Article

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Research on the Inhibition Effect of Coal Spontaneous Combustion by Hydrated Phase Change Materials

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Abstract: In order to the effect of hydrated phase change materials on suppressing coal spontaneous combustion, the thermogravimetric experiment and reaction activation energy analysis experiment were used to explore the changes of combustion characteristic, parameters characteristic temperature and activating energy of gas coal, long flame coal, meagre coal, and lean coal before and after adding hydrated phase change materials. The research results showed that hydrated phase change materials increased the coal samples'characteristic temperature point and have effective inhibitory effects on different stages of oxidation process.However, the effect was best at low temperatures, as hydrated phase change materials undergo phase change and absorb heat when heated at low temperatures, isolating coal from contact with oxygen. The activating energy increased by 1.138 KJ·mol^{-1}～23.048 KJ·mol^{-1} and the mass loss reduced by 1.6%～9.3% after the inhibition of the coal sample,indicating that the oxidation rate of various coal samples can be slowed down and the spontaneous combustion can be suppressed by using hydrated phase change materials.At the same time, this material can also reduce the combustibility index of meagre coal and lean coal, as well as the comprehensive combustion index and maximum loss rate of long flame coal and gas coal.

Keywords: hydrated phase change materials; coal spontaneous combustion; thermogravimetric; activating energy; inhibitory effect

1. Introduction

Due to the characteristics of energy storage in China, coal has always held a relatively important position in China's energy consumption[1-3]. Coal has a natural tendency to spontaneous combustion under certain conditions. There is more residual coal in the goaf due to increased mining intensity, coupled with severe air leakage, making the possibility of residual coal to self ignite increasingly higher.Coal spontaneous combustion can cause huge economic losses[4].Therefore,the mechanism of coal spontaneous combustion must be investigated in order to guarantee the safety of coal mine produce[5-6]. According to the most widely accepted coal oxidation hypothesis by scholars both domestically and internationally[7], the process by which coal's reaction groups react with oxygen to produce heat is known as coal spontaneous combustion. This process increases the temperature of the coal, accelerates the oxidation reaction, and generates more heat overall. When the heat accumulates and reaches the combustion temperature, coal will undergo combustion. Therefore, controlling the release of heat on coal oxidation during the stage of low-temperature is particularly important. According to previous research, existing measures to prevent coal spontaneous combustion have been considered from two aspects: endothermic cooling and oxygen isolation, including grouting[8], injecting gel[9], inert gas[10-11], spraying inhibitor[12-14]. Among them, many scholars are interested in inhibitors because they effectively prevent coal from spontaneously combusting. Currently, various inhibitors have been developed and applied on site both domestically and internationally, and their performance has been studied, including physical and chemical inhibitors.

Huang[15-16] used a controlled temperature experiment system to examine the inhibitor's inhibiting effect on the coal samples' oxidation and spontaneous combustion. Huang also examined the coal samples' inhibition rates at various temperature points. Dong[17] examined the inhibiting effect of enteromorpha-base composite inhibitor on coal samples' spontaneous combustion using in situ fourier infrared spectroscopy and thermal analysis kinetics.It was discovered that coal samples treated with inhibitors had an increase in average activating energy, raising the resistance to coal spontaneous combustion. The coal sample exhibited a higher content of -OH compablue to the raw coal sample. Wang[18] used infrared spectroscopy and temperature programming to examine the inhibitor polyethyene glycol-citric acid's inhibitory effectiveness. The findings demonstrated that polyethyene glycol -citric prevented the synthesis of CO and C_2H_4, the consumption of oxygen, and the oxidation of $-CH_3$ and $-CH_2$. Gao[19] examined the impact of antioxidant-reduced glutathione on coal spontaneous combustion tendency using cross-point temperature and thermogravimetricdifferential scanning calorimetry, which discovered that antioxidant-reduced glutathione has the ability to prevent coal from spontaneous combustion.Xue[20] utilized electron spin resonance and scanning electron microscopy to clarify the inhibition mechanism of antioxidant-type composite inhibitor on coal oxidation.Pan[21] used a C600 microcalorimeter to examined the mechanism and inhibitory impact of inhibitor on oxidation heat release process in coal spontaneous combustion.

Coal spontaneous combustion typically takes 1-3 months to develop.The physical inhibitor unable to perform the functions of oxygen insulation and cooling because of water loss, and the chemical inhibitor will lose its role because it is oxidized by exposure to the air[22-23].The phase change material inhibitor can ensure that its inhibition effect is not weakened in the long latent period, and when the critical temperature is reached by the coal, phase change occurs to absorb coal heat, quickly and effectively close the coal pore, isolate oxygen, moisturize and cool, and inhibit the coal from entering the accelerated oxidation stage[24-26]. Therefore, in order to examine the inhibition effect of hydrated phase change materials on different coal types, this paper used hydrated phase change materials to inhibit four different coal types (gas coal, meagre coal, lean coal and long flame coal). The six characteristic temperatures of the samples were compared based on results of thermogravimetric studies.The changes of coal samples'characteristic temperatures, activation energy and combustion characteristic parameters before and after inhibition were analyzed, and fire extinguishing performance and hydrated phase change materials' advantages were investigated.

2. Experimental principle

To compare the characteristic temperature changes that occur throughout the combustion process of various coal types in order to investigate the inhibitory performance of hydrated phase transition materials on coal spontaneous combustion. The characteristic temperature is one of the most significant indicators of the intensity of the coal oxygen adsorption response, which quantifies the probability of coal spontaneous combustion. The oxidation process may be broken down into four steps based on the characteristic temperature of coal: the stage of water loss and weight loss, the stage of oxygen absorption and weight growth, the pyrolysis stage, and the combustion stage.There will be regular changes in mass loss during the coal combustion process, from initial decomposition to complete combustion to constant mass.The experimental samples' TG-DTG curves can be obtained through thermogravimetric experiments. The coal sample's weight change throughout the oxidation process is represented by the TG curve, and the DTG curve serves as a representation of the TG curve's rate of change or its first-order derivative.It is mainly used to reflect the coal sample's weight change rate during the experimental process.By comparing the two curves, the variation rules of coal samples during the heating process can be accurately analyzed, so as to determine the characteristic temperature points and different thermal oxidation phases of every coal sample as it is being heated. On this basis, the characteristic temperature changes of each combustion stage before and after coal sample inhibition are compared, and the inhibitory performance of hydrated phase change materials on coal spontaneous combustion is ultimately determined.

3. Experimental preparation and scheme

3.1. Treatment of coal sample

Four different coal grades of coal samples were selected and divided into meagre coal, lean coal, gas coal and long flame coal according to the volatile content from low to high. Table 1 showed the industrial analysis findings for the four coal samples.

Table 1. Results of industrial analysis.

Coal sample	M_{ad}/%	A_{ad}/%	V_{ad}/%	FC_{ad}/%
Meagre coal	1.33	4.79	12.36	81.52
Lean coal	1.23	19.16	18.32	61.29
Gas coal	1.89	8.64	39.57	49.9
Long flame coal	4.25	38.94	42.32	14.49

The preparation method of experimental coal samples was to peel and core large coal samples collected on site. Nitrogen separation technology was used and crushed, and 60-80 mesh coal ash was screened and stored as experimental coal samples in a drying oven to prevent physical and chemical adsorption in the air, leading to oxidation reactions.

The four experimental coal samples, which had a different degree of metamorphism,were treated with a hydrated phase change material containing 57.6% aluminum ammonium sulfate dodecahydrate and 42.4% magnesium sulfate heptahydrate[27]. The ratio of coal samples to the resistance material was 4:1. After preparation, let it stand for 12h, and dried it for 72h in vacuum drying oven at normal temperature, and then put it into a coal sample bag, sealed and stored.

3.2. Experimental scheme

Thermogravimetric analysis method was adopted in this performance experimental test, and Shanghai Innuo TGA-1150 thermogravimetric analyzer was used, as shown in Figure 1.

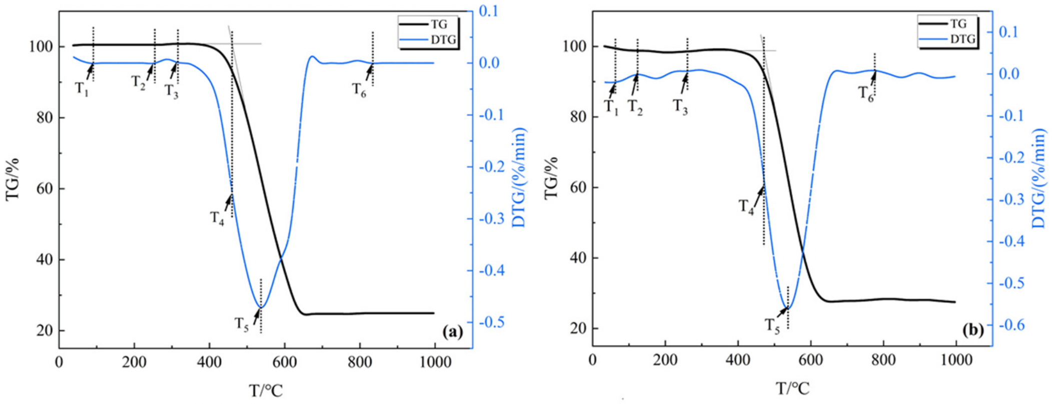
Figure 1. TGA-1150 thermogravimetric analyzer.

The performance test experiment used 8-10mg of coal to heat, with a temperature range of 40-1000℃ and rate of 10℃/min. During the experiment.The gas composed of 78% N_2 and 22% O_2 was continuously injected at a rate of 0.1L/min. The experimental data can be obtained by setting the experimental parameters. Four coal samples with varying metamorphism were evaluated for performance before and after inhibition, and the impact of the inhibitor on these coal samples was investigated[28].

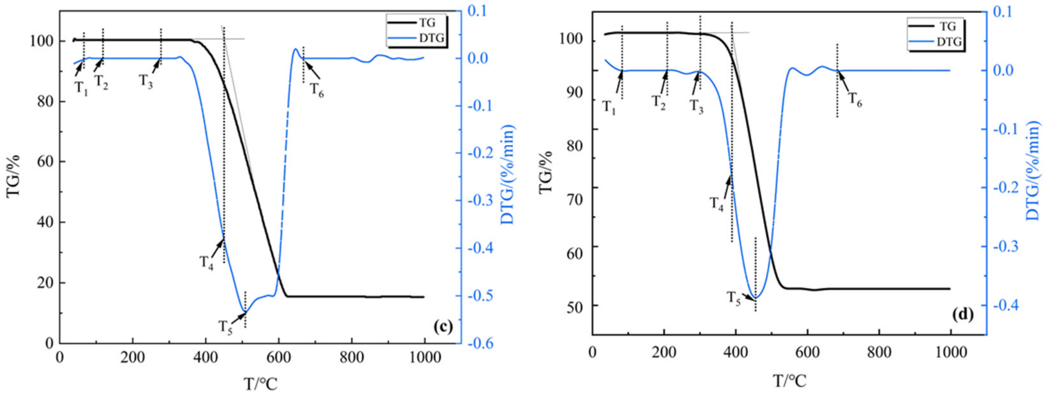
4. Experimental result

4.1. Characteristic temperature analysis

Each coal sample's weight loss reflects the difficulty that it was to burn, and the coal sample's weight loss is directly proportional to the coal's complete combustion.The larger the weight loss, the easier it is for the coal sample to burn completely. Similarly, it can be seen that the weight gain related to oxygen uptake is also proportional to the adsorption capacity of coal samples. Figure 2 and Figure 3 displayed the TG and DTG curves from the experiment.



（a）Meagre coal （b）Lean coal

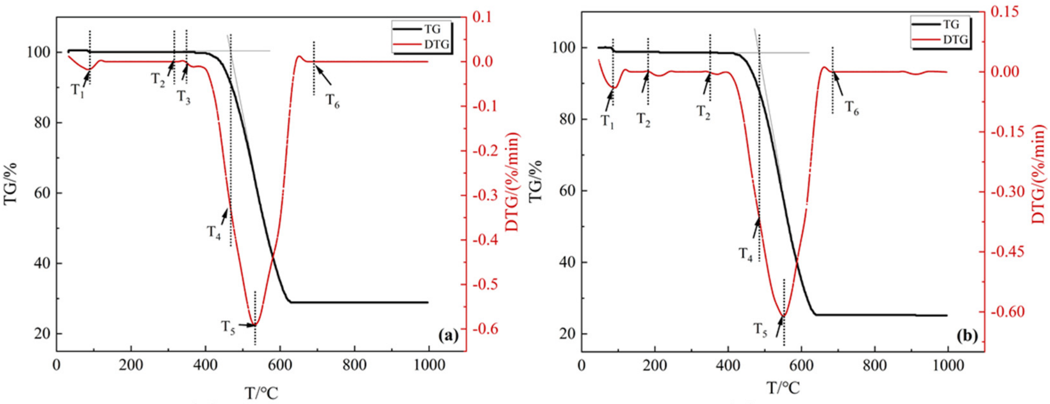


（c）Gas coal （d）Long flame coal

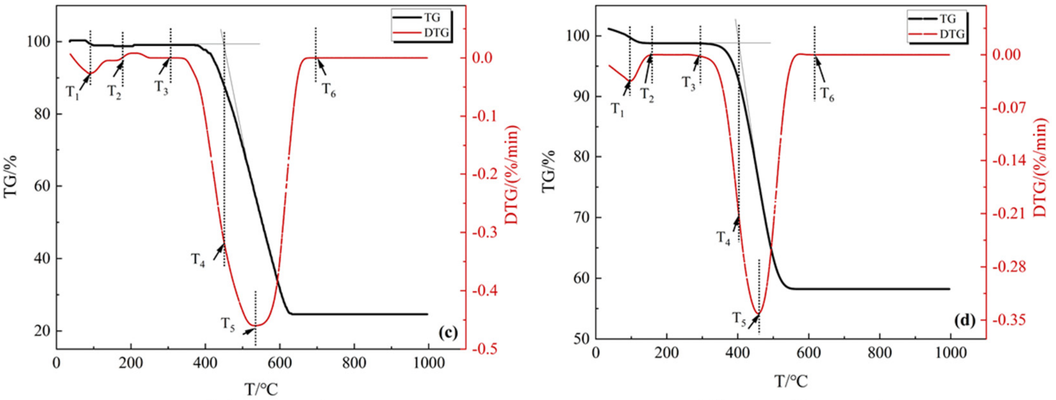
Figure 2. TG-DTG curves of various coal samples.

Figure 2 and Figure 3 showed the curve variations of the various experimental coal samples throughout oxidation heating process.The range of temperatures that corresponds to each of its four oxidation process: The weight loss stage is T_1–T_2. The weight gain stage is T_2–T_3. The pyrolysis stage is T_3–T_4. The combustion stage is T_4-T_6.0

Low-temperature oxidation of the coal sample took place under the thermogravimetric analyzer's temperature program. While the coal sample's water gradually evaporated, it adsorbed O_2 and released CO, CO_2 and other gases. At the beginning, the coal sample's evaporation rate of water was far greater than the rate of O_2 adsorption. So, The rate of weight loss in the coal sample kept increasing. When the critical temperature T_1 was reached, the rate of weight loss in the coal sample was peaked. The T_1 corresponded to the DTG curve's initial peak position, which was also the first temperature point at the velocity of the coal oxygen composite reaction increased. The rate that coal sample's oxygen adsorptive capacity increases with temperature, the thermal weight loss rate of coal sample slowly decreased. When the water evaporation rate of coal sample itself and the oxygen adsorption rate of coal sample reached dynamic equilibrium, the coal sample's rate of thermal weight loss was 0. At this time, the coal sample's water essentially evaporated as the dry cracking temperature T_2 was reached.When the dry cracking temperature T_2 was reached, some active groups started to react with O_2 to generate oxygen containing intermediates which were stored in the coal sample,and he quality started to increase. When the temperature reached the thermal decomposition temperature T_3, the coal's weight gain rate due to oxygen absorption and its own reaction consumption rate reached dynamic equilibrium. The coal sample's thermal weight loss rate again became 0, and its mass growth rate maximized, indicating the end of weight gain stage. After reaching the pyrolysis temperature T_3, the coal sample was oxidized and decomposed, resulting in a significant reduction in quality. The internal energy of coal molecules increased as the temperature kept rising, leading to the thermal decomposition of the circular structure inside the coal molecules. The coal sample's quality continued to decrease, and after reaching ignition temperature T_4, the coal sample started to burn. After exceeding T_4, the coal sample had a violent oxidation reaction, resulting in a significant quantity of gas being released and the primary coal molecules' backbone structure being disrupted, which quickly reduced the coal sample's quality. After reaching the temperature T_5, the coal sample's thermal weight loss rate reached its maximum value. The maximum pyrolysis rate temperature T_5 on the DTG curve corresponded to lowest point. Now, the heated oxidation chemical decomposition reaction was the most intense, generating CO, CO_2, H_2O and other trace gases. The active ingredient in the coal was basically consumed, and the coal combustion rate gradually decreased after this point. Until reaching the burnout temperature T_6, The coal sample's quality tended to stabilize and no longer changes. The TG-DTG curve inclined to a stable value at the T_6, indicating that coal's oxidation and decomposition process had basically over.



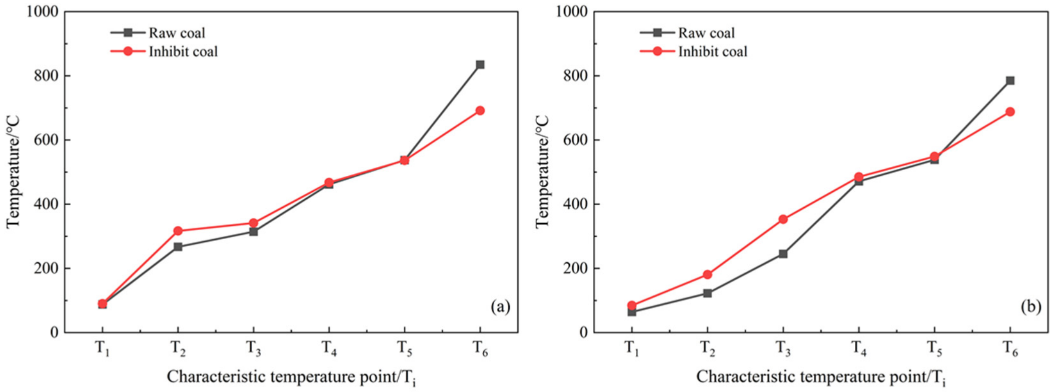
（a）Meagre coal （b）Lean coal



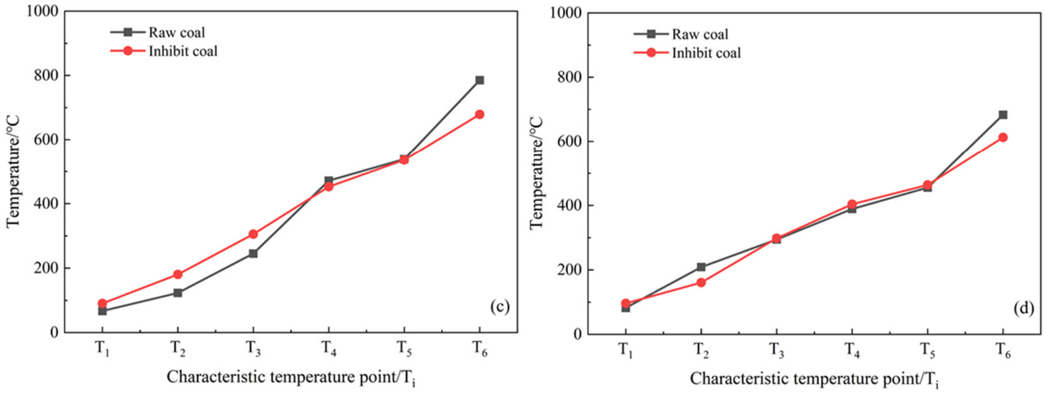
（c）Gas coal （d）Long flame coal

Figure 3. TG-DTG curves of various coal samples with inhibition.

Figure 4 showed the characteristic temperature changes of various coal samples before and after inhibition during the thermogravimetric experiment.After the coal samples were treated with hydrated phase change materials, their critical temperatures (T_1) increased.Lower coal spontaneous combustion grade and lower coal body spontaneous combustion capacity were associated with higher critical temperatures. At low temperatures, hydrated phase change materials exhibited the most effective inhibitory effect on coal spontaneous combustion at temperatures ranging from 60℃ to 90℃. This was because at temperatures ranging from 60℃ to 90℃, hydrated phase change materials underwent phase change when heated to the critical temperature point of phase change, which maximized heat absorption and reduced the rate at which coal's temperature increased, while also isolating oxygen from the coal, resulting in the prevention of coal spontaneous combustion. The inhibited lean coal sample and coal inhibited meager sample had higher thermal decomposition temperatures T_3 and dry cracking temperatures T_2 than the raw coal. The inhibited gas coal sample's the temperature of maximum thermal weight loss rate T_5,the burnout temperature T_6, and T_2 were all higher than the raw coal.The T_2, ignition temperature T_4 and T_5 of the inhibited long flame coal sample were higher than that of the raw coal, indicating that the hydrated phase change material mainly acted on the stages of water loss, weight loss, oxygen absorption and weight gain of the meagre coal and lean coal.It also acted on the stages of water loss, weight loss and combustion stage of gas coal and the stage of water loss, weight loss and pyrolysis of long flame coal.



（a） Meagre coal （b） Lean coal



（c） Gas coal （d） Long flame coal

Figure 4. Different coal samples' characteristic temperature before and after inhibition.

The characteristic temperature points after inhibition were relatively lagging when coal samples before and after inhibition were examined.Among them, the deviation of critical temperature and ignition point temperature was the largest, indicating that hydrated phase change materials had the optimal result during the low-temperature phase of the self-heating oxidation process. The inhibited coal sample's mass loss was 1.6%–9.3% less than that of raw coal,and the rate of oxidation was slowed down.

Figure 5 showed the weight loss rate and its reduction ratio in the thermogravimetric experiment before and after inhibition of various coal samples. The calculation formula of weight loss rate decrease ratio is shown in Eq.(1):

$$\eta = \frac{S_a - S_b}{S_a} \tag{1}$$

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Where, η is the weight loss reduction ratio,%. S_a is the weight loss rate before inhibition,%. S_b is the weight loss rate after inhibition, %.

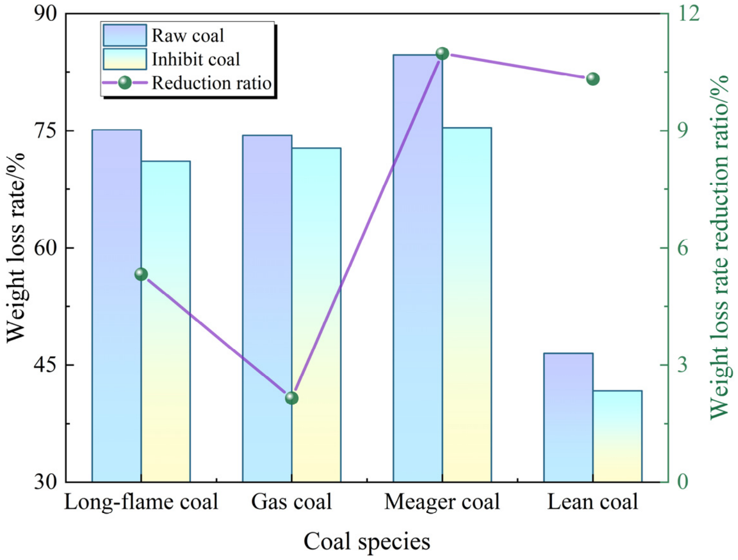


Figure 5. The various coal samples' weight loss rate and its reduction ratio before and after inhibition.

According to the characteristic temperature and weight loss rate before and after coal sample inhibition, the hydrated phase change materials can considerably reduce the weight loss rate of gas coal and long flame coal, making them more appropriate for these types of coal.

4.2. Combustion characteristic parameter analysis

The parameters that describe the properties of coal combustion during combustion are called combustion characteristic parameters, such as combustion intensity, combustion difficulty, combustion rate, ignition performance, and burnout performance. Typically, they are used to reflect the coal's combustion state.The combustion characteristic parameters mainly include the flammability index and the comprehensive combustion characteristic index. Currently, they are also used for studying on the mixed substances, flame-retardant materials and non-coal materials during combustion.

1) The combustion intensity and difficulty of flammable materials are frequently assessed using the flammability index.reflecting their combustion rate, combustion performance, etc. The flammability index is a key indicator that determines the combustible material performance in terms of ignition and combustion. Better ignition stability and combustion performance of flammable materials are indicated by higher flammability index values.The flammability index of the performance testing experiment in this article can be calculated from the maximum combustion rate and ignition temperature. As shown in Eq.(2), the flammability index is directly inversely proportional to the square of the sample ignition point temperature and proportional to the sample's maximum combustion rate.

$$C=\frac{\left(dw/dt\right)_{\max}}{T_i^2} \tag{2}$$

Where, C is the flammability index,%•min^{-1}•K^{-2}. $\left(dw/dt\right)_{\max}$ is the maximum mass loss rate, %/min. T_i is the ignition temperature,K.

2) When assessing the combustible materials' ability to ignite, the comprehensive combustion characteristic index is frequently employed, reflecting the quality of their combustion performance[29]. According to Eq.(3), the sample's comprehensive combustion performance improves with a bigger the comprehensive combustion characteristic index value.

$$S=\frac{\left(dw/dt\right)_{\max}\left(dw/dt\right)_{mean}}{T_i^2 \cdot T_h} \tag{3}$$

Where,S is the comprehensive combustion characteristic index,%•min^{-1}•K^{-3}. $\left(dw/dt\right)_{mean}$ is the average combustion rate,%/min. T_h is the burnout temperature,K.

The combustion characteristic parameters obtained through calculation were shown in Table 2.The flammability index of meagre coal sample and lean coal sample added with hydrated phase change materials significantly decreased compared to the raw coal sample, but the comprehensive combustion characteristic index increased when compared to the raw coal sample. In comparison to the raw coal sample, both the average combustion rate and the maximum mass loss rate increased. When compared to the raw coal sample, the inhibitory gas coal sample and the inhibitory long flame coal sample displayed lower comprehensive combustion characteristic index, lower maximum mass loss rate, higher average combustion rate, and higher flammability index. The comprehensive combustion characteristic index of gas coal and long flame coal, as well as the flammability index of meagre coal and lean coal, can all be lowered by adding hydrated phase change materials.Meanwhile, the maximum mass loss rate of long flame coal and gas coal can be decreased by adding hydrated phase change materials.

Table 2. Combustion characteristic parameters.

Coal sample		T_i /°C	T_h /°C	$\left(dw/dt\right)_{\max}$ /(%/min)	$\left(dw/dt\right)_{mean}$ /(%/min)	C /(%•min^{-1}•K^{-2})	S /(%•min^{-1}•K^{-2})
Raw coal sample	meagre coal	461.7	834.8	-0.47	-0.081	-8.704×10^{-7}	6.36×10^{-11}
	lean coal	471.2	785.2	-0.56	-0.075	-1.01×10^{-6}	7.16×10^{-11}
	gas coal	499.5	664.1	-0.53	-0.102	-8.88×10^{-7}	9.66×10^{-11}
	long flame coal	389.1	683.1	-0.39	-0.049	-8.89×10^{-7}	4.56×10^{-11}
Inhibitory coal sample	meagre coal	467.5	691.8	-0.59	-0.085	-1.08×10^{-6}	9.65×10^{-11}
	lean coal	485.2	687.8	-0.61	-0.090	-1.06×10^{-6}	9.93×10^{-11}
	gas coal	452.5	678.7	-0.46	-0.089	-8.74×10^{-7}	8.17×10^{-11}
	long flame coal	403.6	612.9	-0.34	-0.045	-7.42×10^{-7}	3.77×10^{-11}

4.3. Reaction activation energy analysis

In atmospheric environment, coal will undergo oxidation and spontaneous combustion reaction with air, which is usually called gas-solid reaction. There are various phases to the coal spontaneous combustion, and many small elements are involved in the reaction at each level.During the reaction process, a certain activation energy is required to overcome the corresponding energy barriers and transform into activated molecules. According to calculation and analysis, the activation energy and the spontaneous combustion tendency of coal are related under certain conditions, and there is an inverse ratio between the two.

Based on the above research on Thermogravimetric analysis method, we can study and analyze the coal body's chemical process under conditions of temperature change or isothermal oxidation kinetics of solid materials. To resolve the reaction's activation energy, this experiment uses Coats Redfern integration method to process the thermogravimetric curve[30], and its oxidation reaction kinetics equation is expressed as:

$$\frac{d\alpha}{dT}=\left(\frac{1}{\beta}\right)k\left(T\right)f\left(\alpha\right) \tag{4}$$

Where, β is the heating rate. T is the thermodynamic temperature, K. $f\left(\alpha\right)$ is the mechanism function describing the spontaneous combustion reaction of coal. $k\left(T\right)$ is the reaction rate constant. α is the conversion rate of coal at time t, as shown in Eq.(5):

$$\alpha=\frac{w_0-w_t}{w_0-w_\infty} \tag{5}$$

Where, w_0 is the coal's initial weight ,mg. w_t is the weight at time t,mg. w_∞ is the final weight , mg.

Arrhenius proposed that the rate constant and temperature have the following relationship:

$$k(T)=A\exp\left(-\frac{E}{RT}\right) \tag{6}$$

Where, E is the activation energy, kJ·mol^{-1}.A is the pre-exponential factor.R is the gas molar constant, 8.314J/（mol·K）.

Eq.(7) is obtained by combining Eq.(4) and Eq.(6).

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f\left(\alpha\right) \tag{7}$$

Due to the low temperature at the beginning of the reaction, the reaction rate can be ignored. By integrating Eq.(7), Eq.(8)can be obtained:

$$\int_0^\alpha\frac{d\alpha}{f\left(\alpha\right)}=\frac{A}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)dT \tag{8}$$

Eq.(9) can be obtained by combining the Eq.(8) and the Coats-Redfern equation:

$$\ln\left[\frac{G\left(\alpha\right)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{9}$$

Where, $G\left(\alpha\right)$ is the integral function of the reaction mechanism of coal oxidation process, that is, the original function of $\frac{1}{f\left(\alpha\right)}$.

For the majority of E and the general response temperature range of coal samples, $\frac{2RT}{E}$ is much smaller than 1, $1-\frac{2RT}{E}\approx 1$.Therefore, Eq.(9) can be changed to Eq.(10):

$$\ln\left[\frac{G\left(\alpha\right)}{T^2}\right]=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \tag{10}$$

The general coal oxidation reaction is generally a first order reaction, and the integral function of the reaction mechanism is usually $\ln\left[\frac{\ln\left(1-\alpha\right)}{T^2}\right]$.Therefore, the coal oxidation reaction function obtained in this experiment is shown in Eq.(11):

$$\ln\left[\frac{\ln(1-\alpha)}{T^2}\right]=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \tag{11}$$

Set $\ln\left[\frac{\ln(1-\alpha)}{T^2}\right]$ and $\frac{1}{T}$ are plotted as a function graph, and the slope on the graph is $-\frac{E}{R}$. The activating energy can be obtained by calculation. The intercept on the graph is $\ln\left(\frac{AR}{\beta E}\right)$, which can be calculated to the pre-exponential factor. Figure 6 and Figure 7 showed the correlation analysis of oxidation reactions before and after inhibition in coal samples with four varying intensities of metamorphism.

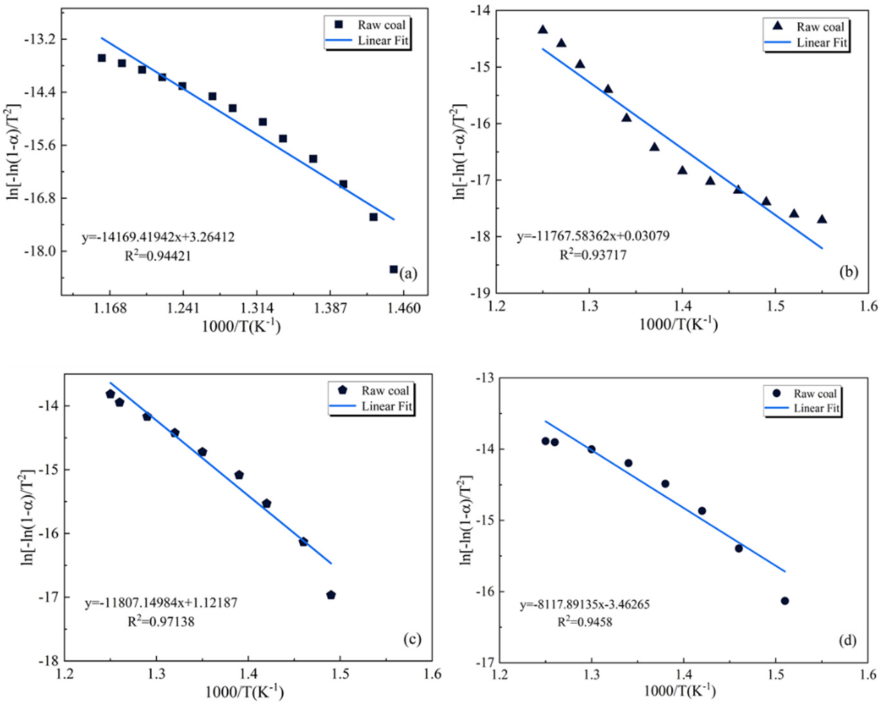
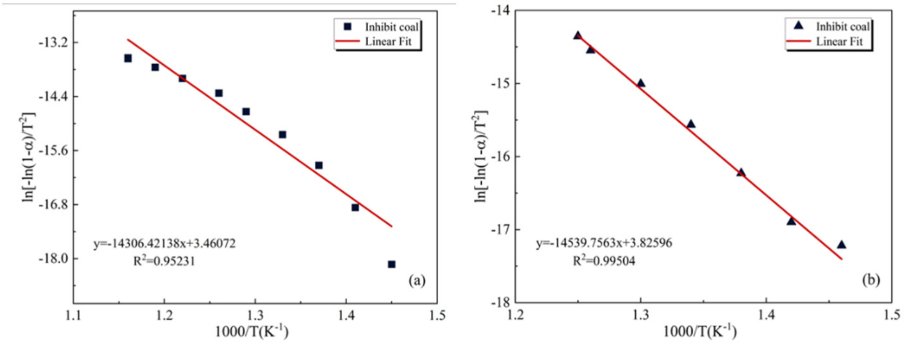


Figure 6. Correlation analysis of oxidation reactions of different raw coal samples.

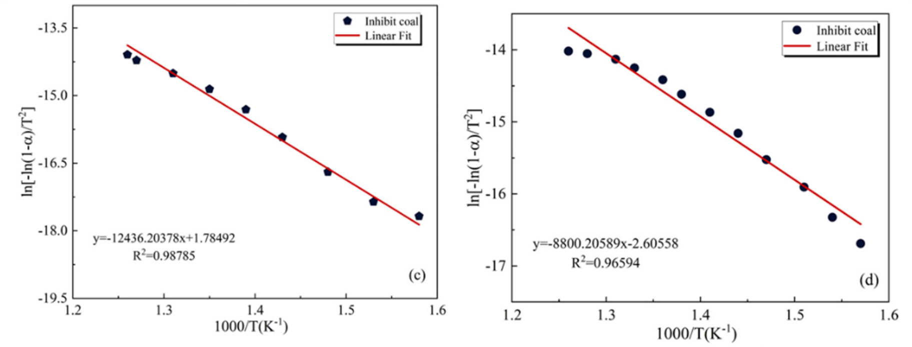
There was a good association between the oxidation reactions of the four coal samples prior to and following inhibition, with correlation coefficients greater than 0.9, indicating that the coal oxidation reaction was well-fitted by this function. As shown in Table 3, pre-exponential factor and activating energy can be obtained by fitting equations.

Table 3. Kinetic parameters of oxidation reaction before and after coal sample inhibition.

Coal sample		Related Coefficient	Fitted equation	Activating energy $(KJ\cdot mol^{-1})$	Pre-exponential factor（10^5）
Raw coal sample	meagre coal	0.94421	y=-14169.41942x+3.26412	117.805	0.3706
	lean coal	0.93717	y=-11767.58362x+0.03079	97.836	0.0121
	gas coal	0.97138	y=-11807.14984x+1.12187	98.165	0.0363
	long flame coal	0.94580	y=-8117.89135x-3.46265	67.492	0.0003
Inhibitory coal sample	meagre coal	0.95231	y=-14306.42138x+3.46072	118.943	0.4555
	lean coal	0.99504	y=-14539.7563x+3.82596	120.884	0.6670
	gas coal	0.98785	y=-12436.20378x+1.78492	103.395	0.0741
	long flame coal	0.96594	y=-8800.20589x-2.60558	73.165	0.0006



（a）Meagre coal （b）Lean coal



（c）Gas coal （d）Long flame coal

Figure 7. Correlation analysis of oxidation reactions of various inhibited coal samples.

Table 3 showed the inhibitory coal samples of meagre coal, lean coal, gas coal, and long flame coal had higher activating energy than their raw coal samples,with increases of 1.138 KJ·mol^{-1}, 23.048 KJ·mol^{-1}, 5.23 KJ·mol^{-1}, and 5.673 KJ·mol^{-1}, respectively. The activating energy of coal sample is a parameter that measures the spontaneous combustion characteristics,which has an inverse relationship with the tendency of coal to spontaneous combustion. Therefore, hydrated phase change materials can reduce the possibility of coal spontaneous combustion. The pre-exponential factor reflects the possibility of collision between activated groups in coal oxidation processes. The bigger the value of pre-exponential factor, the bigger the possibility of collision between activated groups.The pre exponential factors after inhibition were greater than those before inhibition, as shown in Table 3. However, based on the changes in each coal sample's activating energy before and after inhibition, it can be inferred that the increase in pre exponential factor had less impact on coal oxidation reaction than the increase in activating energy.

In summary, hydrated phase change materials had an inhibitory effect on the coal spontaneous combustion effect, which can increase the activating energy of coal and cause the oxidation and combustion process of coal to move backwards.

5. Conclusion

By analyzing the characteristic temperature and weight loss rate, it can be found that hydrated phase change materials had effective inhibitory effects on different oxidation stages of coal samples. During the low-temperature stage, phase change occurs and absorbs heat, isolating coal from oxygen contact, reducing the mass loss of inhibited coal samples by 1.6% to 9.3% compared to raw coal,and slowing down the oxidation rate. Therefore, hydrated phase transition materials showed the best suppression of spontaneous combustion at low temperatures. The addition of hydrated phase change materials can lower the flammability index of meagre coal and lean coal as well as the comprehensive combustion characteristic index of gas coal and long flame coal, according to an analysis of the oxidation characteristic parameters of raw coal samples and inhibited coal samples. In the meantime, hydrated phase transition materials can lower the maximum mass loss rate of gas coal and long flame coal.

By analyzing the oxidation characteristic parameters of raw coal samples and inhibited coal samples, it can be concluded that the addition of hydrated phase change materials can reduce the combustibility index of meagre coal and lean coal, as well as the comprehensive combustion index of gas coal and long flame coal. Meanwhile, the maximum mass loss rate of gas coal and long flame coal can be decreased by adding hydrated phase change materials. The activating energy of coal samples after inhibition treatment has been improved. The coal samples' pre-exponential factors after inhibition were greater than those before inhibition.

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