Influence of Temperature Change on the Change Law of Free Radicals in Coal

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ABSTRACT: This study investigates changes in the concentration and types of free radicals in the process of coal heating, first rising and then falling. Hailar lignite, Panjiang bituminous coal, and Yangquan anthracite were selected as coal test samples. The results show that the lignite’s concentration of free radical changes during heating is greater than that of bituminous coal or anthracite. It clearly shows that lignite is more prone to spontaneous combustion. In the heating and cooling portion of the experiment, the concentration of free radicals during the cooling process was much more than that of free radicals at the same temperature during the heating process. These results obtained from this research study can provide a reference for the prevention and control of the spontaneous combustion of coal with changes in temperature. This study provides a theoretical basis for the prevention and control of spontaneous combustion of coal and the selection of retarding agents and methods in the process of flame retarding by testing the free radical changes of coal at different temperatures. Also, it provides a reference for preventing and controlling coal oxidation with the change in temperature, first rising and then falling.

1. INTRODUCTION

The spontaneous combustion of coal has a serious impact on safe mining and also generates a large amount of harmful gases, such as CO, SO₂, NO₂, CO₂, and H₂S. The harmful gases not only cause serious pollution to the atmospheric environment by forming large-scale acid rain and contributing to the greenhouse effect but also directly endanger the health of humans and other creatures. In recent years, with the development of testing techniques and analysis, research on the mechanism of the spontaneous combustion of coal has made progress. Scholars internationally have come up with theories about the mechanism of coal spontaneous combustion, such as the free radical reaction theory, the electrochemical action theory, the hydrogen effect theory, the base group action theory, the gradual self-activation reaction theory, and the coal oxygen complex action theory.

Using thermal balance analysis, Oreshko confirmed that the oxidation process of coal is composed of four periods and measured and calculated the activation energy in the four periods of the oxidation reaction, showing that the activation energy is the lowest in the first period (57–87 °C) and the highest in the fourth period. Qi et al. analyzed the reaction sequence and thermal properties of aliphatic hydroxyl groups in the coal self-heating process and showed that there were three types of aliphatic alkyl reactions, including oxygen capturing hydrogen, the reaction between aliphatic alkyl groups and hydroxyl groups, and the reaction between aliphatic alkyl groups and oxygen. Wen and Dai held that the thermal oxidation effects of coal are mainly determined by the active molecule species, the quantity of active molecules, and the spatial structure of the coal surface. The research of Ge and Li suggests that after the coal is oxidized at less than 200 °C, the methyl group, methylene, and other side chains of aliphatic hydrocarbons react with oxygen, leading to an increase in oxygen functional groups and a higher proportion of aromatic components. When the temperature is below 200 °C, the aromatic nucleus does not participate in the oxidation. Xu et al. and Qiu et al. have studied the thermal effects of the oxygen functional group of coal during the spontaneous combustion process. Their results suggest that the decomposability of the oxygen functional group of coal is essential to heat generation early in the process of spontaneous combustion. The coal is not oxidized in this period. It is explained that the temperature of coal rose slowly in the initial stage of spontaneous combustion.
Based on the macromolecular structure of coal, Li proposed the free radical reaction mechanism at room temperature, 20 °C. Coal and oxygen have a combined reaction that generates heat, leading to the spontaneous combustion of coal. The coal breaks under the action of an external force, contributing to a large number of cracks and leading to the molecular fracturing of the coal. This fracturing of the coal results in a fracture of the covalent bond, generating many free radicals on the surface of the coal particles and a cracked surface inside the coal, providing the conditions for natural coal oxidation and finally contributing to the spontaneous combustion of the coal. Based on research on the features of free radical reactions, Li also proposed restraining free radicals by adding diphenylamine to restrain the natural oxidation of coal. The mechanism of free radical reactions reveals the chemical process of the combination of coal and oxygen and explains why CO, CO₂, alkane, olefine, alcohol, aldehyde, and other gases are generated at the beginning of the spontaneous combustion of coal. Many scholars study free radicals in coal. Liu et al. have studied the influence that grain size, UV irradiation, and pyrolysis temperature have on the stability of free radicals in coal. The results show that comminution, pyrolysis, and UV irradiation are all effective ways to cause free radicals. Ultrafine comminution has a large influence on the aromatic hydrocarbon radical groups, and UV irradiation can promote the formation of σ-type oxygen free radicals. Wang and Tian have researched the relationship between free radicals, apparent activation energy, and functional groups during the oxidation of coal at less than 120 °C. The results show that hydroxyl related to phenol and alcohol and carboxyl and the double bonds in the aromatic ring have a great influence on the concentration of free radicals. He et al. researched the behavior of free radicals during the process of extracting three kinds of coal solvents. The results show that a decrease in the free radical concentration is attributed to the coupling of free radicals dissolved from the coal at 75 °C. In addition, at a high temperature, an increase in the free radical concentration is attributed to the cracking of weak bonds in coal. Liu et al. researched the free radicals and the bond-cracking behavior during the pyrolysis of coal and found that the quantity of stable free radicals in coal increases with an increase in C %. Qiu and Ikoma have researched the reaction between free radicals, functional groups, and the emission of the index gas CO during the spontaneous combustion of coal. Based on the free radical theory of the spontaneous combustion of coal, it was found that the carbonyl group is the direct active radical group that generates CO during oxidation from 30 to 230 °C. Green and Bandara heated different ranks of coal for a long time at the same temperature and observed the variation in the concentration of the free radicals of different coals. The results show that the free radical concentration of a lower-grade coal does not obviously change after the coal is oxidized for a period of up to 6 months, but the free radical concentration of a higher-grade coal obviously increases. Zhou, Yan, and Liu found that during the pyrogenation of coal, the increase in the concentration of free radicals and g-factor value and the decrease in the line width both indicate that coke experiences condensation with an increase in temperature, leading to the loss of oxygen and an increase in aromaticity. At present, the variation in free radicals caused by temperature mainly focuses on periods at different temperatures and lacks deep research on the variety of free radicals in experiments in which the temperature is raised and lowered.

Therefore, this study adopts the method of laboratory experiments combined with theoretical analysis. The concentrations of free radicals, the g-factor value, and linewidth of lignite, bituminous coal, and anthracite during the heating process and during the heating and cooling process were measured in a laboratory. In addition, the experimental results

| Sample Number | Sample Name       | Sample Made In | Industrial Analysis % |
|---------------|-------------------|----------------|----------------------|
|               |                   |                | M_ads | V_ads | A_ads | FC_ads |
| 1             | lignite           | Inner Mongolia| 25.09 | 30.09 | 7.76  | 36.25  |
| 2             | bituminous coal  | Guizhou        | 1.22  | 26.85 | 5.74  | 66.19  |
| 3             | anthracite       | Shanxi         | 1.86  | 9.02  | 17.17 | 71.95  |

Figure 1. ESR spectrum of Hailar lignite from room temperature to 190 °C.
were analyzed. These two processes can provide a theoretical basis for the prevention and control of spontaneous combustion of coal at different temperatures. In addition, a reference for preventing and controlling the coal oxidation with the change in temperature, first rising and then falling, is provided.

2. RESULTS AND DISCUSSION

2.1. Industrial Analysis Experiment Results. In the industrial analysis test, the three kinds of coal have $V_{daf}$ values of 46.02, 28.86, and 9.14, respectively, fitting the quality of each kind. The results of the industrial analysis of the three samples are shown in Table 1.

2.2. Results and Discussion of the Variation in the Free Radicals of the Coal during the Heating Process. 2.2.1. ESR Spectrum Experiment. The three coal samples of Hailar lignite, Panjiang bituminous coal, and Yangquan anthracite were tested at 20 °C intervals from 25 °C (room temperature) to 190 °C. The measured electron spin resonance (ESR) spectra of each sample are shown in Figures 1−3. The main parameters of each spectrum are shown in Table 2.

2.2.2. ESR Spectrum Analysis. 2.2.2.1. Concentration of Free Radicals $N_g$. The free-radical-concentration change curve of each coal sample during the heating process is shown in Figure 4.

It can be seen from Figure 4 that the free radical concentrations of the three coal samples had increasing trends with increasing temperature. Among them, Hailar lignite had the fastest, Yangquan anthracite the second fastest, and Panjiang bituminous coal the slowest rising rate. It is well known that if the free radical generation rate is greater than the loss rate, the free radical concentration increases, and if the free radical loss rate is greater than the generation rate, the free radical concentration decreases. With an increase in temperature in the range of 110−190 °C, the free radical generation rate of the three coal samples was greater than the loss rate. The covalent bonds in the macromolecules were broken and a large number of free radicals were generated. It can be assumed that the coal was free in the process of oxidation and heating. As the temperature increased, the radical reaction rate
increased. The free radical concentration values of the three coal samples increased as the temperature rose from room temperature to 190 °C: Hailar lignite 329.557 × 10¹⁶/g, Yangquan anthracite 31.867 × 10¹⁶/g, and Panjiang bituminous coal 20.485 × 10¹⁶/g. Therefore, the intensity of the free radical reaction during the oxidation and heating process of coal was Hailar lignite > Yangquan anthracite > Panjiang bituminous coal. The result is consistent with previous studies.37 It indicates that Hailar lignite is more prone to spontaneous combustion than Yangquan anthracite or Panjiang bituminous coal.

### Table 2. Main Parameters of the ESR Wave Spectrum in the Heating Process of Different Samples

| variety of coal         | T/°C  | free radical concentration N_g/(10¹⁶/g) | free radical concentration increase/(10¹⁶/g) | g-value | ΔH/mT  |
|-------------------------|-------|----------------------------------------|---------------------------------------------|---------|--------|
| Hailar lignite          | room temperature | 239.099 | 2.00226 | 0.5444 |
|                         | 50    | 257.935 | 18.836 | 2.00208 | 0.5412 |
|                         | 70    | 258.844 | 19.745 | 2.00207 | 0.5554 |
|                         | 90    | 283.127 | 44.028 | 2.00203 | 0.5621 |
|                         | 110   | 354.899 | 115.8  | 2.00197 | 0.6049 |
|                         | 130   | 413.292 | 174.193 | 2.00191 | 0.6186 |
|                         | 150   | 484.337 | 245.238 | 2.00183 | 0.6223 |
|                         | 170   | 518.685 | 279.586 | 2.00166 | 0.6171 |
|                         | 190   | 568.656 | 329.557 | 2.00159 | 0.6314 |
| Panjiang bituminous coal| room temperature | 257.783 | 2.00178 | 0.4771 |
|                         | 50    | 249.837 | −7.946 | 2.00169 | 0.4543 |
|                         | 70    | 248.248 | −9.535 | 2.00161 | 0.4282 |
|                         | 90    | 245.804 | −11.979 | 2.00156 | 0.4187 |
|                         | 110   | 243.285 | −14.498 | 2.00149 | 0.3906 |
|                         | 130   | 250.919 | −6.864 | 2.00142 | 0.3412 |
|                         | 150   | 261.622 | 3.839  | 2.00133 | 0.3049 |
|                         | 170   | 272.501 | 14.718 | 2.00125 | 0.2921 |
|                         | 190   | 278.268 | 20.485 | 2.00117 | 0.2714 |
| Yangquan anthracite     | room temperature | 163.541 | 2.00194 | 0.4443 |
|                         | 50    | 171.794 | 8.253  | 2.00190 | 0.4419 |
|                         | 70    | 175.928 | 12.387 | 2.00184 | 0.4382 |
|                         | 90    | 175.804 | 12.263 | 2.00177 | 0.4245 |
|                         | 110   | 172.709 | 9.168  | 2.00170 | 0.4077 |
|                         | 130   | 172.103 | 8.562  | 2.00162 | 0.3885 |
|                         | 150   | 176.384 | 12.843 | 2.00154 | 0.3619 |
|                         | 170   | 182.533 | 18.992 | 2.00140 | 0.3412 |
|                         | 190   | 195.408 | 31.867 | 2.00137 | 0.3253 |

#### Figure 4. Change curve for the free radical concentration of each coal sample.

#### 2.2.2.2. Value of the g-Factor. The g-factor value is related to the content of free radicals and impurities in the coal. During the heating process, a change in the g-factor value reflects a change in the type of free radicals.38 The g-factor value of the three coal samples changed with temperature, as shown in Figure 5.

#### Figure 5. g-Factor value change curve of each coal sample.

From Figure 5, the g-factor values of the three coal samples show a decreasing trend. The change in the g-factor value reflects a change in free radical types, indicating that the free radical types of the three coals changed during the process of coal heating and oxidation. With the increase in temperature, the free radical reaction not only changed quantitatively but...
may have also changed qualitatively. The g-factor reduction values of the three coal samples in the range from room temperature to 190 °C were lignite 0.00067, bituminous coal 0.00061, and anthracite 0.00057. Therefore, during the heating process, the fluctuation degree of the g-factor value was in the order Hailar lignite > Panjiang bituminous coal > Yangquan anthracite. The Lande factor g represents the location of molecules resonating in the magnetic field, and its value is equal to the free electron spin value ge for electrons without orbital angular momentum. Therefore, the change in the g-factor value reflects the change in free radical species. The more obvious the change in the g-factor value, the more obvious the change in free radical species. The Hailar lignite g-factor value changed greatly, indicating that the free radical species changed greatly during the heating process, while the free radical species change in Panjiang bituminous coal and Yangquan anthracite was relatively small during the heating process. This is because as the degree of coalification increases, the degree of ring condensation increases while the side chain decreases, and the structure becomes denser and more stable. The degree of coalification of bituminous coal and anthracite is relatively high. The basic structural unit is a fused ring, which contains more than a dozen aromatic, hydrogenated aromatic, and aliphatic rings. The units are connected by oxygen bridges, and the structure is relatively dense, so it is not easy for it to fall off to form free radicals. The basic unit of lignite has only one or two benzene rings or alicyclic rings. It contains more oxygen-containing functional groups, side chains, and bridge bonds. The structure is relatively loose. The group or side chain is more likely to fall off during the heating process, and it is easy for it to fall off to form free radicals.

2.2.2.3. Line Width $\Delta H$. If the symmetry of the radial changes, the line width will change accordingly. If the symmetry of the radical increases, the spin–orbit coupling will increase, the spin–lattice relaxation time will increase, and the line shape will change only slightly. Generally speaking, the more complex the structure of the free radical and the stronger the symmetry, the more stable the free radical. The line width of the three coal samples as the temperature was varied is shown in Figure 6.

It can be seen from Figure 6 that, from the perspective of coal types, the line width is in the order Hailar lignite > Yangquan anthracite > Panjiang bituminous coal. The size of the line width is related to the symmetry of the free radicals. The better the symmetry of the free radicals, the smaller the line width. From the change trend, the line width of Hailar lignite increased with increasing temperature, and the line width increased at most by 0.087 mT during the process of heating to 190 °C. The line width of Panjiang bituminous coal and Yangquan anthracite decreased with increasing temperature in the process of heating up to 190 °C. Also, the line width of Panjiang bituminous coal and Yangquan anthracite decreased by 0.2057 and 0.119 mT, respectively. It can be seen from Figure 6 that with the increase in temperature, the direction of the free radical change in lignite was different from that of bituminous anthracite, indicating that the free radical change mechanism of lignite and bituminous anthracite is different. The line width can show the change in the free radical symmetry, which reflects the change in the free radical species. The smaller the line width, the better the free radical symmetry, and the smaller the free radical species change.

The coalification degree of the three coal samples was different. The coalification degree of lignite was the lowest and that of anthracite the highest, which means that the order of carbon content is anthracite, bituminous coal, and then lignite. The structure of the lignite has the most heteroatoms. After the temperature rises, the chain is split, and the types of free radicals formed by lignite become more and more. Bituminous coal and anthracite have the highest carbon content, resulting in fewer and fewer free radicals, so their curves dropped accordingly. The free radicals produced by bituminous coal and anthracite are mainly C, while the free radicals produced by lignite contain other kinds of elements, such as S and P, so its curve went up accordingly.

2.3. Results and Analysis of Free Radical Changes in the Cooling Process after Heating. 2.3.1. Experimental Results. The temperature of Yangquan anthracite and the coal sample was raised from and then gradually lowered to room temperature. The measured ESR spectrum of each sample is shown in Figure 7. The main parameters of each spectrum are shown in Table 3.

2.3.2. Analysis of the ESR Spectrum. 2.3.2.1. Concentration of the Free Radicals $N_f$. The change in the free radical concentration during the heating process and cooling process of Yangquan anthracite is compared and analyzed, and the change curve is shown in Figure 8.

According to Figure 8, the concentration of free radicals did not decrease with the decrease in temperature during the cooling process. On the contrary, in the range of 190–70 °C, the concentration of free radicals still shows an upward trend as the temperature decreases; until it drops to below 70 °C, the concentration of free radicals began to decrease slowly with the decrease in temperature. During the entire cooling process, the concentration of free radicals is much higher than the concentration of free radicals at the same temperature during the heating process. It shows that the free radical reactions in the heating and the cooling processes are not the same. During the cooling process, the free radical reaction does not weaken with the decrease in temperature. In the range of 190–70 °C, the free radical reaction still shows an upward trend, the covalent bonds of macromolecules in coal are broken, and a large number of new free radicals continue to be produced. After cooling, the oxidation reaction of coal continues, which verifies that the oxidation process of coal is irreversible and can also explain why oxidized coal is more prone to spontaneous combustion.
2.3.2.2. Value of the g-Factor. Figure 9 shows the g-factor value change in Yangquan anthracite during the heating and cooling processes. During the cooling process of coal samples, the g-factor value trended upward and did not decrease with the decrease in temperature. Also, the g-factor value was significantly lower than during the heating process. During the entire temperature change process, the types of free radicals changed significantly. As the coal samples were all centered on carbon atoms during the experiment, there can be no problem changing the central atom, so the change in the g-factor value must have been due to a change in the surrounding groups. The oxidation-reduction reaction of coal occurs during the heating process, and different functional groups in the coal combine with oxygen to generate a large number of new free radicals. Therefore, the change in the g-factor value was mainly due to the change in the type of free radicals. During the cooling process, oxygen continued to participate in the reaction and the g-factor value continued to increase, which also indicates that the free radical reaction continued and a large number of new free radicals were generated.

2.3.2.3. Line Width. Figure 10 shows the comparison of the line width $\Delta H$ of Yangquan anthracite during the heating and the cooling process. During the cooling process, the line width gradually increased with the decrease in temperature, which is the
The reaction is still going on. It provides a reference for the temperature. It indicates that while the temperature decreases, the line width gradually increased with the decrease in temperature. The greater degree than during the heating phase.

Free radicals were constantly changing during this process, to a free radicals could continue to react with oxygen. The types of free radical reactions that occurred during the heating and the cooling processes are not the same, and the types of free radicals generated were also different. As the temperature decreased, the free radical reaction continued. The change in the line width is related to the symmetry of free radicals. The better the symmetry of free radicals, the smaller the line width. During the heating process from 50 to 130 °C, the line width continuously reduced. After 130 °C, the line width sharply; during the cooling process, the line width gradually increased. This is because the free radical reaction did not stop when the temperature dropped from the high temperature to room temperature. Moreover, due to the effect of thermal stress during the cooling process of the coal, there was a temperature difference between the surface and the inside of the coal as well as between different parts of the sample, which caused uneven expansion and contraction and thus the covalent bonds of some macromolecules to break and produce new free radicals. After cooling, the newly generated free radicals could continue to react with oxygen. The types of free radicals were constantly changing during this process, to a greater degree than during the heating phase.

During the heating and the cooling process, the concentration of free radicals still shows an upward trend as the temperature decreases, the g-factor value continued to increase, and the line width gradually increased with the decrease in temperature. It indicates that while the temperature decreases, the reaction is still going on. It provides a reference for the prevention and control of the coal oxidation with the change in temperature, first rising and then falling.

3. CONCLUSIONS

In this study, the influence that temperature has on the variation in free radicals during the coal oxidation process at a low temperature was studied using an ESR spectrometer. Hailar lignite, Panjiang bituminous coal, and Yangquan anthracite were selected as the test samples. The temperature was changed to test the status of the free radical variation and to perform theoretical analysis. The following conclusions were drawn:

1. In the heating process, the order of the rate of increase in the free radical concentration was as follows: Hailar lignite > Yangquan anthracite > Panjiang bituminous coal, indicating that lignite is more prone to spontaneous combustion than anthracite and bituminous coal. The g-factor value of the three coal samples in the order of their degree of fluctuation was Hailar lignite > Panjiang bituminous coal > Yangquan anthracite. The g-factor value of Hailar lignite indicates that the free radical species varied greatly during the heating process, while the free radical species of Panjiang bituminous coal and Yangquan anthracite changed relatively little during the heating process. Therefore, the reaction rate of free radicals is related to the coal species.

2. The concentration of free radicals did not decrease with the decrease in temperature, but it was much higher than at the equivalent temperature in the heating process. This verifies that the oxidation process of coal is irreversible. A high concentration of free radicals also indicates that oxidation reactions are more likely to occur and explains why oxidized coal is more likely to spontaneously ignite.

3. According to the g-factor value and line width, the species of free radicals trended upward during the heating process and did not decrease during the cooling process. The analysis shows that the free radical reaction did not stop when the temperature was lowered. Due to the effect of the thermal stress of the coal body during the cooling process of the coal body, local expansion and contraction were uneven. This caused the breaking of new covalent bonds of macromolecules and produced a large number of new free radicals and results in more characteristics than the change in free radicals in the heating stage.

In this study, free radical changes of coal at different temperatures were measured to provide a theoretical basis for the prevention and control of spontaneous combustion of coal. The experiment of heating up and then cooling down provides a reference for preventing and controlling the coal oxidation with the change in temperature, first rising and then falling.

4. MATERIALS AND METHODS

This study measures and calculates the concentration of the free radical $N_g$, the Lande factor $g$, and the line width $\Delta H$ during the spontaneous combustion process, in which the variation in $N_g$ can directly reflect the variation in the free radical concentration, and $g$ and $\Delta H$ can reflect the variation in the variety of the free radicals. These three parameters can be used to comprehensively analyze the variation law of the free radicals during the two processes. The homolytic bond cleavage forms free radicals, which are atoms or radical groups containing unpaired electrons. Therefore, ESR can be used to investigate it by using the electromagnetic spectrum method to focus on magnetic substances containing one or more unpaired electrons. According to the characteristic parameters of ESR, the test samples can be analyzed quantitatively and qualitatively. The free radical concentration $N_g$, the Lande factor $g$, and the line width $\Delta H$ are the main parameters in this experiment.

4.1. Experiment Materials and Instruments. The materials used in the experiment include Hailar lignite, Panjiang bituminous coal, and Yangquan anthracite. The instruments used in the experiment include a GF-A6 type automatic industrial analyzer, a JEOL JES-FA200 ESR.
spectrum (made in 2009) with a signal amplifier, a jaw crusher, 80 mesh standard sieves, 120 mesh standard sieves, Ziplock bags, 5 × 250 quartz test tubes, 0.1 × 100 capillaries, and so forth.

4.2. Experimental Procedures and Contents. 4.2.1 According to the experimental requirements of the electronic spin resonance spectrometer, three kinds of coal samples were taken for crushing. The coal samples with particle sizes between 80 meshes and 120 meshes were put into sealed bags for later use.

4.2.2 Three kinds of 10 g coal samples with particle sizes of 80–120 mesh were put into a GF-A6 automatic industrial analyzer for industrial analysis and testing. We could know the moisture, ash, volatiles, and fixed carbon in the industrial analysis test. According to the results, we calculated the Vdaf values.

4.2.3 A preliminary heating experiment was carried out. The three kinds of 2 mg samples were put into the JEOL JES-FXA200 ESR spectrometer. The spectra were recorded with the microwave power of 1–2 mW, modulation frequency of 100 kHz, modulation amplitude of 0.1 mT, time constant of 0.1 s, magnetic field sweeping rate of 10 mT/min, and the accumulation times of 2–4. The temperature was programmed at 20 °C intervals between normal temperature and 190 °C, and a correlation analysis was performed according to ESR chromatography.

4.2.4 According to the results of the analysis and the above process, the three kinds of coal samples were subjected to heating experiments. The programmed heating was carried out at 20 °C intervals between normal temperature and 190 °C, and a correlation analysis was carried out according to their respective ESR chromatographies.

4.2.5 The Yangquan anthracite coal was assessed during the heating and cooling process, and its free radical concentration, g-factor value, and line width were compared. A correlation analysis was carried out according to its ESR spectrum.

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