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OXIDATION OF POKROVSKOE COAL IN LABORATORY AND NATURAL CONDITIONS
2. LABORATORY COKING OF EXPERIMENTAL COAL BLENDS

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Abstract

When Pokrovskoe coal oxidized in laboratory conditions (at 140 °C) and in natural conditions (between −1 and +22 °C) is used in coal blends, the bulk density is increased, its plastic–viscous properties are impaired, the expansion pressure is reduced, the content of carbon and hydrogen is reduced, the oxygen content increases, the yield of coke, tar, and benzene falls, and the yield of carbon dioxide, pyrogenetic water, and gas increases. The oxidation is greatest for coal smaller than 0.5 mm. Accordingly, the overall oxidation of the coal is determined not only by the duration and conditions of storage but also by its content of dusty classes. Oxidation reduces the expansion pressure of the coal blends, with loss of mechanical strength of the coke produced. The coke produced from coal blends containing oxidized coal has a higher proportion of isotropic coal, which increases its reactivity and impairs its mechanical and strength after reaction with CO_2.

Keywords: coal; oxidation; expansion pressure; coke quality.

1. Introduction

The oxidation temperature considerably affects the properties of Pokrovskoe coal, as established in [1]. In laboratory oxidation (at 140°C), its plastic–viscous properties and ignition temperature are impaired; in natural oxidation, this change is not as pronounced. The oxidetion processes in natural (between-1 and +22°C) and laboratory (at 140°C) conditions are different. Accordingly, data regarding the change in coal properties in these processes will not be comparable. In the present work, we determine the influence of the content of oxidized Pokrovskoe coal in coking blends on the coke quality and yield of coke and byproducts.

2. Experimental

2.1 Quality of coal blends with Pokrovskoe coal oxidized at 140°C

The oxidation of coal of different rank is basically the same, as shown in [2-3]. It occurs in three main stages: initial oxidation, intense oxidation, and saturation. Accordingly, for laboratory coking, we use Pokrovskoe coal with three levels of oxidation: unoxidized coal (the initial sample); coal after the first stage of oxidation; and coal after intense oxidation. The coal blends used in laboratory coking corresponds to the mean rank composition of coal blends used at Ukrainian coke plants (Table 1).

Coal blend 1 consists of unoxidized coal; coal blend 2 contains Pokrovskoe coal after the first stage of oxidation; coal blend 3 contains Pokrovskoe coal after intense oxidation. Tables 2 and 3 present the properties of coal blends 1–4. Analysis of Table 2 indicates that the ash content, total sulfur content, and volatile matter are practically the same for blends 1–3. However, the bulk density increases from 0.785 t/m^3 for coal blend 1 to 0.794 t/m^3 for coal blend 3 – that is, by 1.15 %.

Table 1 Composition of laboratory coal blends

Supplier	Rank	Content (%) in coal blends 1	2	3
OOO Primugleservis, Russia	G	10	10	10
Selidovdkaya enrichment facility, Ukraine	G	10	10	10
Kalininskaya enrichment facility, Ukraine	Zh	40	40	40
Pokrovskoe mine, Ukraine	K	20^1	20^2	20^3
Uzlovskaya enrichment facility, Ukraine	OS	10	10	10
Krasnyi Brod mine, Russia	KSN	10	10	10

[1] *Unoxidized coal;*[1] *Coal after initial stage of oxidation;*[1] *Coal after intense stage of oxidation*

Table 2. Technological properties of coal blends

Coal blend	Proximate analysis, %			Bulk density, *BD*, t/m^3	Oxidation according to Ukrainian State Standard DSTU 7611:2014		Oxidation according to Russian State Standard GOST 8930
	A^d	S^d_t	V^{daf}		Δt, °C	d_0, %	OK_p, %
1	7.6	1.02	30.8	0.785	1.0	1.9	0
2	7.5	1.05	30.9	0.791	4.0	7.4	0
3	7.8	1.04	31.1	0.794	6.0	9.9	6

Table 3. Plastic-viscous properties of coal blends

Coal blend	Plastometric indices, mm		Roga index	Free-swelling index	Audibert-Arnu dilation				
	x	*y*	*RI*	*FSI*	t_I ,°C	t_{II} ,°C	t_{III}, °C	*a*, %	*b*, %
1	23	14	52	6	388	438	462	26	43
2	25	11	44	4	393	445	456	25	-24
3	29	10	30	3	393	462	-	20	-

The presence of Pokrovskoe coal with different oxidation significantly changes the oxidation of the coal blends. Thus, the oxidation Δt is 4.0°C for coal blend 2 and 6.0°C for coal blend 3, while the degree of oxidation d_o is 7.4 % and 9.9 %, respectively. Petrographic data permit assessment of the influence of the Pokrovskoe coal only after intense oxidation: the oxidation is 6 % in blend 3.

The Roga index falls from 52 for coal blend 1 to 30 for coal blend 3, with corresponding decline in the thickness of plastic layer from 14 to 10 mm and in the free-swelling index from 6 to 3. The Audibert–Arnu softening temperature t_I (the onset of plastic behavior) falls from 388 °C for coal blend 1 to 393°C for coal blend 3; the maximum contraction temperature t_{II} rises correspondingly from 438 to 462°C.

On introducing oxidized coal, the dilatation falls significantly; it is zero for coal blend 3.

On the basis of Table 4, we may say that the use of oxidized coal in the coal blends reduces the content of carbon (from 86.10 to 85.75–85.55 %) and hydrogen (from 5.62 to 5.58–5.55 %) and increases the oxygen content (from 5.29 to 5.66–5.91%). There is practically no change in the nitrogen and total sulfur content.

Table 4. Ultimate composition of coal blends

Coal blend	Content, % C^{daf}	H^{daf}	N^{daf}	S_t^d	O_d^{daf}
1	86.10	5.62	1.97	1.02	5.29
2	85.75	5.58	1.96	1.05	5.66
3	85.55	5.55	1.95	1.04	5.91

2.2 Quality of coal blends with Pokrovskoe coal oxidized naturally

Table 5 present the characteristics of Pokrovskoe coal after open storage for four months (at temperatures between –1 and +22°C). We see in Table 5 that the <0.5 mm size class differs sharply from the others in terms of ash content (A^d=10.3 %) and volatile matter (V^{daf}=27.5 %). The oxidation (Δt=8°C) and degree of oxidation (d_o=17.5 %) are also a maximum for that class-more than double the values for the other size classes.

Table 5. Characteristics of Pokrovskoe coal by size class

Sieve composition		Proximate analysis, %			Oxidation according to DSTU 7611:2014	
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
1–0.5	6.3	8.2	0.81	28.8	3	7.2
<0.5	25.2	10.3	0.75	27.5	8	17.5
Total		8.8	0.81	29.1	4.0	8.9

The <0.5 mm size class has the lowest carbon and hydrogen content and elevated oxygen content, as we see in Table 6 [4-5]. In addition, the aromatic content of the structure and the degree of molecular association are significantly less for the <0.5 mm class.

Table 6. Ultimate composition and structural characteristics of the organic masses of Pokrovskoe coal, by size class

Class, mm	Ultimate composition, %					Aromatic content of the structure	Degree of molecular association
	C^{daf}	H^{daf}	N^{daf}	S_t^d	O_d^{daf}	f_a	cA
>25	90.05	5.55	1.85	0.75	1.80	0.716	0.797
25–13	89.76	5.38	1.86	0.77	2.23	0.742	0.800
13–6	89.27	5.31	1.87	0.85	2.70	0.743	0.799
6–3	89.45	5.29	1.88	0.80	2.58	0.744	0.800
3–1	88.45	5.13	1.88	0.79	3.75	0.746	0.799
1–0.5	88.34	5.08	1.89	0.81	3.88	0.747	0.799
<0.5	78.04	4.65	1.85	0.75	14.71	0.698	0.738
Total	86.34	5.08	1.77	0.81	6.00	0.734	0.786

On that basis, we may determine the change coke quality between coal blend 1 with unoxidized Pokrovskoe coal and coal blend 2 with oxidized coal and assess the potential for mitigating the effect of the oxidized coal in the coal blend by screening out the most oxidized <0.5 mm class (coal blend 3). Table 7 presents the characteristics of the coal concentrates used in the coal blends and also of Pokrovskoe coal concentrate in the following states:

- initial coal (unoxidized);
- partially oxidized coal (storage time – 4 months);
- partially oxidized coal (storage time – 4 months), after removal of the <0.5 mm class.

Analysis of the sample properties indicates that removing the <0.5 mm class from the partially oxidized concentrate reduces its ash content and also increases the volatile matter and the thickness of the plastic layer. In other words, screening out the <0.5 mm class boosts coal quality.

Table 8 presents the composition of the experimental coal blends. We see that only the oxidation and piece size of the coal varies.

Table 7. Characteristics components of coal blends

Supplier	Rank	Proximate analysis, %			Plastometric indices, mm		Mean vitrinite reflectance, %	Petrographic composition (without mineral impurities), %				
		A^d	S^d_t	V^{daf}	x	y	R_0	Vt	Sv	I	L	ΣFC
Sentyanovskaya mine, Ukraine	Zh	5.6	0.95	31.1	22	18	1.06	89	-	9	2	9
Kuzbassrazrezugol' enterprise, Russia	KS	7.4	0.41	25.1	38	10	1.05	33	3	63	1	65
Pokrovskoe mine, Ukraine (initial coal)	K	8.9	0.78	29.0	11	15	1.13	88	0	10	2	10
Pokrovskoe mine, Ukraine (after storage for 4 months)	K	8.8	0.81	29.1	12	12	1.11	86	0	12	2	12
Pokrovskoe mine, Ukraine (after storage for 4 months and removal of <0.5 mm class)	K	8.2	0.80	29.4	12	14	1.12	89	0	10	1	10

Table 8. Composition of coal blends

Supplier	Rank	Content (%) in coal blend		
		1	2	3
Sentyanovskaya mine, Ukraine	Zh	5	5	5
Kuzbassrazrezugol' enterprise, Russia	KS	15	15	15
Pokrovskoe mine, Ukraine (initial coal)	K	80	0	0
Pokrovskoe mine, Ukraine (after storage for 4 months)	K	0	80	0
Pokrovskoe mine, Ukraine (after storage for 4 months and removal of <0.5 mm class)	K	0	0	80
Total		100	100	100

Table 9 presents the characteristics of the experimental coal blends. Analysis indicates that introducing partially oxidized Pokrovskoe coal greatly affects the plastic-viscous properties of the coal: specifically, it reduces the thickness of the plastic layer y from 15 to 10 mm.

Removing the <0.5 mm class increases y to 13 mm. Note also that the ash content of the coal blend is markedly reduced: to 8.0 %.

Table 9. Characteristics of coal blends

Coal blend	Proximate analysis, %			Plastometric indices, mm		Oxidation according to DSTU 7611:2014		Expansion pressure, kPa
	A^d	S^d_t	V^{daf}	x	y	Δt, °C	d_0, %	P_{max}
1	8.5	0.73	28.5	11	15	1.0	2.2	16.8
2	8.4	0.76	28.6	19	10	3.4	7.5	2.7
3	8.0	0.75	28.8	16	13	2.6	6.0	20.1

Removing the <0.5 mm class also reduces the oxidation of the coal blend (in terms of both Δt and d_o). Change in oxidation of the Pokrovskoe coal in the coal blends greatly affects the expansion pressure. In the presence of the <0.5 mm class, it falls from 16.8 to 2.7 kPa. On screening out the <0.5 mm class, the expansion pressure exceeds its initial value, reaching 20.1 kPa.

In Table 10, we note that the presence of partially oxidized Pokrovskoe coal considerably boosts the oxygen content in the coal blend, with decrease in the carbon and hydrogen content. On screening out the <0.5 mm class, the change in ultimate composition is less pronounced.

Table 10. Petrographic and ultimate composition of coal blends

Coal blend	Mean vitrinite reflectance, %	Petrographic composition (without mineral impurities), %					Ultimate composition, %				
	R_0	Vt	Sv	I	L	$\sum FC$	C^{daf}	H^{daf}	N^{daf}	S_t^d	O_d^{daf}
1	1.12	78	1	19	2	20	87.28	5.82	1.90	0.70	4.30
2	1.10	82	1	16	1	17	86.21	5.74	1.89	0.74	5.42
3	1.11	80	0	18	1	18	87.07	5.80	1.91	0.75	4.47

3. Results and discussion

3.1 Laboratory coking of coal blends with Pokrovskoe coal oxidized at 140°C

The change in properties and composition of coal blend containing oxidized coal changes the yield of coke and byproducts (Table 11), as determined in a 20-g laboratory furnace in accordance with State Standard GOST 18635–73.

The use of oxidized coal in the coal blend reduces the yield of tar, benzene, and unsaturated hydrocarbon and increases the yield of carbon dioxide, pyrogenetic water, and coke-oven gas, in accordance with the results in [6]. The yield of coke tends to decline slightly when oxidized coal is added to the blends.

Table 12 presents the results of laboratory coking in a 5-kg furnace designed by UKHIN [7].

The mechanical strength (M_{25}, M_{10}) in drum tests at UKHIN tends to worsen on adding oxidized coal.

Table 11. Yield of coke and byproducts from coal blends

Coal blend	Yield of coke and byproducts, %								
	coke	tar	raw benzene	C_mH_n	NH_3	H_2S	CO_2	H_2O_{pyr}	gas+losses
1	75.42	3.99	1.18	0.55	0.40	0.33	0.53	3.70	13.90
2	75.08	3.87	1.14	0.53	0.42	0.28	0.58	3.80	14.30
3	75.16	3.84	1.12	0.51	0.39	0.25	0.60	3.82	14.31

Table 12. Quality of laboratory coke from coal blends

Coal blend	Yield of coke, B^d, %	Proximate analysis, %			Mechanical strength, %	
		A^d	S^d_t	V^{daf}	M_{25}	M_{10}
1	75.4	10.2	0.87	0.9	93.3	5.6
2	75.0	10.0	0.86	0.5	92.9	6.0
3	75.2	10.4	0.85	0.4	91.8	6.1

3.2 Laboratory coking of coal blends with Pokrovskoe coal oxidized naturally

The use of oxidized Pokrovskoe coal in the coal blends reduces the yield of coke, tar, benzene, and unsaturated hydrocarbon and increases the yield of carbon dioxide, pyrogenetic water, and coke-oven gas (Table 13). Removing the <0.5 mm class restores the product yields to their original values.

Table 14 presents the results of laboratory coking of the experimental coal blends in a 5-kg furnace designed by UKHIN. We see that the use of Pokrovskoe coal oxidized for four months impairs the mechanical strength, with 1.7 % decline in M_{25} and 1.0 % increase in M_{10}.

The total content of anisotropic carbon in the coke falls from 80 to 73 %, while the content of isotropic carbon rises from 4 to 12 %. In other words, the carbon structure of the coke becomes less ordered (Table 15). In Fig. 1, we show the optical texture of the coke [8].

Table 13.Yield of coke and byproducts from coal blends

Coal blend	Yield of coke and byproducts, %								
	coke	*tar*	*raw benzene*	C_mH_n	NH_3	H_2S	CO_2	H_2O_{pyr}	*gas+losses*
1	76.84	2.82	1.08	0.55	0.29	0.24	0.80	4.76	12.62
2	76.50	2.73	0.99	0.50	0.32	0.24	1.24	4.99	12.95
3	76.84	2.80	1.04	0.53	0.36	0.21	1.04	4.78	12.40

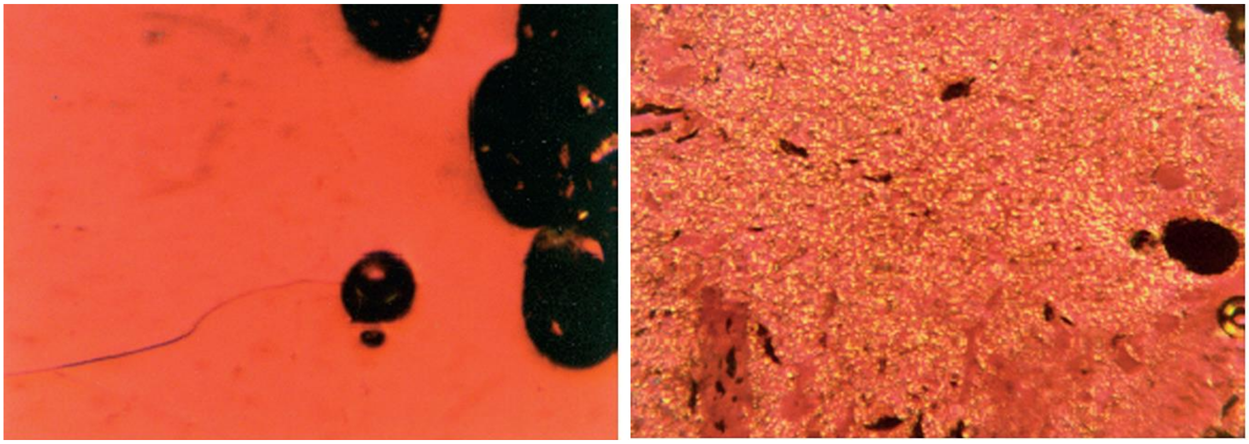
Table 14.Quality of coke from coal blends

Coal blend	Proximate analysis, %			Mechanical strength, %		Reactivity and strength coke after reaction with CO_2, %	
	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 15. Optical texture of coke from coal blends

Coal blend	Inertinite[1]	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

[1] *The inertinite is little changed in thermal destruction and is readily identified in the coke*



a b

Fig. 1 Optical texture of isotropic (a) and anisotropic (b) structure of coke

Our results confirm the earlier conclusion that the mechanical strength of the coke and the expansion pressure of the experimental blends always change in the same direction [9].

As the mechanical strength and content of anisotropic carbon decline, we also note undesirable changes in the reactivity (CRI) and strength after reaction with CO_2 (CSR) of the coke: increase in CRI from 38.6 to 40.5 % and decrease in CSR from 49.1 to 44.9 %.

After screening out the <0.5 mm class from oxidized Pokrovskoe coal, the ash content of the coke in coal blend 3 is reduced by 10.4 %.

In that case, the mechanical strength of the coke in terms of M_{25} and M_{10} is practically the same as for the coke from coal blend with the initial Pokrovskoe coal. Preliminary removal of the <0.5 mm class in the oxidized coal markedly improves CRI and CSR in relation to the coke from blend 1.

4. Conclusions

When Pokrovskoe coal oxidized in laboratory conditions (at 140°C) and in natural conditions (between −1 and +22 °C) is used in coal blend, the bulk density is increased, its plastic–viscous properties are impaired, the expansion pressure is reduced, the content of carbon and hydrogen is reduced, the oxygen content increases, the yield of coke, tar, and benzene falls, and the yield of carbon dioxide, pyrogenetic water, and gas increases.

The oxidation is greatest for coal smaller than 0.5 mm. Accordingly, the overall oxidation of the coal is determined not only by the duration and conditions of storage but also by its content of dusty classes.

Oxidation reduces the expansion pressure of the coal blend with loss of mechanical strength of the coke produced.

The coke produced from coal blends containing oxidized coal has a higher proportion of isotropic coal, which increases its reactivity and impairs its strength and strength after reaction with CO_2.

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, %;*
C^{daf}, H^{daf}, N^{daf}, O^{daf}	*carbon, hydrogen, nitrogen and oxygen in the dry, ash-free 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, %;*
∑FC	*sum of fusinized components, %;*
BD	*bulk density, t/m*^{3}*;*
Δt	*oxidation index, °C;*
d_0	*degree of oxidation, %;*
RI	*index Roga;*
FSI	*free swelling index;*
y	*thickness of the plastic layer, mm;*
t_I	*temperature of softening, °C;*
t_{II}	*temperature of maximum contraction, °C;*
t_{III}	*temperature of final swelling temperature, °C;*
a	*contraction, %;*
b	*dilatation, %;*
OK_p	*oxidation, %;*
P_{max}	*expansion pressure, kPa;*
C_mH_n, NH_3, H_2S, CO_2, H_2O_{pyr}	*unsaturated hydrocarbon, ammonia, hydrogen sulphide, carbon dioxide, pyrogenetic water, %;*
B^d	*yield of coke, %;*
M_{25}, M_{10}	*mechanical strength, %;*
CRI	*coke reactivity index, %;*
CSR	*coke strength after reaction with* CO_2*, %;*
I	*isotropic carbon, %;*
A	*anisotropic carbon, %;*
M	*mosaic carbon, %;*
S	*striated carbon, %;*
P	*plate carbon, %;*
ΣA	*sum of anisotropic carbon, %.*

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