

Study on the Hydrogen Generation Rules of Coal Oxidation at Low Temperature

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Abstract

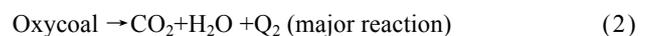
Based on a hydrogen desorption experiment and a comparative experiment of low-temperature coal oxidation performed prior to and after hydrogen desorption, this paper demonstrates the occurrence of hydrogen adsorption in coal at room temperature and reveals that the hydrogen generated in the process of coal oxidation originates from coal oxidation and desorption. The results show that the hydrogen accumulation generated only by coal oxidation and the hydrogen accumulation generated solely by desorption both exhibit a Langmuir-EXT1 function equation relationship with temperature. The result of the present research can provide a theoretical basis for the accurate prediction of spontaneous coal combustion and is of great significance to the prevention and control of coal spontaneous combustion in coal mines, industrial coal storage and transportation.

Keywords: Low Temperature Oxidation; Hydrogen; Desorption; Adsorption; Langmuir-EXT1 Equation

1. Introduction

With the extensive application of fully mechanized caving, fire in coal mines is a serious problem for the coal industry. In coal mines, most fires occur due to spontaneous combustion because of excessive coal residue in the goaf and severe air leakage, etc. [1]. Currently, CO, C₂H₄ and C₂H₂ are commonly used as index gases to monitor spontaneous coal combustion, but few studies have examined the variation of hydrogen as an index gas in the process of coal spontaneous combustion. Vered Nehemia et al. [2] believed that oxidized bituminous coal can release H₂ when the temperature ranges from 40 °C to 115 °C and identified that the hydrogen generation mechanism proceeded via the intermediate product formaldehyde. S. L. Grossman et al. [3], [4], [5], [6] conducted an oxidation experiment on different coal samples within a temperature range of 55 °C to 95 °C and found that coal could produce H₂ at low temperatures during the oxidation process and that the temperature positively correlated with the amount of H₂ generated. Cohen and Haim [7] also found that bituminous coal could generate H₂ during the oxidation process at a room temperature of 40 °C and that the amount of H₂ is in direct proportion to the amount of O₂ consumed. Liang H. D proposed [8] that coal could release hydrogen molecules at room temperature, and Dai G. L [9] analyzed the hydrogen source in goaf. The China University of Mining and Technology (Beijing) [10] identified a relationship between methane and the hydrogen and helium naturally released by

coal. Hydrogen in coal exists in the form of small molecules such as alkanes, hydroxide radicals, carboxyls as well as in branched chains of the aromatic nucleus structure, which is very unstable and can be produced under the effect of thermal shock [11]. When a coal fire occurs, alkane compounds decompose, lose their hydrogen atoms and produce alkene compounds after heating up. However, the product of H free radicals is highly unstable and easily integrates other H radicals into molecular hydrogen. The article by Li et al. introduced the generation mechanism of hydrogen during coal combustion [12], [13]. Vered Nehemia [2] considered that the most probable hydrogen producing reactions during spontaneous coal combustion could be considered as follows:



Zhou F. B et al. [14] proposed a three-stage hydrogen generation model during reignition in a fire zone (as shown in Fig.1).

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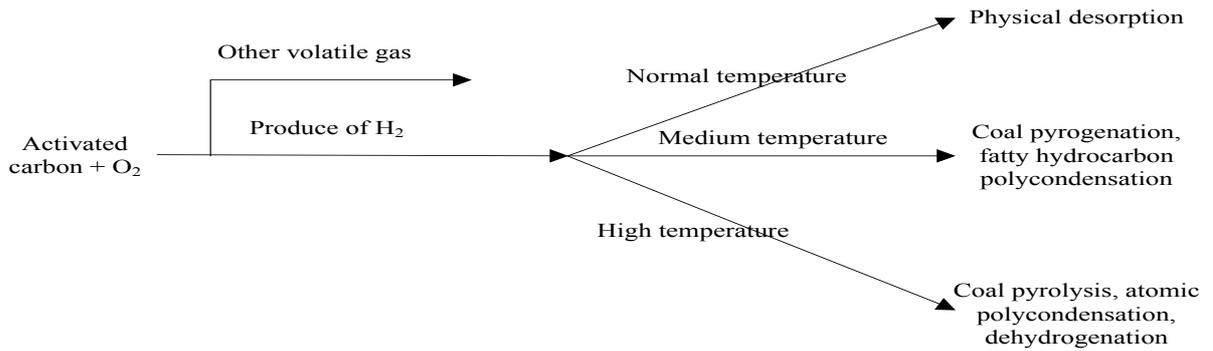


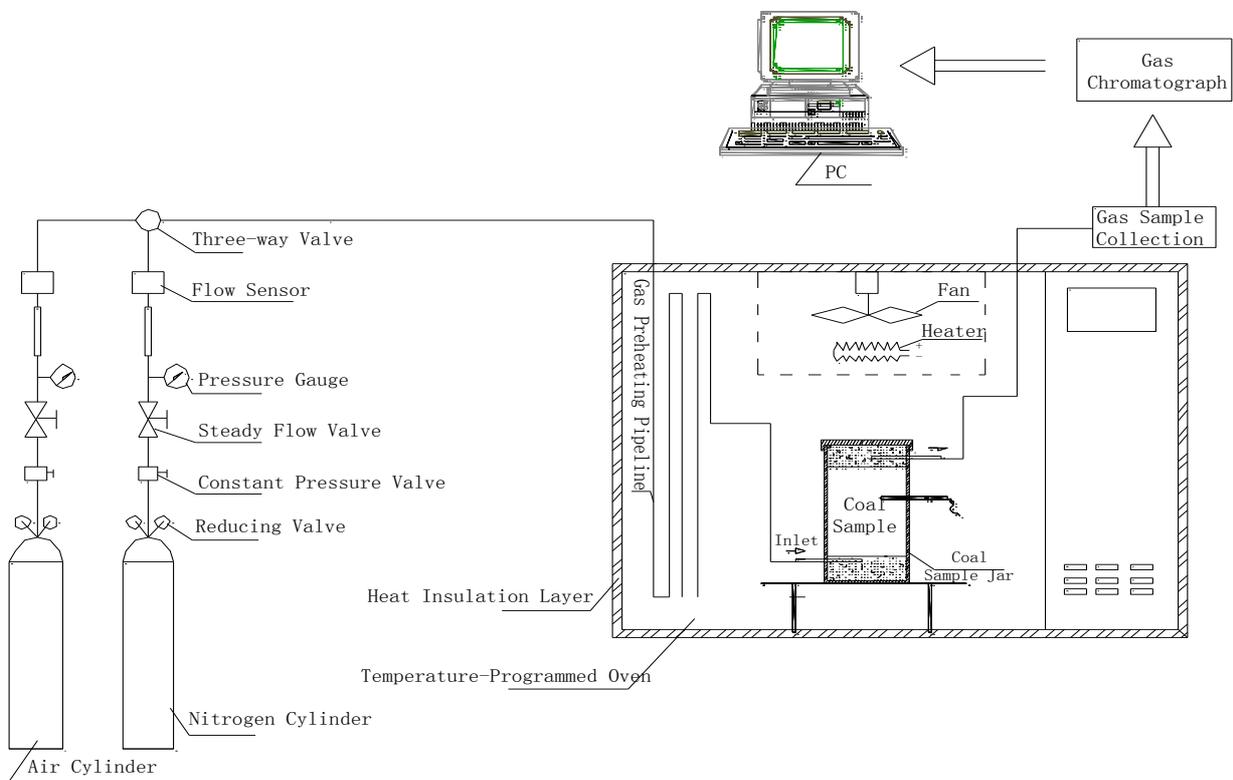
Fig. 1. Three-stage hydrogen generation model during reignition in fire zone

Fig.1 showed that the hydrogen absorbed in coal was discharged into the surrounding atmosphere in small quantities after desorption in the first stage under normal temperature or natural conditions with temperature below 150 °C.

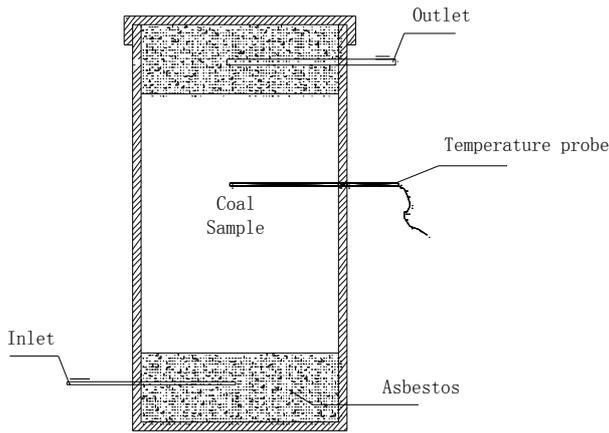
As an important product of coal oxidation at low temperatures, the emergence and variation of H₂ is connected to spontaneous coal combustion. Existing studies of the origin of H₂ are not systematic and exhaustive. Therefore, a systematic analysis of the variation of H₂ in coal oxidation at low temperatures is important to improve and establish a gas index system for the prediction, prevention and control of coal spontaneous combustion.

2. Experimental Installation

To investigate the variation of hydrogen in the spontaneous coal combustion process, a systematic desorption and coal oxidation experiment system was established. As shown in Fig.2, the system consists of a temperature-programmed oven, gas supply system, reaction vessel (coal sample jar), temperature measurement and control system and gas chromatograph. The temperature-programmed oven provides the heating environment for the experiment and ensures the uniformity of the internal temperature field. The gas supply system mainly offers oxygen and nitrogen for coal oxidation and desorption at low temperature in the reaction vessel. The coal sample jar connects the gas supply circuit, the temperature measurement system and the gas vent path. The gas chromatograph detects the types and contents of gases. A 60-m copper pipe was also installed between the gas inlet and the gas supply pipeline as a gas preheating circuit.



(a) Experiment system



(b) Coal sample jar



(c) Temperature-programmed Oven



(d) Gas chromatograph



(e) Bladder of sampling ball

Fig. 2. Integrated test system of temperature programmed for coal spontaneous combustion and desorption

3. Experimental Procedure

3# coal samples from the Dongtan Coal Mine of Yanzhou Coal Mining Company and 1# and 6# coal samples from the Cuijiashai Coal Mine in the Kailuan, Yuzhou mine area were selected as experimental coal samples. Prior to the experiment, the oxide layers on the surfaces of coal samples were stripped, and the coal samples were then crushed and ground. Finally, 25-g particles with a diameter between 40 and 60 were selected as the experimental coal samples. The proximate analysis of coal is shown in Table 1. The test device for proximate analysis is shown in Fig.3.



Fig. 3. Test device for proximate analysis of coal

Tab. 1. Results of proximate analysis of coal

Coal Sample	M _{ad} (%)	V _{ad} (%)	A _{ad} (%)	FC _{ad} (%)
3# Coal from Dongtan Coal Mine	3.11	39.45	8.92	48.52
1# Coal from Cuijiazhai Coal Mine	19.84	32.10	6.01	42.05
6# Coal from Cuijiazhai Coal Mine	18.76	29.02	6.47	45.75

3.1 Desorption of Adsorbed Hydrogen

The jar containing the coal samples was placed into the temperature programmed oven, and the flow of nitrogen was regulated to 200 ml/min. The gas chromatograph was then used to analyze the composition of the gases. When oxygen could no longer be detected in the coal sample jar, the temperature control oven was set to 105 °C, and the coal samples were heated to the same temperature under a steady nitrogen supply. The desorption of adsorbed hydrogen was initiated and continued in the coal samples until hydrogen could no longer be detected. The temperature programmed oven was then closed to cool the internal temperature to room temperature.

The desorption experiment aimed to eliminate the influence of moisture and ensured that there H₂ was not adsorbed on the coal samples during the coal oxidation experiment.

3.2 Oxidation at Low Temperature and Collection of Gas Samples

The valve of the air cylinder was opened, and dry air containing 21% oxygen was infused into the coal sample jar at a flow rate of 150 ml/min. The temperature-programmed oven was then set to 200 °C to heat and oxidize the coal samples. The gas samples were then collected and analyzed at intervals of 15 °C when the temperature of the coal samples was lower than 100 °C and at intervals of 20 °C when the temperature of coal samples exceeded 100 °C.

3.3 Experimental Results

During the desorption experiment at a temperature of 105 °C in the temperature-programmed oven, hydrogen was continuously detected in the reaction vessel; however, hydrogen could no longer be detected after approximately 24 hours of desorption. Therefore, H₂ definitely adsorbed on the coal. The hydrogen generation without desorption in the oxidation experiment, q_{total} , includes two parts, namely the H₂ adsorbed on coal, $q_{desorption}$, and the H₂ generated by coal oxidation, $q_{oxidation}$. The amount of H₂ desorption can be defined as the difference between the hydrogen q_{total} and $q_{oxidation}$ at the same temperature, i.e., $q_{total} = q_{desorption} + q_{oxidation}$. Let $Q_{oxidation}$, Q_{total} and $Q_{desorption}$ be the accumulation of $q_{oxidation}$, q_{total} and $q_{desorption}$ with respect to temperature.

4. Results Analysis

4.1 H₂ Generated by Coal Oxidation without Desorption

Fig.4 shows the relationship between the hydrogen generated by coal oxidation at low temperature (q_{total})

without desorption and the coal temperature. Fig.5 shows the relationship between the hydrogen accumulated ($Q_{oxidation}$) by coal oxidation and the temperature; Fig.6 shows the relationship between the hydrogen accumulated (Q_{total}) without desorption and the temperature; Fig.7 shows the relationship between the hydrogen accumulated ($Q_{desorption}$) by coal desorption and the temperature.

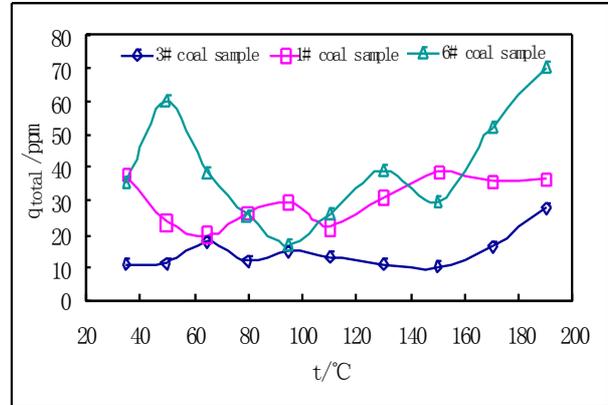


Fig. 4. H₂ generated by the oxidation of coal without desorption

Fig.4 shows that the H₂ generated by the coal oxidation without desorption (q_{total}) did not relate to the temperature for the three types of coal samples studied. Furthermore, q_{total} does not linearly correlate with changes in the temperature. Thus, H₂ cannot be directly used as a gas indicator to predict spontaneous coal combustion.

4.2 $Q_{oxidation}$ of H₂ Accumulation by Coal Oxidation

Fig.5 shows that that the H₂ accumulated due to coal oxidation after desorption, $Q_{oxidation}$, positively correlates with the temperature, and the fitting relationship between $Q_{oxidation}$ and temperature obeys LangmuirEXT1 function model, whose the parameter values are shown in table 2.

The $Q_{oxidation}$ of the 6# coal sample from the Cuijiazhai Mine exhibits a “concave” relationship with the temperature, with a demarcation point at 110 °C. $Q_{oxidation}$ increases more rapidly as the temperature increases from 35 °C ~ 110 °C, while $Q_{oxidation}$ varies slowly as the temperature increases and finally approaches a stable value when the temperature is within the range of 110 °C ~ 190 °C. For the 3# coal sample from the Dongtan Coal Mine and 1# coal sample from the Cuijiazhai Coal Mine, $Q_{oxidation}$ slowly increases as the temperature increases from 35 °C ~ 110 °C, while $Q_{oxidation}$ varies rapidly as the temperature increases from 110 °C ~ 190 °C.

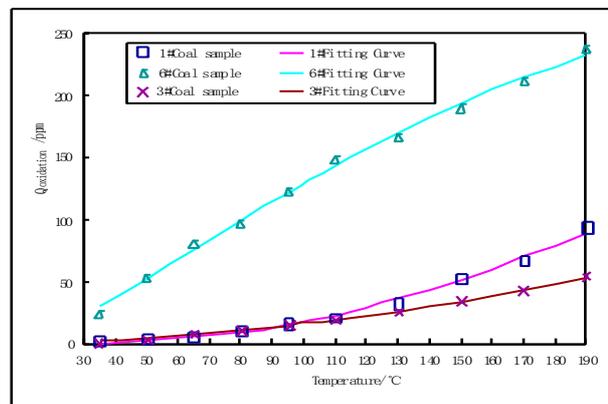


Fig. 5. Relationship between $Q_{oxidation}$ generated by coal oxidation and temperature

Tab. 2. Fitting function between $Q_{oxidation}$ and temperature

Model	LangmuirEXT1			
Function	$y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}}$			
	a	b	c	R2
1#coal sample	265.871	5.68E-08	-2.04665	0.99396
6#coal sample	695.64024	3.61E-04	-0.39335	0.99567
3#coal sample	5848.14538	4.40229E-7	-0.89457	0.98605

4.3 Q_{total} of H₂ Accumulation without Desorption

As shown in Fig.6, the Q_{total} includes not only the hydrogen generated by coal desorption but also by coal oxidation. Q_{total} increases with the temperature, and the relationship between Q_{total} and temperature obeys the LangmuirEXT1 function model, as shown in table 3. Fig.6 shows that the Q_{total} for coal desorption and oxidation smoothly varies with the increasing temperature; it does not show an obvious demarcation point.

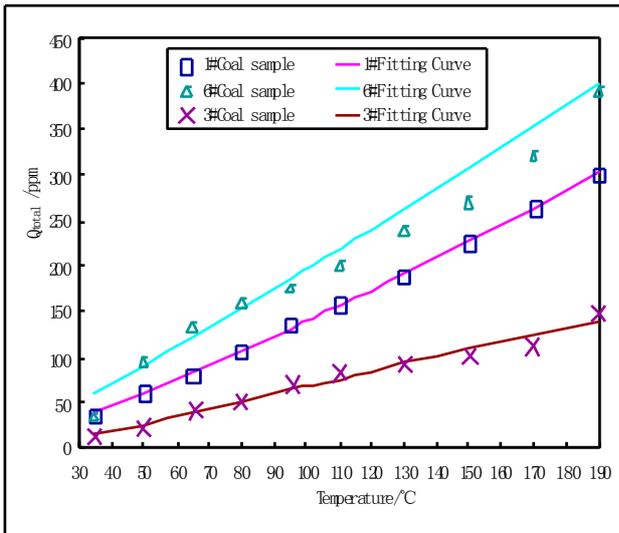


Fig.6. Relationship between Q_{total} excluding desorption and temperature

Tab.3. Fitting function about Q_{total} excluding desorption and temperature

Model	LangmuirEXT1			
Function	$y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}}$			
	a	b	c	R ²
1#Coal sample	7103.8919	6.93E-05	-0.23126	0.99948
6#Coal sample	313048.4175	1.35E-06	-0.31407	0.98530
3#Coal sample	375.04539	1.82958E-4	-0.54042	0.98334

4.4 $Q_{desorption}$ of H₂ Accumulation Generated by Coal Desorption

Fig.7 and table 4 reveal that the fitting relationship between $Q_{desorption}$ and temperature obeys the LangmuirEXT1 function model, i.e., $Q_{desorption}$ positively correlates with the temperature. The values of the parameters are shown in table 4. For the 3# coal sample from the Dongtan Coal Mine and 1# coal sample from the Cuijiashai Coal Mine, $Q_{desorption}$ is a convex function of temperature, with 95 °C as the demarcation point. When the temperature is below 95 °C, $Q_{desorption}$ increases quickly, while it increases slowly above 95 °C.

The properties of the LangmuirEXT1 function indicate that a maximum exists in the “convex” type function, i.e., $\max(Q_{desorption}) = a$. The Langmuir adsorption model for CH₄ adsorbed in coal is assumed as follows: within a certain adsorption system, a dynamic equilibrium can be established between adsorption and desorption. By adopting this hypothesis, the physical meaning of $\max(Q_{desorption}) = a$ can be described as the maximum desorption of H₂ with an increase in the temperature for a given quality of coal sample.

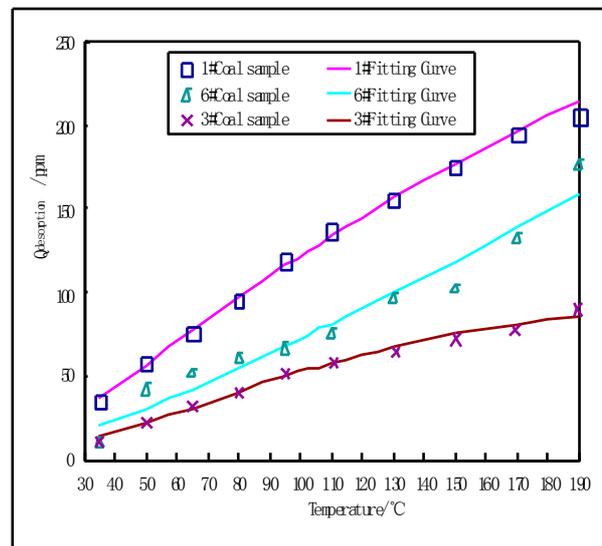


Fig. 7. Relationship between $Q_{desorption}$ and temperature

Tab. 4. Fitting function about $Q_{desorption}$ and temperature

Model	LangmuirEXT1			
Function	$y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}}$			
	a	b	c	R ²
1#Coal sample	464.4509	6.77E-04	-0.36024	0.99604
6#Coal sample	337043.0867	7.15E-09	-1.13563	0.93565
3#Coal sample	127.76787	2.33812E-4	-0.73719	0.98262

5. Conclusions

From the above analysis, the following conclusions can be drawn as follows:

(1) According to the experimental results, this paper demonstrates the adsorption of hydrogen in coal at room temperature and proposes two methods to generate hydrogen during coal oxidation at low temperature — $q_{desorption}$ generated by the desorption of the hydrogen adsorbed to coal and $q_{oxidation}$ generated by coal oxidation.

(2) The hydrogen accumulation generated by coal oxidation ($Q_{oxidation}$) and desorption ($Q_{desorption}$), and the Q_{total} all conform to the LangmuirEXT1 function relationship is shown as follow:

$$y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}}$$

The curves are “concave”, “smooth”, and “convex”, respectively and 95% is the demarcation point in the “concave” and “convex” types.

(3) Based on the LangmuirEXT1 function, the relationship between hydrogen generation and temperature, H_2 can be used as the indicator gas to predict spontaneous coal combustion in order to improve the gas index system of spontaneous combustion prediction. The results provide a theoretical basis for the prevention and control of spontaneous coal combustion in coalmines, open coal yards and industrial coal transportation.

Acknowledgments

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References

1. Ashok K. Singh; R.V.K. Singh; Mahendra P. Singh; Hem Chandra; N.K. Shukla, “Mine fire gas indices and their application to Indian underground coal mine fires”, *International Journal of Coal Geology*, 69, 2007, pp. 192-204.
2. Vered Nehemia; Shoshana Davidi; Haim Cohen, “Emission of hydrogen gas from weathered steam coal piles via formaldehyde as a precursor I. Oxidative decomposition of formaldehyde catalyzed by coal – batch reactor studies”, *Fuel*, 78, 1999, pp. 775–780.
3. S. L. Grossman; S. Davidi; Haim Cohen; “Explosion risks during the confined storage of bituminous coals—Calculation of gaseous hydrogen accumulation in ship”, *Fuel*, 74(12), 1995, pp. 1772-1775.
4. S. L. Grossman; Ina Wegener; Wolfgang Wanzl, “Molecular hydrogen evolution as a consequence of atmospheric oxidation of coal: 3. Thermo gravimetric flow reactor studies” *Fuel*, 73(5), 1994, pp. 762-767.
5. S. L. Grossman; Shoshana Davidi; Haim Cohen, “Evolution of molecular hydrogen during the atmospheric oxidation of coal”, *Fuel*, 70(7), 1991, pp. 897-898.
6. S. L. Grossman; Shoshana Davidi; Haim Cohen, “Molecular hydrogen evolution as a consequence of atmospheric oxidation of coal: 1. Batch reactor simulations”, *Fuel*, 72(2), 1993, pp. 193-197.
7. Cohen; Haim, “Molecular hydrogen formed via low temperature oxidation of bituminous coals as the source of explosions in underground coal mines” // *25th Annual International Pittsburgh Coal Conference, PCC – Proceedings*. USA: CSREA Press, 2008.
8. Liang H. D. “Emission of Molecular Hydrogen from Coal –A Security related Phenomenon for Coal Transportation and Production”, *Mining Safety & Environmental Protection*, 28(2), 2001, pp. 1-3. (In Chinese)
9. Dai G. L., Zhang G. S., Shao H., “Study on Relationship between Hydrogen and Oxidization and Spontaneous Combustion of Coal in Gobs in Xinji Coal Mine”, *Coal Engineer*, 1998 (2), pp. 12-15. (In Chinese)
10. Zhou Q, Jiang H. Q, Liang H. D., “Analysis of the Hydrogen Release from Coalbed Gas, Southern QinShui Basin”, *Nature Gas Geoscience*, 17(6), 2007, pp. 871-873. (In Chinese)
11. Qi W, Zhang L, Zhang L, Shu X Q, Ding Z J, Li G. “Research progress of coal to hydrogen by way of catalytic decomposition process”, *China Coal*, 33(10), 2003, pp. 57-58. (In Chinese)
12. Li Z H, Lin B Q, Zhang L Q, Pan S K, He Y H. “Effects of hydrogen production on gas explosion”, *Journal of China University of Mining & Technology*, 37(2), 2008, pp. 147-151. (In Chinese)
13. Sun X X, Chen J Y. “*The Physical and Chemical Basis of Pulverized Coal*”, Wuhan: Huazhong University of Science and Technology Press, 1991. (In Chinese)
14. Zhou F. B, Li J. H, Liu Y.S, Shao H. “Rules of variation in hydrogen during reignition of underground fire zones of spontaneous coal combustion”, *Mining Science and Technology*, 20(4), 2010, pp. 499-503.