

# Research Progress of Gel Foam Extinguishing Agent in Coal Mines

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**Abstract:** Gel foam extinguishing agent (gel foam) has promising applications in the prevention and management of mine coal spontaneous combustion. Based on the research on coal spontaneous combustion and prevention technology, this article discusses recent studies on using gel foam to extinguish coal mines. The structural properties and principles of gel foam are described briefly. The research developments of three significant varieties of gel foam are then presented in detail, including silicate gel foam, acrylamide copolymer gel foam, and natural polymer gel foam. Meanwhile, the research status of gel foam anti-fire technology's rheological properties, stability property, plugging property, and inhibitory properties are introduced. Furthermore, in conjunction with the research state, the prospects of the research direction of gel foam are proposed, which serve as a reference for future research on gel foam.

**Keywords:** coal spontaneous combustion control; gel foam extinguishing agent; materials research; performance research



**Citation:** Zhang, Y.; Tian, Z.; Ye, Q.; Lu, Y. Research Progress of Gel Foam Extinguishing Agent in Coal Mines. *Fire* **2023**, *6*, 470. <https://doi.org/10.3390/fire6120470>

Academic Editors: Haiyan Wang and Feng Li

Received: 6 November 2023

Revised: 6 December 2023

Accepted: 6 December 2023

Published: 15 December 2023



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## 1. Introduction

Coal is a fossil fuel with great economic potential, but meanwhile, it is threatened by coal spontaneous combustion during coal production [1,2]. Due to the complexity of the coal mining process and the particularity of the environment, coal spontaneous combustion is becoming increasingly frequent [3]. Therefore, coal spontaneous combustion prevention technologies have been widely developed in recent years.

Nowadays, research on preventing and controlling coal spontaneous combustion focuses on three areas. It includes coal natural theory, prevention and control technologies, and field practice. Different technologies, such as grouting, inert gas injection, inhibitor injection, gel injection, foam injection, etc., have been used to control coal spontaneous combustion. Based on the mechanism of action, materials are classified into physical-based, chemical-based, as well as composite retardants [4,5]. Gel foam fire extinguishing agent (gel foam) is an innovative material that combines the advantages of both gel and foam. It exhibits strong practicality and promising application prospects.

In this paper, the research progress of gel foam in recent years was discussed. As shown in Figure 1, the study on coal spontaneous combustion and prevention technologies was introduced first. The structure and principle of gel foam were explained briefly. Then the research developments of three significant varieties of gel foam were presented in detail, including silicate gel foam, acrylamide copolymer gel foam, and natural polymer gel foam. Meanwhile, the research status of gel foam anti-fire technology's rheological properties, stability property, plugging property, and inhibitory properties were introduced. Then, the main challenges and development prospects of gel foam were analyzed, expecting to provide a reference for other researchers.

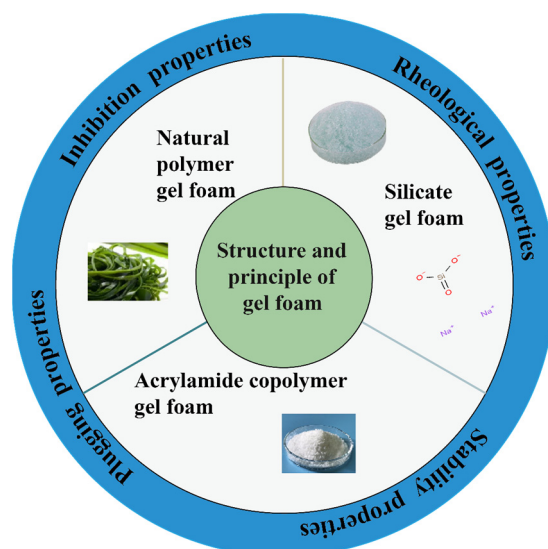


Figure 1. Structure and principle of gel foam.

## 2. Study on Coal Spontaneous Combustion and Prevention Technology

### 2.1. The Mechanism of Coal Spontaneous Combustion

Coal spontaneous combustion is one of the central causes of fire disasters. Due to the spontaneous combustion of coal, a lot of coal resources in the world's major coal mining areas such as South Africa, Europe, the United States, India, and China have been burned [6]. Besides that, harmful gases from coal spontaneous combustion pollute the ecosystem and harm human health, like  $\text{CO}_x$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ , etc. [7,8].

Coal spontaneous combustion has been researched since the 17th century. Various theories have been proposed to explain this phenomenon. Among these, the coal–oxygen composite hypothesis has been recognized by most scholars [9]. Coal spontaneous combustion occurs, which is the result of the joint action between coal and oxygen [10–12]. According to the coal–oxygen compound theory, the reaction of reactive groups with oxygen in coal has been investigated [13–15]. Experimental investigations have confirmed coal adsorbs oxygen. Meanwhile, the oxygen absorbed would react with the reactive groups of the coal to produce new free radicals, thereby generating a chain of water and gas and releasing heat [16–18]. When the heat production rate of coal oxidation is greater than the rate of heat dissipation from the coal to the environment, it will cause the accumulation of heat and make coal oxidation continue, which eventually leads to the spontaneous combustion of coal [19–21]. The reaction of radicals during the spontaneous combustion of coal is a chain cycle process.

### 2.2. Technologies of Prevention and Control of Coal Spontaneous Combustion

#### 2.2.1. Grouting

Grouting is one of the traditional technologies in coal mines for extinguishing fires. The mud is made proportionally from water and non-combustible solids, such as yellow mud or fly ash. It was then transported to the coal seam through an injection pipe [22]. According to the distribution of high-temperature zones in the coal seam, a mud injection system is established to produce mud, which is then transported into the coal seam by a pipeline to extinguish the fire [23]. Mud can cover the coal body, filling internal pores and insulating it from oxygen. However, the mud can easily “pull the ditch” and clog the pipe. In addition, it is difficult to pile up mud to a height, and it cannot solve the fire at a height [24]. However, due to the low cost of grouting, it is still one of the main fire prevention and extinguishing measures.

### 2.2.2. Inert Gas

Currently, CO<sub>2</sub> and N<sub>2</sub> are the main inert gases injected into the fire area. Inert gas can serve the purpose of fire prevention by diluting the oxygen in the fire zone. Inert gas has the advantages of a fast fire extinguishing speed, no pollution, etc. However, due to the severe air leakage in the mining airspace, inert gas cannot be used to extinguish the fire for a long time [25]. It was found that liquid inert gas has a better cooling effect. Currently, liquid inert gas fire prevention technology is being successfully used in many coal mines in China. The liquid inert gas (CO<sub>2</sub>, N<sub>2</sub>), loaded into special tanks, is transported to the site by mining vehicles and then connected to pressurized conveying equipment. It is injected into the area along the borehole using a booster or under pressure [26]. However, a lot of heat has to be absorbed during the evaporation of liquid inert gas. In addition, transporting and handling liquid coal dioxide poses a high risk. Under this condition, Liu et al. [27] developed a new equipment called the Dry-ice Phase Transformation Generator (DPTG) (Figure 2). The principle of the DPTG is based on warm water flowing through a copper pipe and exchanging heat with dry ice. The dry ice quickly changes from a solid to a gaseous state.

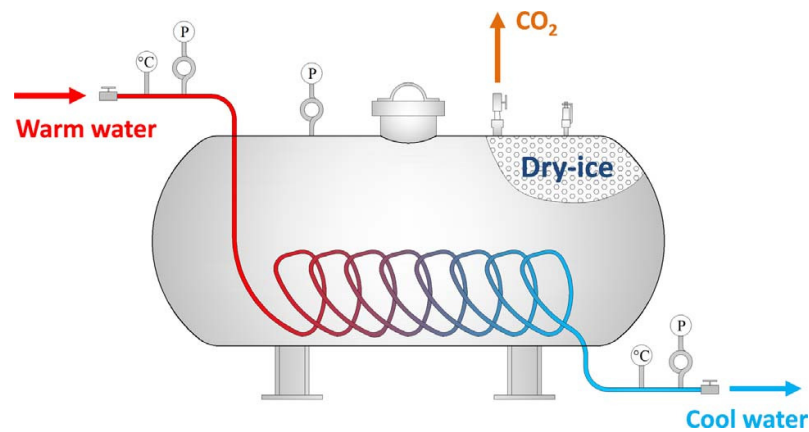


Figure 2. Schematic diagram of Dry-ice Phase Transformation Generator (DPTG) [27].

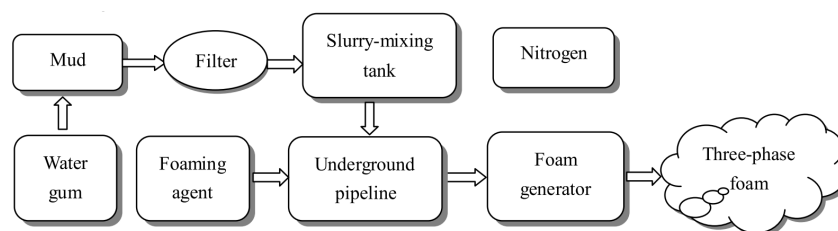
### 2.2.3. Inhibitor

Physical inhibitors are mainly halogen salt inhibitors, phosphate inhibitors, and ammonium salt inhibitors. The halogen salt type inhibitors mainly include CaCl<sub>2</sub>, MgCl<sub>2</sub>, NaCl, etc. [28–30]. These can play a better role in the low-temperature stage of coal oxidation. Physical inhibitors are less expensive and are currently the most commonly used in coal mines. Chemical inhibitors are mainly aimed at preventing the reaction between coal and oxygen, such as polyethylene glycol, anthocyanins, and catechin [31,32]. To offset the disadvantages of a single physical or chemical inhibitor, compound inhibitors offer the advantages of both: They can absorb heat to lower the temperature and effectively break the chain reaction. The compound inhibitors mainly include catechin polyethylene glycol, ascorbic acid–Rosmarinus acid, halogenated salt compound inhibitors, and so on [33,34]. Composite inhibitors have high inhibition efficiency, but the production cost is high, and the synthesis process is complicated. In practice, inhibitors are sprayed onto the coal or directly drill holes and inject inhibitor liquid into the coal wall that has begun to oxidize and heat. Wang et al. [35] examined the spraying process of the inhibitor. He sprayed nitrogen and atomized inhibitor liquid into the goaf for double fire prevention.

### 2.2.4. Foam

Foam is a kind of gas–liquid dispersed system with great importance. It is produced by physical foaming with a foaming device. The three-phase foam was first proposed to prevent the spontaneous combustion of coal in 2004 [36]. The three-phase foam gives full play to the fire protection advantages of yellow mud grouting and nitrogen injection technology. Meanwhile, it has been applied in many coal mines, such as the Longdong Coal

Mine and the Geng Cun Coal Mine in Henan Province [37,38]. In addition, the preparation of three-phase foam in the coal mine site includes two processes (Figure 3): Firstly, the materials are mixed proportionally to form a slurry, and then the slurry is transported to the underground; secondly, a foaming device is used to fully mix and foam the slurry, foaming agent and nitrogen to form a three-phase foam, and the three-phase foam is transported to the area that needs to be prevented from extinguishing the fire [38]. Foam can cover the floating coal in the high place and effectively solve the defect that the grouting technology cannot be poured into the high place. At the same time, it can also be used as a carrier to transport solid phase materials and water to the coal body to improve the resistance effect [39,40].



**Figure 3.** Craft process of infusing the three-phase foam [38].

### 2.2.5. Gel

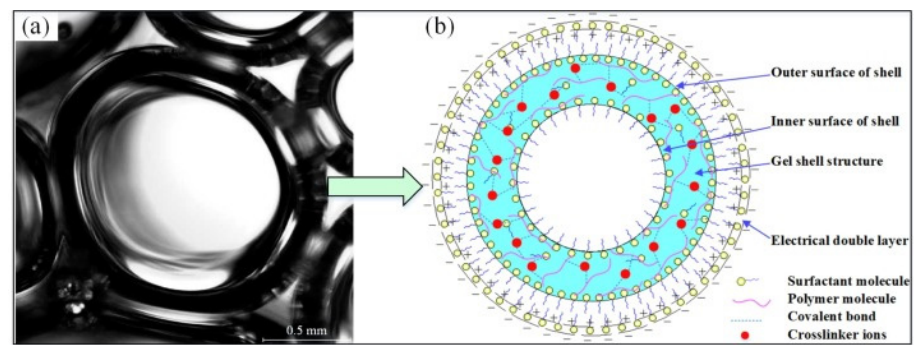
The gel is a special state between solid and liquid. According to the different chemical properties of the base material for preparing gel, it can be divided into inorganic gel, organic gel, and composite gel [41–43]. Gel fire prevention technology is to mix the base material, additives, and water in proportion and then press into the coal seam fire area with a slurry injection system. The solution in a liquid state before gel formation can penetrate the cracks and pores of the coal body. When the solution becomes a gel, it plugs these pores and fissures. The gel has a good water retention effect and absorbs heat through water evaporation to reduce the temperature of the coal. At the same time, the gel can cover the coal body and stop the reaction process between coal and oxygen. However, the flow rate of the gel is small, the fluidity is poor, and the colloid will crack and form fissures after a long period [44].

## 3. Structure and Principle of Gel Foam

### 3.1. Structural Features of Gel Foam

Gel foam is a non-equilibrium structure with gas uniformly dispersed in the gel. It is prepared by mechanical stirring of a gelling agent, cross-linking agent, and blowing agent in a gas [45–47]. In China, gel foam was first used to extract oil to enhance oil recovery. And it was gradually applied to coal mine fire prevention in the 20th century [48,49]. Tian [50] built the constitutive model of gel foam with relevant factors. He carried out a systematic study on the theory and technology of gel foam in coal mines. Qin et al. [51] proposed a multi-phase gel foam combining the gel and three-phase foam. It used fly ash as the base material and explored its weak cross-linking characteristics.

Differing from gel and foam, gel foam is a mixed system with gel as the continuous phase and gas as the dispersed phase [52]. The foam transports the gel-forming material into the coal body, while the foam film contains a large amount of gas and water inside its membrane. After some time, the gel-forming material forms a colloid with a three-dimensional network structure and wraps the foam [53]. As shown in Figure 4, (a) is the structure of the gel foam, and its structural characteristics are shown in (b). The unique formation process and structure of gel foam are applied in coal mine spontaneous combustion control by combining the advantages of both gel and foam.



**Figure 4.** Schematic diagram of single bubble structure in gel-stabilized foam [53].

### 3.2. Principle of Gel Foam Action

Gel foam is a new material based on gel and foam. The principle of spontaneous coal combustion is controlled by preventing or delaying the oxidation process of coal. It is essential to explore the role of gel foam in spontaneous coal combustion and explain its mechanism of action. The action mechanism of gel foam has been divided into three categories based on extensive experimental characterization and analysis [54–56]:

#### (a) The cooling effect [57]

The main component of gel foam is water. When water is transported from the foam to the high-temperature area, it will evaporate quickly due to the high temperature. The temperature of the coal drops because water absorbs a lot of heat as it evaporates, as shown in Figure 5a.

#### (b) The plugging effect

Figure 5b demonstrates the oxygen barrier properties of the gel foam. Gel foams contain gelling and cross-linking agents, which will form a three-dimensional network structure to cover the surface of the coal body after a chemical reaction. When the moisture disappears completely, a gel film is formed, blocking oxygen from coming into contact with the coal [58,59].

#### (c) The inhibition effect

The inhibition of gel foam consists mainly of physical and chemical inhibition. Physical inhibition is usually to prevent the contact of oxygen with coal, using cooling and the oxygen barrier to inhibit the spontaneous combustion of coal; chemical inhibition is to prevent the oxidation reaction of coal from proceeding and to inhibit the oxidative spontaneous combustion of coal by replacing the free radicals of the coal oxygen reaction or by generating a more stable structure with them (Figure 5c) [60].

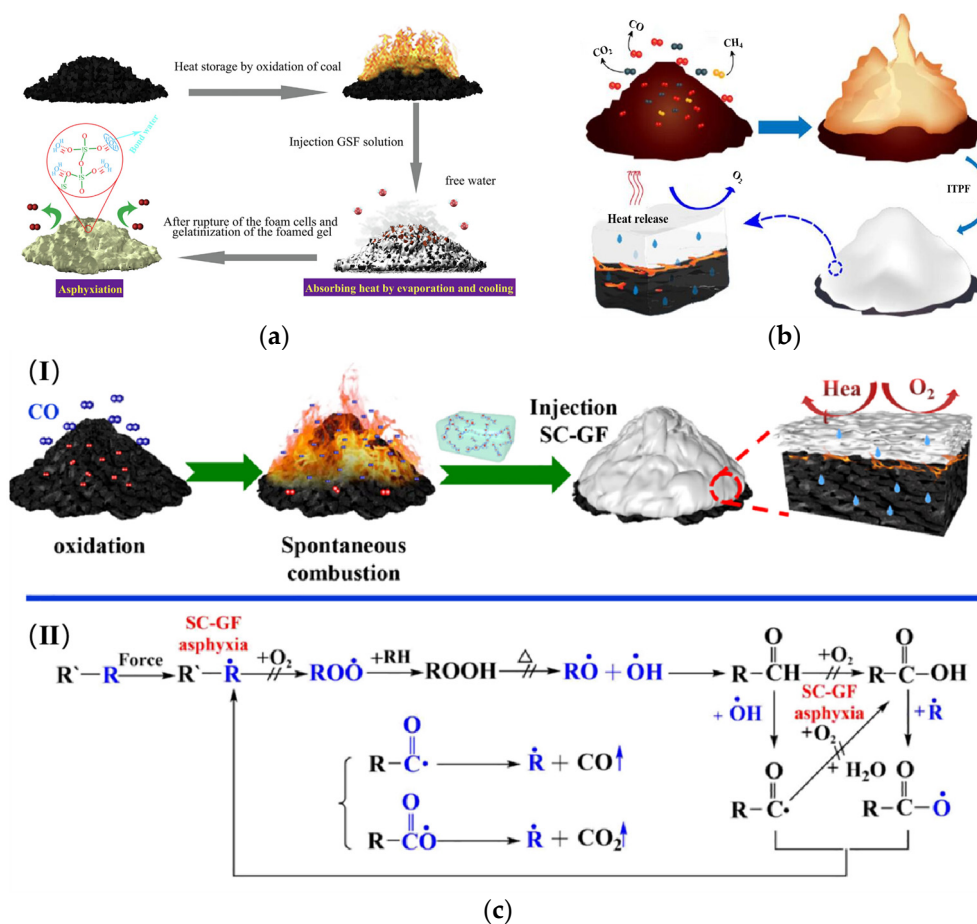


Figure 5. (a) The mechanism of GSF extinguishing coal fire [57]; (b) schematic diagram of gel foam cooling [58]; (c) fire prevention and extinguishing mechanism of SC-GF [60], (I) Visual representation of the process, (II) Mechanism of SC-GF asphyxia.

### 4. Materials Research

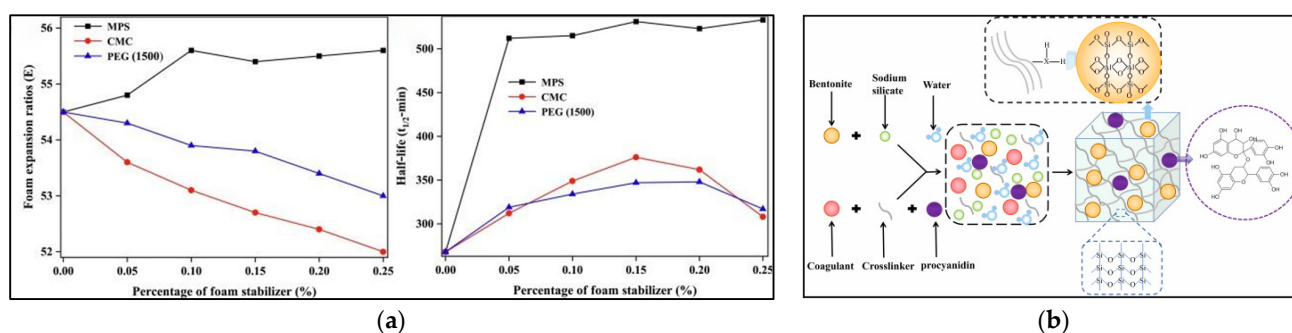
The gel foam component mainly consists of gelling agents, cross-linking agents, foaming agents, and gas sources. Nowadays, gel foams are mainly divided into three categories: silicate gel foam, acrylamide copolymer gel foam, and natural polymer gel foam.

#### 4.1. Silicate Gel Foam

Silicate gel foam is mainly referred to as gel foam with water glass as the gelling agent. In the field of coal spontaneous combustion prevention, the water glass solution is composed of a solid-phase nucleus and a double electric layer. The solid-phase nucleus is mainly a silica aggregate. The bilayer includes an adsorption layer and a diffusion layer. The adsorption layer consists of ionized  $SiO_3^{2-}$  and part of  $OH^-$ , and the diffusion layer is another part of ionized  $OH^-$  [61]. The mechanism of water glass gel foam is similar to that of water glass gel; both are chemical reactions between the gelling agent and the cross-linking agent. However, due to the addition of the foaming agent, the three-dimensional network structure of the gel foam exists uniformly on the foam wall and contains a large number of foams inside. Moreover, water glass gel foam is inexpensive and high-temperature resistant, but there are problems in terms of low strength, poor foam stability, and poor gel solidity.

To improve the problems of water glass gel foam, researchers have developed different kinds of gel foam composite systems with water glass as the base material. Xi et al. [62] prepared a new gel foam using a foaming solution (polyethylene oxide, sodium silicate, sodium dodecyl sulfate, and water) and additives (organic acid and polycaprolactone) as the main raw materials. Researchers investigated the modification of pure water glass gel

foam with polyvinyl alcohol, a polymer long-chain substance. In addition, the molecular chain of polyvinyl alcohol is interspersed between the molecules of sodium silicate, making its intermolecular force stronger, thus improving the disadvantage of the brittleness of pure water glass [63]. Xue et al. [57] investigated a composite foaming agent (CFA) based on two anionic surfactants. On this basis, a foam stabilizer was added to act in combination with the compound foaming agent (CFA). The results showed that the foam stabilizer could improve the stabilization effect of foam, but there were differences in the effect of different foam stabilizers (Figure 6a). Wu et al. [64] introduced a modified water glass gel foam with the incorporation of a film-forming agent and a water-retaining agent. The experiments showed that the modified gel foam had a half-life of up to 40 d at room temperature and a blocking efficiency of 78.35%.



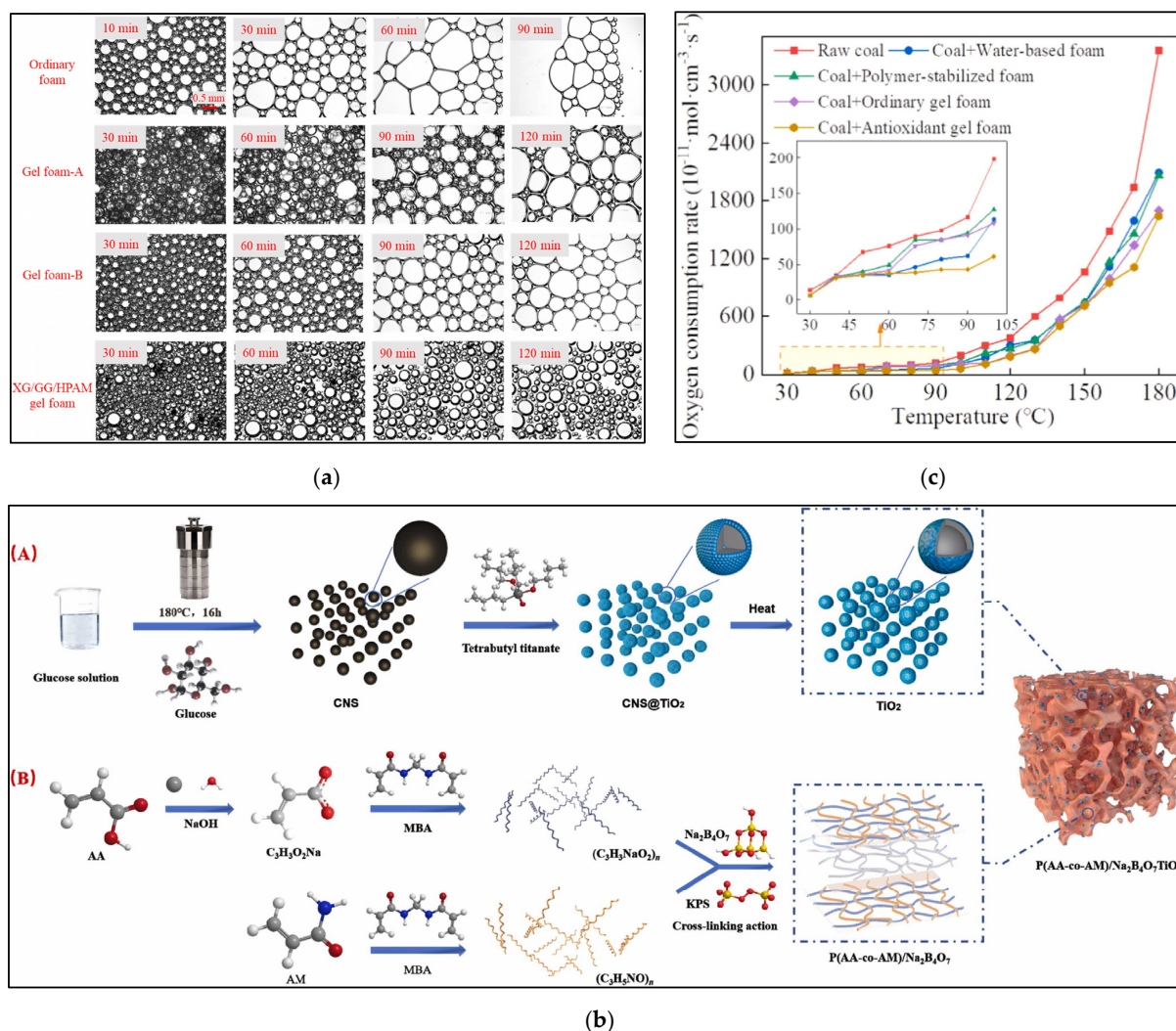
**Figure 6.** (a) Foam stabilizing ability of different foam stabilizers [57]; (b) gelation mechanism of bentonite in the plastic gel [65].

A new gel foam with antioxidant properties has been developed by relevant research scholars recently with the combination of coal spontaneous combustion. Lu et al. [65] prepared a new antioxidant gel foam by adding procyanidins and organic bentonite in a water glass solution (Figure 6b). The results showed that the antioxidant gel foam had denser foam, and the bentonite particles were attached to the foam walls. Meanwhile, the new antioxidant gel foam inhibited the spontaneous combustion of coal by 68.7%, which was the highest among the three. Xue et al. [66] developed a multi-effect synergistic fire extinguishing gel foam by adding a temperature-sensitive capsule of paraffin-encapsulated tea polyphenols to a water glass solution. The results showed that the paraffin underwent a phase change from solid to liquid at 60 °C, leading to the release of the encapsulated tea polyphenols. The H<sup>+</sup> generated by the tea polyphenols reacted with the coal group (–OO) to generate hydrogen peroxide (R–OOH). It prevented the further oxidation of the coal structural group –OO and thus terminated the chain reaction of free radicals in the coal. Lu et al. [67] incorporated sodium dithionite, calcium hydroxide, and activated carbon in a gel foam for a composite deoxygenation gel foam. It has an inhibitory effect on coal oxygen adsorption by blocking the coal radical chain reaction by reducing the alkyl, hydroxyl, and carbonyl groups of coal.

At present, the improvement of water glass gel foam mainly focuses on two aspects: material recombination and antioxidant performance. Water glass gel foam has been treated and reorganized to improve the refractory properties. Meanwhile, it also overcomes the disadvantages of low strength, being easy to break, poor foam stability, and poor water-solidifying properties. Water glass gel foam can react with coal reactive groups when adding antioxidant materials. Therefore, the combination of material reorganization and antioxidant properties will be one of the directions for the development of new water glass gel foam in the future. But its impact on the surrounding environment should also be considered to avoid secondary pollution in the treatment process.

### 4.2. Acrylamide Copolymer Gel Foam

Acrylamide gel foam is commonly used in the preparation of smart gel foams. And polyacrylamide is a widely used polymer commonly used in heavy metal waste treatment, oil extraction, and mineral processing [68]. The polyacrylamide molecule contains amide groups, making it easy to form hydrogen bonds. With good water solubility and high chemical activity, it can be grafted or cross-linked to obtain a variety of modifiers with a branched chain or mesh structure. Shen et al. [69] prepared a gel foam for coal mine fire prevention using polyacrylamide and aluminum citrate as a gel and cross-linking agent, respectively. In addition, the composite polymer gel foam made of xanthan gum, guar gum, and polyacrylamide was created by Fan et al. [70]. This foam was discovered to have a sluggish foam roughening process and a 43.63% higher coal inhibition rate than regular foams (Figure 7a).



**Figure 7.** (a) Foam coarsening process [70]; (b) preparation process flow of (A) H–TiO<sub>2</sub> and (B) gel [71]; (c) the variation of oxygen consumption rate of coal samples with temperature [72].

As well as taking advantage of the characteristics of acrylamide copolymers themselves, monomers such as acrylic acid and acrylamide have been used to combine with other materials to develop multifunctional gel foams. Metal oxides are used as flame retardant synergists in foam systems to enhance the flame effect of foams.

Thus, Li et al. [71] prepared gel foams with a synergistic flame-retardant effect by introducing sodium borate and hollow titanium dioxide (Figure 7b). Among them, hollow titanium dioxide was uniformly distributed on the surface of the gel foam, yielding an



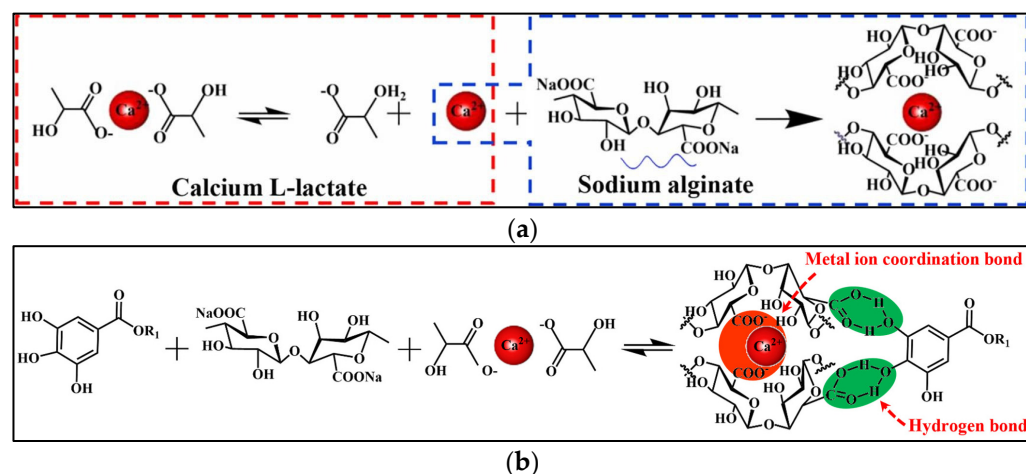
increase in the thickness of the foam liquid film. Ma et al. [72] added a composite inhibitor to the gel foam system. The inhibitor was prepared from procyanidin and a highly absorbent polymer. Meanwhile, it can change the water in the solution from a free state to a bound state, forming a more stable and highly water-retaining skeletal structure. In addition, the inhibition rate of coal can reach 74.48% after this antioxidant gel foam treatment (Figure 7c). Wang et al. [73] introduced soluble starch and N, N'-methylene acrylamide into acrylic monomer to make gel foam. The results showed that the foam gel could effectively reduce the oxidation reaction rate and temperature rise rate in coal, and the inhibition rate of CO reached 64.06%.

In summary, after a grafting or cross-linking treatment of acrylamide copolymer gel foam, the fire prevention performance is greatly improved, and the system strength and temperature resistance are also improved. These gel foams can be combined with other materials to obtain a variety of modifications due to their nature. However, their preparation process, copolymerization requirements, acid and alkali stability, and other factors have restricted their development. So, the field of practical applications is also limited. Acrylamide copolymer gel foam materials need to consider the material supporting technological development to improve the practicality of this type of gel foam.

#### 4.3. Natural Polymer Gel Foam

Natural polymer-based gel foams are gel foams with cellulose or other natural polymers as gelling agents. Most of the raw materials used in natural polymer-based gel foams are widely sourced and diverse, inexpensive, naturally degradable, and less environmentally hazardous. Thus, they have received more attention from researchers in recent years.

Sodium alginate, as a natural linear polysaccharide, has a molecule consisting of an M-unit ( $\beta$ -D-mannuronic acid) linked to a G-unit ( $\alpha$ -L-guluronic acid). The molecular structure contains a large number of hydrophilic groups hydroxyl and carboxyl groups. It is chemically active and can bind to some divalent cations to form a gel system [74]. According to the characteristics of sodium alginate, it is used in gel foam fire prevention technology to prevent coal spontaneous combustion. Han et al. [60] made gel foam with sodium alginate, calcium lactate, tea saponin, and alkyl glycosides. Among that, it forms a stable "eggshell" structure because the carboxylic acid in the sodium alginate reacts with the  $\text{Ca}^{2+}$  ionized from the calcium lactate (Figure 8a). In addition, the accelerated oxidation temperature of coal was delayed from 120 °C to 160 °C, and the CO inhibition rate was 60.5% at 200 °C. On this basis, tannic acid was introduced into this gel foam system to form a double cross-linked structure to enhance the stability of this gel foam. The double cross-linked structure mainly consists of the formation of metal ion coordination bonds between the carboxylate of the sodium alginate and  $\text{Ca}^{2+}$  and the formation of hydrogen bonds between the carboxyl group of sodium alginate and the phenolic hydroxyl group of tannic acid (Figure 8b) [75]. Then, nano-hydroxyapatite (HAP) was introduced into the above gel foam. And hydroxyapatite (HAP) [76], a natural apatite mineral, can hydrolyze  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{OH}^-$  in an aqueous solution. When processed into nanoparticles, it can form an "interfacial barrier" by adsorbing on the foam film. The results showed that the addition of hydroxyapatite could delay the accelerated oxidation temperature of coal from 120 °C to 19 °C, and the CO inhibition rate reached 85.3% at 200 °C [77].



**Figure 8.** (a) Gelation mechanism of SC-GF [60]; (b) double cross-linked stabilization mechanism of SA-Ca<sup>2+</sup>@TA-GF [75].

In addition, natural polymer compounds, such as carboxymethyl cellulose [78], low methoxylated pectin [79], xanthan gum, and galactomannan biopolymer [80], were prepared with a series of gel foams. Wang et al. [81] selected sodium carboxymethyl cellulose (CMC), zirconium citrate (ZrCit), and glucono- $\delta$ -lactone (GDL) to prepare a novel gel foam. The findings showed that the system reduced the rate of oxygen consumption to coal by 81%.

Natural polymer-based gel foams are green, clean, and biodegradable. Therefore, they are one of the directions to develop new gel foams that are green and pollution-free.

However, due to the defects of natural polymer materials, such as the mechanical properties and environmental resistance, the application range is narrow. Modification will be the main direction of future research and development of natural polymer-based gel foams to broaden the application range of natural polymers.

## 5. Performance Research

### 5.1. Rheological Properties

One of the essential features of gel foams entering and controlling the coal seam fire area is the rheological property. Gel foams are pseudoplastic non-Newtonian fluids that have shear-thinning properties. When under the influence of a high shear rate, the orientation of the gel foam's molecular chain would change, and the reticulation structure would be damaged. Meanwhile, the apparent viscosity would drop as the shear rate increases [82,83].

In the laboratory, the primary criterion used to describe the rheology of a gel foam is the apparent viscosity. In this regard, researchers used this parameter to analyze the elements influencing the rheological properties of gel foams [84–87]. Zhang and Qin [84] proposed that with a higher concentration of a thickener and cross-linker mixture, the apparent viscosity rises. The apparent viscosity is inversely proportional to both the shear rate and temperature. Afterward, the apparent viscosity tends to increase and then decrease when the foam foaming multiple is larger. Moreover, the apparent viscosity has variability in sensitivity to acid and alkali and is less sensitive to alkali. Wang [85] contended that when the proportion of gelling agents is larger, the nature of shear thinning is greater. Beyond this, Shen et al. [87] researched the influence of nanoparticles on the rheological properties of gel foam. The presence of nanoparticles increased the system's surface tension and improved the foam's viscoelasticity. It was attributed to the fact that numerous of the system's aggregates had been distributed in the foam film and platform edges. Consequently, the main factors affecting the rheological properties of gel foams include the surfactant type and concentration, the foam foaming multiplier, the concentration and ratio of the gelling agent and cross-linking agent mixture, the temperature, the pH value, added salt, etc. To

aim at a more intuitive study of the rheological properties of gel foam in the coal mine void area, Shi et al. [88] independently established a simplified experimental platform in the coal mine void area. The results showed that the gel foam flowed in an approximately hemispherical shape with the outlet position as the coordinate origin, and the growth of its diffusion hemisphere radius showed a decreasing trend with the decrease of permeation pressure (Figure 9).



**Figure 9.** Stacking process of gel-stabilized foam fluids in X–Z plane [88].

In summary, the rheological properties of gel foam research are mostly focused on the influence of the material components and environmental factors. The rheological properties of gel foam have been initially explored to provide a basis for the in-depth study of the rheological properties. However, no quantitative description of the coordination between the external action and intrinsic surface tension to control the foam flow has been made nor has it been linked to foam rheological properties and structural characteristics. Considering the special characteristics of underground space in coal mines, it is difficult to characterize the parameters such as the percolation and diffusion range, path, and filling height of a gel foam in practice in the laboratory. Hence, it is necessary to simulate to predict the actual situation and analyze the influencing factors of rheological properties. Meanwhile, the correlation between the index parameters needs to be analyzed, and corresponding mathematical models are built.

### 5.2. Stability Properties

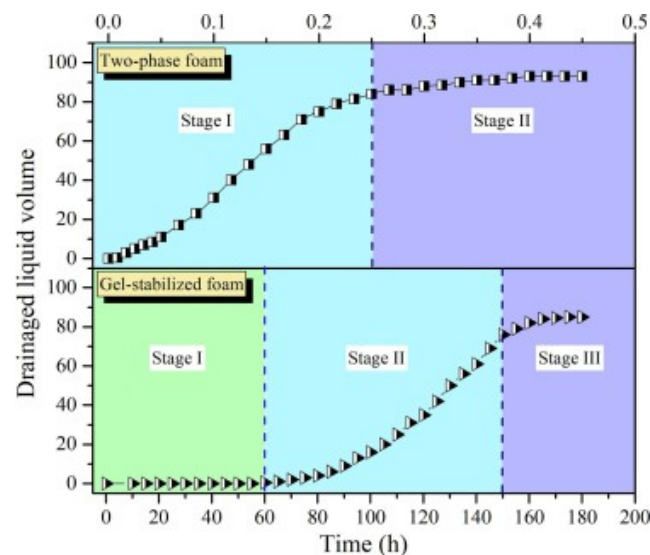
It is well-known that the stability of gel foam is one of the critical factors in preventing spontaneous coal combustion. A more stable gel foam could more easily enter into the coal seam, consequently improving fire prevention performance. In the laboratory, the half-life of the foam is often employed to describe the stability of a gel foam.

It has been demonstrated that the foaming agent type and concentration, foam stabilizer, foam multiple, temperature, pressure, and so on are the main factors affecting the stability performance of a gel foam [89,90]. As the concentration of surfactant increases, the foam generation time and size decreases and then reaches a plateau [91]. Therefore, there is a critical micelle concentration of surfactant. Zhu et al. [92] investigated the effect of surfactants and solid particles on foam membranes. It was found that hydrophilic particles prolonged the life of the membrane and improved the stability of the foam. Xu et al. [93] selected different anionic surfactants to explore the wetting ability of coal. It was found that at low surfactant concentrations, the surface tension is reduced, while the wetting time is shortened.

The structural differences between gel foam and foam have been proven. Zhu [94] proposed gel particles increase the stability of gel foam by changing the curvature and connection mode of the original water-based foam system (“weak rod” to “strong node and weak rod” structure). Furthermore, the three primary processes that impact gel foam stability performance are foam drainage, liquid film rupture, and bubble disproportionation [95,96]. In 2005, Yan’s group reported a kinetic model for the stability of liquid drainage of colloidal gas foam. It can be characterized by [97]:

$$V_t = V_{\max} \frac{t^n}{K^n + t^n} \quad (1)$$

where  $V_t$  is the volume of drained liquid at time  $t$ ,  $V_{\max}$  is the maximum volume of drained liquid,  $n$  characterizes the sigmoidal character of the curve, and  $K$  is equal to the half-life ( $t_{1/2}$ ) of drainage. The kinetic model demonstrated that the two stages of colloidal gas foam are determined by two independent mechanisms. Afterward, following Yan’s study, Shi et al. [98] proposed the liquid drainage of gel foam exists in three stages. The “zero” phase and the long precipitation period are the biggest differences between gel foam and two-phase foam (Figure 10).



**Figure 10.** The comparison of staged drainage curve between traditional two-phase foam and gel-stabilized foam [98].

In addition to the study of the structural stability performance of the gel foam itself, the thermal stability of gel foam has been studied. Chen et al. [99] indicated that surfactants could improve foam stability because of the presence of lamellar liquid crystalline phases. Zhang et al. [89] also proposed that the thermal stability of the gel foam increased with the increase of the concentration of the thickener and cross-linker blends and decreased with the increase of the foaming multiplier. Furthermore, Liu et al. [100] conducted the temperature resistance test and water loss rate experiment to research thermal stability. The gel foam was substantially more temperature resistant than two-phase foam, and the rate of water loss in gel foam was positively connected with temperature.

At present, the stability of gel foam is mainly studied in terms of structural stability and thermal stability. The drainage characteristics, microstructure, and heat and burn resistance of gel foam are analyzed. The difference between the gel foam drainage characteristics and water-based foam is obvious, making the structural stability of gel foam higher. Meanwhile, the thermal stability of gel foam and the influencing factors have also been investigated. However, the influence parameters of gel foam drainage characteristics, the evolution characteristics of foam microstructure morphology, and the mechanism of stability energy have not been studied systematically, so further research is needed.

### 5.3. Plugging Properties

The oxygen-thermal microcirculation effect generated by air leakage in underground coal mines is one of the causes of natural coal ignition. Gel foam can effectively seal air leakage channels and coal fissures to stop or slow down the oxygen-thermal microcirculation effect. So, the research on the plugging property of gel foam is beneficial to promote the application of gel foam in the prevention and control of coal spontaneous combustion.

The gelling property is one of the main factors affecting the plugging property of gel foam. Due to the particularity of the gel foam formation process and the limitation of field pipeline transportation, the gelation time of the system should be controlled. The gelation time is needed after foam formation, before bursting, and not less than the flow time of pipeline transportation. Therefore, the gelling time is the main parameter to characterize the gelling property of gel foam. It has been found that too long or too short of a gelation time of gel foam will lead to the decline of the plugging performance of the gel foam system on coal [101]. Zhang et al. [102] studied the effect of a gelling agent and cross-linker blend of gel foam on the gelling time. The results showed that the increase in the mass concentration of the gelling agent and cross-linker blend would shorten the intermolecular distance.

These can accelerate the molecular collision and promote the enhancement of the cross-linking reaction. Therefore, the gelling time of gel foam is inversely proportional to the mass concentration of the gelling agent and cross-linker blends. Yu et al. [101] tested the effect of different reactant concentrations, temperatures, PH values, and blowing agent concentrations on the gelling time of water glass gel foam using the tilted test tube method. Meanwhile, Li et al. [103] used gelation time and gelation strength as rating indexes to study the effect of the reaction temperature on gel characteristics. Gel time decreased with the increase in reaction temperature, and gel strength was the opposite. It is found that the type and concentration of the gelling agent and cross-linker mixture, temperature, and PH are the main factors of the plugging property of gel foam.

To further study the plugging property of gel foam in underground coal mines, researchers have conducted relevant experimental studies. Ren et al. [21] designed a gel foam plugging property test device. The basic principle is to investigate the plugging property by observing and recording the changing trend of the negative pressure values before and after the gel foam injection device. Shen et al. [69] obtained that the sealing process of gel foam includes three stages via an experimental device designed: high viscosity sealing after the disappearance of shear force in the early stage; formation of a stable pressure-resistant foam wall seal in the middle stage by cross-linking; complete development in the late stage.

At present, the research on gel foam plugging properties mainly includes characteristic parameters, influencing factors, and the plugging process, which is focused on the macroscopic level. However, it lacks systematic research on the microscopic level, such as the gelling formation mechanism and evolution characteristics of the plugging process. In addition, the experimental setup is not optimized. Therefore, how to quantitatively describe the influence of the gelling time on the plugging property, how to link macroscopic characteristics with the microscopic mechanism, and how to optimize the experimental setup of the plugging property are the directions for further research in the future.

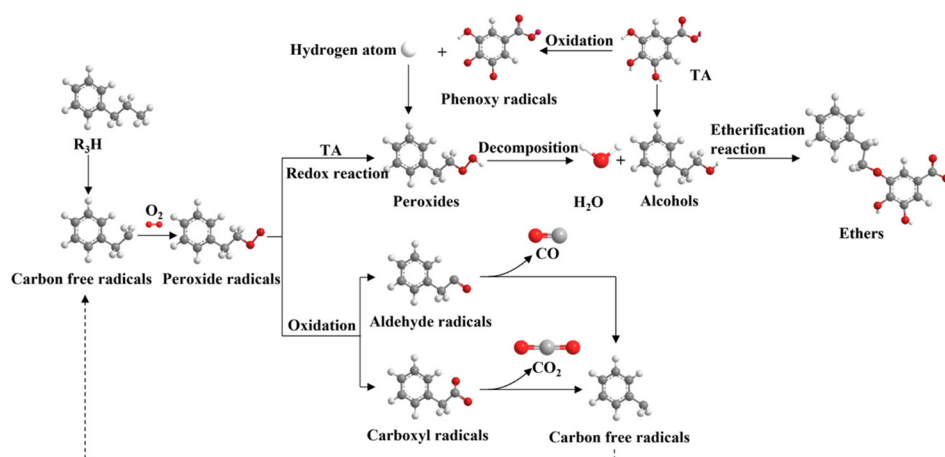
### 5.4. Inhibition Properties

The inhibition property of gel foam is synergized by various properties, such as the rheological property, stability property, and plugging property, which are also some of the important properties affecting gel foam. The inhibition rate is the main parameter to characterize the inhibition effect of gel foam. The release amount of the indicator gas CO and the temperature before and after raw coal treatment are commonly applied to identify the inhibition performance in the laboratory [104]. The development of modern testing technology makes the research field of gel foam resistance properties to be studied from macro and micro angles. Experimental methods, such as the cone calorimeter, TG-DSC, FT-IR infrared spectroscopy, and SEM scanning electron microscope, can be used to explore the resistance performance of gel foam. Those can test the changes in characteristic gas

production, characteristic temperature, microscopic characteristics, and action mechanism of coal samples before and after gel foam.

Accordingly, Li et al. [105] tested the blocking performance of raw coal samples,  $MgCl_2$  coal samples, and gel foam coal samples with a conical calorimeter. The standards are the ignition time, heat release rate, and total heat release rate of coal. The study demonstrated that gel foam had the latest ignition time, the earliest extinguishing time, and the lowest heat release rate and total heat release rate. Wang et al. [106] investigated the blocking effect of gel foam on different particle sizes of coal samples by using the programmed warming experiment method. The results showed that the blocking effect of each particle size of the coal sample by gel foam was in the order of large particle size > medium particle size > small particle size. Lu et al. [107] used a coal self-ignition signature gas determination experimental system and a simultaneous analyzer to test the coal warming rate, the development pattern of signature gas, and the characteristic temperature and thermal effect of coal during pyrolysis of coal samples treated with gel foam, respectively. It was found that the hindering performance of gel foam was better compared with water-based foam and slurry.

The researchers adopted instruments to explore the properties of the gel foam from a microscopic point of view. Huang et al. [108] researched an antioxidant gel foam. The study characterized the functional groups of coal samples treated with the gel foam by the experiment of in situ diffuse reflectance (FTIR) spectroscopy. It was demonstrated that the gel foam reduced the depletion of aliphatic methyl and methylene groups in coal, inhibited the formation of aldehydes and carboxyl groups, and generated stable compound products. The antioxidant materials in the gel foam could inhibit the spontaneous combustion of coal by preventing the chain reaction of some free radicals in the coal. Han et al. [75] proposed a new gel foam and its mechanism in Figure 11. As shown in Figure 11, the coal–oxygen complex reaction is a chain reaction in a continuous cycle. At high temperatures, the alkyl side chains of coal break to form carbon radicals, which form peroxy radicals with oxygen. Peroxy radicals further generate reactive groups and then new reactive groups produce  $CO$ ,  $CO_2$ , and new carbon radicals. However, the TA of the new gel foam can transfer hydrogen atoms to the peroxy radicals to generate stable ether structures. It disrupts the coal chain reaction and thus inhibits spontaneous combustion.



**Figure 11.** The Mechanism of SA- $Ca^{2+}$ @TA-GF inhibiting CSC. [75].

Gel foam resistances are studied by different testing methods and devices. The resistances of gel foam are initially investigated to provide a basis for the mechanism of gel foam fire prevention. However, most of the studies are still in the laboratory stage. Moreover, they are aimed at the resistances of self-developed gel foam materials. A unified evaluation standard and measurement system has not been formed. Meanwhile, considering the complexity of the coal spontaneous combustion mechanism, it is necessary to explore further whether it has practical engineering applicability. Therefore, it is suggested to expand the

scope of research further to provide more comprehensive and objective guidance for the application in practical engineering.

## 6. Prospects

Nowadays, domestic and foreign researchers have carried out a series of studies on the performance and materials of gel foam. They have made certain research results and breakthroughs. However, the situation of mine fire prevention and control in China is still severe. The theoretical research and engineering practical application of gel foam still need to be further explored. For this reason, the following suggestions and outlook are put forward.

### (1) Systematic configuration of gel foam materials

Gel foam is mainly composed of gelling agents, cross-linking agents, foaming agents, and other components. The different components have different effects on the gel foam system. At present, the screening of gel foam formulation is concentrated on the ratio of components under single-factor or multi-factor conditions. The evaluation index of gel foam formulation performance is mainly based on foaming performance and gelling time. However, the uncertainty of the coal spontaneous combustion environment in underground coal mines can lead to differences in the component allocation ratios of the gel foam systems. Therefore, it is necessary to establish a dynamic numerical system. According to the component parameters, rating indexes, and influencing factors, the distribution ratio of each group would be changed over time. In combination with the field and laboratory, the appropriate gel foam formulation is optimized.

### (2) Further basic research on the macroscopic role and microscopic mechanism of gel foam

Gel foam is used in coal spontaneous combustion prevention and control because of its unique structural characteristics and principles. Its mechanism of action is the basis of coal spontaneous combustion prevention and control. At present, scholars have conducted a lot of research on the macroscopic performance of gel foam fire prevention. They also proposed the feasibility of gel foam fire prevention technology for underground coal mine firefighting. However, there is a lack of theoretical basis to reveal the law of gel foam fire prevention. The microscopic mechanism of action of gel foam materials for coal spontaneous combustion prevention has not been systematically studied. Therefore, further research on the mechanism of gel foam fire prevention from macroscopic and microscopic perspectives is needed.

### (3) Research on multi-stage cooperative fire extinguishing technology

Underground coal mine fire zones are classified into small space-defined fire zones, large space-concealed fire zones, and complex fire zones according to the location of the fire source, spatial characteristics, and influence range [109]. Depending on the type of fire, gel foam can be used in combination with other materials. When there is a large space and complex fire, gel foam can be used as a blocking material to partition the fire area. The other materials can be used in conjunction with gel foam to realize multi-stage fire extinguishing. Hence, for the characteristics of different fire zones, a graded collaborative fire extinguishing technology method can be established. It combined with coal spontaneous combustion monitoring technology to achieve the integration between multiple fire extinguishing technologies for effective underground fire extinguishing.

## 7. Conclusions

Gel foam fire prevention technology has obvious advantages for the prevention and control of natural coal fires in underground mines. Gel foam material has good heat dissipation performance of gel and upward accumulation performance of the foam. It provides a new solution for the prevention and control of natural coal fires in underground mines. Among others, the natural polymer gel foam fits well with the concept of green development in China. The research on gel foam technology has shown a good development trend.

This paper also presents an outlook based on the current situation and shortcomings of this research field, hoping that the technology can achieve greater breakthroughs. It provides support for the safe production of China's coal mining industry.

**Author Contributions:** Y.Z.: Methodology, formal analysis, investigation, visualization, writing original draft preparation; Z.T.: Validation, resources, writing—review and editing, funding acquisition; Q.Y.: Investigation, validation, writing—review and editing; Y.L.: Conceptualization, resources, writing—review and editing, supervision, project administration. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by a Project Supported by the Scientific Research Fund of the Hunan Provincial Education Department (19A186).

**Conflicts of Interest:** The authors declare that they have no conflict of interest.

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