Experimental Study on the Inhibition Effects of Nitrogen and Carbon Dioxide on Coal Spontaneous Combustion

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Abstract: Inert gases can effectively inhibit coal spontaneous combustion. In this paper, the inhibition effect of inert gases (N2 and CO2) on coal spontaneous combustion was studied. In the low-temperature oxidation stage, the constant-temperature heat release and apparent activation energy of coal sample were measured and calculated by the C80 micro-calorimeter. In the high-temperature combustion stage, the critical temperature, maximum peak temperature, ignition temperature, and burn-out temperature of coal samples were analyzed by the synchronous thermal analyzer. The results demonstrate that with the decrease of O2 concentration, the oxidation heat release of coal samples drops gradually while the apparent activation energy increases gradually. In the N2 and CO2 atmospheres, as the O2 concentration is reduced to 1.5% and 3%, respectively, the value of apparent activation energy changes from negative to positive, and the spontaneous reaction transits to a nonspontaneous reaction. The TG-DTG (thermogravimetric-derivative thermogravimetric) curve of coal sample in the high-temperature combustion stage indicates that the critical temperature exhibits a W-shaped trend with the decrease of O2 concentration, which also leads to gradual increases of maximum peak temperature, ignition temperature, and burn-out temperature. The above results signify that increasing the inert gas concentration can gradually reduce the oxidation and combustion rate and improve the inhibition effect on coal spontaneous combustion. In addition, when the O2 concentration is the same, the inhibition effect of CO2 on coal spontaneous combustion is superior to that of N2.

Keywords: coal spontaneous combustion; inhibition effect; nitrogen; carbon dioxide

1. Introduction

Coal is an important energy source and chemical raw materials [1–4]. Many disasters may occur in the process of coal mining [5–11]. As one of the main disasters, coal spontaneous combustion (CSC) not only burns vast coal resources and releases toxic gases but also causes casualties [12–14]. In China, 56% of state-owned coal mines have suffered from CSC, accounting for 90–94% of all mine fires [15]. Because coal is a complex organic substance, it will adsorb O2 to undergo a chain reaction and then release heat when exposed to an O2 environment. If the accumulated heat cannot be dissipated, CSC is likely to occur [16]. Therefore, it is of great significance to study the prevention and control technology of coal spontaneous fire to ensure the safety of mine production.

Currently, scholars have carried out extensive researches on prevention and extinguishing materials for CSC, such as gel foam [17], ionic liquid [14], inorganic solidified foam [18], and gel [19], which all
exert satisfactory effects on coal spontaneous fire prevention and control. However, coal spontaneous fires mostly occur in underground concealed spaces. According to statistics, 60% of CSC occurs in the goaf area [15,20]. Due to large space in the goaf area and wide distribution of residual coal, the dangerous areas of CSC present a three-dimensional distribution. Thus, it is difficult to determine the exact location of fire area, which poses a considerable challenge to fire prevention and extinguishing technology of CSC. Inert gases have been gradually applied to CSC prevention and control in the goaf area because of their excellent diffusivity [21–23]. However, many problems still arise in the field application of fire prevention and extinguishing technology of inert gases. For example, inert gas perfusion fails to achieve a satisfactory fire prevention and extinguishing effect; index gases like CO are difficult to be reduced and maintained to below the safety level; the sealed working face is prone to reburn after it is reopened [24]. Hence, an in-depth research on the fire prevention and extinguishing performance of gaseous inert media is essential.

$O_2$ concentration is an important factor affecting the characteristics of CSC [25]. In fact, the technology of fire prevention and extinguishing by inert gases mainly achieves the purpose of inhibiting coal oxidation and spontaneous combustion by lowering the $O_2$ concentration in the environment. In recent years, some scholars have investigated the effect of $O_2$ concentration on the characteristics of coal oxidation and spontaneous combustion under inert gas conditions. Lei et al. [26] studied the inhibition effects of inert gases ($N_2$ and $CO_2$) on open flame coal combustion, with the $O_2$ concentration ranging from 16.39% to 19.01%. The results revealed that $N_2$ reduced the flame area linearly while $CO_2$ reduced the flame area exponentially. In addition, $CO_2$ extinguished fire faster than $N_2$. Shao et al. [27] carried out the contrast experiment of temperature-programmed oxidation of coal samples under the conditions of air, $N_2$–air mixture and $CO_2$–air mixture. In the experiment, the $O_2$ concentration ranged from 17.07% to 17.55%, and the temperature ranged from 20 °C to 110 °C. The inhibition effects of $N_2$ and $CO_2$ on CSC were analyzed by apparent activation energy. Liu et al. [28] studied the thermokinetic characteristics of coal–$O_2$ reaction with the $O_2$ concentration ranging from 3% to 21% in $N_2$–$O_2$ and $CO_2$–air atmospheres through TG-DTG-DSC (thermogravimetric-derivative thermogravimetric-differential scanning calorimetry) experiments. The results showed that the coal–$O_2$ reaction rate could be reduced rapidly by injecting $N_2$ and $CO_2$. Among them, the $CO_2$–air mixture was actually an $O_2$–$N_2$–$CO_2$ mixture, rather than a $CO_2$–$O_2$ mixture. Consequently, the inhibition effects of $N_2$ and $CO_2$ could hardly be truly compared. Deng et al. [29] investigated the characteristic parameters of coal oxidation in the $O_2$–$N_2$ atmosphere and the $O_2$–$CO_2$ atmosphere at low temperatures (30–170 °C) under the $O_2$ concentrations of 4%, 8%, 14%, and 21%, concluding that the $O_2$ consumption rate in the $O_2$–$CO_2$ atmosphere was lower than that in the $O_2$–$N_2$ atmosphere when the $O_2$ concentration was the same.

The oxygen concentration settings in experiments done by other researchers are listed below. Li et al. [30] researched the macro-characteristic indexes of coal samples at different $O_2$ concentrations (3%, 8%, 13%, 17%, and 21%) with the temperature ranging from 30 °C to 500 °C. Ma et al. [31] probed into the thermokinetic characteristics of coal samples when they were heated from 30 °C to 800 °C under the $N_2$ atmosphere with $O_2$ concentrations being 5%, 9%, 13%, 17%, and 21%, respectively. Ren et al. [32] explored the thermodynamic behavior of coal sample oxidation with $O_2$ concentrations being 8%, 14%, and 21% under the $O_2$–$N_2$–$CO_2$ atmosphere and the $O_2$–$N_2$ atmosphere, respectively. Zhang et al. [33] studied the thermogravimetric characteristics of coal oxidation and spontaneous combustion under the $N_2$ atmosphere with $O_2$ concentrations being 5%, 12.5%, and 21%, respectively.

To sum up, most of the current experimental studies focus on an $O_2$ concentration of over 5%, and there is a lack of understanding of the characteristics of inert gas inhibiting coal oxidation and spontaneous combustion under poor $O_2$ conditions. Furthermore, in the laboratory, only oxidation heating experiments in the fire prevention stage (from the room temperature to the target temperature) are performed, whereas the inertiing and inhibition effects of inert gases on high-temperature combusting coal in the fire extinguishing stage are rarely researched on. Therefore, it is necessary to study the fire prevention performance at low temperatures and the fire extinguishing performance at high
temperatures of inert gases under poor O\textsubscript{2} conditions. In this paper, the inhibition effects of inert gases (N\textsubscript{2} and CO\textsubscript{2}) in the low-temperature oxidation stage and the high-temperature combustion stage of CSC under different O\textsubscript{2} concentration conditions were studied with the aid of the micro-calorimeter and the synchronous thermal analyzer. The research was conducted from the perspectives of heat release, activation energy, critical temperature, maximum peak temperature, ignition temperature, and burn-out temperature. The research findings can provide a theoretical guidance for the practical application of technology of fire prevention and extinguishing by inert gases.

2. Experimental Procedure

2.1. Materials

The coal samples used in the experiment were collected from Luxin No.1 Mine and transported to the laboratory after being wrapped with plastic wrap and putting in plastic sealed bags. The lump coal samples were crushed and those with particle sizes of 100–200 meshes and 200–300 meshes were screened out for subsequent experiments. The proximate analysis results of coal samples are shown in Table 1. The purity of O\textsubscript{2}, N\textsubscript{2}, and CO\textsubscript{2} is 99.99%.

Table 1. Proximate analysis results of coal sample.

| Coal Sample | Mad/(wt%) | Aad/(wt%) | Vad/(wt%) | FCad/(wt%) |
|-------------|-----------|-----------|-----------|------------|
|             | 12.445    | 6.18      | 29.01     | 52.365     |

2.2. C80 Micro-Calorimeter

The oxidation heat release properties of coal samples in the N\textsubscript{2} and CO\textsubscript{2} atmospheres under different O\textsubscript{2} concentrations were analyzed by the C80 micro-calorimeter produced by Setaram, France (Figure 1). In the experiment, the amount of coal sample was 1000 mg; the gas flow rate was 50 mL/min; and the O\textsubscript{2} concentration was set at 21%, 10%, 5%, 3%, and 1.5%, respectively. The coal sample was heated from the initial temperature of 20 °C to the constant temperatures 140 °C, 145 °C, and 150 °C, respectively, at a heating rate of 5 °C/min. First, the inert gas was injected. After the heat flow curve was balanced and run for 120 min, O\textsubscript{2} was introduced through the O\textsubscript{2} pipeline flowmeter. During the experiment, the furnace temperature, coal temperature, and heat flow parameters of the coal sample were recorded.
temperature combustion stage of CSC under different O2 concentration conditions were studied with the aid of the micro-calorimeter and the synchronous thermal analyzer. The research was conducted from the perspectives of heat release, activation energy, critical temperature, maximum peak temperature, ignition temperature, and burn-out temperature. The research findings can provide a theoretical guidance for the practical application of technology of fire prevention and extinguishing by inert gases.

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2.3. Synchronous Thermal Analyzer

The inhibition effects of inert gases in the high-temperature combustion stage were studied with the aid of the SDT-Q600 synchronous thermal analyzer produced by TA Company, the USA (Figure 2). In the experiment, the mass of coal sample was 5 mg and the particle size of coal sample was 200–300 meshes. The furnace temperature was raised from 20 °C to 1000 °C at a heating rate of 5 °C/min, with the gas flow rate set at 50 mL/min, and the O2 concentration set at 21%, 15%, 10%, 5%, 3%, and 1.5%, respectively.

Figure 1. C80 micro-calorimeter.

Figure 2. SDT-Q600 synchronous thermal analyzer.
3. Results and Discussion

3.1. Inhibition Effects of Inert Gases in the Low-temperature Oxidation Stage

3.1.1. Constant-Temperature Heat Release

The heat flow curves of coal samples with different O₂ concentrations in the N₂ and CO₂ atmospheres were obtained by the C80 micro-calorimeter, and the overall heat release of coal samples from the heat release stage to the constant temperature stage (a total of 15 h) was acquired by integration, as shown in Figure 3.

![Figure 3. Heat release of coal oxidation in the N₂ and CO₂ atmospheres.](image)

Low-temperature oxidation of coal usually includes two stages: the water evaporation stage and the O₂ adsorption and weight increase stage. The constant temperatures (140 °C, 145 °C, and 150 °C) selected in the experiment belong to the second stage. The O₂ adsorption reaction is an exothermic reaction that causes an increase in the weight of the system. The released heat of coal directly depends on its O₂ adsorption and also indicates the difficulty in coal oxidation reaction. To be specific, the smaller the heat release is, the better the inhibition effect of inert gas in the low-temperature oxidation stage will be. It can be seen from Figure 3 that with the decrease of O₂ concentration, i.e., the increase of inert gas concentration, the heat release of coal gradually decreases at an accelerated rate. This denotes that the O₂ concentration in the fire area should be minimized in order to improve the inhibition effect of inert gas on low-temperature oxidation of coal. In addition, the coal sample in the CO₂ atmosphere always releases less heat than the one in the N₂ atmosphere at the same O₂ concentration, which implies that CO₂ shows a better inhibition effect in the low-temperature oxidation stage than N₂.

3.1.2. Apparent Activation Energy

Activation energy refers to the minimum energy required for the oxidation reaction to proceed. The greater the activation energy, the more difficult the reaction is. For the coal–O₂ reaction, the low-temperature oxidation involves a variety of elementary reactions, and its activation energy usually refers to the apparent activation energy. In this paper, the heat release properties of coal
oxidation under three isotherms (140 °C, 145 °C, and 150 °C) are used to calculate the law of activation energy variation with the O2 concentration.

The time when O2 is injected into the system at different temperatures is defined as the initial exothermic time. Until the temperature is kept at a constant temperature for 15 h, the whole exothermic process is regarded as a complete reaction. That is, the reaction process is 1. According to the Arrhenius Equation:

\[ \ln k = -\frac{E}{RT} + \ln A \]  

where \( A \) is the pre-exponential factor; \( E \) is the activation energy; \( T \) is the temperature of coal sample; \( R \) is the universal gas constant, 8.314 J/mol·K; and \( k \) is the reaction rate constant.

With \( \ln k \) and \( 1000/T \) as straight lines, the activation energy \( E \) and the pre-exponential factor \( A \) are calculated according to the slope and intercept. The calculation results are exhibited in Figure 4.

![Figure 4](image-url)  

**Figure 4.** Activation energy of coal oxidation in the N2 and CO2 atmospheres.

It can be seen from Figure 4 that the activation energy of coal oxidation reaction increases gradually with the decrease of O2 concentration, because N2 and CO2, as inert gases, do not react with coal. With the decrease of O2 concentration, O2 that can participate in the coal oxidation reaction gradually decreases. As a result, the coal oxidation reaction is inhibited, which promotes the reaction difficulty, so the apparent activation energy increases. As the O2 concentration decreases, the value of activation energy transits from negative to positive. A negative value of activation energy indicates that there is no reaction barrier, and the reaction can proceed spontaneously. In contrast, a positive value of activation energy suggests that there is a reaction barrier, and the reaction cannot proceed spontaneously. In the N2 atmosphere, the value of activation energy is positive when the O2 concentration declines to 1.5%, while in the CO2 atmosphere, the value of activation energy is positive only when the O2 concentration drops to below 3%. For the N2 and CO2 atmospheres, the activation energy was negative when the O2 concentration is greater than 1.5% and 3%, respectively, indicating that the inert gases cannot prevent the spontaneous process of the coal–oxygen reaction. The above phenomena demonstrate that under the N2 and CO2 conditions, only when the O2 concentration is reduced to 1.5% and 3%, respectively, can inert gas significantly inhibit the low-temperature oxidation of coal.
Furthermore, it can be observed from Figure 4 that under the same O\textsubscript{2} concentration, the activation energy of coal oxidation reaction in the CO\textsubscript{2} atmosphere is higher than that in the N\textsubscript{2} atmosphere, which implies that CO\textsubscript{2} exhibits a better inhibition effect on the low-temperature oxidation than N\textsubscript{2}. The reason is as follows: during the coal oxidation reaction, coal will simultaneously adsorb O\textsubscript{2} and inert gases. If coal exhibits stronger adsorption capacity for inert gases, then its adsorption capacity for O\textsubscript{2} will be weaker. In the inert gas atmosphere with the same O\textsubscript{2} concentration, the adsorption capacity of coal to CO\textsubscript{2} is stronger than that to N\textsubscript{2}, so the O\textsubscript{2} absorption capacity of coal in the CO\textsubscript{2} atmosphere is weaker than that in the N\textsubscript{2} atmosphere. Therefore, the coal oxidation reaction is inhibited to a greater extent in the CO\textsubscript{2} atmosphere, and the activation energy is greater than that in the N\textsubscript{2} atmosphere.

3.2. Inhibition Effects of Inert Gases in the High-Temperature Combustion Stage

This section primarily presents an analysis on the inhibition effects of inert gases on high-temperature combustion of coal. Thermo-gravimetry is used to investigate the variation characteristics of characteristic temperatures (including critical temperature, maximum peak temperature, ignition temperature, and burn-out temperature) in the oxidation combustion reaction of coal samples in the inert gas atmospheres at different O\textsubscript{2} concentrations.

3.2.1. Critical Temperature

In the CSC process, there is a turning point from low-temperature slow oxidation to rapid oxidation. When the temperature exceeds the turning point, the coal–O\textsubscript{2} reaction rate accelerates and enters the rapid oxidation stage. The temperature at this turning point is called the critical temperature, namely the temperature corresponding to the first peak on the DTG curve of coal sample [34] (Figure 5).

![Figure 5. Definitions of critical temperature and maximum peak temperature.](image-url)
The critical temperature of coal sample implies the starting point of automatic acceleration of coal–O$_2$ reaction, and its value reflects the spontaneous combustion tendency of coal sample. A larger value of critical temperature indicates that coal oxidation combustion is less likely to occur. On the contrary, a small value of critical temperature suggests that the possibility of coal oxidation combustion is very high. According to the DTG curve, the obtained critical temperature values of coal samples with different O$_2$ concentrations in the N$_2$ and CO$_2$ atmospheres are displayed in Figure 6.

![Graph showing critical temperatures of coal sample in N$_2$ and CO$_2$ atmospheres.](image)

**Figure 6.** Critical temperatures of coal sample in the N$_2$ and CO$_2$ atmospheres.

Figure 6 reveals that in the N$_2$ and CO$_2$ atmospheres, the critical temperature of the coal sample presents a W-shaped trend with the decrease of O$_2$ concentration. Specifically, the critical temperature declines at first and increases later, and then repeats that trend again, but its overall trend is to increase with the decrease of O$_2$ concentration. The reason is as follows: at a low O$_2$ concentration, the rate of physical and chemical interaction between the coal sample and O$_2$ is low, and the time for reaching a dynamic equilibrium between the weight increase brought by O$_2$ adsorption and the weight reduction induced by reaction consumption and gas escape lengthens. This signifies that the time required to reach the critical temperature is prolonged, resulting in a higher critical temperature. With the increase of O$_2$ concentration, the probability of contact between active groups in coal and O$_2$ increases, which accelerates the coal–O$_2$ reaction. The amount of O$_2$ adsorbed by the coal sample is balanced with the amount of gas consumed and desorbed in a short period of time. Thus, the value of temperature rise is relatively reduced, which presents a lower critical temperature. With the increases of oxygen consumption and gas desorption volume, the O$_2$ adsorption and reaction rate of coal sample are hindered, leading to a higher critical temperature. As the O$_2$ concentration continues to go up, the O$_2$ concentration gradient formed in the direction of the coal seam thickness increases, so do the O$_2$ diffusion rate and the coal–O$_2$ reaction rate, thus the critical temperature falls. When the O$_2$ concentration continues to rise, the gas concentration gradient will once again hinder the desorption.
and escape of gas products inside the coal sample, thereby inhibiting the coal–O₂ reaction, and causing the critical temperature to rise again.

3.2.2. Maximum Peak Temperature

The maximum peak temperature of coal sample refers to the temperature corresponding to the highest peak in the DTG curve (Figure 5). When the coal sample reaches the maximum peak temperature, the weight loss rate hits its largest, indicating that the coal sample comes to the highest combustion rate. On the basis of the DTG curve, the maximum peak temperatures of coal samples with different O₂ concentrations under inert gas conditions are shown in Figure 7.

![Figure 7. Maximum peak temperature of coal sample in the N₂ and CO₂ atmospheres.](image)

It can be seen from Figure 7 that the maximum peak temperatures of coal samples increase gradually with the decrease of O₂ concentration in the inert gas atmospheres. The reason is as follows: the decrease of O₂ concentration signifies the increase of inert gas concentration, which not only considerably inhibits the formation of active functional groups in the coal structure but also notably suppresses the oxidative cracking of macro-molecular cyclic hydrocarbon structure. Hence, the time required for the coal oxidation and combustion rate to reach the maximum value is prolonged, resulting in a rise of the maximum peak temperature. Figure 7 demonstrates that with the decrease of O₂ concentration, the rate of peak temperature increase is growing. This suggests that increasing the inert gas concentration can delay high-temperature combustion. In addition, a lower O₂ concentration exerts an obvious impact on the peak temperature, namely a better inhibition effect on coal combustion. Moreover, under the same O₂ concentration, the maximum peak temperature in the CO₂ atmosphere is always higher than that in the N₂ atmosphere, which implies that CO₂ shows a better inhibition effect in the high-temperature combustion stage than N₂.

3.2.3. Ignition Temperature and Burn-Out Temperature

The ignition temperature of coal sample, which is the dividing point between coal oxidation reaction and combustion reaction, reflects the difficulty in coal oxidation and combustion. The burn-out
temperature of coal sample, which corresponds to the temperature where the weight of coal sample no longer changes in the combustion stage, represents the duration of coal oxidation and combustion. The ignition temperature and burn-out temperature of coal sample vary with the change of O₂ concentration. The TG-DTG method is usually adopted to determine the ignition temperature and burn-out temperature of coal sample (Figure 8). The maximum peak point of the DTG curve is taken as a vertical line to intersect with the TG curve at Point A. The tangent line of the TG curve is taken at Point A. Point B at the beginning of weight loss on the TG curve is taken as a parallel line. The temperature corresponding to the intersection Point C of the parallel line and the tangent line is the ignition temperature. Furthermore, a parallel line is drawn at the end of weight loss point on the TG curve, and the temperature corresponding to the intersection Point D between the parallel line and the tangent line is the burn-out temperature.

![Figure 8](image_url)

**Figure 8.** Definitions of ignition temperature and burn-out temperature.

The ignition temperature and burn-out temperature of coal samples in the N₂ and CO₂ atmospheres at different O₂ concentrations are exhibited in Figures 9 and 10.
Figure 9. Ignition temperature of coal sample in the N$_2$ and CO$_2$ atmospheres.

Figure 10. Burn-out temperature of coal sample in the N$_2$ and CO$_2$ atmospheres.

Under the inert gas conditions, with the decrease of O$_2$ concentration, the ignition temperatures and the burn-out temperatures of coal samples increase. This indicates that increasing the inert gas concentrations can delay the process of coal oxidation and combustion reaction to a certain extent. The overall reaction rates of coal samples in the high-temperature combustion stage are determined by the gas diffusion rate and the oxidation reaction rate. In the process of coal oxidation and combustion,
the O\(_2\) demand of active structure is fixed. At a low O\(_2\) concentration, the rates of gas diffusion and oxidation reaction are slow, and the time required for oxidation and combustion reaction is prolonged. With the increase of O\(_2\) concentration, the rates of gas diffusion and oxidation reaction are accelerated, and the time required for oxidation and combustion reaction is shortened.

4. Conclusions

In this paper, the inhibition effects of inert gases (N\(_2\) and CO\(_2\)) on low-temperature oxidation and high-temperature combustion of coal samples were investigated. The main conclusions are as follows:

In the low-temperature oxidation stage, with the decrease of O\(_2\) concentration, i.e., the increase of inert gas concentration, the heat release of coal sample gradually drops at an accelerated rate. The O\(_2\) concentration in the fire area should be minimized in order to improve the inhibition effect of inert gas on low-temperature oxidation of coal. The apparent activation energy of coal samples gradually increases with the decrease of O\(_2\) concentration. In the N\(_2\) and CO\(_2\) atmospheres, as the O\(_2\) concentration is reduced to 1.5% and 3%, respectively, the value of apparent activation energy changes from negative to positive, and the spontaneous reaction transits to nonspontaneous reaction.

In the high-temperature combustion stage, the critical temperature of coal sample exhibits a W-shaped trend with the decrease of O\(_2\) concentration, but its overall trend is to increase with the decrease of O\(_2\) concentration. In the inert gas atmospheres, the maximum peak temperature, ignition temperature, and burn-out temperature of coal sample gradually increase with the decrease of O\(_2\) concentration. This signifies that the increase of inert gas concentration can delay the high-temperature combustion reaction of coal, and the lower the O\(_2\) concentration is, the better the inhibition effect on coal combustion will be. Moreover, when the O\(_2\) concentration is the same, the inhibition effect of CO\(_2\) on coal oxidation and spontaneous combustion is superior to that of N\(_2\).

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