

Review

Exploration and Frontier of Coal Spontaneous Combustion Fire Prevention Materials

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Abstract: Mine fires have always been one of the disasters that restrict coal mining in China and endanger the life safety of underground workers. The research and development of new fire prevention materials are undoubtedly important to ensure the safe and efficient production of modern mines. At present, the main inhibiting materials used are grout material, inert gas, retarding agent, foam, gel, and so on. In order to explore the current situation of coal spontaneous combustion (CSC) fire prevention, the existing fire prevention materials were reviewed and prospected from three aspects: physical, chemical, and physicochemical inhibition. The results show that, at present, most of the methods of physicochemical inhibition are used to inhibit CSC. Antioxidants have become popular chemical inhibitors in recent years. In terms of physical inhibition, emerging biomass-based green materials, including foams, gels, and gel foams, are used to inhibit CSC. In addition, CSC fire-fighting materials also have shortcomings, including incomplete research on the mechanism of material action, poor stability of inhibitory properties, low efficiency, and economic and environmental protection to be improved. The future research direction of fire-fighting materials will be based on theoretical experiments and numerical simulation to study the mechanism and characteristics of CSC and develop new directional suppression materials with physicochemical synergies. These findings have extremely important implications for improving materials designed to prevent CSC.

Keywords: fire-fighting materials; coal spontaneous combustion; synergistic inhibition; research status; visualization



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1. Introduction

China's energy structure is characterized by abundant coal resources, which have become the pillar of national economic growth and cannot be ignored to promote rapid economic development [1–3]. However, with the diversity of coal reserves and the complexity of geological structure, coal spontaneous combustion (CSC) is representative of the frequent occurrence of coal mine disasters, which is a serious challenge facing the mining industry [4–6]. Mine fires not only pose direct threats to production safety but also represent one of the primary types of coal mine disasters that lead to substantial economic losses and casualties [7–9]. In recent years, the Chinese government has significantly strengthened its supervision over coal mine safety production and implemented a series of robust measures for comprehensive treatment, resulting in a marked reduction in both frequency and fatality rates associated with such accidents [10]. However, in the face of huge coal production, widely distributed mine networks, coal seams with different mining conditions, and uneven application of safety technology and management effectiveness among regions, CSC still faces serious challenges [11].

Faced with the serious safety hazard of coal mine fire, researchers at home and abroad have made unremitting exploration and successfully developed diversified fire prevention and extinguishing products, including slurry, foam, inert gas, colloid, and chemical retardant [12–15]. These materials are essential in preventing CSC and are integral to ensuring the safety of coal mines. However, despite their significant practical efficacy, certain limitations and deficiencies still persist. In view of this, this paper aims to systematically summarize and deeply evaluate the existing research status of CSC prevention materials, clarify the fire suppression mechanism and inhibition effect of various types of materials, and reveal the problems faced by existing fire prevention materials. This study aims to lay a scientific foundation for the future practice of CSC prevention and control and make targeted recommendations for improvement, with the aim of guiding and optimizing practical operations in this field.

2. Visual Analytics

In order to comprehensively review and summarize the research achievements and development trends in the field of CSC prevention and control materials, we used the core database of Web of Science to conduct an in-depth literature search by keywords “mine fire materials” and “coal spontaneous combustion materials”, and collected a total of 867 relevant research literature. This number indicates that a relatively comprehensive and influential academic system has been established in this field. In order to further analyze the internal correlation and evolutionary trajectory among research hotspots within this domain, we utilized Citespace, a professional literature knowledge mapping tool, for visualization purposes (refer to Figure 1).

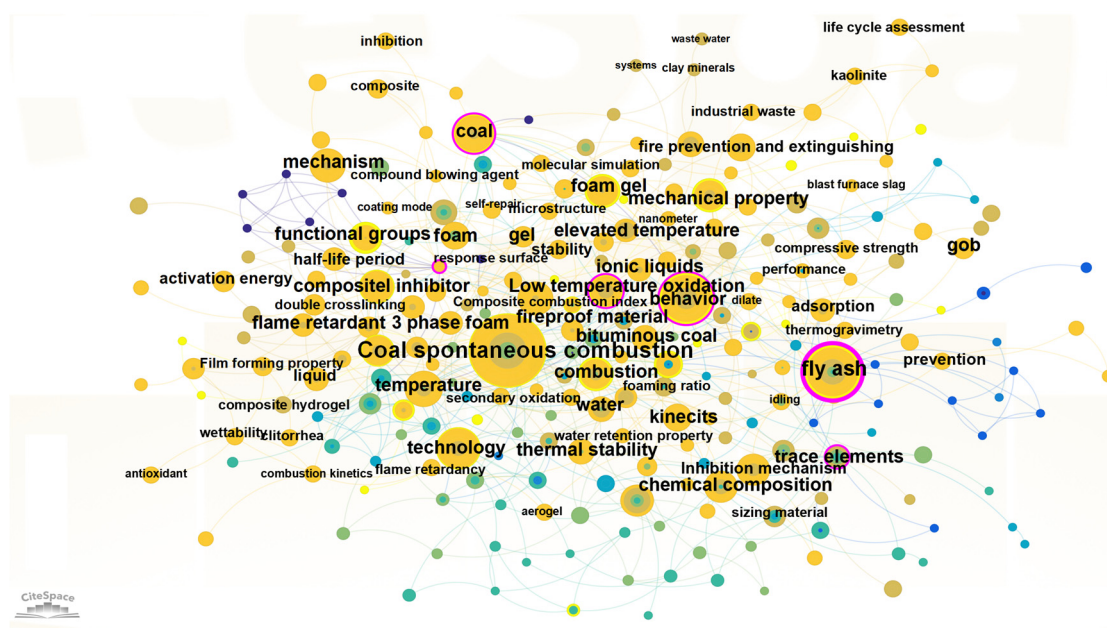


Figure 1. Keyword co-occurrence map.

In this graph, each node represents an individual keyword. The size of the nodes is precisely quantified based on scientometric principles, encompassing occurrence frequency, citation frequency, influence index, and other key indicators for the specified time period or literature collection. Consequently, substantial disparities in node size intuitively disclose the significance and attention attributed to each research topic within the broader academic landscape: larger nodes indicate heightened activity levels, greater influence, or wider scholarly discourse within contemporary research domains. These are considered as focal points of investigation. The color of the node represents the time when the keyword appears, and the darker the color, the earlier the keyword appears.

Figure 1 illustrates a range of prevalent strategies employed for the prevention of CSC. From the color of the keyword nodes, it can be seen that the development of CSC fire-fighting materials has gone through multiple stages, such as grouting, inert gas injection, colloid, inhibitor, foam, and gel foam. In addition, nowadays, researchers mostly use composite materials to synergistically inhibit CSC. When addressing the intricate issue of CSC, researchers tend to employ advanced and efficient fire-prevention measures like colloids, gel foams, and compound retardant agents. As a potential fire prevention medium, it is very important to investigate the basic properties of colloids. Through laboratory testing, scholars have conducted detailed investigations into the fundamental parameters of colloids, such as gelation kinetics, water retention capacity, plugging efficiency, and rheological behavior. These parameters are utilized to evaluate the colloid's ability to infiltrate coal formations, retain moisture content, and seal void spaces. For the inhibition of colloids in the CSC process, thermochemical techniques, including thermogravimetric analysis and temperature programming experiments, will be employed to quantitatively assess the inhibition efficiency of colloids at different temperatures and elucidate their mechanism in suppressing coal oxidation. Foam technology has attracted extensive attention in the field of CSC prevention and control because of its special film-forming properties and excellent durability. It focuses on key indicators, such as the strength and durability of foam film formation (e.g., half-life), with the aim of ensuring that the foam can effectively establish a stable and long-lasting isolation layer on the coal seam surface. This layer serves as a barrier to oxygen diffusion and inhibits coal oxidation and exothermic reactions, thereby enhancing its stability. An ideal foam product should possess outstanding adhesion, expansibility, and anti-evaporation ability while maintaining a long-lasting flame-retardant barrier within complex underground environments. The compound inhibitor synergistically combines diverse components to enhance inhibition efficiency and prolong the duration of inhibitory effects. The purpose of these preparations is to conduct a comprehensive analysis of their chemical inhibition, including determining the effective inhibition time, determining the active site of chemical inhibition, and elucidating the interaction mechanism between chemical inhibitors and coal molecules. It is crucial to elucidate how composite chemical inhibitors can disrupt the oxidation chain process of coal through specific chemical reactions or modify the surface properties of coal to mitigate its oxidation activity. These contents play a decisive role in optimizing formulation design and field application. At present, the research frontier has shifted to the molecular level. For instance, molecular simulation techniques can be employed to elucidate the microscopic interaction mechanism between chemical inhibitors and coal macromolecules and to elucidate how chemical inhibition agents accurately interfere with the thermochemical path of CSC. This theoretical analysis is not only helpful in guiding the design and synthesis of high-performance inhibitors but is also expected to promote the coal spontaneous combustion prevention technology to achieve a new leap of precision and intelligence.

Based on the above overview of the relevant keywords of coal spontaneous combustion anti-fire materials and the elaboration of their respective research focuses, the following will further launch a detailed review of various types of anti-fire materials, in-depth analysis of their working principles, performance characteristics, and practical application effects, in order to fully demonstrate the technical progress and future development direction in this field.

3. Current Situation of Fire Prevention Materials

3.1. Physically Inhibited Material

3.1.1. Grouting Material

The grouting method, commonly employed for the prevention of CSC, entails the blending of clay, crushed gangue, fly ash, and other materials with water to generate a highly mobile slurry. This slurry is then injected into the coal seam through dedicated pipes to effectively wrap the outside of the seam and strengthen the integrity of the coal rock by

plugging existing cracks. Because the grouting technology is simple, safe, and reliable, it is widely used in underground coal mining [16,17].

Wang Deming et al. [18] added the thickening additive KDC (a polysaccharide polymer extracted from natural plants, whose molecular structure is mannuronic acid and guluronic acid) to the mortar to form a loose three-dimensional network structure in water. At a low shear rate, the viscosity was 0.33~2.94 Pa·s. The surface viscosity is less than 0.28 Pa·s at high shear rate. At 0.4% aqueous solution concentration, the viscosity is more than 1500 times that of water. The material has a strong suspension capacity and reduces the flow resistance of the material in the pipeline. Wang [19] utilized fly ash as a substitute for loess and mixed it with water to prepare a fly ash grouting material. Considering economic factors, an optimal formulation consisting of 71 g coal ash, 14 g curing activator, 5–6 g hardening accelerator, and 50–55 g water was determined. This material not only retains the advantages of low cost and convenient production associated with traditional grouting materials but also effectively addresses key issues such as poor controllability and stacking difficulties, demonstrating significant improvement and advantages. Xiao Yang [20], combined with the actual situation of coal mines, proposed to use fly ash instead of loess as mine grouting materials and researched a new type of grouting and injection fire prevention materials (thickening suspending agent JXF1930 and gelling agent FCJ12) to realize the in situ resource utilization of fly ash in pithead power stations, and the performance of the materials is shown in Table 1.

Table 1. Properties of new materials and applicable conditions [20].

Category	Highly Effective Suspension JXF1930	Compound Colloidal Additives FCJ12
Performance	It is added into the slurry to form a thickening colloid so that the fly ash in the slurry is suspended, and the problem of pipeline blockage in the long-distance transportation of high-concentration slurry is solved	It is added to the slurry to form a complex colloid so that the slurry gels in a certain time and then loses its fluidity
Main role	The slurry containing the JXF1930 suspension agent exhibits excellent water retention, permeability, suspension, and compactness properties. It can be effectively encapsulated within coal for prolonged periods without separation during transportation due to its superior fluidity	The slurry, supplemented with FCJ12 gelling agent, can undergo solidification at the designated location to effectively seal the voids within coal deposits and encapsulate high-temperature coal. Allow its accumulated heat to be fully released to prevent the extinguished fire area from reigniting
Use scales	0.10%	0.06%
Usage	Sprinkle evenly into the slurry in the ground grouting pool according to the proportion used	The ZM-5/1.8G coal mine grouting machine proportionally injects it into the grouting pipeline in the vicinity of the underground grouting site
Applicable place	End mining line, eye cutting, gob area, coal field outcrop, surface coal yard, and other large areas of grouting glue to prevent fire	

However, the grouting fire prevention technology also exhibits certain limitations. Firstly, due to the substantial weight of the slurry itself, it is susceptible to gravitational effects, resulting in instances of slurry flow and bursting that restrict its coverage over the coal seam. Secondly, traditional grouting materials possess inadequate water retention capabilities. After the evaporation of water, the grout on the surface of the coal easily dries and cracks, which may produce new air leakage channels, thus affecting the fire prevention and control effect. Additionally, during water evaporation, the exothermic reaction generated by the coal body may pose a risk of water gas explosion under high-temperature conditions. Lastly, although low-concentration slurries exhibit good fluidity characteristics, their treatment area is limited due to sedimentation caused by high solid material density [21].

3.1.2. Gas Material

Inert gas fire prevention technology, as a scientific and effective means of CSC prevention and control, its core principle is to systematically inject inert gases, such as nitrogen and carbon dioxide, which do not easily react with other substances, into those mine areas where there are hidden dangers of spontaneous combustion or signs of spontaneous

combustion have occurred in the early stage [22,23]. The large input of these gases can dilute the oxygen content of the internal environment, effectively reducing the oxygen concentration to a level insufficient to support the continuous oxidation of the coal. In this way, the necessary conditions for maintaining the oxidation reaction chain between coal and oxygen are fundamentally broken, and the potential oxidative heat release process inside coal is inhibited, thus effectively preventing or slowing down the further development of CSC. This technology exhibits exceptional diffusibility, covering the entire fire area rapidly. Moreover, it is non-toxic and non-corrosive, so it plays an important role in the prevention and control of CSC. Since the 1980s, our country initiated the theoretical investigation and practical implementation of N₂ fire prevention and control [24].

Some scholars have conducted numerous theoretical and practical research studies on the suppression of CSC by inert gas. Tang et al. [22] conducted a field test on the compound inert gas of carbon dioxide and N₂ injected into the goaf of a certain working face. The results showed that merely 9 days subsequent to the administration of a composite inert gas, the CO concentration of return air flow decreased significantly from 14.9 ppm to 0.1 ppm, and the CO concentration at the corner of the return air also rapidly decreased from 4821 ppm to 21 ppm. It can significantly reduce the risk of mine fires without endangering the safety of underground workers. Ding [25] conducted an in-depth study on dry air, CO₂, and N₂ to investigate how the inert gases inhibit the mechanism of CSC. The results showed that the ability of coal to absorb oxygen was drastically weakened by the inert gas injection method, thus greatly hindering the coal–oxygen combination reaction and successfully guarding against the phenomenon of CSC. In controlled experiments, we found that the diffusion activity of oxygen was enhanced by 5.89% when carbon dioxide (CO₂) was used as an injection gas relative to nitrogen (N₂), as shown in Figure 2. Therefore, CO₂ was more effective than N₂ in inhibiting CSC. Lei et al. [26] investigated the inhibitory influence of N₂ and CO₂ on CSC under varying flow rates, revealing that both gases effectively suppress CSC; however, CO₂ exhibits superior efficiency due to its ability to not only dilute oxygen but also impede the positive progression of chain reactions, thereby facilitating faster fire control.

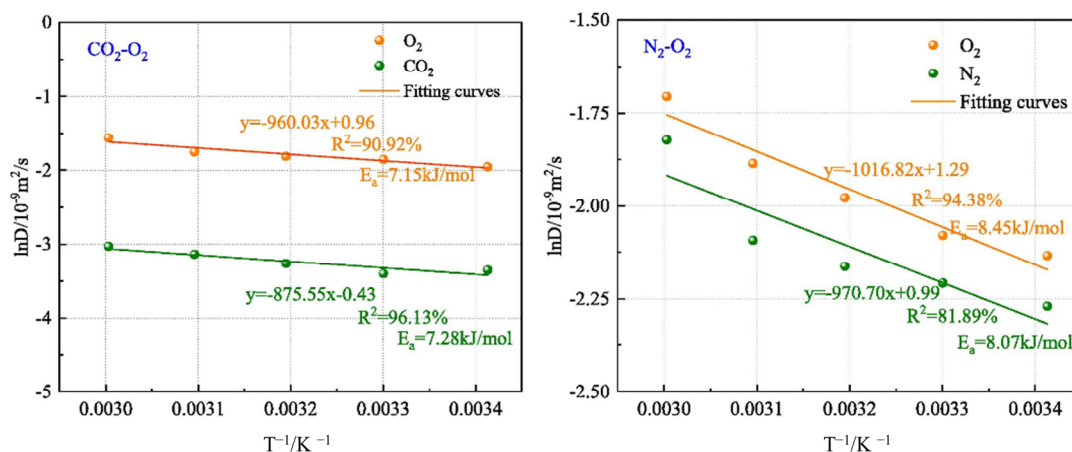


Figure 2. Diffusion activation energy of O₂ in different systems [25].

3.1.3. Colloid Material

In colloidal fire-fighting materials, with the help of drilling technology, the colloidal transport to the designated position after gelling, the surface of the coal is covered by colloidal, plays a role in oxygen blocking and cooling [7,27,28]. Colloidal materials used to inhibit coal spontaneous combustion include gels, corrosion retarding gels, aggregate suspension colloids, and inorganic mineral colloids [29].

Domestic and foreign scholars have widely used a variety of characterization methods to achieve the performance evaluation of gel-based fire-proofing materials, including programmed warming, FTIR infrared spectroscopy, TG-DSC simultaneous thermal analysis,

and SEM. The inhibitory effect of gels on CSC was primarily assessed through the analysis of gas yield, characteristic temperature, heat release, and microstructural changes in untreated and gel-treated coal samples [30,31]. The results are shown in Table 2, and the inhibition of CSC is positively influenced by the gel material.

Table 2. Inhibition effect of different gels on spontaneous combustion of coal.

Author	Gel System	Effect
Huang et al. [32]	Sodium silicate, sodium bicarbonate, and sodium polyacrylate	The optimal ratio of 4%, 5%, and 0.75‰ can increase the oxidation temperature rising zone by 8 m, shorten the length by 20 m, and increase the blocking zone by 28 m
Zhao [33]	The swelling gel was prepared with chitosan, sodium carboxymethyl cellulose (CMC), guar gum, and sodium bicarbonate	The optimal formulations were 0.75 wt%, 2.5 wt%, 0.15 wt%, 0.4 wt% and 0.5 wt% acetic acid. The gel viscosity was 5852 mPa·s, the expansion factor was 0.846, and the strength was 319.925 N/m ² after 6 h of storage. The permeability of loose coal was 93.52%. At 200 °C, the CO ₂ content of coal samples with 1 g of gel is 12,829 ppm, and that of coal samples with 5 g of gel is 23,239 ppm, which is 59.15% and 188.29% higher than that of raw coal, respectively
Zhou et al. [34]	CMC, cross-linking agent aluminum citrate (AlCit), and pH regulator δ -gluconate lactone (GDL)	Compared with the raw coal sample, the cross point temperature is increased by 13.9 °C, the activation energy is increased by 16.34%, and the amount of CO gas produced is reduced by 34.5%
Dong et al. [35]	CMC, Zirconium Citrate (ZrCit) and GDL	When the ratio is 2.5 wt%, 20 wt%, 2 wt%, the gel can effectively inhibit the spontaneous combustion of floating coal. When the ratio is 3 wt%, 20 wt%, 2 wt%, the gel is suitable for sealing and extinguishing fire sources
Wei et al. [36]	Polyvinyl alcohol (PVA), Xanthan gum (XG), and acrylic acid (AA)	Solve the problem of poor mechanical properties of gel materials. The contents of PVA, XG, and AA were 1.5 g, 0.1 g, and 6 g, respectively, and the optimum reaction temperature was 55 °C. Under the optimum conditions, the viscosity was 45 mPa·s, and the surface tension was 30 mN/m

3.1.4. Foam Material

Foam fire prevention technology, an innovative coal fire prevention and control strategy, has demonstrated excellent effectiveness in preventing and controlling CSC [37–39]. The technology is based on a unique foam generation system that produces large volumes of inert foam with high stability through a precise mix of water, foam agents, and, in some cases, inert gas, which is quickly mixed in a specific facility and treated by a foaming unit. These foams not only have excellent flow and spreading properties, which can quickly cover the coal surface and all corners of the mine, but also their internal structure is rich in tiny gas vesicles, which not only insulate oxygen but also form a thermal barrier. It has the characteristics of high viscosity, large acting area, low density, excellent stacking, and flow performance, and is economical and practical. In practice, inert, three-phase, and gel foams are three common types, which show superior fire prevention and extinguishing effects through different modification methods.

Two-Phase Foam

Based on the synergistic mechanism, Li [40] investigated the compound foaming agents ACFA (α -alkene sulfonate sodium: AOS; fatty alcohol polyoxyethylene ether sulfate: AES; hexadecanoate propyl trimethylammonium chloride: YN2031; xanthan gum: XG) and AFA (AOS, XG), and employed the Foamscan system to quantify foam properties. The results demonstrate that ACFA exhibits a faster foam generation rate at lower concentrations with a decay rate of 66.5%. The CO concentration of raw coal at 100 °C is 2287.9 ppm, which decreases to 974 ppm and 726 ppm after treatment with ACFA and AFA, respectively. A new type of foam was proposed by Tang et al. [41], which has high expansibility and good stability. The optimal proportions of sodium dodecyl benzene sulfonate (SDBS), MgCl₂, and guar gum were 2%, 1%, and 0.5%, respectively. In evaluating flame retardant performance, an in-depth analysis is conducted from three key dimensions: functionality, free radical control, and fire protection characteristics. This two-phase system offers advantages such as large foam volume and good fluidity when injected with inert gas for diluting gas concentration and reducing goaf heat in underground mines. However, a two-phase bubble also has some disadvantages, such as fast water erosion and bubble liquid membrane

stability and inert gas, which is vulnerable, especially when addressing hidden dangers related to spontaneous combustion in high areas or deep goaves where its efficacy is limited.

Three-Phase Foam

The concept was first introduced by China University of Mining and Technology [42]. Based on the concept of two-phase foam, solid substances such as fly ash or yellow mud are added to form a solid–liquid–gas three-phase system [43]. The three-phase foam exhibits the characteristics of encapsulation, heat absorption, and dissipation, as well as oxygen isolation, thereby enhancing its effectiveness in suppressing mine fires [44,45]. Zhu et al. [46] selected two anionic foaming agents: sodium dodecyl sulfate (SDS) and SDBS; one cationic foaming agent: cetyltrimethylammonium bromide (CTAB); and two non-ionic foaming agents: lauryl glucoside (APG1214) and coconut oil glucoside (APG0814) to carry out the compounding of the three types of foaming agents. The experimental results show that the foaming properties of anionic, cationic, and non-ionic foaming agents can be optimized when the three foaming agents are formulated according to a specific ratio of 2:1:1. The optimal combination of compound foaming agents was SDBS, CTAB, and APG0814 with a maximum foaming volume reaching 2700 mL. This value was 3.8% higher than the SDBS, CTAB, and APG1214 combination and 10.2% higher than SDS, CTAB, and APG0814 combination; moreover, it exceeded SDS, CTAB, and APG1214 by 12.5%. Wang [47] employed sodium soil as a dispersing agent, whereby the mass fraction of AOS was 0.5%. Sodium soil accounted for 33.3% of the solid particle mass, while the mass fraction of solid particles was 5.0%. A foaming volume of 275 mL and an analyte half-life of 72 min indicate that the three-phase foam under these conditions exhibits excellent foaming and stability. Through an in-depth investigation into its stability mechanism, it was discovered that the addition of sodium soil effectively enhanced particle suspension dispersion and prevented aggregation and sedimentation. Furthermore, incorporating solid particles augmented foam viscoelasticity. The synergistic effect of these two results in a significant increase in stability. Zhang [48] designed a new fire-extinguishing material (SMTP-20) by combining sea mud particles containing inert substances with three-phase foam. SMTP-20, characterized as a thin and tough foam, effectively seals cracks in coal to prevent oxygen ingress, exhibiting 2.19 times higher stability compared to traditional three-phase foams (Figure 3). When conducting dimensional experiments, it was observed that the internal temperature of the coal dropped sharply, reaching a rate of 117 °C/min and rapidly dropping below 100 °C, which demonstrated excellent fire prevention and cooling efficiency. However, it is worth noting that in three-phase foam, a large number of gathered solid particles produce a large extrusion stress on the foam liquid film when flowing, which not only affects the structural stability of the foam but also weakens its ability to seal cracks and prevent air infiltration [49].

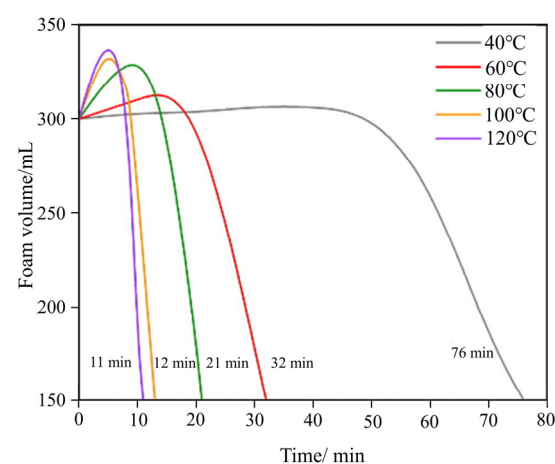


Figure 3. Volume trend of SMTP-20 at different temperatures [48].

Gel Foam

Gel foam technology cleverly combines the lightweight, porous nature of the foam with the highly absorbent expansion capacity of the gel. That is, in the process of forming the foam, the cross-linking agent is cross-linked with the polymer to form a colloid and is adsorbed in the liquid film of the foam to form a dispersion system [50,51]. The key indicators to measure the performance of the gel foam include its foaming ratio, the time required to form the gel, and its own water retention. The inhibitory effects of various systems on CSC are presented in Table 3. Thanks to the distinctive properties of colloids, gel foam exhibits exceptional stability and water retention capabilities, effectively reducing coal temperature while obstructing cracks and pores within the coal matrix to impede oxygen contact. Nevertheless, it is worth noting that the production process of gel foam is relatively intricate and costly, necessitating further attention and resolution.

Table 3. Inhibition of spontaneous coal combustion by different gel foam systems.

Authors	Gel Foam System	Effect
Han et al. [52]	SA (sodium alginate), CL (L-calcium lactate), CFA (tea saponin, alkyl glycoside), and TA (tannic acid)	Compared to the TA-free foam, the half-life was extended from 0.4 to 30 days, and the strength exhibited a remarkable increase of 72.9%. The concentration of CO decreased significantly from 7556.8 ppm to undetectable levels (0 ppm). SA-CA2+@TA-GF elevated the coal temperature by 60 °C during the rapid oxidation stage, achieving an impressive inhibition rate of 79.6% at 200 °C.
Wu et al. [53]	Sodium silicate, polyacrylamide, and film-forming agent	The strength and stability of the sodium silicate gel foam were enhanced. With the optimized formulation, the foaming ratio increased to 3–3.5 times, while the gelation time extended to 480 s. Moreover, the half-life of the gel foam was prolonged to 7 days, and its resistivity reached a remarkable value of 78.35% at 100 °C and 79.6% at 200 °C.
Wu et al. [54]	CMC cellulose, compound foaming agent (α -alkenyl sulfonate sodium; fatty alcohol polyoxyethylene ether sodium sulfate), cross-linking agent	The optimized formulations were 0.7 wt%, 0.7 wt%, and 1.1 wt%, exhibiting a foaming time ranging from 4 to 7 min and a gel time spanning from 3 to 10 min. Low-temperature oxygen consumption of the coal sample decreased by 9.74%.
Qiao et al. [55]	Superhydrophobic nanoparticles, PVA, sodium bicarbonate, and sodium tetraborate	The gel foam (PGF) without the addition of a foaming agent was prepared with a foaming multiple of 3.29 times, exhibiting a half-life exceeding 13 h and water retention for over 15 h at 100 °C. Furthermore, its inhibitory ability remained effective even under high temperatures up to 400 °C.
Xi et al. [56]	Polymer complex (PC) microbial polysaccharide and galactomannan biopolymer, organic boron complex (OBC), homemade anionic surfactant, and non-ionic surfactant foaming agent	The cross-linking time is more than 30 min, and the foam water content is more than 60% after 120 h. The temperature of the burned coal is reduced from about 700 °C to 34.7 °C within 30 min.

3.1.5. Physical Inhibitors

Physical inhibitors are preferred due to their excellent heat dissipation, low preparation complexity, and economic advantages. Common physical resistance agents include CaCl_2 , MgCl_2 , NaCl , NH_4Cl , NH_4HCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, among others. Physical retardant agents inhibit CSC through two primary mechanisms: firstly, they exhibit strong water absorption properties that ensure prolonged wetness of the coal. At high temperatures, a portion of the absorbed water vaporizes and absorbs heat while the remainder forms a liquid film on the coal surface, effectively isolating it from oxygen contact. Secondly, certain inhibitors generate CO_2 during pyrolysis, which not only dilutes oxygen concentration but also absorbs heat generated during the CSC process, thereby inhibiting or retarding coal oxidation [57,58].

Wei [59] successfully prepared a sodium salt microcapsule inhibitor by using the melt dispersion condensation method, using polyethylene glycol 20,000 as the outer wall of the microcapsule and coating the sodium salt inhibitor in the microcapsule. Microcapsule coating technology was employed to reduce the moisture absorption rate of the sodium salt inhibitor at room temperature. If the quality of the core wall ratio is optimized to 1:2, the moisture absorption rate significantly decreases by 67.3%. The initial decomposition temperatures for the sodium salt inhibitor and its corresponding microcapsule form were

measured as 753.1 °C and 384.5 °C, respectively, indicating reduced thermal stability for the microencapsulated sodium salt inhibitor. The inhibition effect of microencapsulated inhibitors at different concentrations is presented in Table 4. Li et al. [60] proposed that the deterioration degree of coal can affect the inhibition effect of halogenated salts. By comparing the characteristic temperature and activation energy of raw coal samples with those with retarding agent added, halogen salt, as a kind of efficient retarding agent, has shown a more significant inhibitory effect on inhibiting the spontaneous combustion of bituminous coal compared with its application on lignite and anthracite. In addition, some scholars [61,62] have studied the inhibition performance of inhibitors based on the solution temperature, action time, injection pressure, and coal temperature changes and found that the traditional salt inhibitors can hardly meet the safety requirements for the prevention of CSC and that the coal itself and the characteristics of the inhibitor, as well as the external environmental conditions, should be considered comprehensively, and the applicable fire prevention materials should be selected according to the target.

Table 4. Average inhibition rate of different concentrations of inhibitors [59].

Inhibitors	Average Inhibition Rate	Inhibitors	Average Inhibition Rate
5% sodium salt inhibitor	24.5	5% sodium salt microcapsule inhibitor	41.5
10% sodium salt inhibitor	36.7	10% sodium salt microcapsule inhibitor	52.8
15% sodium salt inhibitor	46.5	15% sodium salt microcapsule inhibitor	66.6
20% sodium salt inhibitor	57.7	20% sodium salt microcapsule inhibitor	60.8

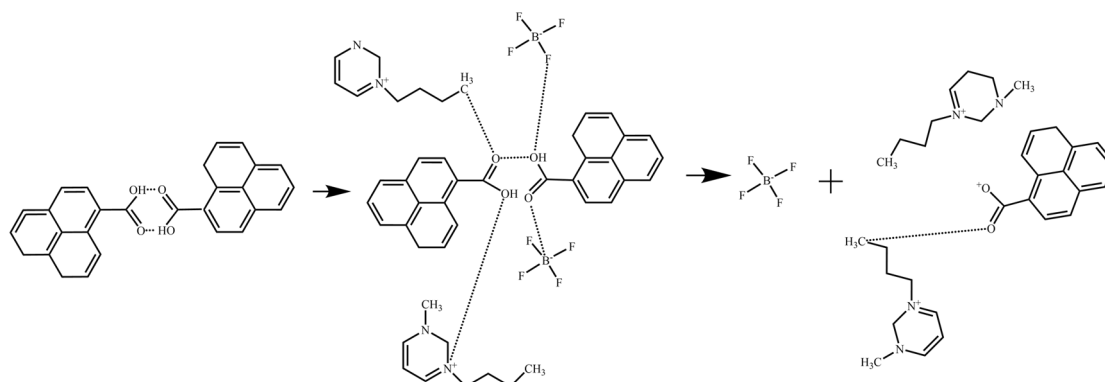
3.2. Chemical Inhibited Material

3.2.1. Chemical Inhibitors

The mechanism of action of chemical inhibitors is that they can penetrate into the molecular structure of coal, closely bind with the active functional groups inside coal, and restrict and passivate these active sites that are easy to trigger chain oxidation reactions by generating more stable ring or cross-linked structures. This process effectively hinders the formation and propagation of free radicals in coal molecules, which are usually the key media to accelerate the coal oxidation process. Through this interventional effect, chemical inhibitors can significantly inhibit the direct contact and reaction between coal and atmospheric oxygen, thus greatly reducing the speed of coal oxidation, effectively controlling and even preventing the occurrence of the CSC phenomenon. The ionic liquid inhibitor, classified as a chemical inhibitor, is primarily employed to prevent CSC through chemical inhibition. Imidazoles represent the most extensively utilized type of ionic liquid inhibitors in this regard. Comprising an imidazole ring group and an anion that replaces the branched hydrogen, these inhibitors exhibit exceptional solubility and inertness [63–66]. The blocking mechanisms of [BMIM][BF₄], [P4,4,4,2]Br, and TEMPO are shown in Figures 4–6. The inhibition effect of each chemical inhibitor is shown in Table 5. Ionic liquids, as a new type of green material to inhibit the spontaneous combustion of coal, can change the microstructure of the coal body, destroying or reducing the active functional groups to reduce the propensity of spontaneous combustion of coal. Additionally, ionic liquids can be easily separated from mixtures and recycled [67]. However, due to its high cost, complex production process, and limited thermal stability, widespread application of ionic liquid in mine fire prevention is currently hindered.

Table 5. Inhibition effect of chemical inhibitor.

Author	Materials	Effect
Li Yiheng [68]	Rare earth hydrotalcites	The -OH group in the inhibitor can react with the oxygen-containing functional groups such as -COO- in the coal, effectively preventing the active -COO- functional groups in the coal from continuing to participate in the oxidation process at low temperatures, reducing the possibility of coal oxidation.
Zhang Yutao [69]	$\text{Zn}_1\text{Mg}_2\text{Al}_1\text{-CO}_3\text{-LDHs}$	The starting exothermic temperature of the coal sample was delayed by 30–60 °C; when the addition amount reached 25%, the heat absorbed in the dehydration and desorption stage was three times that of the original coal sample, and the exothermic amount in the oxidation and combustion process was reduced by 5510 J, and the maximum heat-releasing power was also reduced from 32.96 to 23.5 mW/mg. The inhibition rate increased linearly with the addition of 1% $\text{Zn}_1\text{Mg}_2\text{Al}_1\text{-CO}_3\text{-LDHs}$, and the inhibition rate increased by 1.6%.
Deng et al. [70]	Ionic liquid	The ionic liquid with the greatest effect on independent hydrogen bonding, methylene, and carbonyl groups is [Bmim][BF ₄], and the ionic liquid with the greatest effect on conjugated hydrogen bonding, methyl, and carboxyl groups is [Bmim][I]. Based on the inhibitory effects, the four ionic liquids were ranked in the following order: [Bmim][I] < [Emim][BF ₄] < [Bmim][NO ₃] < [Bmim][BF ₄].
Li et al. [71]	2,2,6,6-Tetramethyl-1-piperidinoyloxy (TEMPO)	The exothermic peak of the raw coal sample appeared at 383 °C, the exothermic peak of the MgCl_2 -treated sample was delayed to 396 °C, and the exothermic peaks of CaCl_2 and TEMPO were delayed to 438 and 452 °C, respectively, and the inhibition of the reactive functional groups such as C-O, C-H, C=O, and O-H in the coal by TEMPO was more significant, which reduced the concentration of the reactive free radicals.
Lv et al. [72]	[BMIM][BF ₄]	The high content of ionic liquids can induce exothermic reactions, thus reducing their inhibitory effect; with the decrease in O ₂ concentration, the inhibitory effect of ionic liquids is enhanced, and the inhibitory effect of ionic liquids is significantly elevated when the O ₂ volume fraction is lower than 10 percent
Sandeep Kumar et al. [73]	NaCl, CaCO ₃ , KI, NaNO ₃ , KCl	According to the results of the flammability temperature (FT) test, crossing point temperature (CPT) test, and differential thermal analysis (DTA), KCl and CaCO ₃ are the most effective inhibitors. At 15% weight ratio of CaCO ₃ , CPT is 35 °C higher than that of raw coal, and at 20% weight ratio of KCl, CPT is 29 °C higher than that of raw coal. At a 20% weight ratio, FT of KCl and CaCO ₃ increased by 15 °C and 40 °C, and DTA increased by 32.01 °C and 31.96 °C compared with raw coal.

**Figure 4.** [BMIM][BF₄] inhibition mechanism [74].

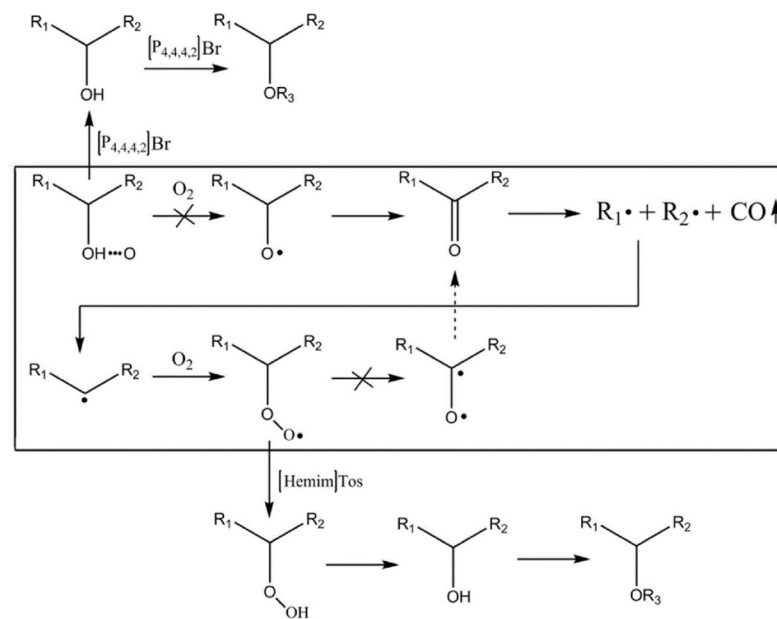


Figure 5. [P4,4,4,2]Br inhibition mechanism [75].

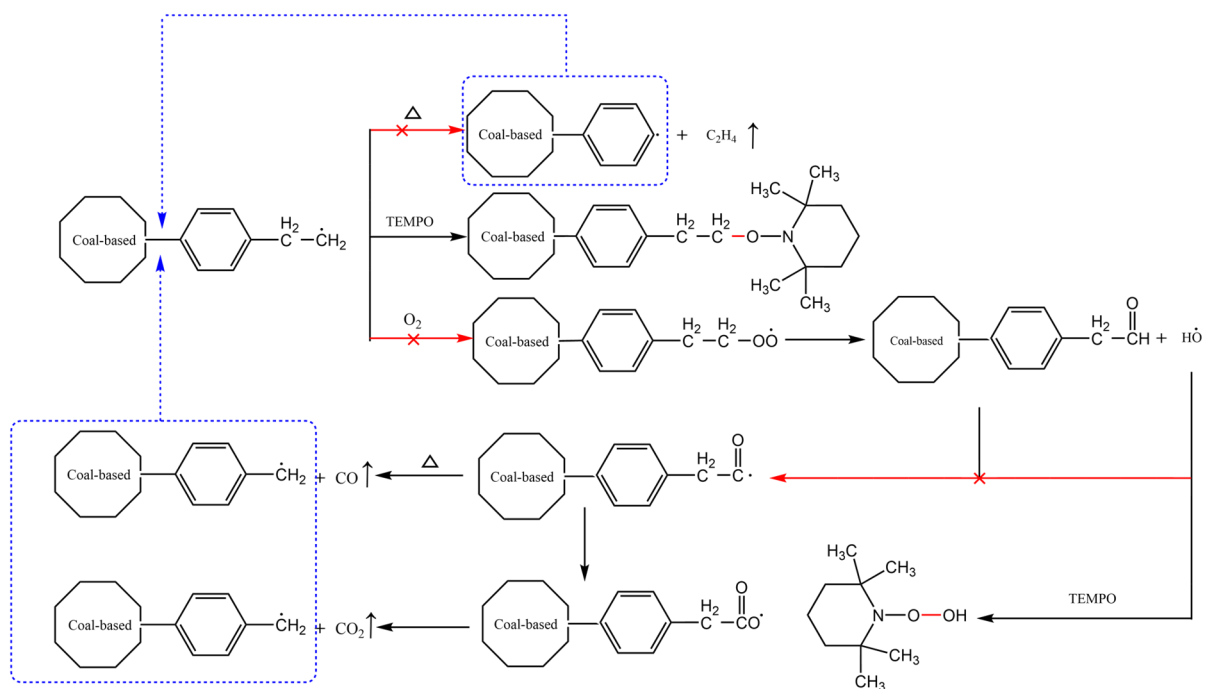


Figure 6. TEMPO inhibition mechanism [71].

3.2.2. Antioxidant Inhibitor

Antioxidants are mainly used to prevent the formation of groups in coal, consume the active chemical groups that easily trigger reactions, and weaken the ability of coal's own oxidation reaction to effectively prevent the occurrence of the CSC phenomenon [76,77]. The antioxidants that inhibit CSC can be classified into inorganic and organic categories. Organic antioxidants include citric acid, polyethylene glycol (PEG), L-ascorbic acid (VC), malic acid, etc., and inorganic antioxidants include urea, chloride, sulfate, and acetate.

Dou et al. [78] conducted a study on the impact of acidic substances. Following the addition of citric acid to three coal samples, the crossing point temperature exhibited an increase of 8–12 °C, accompanied by a corresponding delay in time of 30–40 min. Lu

et al. [79] adopted DL-malic acid as an inhibitor in the study of how to reduce the production of active free radicals during coal oxidation. The experimental results show that compared with untreated raw coal, the cross-point temperature of lignite increases by 15.13 °C, and this temperature of bituminous coal also increases by 13.19 °C. In addition, when the coal samples were treated with 5% and 10% concentration solution, the free radicals in lignite decreased significantly by 57.35%, and the free radicals in bituminous coal also decreased by 53.94%. With the different impregnation times of the inhibitor, the content of aliphatic functional groups in the coal samples can be reduced by up to 41.30%. This change is directly related to the enhanced low-temperature stability of the coal, which means that the treated coal has achieved a significant improvement in thermal stability, confirming that malic acid has a high protective effect on wet coal. In addition, malic acid has a better protective effect on lignite with low metamorphism, especially at low-concentration treatment, and the inhibition efficiency is particularly excellent, which provides a new perspective for optimizing the use of inhibitors according to different coal characteristics. Wang Feng [80] enzymatically treated grape seed meal and combined it with metal ions to form chelates, and the optimal chelation ratio was 1:3. The clearance rates of hydroxyl free radicals and peroxides were significantly increased by 54% and 46%, respectively, compared with those before chelation, 75% and 70%, respectively, compared with that of grape seed meal before enzymolization, and more than 60% and 25%, respectively, compared with a single conventional chemical inhibitor. After treating coal with a gel foam containing a composite inhibitor, oxygen consumption is reduced by 60% compared with raw coal, and the coal crossover temperature is significantly increased by 23 °C. This treatment greatly inhibits the production of CO and C₂H₄ during coal oxidation. Huang [81] combined PEG and proanthocyanidin (OPC) with environmentally friendly characteristics, as shown in Figure 7. The intersection temperature of OPC and PEG increased by 14.3 °C and 17.6 °C, respectively, and the stability of the ether bond increased by 18.41% and 42.71%, respectively. The free radical concentration decreased to 0.1178 Ng/1017 g⁻¹ and 0.1512 Ng/1017 g⁻¹, and the associated and free hydroxyl groups decreased by 24.37% and 59.72%, respectively, indicating that the two inhibitors had significant inhibitory effects. When the samples were treated with OPC and PEG, and the two were mixed at a ratio of 1:2, the crossing temperature increased significantly by 25 °C, showing that there was a highly efficient synergistic effect between OPC and PEG, which greatly improved the oxidation resistance. Qin et al. [82] conducted a thermal analysis experiment aimed at evaluating the efficacy of VC as a flame retardant. The experimental results reveal that VC shows a better inhibition effect than water when coal undergoes a low-temperature oxidation process, which significantly improves the antioxidant performance of coal at this stage. However, due to the decomposition of VC at about 200 degrees Celsius, this property limits its practical application potential in the field of preventing CSC. Figure 8 illustrates the inhibition mechanism of VC and tea polyphenols (TP), highlighting their synergistic effect surpassing the individual inhibitory effects. Li et al. [83] selected six different antioxidants: VC, butylhydroxytoluene (BHT), triphenyl phosphite (TPPI), TEMPO, phytic acid (PA), and ethylenediamine tetraacetic acid (EDTA), to compare the inhibition properties of these inhibitors. The results show that TEMPO exhibits the strongest flame-retardant effect with a high retarding efficiency of 73.08%. In order of inhibition efficiency from high to low, the order is TEMPO, BHT, EDTA, TPPI, and PA.

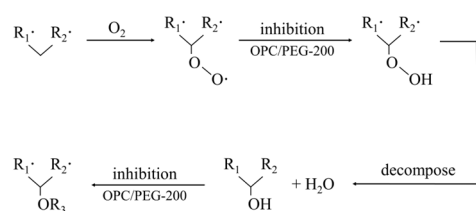


Figure 7. Complex inhibition mechanism of polyethylene glycol and procyanidin [81].

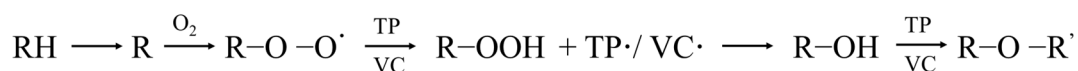


Figure 8. Synergistic inhibition of CSC by VC and TP [84].

Taraba et al. [85] studied the inhibition rate of 14 inorganic antioxidants, such as chloride, urea, and phosphate. The results revealed that urea exhibited a high inhibition rate against CSC, while a 10% uric acid solution demonstrated a low-temperature oxygen inhibition rate of 70%. The effects of inorganic antioxidants at different temperatures vary. Slovak and Taraba [86] mentioned in their study that $CaCl_2$ can effectively slow down the oxidation activity of coal under the temperature of 300 °C. When urea is below 200 °C, it is very effective in inhibiting coal oxidation, but when the ambient temperature exceeds 200 °C, urea instead begins to promote the oxidation process of coal.

3.2.3. Microbial Inhibition

Microbiological technology is gradually showing its application value and spreading in the field of CSC. Li et al. [87,88] conducted a bacterial–coal matching degradation experiment on Zhaotong lignite from Yunnan Province, which was subjected to oxidation by five strains of actinomycetes and nitric acid. Through screening, they identified *Streptomyces chlorophylla* as the dominant degradation bacterium. The degradation of Shengli lignite in Inner Mongolia was performed using *Pingeria xanthosporium*. Kang and Mishra [89,90] found that microorganisms can consume free radicals in coal and decompose sulfides and macromolecular organic substances in coal. Microorganisms consume oxygen through their growth metabolism and proliferation activities, and this natural process helps to slow down the coal oxidation rate and effectively curb the occurrence of the CSC phenomenon.

3.3. Physicochemical Synergistic Inhibition Material

The existing single physical or chemical fire prevention materials have certain shortcomings in solving coal fire disaster problems due to their own shortcomings. At present, scholars at home and abroad have carried out research on new anti-fire materials, and their inhibition mechanism has gradually shifted from single inhibition to compound and collaborative inhibition, combining physical and chemical ways to jointly inhibit the CSC process so as to realize the control of the whole process of CSC.

3.3.1. Composite Foam

Zhang et al. [91] addressed the limitations of limited temporal efficacy and suboptimal efficiency in the early release of retarding agents for preventing CSC by developing a temperature-controlled self-reactive retarding foam using hollow balls as solution carriers. The foam can be generated and released at temperatures ranging from 59 °C to 61 °C, covered by the inhibitor solution, which is approximately 12.9 to 13.9 times smaller than the total area affected. After the foam release, the oxidation heating rate of coal has been significantly controlled, and the inhibition effect reaches 78.7% to 91.6%, which delays the oxidation process of coal by 22 to 35 °C. Through combined foam suppression and inerting effects, the inhibition efficiency against coal oxidation reaches 88.51–97.06% at a temperature of 160 °C. Lu et al. [92] developed a high-performance antioxidant gel material by adding OPC into a gel containing sodium silicate, bentonite, and coagulant. In particular, under the formulation of coagulant and sodium silicate concentrations of 2.5% and 5%, respectively, the prepared gel showed excellent flame-retardant properties. In addition, when the mass ratio of surfactant SDS to SAS was optimized to 1:1, the foaming capacity was dramatically increased to 482 mL, and the stability of the composite foaming agent was significantly enhanced. The inhibition effect of this method on CO was also very significant, and the inhibition efficiency reached 68.7%. In the dimensional experiment, the rapid drop from 727 °C to the ambient temperature was achieved within 1850 s. By utilizing foam as a carrier for chemical retarder transportation, the composite foam takes advantage of its large flow capacity, wide diffusion range, and excellent stacking properties to effectively

cover the area prone to CSC and ensure full contact between the chemical retarder and coal body, thereby maximizing their synergistic effect.

3.3.2. Composite Gel

Wang [93] selected a highly absorbent resin polymer (SP) in combination with ascorbic acid (A) to create a cage-type composite inhibitor material with dual physical and chemical effects. Experimental data revealed that the inhibition system demonstrated the best inhibition efficacy when the mass ratio of SP to A reached an optimal 1:5 and the mass percentage of the composite inhibitor in the whole was 10%. Moreover, this compound inhibitor exhibited remarkable capability in reducing the presence of methyl, methylene, aromatic hydrocarbons, and hydroxyl groups, thereby inerting its oxidation activity. Xue et al. [94] prepared a novel composite corrosion inhibitor by grafting oligo-PC radicals onto a sodium acrylate and acrylic acid copolymer, followed by combining it with polyphosphoric acid (APP). The concentration of free radicals decreased by 6.00%, the heat release of coal decreased significantly by 62.83%, and the activation energy increased by 13.93%. These data strongly prove the excellent results of the gel in enhancing the chemical stability of coal and effectively delaying the corrosion process. Huang et al. [95] prepared a modified antioxidant-based hydrogel with sodium acrylate, tert-butyl hydroquinone (TBHQ), and montmorillonite, and TBHQ significantly reduced $-CH_3$, $-CH_2-$, $-OH$, and $-COOH$ while increasing the number of ether bonds. The thermal mass loss rate decreased by 0.84%/min and the dry cracking temperature increased by 52.8 °C. The results show that the thermal stability of the coal sample is significantly improved, and the oxidation loss is reduced.

3.3.3. Compound Inhibitor

The composite inhibitor can play a synergistic role through the combination of various inhibitor components and significantly improve the inhibition effect. Table 6 shows the inhibition effect of various compound chemical retardants on CSC.

Table 6. Inhibition effect of composite inhibitors.

Authors	Composite Inhibitors	Effect
Wang et al. [96]	MgCl ₂ , CaCl ₂ , N, N-dibenzylhydroxylamine (DBHA), BHT	The release of CO decreased by 88.7% at 128 °C. The inhibition rate reached 82.5% at 100 °C. Reducing hydroxyl, methyl, and methylene groups and carbonyl-containing active components in coal. The relative content of aromatic ketones decreased significantly. The oxygen adsorption process of the coal body is shortened, and the adsorption capacity is reduced. The activation energy was increased by 53.2% during oxygen inhalation
Jiao [97]	IOxidant microcapsule compound inhibitor, tea polyphenol, polyethylene glycol 20,000, Pentaerythrityl tetrastearate	When the mass ratio of polyethylene glycol 20,000 and pentaerythrityl stearate is 1:1, 1:2, and 1:3, the microcapsule wall material obtained by the combination of polyethylene glycol 20,000 and pentaerythrityl stearate has better hydrophobicity. When the wall-material ratio was 1:1 and the core-wall ratio was 1:1, the coating rate of microcapsule material was the highest. When the wall-material ratio was 1:1 and the core-wall ratio was 1:1, the inhibition rate reached 76.8%, which was 11.4% higher than that of single tea polyphenol. The cross point temperature was increased by 43 °C compared with the raw coal
Huo [98]	MgCl ₂ , BHT, TPPI, and polyethylene glycol 400	The optimal quality fractions were 10.26%, 3.15%, 2.09%, and 0.58%, respectively. The optimal quality fraction of P&C was 12% of coal. The cross point temperature of the coal sample was increased to 155.08 °C, 22.48 °C higher than that of the raw coal sample
Xue [99]	Melatonin, polyacrylate-alginate sodium	When 6 wt% melatonin was added to the coal, the inhibition effect was the best. When the optimal mass ratio of melatonin and polyacrylic acid-sodium alginate was 1:4, it could effectively inhibit the generation of CO, increase the crossing point temperature of coal oxidation, reduce the oxygen consumption rate at 70 °C, and significantly reduce the risk of CSC

Table 6. Cont.

Authors	Composite Inhibitors	Effect
Huang et al. [100]	Tea polyphenols, halloysite nanotubes	The maximum heat absorption was 67.15 J/mg, the shortest heat release interval was 120.22 °C to 572.22 °C, and the minimum total heat release was 2536.73 J/mg. Lower the hydroxyl content and reduce the number of aliphatic functional groups converted to carbonyl and carboxyl groups
Xi et al. [101]	Compound antioxidant containing superoxide dismutase (SOD)	The results showed that the energy barrier of SOD for eliminating peroxy radicals was 31.3 kJ/mol, and SOD could automatically eliminate peroxy radicals at room temperature.
Zhang et al. [102]	Rare earth hydrotalcite, halogen salt	The activity of acid functional groups such as -COOH in coal is weakened due to weak hydrogen bonds between -OH and acid functional groups such as -COOH in rare-earth hydrotalcite laminates. Mg^{2+} is complexed with -COO- in coal molecules to form -COOMg-, resulting in reduced C=O activity in -COO-. Compared with the raw coal, the peak temperature of the coal is shifted back by 50–60 °C, the T_1 temperature is shifted back by 90–100 °C, and the total heat release is reduced by 19–27 kJ·g ⁻¹ .
Zhang [103]	Polyethylene glycol 6000, LDHs	Increase the inhibition time. The best effect was obtained when the core wall ratio was 1:5. The critical temperature and maximum weight loss temperature were increased by 8.8 °C and 33.6 °C, respectively. The apparent activation energy of water evaporation and gas desorption stage was increased by 13.42 kJ/mol. The thermal decomposition stage and combustion stage increased by 88.64 kJ/mol
Pan et al. [104]	Sodium dodecyl sulfate, sodium laurylsulfonate, flame-retardant compound (CaCl ₂ , MgCl ₂ , NaHCO ₃ , (NH ₄) ₂ HPO ₄ , CO(NH ₂) ₂), XG	The higher the concentration of compound inhibitor, the better the effect; the 20% inhibitor solution has the most significant effect. The inhibition rate is 85.92%, and the average inhibition rate is 15 times that of water. The oxidation inhibition effect of coal samples after water treatment can be observed only at 140 °C, and the oxidation rate increases with the increase in temperature. Chloride ions and phosphate elements break down into ions and small molecules, forming stable substances with free radicals, reducing the number of free radicals, and preventing spontaneous combustion.

4. Conclusions

Based on the in-depth analysis of CSC fire-prevention materials, a series of quantitative and network analyses is carried out by using visualization software CiteSpace, revealing the frontier trend, cooperation network, and key nodes of mine fire prevention materials research. The fire-fighting mechanism and inhibition effect of existing fire-fighting materials are summarized and sorted out, and the conclusions are as follows:

- (1) The keyword co-occurrence map of CSC fire-fighting materials was obtained through CiteSpace visual analysis. Through the Atlas network, it is concluded that the development of CSC fire-fighting materials has experienced several stages, such as grouting, inert gas, colloid, retarder, foam, and gel foam. The characterization methods of CSC prevention and control by each inhibitory material were analyzed. Through the keyword network, it is concluded that the current research frontier focuses on the verification of the inhibition mechanism of different inhibition materials by molecular simulation.
- (2) The existing CSC fire-fighting materials can be divided into physical inhibition, chemical inhibition, and physicochemical coordination inhibition according to the form of action. These materials reduce the oxidation rate of coal and inhibit CSC by diluting oxygen, isolating oxygen, and hindering chain reaction.
- (3) In terms of application, composite inhibitors, environmentally friendly foams, gels, gel foams, etc., not only improve flame retardant efficiency but also show great potential in environmental protection and durability. In addition, the synergistic mechanism of compound antioxidants enhances the flame-retardant effect, reveals the microscopic mechanism of chemical inhibitors, and provides theoretical guidance for the design of high-performance inhibitors. In the future, the use of microbial inhibition of CSC will show environmental friendliness and long-term action, which is a frontier direction worthy of attention, and its management strategy and potential application deserve further exploration.

5. Existing Problems and Development Trends

Well-known scholars at home and abroad have conducted extensive research on various kinds of suppression materials to prevent CSC disasters. Currently, a relatively comprehensive system has been established. However, the situation regarding the prevention and control of CSC disasters within our country remains severe, requiring further enhancement of the research system for preventing and controlling mine fires.

- (1) Affected by factors such as the increasing depth of mining and the complex and dynamic mining environment, CSC prevention and control pose significant challenges. The existing fire prevention materials still fail to fully meet the requirements for effective fire prevention and control. Therefore, developing novel fire prevention materials with prolonged resistance life, enhanced fire prevention efficiency, and simplified manufacturing processes is a pressing issue that needs to be addressed.
- (2) The retarding effect of the same coal varies when subjected to the same fire-proof material. Therefore, it is imperative to analyze the alterations in key functional groups, free radicals, reaction pathways, and other factors during the retarding process while comprehensively elucidating the mechanism underlying CSC.
- (3) Some materials may decompose into toxic and harmful substances when exposed to heat, which can potentially exert significant ramifications on human health and the ecological environment. Additionally, fire-fighting materials may adhere to coal surfaces and form complex solid impurities, potentially leading to soil and water pollution as well as increased secondary treatment costs. Further research is needed to investigate these potential effects.
- (4) Through continuous exploration and innovation, the use of refractory materials with strong popularity and excellent fire protection effect can implement accurate and efficient flame-retardant strategies for different types of coal, greatly enhancing the overall effectiveness of fire prevention measures.

As a valuable fossil fuel, coal is expected to undergo advancements in cleanliness, efficiency, and refinement in the future. Additionally, re-mining or reuse of coal reserves within closed mining areas will emerge as a prominent development trend. Therefore, the prevention and control of re-mining fires in closed mining areas should also be considered in planning. In addition, firefighting materials in other fields need to be actively explored and evaluated for their usefulness and effectiveness in CSC prevention and control applications. Given that coal serves as the predominant energy source in our nation, ensuring effective prevention and management of CSC holds significant long-term implications. Consequently, enhancing fire prevention systems within coal mines becomes imperative.

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