Means of protecting materials from spontaneous coal combustion: current developments, mechanisms, classifications, and prospects

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Abstract: Spontaneous coal combustion poses serious threats to the world and especially to China, the world’s largest coal producer and user. Apart from spurring monetary losses in national exchequers and resource losses for countries, spontaneous coal combustion results in a loss of life, which cannot be measured based on costs. Innumerable researchers and scholars in China and abroad have paid considerable attention to studying means of protecting materials from spontaneous coal combustion. A variety of materials that prevent spontaneous coal combustion have been developed. The goal of this paper is reveal the academic literature on spontaneous coal combustion. In this comprehensive review, mechanisms of spontaneous coal combustion, research findings and advantages and shortcomings of materials that prevent spontaneous coal combustion are explored. In view of different coal mining conditions and material properties, materials that prevent spontaneous coal combustion are classified in accordance with material phases. The development of various coal fire extinguishing materials is discussed. Our comprehensive review can thus be used to prevent and control spontaneous coal combustion and to curtail the currently frequent disasters resulting from spontaneous coal combustion.

Keywords: spontaneous coal combustion; damage; materials; mechanism; research status; criteria.


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1 Introduction

Spontaneous coal combustion continues to pose significant threats to the mining and storage industries (Beamish et al., 2013) and threatens the safety of coal mining and transportation. Figure 1 illustrates coal fire scenarios and their hazards surrounding a working face. According to statistics, spontaneous coal combustion hazard levels for Chinese state-owned coal mines exceed 51.3% and more than 90% of cases of spontaneous coal combustion result in coal fire disasters. Gas and coal dust explosion accidents induced by spontaneous coal combustion occur frequently, posing serious threats to the security of residents and properties, impeding the sustainable development of the coal mining industry and affecting social stability. More than 42 billion tons of high quality coal has been lost as a result of spontaneous coal combustion. These losses increase at a rate of 20–30 million tons each year. Idle resources also account for over 2 billion tons each year and direct financial losses amount to more than tens of billions of Yuan. As a result of spontaneous coal combustion, large volumes of greenhouse and toxic gas are emitted, which can result in both health and environmental hazards. Indirect losses resulting from spontaneous coal combustion (e.g., loss of land resources, air pollution, destruction of natural ecological environments, restricted social activities, etc.) are difficult to estimate. On November 18th, 2001, long-term coal retention in the –624 level coal bunker of the Qiwushengjian Coal Mine in Shandong Province (China) caused gas explosion, resulting in four workers killed and one seriously injured. On March 5, 2008, in Jinan Coal Mine in Jilin Province (China), a partial roof collapse occurred after spontaneous combustion, resulting in 17 asphyxial deaths due to being blocked in the roadway. On August 18, 2007, in the 695 workface of Pinghu Mine of Jiangxi Province (China), the spontaneous combustion caused gas explosion, causing two draegermen...
injured and the mine closed (Xu, 2008). Since 2000, the self-ignition tendency of the coal seam of Pingmei No. 8 Mine in Pingdingshan city of Henan Province (China) has become more and more serious, and 11 severe spontaneous combustion and fire accidents have occurred (Zhang, 2009). On October 15, 2011, coal fire in the workface of the Laoyingtang Coal Mine in Chongqing city (China) killed four people. On March 29, 2013, in the Babao Coal Company of Jilin Province (China), air leakage in the gob caused coal spontaneous combustion and gas explosion, leading to 36 people killed, 12 injured and direct economic loss of 47.089 million Yuan. On June 3, 2014, a gas explosion caused by the spontaneous combustion of coal in the gob area occurred in the Yanshitai Mine of Chongqing city (China), resulting in 22 people killed and one person injured. The spontaneous combustion of the Shirenpo coal seam in Lvhe Town of Yunnan Province (China) that began in 1958 has lasted more than half a century, which wasted huge amount of coal resource, released huge amounts of toxic and harmful gas, caused land subsidence and huge economic losses, and affects the life and property safety of the local people (Liu and Zhang, 2017). Mine fire prevention and control are thus arduous tasks in terms of promoting safe coal production. In recent years, numerous materials designed to prevent spontaneous coal combustion have been widely applied worldwide with considerable success. However, due to different mining conditions and the various characteristics of fire retardants, fire retardants are currently lacking.

Spontaneous coal combustion occurs most frequently in exposed and underground coal seams. Low-temperature oxidation reactions involving coal have been studied for a long time, and especially in relation to spontaneous coal combustion phenomena. Spontaneous coal combustion involves a redox reaction between coal and air and considerable heat is produced as a result. When heat released through oxidation reactions cannot dissipate efficiently, heat accumulates and coal temperatures increase. When the critical temperature (60–80ºC) is reached, coal temperatures increase rapidly and coal begins to smoulder and burn. Understanding coal oxidation rates at low temperatures is thus critical for predicting spontaneous combustion episodes. It is vital to prevent such phenomena from occurring. Several factors shape spontaneous coal combustion occurrence (i.e., coal ranks, coal oxygen content, air flow rates, particle sizes, coal moisture content, air humidity, etc.). Generally speaking, low rank coal is much more susceptible to spontaneous combustion. Heat released through oxidation reactions can be removed rapidly via air flows as a result of stronger convective heat transport mechanisms; moisture in the coal in turn evaporates, extracting heat from the coal, and when coal includes more oxygen functional groups, spontaneous combustion occurs more readily. Air humidity and coal water vapour absorption and desorption heat levels are very strong controlling factors of coal spontaneous heating. Rates of heat release in such circumstances are dependent on the partial pressure of water vapour in the air and in coal. Generally speaking, the rate of oxidation is dependent on the effective surface area per unit of coal particle volume. This rate of oxidation increases with decreasing particle diameter until a critical value is reached. Therefore, oxidation-reduction between coal and oxygen gas in the air occurs and heat is generated. This accumulates when heat released by oxidation-reduction cannot be effectively lost. This causes coal temperatures to rise, resulting in spontaneous coal combustion.
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Figure 1 Coal fires and their hazards surrounding a working face, (a) cracks produced by fires occurring on the ground (b) roofs falling off working faces (Fu-bao et al., 2015) (c) burning coal (d) smoke generated through spontaneous coal combustion (Yang et al., 2014) (see online version for colours)

Spontaneous coal combustion occurs in numerous countries such as China, New Zealand, South Africa, Colombia (Quintero et al., 2009), Australia, the USA, etc. Where there is a coalfield, spontaneous coal combustion occurs. China is the largest coal producer in the world. Incalculable hazards have resulted from spontaneous coal combustion. Numerous experts, scholars and researchers in China and overseas have dedicated considerable time, energy, and money to the study of spontaneous coal combustion in China. Several methods and materials for preventing spontaneous coal combustion have also been explored and developed. This paper comprehensively reviews mechanisms of spontaneous coal combustion, research findings and progress made in terms of fireproofing coal around the world and with a particular focus on China. It is worth noting that all fire retardants are categorised as soft materials, gel and slurry materials or solid materials on the basis of new criteria. In addition, this paper discusses limitations and the development of fire retardants.
To the best of our knowledge, this paper is the first to review materials that prevent spontaneous coal combustion. We deliver:

1. A comprehensive overview of recent spontaneous coal combustion research including studies on mechanisms, conditions, development tendencies and fireproofing and fire retardant materials.

2. A critical discussion of the strengths and weakness of fireproofing and fire retardant materials that could be used to prevent coal fires and to promote safe coal mining.

2 Mechanisms of spontaneous coal combustion

The most significant obstacle to understanding and studying mechanisms of spontaneous coal combustion pertains to complex intrinsic and extrinsic factors that affect spontaneous coal combustion. Many factors have been studied by various researchers, including temperatures, particle sizes, surface areas, coal-pore structures, moisture content levels, coal ranks and ambient air compositions. Some of the main influencing factors involved are summarised (Table 1).

Table 1 Main factors influencing spontaneous coal combustion

<table>
<thead>
<tr>
<th>Intrinsic factors (nature of coal)</th>
<th>Extrinsic factors (atmospheric, geological and mining conditions)</th>
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</thead>
<tbody>
<tr>
<td>Pyrites</td>
<td>Temperature</td>
</tr>
<tr>
<td>Moisture</td>
<td>Moisture</td>
</tr>
<tr>
<td>Particle sizes and surface areas</td>
<td>Barometric pressure</td>
</tr>
<tr>
<td>Rank and petrographic constituents</td>
<td>Oxygen concentrations</td>
</tr>
<tr>
<td>Chemical constituents</td>
<td>Bacteria</td>
</tr>
<tr>
<td>Mineral matter</td>
<td>Coal seams and surrounding strata</td>
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<td></td>
<td>Working methods</td>
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<td>Ventilation systems and air flow rates</td>
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<td>Timbering</td>
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<td></td>
<td>Roadways</td>
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</table>

Spontaneous coal combustion is an extremely complex physio-chemical process with numerous effects. Researchers in China and abroad have made great progress in putting forward several theories on spontaneous coal combustion over the past 200 years. Owing to its complexity, mechanisms of spontaneous coal combustion remain only partially understood. However, one theory on complex reactions between coal and oxygen is widely acknowledged. Figure 2 presents three series of experiments involving the preparation of coal samples, desorption under nitrogen from unoxidised coal (series 1 in Figure 2), drying under nitrogen at 65°C, oxidation at various temperatures (series 2 in Figure 2), and desorption after oxidation under nitrogen (series 3 in Figure 2). Low-temperature oxygen in coal and a temperature threshold for the thermal decomposition of coal have been confirmed through three series of experiments (Figure 2), and two parallel reaction sequences have also been supported. Several studies
suggest that low-temperature coal oxidation constitutes a primary source of heat that leads to spontaneous coal combustion.

**Figure 2** Schematic diagram illustrating the three series of experiments performed

![Diagram](image)

The likelihood of spontaneous coal combustion occurring is high when heat accumulates and when temperatures reach 350 K or higher. The majority of heat is generated through exothermic low-temperature oxidation reactions while mass and heat transport play major roles in determining the magnitude of temperature increases in a given situation. The oxidation of coal at low temperatures is a complex phenomenon involving the transport of O₂ through coal pores, gas adsorption, the formation of gaseous and solid products and changes in heat levels. As is the case for most oxidation reactions, coal oxidation at low temperatures involves exothermic reactions (Figure 3 and Figure 4).

**Figure 3** Time-temperature curve

![Graph](image)

*Source: Quintero et al. (2009)*
It is clear that low temperature coal oxidation is mainly dependent on the temperature and rate of oxygen consumption (Krishnaswamy, 1996). Effects of particle size on oxidation rates of coal have also been studied by numerous scholars (Kaji et al., 1985). Figure 4(a) illustrates the influence of particle sizes on $T_{acrit}$ where $T_{acrit}$ is the critical ambient temperature, and Figure 4(a) shows that the $T_{acrit}$ of all the four coals increases as particle sizes increase, providing evidence for the above conclusion on effects of particle sizes and of intrinsic properties of coal on spontaneous combustion. Rates of $T_{acrit}$ increase for the four coals differ and impacts of particle sizes on Prima coal are very significant, though limited effects result for South Banko coal and Tanjung Enim coal. Thus, the larger the particle size, the steeper the curve and the longer the ignition temperature period becomes. Figure 4(b) and Figure 4(c) show $QA$ and $E_a$ values for different particle sizes where $QA$ is the oxidation heat level, $J \cdot kg^{-1}$, and $E_a$ is activation, $J \cdot mol^{-1}$. Figure 4(b) and Figure 4(c) show that $QA$ and $E_a$ trends for the same coal sample are roughly the same (there may be a relationship between $QA$ and $E_a$ which is explored elsewhere). Many experimental findings demonstrate that rates of oxygen consumption by coal at low temperatures are mainly dependent on intrinsic properties of coal itself and on the oxygen absorption capacity of coal pores (Carras and Young, 1994). The authors have applied crossing point methods (Chen and Chong, 1995) to evaluate the kinetic parameters of coal using data derived from oven heating experiments.

The capacity for a coal sample to take up $O_2$ is typically determined from the rate of oxygen consumption. Figure 5(a) shows that temperatures increase during coal oxidation and that oxygen concentrations decrease. At the same time, concentrations of carbon monoxide, a product of coal oxidation, rises as is shown in Figure 5(b). The rate of oxygen consumption can be expressed in terms of the external surface area of coal particles or particle diameters as confirmed by Figure 6. Finally, the relationship between rates of oxygen consumption and coal particle size can be written as (Yang et al., 2014):

$$ R_{O_2} = \frac{m_1}{d}(1 - e^{-m_2d}) $$  \hspace{1cm} (1) 

where $d$ is the mean particle diameter and $m_1$ and $m_2$ are empirical constants. Equation (1) predicts an intuitive trend where with diminishing particle diameters, the rate of oxygen consumption approaches a constant value. Rates of oxygen consumption with oxidation time have also been studied. The dependence of the rate of oxygen consumption on time takes the following form:

$$ R_{O_2} = b_1m_3t^{b_1-1} $$  \hspace{1cm} (2) 

where $t$ is time and $b_1$ and $m_3$ are experimentally determined constants with $b_1$ ranging from 0.6 to 0.8 and with $m_3$ ranging from 0.04 to 0.4.

Numerous studies show that coal oxidation occurs through a reaction sequence involving multiple steps: the chemisorption of oxygen on pore surfaces, the formation of unstable carbon-oxygen complexes, the decomposition of unstable solid oxygenated intermediates to gaseous products and stable solid complexes, the degradation of stable complexes and the generation of new active sites for oxidation following the decomposition of these complexes (Wang et al., 2003). It is widely acknowledged that the first phase involves the chemical adsorption of oxygen onto coal surfaces. Chemical
reaction and adsorption processes occurring during coal oxidation are not simple. With the participation of oxygen, some uncontrollable reactions produce carbon oxides. As is shown in Figure 7, at least two parallel reactions are responsible for the production of carbon oxides. The reaction mechanisms of each step are described below (Palmer et al., 1990; Wang et al., 2002a).

Figure 4 (a) Effects of particle sizes on critical ambient temperatures (b) Reactivity levels (c) Activation energy levels for prima, Pinang, South Bangko and Tanjung Enim coals
Figure 5  Concentrations of oxygen and carbon monoxide in self-heating coal in an adiabatic heating oven


1 Sorption sequence:
   a  Coal + O₂ → coal-oxygen intermediates → CO₂ + unreactive species (25–95°C).
   b  Coal + O₂ → CO₂ + carboxyl + carbonyl + unreactive species (60–90°C)
      Carboxyl species → CO₂
      Carbonyl species → CO.

2 Direction burn-off reactions:
   a  Coal + O₂ → CO₂, CO (25–95°C).
   b  Coal + O₂ → CO₂, CO + other species (H₂O, etc.) (60–90°C).
However, there is no direct evidence that supports this hypothesis, and a large number of experimental techniques have been employed to study such problems. An overview of experimental techniques used to study low-temperature oxidation and spontaneous coal combustion is shown in Table 2.

**Figure 6** A typical trend illustrating the effect of particle sizes on rates of oxygen consumption

![Graph showing the effect of particle sizes on rates of oxygen consumption]

*Source: Akgün and Arisoy (1994) and Wang et al. (2002b)*

**Figure 7** Product of oxidation and desorption experiments conducted at 343 K; particle sizes of between 0-0.5 mm; oxidation experiments performed with $O_2 = 20.9$ vol. %

![Graph showing the product of oxidation and desorption experiments]

*Source: Akgün and Arisoy (1994) and Wang et al. (2002b)*
Table 2  Overview of experimental techniques used to study low-temperature oxidation and spontaneous coal combustion

<table>
<thead>
<tr>
<th>Experimental method</th>
<th>Applicable temperature range</th>
<th>Parameters measured</th>
<th>Major futures</th>
<th>Typical work reported in the literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermogravimetric analysis (TGA)</td>
<td>&gt; 100ºC (insensitive while operating at lower temperatures)</td>
<td>Mass changes (TG and DTG data)</td>
<td>Mass variation reflecting the adsorption of O2 and the production of the oxidation products in both the gas and solid phases.</td>
<td>Marinov (1977a, 1977b)</td>
</tr>
<tr>
<td>Adiabatic Calorimeters, and differential thermal analysis (DTA)</td>
<td>No restrictions</td>
<td>Temperature rise in coal samples</td>
<td>Heat released during the oxidation process, accounting for the overall effects of physical and chemical processes. Available for calculating the apparent kinetic data for O2 consumption by simplifying the reaction mechanism of coal oxidation.</td>
<td>Chen and Stott (1993)</td>
</tr>
<tr>
<td>Other heat-based Measurements, i.e., basket heating, crossing-point temperature and Chen’s method</td>
<td>&gt; 100ºC (impossible to observe the initial stage of self-heating process)</td>
<td>Critical temperature of self-heating or auto-ignition of coal</td>
<td>Evaluation of self-heating and spontaneous combustion of coal for industrial purposes</td>
<td>Bowes and Cameron (1971); Graham (1914)</td>
</tr>
<tr>
<td>Isothermal flow reactor and ‘oxygen adsorption’</td>
<td>No restrictions</td>
<td>Consumptions of O2 and formation of gaseous products</td>
<td>Time-dependent rate of consumption of O2 and the rate of formation of gaseous oxygen products. Appropriate for examining the reaction steps and intrinsic kinetic data of the reactions</td>
<td>Graham (1914); Krishnaswamy (1996)</td>
</tr>
<tr>
<td>Titration, IR FTIR, XPS, SIMS, and EPR/ESP</td>
<td>No restrictions</td>
<td>Concentration of solid oxygenated species formed at coal surface</td>
<td>Identification of solid oxygenated species formed at coal surface reliable information for testing the proposed elementary mechanism and quantifying the rate parameters</td>
<td>Dack et al. (1984); Zhou et al. (2006)</td>
</tr>
</tbody>
</table>

During the incubation of spontaneous coal combustion, low temperature oxidation occurs on coal surfaces, which in turn decreases the ignition point. Heat is released as a result of the oxygen physical adsorption of coal, and more heat is released as a result of chemical adsorption and due to chemical reactions occurring between coal and oxygen. Heat accumulates when more heat is released than is lost, initiating the self-heating stage. Spontaneous coal combustion occurs at the end.
It is important to understand the reaction kinetics of coal oxidation processes that occur at low temperatures (Wang et al., 2003). The reaction rate of coal oxidation in terms of oxygen consumption is normally expressed by the conventional Arrhenius equation as follows:

\[
\frac{d\rho_{\text{ox}}}{dt} = \rho_{\text{ox}}^0 A \exp \left( \frac{-E}{RT} \right)
\]

where \( \rho_{\text{ox}} \) is the oxygen density of the gas phase, and the linear dependence of reaction rates on oxygen density is experimentally valid. According to equation (3), the rate of coal oxidation is regarded as a function of coal temperature \( T \). Numerous studies show that coal oxidation, a complex phenomenon, is not sufficiently expressed by a simple Arrhenius equation. Low-temperature coal oxidation is considered to occur predominantly along internal coal pore surfaces. Chemisorption is the only significant process that occurs during initial phases of coal oxidation. Stable surface complexes form and cover active sites on the surface. The number of available reactive sites in turn decreases to a limited value. Consequently, the rate of oxidation product formation decreases with the extent of oxidation. As a result, the reaction rate of fresh coal should be expressed as a function of time and temperature (Akgün and Arisoy, 1994; Wang et al., 2002b).

On the other hand, in recent decades numerous scholars have studied the chemical structures of coal and have put forward several coal molecular structures and models. According to its chemical structures, a variety of primary and secondary active groups are found in coal. Oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, methoxyl groups and non-active oxygen affect coal properties significantly, causing more heat to be released through oxidation reactions between coal and oxygen and rendering coal more combustible.

Methylene groups significantly contribute to spontaneous coal combustion, and thus methylene structures must be disposed of first to suppress spontaneous coal combustion effectively. The degree range of gas coal is the largest, showing that gas spontaneous coal combustion is largely affected by active groups. These results should prove helpful for identifying functional groups that deeply shape low temperature coal oxidation.

3 Classification and using standard materials that prevent spontaneous coal combustion

3.1 Development of materials that prevent spontaneous coal combustion

Preventing and controlling coal fires is an arduous task in terms of safe coal production owing to the enormous financial losses and casualties that result from spontaneous coal combustion incidents. Several scholars have studied fire-fighting technologies related to the coal industry over the past 200 years. Such research has mainly focused on traditional technologies that prevent and control coal fires. The purpose of prevention work is to prevent the occurrence of coal fires associated with underground and surface coal mining, and this has become a major issue. In recent years, a series of extinguishing materials that prevent spontaneous coal combustion have been widely used throughout the world, including inert gases such as ammonia and carbon dioxide emitted into closed spaces that
dilute concentrations of oxygen (inert gas extinguishing technologies). Yellow mud, hydraulic hitch mortars, coal ash and similar materials are also used as filling materials to perfuse coal through extinguishing technologies of inorganic solidified material. Soaking fluids of inorganic salt, inhibitors of calcium hydroxide and other halides are used as inhibitors (coal fire retardant technologies) and chemical gels, complex gels and multi-phase foam are used as new extinguishing technologies.

3.2 Classification according to phases

Some materials are mainly composed of gas-phase materials of high bulk levels and low density (e.g., inert gases and foams). Some materials mainly consist of fluid-phase low bulk, high-density materials (a variety of gels and slurries). Other solid-phase materials used as main components block air leaks and strengthen the coal body (polyurethane and foaming cement). In conclusion, fire prevention materials can be classified based on phases.

1 Soft materials (Zhou et al., 2006). Soft materials mainly include inert gases and foams with gas-phase materials. Figure 8 shows three-phase foam materials. Their high bulk and limited weight levels allow them to prevent and control fires in large spaces when a fire’s positioning is not certain. Such materials and technologies are widely used in closed spaces exposed to exogenous mine fire and spontaneous coal combustion. This technology must be applied to closed spaces where the heat capacity of inert gases is low with limited heat absorbed from coal and with long fire-fighting cycles and a high likelihood for reburning (Chen and Wang, 1996).

Soft materials are widely applied to closed spaces exposed to exogenous mine fires and spontaneous coal combustion, and three-phase foam is used to prevent and extinguish large fires in goafs to prevent spontaneous coal combustion at a deep dip angle and to target high altitude or unknown fire positions (Chen and Wang, 1996).

The extinguishing mechanism of inert gases is said to be thermal rather than chemical, which can be understood qualitatively on the basis of the Damkohler criterion for extinction.

\[
D = \left( \frac{1}{v} \text{ or } \frac{1}{\alpha} \right) c_F c_0 e^{-\frac{E}{RT}}
\]

where \(c_F\) is the fuel concentration in mg/cm\(^3\), \(c_0\) is the oxygen concentration in g/cm\(^3\), \(E\) is the activation energy level of the reaction in cal/mol, \(R\) is the ideal gas constant in cal/mol K, \(l\) is the characteristic length, \(v\) and is the characteristic velocity. As equation (4) shows, injected liquid nitrogen is believed to isolate the oxidiser and to thereby reduce \(D\) by reducing the oxygen concentration \(c_0\) in the gas. Cooling condensed fuel tends to reduce \(c_F\) as well as the flame temperature \(T\) in the above equation, thereby reducing \(D\); blowing out a flame increases \(v\), and this has a strong effect on \(D\) (Watanabe and Zhang, 2001).

The extinguishing mechanism of foam: extinguishing foam is simple and stable, and in turn fire can be extinguished successfully (Dack et al., 1984). As foam cells rupture, fly ash and mud, as a result of viscosity levels, can uniformly cover coal in
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the goaf and can minimise further coal oxidation (Zhou et al., 2005). The foam can quickly and effectively extinguish a fire in a large area. The structural model of three-phase foam is shown in Figure 9 and Figure 10.

**Figure 8** Three-phase foam materials for preventing and controlling spontaneous coal combustion, (a) three-phase foam produced in situ (Zhou et al., 2006) (b) three-phase foam produced in a roadway (see online version for colours)
Figure 9  Schematic of the homemade column for three-phase foam generation (see online version for colours)

Notea: (1) Venturi tube, (2) jet regulator and (3) impeller; the FA particle size is exaggerated for clarity.

Source: Qin et al. (2014)

Figure 10  A structural model of three-phase foam for attaching FA particles to N₂-water interfaces by tuning surface-wetting properties, (a) schematic illustration of the stabilisation of gas bubbles with fly ash particles (b) the adsorption of partially lyophobic FA particles at the gas-liquid interface, illustrating the balance in tension responsible for the attachment of particles (c) a potential approach for tuning wetting properties of originally hydrophilic particles to absorbed SBDS molecules (see online version for colours)

Source: Qin et al. (2014)

2 Gel and slurry materials (Colaizzi, 2004; Xu et al., 2012). The phase of the materials is described as follows: fluid with liquidity; aggregated; and a strong capacity for heat absorption, coverage and oxygen isolation (see Figure 11 and Figure 12). This material can be applied to small fires and to fires found in certain areas. Grout can wrap coal and can prevent coal exposure to oxygen while gel can conglutinate with a roof, decreasing the porosity of goaf and increasing the resistance of air leaks. However, these materials may, for instance, easily dehydrate, decrease in bulk after dehydration, or lack solidification, negatively affecting coal quality and the working
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face and compromising the prevention and control of spontaneous coal combustion for top coal and coal pillars (Wang et al., 2010). It is extremely difficult to transport gel materials through mine tunnels. To a certain extent, coagulants pollute underground coalmines with ammonia. Such materials should be used to prevent and extinguish large area fires in goafs through simple production processes at relatively low cost and that they can be applied in many locations to prevent and control mine fires (e.g., chain pillar, collapse-danger area, fault zone, open-off cut, goaf, roadway and working face fires).

Figure 11 Photographs of sand-suspended colloids of different concentrations, (a) concentration of 0.2% (b) concentration of 0.4% (c) concentration of 0.5% (see online version for colours)

Source: Xu et al. (2012)
Several materials can be used to extinguish an outcrop fire, including (a) silicone, (b) fly ash composite gel, (c) loess composite colloids and (d) polymer colloids (see online version for colours).

The extinguishing mechanism of grout: lightweight grout is extremely heat resistant and flowable and can be applied directly to a red-hot coal fire without causing steam explosions or grout flash sets. Once in contact with a fire, grout encapsulates burning material, thereby removing heat and fuel and filling void spaces and passages, thus effectively acting on sources of oxygen. By directly addressing all three critical fire propagation elements with comparatively little land disturbance, this relatively new technological tool surpasses traditional coal fire control methods (Colaizzi, 2004). When applied similar to shotcrete to exposed coal seams, grout can limit the amount of oxygen introduced and can shorten the oxidation process. Grout injections into cracks, vents and cut-off trenches stall or prevent continued growth. When grout is injected directly into fire zones, air intake areas and exhaust sites, fires can be successfully extinguished (Colaizzi, 2004).

Solid materials. These materials are mainly of the solid phase and include solidified organic polymer materials and solidified inorganic solidified materials. Inorganic solidified foam is shown in Figure 13. The former consists mainly of polyurethane
and of modified polyurethane while the latter are mainly composed of foaming cement. The principal function of these materials is to consolidate a coal body through the use of sealing and filling materials. Solid materials can enhance the extinguishing functions of soft materials and gel or slurry materials as auxiliary materials. While the air tightness and compressive strength of polyurethane meets air seal requirements, as polyurethane solidifies so quickly, it cannot fill large areas as a seal-filling material (Yang, 2005). Inorganic solidified materials can cover a shortage of polyurethane solidified materials. Inorganic solidified material generation to solidification occurs over 20 to 60 min, and thus such materials meet airtightness requirements and can fireproof areas such as cavities in falling roofs, roadway partition areas and relaxation zones. Solidified polymer materials are only applied to small, enclosed spaces while inorganic solidified materials can be applied to both small, enclosed spaces and large spaces (Xu et al., 2012).

Figure 13  Inorganic solidified foam, (a) solidified foam after drying (b) solidified foam after cellulose addition (c) zoomed-in image of the bubble cross-section (see online version for colours)

Source: Qin and Lu (2013)
The extinguishing mechanism of macromolecule materials: macromolecule organic materials extinguish coal fires by sealing fire areas off. Such materials include organically-based chemicals such as those composed of urea formaldehyde polymers or organic agents. Polyurethane foam has been applied to a coalmine roadway as an air leak sealant. As organic products are more costly than inorganic foam, they are used less.

The extinguishing mechanism of inorganic materials: organic solidified foam effectively controls fires but its costs and environment prevention requirements are high. Solidified materials with high foaming solidification potential are needed to fill and plug to prevent and control spontaneous coal combustion (Qin and Lu, 2013). Calcium chloride and urea limit heat changes during coal oxidation at ambient temperatures. CaCl₂ has been found to shift activation energies $E_a$ to higher values relative to those of untreated coal for the temperature range studied. At temperatures of less than 200°C, the presence of urea spurs an increase in $E_a$ levels (Slovák and Taraba, 2012).

3.3 Classification according to retardant properties

Conditions of spontaneous coal combustion can be divided into physical and chemical conditions. As a result, according to retarding mechanisms, inhibitors can be classified as physical (Slovák and Taraba, 2012; Li et al., 2012) or chemical inhibitors (Beamish et al., 2013). Physical inhibitors prevent and control mine fires by altering the environmental and physical attributes of coal. Chemical inhibitors also prevent spontaneous coal combustion via chemical reactions to reduce or destroy coal low-activation energy groups.

1 Physical inhibitor. A physical inhibitor cuts off oxygen supplies and decreases reaction temperatures. Some physical inhibitors such as yellow mud and inert gas serve as a protective layer to limit contact with oxygen by covering surface active coal sites (Zhan et al., 2011). Figure 14 shows an inert gas nitrogen-generating machine. Some physical inhibitors such as colloidal formulations can supply water to decrease coal heating rates while water evaporates into steam, carrying away tremendous amounts of heat (Beamish et al., 2012). Other physical inhibitors can react with active coal sites to generate a stable link that enhances coal stability (e.g., water absorbing salts) (Slovák and Taraba, 2012).

2 Chemical inhibitor. Chemical inhibitors can change the chemical properties of coal to prevent spontaneous coal combustion (e.g., sodium persulfate). Some chemical inhibitors can capture free radicals generated through coal oxidation to break the chain reaction between coal and oxygen. Some chemical inhibitors can prevent and control spontaneous coal combustion by destroying coal functional groups, by strengthening coal capacities for water storage or be improving reaction conditions (Zhao et al., 2008; Wang et al., 2012). Figure 15 presents the chemical structures of certain ionic liquids.
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Figure 14  Mobile nitrogen-generating machine (see online version for colours)

Figure 15  Structures of six ionic liquids: [AOEmim] [BF₄], [HOEmim] [BF₄], [Bmim] [AC], [Emim] [AC], and [Bmim] [OTf]

Source: Wang et al. (2012)

While research on physical inhibitors is relatively well established, we are only beginning to investigate chemical inhibitors, and further research on this subject is needed. Both physical and chemical inhibitors are applicable in different situations. It is necessary to identify appropriate carriers that can transport physical or chemical inhibitors to flammable areas. Physical inhibitors affect the first stages of spontaneous coal combustion while chemical inhibitors mainly affect the second and third stages of spontaneous coal combustion. A compound can affect all three stages of spontaneous coal combustion after a physical inhibitor is compounded with a chemical inhibitor. Resulting inhibitory effects are thus superior, as conditions for spontaneous coal combustion can be changed. This compound may thus be used for
spontaneous coal combustion prevention in the future (Li et al., 2012). In order to prevent and control the spontaneous coal combustion in the future, the compound can affect all three stages of spontaneous coal combustion after a physical inhibitor is compounded with a chemical inhibitor will be mainly studied. And the most focus tasks at the moment in order to prevent and control the spontaneous coal combustion are that further study on the mechanisms of spontaneous coal combustion, the research of monitoring and appraising method in spontaneous combustion of coal, the mechanism of retardant, the classification of materials that prevent spontaneous coal combustion and the comparison of retardant effect.

3.4 Indicators to evaluate these methods of preventing and controlling spontaneous coal combustion

To evaluate these methods of preventing and controlling spontaneous coal combustion, many indicators and factors should be considered. In order to evaluate these methods more accurately, we should not only take a single influencing factor as the criterion, but we should also consider the common action of all kinds of factors. The indicators to be considered generally include mechanism of coal spontaneous combustion prevention and control, the effect of fire-fighting methods, time stability, crafting process, safety and reliability, economic benefits and so on.

4 Discussion

The mechanism of spontaneous coal combustion is extremely complex, and current research theories describe its mechanism based on chemical reactions between coal and oxygen and based on chemical structures of coal by analysing properties and mechanisms of spontaneous coal combustion from a certain angle. However, no theories have yet comprehensively revealed the mechanism of spontaneous coal combustion. Further research on spontaneous coal combustion should be conducted in the future.

In recent years, studies on materials that prevent spontaneous coal combustion have achieved prominent results, and a series of materials have been applied in China and overseas. Traditional technologies of spontaneous coal combustion prevention and control mainly include inert gas extinguishing technologies, inorganic solidified material extinguishing technologies, and retardant coal fire prevention technologies. Traditional technologies are limited in their capacities to prevent and control spontaneous coal combustion. In addressing the flaws of traditional materials, new extinguishing materials such as chemical gels, complex gels and multi-phase foam have been developed. Considerable progress with new extinguishing materials has been achieved in China in recent decades. However, coal fire prevention and extinguishing technologies lag behind coal exploitation technologies. To limit the frequency of disasters resulting from spontaneous coal combustion, it is necessary for related departments to invest in related research and to popularise new coal fire extinguishing technologies.

At present, classifications of materials that prevent spontaneous coal combustion are not unified. Extinguishing materials are thus categorised based on material phases in this paper: soft materials, gel and slurry materials and solid materials. Some materials are mainly composed of gas-phase materials with high bulk levels and limited density (inert gases and foams). Some materials mainly consist of low-bulk and high-density
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fluid-phase materials (gels and slurries). Other materials composed of mainly solid-phase materials are used to block air leaks and to strengthen a coal body (polyurethane and foaming cement). In conclusion, fire prevention materials can be classified on the basis of phases. Inhibitors can also classified as physical or chemical inhibitors depending on retardant mechanism involved. Physical inhibitors prevent and control spontaneous coal combustion by changing the surrounding coal environment or by destroying physical conditions that support spontaneous coal combustion. Chemical inhibitors prevent and control spontaneous coal combustion through a series of chemical reactions that can change or destroy the chemical reaction chain involved in spontaneous coal combustion.

5 Conclusions

Spontaneous coal combustion poses serious threats to the world and especially to China, New Zealand, South Africa, Colombia, Australia, and the USA. Apart from monetary losses to national exchequers and resource losses incurred by countries, spontaneous coal combustion results in casualties, which cannot be measured as a monetary cost. Thus, despite its complexities, international and Chinese experts and scholars have devoted themselves to the study of spontaneous coal combustion. Considerable progress has been made through hard work conducted over recent decades.

The mechanism of spontaneous coal combustion, an extremely complex physio-chemical process affected by numerous factors, has been studied intensively. Researchers around the world have made great progress and have put forward several theories on spontaneous coal combustion over the past 200 years. The theory of complex action between coal and oxygen is widely acknowledged. Low temperature oxidation occurs along coal surfaces, which in turn decreases the ignition point. Heat is released as a result of physical coal oxygen adsorption and more heat is released as a result of chemical adsorption and chemical reactions between coal and oxygen. Heat accumulates when more heat is released than is lost, initiating the self-heating stage. Spontaneous coal combustion occurs as a result. Regarding the chemical structures of coal, oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, methoxyl groups and non-active oxygen affect coal properties significantly, causing more heat to be released through oxidation reactions between coal and oxygen and rendering coal more combustible.

Several scholars have studied coal fire-fighting technologies over the past 200 years. In recent years, a series of extinguishing materials that prevent spontaneous coal combustion have been widely used worldwide, including extinguishing technologies of inert gas, extinguishing technologies of inorganic solidified materials, retardant coal fire prevention technologies and new extinguishing technologies.

According to the existing literature and data and on the basis of properties and applications, mine fire extinguishing materials are divided into soft materials, gel and slurry materials and solid materials. These criteria for classification are mainly based on material phases. Various characteristics and applications are found among the same types of materials. As a result, it is necessary to select proper extinguishing materials in accordance with specific conditions. According to retardant mechanisms, coal fire extinguishing materials can be classified as physical or chemical inhibitors. Physical inhibitors prevent and control mine fires by changing environmental and physical coal
conditions. Chemical inhibitors also prevent spontaneous coal combustion through chemical reactions that reduce or destroy coal low activation energy groups. Physical inhibitors cut off oxygen supplies and decrease reaction temperatures, in turn affecting the first stage of spontaneous coal combustion. Chemical inhibitors on the other hand mainly affect the second and third stages of spontaneous coal combustion. At present, while research on physical inhibitors is relatively established, we are only beginning to investigate chemical inhibitors, and further research on this subject is needed.

Compounds can affect all three stages of spontaneous coal combustion after physical inhibitors are compounded with chemical inhibitors. This property improves inhibitory effects because conditions of spontaneous coal combustion can be changed. Therefore, compounds may represent the future of spontaneous coal combustion prevention.

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