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EVALUATION OF HEAT OUTPUT OF COAL OXIDATION AT RELATIVELY LOW TEMPERATURE[*]

Summary. Coal spontaneous combustion is related with the heat output of coal under the low temperature. But the heat output is small and it is very difficult to directly measure. Based on the laboratory experiments of coal spontaneous combustion, this paper put forward a new method to evaluate the maximum $q_{\min}(T)$ and minimum $q_{\max}(T)$ specific heat output of coal with bond energy changes of gases at relatively low temperature. It was found that the specific heat output of coal is close the minimum $q_{\min}(T)$ under 85¡æ and . But if the temperature is higher 85¡æ, the specific heat output of coal is close the maximum $q_{\max}(T)$. It's significance to predict self-ignition of coal.

OCENA ILOŚCI WYDZIELANEGO CIEPŁA W PROCESIE UTLENIANIA SIĘ WĘGLA W NISKICH TEMPERATURACH

Streszczenie. W artykule przedstawiono badania nad samozapaleniem się węgla. Związane jest ono z wydzielaniem się ciepła z węgla w niskich temperaturach. Przedstawiono wyniki badań laboratoryjnych i określono granice wydzielania się ciepła z węgla.

The spontaneous combustion of coal is very serious in China. It can be found in almost all the coal-mining districts from north-east to north-west, which causes great consumption of coal resources. As it goes on, the self-ignition of coals leads to heavy pollution in China. So it's significance to study the process of spontaneous combustion. In the recent years, many laboratory studies of spontaneous combustion parameters of coal at relatively low temperature(as low as below 100¡æ) were widely conducted in the word. The minimum self-

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heating temperature of coal is determined using adiabatic heating oven at the Bureau of Mines in the American[1]. Adiabatic oxidation techniques have traditionally been used at the university of Nottingham in England to investigate the problem of spontaneous combustion[2]. Four methods(static isothermal, ignitability, adiabatic and dynamic) have been used to compare the relative liability of coal to spontaneous combustion and investigate the mechanism in Canada[3]. The critical temperature of coal is determined using nonisothermal dynamic method in Turk[4]. An adiabatic calorimeter has been designed to enable the spontaneous combustion propensity of coal in South Africa[5]. Japanese proposed a new method 'exposure equivalent-time' for estimating the heat generation rate of coal[6].

Coal spontaneous combustion is directly related with the heat output of coal. But the heat output of coal is small at the relatively low temperature and it is very difficult to directly measure. Although the scientists have involved in the research about the heat output of coal for some years and got a few accomplishments in the word, there still leave much many problems to determine exactly the heat output of coal. The article put forward a new method to evaluate heat output of coal according to the laboratory experiments of coal spontaneous combustion.

On the basis of the experiments for simulation of spontaneous combustion in coalbeds or in stockpiles out in laboratory oven XK-2, to measure the parameters, like the amount of oxygen adsorption, velocity of oxygen consumption, producing rates of CO and CO2 ,and so on, may be evaluated respectively. Then according to the bond energy changes of the gases in the process of coal oxidation, heat output of coal can be evaluated.

1. Laboratory oven of coal spontaneous combustion

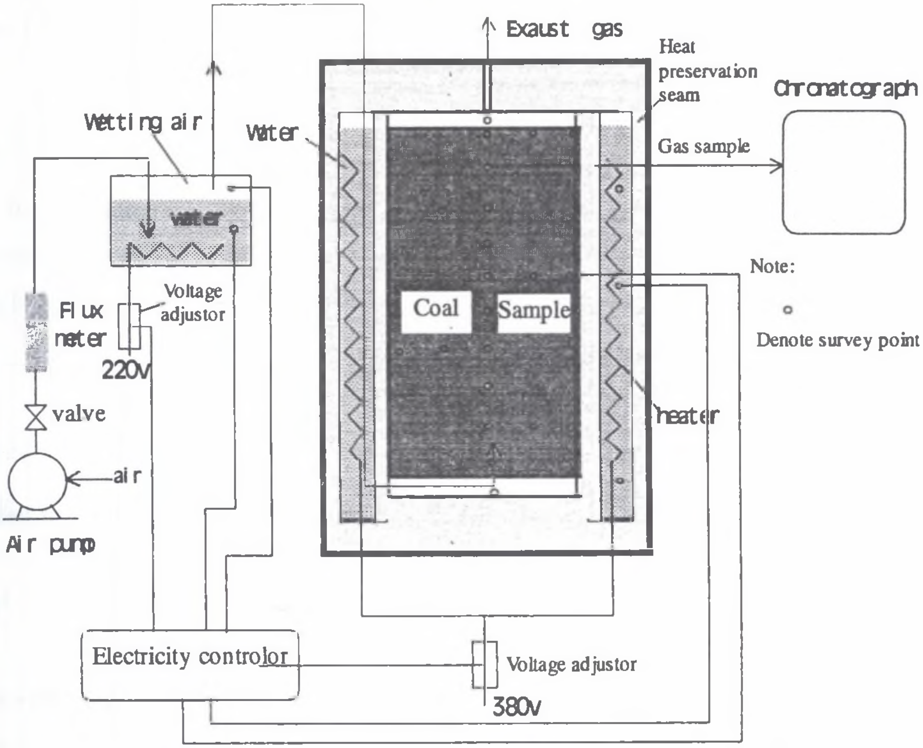


Fig. 1. Schematic diagram of experimental unit to examine self-heating of coal

1.1. Structure of the oven

The laboratory oven (XK-2) to examine coal spontaneous combustion of a 0.5 ton coalbed ,is comprised with oven body, air supply system and control and test system (see figure 1). Oven body is column which internal diameter is 0.6m and height is 1.8m. The top and bottom of the oven have 10¡«20cm free space which assure gas evenly flowing. The wall of the oven is constructed with absolute layer and the water layer in which heaters and preheat air pipe are installed. 32 temperature sensors and 10 pumping gas pipes are disposed in the oven. In the process of experiment, the gas samples which are taken out from coal are analyzed by gas chromatograph, the temperatures in the oven are automatically gauged and the ambient temperature is automatically controlled by a computer.

1.2. Characteristics of the laboratory oven Xk-2

1. Coal spontaneously heats and lead it's temperature to rise in the oven.
2. Store up and scatter conditions in the oven are analogous to real coal pile by any possibility.
3. The intensity of air-leakage, air flow temperature and wet of water can be controlled.
4. The total weight and size of coal are reasonable.
5. The initial temperature in the experimental is same with wall rock temperature.

2. Gas changes in the coal oxidation

2.1. The velocity of oxygen consumption

Supposing air flows along one direction and neglecting diffusion of oxygen and unsteady change, the velocity of oxygen consumption for unit volume is derived.

$$V_{O_2}(T)/n = u \cdot \frac{dC}{dZ} \tag{1}$$

Where, $Vo_2(T)$ denotes the velocity of O_2 consumption in the real oxygen concentration, mol/(cm^3.s); C denotes the concentration of oxygen; n is porosity of coal; u is the velocity of air flow and Z is distance of two point in the oven.

Generally, we consider the velocity of oxygen consumption is direct proportion with the oxygen concentration. *viz,*

$$V_{O_2}(T) = K \cdot C \tag{2}$$

where K denotes chemical reaction constant.

Therefore,the consupmtion rate of oxygen in the fresh air (oxygen concentration is 21%) can be expressed.

$$V_{O_2}^{0}(T) = \frac{C_0}{C} \cdot V_{O_2}(T) \tag{3}$$

$$dC = -V_{O_2}^{0}(T)/n \times \frac{C}{C_0} \times \frac{S \cdot n}{Q} dz \tag{4}$$

$$V_{O_2}^{0}(T) = \frac{Q \cdot C_0}{S(z_{i+1} - z_i)} \cdot \ln \frac{C_i}{C_{i+1}} = 1657.86 \times Q \times 10^{-11} \times \ln \frac{C_i}{C_{i+1}} \tag{5}$$

where Q is the air flux; S is the section area of oven.

Based on the oxygen concentration and the air flux in the oven, the velocity of oxygen consumption can be evaluated

2.2. Producing rate of CO¡¢CO$_2$

In the experiment oven, the concentration of oxygen gradually decreases alone the direction of air flow, but the concentration of CO or CO2 increases. The producing rate of CO CO$_2$ is approximately direct proportion to the concentration of oxygen. *viz,*

$$V_{CO}(T) = \frac{C}{C_0}\cdot V_{CO}^0(T) \tag{6}$$

Where, *Vco(T)* denotes the producing rate of CO in the real oxygen concentration, mol/(cm^3.s); $V_{CO}^0(T)$ denotes the producing rate of CO in the fresh air (oxygen concentration is 21%); C_0 is the oxygen which concentration is 21%.

Based on the equation (4), the concentration of oxygen is derived.

$$C = C_i\cdot e^{-\frac{V_{O_2}^0(T)\cdot S}{Q\cdot C_0}\cdot(z-z_i)} \tag{7}$$

Where, C_i and Z_i is a concentration of oxygen and a distance from inlet to one point in the oven.

$$\because dC_{co} = \frac{V_{CO}(T)}{n}d\tau, d\tau = \frac{dz}{u}, u = \frac{Q}{S\cdot n} \tag{8}$$

$$C_{co}^2 - C_{co}^1 = \int_{z_1}^{z_2}\frac{V_{co}(T)}{u\cdot n}dz = \int_{z_1}^{z_2}\frac{S}{Q}\cdot\frac{C\cdot V_{co}^0(T)}{C_0}dz = \frac{S\cdot V_{co}^0(T)}{Q\cdot C_0}\int_{z_1}^{z_2}C_1\cdot e^{-\frac{V_{O_2}^0(T)\cdot S}{Q\cdot C_0}(z-z_1)}dz \tag{9}$$

So

$$V_{co}^0(T) = \frac{V_{O_2}^0(T)\cdot(C_{co}^2 - C_{co}^1)}{C_1\cdot[1-e^{-\frac{V_{O_2}^0(T)\cdot s\cdot(z_2-z_1)}{Q\cdot C_0}}]} \tag{10}$$

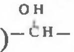
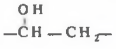
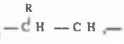
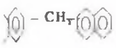
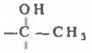
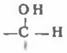
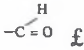
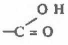
Similarly, the producing rate of CO$_2$ is derived.

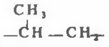
$$V_{co_2}^0(T) = \frac{V_{O_2}^0(T)\cdot(C_{co_2}^2 - C_{co_2}^1)}{C_1\cdot[1-e^{-\frac{V_{O_2}^0(T)\cdot s\cdot(z_2-z_1)}{Q\cdot C_0}}]} \tag{11}$$

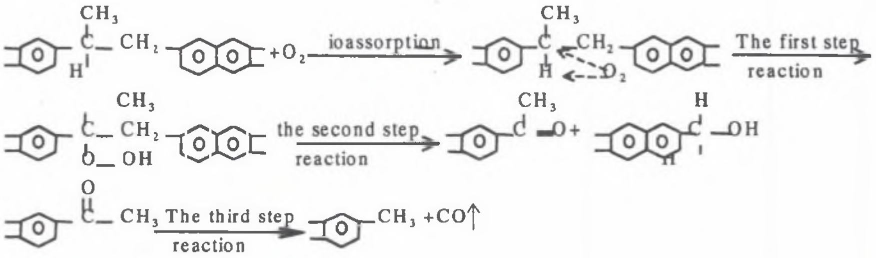
Based on the concentrations of CO and CO_2 in the experiment oven, the producing rate of CO and CO_2 can be evaluated.

3. Evaluation of heat output of coal with bond energy changes

3.1. Bond energy changes of CO¡¢CO_2

According to the organic chemistry theory, the bridge bonds such as 1) $-CH_2-O-$, 2) $-\overset{OH}{CH}-$, 3)  $-\overset{OH}{CH}-CH_2-$ 4) $-\overset{R}{CH}-CH_2-$ and so on, and side chains ,such as 1) ,2) $-\overset{OH}{C}-CH_3$,3) $-\overset{OH}{C}-H$,4) $-\overset{H}{C}=O$ £¬5) $-\overset{OH}{C}=O$ and so on, are liable to react with oxygen at relative low temperature.

The oxidation process of the bridge bond is illustrated with  $-\overset{CH_3}{CH}-CH_2-$.



The bond energy changes of reaction process can be evaluated as follow equation.

$$\Delta H = \sum bond\ energy\ of\ products - \sum bond\ energy\ of\ reac\tan ts \\ - \sum s\tan dard\ enthalpy\ of\ atom \tag{12}$$

$$\text{The first step}: \Delta H_{31} = (\varepsilon_{C-O} + \varepsilon_{O-O} + \varepsilon_{O-H}) - \varepsilon_{C-H} - 2\Delta_{O_2} = 59(kJ/mol)$$

$$\text{The second step}: \Delta H_{32} = \varepsilon_{C-O} - \varepsilon_{O-O} - \varepsilon_{C-C} = 253(kJ/mol)$$

$$\text{The third step}: \Delta H_{33} = \Delta_{CO} - \varepsilon_{C-O} - \varepsilon_{C-C} = -14.8(kJ/mol)$$

where, ε is bond energy,kJ/mol. Δ is the standard enthalpy of atom,kJ/mol.

The tall reaction heat of the bridge bond producing CO is

$$\Delta H_{CO}^{3} = \Delta H_{31} + \Delta H_{32} + \Delta H_{33} = 59 + 253 - 14.8 = 297.2(kJ/mol)$$

Similarly, the tall reaction heat of other bridge bond is evaluated.

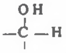
$$\Delta H^{1}_{CO_2} = 59 + 290.7 + 103.7 = 453.4 kJ/mol$$

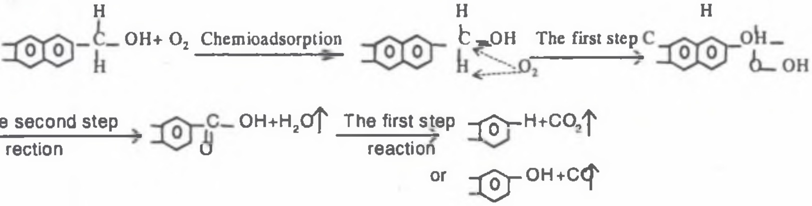
$$\Delta H^{2}_{CO_2} = 59 + 253 + 103.7 = 415.7 kJ/mol$$

$$\Delta H^{2}_{CO} = 59 + 253 - 14.8 = 297.2 kJ/mol$$

$$\Delta H^{3}_{CO} = 59 + 253 - 14.8 = 297.2 kJ/mol$$

$$\Delta H^{4}_{CO} = 59 + 253 - 14.8 = 297.2 kJ/mol$$

The oxidation process of the side chain is illustrated with  $-\overset{OH}{\underset{|}{C}}-H$ as a example.



If CO is produced in the oxidation process of coal, the reaction heat of every step is

The First step : $\Delta H_{51} = (\varepsilon_{C-O} + \varepsilon_{O-O} + \varepsilon_{O-H}) - \varepsilon_{C-H} - 2\Delta_{O_2} = 59(kJ/mol)$

The second step : $\Delta H_{52} = \Delta_{H_2O} + \varepsilon_{C=O} - \varepsilon_{C-O} - \varepsilon_{O-O} - \varepsilon_{O-H} - \varepsilon_{C-H} = 290(kJ/mol)$

The third step : $\Delta H_{53} = \Delta_{CO_2} + \varepsilon_{C-H} - \varepsilon_{C-O} - \varepsilon_{H-O} - \varepsilon_{C=O} - \varepsilon_{C-C} = 103.7(kJ/mol)$

Or $\Delta H'_{53} = \Delta_{CO} - \varepsilon_{C=O} - \varepsilon_{C-C} = -14.8(kJ/mol)$

Similarly, if CO$_2$ is produced in the oxidation process of coal, the tall reaction heat of other bridge bond can be evaluated too.

$$\Delta H^{5}_{CO_2} = 59 + 290 + 103.7 = 452.7 kJ/mol$$

$$\Delta H^{5'}_{CO} = 59 + 290 - 14.8 = 334.2 kJ/mol$$

$$\Delta H^{6}_{CO_2} = 59 + 290 + 155.8 = 504.8 kJ/mol$$

$$\Delta H^{7}_{CO_2} = 59 + 365.1 = 424.1 kJ/mol$$

Because the process of the , the average reaction heat of£º

¢Ù¡¡producing 1 mol CO, the average of the reaction heat is

$$\Delta H_{CO} = (\Delta H^{4}_{CO} + \Delta H^{3}_{CO} + \Delta H^{2}_{CO} + \Delta H^{5'}_{CO})/4 = 306.45 kJ/mol$$

¢Ú¡¡producing 1 mol CO$_2$, the average of the reaction heat is

$$\Delta H_{CO_2} = (\Delta H^{1}_{CO_2} + \Delta H^{2}_{CO_2} + \Delta H^{5}_{CO_2} + \Delta H^{6}_{CO_2} + \Delta H^{7}_{CO_2})/5 = 450.14 kJ/mol$$

producing 1 mol H$_2$O, the average of the reaction heat is

$$\Delta H_{H_2O} = \Delta H_{61} + \Delta H_{62} = 59 + 290 = 349 kJ/mol$$

¢Û¡¡the heat of chemisorption is

$$\Delta H_{\text{lü}} \le \Delta H_{11} = 59KJ/mol$$

Based on the chemistry theory, the heat output of coal oxidation can be evaluated with the bond energy changes of chemical reaction and the chemisorption heat.

The products of coal oxidation are mainly CO and CO_2 under the low temperature. If the bond energy changes of O_2,CO and CO_2 in the coal oxidation are estimated, the heat output of the coal may be evaluated In the light of equation (9). But because the reaction between coal and oxygen is very complicated, the bond energy changes are only determined in line some main reaction equations. In accordance with analysis and calculation, the chemisorption heat is about 58.8kJ/mol,the bond energy change of producing 1mol CO is 297.0kJ/mol,and the bond energy change of producing 1mol CO_2 is 446.7kJ/mol.

3.2. Estimate of the heat output of coal

Supposing the oxygen which are consumed in the coal oxidation are all changed to CO and CO_2 , the maximum heat output of the coal is evaluated . *viz,*

$$q_{max}(T) = \frac{V^0_{CO}(T)}{V^0_{co}(T) + V^0_{CO_2}(T)} \cdot V^0_{O_2}(T) \cdot q_{co} + \frac{V^0_{CO_2}(T)}{V^0_{co}(T) + V^0_{CO_2}(T)} \cdot V^0_{O_2}(T) \cdot q_{co_2} \tag{13}$$

Where, q_{max} is he maximum heat output of the coal£¬J/(cm^3.s). q_{CO} and q_{CO_2} is bond energy change of producing 1mol CO and 1mol CO_2 respectively. $V_{CO}(T)$ and $V_{CO2}(T)$ is the producing rate of CO and CO_2,mol/(cm^3.s).

But the oxygen which is consumed is not all change to CO and CO_2£¬the real heat output of coal is smaller the value of evaluation. On the other hand, if the remain oxygen is all chemically adsorbed by coal, the minimum heat output can be evaluated. *viz,*

$$q_{min}(T) = q_{\text{lü}} \cdot [V^0_{O_2}(T) - V^0_{co}(T) - V^0_{CO_2}(T)] + q_{co} \cdot V^0_{co}(T) + q_{co_2} \cdot V^0_{CO_2}(T) \tag{14}$$

Obviously, the remain oxygen can not only be chemically adsorbed by coal, but also react chemically with coal. And the reaction heat is larger than the heat of chemisorption. Therefore, the real heat output of coal is larger the value of evaluation.

So the real heat output of coal is between above two evaluations.

$$q_{min} < q_O(T) < q_{max} \text{ ¡£}$$

4. Example

The authors used spontaneous combustion oven (XK-2) to simulate *Dongtan* 3# coal. The experimental conditions listed on table 1.The result is shown in table 2.

Table 1

Conditions of spontaneous combustion experiment for coal sample

Name	Weight (Kg)	Thick (m)	partical size (mm)	porosity (%)	air leakage intensity ($m^3/(m^2min)$)	Initial temprature (¡æ)
Dongtan3#	400.6	14.8	<30	34.4	0.0026	21

Table 2

Evaluation of heat output of coal under the experimental conditions (d_{50}=4.74mm)

Time (day)	temperature (¡æ)	¦¤T/¦¤Ó ¡æ/h	$V_0(T)$ ¡Á10^{+11}	$V^0_{CO}(T)$ ¡Á10^{+11}	$V^0_{CO_2}(T)$ ¡Á10^{+11}	q_{min} ¡Á10^{+5}	q_{max} ¡Á10^{+5}
1	21.48	0.057	24.97	0.20	0.58	1.76	10.58
3	24.21	0.057	27.58	0.21	0.71	1.97	11.79
5	26.86	0.055	28.68	0.18	0.64	2.00	12.30
7	29.69	0.059	30.98	0.19	0.67	2.15	13.27
9	32.86	0.066	31.81	0.21	0.72	2.22	13.62
11	36.65	0.079	33.69	0.24	0.81	2.38	14.40
12	38.40	0.073	38.28	0.27	0.95	2.71	16.40
13	40.58	0.091	43.76	0.29	0.97	3.05	18.70
14	43.03	0.102	45.55	0.32	1.13	3.23	19.53
15	45.31	0.095	49.07	0.31	1.05	3.40	20.98
16	48.36	0.127	52.96	0.35	1.12	3.67	22.58
17	51.79	0.143	56.93	0.29	1.28	3.95	24.68
18	54.93	0.131	61.69	0.43	1.72	4.45	26.62
19	58.74	0.159	59.62	0.48	2.13	4.51	25.85
20	62.89	0.173	64.16	0.51	2.57	4.96	27.99
21	67.76	0.162	71.55	0.56	2.81	5.50	31.20
22	72.63	0.203	81.94	0.65	3.10	6.26	35.65
23	78.32	0.237	115.99	1.28	5.23	9.29	50.09
24	85.06	0.281	143.54	2.46	9.34	12.89	61.76
25	94.61	0.398	186.01	4.83	14.38	18.04	78.94
26	107.25	0.527	234.93	7.34	20.81	24.18	99.41
27	124.87	0.734	458.86	16.75	37.18	46.45	191.03
28	150.14	1.053	747.52	40.83	89.73	90.98	310.98
29	195.87	1.905	1463.42	85.14	213.95	194.97	614.42

In terms of table 1, the critical temperature of spontaneous combustion is about 78~85 ¡æ. If the coal temperature is lower the critical temperature (<85 ¡æ), the velocity of oxygen consumption is mainly chemisorption of coal and the specific heat output of coal is close the minimum $q_{\min}(T)$. But if the coal temperature is higher the critical temperature (>85 ¡æ),the velocity of oxygen consumption is mainly react chemically and the specific heat output of coal is close the maximum $q_{\max}(T)$.

Conclusion

1. At relatively low temperature, the specific heat output of coal is small. It is difficult to gauge the heat.
2. In terms of the bond energy changes in the process of spontaneous combustion experimental of the coal, the specific heat output of coal can be devaluated.
3. Under 85¡æthe specific heat output of coal is close the minimum $q_{min}(T)$. But if the temperature is higher 85¡æ, the specific heat output of coal is close the maximum $q_{max}(T)$.

REFERENCE

1. Smith A.C.,Lazzara C.P.: Inhibition of Spontaneous combustion of coal, Report of investigation –Unites States. Bureau of mines, Pittsburgh, PA, USA 1988: 41.1-41.4.
2. Ren, T.X.;Richards,M.J.: Computerised system for the study of the spontaneous combustion of coal. Mining engineer (Longdon) v154 n398 nov 1994. P121-127.
3. Feng K.K. Spontaneous combustion of Canadian coals. CIM Bulletin. 1985,78(5):71-75.
4. Btooks Kevin, Svanas Nicoloas,Glasser David. Critical temperatures of some Turkish coals due to spontaneous combustion. Journal of Mines, Metals & Fuels. 1988,36 (9) :434-436.
5. Gouws M.J.,Gibbon G.J. ,Wade L., Phillps H.R. Adiabatic apparatus to establish the spontaneous combustion propensity of coal. Mining science & technology 1991,13 (3):417-422.
6. Sasaki,Kyuro; Miyakoshi,Hiroshi; Otsuka,Kazuo: Spontaneous combustion of coal in the low temperature range-application of exposure equivalent-time to numerical analysis. Nippon Kogyo Kaishi/Journal of the Mining and Metallurgical Institute of Japan v103 n 1197 Nov 1987 p771-775.
7. Miyakoshi Hiroshi,Isobe Toshiro, Otsuka Kazuo, Relationship between heat by oxygen adsorprion and physico-chemical properties of coal:study on spontaneous combustion of coal(1first report). Joural of the Mining and metallurgical Institute of Janpan v100 n1158 Aug 1984 p643-650.
8. Xing Qiyi & Zhou Zhengbian. Foundation of organic chemistry,Beijing, the people eduction press, 1980, 62~70.
9. Xu Jingcai & Deng Jun,Danger of Losing Coal Spontaneous Combustion Prediction in Comprehensively Mechanized Roof -coal Caving face, Journal of FuXing Mining Institut, 1997,16(3),180-183.
10. Xu Jingcai, Wen hu, Deng Jun: Determination of oxidation zone in mined out areas, fourteenth Annual International Pittsburgh Coal Conference & Workshop Proceedings,1997,9.

Recenzent: prof. dr hab. inż., dr h.c. Bernard Drzęźla

Podsumowanie

Samoistne zapalenie się węgla związane jest z wydzielaniem się ciepła z węgla w niskich temperaturach. Ilościowo jest ono małe i trudne do bezpośredniego zmierzenia. Na podstawie doświadczeń laboratoryjnych samoistnego zapalenia się węgla przedstawiono metodę oceny maksymalnego $q_{max(T)}$ i $q_{min(T)}$ wydzielania się ciepła wraz ze zmianami energii gazów przy względnie niskich temperaturach. Ma to istotne znaczenie dla przewidywania samozapłonu węgla.