Research Article

Experimental Research on the Performance of the Macromolecule Colloid Fire-Extinguishing Material for Coal Seam Spontaneous Combustion

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Coal resources are rich in China. They are mainly concentrated in the northwest region. But these resources also make the situation of spontaneous coal combustion hazards most serious in this area. Affected by the arid and semiarid climate, the water resource in this area is relatively scarce. In order to improve the utilization rate of water, a macromolecule colloid for coal mine fire fighting was developed in this research. The main components of the macromolecule colloid and the principle of gel formation were analyzed. The physical and chemical properties of the macromolecule colloid were analyzed by the time of gelation and the water loss. The water content of the macromolecule colloid was as high as 99%. The inhibition performance of the macromolecule colloid on coal fire was studied by the programmed heating device. The experimental results show that the macromolecule colloid has a significant inhibitory effect on the heating rate, oxygen consumption rate, and gas production rate. It inhibits the coal-oxygen composite by increasing the activation energy (Ea) of coal, which also has the effect of wrapping coal to isolate oxygen. The inhibition performance of the macromolecule colloid on coal fire disasters is better than that of water, water glass, loess compound colloids, and other traditional fire-extinguishing materials.

1. Introduction

The spontaneous combustion of coal in underground longwall gob areas represents a significant hazard associated with the coal industry in the world [1]. This phenomenon can affect mine production such that major economic losses incur and also may lead to gas explosions with the potential for heavy casualties. Ellyett and Fleming believe that Australia’s Burning Mountain coal field has been burning for more than 6,000 years. Since the era of Herodotus, Tajikistan’s Ravat coal field fire has been burning for more than 2,000 years [2]. In coal-producing countries, especially in China [3–6], the United States [7–9], Australia [1, 10, 11], India [12–14], South Africa [15, 16], and so on, the coal field fire is more serious. Coal fire disaster not only burns a lot of coal resources directly, which threatens the safety of miners and results in large economic losses [17], but also seriously endangers the ecological environment (for example, air pollution, surface heat disasters, and groundwater pollution).

In order to control coal fire disasters, researchers in various countries have developed a variety of fire-fighting technologies such as water injection [18, 19], stripping [3], grouting (yellow mud slurry, fly ash slurry, and cement slurry) [20], three-phase foam perfusion [21], multiphase foam [22], composite gel (loess compound colloids and fly ash composite colloids) [23, 24], and ionic liquids [25]. These methods have achieved tangible results in controlling coal fires but also have some shortcomings. For example, the flow of water will increase the porosity of the coal, and the air will flow more easily into the void after evaporation. An explosion accident occurs easily when water encounters a
high-temperature coal fire area (as shown in Figure 1). It will cause secondary disasters. For the higher position of the coal field fire, the effect of grouting technology is not good because of its limited spreading range. The instability of the foam limits the performance of the three-phase foam and the multiphase foam. Water glass can be easily dehydrated and shrunk, finally into powder. The cost of using the composite gel technology for fire fighting is very high in areas where there is lack of loess and fly ash.

Coal resources are mainly distributed in the western and northern regions of China. As shown in Figure 2, the coal production of six provinces (autonomous regions), which are Shanxi, Shaanxi, Inner Mongolia, Ningxia, Gansu, and Xinjiang, accounted for 78.69% of the national coal production. The above areas are typical of arid or semiarid climate, with less water and serious desertification. Because of the thick coal seam, burial shallow, serious abuse, and other factors, the coal fire disaster in these regions is more serious [26]. The direct combustion of coal quantity each year due to coal fire is 20 million tons. In 2010, the coal fire of China has been included in the “five global sustainable ecological disasters” by “Foreign Policy” [27].

In order to effectively control the coal fire disaster, improve the utilization of water, and overcome the shortcomings of traditional fire-fighting methods, this paper provides a macromolecular gel colloid for controlling the spontaneous combustion of coal in coal mines.

2. Macromolecular Colloid and Its Mechanism of Inhibiting Coal Oxidation

2.1. Macromolecular Colloid Composition and Gelling Principle. The macromolecular materials in this study were provided by Xi’an Tianhe Mining Technology Co., Ltd. Their main components are linear polymer materials and transition-metal high-valent ion solutions, such as copolymers of acrylic acid, vinyl acetate, and solution containing Al³⁺. In order to master the main components and structure of macromolecular colloids, a Spectrum One Fourier transform infrared spectrometer was used to analyze them, as shown in Figure 3. According to the position analysis of the absorption peak in Figure 3, the main contents of the macromolecular colloid are Mg²⁺, Ca²⁺, AlO₂⁻, COO⁻, CH₂O, and so on.

When the macromolecular material encounters water, swelling occurs, which causes a large amount of water to be controlled within the macromolecular colloid. Since the material has some crosslinking bonds, it could not be dissolved and eventually form gel clumps. Macromolecular colloids are mainly composed of organic and inorganic components. Organic components are mainly a mesh structure, and part of the molecular formula is shown in Figure 4.

2.2. Mechanism of Inhibiting Coal Oxidation. The oxidation starts from the surface of the coal. The first step is the contact of coal and oxygen, in which physical adsorption occurs, followed by the chemical adsorption and chemical reaction, which release heat. The process of chemical reaction also produces a large number of active groups and free radicals so that the chemical reaction continues. The fire suppression of macromolecular colloids is to suppress all aspects of coal-oxygen composites, thus effectively reducing the heat generation and releasing heat accumulated in the coal.

2.2.1. Reduction of Physical Adsorption. The macromolecular colloid can wet the coal surface and turn the gas-solid interface into the liquid-solid interface. Therefore, the macromolecular colloids isolate coal and oxygen, which reduce or prevent the physical adsorption of coal on oxygen.

2.2.2. Prevention of Chemical Adsorption and Chemical Reactions. The process of coal-oxygen chemical adsorption is that the electron cloud in the coal enters the two unpaired electron orbitals of the oxygen molecules, and the electron cloud is covered to produce the π complex and the σ complex; meanwhile, the adsorption heat is released. The reaction process is shown in Figure 5.

Macromolecular colloids contain a variety of ions and molecules, some of which are electrophilic reagents. The electrophilic reagent is usually located on the colloidal network. It can adsorb with the active structure of coal and even produce complex compounds. However, its complex can no longer undergo electrophilic substitution or oxidation with aromatic rings. Moreover, the function of the colloid and the active structure stop in the first step. The second step is slow. The product is predominantly a π complex, and the amount of σ complexes is very small. The process produces little heat. The reaction process is shown in Figure 6.

3. Study on Physical Properties of Macromolecular Materials

3.1. Gel Time of the Macromolecular Materials. The preparation of different concentrations of macromolecular colloids is shown in Table 1. First, the macromolecular material and water are weighed, and then the macromolecular material is poured into the water and mixed continuously with a glass rod. The gelling time is measured by using a stopwatch, and the results are shown in Figure 7. It can be seen that when the concentration is a few thousandths, they can be gelled smoothly. It shows that the water absorption property of the macromolecular material is stronger. At 20°C, the gelling time of the macromolecular material decreases with the increase of the concentration.

The ratio of the macromolecular material to water was set at 1.0% to prepare a macromolecular colloid. The experimental temperature was adjusted by the HH-M6 digital water bath, and the temperature was controlled at 20°C, 40°C, 60°C, 80°C, and 100°C respectively. The macromolecular material, which was weighed, was slowly added to the water and stirred continuously with a glass rod. The gel time was measured with a stopwatch. The results are shown in Figure 8. The time of gelation of macromolecular fire-extinguishing materials is greatly affected by temperature. The gel time is almost linearly decreasing with increasing temperature. After 45°C, the gel time is reduced to less than 10 s.
3.2. Viscosity of the Macromolecular Materials. Figure 9 shows the plots of viscosity versus time for the macromolecular materials at different concentrations. For each concentration, the viscosity of macromolecular materials decreases rapidly within 30 mins, and then the rate of the decline is gradually decreased. Approximately 250 hours later, the viscosity increased slightly because of the increase of concentration of the macromolecular materials caused by the loss of water. Subsequently, the above-mentioned...
A reciprocating trend occurs continuously until the content of water is small and the surface is dry. In addition, the viscosity of the macromolecular materials increases with the increase of the concentration. When the concentration increases to 1.2%, the initial viscosity of the macromolecular material increases significantly, which is about ten times higher than 1.0%. Under such conditions, because of its large flow resistance, it is difficult to transport the colloid to the desired self-ignition area, further affecting the fire-prevention effect.

3.3. Rate of Water Loss. Macromolecular colloid is a high water-retaining material, and about 99% of its composition is water. The water retention of macromolecular colloids is a key factor in fire fighting. Therefore, according to the change of the mass of the colloid, the average water loss per unit time is measured. The experimental environment temperature is 20°C. The colloidal concentrations of the macromolecular colloid were 0.4%, 0.6%, 0.8%, 1.0%, 1.2%, and 1.4%, respectively. As shown in Figure 10, it can be seen that the six curves are substantially coincident. With the increase of time, the average water loss decreases first, and when it
reaches a certain threshold, it starts to increase and then decrease. This shows that colloidal concentration has little effect on the rate of water loss.

A macromolecular colloid with a concentration of 1% was prepared. The macromolecular colloids were placed in a water bath at different temperatures (20°C, 40°C, 60°C, 80°C, and 100°C). And then the changes of the mass of the macromolecular colloid with time were measured. The results are shown in Figure 11. It can be seen that the average water loss rate of the macromolecular colloid increases with increasing temperature. The average water loss rate for each temperature condition has a maximum value. The peaks were 0.57 g/h, 1.47 g/h, 3.99 g/h, 7.34 g/h, and 10.49 g/h, respectively.

4. Study on Fire-Fighting Performance of Macromolecular Colloids

4.1. Experimental Equipment and Process. In this paper, a self-designed temperature-programmed experimental system was used to test the performance of the macromolecular colloid. The experimental system is shown in Figure 12(a) [28]. The system mainly includes four process: gas supply, temperature control, gas analysis, and tail gas treatment. The loading capacity of the self-made coal sample tank is 1,000 g, and the structure is shown in Figure 12(b).

The selected coal samples were mixed with water, water glass colloid (WGC), loess compound colloid (LCC), fly ash composite colloid (FACC), and macromolecular colloid (MC) (as shown in Table 2), then soaked for 12 hours, and finally placed on a 0.5 mm wire mesh. After no water dropping, they were loaded into a coal sample tank to begin the experiment. Water glass and gelling agents are from Xi’an Tianhe Mining Technology Co., Ltd.

The treated coal sample was charged into an experimental furnace, and nitrogen gas was introduced for 30 minutes. Then, the air was allowed, and the flow was set to 120 ml/min. The experiment started from 25°C to 170°C, and the heating rate was 20°C/h. When the temperature of the coal sample was higher than 10°C, the gas in the coal sample tank was analyzed by gas chromatography.

4.2. Results and Discussion. The experiment was carried out in the Key Laboratory of Mine and Disaster Prevention and Control of Ministry of Education. The ambient temperature was 20.0–25.0°C, the relative humidity was 58.0–70.0%, and the atmospheric pressure was about 101.0 kPa.

4.2.1. Effects of Macromolecular Colloids on Heating Rate. The study of Xu et al. [29] showed that the temperature-programmed experimental method is a technique for short-term testing of spontaneous coal combustion. Spontaneous coal oxidation combustion is a dynamic process of nonlinear development [30, 31].

It can be seen from Figure 13 that the coal temperature increases gradually [32], and the heating process is divided into three stages (I: <90°C, II: 90–100°C, and III: >100°C). The resistance effect of various fire-prevention materials is mainly reflected in stage II. From 90°C to 100°C, each coal sample (No. 1, No. 2, No. 3, No. 4, No. 5, and No. 6) requires 48 min, 55 min, 826 min, 373 min, 550 min, and 921 min, respectively. This shows that the resistance effect of the macromolecular colloid is significantly better than that of other fire-prevention materials.

4.2.2. Effects of Macromolecular Colloids on Oxygen Consumption Rate. As can be seen from Figure 14, the oxygen consumption rate of coal samples (No. 1, No. 2, No. 3, No. 4, No. 5, and No. 6) increased with increasing temperature [33]. The oxygen consumption rate of the raw coal (No. 1) was greater than the oxygen consumption rate of the treated
coal samples (No. 2, No. 3, No. 4, No. 5, and No. 6). When the coal sample temperature was below 60°C, the difference in the rate of heating of various coal samples was small. After 80°C, the heating rate of the coal sample treated with the macromolecular colloid (No. 6) was significantly smaller than that of other coal samples (No. 1, No. 2, No. 3, No. 4, and No. 5).

4.2.3. Effects of Macromolecular Colloids on CO. Dou et al. [34], Xu et al. [29], and Deng et al. [28] studies showed that the emission of CO has a significant dependence on temperature. So, CO has been considered as an effective means of tracking or predicting coal spontaneous combustion. Accordingly, we studied the CO concentration of the raw coal sample and the treated coal sample at various temperatures. The results are shown in Figure 15.

As can be seen from Figure 15, the amount of CO produced by the treated coal samples (No. 2, No. 3, No. 4, No. 5, and No. 6) was much lower than the amount of CO produced by the raw coal sample (No. 1), and among them, No. 6 produced the smallest. This shows that the macromolecular colloid effectively inhibits the oxidation process of coal.

4.2.4. Effects of Macromolecular Colloids on Activation Energy ($E_a$). According to the kinetic theory of reaction, the $E_a$ in each reaction was different. The lower the $E_a$ is, the easier the reaction is and the faster the reaction rate is. Therefore, $E_a$ could be used as an indicator of spontaneous coal combustion propensity [35].

According to the literature [30], the reaction process of coal oxidation and temperature rising can be described as

$$\text{Coal} + \text{O}_2 \rightarrow a\text{CO} + b\text{CO}_2 + \text{others} \quad (1)$$

According to Arrhenius’ law, the rate of oxidation at any coal temperature is shown as
\[ r(T_k) = r(O_2) = \frac{r(CO)}{a} = \frac{r(CO_2)}{b} = k_0 C_{O_2}^m \exp\left(-\frac{E_a}{RT_k}\right). \]  
\[ (2) \]

where \( r(a) \) is the reaction rate (mol/(m\(^3\)·s)), \( T_k \) is the temperature of coal (°C), \( a \) and \( b \) are coefficients, \( k_0 \) is the exponential factor, \( C_{O_2} \) is the molecular strength of oxygen in air (mol/m\(^3\)), \( m \) is the reaction series, \( E_a \) denotes the activity energy (kJ/mol), and \( R \) is the gas constant (8.314 J/(°C·mol)).

During the experiment, it is assumed that the air flows along the longitudinal direction of the coal sample tank, that is, the positive direction of \( y \), as shown in Figure 12(b). The rate of CO generation at any point in the \( y \) direction is

\[ dV_{CO} = \frac{S \cdot ak_0 C_{O_2}^m \exp\left(-E_a/RT\right)}{k \cdot v_{air}} dy, \]  
\[ (3) \]

where \( V_{CO} \) is the CO concentration (ppm), \( S \) is the sectional area of the coal sample tank (m\(^2\)), \( v_{air} \) is the airflow velocity (m\(^3\)/s), and \( k \) is the concentration conversion coefficient \((22.4 \times 10^8)\).

Integrating the above formula (3), we obtain

\[ \int_{P_{in}}^{P_{out}} dV_{CO} = \int_{0}^{t} \frac{S \cdot ak_0 C_{O_2}^m \exp\left(-E_a/RT\right)}{k \cdot v_{air}} dy, \]  
\[ (4) \]
where $P_{\text{out}}$ is the CO concentration at the exit of the coal sample tank (ppm) and $L$ is the height of the coal sample.

From formula (4), we obtain

$$\ln P_{\text{out}} = -\frac{E_a}{R} \cdot \frac{1}{T_k} + \ln \frac{a L k S C_O^m}{k \cdot v_{\text{air}}}. \quad (5)$$

According to the relationship between $\ln(P_{\text{out}})$ and $1/T_k$ in (5), the apparent activation energy ($E_a$) can be calculated [29, 35, 36]. Figure 16 shows the linear relationship between $\ln(P_{\text{out}})$ and $1/T_k$ for six coal samples (No. 1, No. 2, No. 3, No. 4, No. 5, and No. 6).

The $E_a$ of the corresponding coal sample is obtained by substituting the slope value fitted in Figure 16 into equation (5). The results are shown in Table 3.

<table>
<thead>
<tr>
<th>Coal sample</th>
<th>No. 1</th>
<th>No. 2</th>
<th>No. 3</th>
<th>No. 4</th>
<th>No. 5</th>
<th>No. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>68.26</td>
<td>74.79</td>
<td>96.59</td>
<td>83.90</td>
<td>88.71</td>
<td>102.00</td>
</tr>
</tbody>
</table>

5. Conclusions

A macromolecular colloid for coal seam fire fighting was developed, and its physical and chemical properties and flame suppression performance were analyzed. The following conclusions are drawn from this study:

1. The macromolecular material has some crosslinking bonds. When it encounters water, it will swell and cannot be dissolved, and a lot of water is controlled in the macromolecular colloid. Macromolecular colloid is better than that of water, water glass, loess compound colloids, and fly ash composite colloids. The flame-retardant ability of several materials from large to small is macromolecular colloids, water glass colloids, fly ash composite colloids, loess compound colloids, and water.
materials and water can be mixed into a mixture of macromolecular colloids. The colloid mainly consists of organic and inorganic components. Organic components are mainly mesh structures.

(2) The concentration of a few thousandths of the macromolecular materials can be successfully formed into gel. This shows that the macromolecular materials have a stronger water absorption property. With the increase of concentration, the gel time of the macromolecular colloid gradually decreases. With the increase of temperature, the gel time of macromolecular colloid gradually decreases.

(3) The concentration has little effect on the water loss of macromolecular colloids. The effect of temperature on the water loss of macromolecular colloids is higher. The higher the temperature is, the higher the water loss value is.

(4) The heating rate of coal samples treated with macromolecular colloids is lower than that of coal samples treated with other fire-extinguishing materials. The rate of oxygen consumption, the rate of CO generation, and the rate of CO₂ generation of the coal treated by macromolecular colloids are lower than those of the coal treated by other fire-extinguishing materials. Macromolecular colloids suppress the oxidation and temperature rising by increasing the $E_a$ and they also have the ability of wrapping oxygen.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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