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Research article

Experimental study on thermo-responsive inhibitors inhibiting coal spontaneous combustion

Chuanbo Cui[a,b], Shuguang Jiang[a,b,c,*], Hao Shao[a,b], Weiqing Zhang[c], Kai Wang[a,b], Zhengyan Wu[a,b]

[a] Key Laboratory of Coal Methane and Fire Control (China University of Mining & Technology), Ministry of Education, Xuzhou 221116, China
[b] School of Safety Engineering, China University of Mining & Technology, Xuzhou 221116, China
[c] State Key Laboratory of Coal Resources and Safe Mining, China University of Mining & Technology, Xuzhou 221116, China

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ABSTRACT

Due to its strong fluidity and easy evaporation characteristic, high water-cut physical inhibitors (HWPIs) cause the decrease in moisture content of coal, so that its inhibitory effect on coal spontaneous combustion weakens or even fails. Aiming at solving the problem, this paper proposes to inhibit coal spontaneous combustion using thermo-responsive inhibitors (TRIs). These inhibitors are sensitive to specific temperatures and can retain their effects as long as the temperatures have not been reached. Besides, when the temperatures are reached, they are able to absorb heat and undergo physical and chemical changes to release H_2O and inert gases (defined as gases that are not involved into the coal oxidation reaction in this paper) such as NH_3 and CO_2, so as to inhibit the low-temperature oxidation of coal. Based on the temperature-programmed experiment of coal spontaneous combustion, this paper analyzed the effects of types and amounts of TRIs on coal spontaneous combustion by using differential scanning calorimetry (DSC), scanning electron microscope (SEM), thermogravimetry-derivative thermogravimetric analysis-differential scanning calorimetry (TG-DTG-DSC) and nitrogen adsorption test methods. The results show that $CaCl_2•6H_2O$ achieves the most stable inhibitory effect, as its inhibiting rate rises steadily in the heating process to reach a maximum value of 79.9% at 200 °C.

1. Introduction

Underground coal fire is a difficult and persistent problem worldwide, which is mainly associated with coal spontaneous combustion [1,2]. It is well known that coal reacts with O_2 in air to release heat, even in ambient conditions. Large-scale spontaneous combustion of coal areas occurs more frequently, increasing channels of air leakage to the goaf [3]. Among China's state-owned collieries, 56% of the mines have been jeopardized by the combustion which leads to huge personal casualties, economic losses and massive environmental contamination [4,5].

Retarding coal spontaneous combustion is therefore highly desirable. Physical inhibitors are widely used to prevent or extinguish coal mine fires. At present, a wide range of inorganic salts such as NaCl, $MgCl_2$ and $CaCl_2$ have been considered [6–9] for use in this role. Smith et al. [10] studied the inhibitory effects of ten kinds of additives on the spontaneous combustion of bituminous coal and found that $NaNO_3$, NaCl and $CaCO_3$ achieved the most optimal effects. Clemens et al. and Kadioglua et al. [11,12] studied the effect of moisture on the combustion. Liodakis et al. [13] discovered that diammonium phosphate and ammonium sulfate can effectively prevent the spontaneous ignition properties of *Pinus halepensis* pine needles. Anthony et al. [7], Yucel et al. [15], Zhang et al. [16] and Li et al. [17] studied the influence of moisture on the combustion. Zhan et al. [18] concluded that Na_3PO_4 can improve the thermal stability of coal and effectively inhibit the generation of free radicals. Taraba et al. [19] and Vaclav et al. [7] revealed that urea can effectively inhibit coal self-heating and spontaneous combustion. The process of coal spontaneous combustion is generally divided into three periods, namely, preparation period, self-heating period and combustion period. Coal spontaneous combustion requires the accumulation of heat. In the preparation period, with both a low initial ambient temperature and a low coal oxidation rate, just a small amount of heat is generated, so a relatively long heat storage process is required. After going through the preparation period, the coal is oxidized at a higher rate, and the heat generated by oxidation keeps raising the coal temperature. After the coal temperature reaches the critical temperature, the amount of heat generation exceeds that of heat release, so that the coal temperature rises sharply to reach the ignition

* Corresponding author at: Key Laboratory of Coal Methane and Fire Control (China University of Mining & Technology), Ministry of Education, Xuzhou 221116, China.
E-mail address: jsguang@cumt.edu.cn (S. Jiang).

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point of coal. The above inhibitors are mixed with water to be prepared as a certain concentration of solution called high water-cut physical inhibitors (HWPIs). These inhibitors, however, retard coal oxidation merely by creating a barrier to O_2 and adsorbing heat via water evaporation. Nevertheless, water will evaporate in large quantity under the influence of temperature with the passage of time. Therefore, these compounds typically exhibit low efficiency and short active lifetimes [14,20]. Cui et al. [29] proposed a technique of encapsulating HWPI in thermo-responsive secundine (TS). It overcomes the defects of the existing inhibitors which are unable to control spontaneous combustion in coal seams or goaf due to their strong fluidity, short inhibitory function time, corrosivity, etc.

Some researchers injected inert gases (N_2 and CO_2) into the goaf to inhibit coal spontaneous combustion, which indeed worked [21,22]. Since inert gases are non-toxic and inexpensive and do not participate in the oxidation reaction, injecting them into a limited space can lower the O_2 concentration. Nevertheless, the mobile inert gases diffuse and then disappear with the passage of time, so that their inhibitory effects quickly weaken or even fail. Furthermore, since coal spontaneous combustion requires a long heat storage time from the preparation period to the self-heating period, the optimal time for inert gas injection can hardly be determined.

To solve problems of short inhibitory lifetime of HWPI and difficult determination of optimal time for inert gas injection, a new type of inhibitor is required. This inhibitor not only possesses a retainable inhibitory effect over the long storage time, but also can automatically exert its inhibitory effect when the coal temperature approaches the critical temperature of spontaneous combustion. This paper proposes to inhibit the combustion by using thermo-responsive inhibitors (TRIs) which are sensitive to temperature. When the coal temperature gets close to the critical temperature, TRIs may absorb heat and release liquid H_2O, gases such as NH_3 and CO_2 and salts to cover the coal.

In addition, TRIs are not easy to fail before the coal temperature approaches the critical temperature. Besides, in the case of emergencies such as an occurrence of the combustion in a mine goaf, a TRI can be directly spread into the goaf without bothering to prepare a solution, so it is convenient and fast to be applied. The mechanism of TRI for inhibiting the combustion mainly lies in three aspects: First, both the thermal decomposition of TRI and the evaporation of water produced by the decomposition will absorb a large amount of heat. Second, the liquid water and salts produced will wrap the coal to isolate it from O_2. Third, the CO_2, NH_3 and other inert gases produced will lower the O_2 concentration.

2. Materials, system and procedures

2.1. Experimental materials

The fresh coal used in the present experiment was supplied by Longdong Mine, Xuzhou city, China, and sealed in sealing bags to be transported to the laboratory. The interior part of the coal was ground and sieved to particle sizes of between 0.18 mm and 0.38 mm and then dried under vacuum for 24 h at 40 °C. The technical parameters of Longdong coal is listed in Table 1.The true density of the coal sample is 1.99 g/cm^3.

The TRIs used in this paper are $CaCl_2{\cdot}6H_2O$, $MgCl_2{\cdot}6H_2O$, $Na_2S_2O_3{\cdot}5H_2O$, $NaHCO_3$ and $CO(NH_2)_2$. Among the 5 temperature-sensitive materials, the first three will melt to release crystal water when heated, and $MgCl_2{\cdot}6H_2O$ can even produce HCl when heated to a certain temperature. The latter two will decompose into different decomposition products. These materials were ground to the diameter of 0.18–0.38 mm and then sealed to be stored under low temperature. The HWPI adopted in this study is a $CaCl_2$ solution at the concentration of 20%.

Table 1
Technical parameters of Longdong coal.

Proximate analysis (%)				Ultimate analysis (%)				
M_{ad}	A_d	V_{daf}	FC_{ad}	O_{daf}	C_{daf}	H_{daf}	N_{daf}	S_{td}
2.38	25.32	40.96	43.04	13.42	78.49	5.10	1.45	1.15

2.2. Experimental system

The testing system simulating coal acceleration combustion consists of a temperature-programmed system and a data acquisition system. Composed of a PC, a data collection, an indicator gas analysis system, a thermocouple, and an electronic balance, the data acquisition system can simultaneously collect the concentration of gases generated by coal oxidation. Among them, the indicator gas analysis system includes a high-precision CO sensor, a CO_2 sensor, an O_2 sensor and a signal processing module. As the indicator gas analysis system can collect the concentration of indicator gas in real time, it is more efficient and convenient than a gas chromatograph.

2.3. Experimental procedures

2.3.1. Effect of water evaporation on the inhibitory effect of HWPI

Underground mine goafs are prone to spontaneous combustion. To solve this problem, people generally adopt the method of spraying HWPI to the goaf. However, due to the strong mobility of HWPI, air leakage and higher temperature in the goaf, the water in residual coal will not only flow away, but also decrease with the evaporation of moisture. The drop of water content in coal will seriously affect the inhibitory effect of HWPI. The following experiment was performed to study the effect of water evaporation on the inhibitory effect of HWPI:

Step 1: 20 g of raw coal was taken and averagely divided into 4 pieces. Among them, a piece without addition of reagent was taken as the raw coal sample. Another piece was added with 1.8 g of HWPI and allowed to settle for 1 h after being stirred evenly. The initial water content of the sample was 21.18%.

Step 2: For the rest 2 pieces, each was added with 1.8 g of HWPI and allowed to settle for 1 h after being stirred evenly. Next, the 2 samples were dried in a vacuum drying oven at 40 °C constant temperature for 12 h and 24 h, respectively, after which they were taken out to be weighed by an electronic balance and have their water contents calculated.

Step 3: The 4 samples were respectively put into the reaction vessel for performing the temperature-programmed experiment. The experiment, which was based on the experimental system shown in Fig. 1, was aimed at detecting the concentration of indicator gas and the amount of water evaporation in the temperature-programmed process.

2.3.2. Contrast experiment on inhibitory lives of TRI and HWPI

9 g of $CaCl_2{\cdot}6H_2O$ was taken and averagely divided into 3 pieces. Next, they were evenly mixed with 5 g of dried raw coal. The 3 coal samples were dried in a vacuum drying oven at 40 °C constant temperature for 0 h, 12 h and 24 h, respectively, after which they were taken out to be weighed. Then, the 3 samples were respectively put into the reaction vessel for performing the temperature-programmed experiment. The experimental conditions were the same as Step 3 in Section 2.3.1. Finally, the other 4 TRIs were taken for performing the contrast experiment in accordance with the same steps.

2.3.3. DSC test of TRI

A TRI is characterized by its sensitivity to temperature. With the rise of temperature, a TRI will absorb heat and decompose to produce gases, water or crystal water. In order to accurately grasp the endothermic and exothermic properties of TRI, a DSC test was conducted on the samples through the NETZSCH DSC200F3 instrument produced in Germany.