Research Article

Study on the Effect of Polysulfide Content on the Micromorphology and Spontaneous Combustion Characteristics of Coal

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This paper aimed to study the effect of the polysulfide content on the micromorphology and spontaneous combustion characteristics of coal, in order to develop more targeted prevention and treatment strategies. To this end, this study selected the method of mixing different sulfides with very low sulfur content raw coal to prepare the coal samples to be tested. Various parameters, such as true density, porosity, micromorphology, and oxygen uptake of the different sulfur samples, were tested. The results reveal that sulfide had a certain expansion effect on the coal body and improved the pore structure of coal, and the porosity increased with the increase of the sulfur content. After adding iron (II) disulfide (FeS2) and iron (II) sulfide (FeS) powder to the original coal sample, the number of fine particles on the surface increased significantly. After increasing the oxidation temperature, the lamellar structure disintegrated, and the massive coal body was broken into several fine particles, which promoted the spontaneous combustion of coal. Polysulfide promotes the low-temperature oxygen absorption of coal and shortens the natural firing period of coal. FeS has a slightly greater effect on increasing the tendency of coal to spontaneously combust and shortening the shortest natural firing period of coal. Before the addition of FeS2 and FeS to the coal samples, the coal production amount was not much different below 80–90°C, and then, the gap gradually widened. Under the same temperature condition of coal, carbon monoxide (CO) production basically occurred first as the sulfur content increased. When FeS2 and FeS were added, the sulfur content of the coal samples was 3 and 4%, respectively, and the production of CO and ethene (C2H4) was the largest. Although the peak areas of aliphatic hydrocarbon, aromatic hydrocarbon, hydroxyl group, and carbonyl group in the coal samples with FeS were different, they all reached their maximum value when the sulfur content was 4%.

1. Introduction

The sulfur content in China’s coal resources varies greatly, ranging from 0.04 to 9.62%. According to the sulfur content, coal resources can be divided into low sulfur coal (<1%), medium sulfur coal (between 1 and 2%), and high-sulfur coal (>2%). The content and distribution of sulfur in coal are closely related to the coal formation age and coal-forming environment [1, 2]. With the continuous expansion of underground mining, I-beams, anchor rods, nets, and other iron-containing materials are widely used, and ferrous sulfide (FeS), which is a combustible product of the corrosion of sulfur and sulfide with iron and its oxides in coal [3–5], has gradually become a common sulfide present in mines. The oxidation of inorganic sulfur in coal produces a lot of heat, promotes the process of spontaneous combustion of coal, and significantly shortens the natural combustion period of coal [6, 7]. In addition, the original hydrogen sulfide (H2S) gas in some coal is also flammable and produces a blue flame when burning [8–10].
The mutual conversion between different sulfur-containing substances is a very complex reaction system. Depending on different factors, such as temperature, oxygen concentration, and environmental pH, whether other substances are involved, different reactions will occur and different substances will be generated [11]. Under certain conditions, various substances can be converted into each other. However, usually, the underground environment of a coal mine is extremely complex, and the chemical composition of the coal body is diverse [12, 13]. Various factors work together to enable the presence of multisulfide in the underground coal body, which has a certain effect on the law of coal spontaneous combustion. The multisulfide complex reaction system has been preliminarily established. As shown in Figure 1, complex reactions of FeS2, FeS, and H2S of coal spontaneous combustion. kX_hel multisulfide complex underground coal body, which has a certain effect on the law of the coal body is diverse [12, 13]. Various factors will enter the pore of the coal macromolecule and gradually condense into Fe(OH)3 micelles to fill the pores, thereby reducing the effective pore volume of the coal particles, ultimately increasing its true density, and reducing its porosity. Also, the greater the sulfur content of coal is, the greater the plugging effect is, and with the increase of the temperature, this effect is more pronounced.

Some Chinese high-sulfur coal mines (Shenhua Wulan Coal Mine, Laoshidian Coal Mine, etc.) once had blue flame and flue gas, but the concentration of carbon monoxide (CO) at the upper corner of the working face did not exceed the standard and was even 0, and the cause of ignition was not completely clear. Therefore, the study of the influence of multiple sulfides (mainly FeS2, FeS, and H2S) on the physical structure and spontaneous combustion characteristics of coal has an important guiding significance for the analysis of the influence of multiple sulfides on the natural combustion law of coal and fire prevention and extinguishing work in the process of high-sulfur coal seam mining.

2. The Effect of Coal Porosity

As a kind of porous medium, there are a lot of pores in the coal body, and the proportion of the pore volume of the total volume of the coal body is the porosity of coal [18]. The porosity of coal has an important effect on the coal-oxygen composite reaction in the low-temperature oxidation stage. The larger the porosity of coal is, the larger the coal surface area involved in the coal-oxygen composite reaction will be, which is more conducive to the coal-oxygen composite reaction. The true density of coal refers to the ratio of the true weight to the true volume of the coal [19, 20]. For the same coal sample, the higher the true density is, the smaller the porosity is, and the two are inversely proportional [21–24].

Coal blocks were crushed and ground into coal samples smaller than 0.2 mm, which were divided into 9 groups with different sulfur contents according to the test scheme and two samples for each group. One part was left untreated, and the other was cooled after 8 hours of oxidation and heating in an air blast high-temperature chamber at 180°C. The true density of coal before and after oxidation was tested according to GB/T23561.2-2009 “Methods for the determination of physical and mechanical properties of coal and rock—Part 2: Methods for the determination of true density of coal and rock,” and the process setup is shown in Figure 2.

The experimental results of the true density test shown in Table 1 and Figure 2 reveal that the true density increases to varying degrees when FeS2 and FeS are added to the original coal samples before the increase of the oxidation temperature. With the increase of the sulfur content, the true density increases and the porosity decreases. The experimental results of the true density test shown in Table 1 and Figure 3 reveal that the true density increases to varying degrees when FeS2 and FeS are added to the original coal samples before the increase of the oxidation temperature. With the increase of the sulfur content, the true density increases and the porosity decreases. With the same sulfur content, the true density of the coal samples with FeS is higher than that with FeS2. This is due to the high porosity of the coal, with many pores on its surface and inside, and also that the added sulfide is solid powder, so the addition of sulfide reduces the number of pores in the coal sample per unit mass, while the added FeS mass is greater than that of FeS2 with the same sulfur content.

The results in Table 1 and Figure 2 also reveal that the change rule of the true density and porosity of coal samples after oxidation and heating is basically the same as that before heating. In the process of oxidation and heating of a coal sample, ferrite compounds react with oxygen and release heat. Ferric hydroxide (Fe(OH)3), one of the reaction products, will form a sol in the presence of water, with a particle radius of between 10^{-7}−10^{-5} cm, and a pore radius of the coal macromolecule of 10^{-5} cm. Thus, the Fe(OH)3 sol will enter the pore of the coal macromolecule and gradually condense into Fe(OH)3 micelles to fill the pores, thereby reducing the effective pore volume of the coal particles, ultimately increasing its true density, and reducing its porosity. Also, the greater the sulfur content of coal is, the greater the plugging effect is, and with the increase of the temperature, this effect is more pronounced.

In this test, the coal sample was not humidified, and its water content was the natural water content. If the coal containing sulfur under the shaft is in a humid environment and there is a risk of natural combustion, the effect of sulfur compounds on the reduction of its porosity will be more obvious.

3. The Influence of the Microscopic Morphology of Coal

Scanning electron microscopy (SEM) is usually used to examine the microscopic morphology of substances. In this study, SEM was used to examine the microscopic morphology of coal samples with different sulfur contents before and after heating using a Hitachi S-3400N scanning electron microscope (Hitachi Ltd., Tokyo, Japan). The SEM images of raw coal samples and coal samples with FeS2 and FeS added before and after the increase of the oxidation temperature (the increasing oxidation temperature conditions were the same as those for the true density test) were recorded at a magnification of 10,000x, and the images are displayed in Figures 4–6.

Through continuous observation with a moving lens, representative images with a magnification of 10,000x were selected for analysis.
The images in Figure 4 reveal that the surface of the raw coal sample before and after the oxidation and heating exhibits a lamellar structure, and there is a small pore structure on the surface. After heating, the pore structure on the surface of the raw coal sample expands compared with that before heating, and the cracks increase. The surface of the coal sample is partially oxidized, and the surface of the coal sample is cracked as a whole.

The images in Figure 5 show that after adding FeS₂ powder to the raw coal sample, the microscopic morphology of the coal sample surface changes from that before adding FeS₂. In particular, the number of fine particles on the coal surface increases significantly, and such increase in the number of fine particles increases the contact area between the coal and oxygen, which is conducive to natural combustion. After the oxidation temperature increases, the number of fine particles increases, and...
the original massive area becomes loose. Cracks appear on the surface of both the massive coal and the particles, which sets up the conditions for further accelerated oxidation.

The images in Figure 6 reveal that after the addition of the FeS powder to the raw coal sample, the surface becomes smooth and exhibits an obvious lamellate distribution, and deep cracks are found between each lamellate. After the oxidation temperature increases, the lamellar structure is clearly disintegrated, and the block of coal is broken into numerous fine particles. The thin layer of fine particles loosens the structure of the coal seam and increases the air leakage velocity and oxygen content in micropores, further promoting the spontaneous combustion of coal.
4. The Effect of the Tendency of Coal Spontaneous Combustion

The spontaneous combustion of coal is directly related to the adsorption of oxygen by coal. In this study, the ZRJ-1 briquette spontaneous combustion tester is used to test the influence of the sulfur content on the dynamic oxygen uptake of coal under different temperature conditions. During the experiment, fresh large coal samples were taken, and then, the coal core of 100–150 g was used. The coal was crushed to less than 0.2 mm particles within 20 min, and particles of 0.1–0.15 mm accounted for more than 70% [5–8]. Eight groups of coal samples with a sulfur content of 2, 3, 4, and 5% were prepared by adding FeS2 and FeS, and the raw coal sample was considered to have approximately the sulfur content of 0%. There were 9 groups in total.

The oxygen intake levels of coal samples with different sulfur contents at 30°C shown in Table 2 reveal that with the increase of the sulfur content in the coal sample, indicating that the sulfur content promotes the physical oxygen uptake of coal, with a maximum increase of about 15.33 and 21.90%.

With the increase of the sulfur content of the coal sample, the oxygen absorption, as measured by chromatography, initially increases and then decreases. This finding indicates that within the usual sulfur content range of coal seam, there is a sulfur content value that has the strongest promoting effect on the oxygen absorption measured by chromatography of the coal sample, which has the greatest enhancing effect on the spontaneous combustion tendency of coal. With the same sulfur content, the chromatographic oxygen uptake at 30°C of the coal samples containing FeS is higher than that of coal samples containing FeS2, indicating that the promoting effect of FeS on the spontaneous combustion tendency of coal is slightly greater than that of FeS2 under the same experimental conditions. For the FeS coal sample, the peak value of oxygen absorption is about 4% of sulfur content, while for the FeS2 coal sample it is about 3%.

5. The Effect of the Coal Spontaneous Combustion Mark Gas

The effect of sulfur compounds with different sulfur contents on the generation regularity of the symbol gas of coal spontaneous combustion was studied by a programmed temperature experiment. Fresh large-lump coal samples were shelled, cored, and crushed, and four kinds of coal particles with a particle size of 0–1 mm, 1–3 mm, 3–5 mm, and 5–10 mm were selected to prepare mixed coal samples required for the temperature-programmed characteristic experiment according to the mass ratio of 1:1:1:1. Then, the correct weight of the FeS2 or FeS powder sample was evenly mixed with the coal sample according to the designed sulfur content. Each sample weighed 1,000 g [25, 26]. The prepared coal sample was slowly loaded into the coal sample tank and then placed into the programmed heating furnace. During the experiment, dry air was injected into the coal sample tank at a flow rate of 130 mL/min; then the gas was taken for every 10°C increase and analyzed by gas chromatography.

5.1. Rule of CO Production. CO is the earliest oxidized gas product in the process of coal spontaneous combustion and runs through the whole process. After adding FeS2 and FeS, the change of CO production in coal samples with different sulfur contents with the coal temperature is shown in Figure 7.

The results in Figure 7(a) show that before the temperature of the coal samples with added FeS2 and FeS reaches 80–90°C, there is little difference in the amount of CO produced in each coal sample. Above 80–90°C, the difference gradually increases. Under the same coal temperature condition, the amount of CO produced usually increases first and then decreases with the increase of the sulfur content. In the case of the two additives, when the sulfur content is 3 and 4%, respectively, the coal sample produces the largest amount of CO, the raw coal sample is the smallest, and the rest is between the two, with some staggered overlap, which is basically consistent with the change rule of oxygen intake. Compared with the CO production data with the same sulfur content with different sulfur compounds, when the sulfur content is 2 and 3%, the CO production in the coal sample with added FeS2 is slightly higher than that in the coal sample with added FeS. When the sulfur content is 4 and 5%, the result is the opposite to that obtained when the sulfur content is 2 and 3%. The difference between the two is the largest when the sulfur content is 4%.

5.2. Rule of Ethylene (C2H4) Production. The appearance of C2H4 indicates that the coal spontaneous combustion has entered the accelerated oxidation stage, which is generally used as the index of coal spontaneous combustion. After adding FeS2 and FeS, the C2H4 production of the coal samples with different sulfur contents varies with the coal temperature, as shown in Figure 8. When FeS2 is added, the production of C2H4 is less regular, and the temperature at which C2H4 appears for the first time does not change in the process of programmed heating, which is at 80°C. The C2H4 production of each coal sample with sulfur content is clearly higher than that of the raw coal sample, but their curves overlap at many points. Therefore, under the condition of the same coal temperature, the variation rule of C2H4 production with sulfur content is not clear, but it can be seen that when the sulfur content is 3%, the C2H4 production is the maximum in the whole process.

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<th>Table 2: Chromatographic oxygen intake of coal samples with different sulfur contents at 30°C.</th>
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<td>Sulfide species</td>
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The regularity of \( \text{C}_2\text{H}_4 \) production of the coal samples with added FeS is clearly better than that with added FeS\(_2\), and the overlapping of curves is significantly reduced. The temperature of \( \text{C}_2\text{H}_4 \) in the coal sample with a sulfur content of 4\% was increased to 70°C for the first time, which indicated that it had a significant promoting effect on the spontaneous combustion of coal. At the same coal temperature, with the increase of the sulfur content, \( \text{C}_2\text{H}_4 \) production usually increases first and then decreases, and the \( \text{C}_2\text{H}_4 \) production reaches its maximum when the sulfur content is 4\%.

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6. The Effect of the Shortest Spontaneous Combustion Period of Coal

The shortest spontaneous combustion period in coal experiments refers to the time from coal exposure to air to coal spontaneous combustion, which can better characterize the risk of coal spontaneous combustion [27, 28]. The variation trend of the coal spontaneous combustion period with sulfur content is shown in Figure 9.

The data in Figure 8 show that with the increase of the sulfur content, the coal spontaneous ignition period generally exhibits a decreasing trend, indicating that sulfur plays a promoting role in the natural combustion of coal. In addition, for the coal samples with added FeS\(_2\), the minimum value is 14.23 when the sulfur content is 3\%, and for the coal samples with added FeS, the minimum value is 13.24 d when the sulfur content is 4\%. The promoting effect of the added FeS is greater than that of the added FeS\(_2\). Therefore, in the daily fire prevention work, it is necessary to detect the content and type of sulfur in the coal seam at any time to prevent the occurrence of the natural combustion of coal.

7. The Influence of Distribution of Main Active Groups in Coal

The distribution characteristics of coal samples with different contents of sulfide functional groups and the variation characteristics of each functional group during oxidation are analyzed by \emph{in situ} Fourier transform infrared (FTIR) spectroscopy. Then, the real-time change rule of the groups in the reaction process of coal is obtained, which provides the basis of the microstructure distribution and change for the study of the effect of different sulfides on the distribution of the main active groups in coal [29, 30]. The \emph{in situ} FTIR spectroscopy analysis was performed on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a smart diffuse reflectance accessory, sample reaction tank, temperature control device, gas supply device, and water cooling device, as shown in Figure 10.

The infrared spectra of the functional groups of coal samples with different sulfides in the coal oxidation process that change with time are shown in Figure 11. The chemical activity of coal is determined by its composition and content of functional groups. The content of each functional group in coal can be determined by quantitative analysis of infrared spectra of coal samples. The quantitative analysis method of an infrared spectrum is mainly based on Lambert-Beer law, expressed as follows:

\[
A(\nu) = \log \frac{1}{T(\nu)} = K(\nu)bc,
\]

where \( A(\nu) \) is the absorbance of the sample spectrum at the wavenumber \( \nu \), \( T(\nu) \) is the transmittance of the spectrum of the sample at the wavenumber \( \nu \), \( K(\nu) \) is the absorbance coefficient of sample at the wavenumber \( \nu \), \( b \) is the thickness of the sample, and \( c \) is the concentration of the sample. There are two kinds of
quantitative analysis methods based on Lambert-Beer law: one is based on peak height; the other is based on peak area. The peak area value of the infrared absorption spectrum is less affected by the factors of sample and instrument than the peak height value. Therefore, in this study, the method of peak area is used to quantitatively analyze the content of each functional group in the coal samples.

The peak area values of the main functional groups of the coal samples with different sulfur contents at different temperatures were obtained by the fitting method. As shown in Table 3, the main functional groups in the coal structure include aromatic hydrocarbons, aliphatic hydrocarbons, and various oxygen-containing functional groups (mainly hydroxyl and carbonyl groups).

The peak area of aliphatic hydrocarbon and aromatic hydrocarbon of the FeS coal samples generally increased first and then decreased with the sulfur content, while the peak area of the hydroxyl and carbonyl groups decreased first and then increased, reaching its maximum value when the sulfur content was 4%. With the addition of FeS\(_2\), the peak area of the aliphatic hydrocarbon increased first and then decreased with the sulfur content, the peak area of the aromatic hydrocarbon increased first and then decreased with the sulfur content, and the peak area of the hydroxyl

Figure 8: Ethylene (C\(_2\)H\(_4\) generation) rules of coal samples with different sulfur contents in the process of programmed heating (a) with FeS\(_2\) and (b) with FeS.

Figure 9: The variation trend of the shortest spontaneous combustion period of coal with the sulfur content.
and carbonyl groups increased first and then decreased, reaching its maximum value when the sulfur content was 4%.

8. Conclusion

From the study of the effect of various sulfides on the physical structural properties of coal, such as porosity and microstructure, as well as its spontaneous combustion tendency, spontaneous combustion mark gas, and spontaneous combustion period, the following conclusions are drawn:

(1) Sulfide can expand coal and improve its pore structure. The true density decreases with the increase of the sulfur content, while the porosity

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(1) Sulfide can expand coal and improve its pore structure. The true density decreases with the increase of the sulfur content, while the porosity
of the sulfur content, oxygen uptake increases first and then decreases, and there is a sulfur content level that enables the coal to have its maximum oxygen uptake value. It is preliminarily determined that the optimal sulfur content of the spontaneous combustion of coal samples with the addition of FeS$_2$ and FeS is 3% and 4%, respectively. Under the same coal temperature condition, the CO production of the coal samples increases first and then decreases with the increase of the sulfur content.

When there are two kinds of additives with a sulfur content of 3% and 4%, respectively, the coal sample produces the largest amount of CO, and the law of CO generation is basically consistent with the change law of oxygen intake. The C$_2$H$_4$ production of the coal samples with various sulfur contents is greater than that of the raw coal samples, and there are many overlapping points. When the sulfur content of the coal samples with FeS$_2$ and FeS is 3% and 4%, respectively, the C$_2$H$_4$ production is the largest.

Sulfur promotes the spontaneous combustion of coal, and the effect of adding FeS$_2$ is greater than that of adding FeS.

The peak area of the aliphatic hydrocarbon and aromatic hydrocarbon of FeS$_2$ coal samples generally increased first and then decreased with the sulfur content, while the peak area of the hydroxyl group and carbonyl group decreased first and then increased and reached the maximum value when the sulfur content was 4%. With the addition of FeS$_2$, the peak area of the aliphatic hydrocarbon increased first and then decreased with the sulfur content, the peak area of the aromatic hydrocarbon increased first and then decreased with the sulfur content, and the peak area of the hydroxyl and carbonyl groups increased first and then decreased, reaching its maximum value when the sulfur content was 4%.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there are no conflicts of interest.

References


