abrasion and fragmentation, respectively, %.*

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