**ABSTRACT:** In this paper, an active colloid (AC) with a three-dimensional network framework, prepared from stimulated fly ash (FA) component by an acid–base compound chemical method, was proposed for prevention of coal mine fire. During the stimulation process, the active substance in fly ash can be released and transformed into effective components for fire prevention. Research results show that Al$^{3+}$, Fe$^{3+}$, and Ti$^{4+}$ from FA can serve as metal cross-linking agents to graft-copolymerize with sodium carboxymethyl cellulose. Mg$^{2+}$ and Ca$^{2+}$ can be formed into halogenated salts that are encapsulated by composite colloids and cooperate with them to participate in fire prevention. The remaining fly ash solid particles served as an inert component can be fixed in the framework to encapsulate more water, improving the colloid’s strength and water retention. The content of the active component was measured by inductively coupled plasma (ICP) emission spectroscopy to evaluate the stimulation effect of fly ash. The gel time, viscosity, water retention, and other performance parameters were determined for evaluation of physical characteristics. The fire-prevention performances of AC were also determined by the inhibition performance test, thermogravimetric analysis, and infrared spectroscopy. Moreover, the fire-prevention mechanism of AC was also explored. These results showed that the AC prepared from the stimulated fly ash component can greatly inhibit the spontaneous combustion of coal and can be chosen as a potential material for prevention of coal mine fire caused by spontaneous combustion of coal.

1. **INTRODUCTION**

The spontaneous combustion of coal is a key safety issue in the mining, storage, and transportation of coal, which continues to severely restrict the development of the coal industry. Along with safety concerns, it can also cause significant environmental problems, such as the emission of greenhouse gases and hazardous trace elements. To decrease risks to humans and the environment, researchers have proposed several technologies and methods to prevent this hazard, including yellow mud grouting, spraying chemical inhibitors, pressure injection of colloids, etc. Among them, colloid injection technology is widely used because of its convenient operation and ability to inhibit the spontaneous combustion of coal via a variety of effective pathways.

In recent years, many new fire-fighting materials have been developed. How to match different components to play a synergistic role has become a research hotspot in the field of fire prevention all over the world. Yang et al. prepared colloidal particle-stabilized foam with sodium alginate, fly ash (FA), and aqueous foam, showing good inhibition performance. Xi et al. prepared a novel plugging material with cement, fly ash, graphene oxide, and other additives to prevent spontaneous combustion of coal by efficiently plugging the cracks in coal and rock mass. Yan et al. proposed an intumescent flame retardant, which can show good inhibitory effects during all stages of coal oxidation. Wang et al. selected inorganic salt such as magnesium chloride and calcium chloride to combine with free radical scavengers N,N-dibenzylhydroxylamine and 2,6-di-tert-butyl-4-methylphenol to form a composite inhibitor. Christopher et al. studied the effect of inorganic phosphate Pi and sulfonate mixed with surfactants on coal spontaneous combustion and found that inorganic salts can destroy free radicals generated during coal oxidation and surfactants can prevent coal from contacting with oxygen. Dou et al. studied the inhibitory effect of catechin and poly(ethylene glycol) on coal and found that they could generate more stable ether bonds in coal.

However, from a wide amount of literature, most of the fire-extinguishing materials are based on industrial raw materials or chemical reagents prepared by physical or chemical cross-linking reactions, rarely using industrial solid waste. Fly ash is the main solid residue of coal-fired power plants, which causes serious environmental pollution if discharged without treatment. Due to its low price, unique structure, and high recycling
value, fly ash has attracted extensive attention from researchers, especially in ceramics, architecture, agriculture, and other fields.12−14 Fly ash shows good physical and chemical activity after activation, and these effective components can serve as a synergistic flame retardant for fire extinguishment. The main chemical components of fly ash are SiO2, Al2O3, CaO, Fe2O3, MgO, TiO2, K2O, and Na2O, and the total content is usually more than 85%. After activation, SiO2 can be converted to silicate ion; Al2O3, Fe2O3, and TiO2 can be converted into high-valence Al3+, Fe3+, and Ti4+, which can be used as cross-linking agents to synthesize colloids; CaO and MgO can be converted into divalent Ca2+ and Mg2+, which are effective inhibitors of spontaneous combustion of coal. The residual solid component is a flame retardant inert material, and the activation process can improve the suspension and fluidity of solid components of fly ash.

In this study, a composite acid–base chemical activation method was used to stimulate the activity of fly ash, and the activation effect was evaluated. The AC was prepared by the graft copolymerization of activated fly ash with sodium carboxymethyl cellulose and a slow H+ release agent. The gelation time, viscosity, and water retention of the gel were investigated. The fire suppression properties were evaluated by blocking property experiments, thermogravimetric analysis (TGA), and specific surface area measurements. The inhibition mechanism based on the synergistic effect of active components from ash fly ash was also explored based on experimental results. These results showed that the AC prepared from the stimulated fly ash component can greatly inhibit the spontaneous combustion of coal and can be chosen as a potential material for prevention of coal spontaneous combustion.

2. EXPERIMENTAL SECTION

2.1. Preparation of Active Collide from Fly Ash

2.1.1. Stimulation of Fly Ash. The fly ash (FA) used in this study was obtained from the Yulian power plant and was of first grade. The chemical composition and content of FA are shown in Table 1. During the composite gel preparation, fly ash acts as a cross-linking agent. In this study, fly ash was activated by a compound acid–base activation method. Fly ash (300 g) was added to 200 mL of sodium hydroxide solution with concentrations of 1.5 M. After mixing evenly, it was placed at ambient temperature with a soak time of 3−4 days. After that, a 2 M hydrochloric acid solution was added to the alkali-activated fly ash solution. After rapid stirring, the solution was yellow-green and accompanied by bubbles, indicating that the internal active components in fly ash were dissolved under acidic conditions to stimulate the activity of fly ash.

2.1.2. Determination of the Active Component Content. During stimulation, a sand core filter device equipped with a 0.22 μm filter membrane was used to filter the acid–base fly ash solution (ABFA), and the filtrate with the active component was obtained. A PerkinElmer Avio 500 inductively coupled plasma-optical emission spectrometry (ICP-OES) instrument was used to detect the concentration of various ions in the filtrate. After diluting the acid filtrate tenfold, the concentrations of Al3+, Fe3+, Ti4+, and Mg2+ were determined. After 100-fold dilution, the concentration of Ca2+ was determined. The results are shown in Table 2.

### Table 1. Composition and Content of Fly Ash

| sample      | SiO2  | Al2O3 | Fe2O3 | CaO  | K2O  | TiO2 | MgO  | Na2O | SO3 | P2O5 | Cl | NiO |
|-------------|-------|-------|-------|------|------|------|------|------|-----|------|----|-----|
| Yulian FA   | 53.97 | 31.15 | 4.16  | 4.01 | 2.04 | 1.13 | 0.89 | 0.73 | 0.67 | 0.13 | 0.11 |     |

### Table 2. Concentration of Metal Ions Released from Fly Ash after Acid–Base Activation

| sample      | Al3+ | Fe3+ | Ti4+ | Mg2+ | Ca2+ |
|-------------|------|------|------|------|------|
| Yulian ABFA | 187.1| 73.37| 5.108| 145  | 105.7|

2.1.3. Preparation of AC. AC was prepared from a solution containing sodium carboxymethyl cellulose (CMC), activated fly ash, chelating agent citric acid, and H+ sustained-release agent gluconic acid-δ-lactone (GDL). CMC solutions with concentrations of 2, 2.5, and 3% were prepared by dissolving CMC in deionized water, stirring strongly, and standing until completely dissolved. Citric acid was added to the activated fly ash solution, and the pH was adjusted to 6 with 0.5 M NaOH solution to prepare the activated fly ash cross-linking agent. The CMC solution, activated fly ash cross-linking agent, and GDL were stirred strongly and mixed evenly to prepare the composite gel. AC materials with different proportions of CMC (2, 2.5, and 3%) were labeled as AC-1, AC-2, and AC-3, respectively. The volume of activated fly ash solution was 30% of the CMC solution, the volume of citric acid was 1% of activated fly ash solution, and the volume of GDL was 5% of the CMC solution.

2.2. Determination of Physical Characteristics

2.2.1. Gelation Time. The gelation time was measured by the drip counting method. The well-mixed cross-linking system was quickly poured into a funnel, where it was allowed to flow naturally into another container. The time of this process was called the funnel dripping time. The cross-linking system was poured into the funnel again, and the above operation was repeated until the dripping time was 50% more than that of the previous one. The duration of the whole experiment was the gelation time.

2.2.2. Viscosity Test. The viscosity of the colloid was measured by an NDJ-4 rotary viscometer. During the experiment, the activated fly ash gel cross-linking system with different proportions was added to a beaker and stirred until the cross-linking system completely reacted. Then, the beaker was placed under the rotor of the viscometer so that the rotor was completely immersed in the gel cross-linking system. The rotor showed the viscosity of the gel cross-linking system in real-time during rotation. The viscosity data were recorded every 10 min and stopped after 100 min.

2.2.3. Water Retention of Gel. Weigh 100 g of each of the three gels and put them into the temperature-program control box at the same time as the water. The temperature range was 50−180 °C, and the heating rate was 1 min/°C. As the temperature increased by 10 °C, the beaker was removed and weighed. After weighing, it was immediately returned to the temperature-programmed control box. The weight loss rate of the gel was calculated as follows.
where $\eta$ is the heat loss rate of gelatin, %; $m_0$ is the initial mass of the gel, g; and $m_1$ is the mass of the gel at a specific time, g.

2.2.4. Permeability of Gel Materials. A homemade infiltration device is adopted to test the permeability of gel materials, and the schematic diagram of the device is shown in Figure 1. The crushed coal particles with a particle size of 0.1–0.2 cm were uniformly placed in the device. Water, AC-I, AC-II, and AC-III were poured evenly on crushed coal in a cone-shaped container. After 30 min, the mass of the gel was measured, and the permeability was taken as the ratio of the gel mass to the initial mass at the outlet.

2.2.5. Thermal Stability Test. Three kinds of gel materials were placed in a vacuum drying oven, dried for 24 h at 40 °C, and ground into a solid powder. To test its thermal stability, the dried gel powder (10 mg) was placed in a thermogravimetry–differential scanning calorimetry (TG–DSC) analyzer. The temperature range was 30–650 °C, the heating rate was 10 °C/min, and the air flow rate was 50 mL/min.

2.3. Characterization of Fire Prevention. 2.3.1. Inhibition Performance. Ximeng lignite was selected as the coal sample in the experiment, which has low metamorphism and easy and spontaneous combusts. After crushing the coal sample, a sample with a particle size of 40–60 mesh was selected. The coal sample (40 g) was weighed and mixed with AC-I, AC-II, and AC-III colloidal solutions, and then temperature-programmed experiments were carried out. In the experiments, an air flow of 80 mL/min was introduced, the heating rate was 1.0 °C/min, and the temperature range was 30–200 °C. The concentration of gaseous products at the outlet was recorded at every 10 °C increase in temperature until the final temperature was reached.

2.3.2. Thermogravimetric Analysis. A sensitive thermogravimetric analyzer (TGA) (NETZSCH STA 409 C) equipped with an Al$_2$O$_3$ ceramic crucible (flat tray) was employed to measure the weight and heat change. During the experiment, 10 mg of lignite raw coal with a particle size of 40–60 mesh and 10 mg of coal treated with 1 mg of AC-III colloid solution were prepared and put into an alumina crucible, respectively. The TG–DSC curves of coal samples were obtained by injecting dry air with a flow rate of 50 mL/min, setting the heating rate of the furnace to 10 °C/min, and heating from room temperature to 800 °C.

2.3.3. Filling Capacity. The filling property of activated colloid on the surface of coal particles is determined by measuring the difference between the specific surface areas of the lignite raw coal and the AC-III gel-treated coal sample. The test of specific surface area was determined with a BeiShiDe 3H-2000PS4-type specific surface area analyzer. During the test, 3.00 g of coal samples with a particle size range of 20–60 mesh was weighed and heat-treated at a constant temperature, and gas desorption was carried out in vacuum. The net weight was input into the analysis station to test the $N_2$ adsorption process and adsorption capacity of coal samples in the range of saturated vapor pressure at liquid nitrogen temperature.

2.3.4. Changes of Active Functional Group. The functional groups of lignite raw coal and coal samples treated with AC-III gel were determined by a Bruker VERTEX 70 infrared spectrometer. In the experiment, the wavenumber range of Fourier transform infrared (FTIR) was 4000–500 cm$^{-1}$, the resolution was 2.0 cm$^{-1}$, and the scanning time was 40 s. The background spectrum was determined by dry KBr. The samples were heated from 30 to 210 °C at a heating rate of 1 K/min, and infrared spectra were measured every 15 °C increase in temperature.

3. RESULTS AND DISCUSSION

3.1. Gel Properties. 3.1.1. Gelation Time. The gelation time is the most stringent requirement for practical production and has the greatest impact on fire prevention and extinguishment. Generally, the gelation time is defined as a period of time from the initial state to the sudden change in the flow state, which reflects the changes in the colloidal morphology of the gel material. The experiments showed that three different proportions of gel materials formed a stable gel structure (AC-I, AC-II, AC-III gel). AC-I gel had strong mobility and obvious dehydration after a week. AC-II and AC-III gels had strong stickiness on the surface of the container. After placing for 1 week, a dense film appeared on the surface to wrap the entire colloid, and there was no obvious dehydration. The experimental results showed that the gelation times of AC-I, AC-II, and AC-III gel were 56, 31, and 22 min, respectively. The gelation times showed that the critical micelle concentration (CMC) increased from 2 to 3%, and the gelation time shortened by 60.7%. This is because when the concentration of the CMC solution was low, there were fewer linear CMC macromolecules. This led to a lower cross-linking density, and the graft copolymerization reaction was slower. The probability of collision between metal ions in the activated fly ash solution and the CMC linear macromolecules was smaller, so the reaction time was long; however, upon increasing the CMC concentration, the number of linear macromolecules in the gel system increased. The cross-linking
sites provided for metal ions in activated fly ash solution increased, the gelation reaction accelerated, and the gelation time shortened significantly.

3.1.2. Viscosity of the Gel. In mine fire prevention and extinguishment, the viscosity of the colloid in its initial state is an important parameter for evaluating the fluidity of the colloid and the condition of the colloid wrapping coal in a coal seam. The viscosity changes of the three kinds of gels were tested, and the results are shown in Figure 2. The relative change was obtained by the viscosity of the gel at the special time minus its viscosity at the initial state (t = 0).

It can be seen from the diagram that the viscosity of the system increased upon increasing the CMC concentration, and the viscosity of the gel system with 2.5 and 3% CMC increased rapidly. The gel viscosity changed with the interaction time of the colloid components, and it could reach the mutation point when the interaction time was close to the gelation time, and then, a gel material was formed. According to the data in Figure 2, the three gels showed their interaction time at around 65, 35, and 25 min, respectively. This result was similar to the gelation time. Also, the viscosity of the 3% CMC gel system showed its mutation point at around 25 min, which was much less than those of the other two gels. This is because the CMC content in AC-III is high than those in the rest gels, and the CMC component can promote the cross-linking reaction rate during the gelation process. When the CMC concentration was 2%, the viscosity of the colloidal system increased slowly, the active molecules in the solution were relatively independent, the interaction between molecules was low, and no obvious reaction occurred.

3.1.3. Water Retention of the Gel. The main component of the activated fly ash colloidal material is water. During the gelation process, water is wrapped by the three-dimensional network formed by a colloid, which decreases its fluidity. During mining applications, the gel is affected by the temperature, resulting in a series of physical and chemical transformations; therefore, the water retention of colloidal materials at different temperatures is an important index for evaluating the colloidal properties.

Figure 3 shows the weight loss of water and colloids of different proportions when heated. It can be seen that before 100 °C, the weight loss rate increased slowly upon increasing the temperature. Above 100 °C, the weight loss rate of water increased significantly, and the weight loss rate of three kinds of gels was lower than that of water. This indicates that these three kinds of gels had water retention properties. When the temperature reached 180 °C, the weight loss rates of AC-I, AC-II, and AC-III gel were 51.34, 45.75, and 38.87%, respectively. The weight loss rate of the AC-III gel was the lowest, and the water holding capacity was the strongest.

In the traditional fly ash slurry, water only adheres to the surface of the fly ash particles, and there is no three-dimensional network structure in the fly ash slurry. This leads to poor water retention in traditional fly ash slurries. In the activated fly ash gel, many carboxyl groups in the CMC structure reacted with the high-valence metal cations in the activated fly ash cross-linking agent to form a three-dimensional structure, which encapsulated the internal water molecules and reduced the evaporation rate of water; therefore, the water retention of activated fly ash gel increased significantly, and the change in the moisture content was relatively slow.

3.1.4. Gel Permeability. During the injection of colloidal material, the colloidal material must penetrate the broken coal and maintain encapsulation to isolate oxygen and fill the air leakage channels. The experimental results of the permeability of the colloidal materials are shown in Table 3.

It can be seen from the table that the water permeability was as high as 95.23%, indicating that almost no water existed in

### Table 3. Permeability of Each Experimental Material

| material  | water permeability (%) | AC-I | AC-II | AC-III |
|-----------|------------------------|------|-------|--------|
| permeability (%) | 95.23 | 65.83 | 48.54 | 30.37 |
the coal. The permeability of gel materials with different concentration ratios was also different. The permeability of the AC-III gel was 30.37%, which is 1/3 of the water permeability and 37.4% lower than that of the AC-II gel. This indicated that the AC-III gel stayed in the pores and cracks of coal, wrapped coal, and reduced its contact with oxygen. This effectively weakened the reaction between coal and oxygen and inhibited the spontaneous combustion of coal.

3.1.5. Thermal Stability of the Gel. The TG−DSC analysis results of the dried gels are shown in Figure 4. According to changes in the gel mass and heat, the TG−DSC curves were divided into three stages. The mass loss of the first stage (<169 °C) was about 10%. The whole stage was endothermic and was caused by the evaporation of free water and crystal water in the gel. In the second stage (169−294 °C), the mass loss was about 8%, and a small amount of heat was released due to the cleavage of glycoside chains and cellulose chains. The mass loss during the third stage (294−511 °C) was about 22% due to the gradual carbonization of organic components in the gel at higher temperatures. Therefore, it can be seen that the cellulose chain was not easily cracked at low temperatures, and the structure of the gel was only slightly damaged below 200 °C, showing its good thermal stability.

3.2. Fire-Prevention Characteristics. 3.2.1. Determination of Index Gas. Gas-phase products are often released during the coal oxidation reaction. At present, the commonly used indicator gases are CO and CO₂. Because of its early appearance and easy detection, CO is often used as the main indicator of the spontaneous combustion of coal, while CO₂ is used as an auxiliary indicator. This experiment mainly investigated the generation of CO and CO₂, and the results are shown in Figure 5.

It can be seen from the diagram that the trends of CO and CO₂ produced by coal samples treated with the colloid were similar and all were lower than that of raw coal. The least amounts of CO and CO₂ were released from coal samples treated by the A-III colloid. At 210 °C, the CO concentration of raw coal increased to 56 463 ppm, while the CO concentrations of coal samples treated with AC-I, AC-II, and AC-III increased to 49 076, 45 545, and 43 692 ppm, respectively. Compared with raw coal, these were decreased by 13.08, 19.34, and 22.62%, respectively. The results showed that all three kinds of gels inhibited the spontaneous combustion of coal, and the AC-III gel was more effective at inhibiting the spontaneous combustion of coal than other gels.

3.2.2. Mass and Heat Changes. TG−DSC curves of raw coal and AC-III treated coal are shown in Figure 6. It can be seen that due to the water retention and plugging effect of the colloid, the temperature at each stage of coal samples treated with the colloid lagged to different degrees. The curve of the coal sample with colloid began to stabilize at about 120 °C and entered the dynamic equilibrium stage, which was about 15 °C higher than that of raw coal. Upon increasing the temperature, the raw coal first entered the combustion stage, at which time the quality of the coal sample decreased rapidly, while the coal sample treated by the colloid entered the combustion stage about 20 °C higher than the raw coal sample.

It can be seen from the DSC curve that the curve change trend of the coal sample treated by the colloid was basically the same as that of raw coal. Before 120 °C, the DSC curve of the colloidal coal sample was negative, and the coal sample underwent water loss and heat absorption, lagging by about 30 °C compared with the raw coal sample. As the exothermic reaction proceeded, the coal sample gradually released heat. The exothermic peak of the coal sample treated by colloid was 612 °C, which is about 40 °C lower than that of raw coal, and the area of the exothermic peak was smaller than that of raw coal. The results show that the water retention and plugging properties of the colloid slowed the compound reaction rate of coal and oxygen and inhibited the low-temperature oxidation stage of the spontaneous combustion of coal.

Figure 4. Thermal analysis results of the activated fly ash gel material.

Figure 5. Emission trends of CO and CO₂.

Figure 6. TG−DSC curves of raw coal and AC-III treated coal.
3.2.3. Filling Capacity. The specific surface area was determined by the pore structure of coal, and the micropores and pores contributed more to the specific surface area. If there are many micropores and pores in coal, its specific surface area will be higher, which will provide more active sites for oxygen and make the coal more prone to spontaneous combustion. Therefore, the specific surface area can explain the inhibitory effect of the gel on the spontaneous combustion of coal from a microscopic perspective. The specific surface areas of XM raw coal and gel-treated coal samples are shown in Table 4.

As can be seen from the table, compared with that of raw coal, the specific surface areas of the colloid-treated coal samples decreased by 4.70, 12.42, and 19.63%, respectively. The reason is that the water and fly ash particles in the gel filled the pores on the coal's surface. Colloids have a high viscosity and can effectively encapsulate coal particles, which further decreases the specific surface area of coal samples treated by colloids. The specific surface area of coal samples treated with AC-III was the lowest, which indicates that increasing the CMC concentration greatly improved the filling and encapsulation effects of the gel.

Table 4. Specific Surface Area Test Results

| Sample         | Coal  | AC-I + coal | AC-II + coal | AC-III + coal |
|----------------|-------|-------------|--------------|---------------|
| Specific surface area (m²/g) | 5.96  | 5.68        | 5.22         | 4.79          |

Figure 6. TG–DSC curves of raw coal and AC-III-treated coal.

3.2.4. Changes of Active Functional Groups. The FTIR spectra of two kinds of samples at 30, 60, 90, 120, and 150 °C are shown in Figure 7. Comparing the FTIR spectra of coal samples at different temperatures shows that the effect of temperature on the surface-active functional groups of coal was mainly reflected by changes in the peaks in the ranges of 3100–2800 and 1850–1000 cm⁻¹. These peaks correspond to the absorption vibration of aliphatic C–H components and the stretching vibration region of aromatic C=O compounds, respectively. The peak areas of different vibration ranges were calculated by Peak-fit software, and the stability of the aromatic C=C content during heating was used to quantitatively standardize the peak areas of other functional groups; that is, the absorption peak area of functional groups at each temperature was divided by the absorption peak area of functional groups at the initial temperature. The standardization results are shown in Figure 8.

As can be seen from Figure 8a, the content of aliphatic C–H components such as –CH₃ and –CH₂– in raw coal samples and gel-treated coal samples decreased upon increasing the temperature. This is due to the strong reactivity of the methyl and methylene components, which participated in the early low-temperature oxidation of coal as the temperature increased, which decreased the peak area. Before 120 °C, the consumption rate of methyl and methylene groups in coal samples treated with colloid was slower than that of raw coal. This was because the colloid had good water retention and the film that formed on the coal surface of the colloid isolated

Figure 7. Infrared spectra of raw coal and AC-III-treated coal at different temperatures.
contact between the air and coal samples. This effectively inhibited the participation of methyl and methylene groups in the oxidation reaction. After 120 °C, the gel inhibition effect gradually weakened due to the evaporation of water in the gel. The contents of aliphatic C−H components in the raw coal samples and gel-treated coal samples were basically the same.

It can be seen from Figure 8b that the C=O content in the coal sample increased upon increasing the temperature, which indicates that during the oxidation of coal, hydroxyl, methyl, methylene, and other adsorbed groups were oxidized by oxygen to form products containing C=O functional groups. In addition, the C=O content of gel-treated coal samples increased less than that of raw coal, indicating that after the addition of the gel, the reaction between coal and oxygen was suppressed, which slowed the growth rate of C=O groups. After 120 °C, the water in the gel evaporated completely, and the C=O content of the gel-treated coal samples and raw coal was basically the same. This indicated that colloidal materials inhibited the early oxidation process of coal mainly by retaining water, wrapping coal, and forming a thin film to isolate oxygen before 120 °C.

3.3. Fire-Prevention Mechanism. Based on the experimental results, a schematic diagram of active colloid prepared from the stimulated fly ash component is shown in Figure 9. In the stimulation process, active substances in fly ash can be released and transformed into effective components of fire prevention. Among these active ingredients, Al³⁺, Fe³⁺, and Ti⁴⁺ can be used as cross-linking agents to graft-copolymerize with CMC linear polymer chains to form a three-dimensional network framework structure. Mg²⁺ and Ca²⁺ can be formed into halogenated salts that are encapsulated by composite colloids and cooperated with them to participate in inhibition. The remaining fly ash solid particles serving as an inert component can be fixed in the framework to encapsulate more water and improve the colloid’s strength and water retention.

When the AC acts on the coal body, it can cover the coal body, reduce the probability of coal−oxygen contact, isolate oxygen, and terminate the chain reaction of spontaneous combustion of coal. Large amounts of water, fly ash particles, and chemical inhibitors are encapsulated in the AC. These effective components will be released when AC is fractured due to high temperatures. At the same time, the residual fly ash particle has a good microaggregate effect, which fills the pores of coal particles with water. This reduces the specific surface area of coal, further preventing contact between coal and oxygen and reducing the number of active sites on the surface of coal. The released inhibitor will participate in the coal−oxygen reaction and form a stable chain, which inhibits the reaction of coal surface-active free radicals with oxygen. The chemical reaction equation can be described as follows.

![Figure 8](https://example.com/fig8.png)

Figure 8. Change trends of active groups during heating. (a) Aliphatic C−H content. (b) C=O containing groups.

![Figure 9](https://example.com/fig9.png)

Figure 9. Schematic diagram of fly ash colloid preparation.
Compared with that in raw coal, the content of aliphatic C–H components such as methyl and methylene groups increased and the C=O content decreased in the treated coal. This effectively reduced the reaction rate of active functional groups and the tendency of the spontaneous combustion of coal. This is due to the multifaceted inhibition of the composite colloid, as shown by the inhibition mechanism in Figure 10.

4. CONCLUSIONS

An active colloid with a three-dimensional network framework was proposed for prevention of coal mine fire. The effective components of fire prevention in fly ash were activated by a chemical method, and then, the active colloid was prepared by graft copolymerization using activated fly ash solution, sodium carboxymethyl cellulose, a H+ slow-release agent, and a metal-ion chelating agent. Al³⁺, Fe³⁺, and Ti⁴⁺ were used as cross-linking agents to synthesize activated colloids, which cooperated with halogenated salt inhibitors formed by Mg²⁺ and Ca²⁺ to participate in inhibition. Experimental results showed that 3% CMC could provide more cross-linking sites for the metal ions activated in fly ash solution with good gel properties. Compared with those of raw coal, the index gas, specific surface area, and C=O functional group content of coal samples treated by AC were reduced. The AC can inhibit spontaneous combustion of coal mainly through the following four aspects: (1) wrap coal blocks, isolate oxygen, and inhibit coal–oxygen reaction; (2) release water, reduce temperature, and extinguish fire; (3) the microaggregate effect of micro fly ash solid particles can fill the voids of coal and reduce the specific surface area of coal; (4) and release inhibitor ions, participate in coal–oxygen reaction, and inhibit the reaction between coal surface active groups and oxygen. These results showed that the AC prepared from the stimulated fly ash component can greatly inhibit the spontaneous combustion of coal and can be chosen as a potential material for fire prevention.

Figure 10. Diagram of inhibition mechanism for the fly ash composite colloid.

R – O – O’ + MgCl₂/CaCl₂ + H₂O
→ ROCl + Mg(OH)₂/Ca(OH)₂ + HCl

(2)

R – O – O’ + HCl → ROCl + OH’

(3)

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Notes
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