



## Full Length Article

# An intelligent gel designed to control the spontaneous combustion of coal: Fire prevention and extinguishing properties



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## ABSTRACT

A new type of mining fire-extinguishing material designed to prevent the spontaneous combustion of coal is presented. Through the graft copolymerization of corn straw, 2-acrylamide-2-methylpropanesulfonic acid (AMPS), and acrylic acid (AA), a corn straw-co-AMPS-co-AA hydrogel was synthesized. A chemical foaming agent was then added to the hydrogel, resulting in a self-foaming gel, which was subsequently mixed with expandable graphite to create an intelligent gel. Compared to temperature-sensitive and polyacrylamide gels, this intelligent gel exhibited good thermal stability, as well as adhesion and swelling at high temperatures. Fire-extinguishing experiments revealed that the intelligent gel could cover the surface of burning coal, thereby significantly reducing the ignition source temperature, thermal radiation, and amount of CO generated. Infrared spectrum analysis showed that the IG sample with 10% expanded graphite could inhibit the oxidation of the hydroxyl group during the heating process. The fire-extinguishing performance of the intelligent gel was found to be superior to those of the other gels, as it prevented re-ignition. Thus, this gel is an ideal fire prevention and control material, especially for controlling the spontaneous combustion of coal.

## 1. Introduction

The spontaneous combustion of coal is one of the main threats to safety in coal mines. The resulting fire can cause casualties and significant property loss, as well as serious environmental pollution [1–3]. Methods for preventing spontaneous coal combustion include: (i) grouting [4–5]; (ii) spraying an inhibitor, chemical fog, gel fog, or inert gel fog [6–8]; (iii) pressure equalization [4]; (iv) injection of inert gases [9–12], gels [13–15], foam, or three-phase foams [16–19]; and (v) air sealing using clay composite slurries [20], inorganic foams [21–23], or polymer materials (such as phenolic foams, polyurethane or urea formaldehyde foams, and polyurethane elastomers) [24–28]. These techniques play a key role in safeguarding mining production. However, several issues related to these techniques remain unresolved. For instance, inert gases diffuse readily because of air leakage and tend to leave the injection area. Further, gels have low fluidity and a small penetration range. In addition, three-phase foams do not cure readily and are only stable for 8–12 h, while organic foams are expensive and exothermically reactive and can thus trigger spontaneous coal combustion. Given these drawbacks of the existing fire-extinguishing materials, there is a need for novel materials that improve the efficiency of

spontaneous coal combustion prevention.

Hydrogels are polymers with three-dimensional structures and are constituted of cross-linked and hydrophilic macromolecular compounds [29–31]. Compared to pure water, they offer clear advantages with regard to water binding as well as cooling and sealing. Currently, hydrogels are being used ubiquitously in forest and coal mine fire prevention [13–14]. To improve their fire-extinguishing efficiency, Qin et al. synthesized a novel, multi-phase foaming gel [32–34]. This material was fabricated by mechanically stirring fly ash (a foaming agent), nitrogen (a thickening agent), and a cross-linking agent. The obtained gel exhibited good fire-extinguishing properties [32]. Wang et al. prepared a foaming gel that exhibited mechanical foaming [35]. Chemical foaming is another effective way of introducing a porous structure into a gel and involves including specific chemicals that react with an acid or decompose at elevated temperatures to produce gases. These reactions produce bubbles during the polymerization process, yielding polymers with a porous structure [36]. Kabiri et al. synthesized a super-absorbent intelligent hydrogel using acetone and NaHCO<sub>3</sub> as the foaming agents [36]; this gel was reported to respond quickly to temperature changes and allowed up to 90% of the water present in it to evaporate within 10 min, making it a good coolant material for the fire

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area.

Expandable graphite (EG) is a crystalline compound obtained by the physical or chemical insertion of non-carbon reactants between graphite layers. Upon exposure to high temperatures, the reactants decompose between the layers, and the graphite begins to expand. This process is completed at 1000 °C, with the final volume being more than 200 times the original one. EG is an excellent insulator, releases negligible heat, loses negligible mass, and produces negligible smoke in fire [27]. It is currently used as a sealing and flame-retarding material [24]. When EG is added as an aggregate to a hydrogel, it may expand and prevent air leakage at high temperatures.

Crop straw is a natural and renewable resource that can be derived from a wide range of materials. It is also inexpensive and biodegradable [37]. Currently, crop straw is used to prepare animal feed and alcohol. However, some straw is incinerated, which amounts to resource wastage and causes environmental pollution [38]. The preparation of hydrogels using a simple straw pretreatment process allows for more effective use of this natural resource and reduces the cost of the gels.

In this study, we propose a self-foaming, intelligent gel (IG) that expands at high temperatures. This hydrogel is prepared from corn straw, a foaming agent, and EG. Compared to traditional hydrogels, the IG offers the following advantages: it can react to release an inert gas, thereby extinguishing the fire, and its porous structure allows for a quick response to temperature changes, causing rapid loss of its water content at high temperatures. This effectively cools the fire. Moreover, when all the water in the IG has evaporated, the EG in the IG expands rapidly, wrapping and sealing the high-temperature fire source.

The fire-extinguishing mechanisms of the IG were analyzed by comparing its foaming properties, high-temperature (380 °C) swelling, adhesion, thermal stability, and fire-extinguishing characteristics to those of temperature-sensitive gels comprising poly(N-isopropylacrylamide-co-acrylic acid-co-2-acrylamide-2-methylpropane-sulfonic acid) as well as those of polyacrylamide gels.

## 2. Experimental

### 2.1. Experimental materials

The coal used for the combustion tests was bitumite with an ignition point of 400 °C. The coal was burned through smokeless combustion.

### 2.2. Gel preparation

#### 2.2.1. Preparation of intelligent gel (IG)

Dried corn straw was crushed and segregated using a 40-mesh sieve. The resulting powder was alkalinized by being mixed with a 15 wt% aqueous NaOH in an isothermal water bath at 55 °C for 2.5 h. It was then bleached with H<sub>2</sub>O<sub>2</sub>, dried, and crushed to obtain cellulose.

The thus-obtained cellulose was immersed in a 17.5% aqueous NaOH solution and stirred for 1 h; this was followed by 3 h of soaking. The cellulose was then separated and washed thoroughly with deionized water. It was subsequently filtered and dried to a constant weight, resulting in alkaline fibers. The alkaline fibers (1.6 g) and deionized water (100 mL) were mixed in a 250 mL three-necked flask and stirred for 10 min at 40 °C under a nitrogen atmosphere. A known amount of KPS (0.05 g) was then added to the mixture. After a reaction time of 20 min, the AMPS monomer (4.8 g) was added. After an additional 4 h, the product was removed from the three-necked flask, cooled, washed with water and ethanol, and dried to a constant weight to obtain sulfonic cellulose [37].

The obtained sulfonic cellulose (1 g) was dissolved in water (10 mL) under nitrogen at 80 °C and gelatinized for 10 min. It was then cooled to 40–60 °C and KPS (0.1 g) was added, followed by acrylic acid (7 g) that had been neutralized with NaOH. The mixture was allowed to react for 1–2 h, and the cross-linking agent MBA (0.05 g) was subsequently added to it. After the solution had gelled and the odor of acrylic acid

**Table 1**

Formulation and processing parameters of the self-foaming hydrogel. AA: acrylic acid; KPS: potassium persulfate; MBA: N, N-methylenebisacrylamide.

Pretreated straw (g)	AA (g)	MBA/AA (%)	Na <sub>2</sub> CO <sub>3</sub> (g)	KPS/AA (%)	Neutralization value (%)	T (°C)
1	6	0.8	0.25	1.5	70	50

had faded, a Na<sub>2</sub>CO<sub>3</sub>/AcOH mixture was added to the solution as a foaming agent. The resulting mixture was stirred for 2 min at a polymerization temperature of 50 °C. The gel was removed, cut into pieces, and dried at 90 °C. Subsequently, it was ground to a powder and sieved through an 80-mesh sieve. The resulting gel granulates were sealed in a bag for subsequent use. The formulation for the self-foaming hydrogel is listed in Table 1, while Scheme 1 illustrates the mechanism of graft copolymerization.

To finally prepare the IG, EG was added to the self-foaming gel particles; this was followed by the addition of water. Three types of IG having EG contents of 5 (IG-I), 10 (IG-II), and 15% (IG-III) were prepared (Table 3).

#### 2.2.2. Preparation of temperature-sensitive hydrogel (TSG)

- (1) Sweet potato starch (5 g) and distilled water (70 mL) were added to a 250 mL three-necked flask and stirred well. The mixture was then heated and gelatinized in an isothermal water bath at 80 °C for 0.5 h under magnetic stirring using a stir bar.
- (2) An 80 wt% acrylic acid solution (25 mL) was prepared and neutralized with 40% NaOH, resulting in a solution of sodium acrylate (SA, pH = 7). The SA solution was stirred and cooled to 25 °C. Then, NIPAM (5 g) and AMPS (3 g) were added under stirring to produce solution I.
- (3) Solution I was added to the gelatinized starch. Subsequently, 30% ammonium persulfate (15 mL) and MBA (0.05 g) were also added. This mixture was heated in a water bath at 70 °C using a thermostat with a magnetic stirrer and kept under a nitrogen atmosphere until gelation occurred. The gel was then cut into small pieces, dried, crushed into a powder, and separated using a 60-mesh sieve. The formulations and process parameters for producing the temperature-sensitive hydrogel are listed in Table 2.

In this study, the fire-extinguishing properties of the IG, TSG, and PAM gels were compared. The specific proportions used are shown in Table 3.

### 2.3. Performance testing

#### 2.3.1. Determination of hydrogel microstructures

The self-foaming and temperature-sensitive gels were cut into pieces using scissors and dried isothermally to a constant weight. The dried gel samples were sputter-coated with gold, and their morphologies were observed using a S-3500N scanning electron microscopy (SEM) system (Hitachi, Japan), with magnifications of 5–300,000 and a secondary electronic resolution of 3.0 nm, at 10 kV.

#### 2.3.2. Examination of hydrogel foaming properties

Solutions of the IG, TSG, and PAM gels (2%) were prepared and poured into graduated cylinders, which were then placed in a drying oven in air in order to observe their foaming behaviors at various temperatures.

#### 2.3.3. Hydrogel penetration

At ambient temperature, the times required for equal volumes of the intelligent, temperature-sensitive, and ordinary gels to flow through

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