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Study on Preventive and Control Effect of Composite Flame Retardants on Coal Spontaneous Combustion Based on the Heating Spontaneous Combustion Test

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Coal spontaneous combustion seriously affect the safety of coal production enterprises, and using flame retardants is an important means to prevent coal spontaneous combustion. Based on the heating spontaneous combustion test, the effects of retardants, including $MgCl_2$ flame retardant and secondary aromatic amines, on the long flame coal of Yima, bituminous coal of Pingdingshan and Yangquan anthracite are tested in this paper. The experimental results show that both kinds of flame retardants have good effects. The effect of the spontaneous combustion flame retardants on Yima long flame coal and Pingdingshan bituminous coal is better than that of $MgCl_2$ flame retardant, but $MgCl_2$ flame retardant has better effects on Yangquan anthracite. Moreover, the flame retardant mechanism of the two kinds of flame retardants is different. $MgCl_2$ flame retardant absorbs water vapor in the air, while the secondary aromatic amine flame retardant will react with the free radicals generated by coal under high temperature, thereby cutting off the chain of coal oxidation reaction.

1. Introduction

Coal is the most important fossil energy in China. Spontaneous combustion of coal is a common phenomenon of coal seam, which exists in nearly three quarters of the coal seams in China. According to incomplete statistics, the fires caused by coal spontaneous combustion accounts for 97% of the natural fires (Gürdal et al., 2015; Pelucchi et al., 2017). Spontaneous combustion of coal seam not only causes economic loss, but also causes serious pollution to the environment (Xu et al., 2012). It is necessary to have corresponding fire preventing and fighting measures in order to prevent spontaneous combustion of coal in the process of coal mining (Pandey et al., 2015). The degree of coal spontaneous combustion is closely related to the composition and structure of coal. The chemical structure, characteristics of surface functional groups, carbonization degree, moisture content, sulfur content and pore structure of coal determine the low temperature spontaneous combustion ability of coal (Lin et al., 2017; Parsa et al., 2017).
At present, the researches on coal spontaneous combustion flame retardants are attracting more and more attention. Flame retardants commonly used at home and abroad include gypsum slurry injection grouting, inert foam plugging, anti-spontaneous combustion flame retardants, powdered flame retardants and gel, etc (Du et al., 2014; Xi and Li, 2016). It is found that most of the researches focus on the study of physical flame retardants, not the chemical flame retardants in inhibiting the spontaneous combustion of coal seam. And the existing researches only give the qualitative analysis, without discussing the mechanism (Qin et al., 2016). It is necessary to understand the chemical kinetic mechanism and kinetic model of coal spontaneous combustion in order to study the mechanism of chemical flame retardant on spontaneous combustion of coal (Sahu et al., 2012). Based on the heating spontaneous combustion test, three representative coal samples and two kinds of flame retardants are selected as the research object to study the kinetic mechanism of flame retardant on coal spontaneous combustion through kinetics.

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2. Preparation and Experiment of Coal Samples

Three kinds of typical coals were selected as samples in the experiment, including Yima long flame coal, Pingdingshan bituminous coal and Yangquan anthracite. The industrial analysis of the three coal samples is shown in Table 1. The spontaneous combustion flame retardant and $MgCl_2$ flame retardant were selected for the experiment. Weigh 50g (as accurate as to 0.01g) experimental coal sample with a balance and put it into a reaction tube with asbestos at the bottom of the tube. Add flame retardant in proportion, turn on the thermostat, connect the gas path, start the compressor, and use a float flow meter to measure the air flow rate to ensure that the air flow rate is controlled at 160 ml / min. Turn on the temperature switch to raise the temperature to 150 ° C. Then the CO content released from the reaction tube would be automatically recorded by a gas analyzer. The flame retardant curve was drawn according to the measurement value of CO release, and the flame retardant rate of the flame retardant to coal spontaneous combustion was calculated.

Table 1: Industrial analysis of coal samples

Sample	Moisture/%	Ash content/%	Volatile/%	Fixed carbon/%
Yima long flame coal	11.53	17.13	39.22	32.12
Pingdingshan bituminous coal	6.78	15.18	24.28	53.76
Yangquan anthracite coal	1.77	5.62	13.72	79.99

3. Experimental Study on Thermal Characteristics of Coal Spontaneous Combustion and Flame Retardancy

3.1 Comparison of spontaneous combustion characteristics of original coal samples

With a composition of N, H, O and C atoms, the coal will show different spontaneous combustion activity with different atom contents (Peng et al., 2016). There is a characteristic temperature in the process of spontaneous combustion of coal, the higher the characteristic temperature is, the more conditions the coal spontaneous combustion will require, and the more difficult the spontaneous combustion phenomenon will occur. As can be seen from the Figure 1 showing the TG-DTG-DSC curves of three kinds of coal samples, 7 characteristic temperature points can be obtained from each coal sample: T1 - upper adsorption temperature; T2 - critical temperature; T3 - dry cracking temperature; T4 - growth temperature; T5 - combustion temperature; T6 - maximum temperature of weight loss rate; T7 - burnout temperature. Among them, T5 represents the thermal stability of coal. It can be seen from the figure that Pingdingshan bituminous coal has the highest adsorption temperature, followed by Yima long flame coal and Yangquan anthracite coal.

3.2 Effect of heating rate on spontaneous combustion and flame retardancy of coal

In this paper, the spontaneous combustion of three kinds of original coal samples and the flame retardancy of coal after adding $MgCl_2$ flame retardant and spontaneous combustion agent are studied after the heating rate is increased from 10 ℃ / min to 20 ℃ / min. Table 2 shows the thermal characteristic value of original coal samples at different heating up rates, and Table 3 shows the thermal characteristic value of coal samples with flame retardants at different heating up rates. It can be seen from Table 2 that the spontaneous combustion reaction of original coal samples is sensitive to the heating rate. The maximum weight loss rate, the maximum exothermic point and the maximum heat loss of coal samples are reduced after adding flame retardant to them. In addition, after the addition of flame retardant, the range of weight loss of coal samples expands and the maximum point of weight loss also increases.

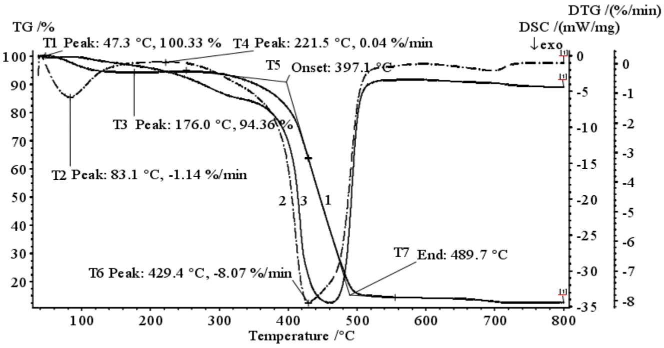
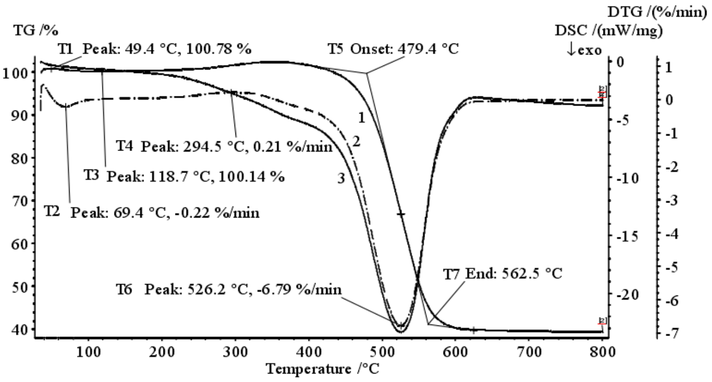
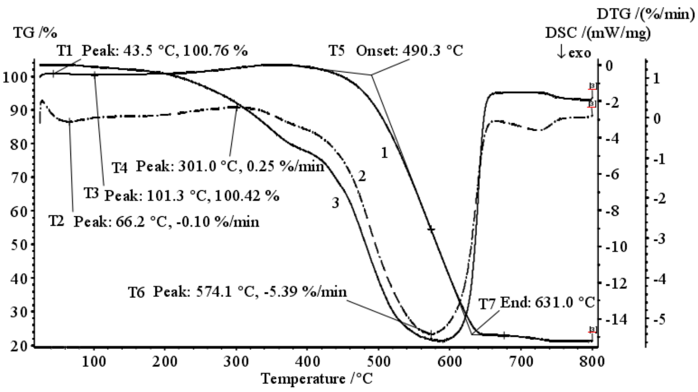


Figure 1: The TG-DTG-DSC graph of coal samples: (a) Yima long flame coal



(b) Pingdingshan bituminous coal



(c) Yangquan anthracite coal

Figure 1: The TG-DTG-DSC graph of coal samples

Table 2: Thermal characteristic values of natural coal under different temperature gradient

Heating rate (°C·min^{-1})	Weight gain range/°C	Weight loss range/°C	Maximum weightlessness point/°C	Maximum weight loss rate (%·min^{-1})	Maximum exothermic point/°C	Maximum loss heat (mW·mg^{-1})
10	83.1-252	252-489.4	429	8.07	461	37.48
20	96.8-242.8	242.8-544.5	446.3	9.92	511.5	39.72

Table 3: Thermal characteristic values of inhibited coal under different temperature gradient

Heating rate (°C·min^{-1})	Weight gain range/°C	Weight loss range/°C	Maximum weightlessness point/°C	Maximum weight loss rate (%·min^{-1})	Maximum exothermic point/°C	Maximum loss heat (mW·mg^{-1})
10	83.3-294	294-503.8	447.6	7.76	470.6	35.79
20	97.3-242.4	242.4-568.7	475.7	9.42	532.8	38.73

4. Comparative Study of Spontaneous Combustion and Flame Retardant Efficiency of Coal at Constant Temperature

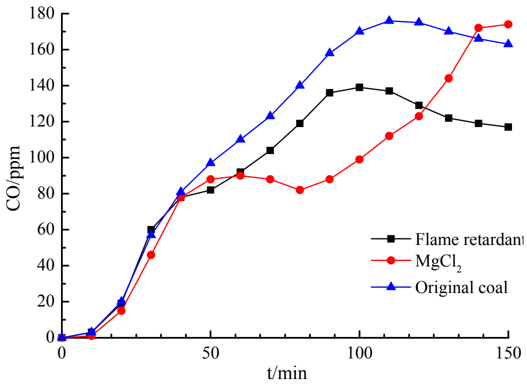
4.1 Comparison of flame-retardant efficiency of flame retardant to coal spontaneous combustion

At present, the index to measure coal spontaneous combustion is CO. The reliability coefficient of coal spontaneous combustion degree is high with CO as index, and the output of CO is closely related to coal temperature (Ozdeniz, 2010; Yang et al., 2015). In this paper, the flame retardant curve is drawn according to the amount of CO measured by the gas analyzer automatically with temperature constant at 1,150 □ based on the heating spontaneous combustion test. The flame retardant rate of the flame retardant is defined as Formula 1.

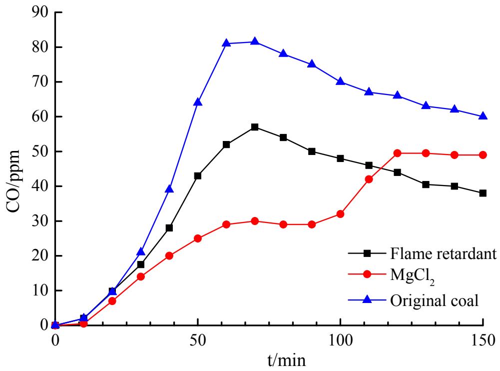
$$E=(S_1-S_2)/S_1\times 100\% \quad (1)$$

Where, E is the flame retardant rate of the flame retardant /%; S_1 is the total CO concentration released by the original coal sample within 150 min / ppm·min; S2 is the sum of CO concentration released in 150 min by the original coal sample with a flame-retardant / ppm·min.

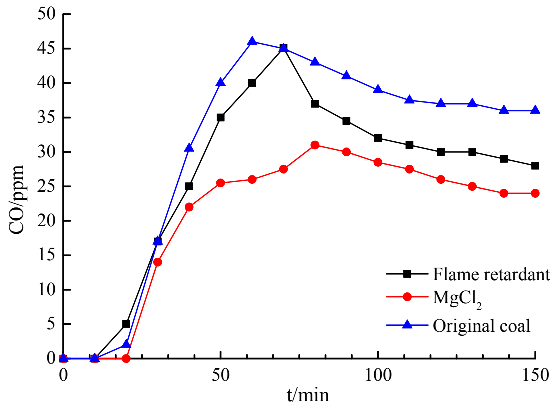
Figure 2 is the flame retardancy curve of spontaneous combustion of the same coal sample with different flame retardants. Figure 2 (a) shows the flame retardancy curve of Yima long flame coal, from where it can be seen that the flame retardants work starting from the 30min, and the flame retardant effect reaches the strongest at about 80min after adding $MgCl_2$ flame retardant, then the flame retardant effect is weakened, and shows negative flame retardancy at 140min. The flame retardant effect becomes obvious starting from the 40min after adding flame retardant and becomes stronger 100min after adding flame retardant. Figure 2 (b) shows the flame retardancy curve of Pingdingshan bituminous coal, from where it can be seen that the flame retardant works from the first 15min and both flame retardants show good flame retardant effect.



(a) Yima long flame coal



(b) Pingdingshan bituminous coal

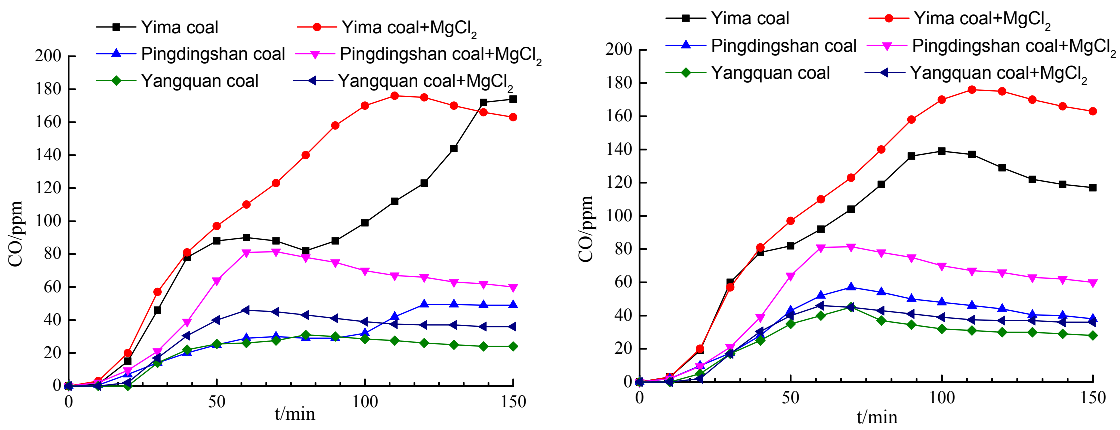


(c) Yangquan anthracite coal

Figure 2: Inhibitory curves that different inhibitors inhibit coal samples

Figure 3 shows a flame retardancy curve for spontaneous combustion of different coal samples, from where it can be seen that the total CO release of coal samples with flame retardant reaches its peak at 75min, the flame retardant effect of the spontaneous combustion flame retardant on Yima long flame coal and Pingdingshan bituminous coal is better than that of $MgCl_2$ flame retardant, and $MgCl_2$ flame retardant has better flame retardant effect on Yangquan anthracite. Table 4 shows the flame retardant rate and total flame retardant rate of three kinds of coal samples at different combustion stages, where E1 is the flame retardancy of coal in the early stage of spontaneous combustion, E2 is the flame retardancy of coal in the latter stage of spontaneous combustion, and E is the total retardant rate of coal in the whole spontaneous combustion stage.

It can be seen that the both kinds of flame retardants have the best effect on the flame retardancy of Pingdingshan bituminous coal.



(a) $MgCl_2$ *(b) Flame retardant*

Figure 3: Resistance of flame retardant to different types of coal spontaneous combustion curve

Table 4: Inhibitory rate of inhibitors to three kinds of coal in different spontaneous combustion stages

Flame retardant	Yima coal			Pingdingshan coal			Yangquan coal		
	E_1	E_2	E	E_1	E_2	E	E_1	E_2	E
$MgCl_2$	27.9	19.7	25.6	64.3	31	80.4	27.1	32.3	29.1
Flame retardant	13.2	25.8	20.6	30.3	33.6	49.5	14.7	19.4	16.5

4.2 Analysis of flame retardant mechanism of flame retardants

The groundwater is a good flame retardant. The surface of coal is covered by water film, which blocks oxygen and reduces the internal temperature. With the increase of moisture on the surface of coal, the effect of blocking coal spontaneous combustion is increased. When the coal surface moisture decreases, the external moisture of the coal will change from the original flame retardant effect to a catalytic effect, which will promote the spontaneous combustion and oxidation of the coal. $MgCl_2$ flame retardant is an inorganic salt flame retardant with good water absorption and moisturizing properties, which absorbs water vapor in the air to generate water vapor film on the coal seam surface, thereby reducing the evaporation and temperature rising rate of water, so as to achieve the purpose of spontaneous combustion of coal. The spontaneous combustion flame retardant is a kind of secondary aromatic amine flame retardant, containing group -NH. The effect of this flame retardant mainly happens in the later stage, which is not obvious at the early stage of coal oxidation. The coal generates reactive radicals at high temperature, which will react with the -NH group provided by the secondary aromatic amine flame retardant, thereby cutting off the reaction chain of coal oxidation.

5. Conclusions

In this paper, the flame retardant effect of $MgCl_2$ flame retardant and secondary aromatic amine flame retardant on three kinds of coal samples is studied based on the heating oxidation test. The specific conclusions are as follows:

From the TG-DTG-DSC curve of the three coal samples, it can be seen that Pingdingshan bituminous coal has the highest adsorption temperature, followed by Yima long flame coal and Yangquan anthracite coal.

The flame retardant effect of the spontaneous combustion flame retardant on Yima long flame coal and Pingdingshan bituminous coal is better than that of $MgCl_2$ flame retardant, and $MgCl_2$ flame retardant has better flame retardant effect on Yangquan anthracite.

Moreover, the flame retardant mechanism of the two kinds of flame retardants is different. $MgCl_2$ flame retardant absorbs water vapor in the air to generate water vapor film on the coal seam surface, thereby reducing the evaporation and temperature rising rate of water, so as to achieve the purpose of spontaneous combustion of coal. The effect of spontaneous combustion flame retardant mainly happens in the later stage, which is not obvious at the early stage of coal oxidation. The coal generates reactive radicals at high temperature, which will react with the -NH group provided by the secondary aromatic amine flame retardant, thereby cutting off the reaction chain of coal oxidation.

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