Experimental Study on Primal CO Desorption Effect Factors: External Causes

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Carbon monoxide (CO) is a commonly used indicator gas to predict the risk of coal spontaneous combustion. However, the occurrence of primal CO in coal seam may result in error of prediction. Therefore, identifying the primal CO in coal seam is crucial to improve the accuracy of coal spontaneous combustion prediction. This paper conducts a laboratory experiment to research the regularities of primal CO desorption. Four analysis factors are introduced to represent the CO emission characteristics in different desorption stages. The result indicates that CO generated by different coal samples' oxidation has big differences. Ambient temperature has little effect on CO initial emission concentration. CO concentration in the first one and first ten desorption hour increases regularly with the increase of crushing time, primal CO cannot be ignored especially in high temperature coal mines.

1. Introduction

Coal spontaneous combustion is a kind of serious accident that results in large number of safety problems, severe environment pollution and significant property loss (Alberto and Enrico, 2016; Barraza-Burgos et al., 2015; Hower et al., 2013; Tomohiko et al., 2016; Monika and Agnoeszka, 2016). Indicator gas technique is a commonly used method to predict coal spontaneous combustion. Recently, a number of researches have been conducted on gas productions during coal self-heating process (Mao et al., 2013; Qin et al., 2013; Wang ei al. 2015). Generally, scholars attribute the differences of coal self-heating reaction rate and productions to the effects of internal factors (coal physical properties, particle size and so on) and external factors (temperature, moisture content of air, O_2 concentration and so on) (Taraba and Pavelek, 2014). Therefore, the regularity of coal spontaneous combustion is mainly revealed by monitoring the gaseous productions with various conditions (Yuan and Smith, 2011; Carras et al., 2009; Jim et al., 2016). The results of these researches indicates that CO is produced at the very early stage of coal oxidation, and the amount of CO released is independent of airflow (Nugrohom, 2000).

However, the generation of CO isn't solely caused by coal self-heating. When organic matters buried, many complex physical and chemical reactions resulted in carbon element accumulation and volatile vocalization, in conditions of high temperature, high pressure and biological action. This is an important factor to cause CO generation (Jiang et al. 2010). Gases produced in coal-forming process are mainly hydrocarbon gases, but non-hydrocarbon gases including CO also accounts for a big proportion. CO concentration in coal seam varies with environmental complexity and coal molecular structure (Tselev et al. 2014).

Many scholars believe that CO_2, CO, H_2O and other non-hydrocarbon gases are produced by free radical crosslinking reaction in the process of coal-forming. By analyzing the composition of coal seam gases, researchers found that H_2S, CO, N_xO and some rare gases show abnormal high concentration in some special conditions (Solomon et al., 1990; Mae et al., 2002; Wang et al. 2008; Schoell, 1980).

Research on coal seam gas desorption has been experienced hundreds of years, but research on the relationship between coal and coal seam primal CO is in early development stage. Cygankiewicz studied on CO adsorption and desorption of hard coal and the result shows that CO adsorption of hard coal is an irreversible process, isotherm adsorption under the condition of low pressure cannot be overlapped, the CO adsorption of hard coal is influenced by carbon, oxygen elements and coal rank. High oxygen content and low

carbon content coal sample could adsorb more CO (Cygankiewicz et al., 2007). Guo conducted pure CO isothermal adsorption experiments of coal in different temperature conditions (t≤50℃), and concluded that CO adsorption of coal samples decreased with the increase of temperature in the experimental test of low temperature and low pressure conditions, CO adsorption quantity increased with the increase of temperature in high pressure conditions, Guo believes chemical adsorption happens (Xiao, 2007).

Primal CO emission can cause errors for CO as coal spontaneous combustion prediction indicator gas. In this paper, laboratory experiments were conducted to monitor CO concentration, 4 analysis factors were determined to represent the characteristics of CO emission in different stages, the CO emission changing regulations with exogenous causes were analyzed. The experimental results have implications for the coal self-heating prediction.

2. Experimental

2.1 Coal seam primal CO desorption experimental device

This test system was proposed to control the degree of broken coal samples by adjusting the coal sample crushing time, to adjust and change the ambient temperature using programmed temperature control box, to change atmosphere environment using valve system, to realize airtight environment using sampling jug. Experiments were conducted in 6 conditions: 1)Charging with pure nitrogen, break each coal sample for 3h at 25℃ with the best grinding rate (A), 2)Charging with pure nitrogen, break each coal sample for 2h at 30℃ with the best grinding rate (B), 3)Charging with pure nitrogen, break each coal sample for 3h at 30℃ with the best grinding rate (C), 4)Charging with pure nitrogen, break each coal sample for 3h at 35℃ with the best grinding rate (D), 5)Charging with air, break each coal sample for 3h at 30℃ with the best grinding rate (E), 6)Charging with pure nitrogen, break each coal sample for 4h at 30℃ with the best grinding rate (F). Collect one gas sample each hour in the first 10 hours, and collect the 11th sample after 24 hours desorption. Analyze the desorpted gas components using gas chromatograph (GC).

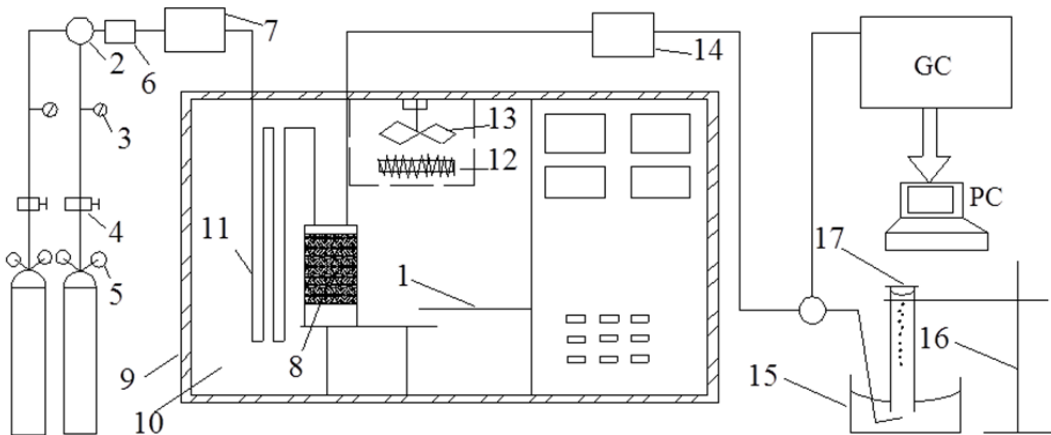System structure and composition is shown in Figure 1.

Figure 1: Coal seam gas isotherm desorption and gas analysis device testing system. 1-force pump 2-tee junction 3-pressure gage 4-pressure maintaining valve 5-pressure reducing valve 6-dust remover 7-inlet mixing warehouse 8-coal sample jug 9-thermal insulating layer 10-programmed temperature control box 11-gas preheating tubes 12-heater 13-fan 14-outflow gas filter chamber 15-water channel 16-iron support 17-gas collection measuring cylinder

2.2 Ultimate analysis and proximate analysis

Coal samples were collected at workface from Xingtao coal mine (1#), Donghuantuo coal mine (2#), Linnancang coal mine (3#), Xixizhuang 1# coal mine (4#), Xixizhuang 5# coal mine (5#) and Dashucun coal mine (6#). The proximate analysis was conducted using GF-A6 automatic proximate analysis device. The ultimate analysis was conducted using vario MACRO CHNS ultimate analysis device. The ultimate analyses and proximate analyses are given in Table 1.

Table 1: The ultimate analyses and proximate analyses results

Properties	1#	2#	3#	4#	5#	6#
Ultimate analysis (wt%)						
C	66.19	72.485	72.335	60.95	76.805	84.65
H	5.031	5.359	5.815	5.306	3.566	4.117
N	1.313	1.558	1.666	0.854	1.116	1.811
S	0.852	0.808	0.582	0.204	0.814	0.354
O	13.57	9.424	11.02	22.265	4.575	2.6
C/N	50.4	46.525	43.43	71.39	68.83	46.76
Proximate analysis (wt%)						
Moisture	3.41	3.18	2.84	17.76	2.37	0.81
Ash	9.45	7.97	7.49	5.945	11.44	5.18
Volatile matter	32.98	33.51	35.98	30.85	9.515	8.915
Fixed carbon	55.62	56.66	54.94	51.99	77.18	85.22

3. Results and analysis

3.1 Analysis factors

By fitting the CO desorption concentration with time, CO gas desorption concentration distribution model is:

$$y = cx^{-b} \tag{1}$$

Where x is time, y is CO desorption concentration. The fitting degree is 0.96.

To further investigate the effects the external causes on CO desorption in different stages, CO concentration at the 1st hour is selected to be primal CO initial desorption analysis index, use I_c for short. I_c represents the coal seam CO initial desorption concentration. Use exponential term of fitted equation as the primal CO desorption decay factor, use I_a for short. I_a represents the degree of coal seam CO desorption concentration attenuation. The sum of desorption quantity of the first 10h (add up the values of the first 10 sampling) is selected to be the primal CO emission quantity factor, use I_{Q10} for short. The value of the 11th sampling is selected to be the primal CO desorption quantity during 10-24h, use I_{Q10-24} for short. I_a and I_{Q10-24} are factors represent CO desorption regulation, I_c and I_{Q10} are factors represent CO emission quantity.

3.2 Ambient temperature

Different analysis factors of various coal samples change with temperature are shown in Figure 2.
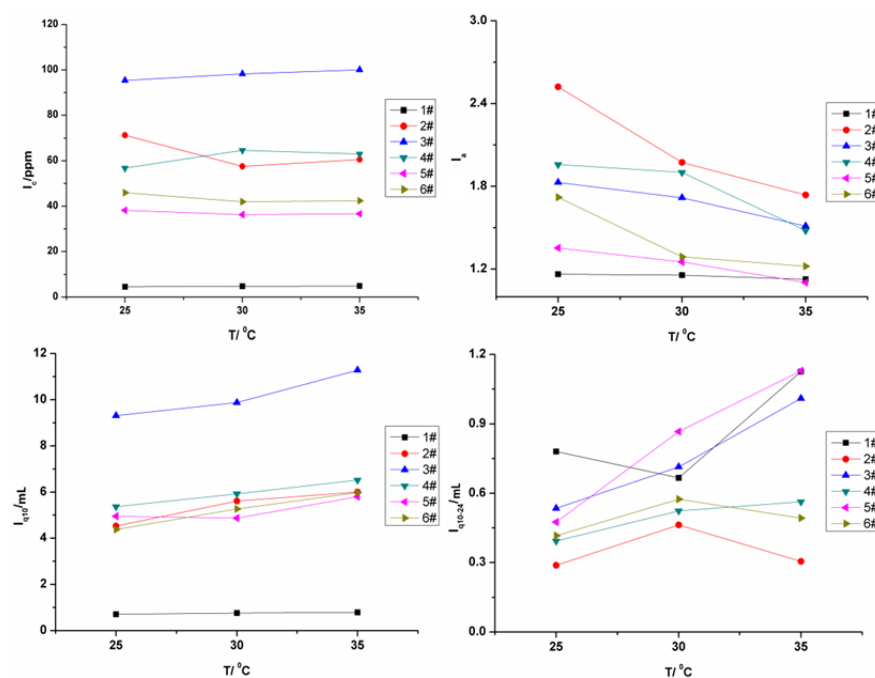

Figure 2: Influence of ambient temperature on CO analysis factors

Some of the analysis factors regularly change with ambient temperature. In Figure 2, I_c has little change with temperature rise, which mainly because the effect of temperature on CO desorption is sustainable, 1 hour is too short to change the desorption rate. I_a decreases with the increase of ambient temperature, the rise of temperature is advantageous to CO gas desorption, so desorption decay rate decreases rapidly with temperature raise. I_{Q10} basically increases with the increase of temperature, 5# coal sample slightly decreases in 25-30℃, primal CO desorption increases with the raise of temperature in the first 10 hours, which is in accordance with the change of decay rate, the higher temperature, the higher primal CO desorption rate. I_{Q10-24} of 3#, 4# and 5# coal samples persistently increases with the temperature raise, 2# and 6# coal samples first increase and then decrease with increase of temperature. The primal CO residual quantity after 10 hours desorption may be affected by characteristics of coal samples.
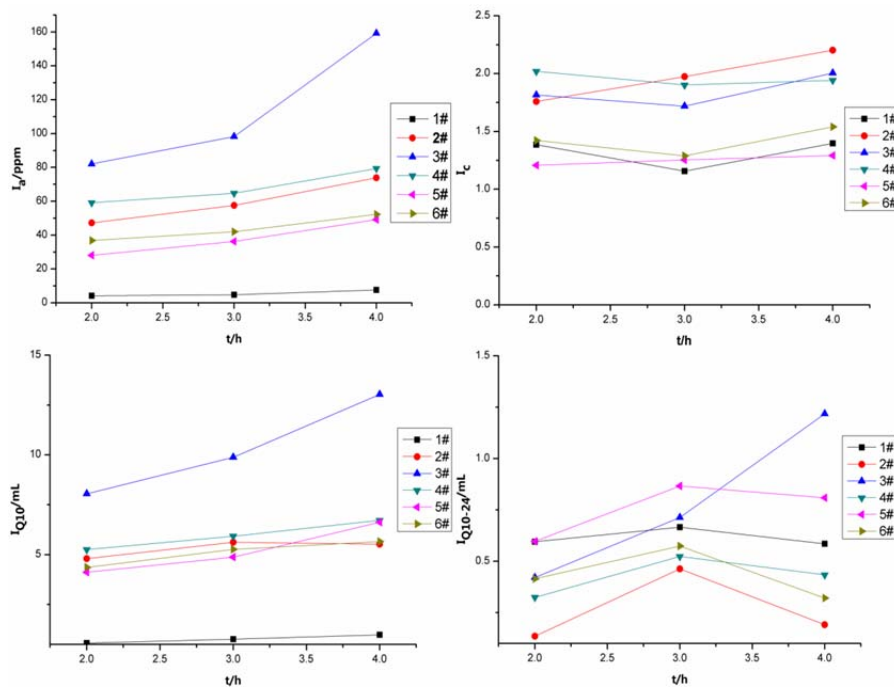
3.3 Degree of crushing

Figure 3: Influence of crushing degree on CO analysis factors

Coal samples were crushed in ball mill at the same rotate speed for 2h, 3h and 4h, different analysis factors of various coal samples change with crushing time are shown in Figure 3. Some of the analysis indexes change very regularly with crushing time.

Crushing time has great influence on I_c and I_{Q10}, I_c and I_{Q10} increase with the increase of crushing time, Which is mainly because that longer crushing time creates more coal grains and larger free surface, the CO emission path inside the coal grains becomes shorter. Increase of crushing degree can reduce the dead space in coal grains, which makes primal CO desorption more easily.

With crushing time raise, I_a basically decreases first and then increase, I_a of 2# and 5# coal samples increases continuously, which may be because that the decay rate is affected by crushing degree and the residual CO quantity. When crushing time is short, the small coal grain free surface, the long desorption path inside coal grain and the large dead space make CO unable to desorb. When crushing time is long, the higher crushing degree, the larger coal grain free surface and the shorter emission path make CO easier to desorb, but the less residual CO volume increase the desorption decay rate.

I_{Q10-24} increases first and decreases with the increase of crushing time, I_{Q10-24} of 3# coal sample continues to increase with crushing time raise, the reasons of long and short crushing time leading to low I_{Q10-24} are similar with the change of I_a value.

3.4 Ambient atmosphere

Plot Figure 4 (a) by the coal samples on the horizontal axis and the I_{Q10} ratio and I_{Q10-24} ratio in different E (air charging conditon) and C (N_2 charging condition) experimental conditions on the vertical axis, plot Figure 4 (b)

by the time on the horizontal axis and the difference of CO desorption in N_2 and air charging conditions on the vertical axis.

As can be seen in Figure 4 (a), I_{Q10-E}/I_{Q10-C} is between 2 and 4 except 1# and 4# coal sample, CO desorption in the first 10 hours takes a great proportion in primal CO quantity, especially in the initial stage of desorption, primal CO desorption quantity is larger than CO generated by oxidation, maybe the large content of CO is caused by crushing process. 1# coal sample has low primal CO quantity and high oxidized CO quantity, so abnormally high CO content detected after crushing maybe reduced by low temperature oxidation. 4# coal sample is brown coal, has high primal CO and is easily to be oxidized in low temperature, CO content produced by oxidation is 5-10 times as other coal samples, I_{Q10-E}/I_{Q10-C} in air and N_2 charging condition is very high, high content CO detected after coal crushing should be considered caused by low temperature oxidation.
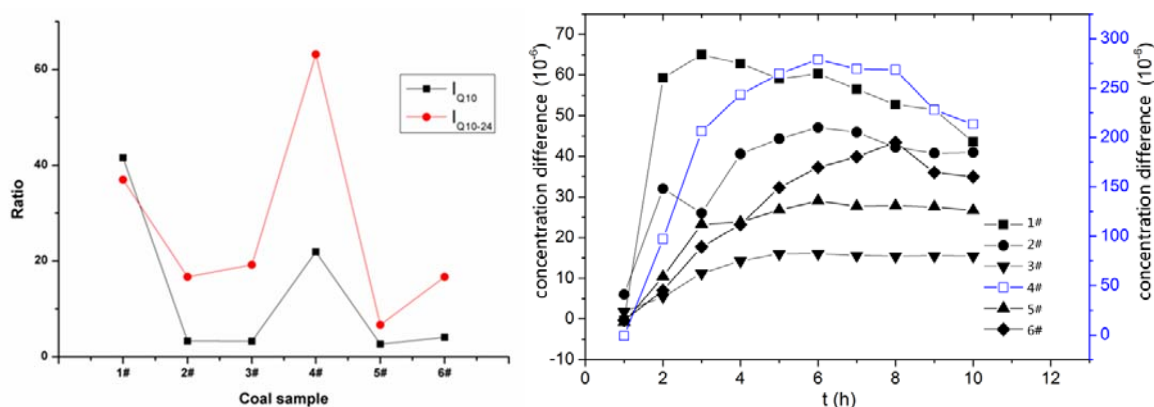

Figure 4: (a) IQ10-E/ IQ10-C and IQ10-24-E/ IQ10-24-C; (b) CO concentration difference in E and C experimental conditions

The difference in Figure 4 (b) means the CO content produced by oxidation in 30℃. All 6 coal samples CO content difference increase first and then decrease with time, but the decrease extent is limited. 4# and 1# coal sample has low metamorphic grade and easily to be oxidized, 4# coal sample produces 300×10^{-6} CO. 1# coal sample has low primal CO content, also produce 70×10^{-6} CO by oxidation. The other 4 coal samples are high metamorphic coal samples, CO concentration produced by oxidation is significantly lower than 1# and 4# coal samples, CO produced by oxidation of 5# coal sample is even lower than primal CO content. Most CO content is inclined to be produced by oxidation in low metamorphic coal seam in low temperature, the unusual high CO concentration in high metamorphic coal seam should be considered caused by primal CO emission.

4. Conclusion

Laboratory experiments were conducted to test the impact of external causes on primal CO desorption. Based on preliminary analysis, the quantity of CO desorption decreases exponentially with time goes by. Four analysis factors (I_c, I_a, I_{Q10} and I_{Q10-24}) are introduced to represent the characteristics of CO desorption regulations and desorption quantity.

Ambient temperature has little effect on CO initial emission concentration, but the decay rate of primal CO desorption decreases with the increase of temperature, higher ambient temperature is more advantageous to CO gas desorption.

Crushing time could significantly change coal free surface, emission path and the dead space of coal, CO desorption quantity increases regularly with the increase of crushing time, but the variation of desorption is ambiguous for some coal samples, which may be because of the lack of primal CO. The change laws of coal free surface, porosity and specific surface area which changes with crushing time on primal CO desorption should be further studied and investigated.

By comparing the CO desorption concentration in N_2 and air conditions, the primal CO concentration should not be ignored especially in low metamorphic coal seam. The result of this study indicates that coal seam primal CO concentration maybe high enough to mislead the indicator gas analysis results. When applying indicator gas method, the primal CO desorption should be taken fully consideration, especially in coal seam with relatively high ambient temperature and high ground stress.

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