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Characteristics of polymorphic foam for inhibiting spontaneous coal combustion

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ABSTRACT

For inhibiting the spontaneous combustion of coal, a technique using polymorphic foam (PF) synthesized from a sol foam/polycaprolactone (SFP) solution and organic acid is described. This study includes zeta potential measurements of the SFP solution and formation of the PF, and a differential scanning calorimeter/thermogravimetric, X-ray diffraction, X-ray photoelectron spectroscopy and infrared analysis of the PF. It was found that the PF solution that included a polycaprolactone concentration of 0.7 wt% had the strongest electrostatic repulsion. Within 30 s of the organic acid being injected into the SFP solution, an aqueous foam was generated via injecting gas, subsequently, within 2–3 min, the PF could form due to the chemical reaction between sodium silicate and the organic acid. The PF had the properties of adsorbing the significant heat produced by coal low-temperature oxidation, wrapping in coal from oxygen ingress by the colloid-fused polycaprolactone, providing the moisture for coal to inhibit coal self-heating. The PF could maintain a weight of 12% non-flammable residue, composed of mainly SiO_2 and a small amount of Na_2CO_3, forming a thermally stable coating layer on the surface of the combustible to extinguish fire. The PF mainly contained C–O and C=O functional groups, resulting in its surface being much more hydrophilic. It also inhibited the formation of new $-CH_2/CH_3$ and –OH functional groups in the process of coal low-temperature oxidation. It was concluded that PF has the potential to prevent and control the spontaneous combustion of coal.

1. Introduction

Statistics show that coal production for China in 2015 was 3.75 billion tons. Although this was the 3.3% less than in 2014, it still accounted for 64.0% of total domestic energy consumption [1]. Coal transportation, including imports and exports, plus the coal inventory of coal enterprises, account for up to 0.31 billion tons, which equates to 8.3% of raw coal production [2]. With such a huge amount of coal storage and transportation, safety issues cannot be ignored.

Coal fire is one of the major hazards in coal storage and transportation. The spontaneous combustion of coal causes annual coal losses of up to 10–20 million tons [3]. This not only affects coal quality [4,5], but also releases many greenhouse gases that pollute the atmosphere [6]. To control or prevent the spontaneous combustion of coal, various technologies have been used, including injecting gel [7–10], pouring slurry [11–13] and the use of inhibitors [14,15]. However, these techniques are mainly used to suppress heating in goaf areas and are not suitable for coal stockpiles because the non-flammable media included in the extinguishing agent can affect coal quality, leading to it becoming unacceptable for the end user. Water spray is the most traditional method for firefighting [16]. However, water only flows along low-lying areas and cannot cover the coal in higher places to suppress self-heating.

Aqueous foam technology is a well-known method to control the spontaneous combustion of coal. In 1949, Brady first studied the characteristics of aqueous foam [17]. In 1956, Jacobi et al. reported the use of foam technology in firefighting [18]. With the progress of surface-interfacial chemistry, aqueous foam technology is becoming more and more powerful. Aqueous foam is a dispersed system of gas bubbles in a continuous liquid that is generally metastable, both kinetically and thermodynamically. Therefore, foam liquid films easily rupture under external interference, resulting in poor fire extinguishing. In order to obtain more stable foam, Garrett et al. utilized latex nanoparticles to stabilize aqueous foams in surfactant solutions composed of sodium dodecyl sulfate (SDS), sodium bis-octyl sulphosuccinate and an ethoxylated octyl phenol [19]. Binks et al. utilized a mixture of silica nanoparticles to stabilize aqueous foams in cationic surfactant solutions of didecyldimethylammonium bromide and cetyltrimethylammonium

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bromide [20]. Sun et al. used partially hydrophobic modified silica nanoparticles to increase aqueous foam stability in SDS solutions [21]. Alargova et al. applied polymer microrods (obtained from the synthesis of SU-8, γ-butyrolactone, glycerol and ethylene glycol) to stabilize aqueous foams in SDS solutions [22]. Zhao et al. added a dispersed particle gel to tetradecyl hydroxyl sulfobetaine solutions with the aim of obtaining more stable three-phase foams [23].

Research into aqueous foam-based technologies for fire control has acquired obvious results, but there are several shortcomings in the application process. Firstly, when aqueous foam is sprayed to extinguish fire, due to air disturbances caused by fire plumes, foam film can easily rupture, resulting in poor fire control. Secondly, when aqueous foam is sprayed to high-temperature fire areas, it adsorbs heat and is highly susceptible to vaporization.

Taking the previous research results into account, polymorphic foam (PF), as an efficient approach to inhibit the spontaneous combustion of coal, is studied.

2. Materials and methods

2.1. Materials

The main materials used in this study are listed as follows: industrial-grade polycaprolactone (PCL; Letai chemical, particle size <38.5 μm); industrial-grade polyethylene oxide (PEO, Letai chemical, particle size <38.5 μm); sodium silicate solution (Na_2O, ∼10.6%, SiO_2, ∼26.5%, Letai chemical); sodium dodecyl sulfate (SDS; Aladdin, 99%); industrial-grade organic acid (Letai chemical, ∼85%); distilled water and the coal sample (Nanjing Wharf, Tianjin Port, China, particle size <0.15 mm).

PF was synthesized from a sol foam/polycaprolactone (SFP) solution and organic acid. The aqueous foam solution was mainly comprised of sodium silicate, SDS and distilled water. The sol foam (SF) solution was mainly comprised of PEO and the aqueous foam solution. The SFP solution was prepared by adding PCL into the SF solution at concentrations of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/L, respectively.

2.2. Methods

The ζ potentials of the SFP solutions were measured by a Malvern Zetasizer (Nano ZS90). Each sample was sonicated for 15 min, and then put into a testing cell, which was set to stand at 25 °C for 120 s, to measure the ζ potential. Each sample was measured five times and averaged. The ζ potential value was automatically calculated according to the Smoluchowski equation by the Zetasizer.

PF combustion was measured by an SDT Q600 simultaneous differential scanning calorimeter/thermogravimetric analyzer. During the experiment, the sample was placed in an alumina crucible and heated from 25 to 600 °C at a rate of 10 °C/min. An industrial grade air bottle was used for conducting the combustion experiment.

The crystalline phases of PF were determined by X-ray diffraction using a Rigaku Dmax-2500 with a voltage of 40 kV, a current for 150 mA, scanningMode for 2 theta/theta and Cu Ka radiation.

X-ray photoelectron spectroscopy (XPS) was carried out using an ESCA Lab 250Xi-ray photoelectron spectrometer with Al K Alpha radiation. The survey scanning transmission was 50.0 eV with a 1.000 eV step size. The C 1s sub-peak scanning transmission was 30.0 eV with a 0.100 eV step size.

The functional groups in the coal and blend of PF and coal were analyzed using a Nicolet 6700 DRIFTS by Nicolet in USA with wave number range from 650 to 4000 cm^{-1} and resolution of 4 cm^{-1}. During analysis, pure ground KBr was first collected as a baseline reference spectrum, after which either sample was placed into the reaction chamber connected to a temperature controller and the dome was installed, then dry air flowed into the reaction chamber, and the chamber was heated to 200 °C at a heating rate of 1 °C/min. Each spectrum was collected with 64 scans and at 30-s intervals.

3. Results and discussion

3.1. Zeta potential

The ζ potential provides an important parameter in charge dispersed systems near a solid surface [24]. Fig. 1 shows the ζ potential of the SF solution with different PCL concentrations.

The ζ potential value of the SF solution gradually decreases with increasing PCL concentration until the ζ potential reaches -39.3 mV at a particle concentration of 0.7 wt%. After this point, the ζ potential increases. Therefore, a particle concentration of 0.7 wt% is the critical value for the complete dispersion in the SF solution. In effect, the polymeric PEO, with a longer molecular chain due to the polymerization of PEO and water, can wrap up the particles of the adsorbed surfactant anions [25]. This means that the polymeric PEO coats the particles masking the adsorbed surfactant anions [26,27]. This phenomenon also results in more particles being wrapped up in the SF solution. At low PCL concentrations, the surfactant anions adsorb on the particle surfaces through hydrophobic interactions and the particles become more hydrophilic, resulting in a strong negative charge. At high PCL concentrations, only small selections of the particles are dispersed in the SF solution, most of which are flocculated inside the SF solution. At moderate PCL concentrations, the hydrophobic particles, when they adsorb the appropriate amount of surfactant molecules, can be exposed to the air-water interface.

3.2. Formation of polymorphic foam

The formation of PF focuses on injecting gas into the SFP solution and the chemical reaction of sodium silicate and organic acid. Fig. 2 shows the chemical mechanism for the step-by-step formation of PF. In the first step (shown in Fig. 2a), the SF solution consisting of sodium silicate, SDS, PEO and distilled water is prepared, and their concentrations are 20, 20, 1 and 959 g/L, respectively [28]. It is well known that the anionic SDS surfactant reduces the surface tension of the solution, resulting in increasing gas content inside the liquid flow to form the foam [29]. Polymeric PEO, polymerizing with water to form a longer molecular chain [25], can enhance the viscoelasticity of the foam to that of conventional foams used for extinguishing fires. For the second step (shown in Fig. 2b), the SFP solution is prepared when PCL is added to the SF solution. The hydrophobic particles adsorbing the appropriate amount of surfactant molecules can be dispersed into the SF solution, with the critical concentration of 7 g/L. PCL has thermoplastic properties and it gradually fused into a colloid with increasing temperature, and the fused colloid can wrap in coal from oxygen ingress to retard the self-heating of coal [3]. In the third step (shown in Fig. 2c), there is the PF solution as organic acid is added into the SFP solution. For the fourth step (shown in Fig. 2d), within 30 s of the organic acid injection into the SFP solution, before the surface properties of SFP solution do not change, the aqueous foam must be generated via injecting gas. The final step (shown in Fig. 2e) involves the formation of PFs within 2–3 min of generating the aqueous foams later, and sodium silicate will be converted to silica due to the chemical reaction with the organic acid [30].