Effects of Moisture and Associated Pyrite on the Microstructure of Anthracite Coal for Spontaneous Combustion

Cai-Ping Wang, Nan-Nan Yang, Yang Xiao,* Zu-Jin Bai,* Jun Deng, and Chi-Min Shu

ABSTRACT: To explore the micromechanism of the structural changes of anthracite due to heat accumulation by water and pyrite, during oxidation, anthracite with coal samples was selected in this work from Baijiao Coalmine, Sichuan, China. The samples were added with water of 1, 5, 10, 15, and 20 mass % and pyrite of 1, 2, 4, and 6 mass % and were conducted to experimented torts. As compared with the raw coal sample, the effects of water and pyrite on the microstructure of anthracite were studied. The results indicate that the oxygen-containing functional group of coal increases with the addition of water. The content of the aromatic structure in coal was thought to be due to water and pyrite synergistic effects. The synergistic effect of water and pyrite accelerates the oxidation process of seven types of active groups in coal samples. The water content was 10–15 mass %, and the associated pyrite content was 2–4 mass %; the contribution to the oxidation activity of the main active groups of coal was the largest under oxidizing conditions.

1. INTRODUCTION

Under the conditions of high humidity, the reaction of the surface-active groups and the associated pyrite in anthracite produces Fe(OH)$_3$ colloids$^{1,2}$ that adhere to the coal surface, which causes coal porosity to decrease and heat dissipation capacity to weaken. The heat released in the reaction process is continuously gathered, causing coal to reach the self-ignition point under certain conditions, which leads to the occurrence of fire.$^{3,4}$ Therefore, approaching the effect of high sulfur content and high humidity conditions on the microstructure of anthracite is an urgent scientific issue to be solved. Therefore, it is necessary to study the microscopic mechanism of coal spontaneous combustion.

In a humid environment, the change of coal porosity leads to certain changes in the microstructure of coal.$^{5-8}$ The main characteristics of coal spontaneous combustion were changed in the microscopic mechanism.$^{9-11}$ The change trend which affected the microstructure was mainly the evolution of aromatics$^{6,8}$ by extracting the internal and external moisture content of coal; the evaporation temperature of internal water was higher than 100 °C, and the evaporation loss of external water was usually 40–50 °C.$^{12}$ Therefore, the water content of the coal sample obtained by soaking was the external water, and the water affects the coal oxidation reaction temperature at 30–70 °C.$^{13}$ Onifade and Genc$^{17}$ showed that water was the main factor affecting coal spontaneous combustion. Li et al.$^{18}$ concluded the effects of external moisture for coal spontaneous combustion with the promotion of 0–9% as well as the inhibition of 9–25%. In terms of microstructure, the number of −OH and C=O groups of coal samples, and side-chain lengths, was enhanced with increasing water.$^{19}$ Under the action of water, the content of hydroxyl and aromatic hydrocarbons in coal increased significantly and the temperature at which fat-based and oxygen-containing functional groups participate in the reaction decreased.$^{20,21}$ Song et al.$^{22}$ studied the effect of soaked time on the low-temperature oxidation process of coal, and the soaked time was directly proportional to the concentration of free radicals and the amount of CO generated and inversely proportional to the activation energy of the coal sample; proper water can promote spontaneous combustion of coal.$^{23,24}$

Sulfur exists in coal in the form of pyrite, sulfate, and organic sulfur, among which pyrite has the greatest impact on coal spontaneous combustion.$^{25}$ Deng et al.$^{26}$ found that under the separate action of different microstructure contents and pyrite, low-temperature oxidation can enhance the apparent activation energy of coal. Meanwhile, Zhang et al.$^{27}$ concluded that Fe$_2$O$_3$ and C can form (Fe, C), which then caused the crushing and erosion of the coal surface wall. Pyrite changed the coal structure by activation energy shift, and apparent activation energies of the coal samples declined with higher pyrite contents. Pyrite promotes the interaction between water vapor...
and carbon and enhances the rate of gasification reactivity by inhibiting the growth of heavy aromatic structures, catalyzing the graphitization process, and enhancing the surface chemical properties. Therefore, the spontaneous combustion of coal can be promoted by pyrite.28−30 Li et al.31 found that pyrite has the greatest influence on the spontaneous combustion of coal under the action of water. Because the pyrite oxidation reaction consumes water, there was a mutual effect of accelerated heating as less heat was used up in water evaporation.32 During the reaction, the content of the main functional groups in coal changes.33,34 At present, most of the effects that existed on pyrite and water on coal spontaneous combustion are based on the single-factor effect to study the occurrence and development of coal spontaneous combustion. This article aims at studying the synergistic effect of different proportions of pyrite and water, through studying the changes of the coal microstructure, and then ascension of the elaboration of the coal spontaneous combustion mechanism. The research results could provide inhibiting effects from the microscopic view and the theoretical basis for anthracite spontaneous combustion. It has an important scientific value and a practical guiding significance for further research on the prediction and scientific prevention and control of spontaneous combustion of high-sulfur anthracite.

2. RESULTS AND DISCUSSION

2.1. Microcrystalline Structure of Samples. Using X-ray diffraction (XRD) and MID Jade software to analyze the crystalline structure, the XRD patterns of the coal samples with different water contents were obtained, as shown in Figure 1.

![XRD atlas of coal samples with different water and pyrite contents](image-url)

Figure 1. XRD atlas of coal samples with different water and pyrite contents: (a) 1 mass % water, (b) 5 mass % water, (c) 10 mass % water, (d) 15 mass % water, and (e) 20 mass % water.
The XRD spectra of each sample show certain regularity. The 002 and 100 diffraction peaks exist in the range of 2θ = 20–30 and 40–50°, respectively. S represents the area corresponding to the diffraction peak, and it is the intensity of the diffraction peak. According to the analysis of the diffraction spectrum, a peak appears on the left side of the 002 peak. This peak has a different shape from the 002 peak and is asymmetric around the 002 peak. The reason is believed to be due to the saturated lipid chain or lipid in the coal structure. In these samples, the 002 diffraction peaks appear to be upright and tend to be symmetrical. The 100 diffraction peak is generally considered to be formed by the degree of condensation of the aromatic ring and can reflect the size of the aromatic ring carbon mesh layer. The influence of minerals on the spectrum is mainly manifested as spikes in other positions in XRD. Because the aromatic microcrystalline structure present in different coal samples is destroyed by Fe(OH)_3 produced by pyrite and water, the position and intensity of the peaks are similar and different. When the water content was 1 mass %, the XRD patterns of the pyrite coal samples with different contents showed the same diffraction peak. There was a difference in the peak position and peak intensity, and the main structure of the peak had not changed significantly. It shows that the addition of different pyrite contents did not have a significant effect and cannot change the microcrystalline structure of the coal samples. Meanwhile, the XRD curve of the coal samples with different water contents also showed the same regular diffraction peak spectrum. It shows that the different water contents had little effect on the microcrystalline structural properties of the coal sample.

There are aromatic microcrystalline structures in coal, which can be compacted or dispersed. Generally, the parameters of aromatic layer spacing d_m, stacked height L_c, and effective stacking aromatic sheet M_e were used to characterize the structural characteristics of the aromatic crystallites and are calculated as follows38

\[
d_m = \frac{\lambda}{2 \sin \theta_{002}} \quad (1)
\]

\[
L_c = \frac{K_a \lambda}{\beta_{002} \cos \theta_{002}} \quad (2)
\]

\[
M_e = \frac{L_c}{d_m} \quad (3)
\]

where \( \lambda \) is the X-ray wavelength, and the copper target is 1.540 Å; \( \theta_{002} \) and \( \theta_{100} \) are the Bragg angles corresponding to the 002 and 100 peaks (°), respectively; \( \beta_{002} \) and \( \beta_{100} \) are the half-width heights corresponding to the 002 and 100 peaks (rad), respectively; and \( K_1 \) and \( K_2 \) are the crystallite shape factors, with \( K_1 = 1.84 \) and \( K_2 = 0.94 \).

The coalification degree P is used to describe the percentage of condensed aromatic layer rings in coal as well as determine the relative content of the aromatic layer and fat layer stacking structures and is expressed as follows (d_m is 3.975 × 10^{-7} nm)

\[
P = \frac{3.975 - d_{002}}{3.975 - 3.345} \times 100\% \quad (5)
\]

where \( P \) is the degree of coalification and \( d_{002} \) is the layer spacing of the aromatic layer (×10^{-7} nm).

By smoothed and data processing of the map through Jade 6.0, the microcrystalline structural parameters of the coal samples with water contents of 1, 5, 10, 15, and 20 mass % were obtained. The calculation results and change trend are shown in Figure 2.

**Figure 2.** Microcrystalline structural parameters of coal samples with water contents of 0, 1, 2, 4, and 6 mass %.

Under the same water content, the effects of different proportions of pyrite on the microcrystalline structure of coal were compared. Taking the 5 mass % water content as an example, the layering interval \( d_m \) of the aromatic lamina generally increases with the increase of the pyrite content. However, the variation ranges of the elongation \( L_c \), effective stacked number of aromatic tablets \( M_e \), and coalification degree \( P \) were small. The content of aromatic structures was the highest in the sample of W5P4, but the overall change was small. The results showed that the addition of pyrite had little effect on the aromatic microcrystalline structure of the coal samples. In W1P6, the aromatic content of the coal sample was high, while the W5P4, W10P6, W15P0, and W20P4 coal samples had the highest aromatic structure contents. However, the overall change of the aromatic microcrystalline structures of the coal samples was not obvious. Furthermore, the water content in this range had little effect on the aromatic crystalline structure of coal.

Under the same conditions of pyrite contents, the effects of different proportions of moisture on the microcrystalline structure of coal were compared. Taking the pyrite content of 2 mass % as an example, the interlayer spacing \( d_m \) of the aromatic layers in coal decreased, while the stacked height \( L_c \) fluctuated. The content of aromatic structures in the sample gradually increased, whereas the content of fat structures gradually decreased. However, the overall change was relatively small, indicating that there was no significant change in the coal sample microcrystalline structure. In W20P0, W10P1, W20P2, W20P4, and W10P6, the content of aromatic structures in the sample was the largest, but the overall change was small. Therefore, the content of pyrite had little influence on the aromatic microcrystalline structure of coal. The maximum effects of the different water and pyrite contents on the microcrystalline structure of coal samples are listed in Table 1.

The influence of the different water and pyrite contents on the microcrystalline structure of the coal samples was found to be insignificant, and the mineral composition had not changed.
The addition of different water and pyrite contents had different effects on the structural parameters of the aromatic microcrystals of the sample. When the content of pyrite was 6 mass % and the water content was 10 mass %, the aromatic structure content in the sample was the highest. In summary, the influence of water and pyrite on the microstructure of coal is derived from the pore structure, aromatic microcrystalline structure, and fatty structures.

### 2.2. Evolution Behaviors of Reactive Groups

Through the Fourier transform infrared (FTIR) spectroscopy experiment, the infrared spectra of the experimental coal samples under the influence of different water and pyrite contents were obtained, as shown in Figure 3. At room temperature and with the increase of the water and pyrite contents, the hydroxyl groups such as $–\text{OH}$ shifted, and elements such as Fe and S in pyrite greatly influenced the groups of $1300–400$ cm$^{-1}$. Figure 4 shows the infrared spectra of the W20P4 and W5P4 coal samples during the oxidation process. The infrared spectrum is mainly manifested as a variety of substituted aromatic hydrocarbons with peak positions at $700–900$ cm$^{-1}$, methylene groups at $1439–1449$ cm$^{-1}$, aromatic ring C=C structures at $1599–1605$ cm$^{-1}$, free hydroxyl at $3684–3697$ cm$^{-1}$, and intramolecular hydrogen bonds at the positions of $3624–3613$ cm$^{-1}$. The strength of chemical groups increases or decreases, and the peak position shifts. During the oxidation of coal, because of oxygen participating in the reaction, the content of different chemical groups varied, the apparent activation energy changed, and the oxygen consumption increased with the increasing temperature.

### 2.2.1. Aromatic Hydrocarbons

It can be found from Figure 3 that the aromatic hydrocarbons of the experimental coal samples were mainly distributed in the intervals of $1594–1599$ and $900–700$ cm$^{-1}$. Combined with the crystal structure analysis using XRD, it was shown that affected by water and pyrite, the aromatic ring of the aromatic structure in the coal molecule significantly changed, and the stability was affected. Additionally, from Figure 4, it was concluded that during the low-temperature oxidation of coal, when the temperature rose, the aromatic microcrystalline structure formed, and the specific surface area increased. In the infrared spectrum, a variety of substituted aromatic hydrocarbons from $700$ to $900$ cm$^{-1}$ were mainly located on the aromatic nuclei of $756$ cm$^{-1}$, the number of type III hydrogen atoms on the aromatic nucleus, and the intensity of the absorption peak of each coal sample exhibited an overall increasing trend with the increasing temperature. The higher the temperature, the slower the increasing rate tended to be. As water increased, the temperature required to reach the maximum value gradually decreased. As the water content reached $20$ mass %, with the increase of temperature, the absorption peak intensity of the type IV hydrogen atoms of the coal samples showed a downward trend. Within the ranges of $0.0034–0.0249$, $0.0223–0.0213$, $0.0330–0.0368$, $0.0551–0.0168$, and $–0.0472$ to $–0.0435$, the contents of water and pyrite were below 15 and 4 mass %, respectively, and their effect on the type IV hydrogen atoms was greater. In W15P4, the oxidation promotion effect was maximized. In W20P6, the promotion effect was not apparent, and the consumption of the reaction was greater than the production. It was shown that the water contents were too high, and the water complex produced by coal and water interacted with Fe(OH)$_3$, produced by pyrite, which reduced the number of class IV hydrogen atoms on the aromatic core. As the abrupt temperature point of the absorption peak of each coal sample reached the lowest in W15P4, it played a certain role in promoting the oxidation process of the type IV hydrogen atoms.

#### 2.2.1.2. Type III Hydrogen Atoms

Figure 5b shows a graph of the intensity change of the type III hydrogen atoms on the aromatic nucleus at $810$ cm$^{-1}$. It can be found that the intensity of the absorption peak of the type III hydrogen atoms of each coal sample showed an overall increasing trend with the increase of temperature. The changes in the intensity of the type III hydrogen atoms were within the ranges of $–0.0208$ to $+0.001$, $–0.007$ to $–0.0036$, $0.0214–0.0212$, $0.0045–0.0035$, and $–0.0299$ to $–0.0164$; taking the 10 mass % water content as an example, with the increase of temperature, the accumulation of heat accelerated the generation of type III hydrogen atoms, which participated in the oxidation. At the water content of $20$ mass %, the consumption of type III hydrogen atoms in the pyrite-containing coal samples was greater than the amount of production, inhibiting the generation of type III hydrogen atoms. The water contents were below $15$ mass %, and the different contents of pyrite synergistically interacted; the promotion of the generation of type III hydrogen atoms was greater and reached a maximum in W15P2. In W20P6, the consumption of the oxidation reaction was greater than the generated amount. This indicates that the water and pyrite contents were too high, and the number of type III hydrogen atoms on the aromatic nucleus decreased. In addition, W10P2 had the lowest abrupt temperature point of the absorption peak of each coal sample.
which had a certain role in promoting the oxidation process of type III hydrogen atoms.

2.2.1.3. Type I Hydrogen Atoms. Figure 5c shows a graph of the intensity change of the type I hydrogen atoms on the aromatic nucleus of 872 cm$^{-1}$. It shows that the changes in the strength of each coal sample during the heating and oxidation processes were in the range of $-0.0323$ to $-0.0092$, $-0.0171$ to $+0.0134$, $0.0229$ to $0.0190$, $0.0180$ to $0.030$, and $0.030$ to $0.0066$; the five coal samples with the largest changes were W15P2, W15P4, W10P6, W15P1, and W10P0, respectively. The water contents were below 15 mass % and the pyrite contents were 6 mass %, and both had a certain effect on the generation of type I hydrogen atoms in W10P2. At this time, this oxidation promotion effect was maximized. By taking the 10 mass % water content as an example, the intensity change of the type I hydrogen atoms became larger with the increase of temperature, implying that when synergistically acting with appropriate pyrite, the generation of type I hydrogen atoms can be accelerated and they participate in oxidation. The peak temperature of the absorption peak of the W10P6 coal sample was 63 °C when it reached the lowest point, disclosing that W10P6 promoted the generation of type I hydrogen atoms at 60 °C. However, after 100 °C, the water and pyrite contents had little effect on the formation of type I hydrogen atoms.
This indicates that there were less active type I hydrogen atoms at 100–200 °C; thus, the oxidation reaction was slow.

2.2.1.4. Structural Change Characteristics of Aromatic Ring C=C. As shown in Figure 6a, the intensity changes of aromatic ring C=C were 1599–1605 cm⁻¹. The aromatic ring C=C structure in each coal sample generally demonstrated a decreasing trend with the increase of temperature, and the decreases in the intensity changes were −0.0194 to +0.0203, −0.0211 to +0.0219, −0.0211 to −0.0216, +0.0056 to −0.0033, and −0.0497 to −0.0465. The five coal samples with the largest changes were W20P2, W20P0, W10P2, W1P4, and W5P4. This illustrates that the aromatic ring C=C participated in the oxidation reaction or decomposition consumption during the low-temperature oxidation of coal, and the consumption was greater than the amount of reaction generated, indicating that pyrite and water as a whole can reduce the number of aromatic ring C=C structures. The water content was below 20 mass %, and the pyrite content was below 6 mass %; the consumption effect on the aromatic ring C=C structure was strong, and in W20P4, the promotion of this effect was maximized. However, it can be seen that the water content was 15 mass %, the effect tended to stabilize, and the influence on the number of aromatic ring C=C structures was small.

2.2.2. Aliphatic Hydrocarbons. Methylene easily participates in the coal–oxygen complex reaction and is one of the
main substances that causes coal spontaneous combustion. Therefore, the variation law of the 1439−1449 cm$^{-1}$ spectrum peak, where methylene is located, was selected for analysis, as shown in Figure 6b.

Overall, methylene in each coal-like aliphatic hydrocarbon decreased with increasing temperature. The reduction intensity changes were within the ranges of $-0.0674$ to $-0.0517$, $-0.0511$ to $-0.0530$, $-0.0262$ to $+0.0228$, $-0.0024$ to $-0.0025$, and $-0.1119$, and the five coal samples with the largest changes were W20P2, W20P6, W10P1, W10P2, and WSP6. Aliphatic methyl can participate in the reaction at a lower temperature to consume a part of the methylene group, indicating that pyrite and water together can reduce the number of fatty hydrocarbon methylene structures. When the water was below 20 mass % and the pyrite was below 6 mass %, the consumption of methylene in the aliphatic hydrocarbons was stronger, and in W20P2, this reaction to promote consumption was maximized.

2.2.3. Oxygen-Containing Functional Groups. 2.2.3.1. Characteristics of Free Hydroxyl Groups. The infrared spectra of 3684−3697 cm$^{-1}$, obtained during the low-temperature oxidation of the experimental coal samples, were analyzed. Meanwhile, the characteristic curves of the free hydroxyl groups of the different coal samples are shown in Figure 6c. In addition, the absorption peak intensity of the free hydroxyl groups of the coal samples generally increased first and then gradually decreased. The changes in the free hydroxyl strengths were in the ranges of $0.0250$ to $0.0197$, $-0.0076$ to $-0.0154$, $+0.0060$ to $-0.0043$, $+0.0023$ to $-0.0149$, and $-0.0472$ to $-0.0435$. The five coal samples with the largest changes were W1P4, W1P0, W1P6, W5P6, and W1P2. This is mainly because the interaction between pyrite and water in the oxidation process would promote the oxidation of certain groups to form hydroxyl groups. The hydroxyl group itself had high activity and reacted with oxygen or alkyl groups in the coal molecules. It caused the hydroxyl content to first increase and then decrease. The water was below 5 mass % and the pyrite was below 6 mass %; the effect on the free hydroxyl was greater, and the water content was 1 mass %; the effect of promoting the formation of free hydroxyl was maximized. It was indicated that a small amount of water and pyrite can accelerate the oxidation rate of free hydroxyl groups, which was helpful to the reaction. An excessively high water content would inhibit the reaction. Therefore, the synergistic effect of water and pyrite on free hydroxyl groups was mutual.

2.2.3.2. Intramolecular Hydrogen Bond Variation Characteristics. The intramolecular hydrogen bonding at the 3624−3613 cm$^{-1}$ position in the infrared spectra of the experimental coal samples during low-temperature oxidation was analyzed, and the changes in the intramolecular hydrogen bond strength of the different coal samples were obtained, as shown in Figure 7.

The intramolecular hydrogen bonds of each coal sample showed a decreasing trend with increasing temperature, and...
the strength reduction amounts were $-0.0294$ to $-0.0515$, $-0.3992$ to $-0.0559$, and $-0.0150$ to $-0.0559$, and within the range of $+0.0660$ to $-0.0636$ and $-0.6177$ to $-0.4570$. The five coal samples with the largest changes were W20P2, W20P6, W15P1, W15P4, and W5P4, indicating that the intramolecular hydrogen bonding with high activity was exceptionally unstable, and could participate in reaction consumption at lower temperatures. Furthermore, it was shown that the synergistic effect of water and pyrite accelerates the consumption of intramolecular hydrogen bonds, which ultimately leads to a decrease in their number.

Compared with other active groups, less energy was required to complete the reaction first, and there was no obvious linearity with the extent of the pyrite and water relationship, but there were stage characteristics. The pyrite and water ($<$20 mass %) contents had a strong effect on the consumption of intramolecular hydrogen bonds, and in W20P4, the reaction to promote this consumption was maximized. When the water increased to 15 mass %, the mutation temperature of intramolecular hydrogen bonding was advanced from approximately 70 to 100 °C, and the reaction rate was accelerated, indicating that the proper amount of water and pyrite can shorten the oxidation history of intramolecular hydrogen bonding. Therefore, the effect of water and pyrite on the hydrogen bonding in coal molecules was mainly reflected before the low-temperature stage of 100 °C, and there was a reaction acceleration critical point with a water content of 15 mass %.

### 2.3. Induction Mechanism.

The study of the coal molecular structure has an important guiding significance for revealing the microscopic mechanism of coal, and by destroying the active groups, interrupting the oxygen chain reaction of coal, and reducing the oxidation exothermal, it can fundamentally prevent the spontaneous combustion of coal. Through XRD experiments, the changes of various parameters of the aromatic layer in coal under different water and pyrite ratios were studied, and they show that the microcrystalline structure of coal has no inherent relationship with water and pyrite. The FTIR experiment was used to characterize the evolution of active groups in aromatic rings, aliphatic hydrocarbons, and oxygen-containing functional groups in coal. Further research, it is inferred that the influence mechanism of water and pyrite on the microstructure of coal is shown in Figure 8. With the increase of water content, anthracite reacted with the associated pyrite at high humidity. First, the coal surface reacted with FeS2, O2, and H2O to release a certain amount of heat, and then, FeSO4 reacted with H2O and O2 to form a Fe(OH)3 colloid, resulting in an increase in the true density and a decrease in the porosity. The released heat quickly traveled throughout in coal, and under the influence of water, methylene of coal would first form a methyl group during the reaction. Finally, C2H2, C2H6, CH4, and other gases predicted were generated. For instance, the reaction generated −OH, which eventually yielded water, continued to function in coal and formed active groups in the type IV, III, and I hydrogen atoms, C═C, CH2, and free hydroxyl −OH, and the intramolecular hydrogen bond −OH was more active. At 30–200 °C, type IV and III hydrogen atom consumption was greater than the quantity produced. Resulting in the 10 mass % water and 6 mass % pyrite contents at 60 °C, the pyrite interactions promote the generation of type I hydrogen atoms. The aromatic hydrocarbon of the methylene partial reaction resulted in a decrease in the methylene content, and a carbon double-bond rupture in response, causing the final carbon double-bond content to decrease and the free hydroxyl content in coal to increase. The intramolecular consumption effect was stronger as the hydrogen bond content decreased, and the reaction process of heat accumulation, the effect of which led to coal spontaneous combustion, releases CO, CO2, and other gases.

### 3. CONCLUSIONS

The ratio range and reaction mechanism of the influence of water and pyrite on coal activity obtained in this paper can provide a theoretical basis for the development of new environmentally friendly barrier materials. The specific results are as follows:

- The synergy between water and associated pyrite was hardly to cause changes in the microcrystalline structure of coal samples, and it was also difficult to affect the types of minerals in coal samples. This also implies that the microcrystalline structure of coal has no inherent relationship with water and pyrite.
- With the water contents of 10–15 mass % and the pyrite contents of 2–4 mass %, a series of synergistic effects between the two are produced. These synergistic effects greatly promote the generation of type IV and III
hydrogen atoms and free hydroxyl groups but inhibit the number of active atoms in the aromatic ring C=C structure and the formation of methylene groups and intramolecular hydrogen bonds.

- The synergy between water and pyrite could increase the number of active atoms, resulting in enhanced oxidation activity of anthracite. In addition, the oxidation activity of the main active groups of coal appears the strongest when the water content is 10–15 mass % and the associated pyrite is 2–4 mass %.

4. EXPERIMENTS AND METHODS

4.1. Sample Preparation. The coal sample selected for the experimental tests was anthracite from Baijiao Coalmine, Sichuan province, China, with the characteristics of high sulfur and high humidity. The coal sample was extracted from the coal core and then sealed, stored, and shipped back to the laboratory. First, anthracite was crushed to a size of less than 200 mesh and divided into 25 parts, each of which had a mass of 100 g. Next, the 25 coal samples were dehydrated. After that, the coal samples were vacuum-dried at 30 °C for 48 h and added sequentially to the different proportions of water required by the experiment for uniform mixing. After sealing, the samples were placed in a cool place for approximately 1 week to allow for water absorption. The experimental coal samples with the external water contents of 1, 5, 10, 15, and 20 mass % could then be approximately obtained.

Pyrite was crushed to a size of less than 0.075 mm. Then, contents of 0, 1, 2, 4, and 6 mass % were added to the experimental coal samples. Orthogonally different proportions of pyrite and coal samples with different proportions of water could get coal samples with different proportions of water and pyrite as follows: W1P0, W1P1, W1P2, W1P4, W1P6, WSP0, WSP1, WSP2, WSP4, WSP6, W10P0, W10P1, W10P2, W10P4, W10P6, W1SP0, W1SP1, W1SP2, W1SP4, W1SP6, W1SP0, W20P1, W20P2, W20P4, and W20P6. W and P represent water and pyrite; industrial analysis and elemental analysis were used to verify the water contents and pyrite contents of the prepared coal sample.

4.2. Coal Quality Analysis. A Vario EL III (Elementar, Frankfurt, Germany) was used to determine the contents of C, H, O, N, and S of raw coal, which were 90.47, 3.21, 1.51, 2.80, and 1.40%, respectively. The contents of water, ash, and the main active groups of coal were 90.47, 3.21, 1.51, 2.80, and 1.40%, respectively. The programmed heating experiment was conducted in an air atmosphere with the flow rate of 100 mL/min, a heating rate of 2 °C/min, a scanning wave number range of 650–4000 cm⁻¹, and a resolution of 4 cm⁻¹. Infrared spectra were recorded when the temperature reached 30 °C, and liquid nitrogen was used for cooling.

4.3. XRD Experiment. An XRD-7000 (Shimadzu, Kyoto, Japan) was used to load coal samples onto an aluminum frame for XRD to obtain the diffraction patterns of the different coal samples using copper–palladium radiation, the continuous scanning mode, a tube pressure of 40 kV, a tube flow of 30 mA, a scanning angle of 2 of 10–80°, and a scanning speed of 4°/min. Finally, the XRD patterns of samples with different water and pyrite contents were obtained.

4.4. FTIR Experiment. In situ infrared spectroscopy was performed using a VERTEX 70 (Bruker, Karlsruhe, Germany) check reflectance infrared spectrometer. At room temperature, to reduce the interference of scattering peaks, the samples were mixed with KBr powder at a ratio of 1:200 to obtain test samples. Then, the samples were tested. The start and end temperatures of the oxidation experiment were 30 and 200 °C, respectively. The synergy between water and pyrite could increase the number of active atoms, resulting in enhanced oxidation activity of anthracite. In addition, the oxidation activity of the main active groups of coal appears the strongest when the water content is 10–15 mass % and the associated pyrite is 2–4 mass %.

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4.3. XRD Experiment. An XRD-7000 (Shimadzu, Kyoto, Japan) was used to load coal samples onto an aluminum frame for XRD to obtain the diffraction patterns of the different coal samples using copper–palladium radiation, the continuous scanning mode, a tube pressure of 40 kV, a tube flow of 30 mA, a scanning angle of 2 of 10–80°, and a scanning speed of 4°/min. Finally, the XRD patterns of samples with different water and pyrite contents were obtained.

4.4. FTIR Experiment. In situ infrared spectroscopy was performed using a VERTEX 70 (Bruker, Karlsruhe, Germany) check reflectance infrared spectrometer. At room temperature, to reduce the interference of scattering peaks, the samples were mixed with KBr powder at a ratio of 1:200 to obtain test samples. Then, the samples were tested. The start and end temperatures of the oxidation experiment were 30 and 200 °C, respectively. The programmed heating experiment was conducted in an air atmosphere with the flow rate of 100 mL/min, a heating rate of 2 °C/min, a scanning wave number range of 650–4000 cm⁻¹, and a resolution of 4 cm⁻¹. Infrared spectra were recorded when the temperature reached 30 °C, and liquid nitrogen was used for cooling.

4. EXPERIMENTS AND METHODS

4.1. Sample Preparation. The coal sample selected for the experimental tests was anthracite from Baijiao Coalmine, Sichuan province, China, with the characteristics of high sulfur and high humidity. The coal sample was extracted from the coal core and then sealed, stored, and shipped back to the laboratory. First, anthracite was crushed to a size of less than 200 mesh and divided into 25 parts, each of which had a mass of 100 g. Next, the 25 coal samples were dehydrated. After that, the coal samples were vacuum-dried at 30 °C for 48 h and added sequentially to the different proportions of water required by the experiment for uniform mixing. After sealing, the samples were placed in a cool place for approximately 1 week to allow for water absorption. The experimental coal samples with the external water contents of 1, 5, 10, 15, and 20 mass % could then be approximately obtained.

Pyrite was crushed to a size of less than 0.075 mm. Then, contents of 0, 1, 2, 4, and 6 mass % were added to the experimental coal samples. Orthogonally different proportions of pyrite and coal samples with different proportions of water could get coal samples with different proportions of water and pyrite as follows: W1P0, W1P1, W1P2, W1P4, W1P6, WSP0, WSP1, WSP2, WSP4, WSP6, W10P0, W10P1, W10P2, W10P4, W10P6, W1SP0, W1SP1, W1SP2, W1SP4, W1SP6, W1SP0, W20P1, W20P2, W20P4, and W20P6. W and P represent water and pyrite; industrial analysis and elemental analysis were used to verify the water contents and pyrite contents of the prepared coal sample.

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