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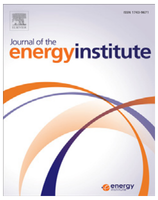

Experimental investigation of applying $MgCl_2$ and phosphates to synergistically inhibit the spontaneous combustion of coal

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ABSTRACT

Spontaneous fire hazard in underground collieries threatens the safe production of coal. Thus, globally, there is a growing interest in identifying and adapting novel methods for inhibiting the spontaneous combustion of coal. Although Cl-containing minerals exhibit retardant properties in the low-temperature range, they fail to control the combustion of coal at high temperatures. Therefore, to control the fire hazard caused by spontaneous combustion of coal at high temperatures effectively, phosphates and $MgCl_2$ were innovatively used as synergistic inhibitors for suppressing self-ignition of coal. Laboratory tests such as thermal analysis, infrared spectrum analysis and oxidation analysis were performed to evaluate the behavior of coal samples before and after treatment. Experimental results indicated that the combined utilization of $MgCl_2$, $Zn_3(PO_4)_2$, and $(NH_4PO_3)_n$ could significantly reduce the heat emission during coal combustion, as well as the yield rate of CO. The optimal effect can be obtained with a Cl-to-P ratio of 2:1. In addition, functional groups such as $-OH$ and $-CH_2-$ in treated samples decreased markedly. Hence, underground coal fire can be prevented more effectively using a combination of Cl and P, instead of using Cl-based retardants alone.

1. Introduction

Spontaneous combustion of coal frequently occurs during the production, transportation, and storage of coal, and is a challenging problem worldwide [1,2]. This generally occurs in underground coal mines and is often accompanied by the emission of hazardous gases such as CO [3,4]. Moreover, the flammable gas (CH_4) in goaf easily undergoes combustion due to the self-ignition property of coal, thereby causing serious accidents [5]. Therefore, prevention of the spontaneous combustion of coal is of great significance for the safe production of coal. Spontaneous combustion of coal is triggered by various factors. For example, the external ventilation and accumulation of heat affect the occurrence and development of spontaneous combustion [6,7]. Besides, internal factors [8,9] such as coal rank, moisture, sulfur content, petrographic characterization, and pore structure are reported to be responsible for spontaneous combustion. To effectively prevent coal from undergoing spontaneous combustion in underground coal mines, several techniques have been developed. For example, Dou et al. [10] weakened the low-temperature oxidation of coal using catechin and poly (ethylene glycol) as chemical inhibitors. Using polyethylene as a new inhibitor, Li et al. [11] remarkably reduced the amount of CO generated by lignite during low-temperature oxidation, which limited the combustion of lignite. Qi et al. [12] reported that a controlled-release inhibitor made from halogen inhibitors, catechin, co-polymer, solvent, and surfactant could affect the crossing-point temperature of coal. It is widely acknowledged that the low-temperature oxidation is the most important period in the spontaneous combustion of coal, so inhibiting this process is of vital importance for controlling spontaneous combustion of coal. At present, the most extensively used chemical method for inhibiting the spontaneous combustion of coal in field application is spraying cheap but efficient inorganic salts such as $MgCl_2$ and $CaCl_2$ [13,14]. These chlorides show favorable inhibition effects at low temperatures. It has also been reported that chlorides can facilitate the combustion of coal by increasing the combustion rate of coal powders at high temperatures [15]. These results indicate that inorganic chlorides can merely inhibit the spontaneous combustion of coal in the initial period, but these fail to control the spread of fires as the temperature of coal rises. By contrast, phosphorous-containing inhibitors

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show preferable flame-retardant effects at high temperatures (>150 °C), but present weak flame-retardant effects at low temperatures [16]. Compared with using only kind of inhibitor, applying a combination of two kinds of inhibitors can more effectively control the spontaneous combustion of coal. For the combustion of some oxygen-containing polymers, halogen–phosphorus combination shows a favorable flame-retardant effect [17]. For example, when applying flame-retarded polyethylene terephthalate (PET) materials in bromine–phosphorus systems, the amount of inhibitor used is much less than that utilized in conventional bromine–antimony systems [18]. It is also reported that adding tribromophenyl acrylate and triphenyl phosphate in polyurethane can effectively retard combustion [19]. Therefore, in this work, the synergistic effect of chlorides and phosphates on inhibiting the spontaneous combustion of coal was investigated and the optimal flame retardant effect was analyzed.

2. Experimental

2.1. Sample preparation

Samples for this study were collected from No. 8 coal seam in Xiqu colliery, Shanxi, China. The technical parameters and elemental composition of these samples are presented in Table 1. The fresh lump coal was crushed and filtered through a mesh sieve to select only those with particle size between 0.18 mm and 0.25 mm, which were then dried sufficiently and stored for later use. The chemical reagents used in the experiment were from Sinopharm Chemical Reagent Co., Ltd. Magnesium chloride ($MgCl_2$), zinc phosphate [$Zn_3(PO_4)_2$], and ammonium polyphosphate $(NH_4PO_3)_n$ of different masses were then added separately in deionized water to prepare the corresponding solutions of weight percent 20 wt%. Afterward, 40 g coal samples were placed in a beaker into which 100 ml of the prepared solution was added. The mixture was thoroughly stirred and the solution was allowed to stand for 24 h. Finally, the coal samples were placed in a vacuum oven and dried at 313 K for 12 h. These oven-dried samples were then used for experimental analysis.

2.2. Programmed heating test

Coal samples (30 g) were placed in a reactor (5 cm × 10 cm) and heated from room temperature to 473 K at a rate of 1 K/min through temperature-programming. The experimental device is illustrated in Fig. 1. In this process, dry air was passed through the reactor at a speed of 20 l/min. Once the temperature reached 333 K, 5 ml of gas was extracted from the reactor every time when the temperature was raised by 20 K to measure the CO concentration using the GC-950 gas chromatography. Based on the test results, the inhibition effect of the inhibitor with different ratios on the oxidation of the coal sample was evaluated.

2.3. TG/DSC test

To study the characteristic temperature of coal at low temperatures, the NETZSCH STA 449F5 simultaneous thermal analyzer was used. Based on the test results, thermo-gravimetry (TG), derivative thermo-gravimetry (DTG), and differential scanning calorimetric (DSC) curves were drawn. During the detection process, coal samples were heated from room temperature to 1073 K at rates of 5 K/min, 10 K/min, and 15 K/min in an atmosphere of air, respectively.

2.4. Infrared spectroscopy

Using an infrared spectrometer (Bruker VERTEX 70), 1 g coal samples were scanned 32 times in the range of 500–4000 cm^{-1} to obtain the infrared spectra. Based on these spectra, changes in the functional groups on coal surface before and after the proposed treatment were analyzed.

3. Results and discussion

3.1. Thermal analysis

As illustrated in Fig. 2, when drying the coal samples in air, increase in temperature caused the samples to lose moisture and volatile content continuously, allowing them to dry and crack easily. Under these conditions, certain amounts of gaseous products were also

Table 1
Basic parameters of coal samples.

Proximate analysis	%
M_{ad}	0.46
A_d	10.64
V_{daf}	21.18
FC_d	70.43
Ultimate analysis	
$S_{t,ad}$	2.07
O_{daf}	4.32
C_{daf}	87.33
H_{daf}	4.61
N_{daf}	1.43
Coal rank	Bituminous coal

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