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IMPACT OF OXIDATION ON THE EXPANSION PRESSURE OF COAL

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Abstract

Experiments show that the oxidation of bituminous coal from the Zasyad'ko mine at 60°C in laboratory conditions increases its expansion pressure from 5.2 to 30.0 kPa in 28.3 days. Oxidation occurs in stages, as already demonstrated for Ukrainian and imported coal of different metamorphic stages on oxidation in the laboratory and in industrial trials at other temperatures. The rate constant in the initial stage of oxidation is $0.4095 \cdot 10^{-4} min^{-1}$ at 60°C.Saturation of the middle stage metamorphism coal with oxygen on oxidation increases the viscosity of the plastic mass that forms and increases the volume of gas and vapor products. Ultimately, that results in increase in the expansion pressure as the coal is oxidized.

Keywords: coal; oxidation; expansion pressure; plastic-viscous properties.

1. Introduction

Prolonged industrial experiments (lasting six months or more) on the natural oxidation of Donetsk coal during heap storage in the open at coke plants indicate that storage of bituminous coal (Zh coal) for up to 200 days improves its coking properties (the crushability I_{40} and grindability I_{10}) [1–5]. We may suppose that this improvement in coking properties is due to increase in the expansion pressure of the coal.

In the present work, we investigate the increase in expansion pressure of bituminous coal on natural oxidation.

2. Experimental

In the experiments, bituminous coal from the Zasyad'ko mine (Donetsk Basin), crushed to the <3 mm class (100%), is oxidized in a drying chamber at 60°C with free access of atmospheric oxygen. The oxidation temperature of 60°C is selected on the basis of literature data [6-7].

In the experiment, the coal is constantly mixed to ensure uniform oxidation. At intervals, samples are taken from the coal, and the oxidation index Δt is determined. If Δt changes by 2–3°C, we conduct technical, petrographic, and plastometric analysis and determine the actual coal density, expansion pressure, Roga index, free-swelling index, Audibert-Arnu dilation, and Gieseler plasticity.

The coal was sampled and tested for oxidation determination according to DSTU 7611:2014 «Coal. Method for the determination of oxidation and degree of oxidation» [8]. The principle of the method is to compare the temperatures of ignition of initial tested coal, reduced and oxidized coal.

The installation for determination of coal oxidation is a laboratory complex (Fig.1) comprising electric furnace 1, copper block 2, thermocouples 3 and 4, furnace temperature regulator 5, four sets of test tubes 6, burettes 7, glasses 8, two laboratory supports 9. The main component of the installation is an electric furnace with copper block where the coal sample is heated in order to determine its ignition temperature.

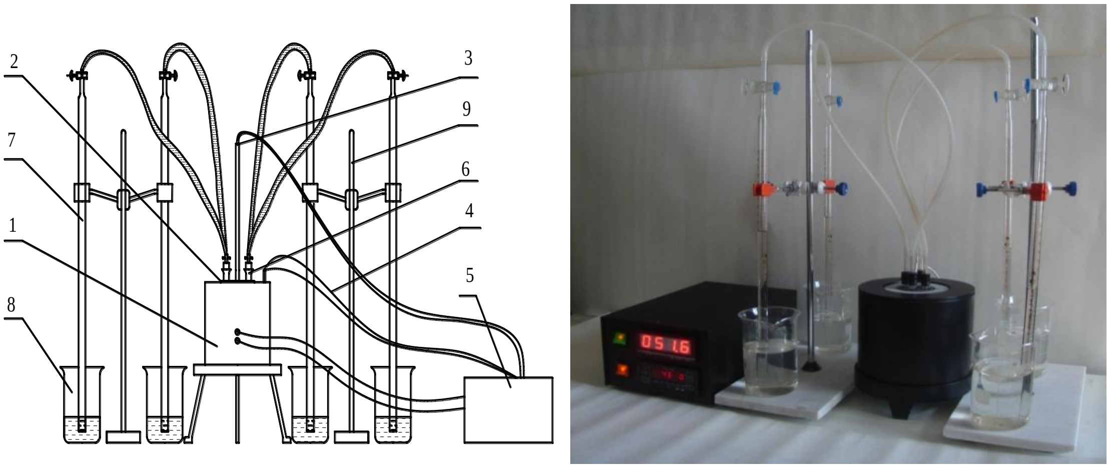

Fig. 1 Installation for determine of coal's inflammation temperature: 1 – electric furnace; 2 – copper block; 3, 4 – thermocouples; 5 – furnace temperature regulator; 6 – test tubes; 7 – burettes; 8 – glasses; 9 – laboratory supports

During the experiment a sample of coal with a particle size of less than 0.2 mm is used. To perform a test a sample of test specimen weighing 0.5 g is thoroughly mixed with 0.25 g of sodium nitrite ($NaNO_2$) and transferred to a dry test-tube. To determine the ignition temperature of the test sample of reduced coal a sample weighing 0.5 g is mixed with 0.25 g of sodium nitrite ($NaNO_2$) and 0.0125 g of benzidine (4.4-diaminodifenol). The resulting mixture is transferred into a dry test-tube. The test-tubes are closed up with rubber stoppers with glass tubes inserted into, which are connected to burettes with rubber (silicone) tubes; burettes are filled with water and then the open end is immersed into a glass of water to a depth of 20–30 mm. The system is checked for leaks. The burette is connected to a test-tube turning the tap.

The test-tubes are dropped into a block of a device which enables simultaneous heating of the four test-tubes. In the centre of the block a recording unit of thermocouple is set which generate heating at a rate of 5°C/min. At the moment of explosion (ignition of the coal tested), which is accompanied by a sharp decrease of the water level in the burette as a result of the pressure of gases evolved, the registration of temperature is taken.

According to the above-mentioned standard, the assessment of coal oxidation is based on the following parameters:

Coal oxidation (*Δt,* °C) is a difference in ignition temperatures between reduced and initial tested coal, as it is calculated according to (1):

$$\Delta t = t_{ig.r} - t_{ig} , \qquad (1)$$

where $t_{ig.r}$ is an ignition temperature of reduced coal, °*C*; t_{ig} is an ignition temperature of initial tested coal, °*C*.

Degree of coal oxidation (d_o, %) is calculated as follows:

$$d_o = \frac{t_{ig.r} - t_{ig}}{t_{ig.r} - t_{ig.o}} \cdot 100 \qquad (2)$$

where $t_{ig.r}$ is an ignition temperature of reduced coal, °*C*; t_{ig} is an ignition temperature of initial tested coal, °*C*; $t_{ig.o}$ is an ignition temperature of oxidized coal, °*C.*

Determination the size of expansion pressure of the investigated tests of coals was conducted on worked out in the Ukrainian State Research Institute for Carbochemistry to the laboratory setting on determination of expansion pressure the coals and coal blends (Fig.2) [9].

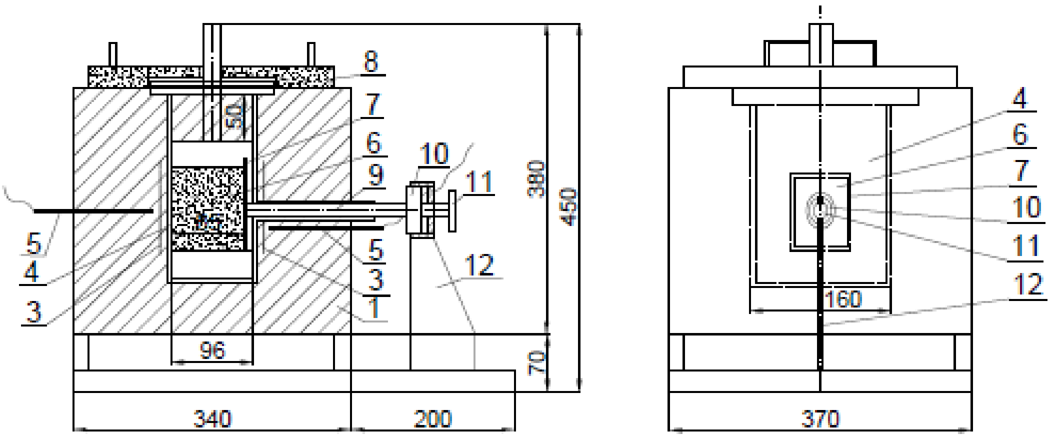

Fig. 2 Laboratory equipment for determination of expansion pressure the coals and coal blends: 1 – foundation; 2 – oven; 3 – heater element; 4 – retort; 5 – thermocouple; 6 – the coal loading; 7 – plate; 8 – lid; 9 – quartz kernel; 10 – pressductor; 11 – screw; 12 – bracket

The method of determination the expansion pressure consists in the two-sided heating of chamber electro-oven, with experimental coal hinge-plate 7 in a metallic retort 4, at the temperature of warming walls: front–880°C; back–600°C; arising up in process of coking expansion pressure the coal loading 6, passed from a plate (walls coking chambers) 7 through quartz kernel 9 on a piezoelectric pressductor 10.

Parameters the preparation of coal (blend) are shown in the table 1.

Table 1. Parameters the preparation of coal (blend)

Charge mass, kg	Grain size distribution, %	Moisture content of coal (blend), %	Charge density g/cm^3
0,600±0,002	80,0±3,0	10,0±0,2	0,80±0,01

The actual coal density is determined because it is directly related to the structure of the coal's organic mass [12].

The actual density d_r^{daf} of dry, ash-free coal is calculated from the formula

$$d_r^{daf}=\frac{100d_r^d-2.6A^d}{100-A^d}\ , \qquad (3)$$

where d_r^{daf} is the actual density of dry coal, g/cm^3; A^d is the coal's ash content, %; the factor 2.6 represents the presumed actual density of the mineral matters in the coal, g/cm^3.

The experiment ends when the plastic-layer thickness y=17 mm for the oxidized coal. That is the limiting permissible value for Zh coal according to Ukrainian State Standard DSTU 3472–96 "Brown coals, hard coals and anthracite. Classification".

3. Results and discussion

Tables 2–4 present the change in technological properties, petrographic characteristics and plastic-viscous properties of the bituminous coal in oxidation.

Table 2.Variation in the properties of bituminous coal during oxidation

Oxidation time, min	Approximate analysis,%			Actual density, g/cm^3		Expansion pressure	Characteristics in DSTU 7611:2014	
	A^d	S_t^d	V^{daf}	d_r^d	d_r^{daf}	P^H_{max}, kPa	Δt, °C	d_0, %
0	7.4	1.84	31.2	1.378	1.280	5.2	3	9.3
16260	7.4	1.85	31.4	1.358	1.259	10.5	5	15.6
36480	7.1	1.87	31.5	1.316	1.218	18.5	7	21.9
40800	6.9	1.88	31.6	1.293	1.196	30.0	10	29.4

Table 3 Variation in the petrographic characteristics of bituminous coal during oxidation

Oxidation time, min	Petrographic composition (without mineral impurities), %					Mean vitrinite reflectance R_{0}, %	Metamorphic stage in terms of vitrinite, %					
	Vt	*Sv*	*I*	*L*	ΣLC		0.50-0.64	0.65-0.89	0.90-1.19	1.20-1.39	1.40-1.69	1.70-2.59
0	90	0	8	2	8	1.05	0	3	94	1	2	0
16260	93	0	6	1	6	1.07	0	0	99	1	0	0
36480	93	1	5	1	6	1.07	0	1	97	2	0	0
40800	92	1	6	1	7	1.08	0	0	94	5	0	0

Table 4. Variation in the plastic-viscous properties of bituminous coal during oxidation

Oxidation time, min	Plastometric indices, mm		Roga index *RI*, points	Free-swelling index *FSI*	Audibert-Arnu dilation					Gieseler plasticity				
	x	*y*			t_{I}, °C	t_{II}, °C	t_{III}, °C	*a*, %	*b*, %	t_{p}, °C	t_{max}, °C	t_{f}, °C	*Δt*, °C	F_{max}, ddpm
0	4	21	83	81/2	373	426	490	27	212	395	452	488	93	1093
16260	11	18	83	81/2	374	425	488	30	193	400	451	487	87	876
36480	15	18	77	81/2	375	425	485	28	187	406	448	485	79	539
40800	16	17	76	81/2	376	427	485	24	183	409	447	484	74	120

With increase in the oxidation time (Table 2), the characteristics defined in Ukrainian State Standard DSTU 7611:2014increase sharply: the oxidation index *Δt* from 3 to 10°C; and the degree of oxidation d_0 from 9.3 to 29.4%.

In Figs. 3 and 4, we show the variation in the oxidation over time. Analysis indicates that oxidation passes from the initial stage to intense oxidation at point *1* [8, 11]. This confirms that oxidation occurs in stages, as already demonstrated for Ukrainian and imported coal of different metamorphic stages on oxidation in the laboratory and in industrial trials at different oxidation temperatures [8, 11].

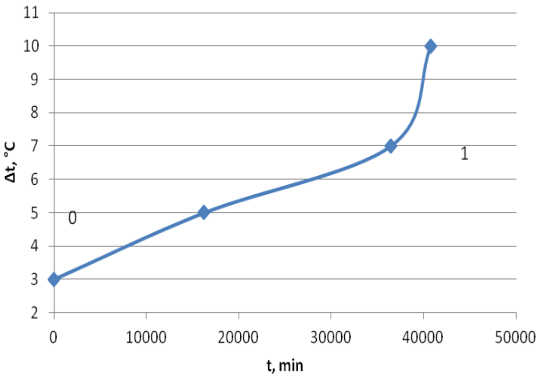

Fig. 3 Time dependence of the oxidation index

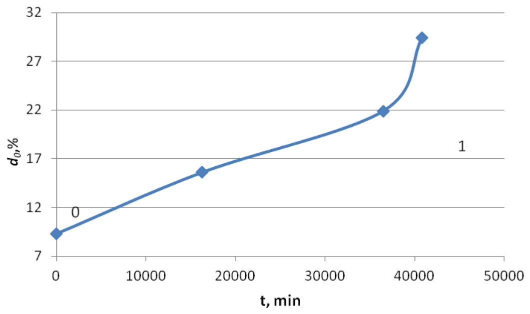

Fig. 4 Time dependence of the degree of oxidation

On the basis of the assertion that the oxidation rate of coal in the initial stage is limited by diffusion, we calculate the oxidation rate of bituminous coal for a first-order reaction [10, 14]

$$k_{0-1}=\frac{2.3}{\tau}\log\left(\frac{c_0}{c_1}\right) , \qquad (4)$$

where τ is the reaction time; c_0 is the initial concentration of the unoxidized coal; and c_1 is the concentration of the unoxidized coal at point *1*.Equivalently

$$k_{0-1}=\frac{2.3}{\tau}\log\left(\frac{100-d_{0,0}}{100-d_{0,1}}\right) , \qquad (5)$$

where τ is the reaction time, min; $d_{0,0}$ is the degree of oxidation at point 0, %;$d_{0,1}$ is the degree of oxidation at point 1, %.

The calculated rate constant in the initial stage of oxidation at 60°C is $0.4095 \cdot 10^{-4}$, min^{-1}.

In Figs. 5 and 6, we show the expansion pressure as a function of the degree of oxidation. For those curves, R^2= 99.4 and 98.4%, respectively. On the basis of Figs. 5 and 6, we conclude that the oxidation of bituminous coal at 60°C significantly increases the expansion pressure: from 5.2 to 30.0 kPa (by a factor of 5.8) over ~28.3 days. The increase in the expansion pressure of bituminous coal on oxidation must be explained in terms of change in its technological properties, petrographic characteristics and plastic-viscous properties.

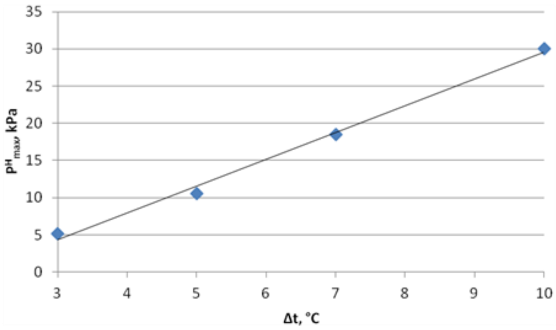

Fig. 5 Dependence of the expansion pressure on the oxidation index of the coal

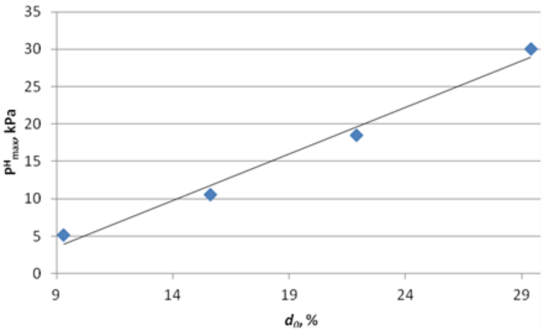

Fig. 6 Dependence of the expansion pressure on the degree of oxidation of the coal

Analysis of Table 2 indicates that the yield of volatiles matters is constant throughout the given period. At the same time, the actual coal density falls markedly from 1.280 to 1.196 g/cm^3 (by 6.6%).

This must be due to variation in the elementary composition of coal: most authors [12–15] who have studied the effect of aerial oxidation have in general reported decrease in carbon, and increase in oxygen content.

These changes in the coal's organic mass do not affect the petrographic characteristics of coal samples with different degrees of oxidation. At the same time, the plastic-viscous characteristics change significantly during oxidation.

Thus, in the given period, the plastic-layer thickness declines from 21 to 17 mm; the Roga index falls from 83 to 76; and the dilation index b is reduced from 212 to 183%. There are also extensive changes in the Gieseler plasticity. Thus, the transition temperature to the plastic-viscous state increases from 395 to 409°C; the residence time of the coal in the plastic-viscous state Δt falls from 93 to 74°C; and the fluidity F_{max} of the plastic mass declines from 1093 to 120 ddpm.

As we know, the expansion pressure reflects the gas pressure in the charge bounded by the plastic layer. Of course, other conditions being equal, that pressure will be larger in the presence of larger volumes of gas products and in less permeable plastic layers.

Laboratory research has shown that 1% increase in oxygen content within the coal reduces the yield of tar by 0.146%, that of benzene by 0.075%, and that of unsaturated compounds by 0.013%, while the yield of carbon dioxide increases by 0.027%, that of pyrogenetic moisture by 0.053%, and that of coke-oven gas by 0.323% [16].

Since the molecular mass of the carbon dioxide, pyrogenetic moisture, and coke-oven gas is markedly less than that of the tar, benzene, and unsaturated compounds, we may suppose that, with practically the same yield of volatiles (V^{daf}= 31.2–31.6%) from bituminous coal with different degrees of oxidation (Table 2), the volume of gaseous products from the thermal destruction of the coal's organic mass will increase with increase in its degree of oxidation.

As already noted, the decrease in viscosity of the plastic mass is determined by the Gieseler method. In Fig. 7, we show the dependence of the expansion pressure on the maximum Gieseler fluidity. For that line, R^2 = 99.87%. Analysis of Fig. 7 indicates that increase in the viscosity of the bituminous coal (decrease in its fluidity) as a result of oxidation, like increase in the volume of gas products, boosts the expansion pressure.

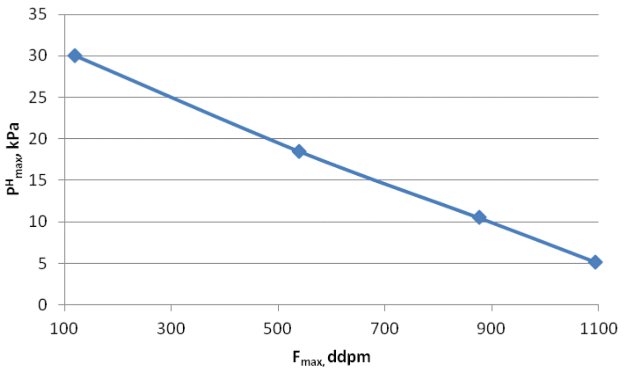

Fig. 7 Dependence of the expansion pressure on the maximum Gieseler fluidity of the coal

Finally, we should note the use of an original method to establish pronounced increase in the maximum expansion pressure of oxidized Zh coal in [17]. The increase in the expansion pressure was linked to increase in the viscosity of the plastic mass formed by the bituminous coal, as well as the properties of the coal and the dynamics of gas liberation.

4. Conclusions

1. Experiments show that the laboratory oxidation of bituminous coal from the middle stage metamorphism coal at 60°C leads to increase in the expansion pressure from 5.2 to 30.0 kPa in ~28.3 days
2. We suggest that saturation of the bituminous coal with oxygen on oxidation increases the viscosity of the plastic mass that forms and increases the volume of gaseous products. Ultimately, that results in increase of the expansion pressure as the coal is oxidized.

Symbols

Zh coal	*bituminous coal from the middle stage metamorphism coal;*
I_{40}	*crushability coke;*
I_{10}	*grindability coke;*
Δt	*coal oxidation;*
d_o	*degree of coal oxidation*
DSTU	*Ukrainian State Standard;*
$t_{ig.r}$	*an ignition temperature of reduced coal, °C;*
t_{ig}	*an ignition temperature of initial tested coal, °C;*
$t_{ig.o}$	*an ignition temperature of oxidized coal, °C;*
d_r^{daf}	*actual density of dry, ash free coal;*
A^d	*ash content of coal;*
y	*thickness plastic layer of coal;*
τ	*the reaction time;*
c_0	*the initial concentration of the unoxidized coal;*
c_1	*the concentration of the unoxidized coal at point 1*
$d_{0,0}$	*the degree of oxidation at point 0;*
$d_{0,1}$	*the degree of oxidation at point 1;*
F_{max}	*the fluidity of the plastic mass;*
V^{daf}	*yield of volatiles from coal.*

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