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Research Progress on Spontaneous Combustion Characteristics of Coal

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Abstract: Based on coal spontaneous combustion characteristics under different influence differ greatly. The oxidation mechanism of coal is reviewed. The surface active functional groups of coal which influence the spontaneous combustion characteristics of coal were studied. The factors affecting spontaneous combustion of coal were analyzed, including volatile matter, ash, moisture content and metal elements. It provides reference and guidance for further study of coal spontaneous combustion characteristics.

Keywords: Coal spontaneous combustion, Low-temperature oxidation of coal, Influencing factors.

1. Introduction

Coal mine fire would produce smoke and soot, which would affect the work efficiency and health of workers. And coal mine fire would produce large amounts of greenhouse gases, greenhouse gas emissions easily for open-pit coal mine, impact on atmospheric environment, for underground coal mine, gas emissions is not easy, but in the accumulation of roadway, the action of external force would appear deflagration, pouring, gas suffocation accidents, easy to cause the secondary accidents. Some coal mines with high sulfur content would emit a large amount of sulfur oxides after spontaneous combustion, which would cause acid rain and other hazards[1-2].

Moreover, the season has a certain influence on the opencast coal mine. In the season of drought, high temperature and strong wind, fire is more likely to occur. In the process of coal accumulation, the factors caused by these seasons would reduce the evaporation of water in the coal, and fully react with oxygen, saving the heat generated by oxidation. When the heat reaches the ignition point of the coal itself, it would lead to spontaneous combustion[3-4].

Once a coal fire occurs, it is very difficult to extinguish the fire due to the high temperature and ventilation of the roadway. Therefore, preventing coal fire is very important in coal mining and storage[5]. The accident injury caused by fire accident is aggravated, so it is very important to explore the influencing factors of coal low-temperature oxidation process.

2. Theory of Coal Spontaneous Combustion Mechanism

By studying the complex physical and chemical reactions in the process of coal oxidation, many scholars have explored the mechanism of coal oxidation and obtained a variety of hypotheses of coal spontaneous combustion.

(1) Pyrite theory: it was put forward by British scholars Plolt and Berzelius in the 17th century. They believed that the spontaneous combustion of coal was mainly due to the fact that iron disulphide in coal reacted with oxygen and water around to release heat and accumulated enough heat to make coal spontaneous combustion [6,7].

(2) Bacterial causation theory: It was proposed by British scholars Potter and M.c., et al., in 1927, and they mainly believed that coal spontaneous combustion was caused by bacterial fermentation, which made coal generate heat and make coal spontaneous combustion under the condition of continuous heat storage [8].

(3) Phenolic origin theory: It was proposed that unsaturated phenolic compounds in coal are oxidized by oxygen in the air, leading to spontaneous combustion of coal .

(4) Theory of free radical action: It was proposed that when coal is subjected to external force, covalent bond of coal itself would be broken, and when covalent bond is broken, a large number of free radicals would be generated. Free radicals may exist not only on the surface of coal, but also in cracks formed when coal is damaged. These free radicals react with oxygen to cause spontaneous combustion.

(5) coal-oxygen complex theory [9,10] : According to this theory, when the coal sample is completely exposed in the atmosphere, it may react with oxygen in the air, and certain heat would be generated in the reaction. When the generated heat accumulates to a certain extent, the temperature of the coal seam would continue to rise, which may lead to spontaneous combustion of the coal seam. However, not all coal would spontaneously ignite after the oxidation process. This hypothesis has been proved in laboratory and field practice.

Academic experts at home and abroad have done a lot of experiments to explore whether coal spontaneous combustion is related to oxygen. They take the oxygen consumption and consumption rate of coal in the process of spontaneous combustion as the basis, and put forward the coal-oxygen composite theory of coal spontaneous combustion. The Chinese Coal Research Institute put forward the chromatographic oxygen absorption identification method, which determines the difficulty of coal spontaneous combustion by measuring the oxygen absorption of 1g coal under the test conditions by the coal spontaneous combustion instrument. It can be seen from the previous academic research results that the coal-oxygen composite theory has a positive effect on the judgment of the tendency of coal spontaneous combustion, but there is no in-depth explanation of the principle of coal spontaneous combustion in these literatures.

Many scholars have proposed many reaction models based on the action hypothesis of coal samples, such as those proposed by Kam [11], Karsner[12] and Itay[13]. In these

reaction models, they all believe that an important reaction process in the process of coal spontaneous combustion is coal oxidation adsorption reaction.

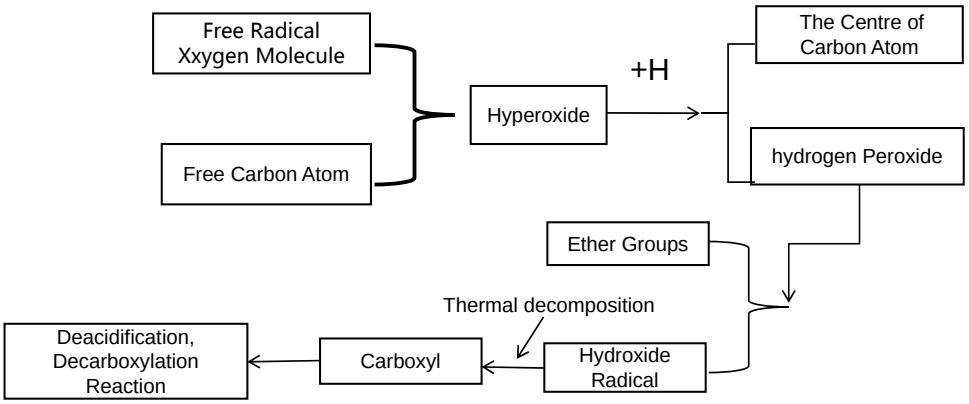

Figure 1. Reaction process of coal oxygen adsorption

3. Study on Surface Active Functional Groups of Coal

Since coal molecular structure was studied by many scholars in the early 20th century, many models of coal molecular structure have been proposed. In these models, there are more or less some differences, but some basic views are consistent, for example: (1) the aggregate composed of aromatic structure is the main structure of coal; (2) The connection mode between aromatic groups and aromatic groups is bridge bond; (3) Many different kinds of chemical structures are connected by bridge bonds, and fatty structures account for a large proportion;(4) the coal structure contains O, N, S and other structures, N mainly exists in heterocycles, and a small part exists in the outer groups of aromatic rings. The oxygen atom groups are mainly in the form of phenolic hydroxyl group, alcohol hydroxyl group, methoxy group, carbonyl group and furanone. The existing form of S, compared with the existing form of N, also exists in the sulfide bond and other structures; (5) there are some small molecular structures in the main structure of coal, which are not closely related to the main body and are called free phase structures. They may be embedded in the main structure, or they may maintain different degrees of weak ties with the main structure of coal by hydrogen bonds or van der Waals forces.(6)The chemical structure of coal contains free radicals with different reactivity, and their types and quantities are different[14].

Researchers at home and abroad have proposed hundreds of macromolecular structure models of coal, and the main research methods include industrial analysis, elemental analysis, nuclear magnetic resonance carbon spectroscopy,X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy (HRTEM) . The industrial analysis and elemental analysis are indispensable methods to explore the coal molecular model[15].

From the perspective of the macromolecular structure of coal, first carries on the determination of industrial analysis and elemental analysis, secondly combining the 13 C nuclear magnetic resonance (NMR) spectrum, X ray photoelectron spectroscopy and Fourier transform infrared spectroscopy analysis results, such as its chemical structure model was constructed. The simulation results show that the model can reflect the structural characteristics of macromolecules well.The chemical structure of coal is relatively complex. Active structures in coal include free radicals and active functional groups, etc. The actual process of coal oxidation reaction also includes the reaction between active functional groups in coal and oxygen and the reaction between secondary active structures[16,17].

Hydroxyl group, carboxyl group, carbonyl group, aliphatic hydrocarbon group, N and S exist as active structures in the functional group structural unit group. The main active reaction front orbitals focus on oxygen-hydrogen bond and C-H bond, which provides the chemical bond basis for the priority reaction for the determination of all reaction sequences of functional group structural unit [18]. Hydroxyl group is the most active oxygen-containing functional group, which is involved in coal-oxygen complex reaction at low temperature. Carboxyl compounds are important transition products of coal-oxygen complex reaction, and the content of C=O also increases greatly in this process. The chemical properties of adipose ether are more active than aromatic ether[19].

The main factor affecting whether coal is prone to spontaneous combustion is the number of active groups involved in the reaction. Different active groups, such as hydroxyl, methyl, methylene, etc., have different oxidation properties [20].

In the coal experienced a long time under the geological action and external force formation, and after these processes still exist in the coal groups belong to the original group. Coal is a macromolecular organic structure. Although the volatile fractions of coal samples with different metamorphic degrees are different, the primary groups exist in the coal body, and their quantities may be different, which are mainly related to volatile fractions [21,22].

The groups in coal are all related to the inherent characteristics of coal, weak transitivity of groups, delocalization of unpaired electrons in aromatic structure and other factors. The primary group can survive because it is in a relatively closed underground environment for a long time and does not have the conditions for oxidation reaction. When mining coal, a large amount of air flows into the underground, and the coal seam is in full contact with oxygen, and the more active groups would participate in the reaction, resulting in the reduction of their number [23].

While the more active groups are reduced, some groups that do not exist originally would be generated, and these groups are called secondary groups. In addition, the transport process by the external influence or reaction with the air formed group also belongs to the secondary group. Secondary

groups mainly include groups with carbon atoms as the center of the structure and heteroatomic groups. The heteroatomic groups are mainly groups with oxygen, nitrogen and sulfur as the center of the structure, as well as a small number of groups containing metal ions.

Table 1. Source of primary group in coal[23]

Variety	Form the Source	Main Way
1	Sedimentary metamorphism,air oxidation or enzymatic action of organic sediments during coal formation	Organic matter reaction generates -COOH, C=O, -OCH_3, -OH, and side chain reaction generates H_2O, CO_2, CH_4, etc. Side chain breaks; Later, other reactions form groups that do not participate in the reaction and survive
2	Chemical bonds undergo thermal cleavage over hundreds of years at 200°C	In the most important form, according to the burial depth and temperature gradient, the coal formation period is often in the metamorphic environment of 200□ or slightly lower, although this temperature is not high, but the chemical bond in this temperature for a long time would occur thermal cracking and form various groups.
3	Chemical bonds in coal are broken by millions of years of natural radiation	Studies have shown that only when high rank coal (C% > 85%) is placed in a radioactive environment, the group concentration in coal would change significantly. There is some debate about whether the chemical bond breaks in coal are caused by radiation

4. Influencing Factors of Coal Spontaneous Combustion

The process of coal spontaneous combustion, the conditions of coal itself have a great influence on coal spontaneous combustion, including the volatile matter, ash and moisture content of coal, etc. In addition, under long-term geological conditions, the associated metal elements in coal would also affect coal spontaneous combustion.

(1) The effect of particle size

The pore structure of coal samples would affect the natural propensity of coal, and the larger the specific surface area of coal, the easier it was to spontaneously ignite[24].

(2) The Influence of Moisture

Due to the complex geological and hydrological conditions of the mine, the mechanism of action of original moisture in coal on coal spontaneous combustion process presented phased characteristics with the development of coal spontaneous combustion process[25].

(3) The influence of minerals

The results show that manganese and iron ions promote the combustion of coal, while calcium and magnesium ions inhibit the spontaneous combustion of coal.The Ca2+ could form complexes with active groups in coal through infrared spectrum and TG results, which increased the activation energy of coal to a certain extent, thus making coal less prone to spontaneous combustion. The manganese ions could promote the generation of free radicals through electron transfer, and phosphorus could inhibit the oxidation of coal by trapping free radicals. In addition, the content of Mn and P in 18 coal fields in China is investigated, and the investigation finds that the coal mine containing more P has fewer spontaneous combustion accidents[26].

(4) The influence of oxidation temperature and time

The temperature rise rate of coal is 0.2, 0.4 and 0.6 ℃/min in the process of low temperature oxidation. When the temperature rise rate is lower, the oxidation activation energy of coal would be smaller and spontaneous combustion would be easier. Besides, compared with the high temperature rise rate, coal would burn more completely and release higher heat in the process. Temperature is one of the main reasons affecting the degree of coal metamorphism. Temperature would cause chemical changes in the aromatic structure of coal, resulting in the reduction of functional groups and bonds, chain shortening and polycondensation, thus increasing the degree of coal metamorphism and making it more stable, and the number of oxygen molecules combined with it would decrease, and the oxygen consumption would also decrease[27].

(5) The Effect of Sulfur Content

The content of some active functional groups in the coal sample with pyrite increased compared with the blank sample. Moreover, the experiment proved that pyrite would accelerate the spontaneous combustion process of coal gradually and promote the spontaneous combustion of coal[28].

(6) The Effect of Oxygen Concentration

The accelerated oxidation stage of coal spontaneous combustion could be delayed by reducing the oxygen concentration, and the critical oxygen volume fraction value of coal spontaneous combustion was 9%. The carbon-oxygen group was the oxidation intermediate functional group of CO generated by low-metamorphic coal oxidation at low temperature by comparing the functional groups of coal samples treated with and without oxygen isolation heating. When the coal rank increased, the coal would be less likely to spontaneous combustion and more difficult to burn out, while when the coal sample of the same rank increased with the oxygen volume fraction, the coal oxygen reaction was more likely to occur. Compared with gas and coal, C2H6 is more sensitive to changes in test conditions. When oxygen concentration changes, the initial temperature generated by C2H6 would also change, so C2H6 can be used as an indicator gas to judge the degree of spontaneous combustion of coal[29].

(7) The influence of coal and rock composition

According to the relevant theories of coal petrology, the macroscopic components of coal include bright coal, dark coal, mirror coal and silk carbon. While silk carbon is the least easily oxidized. However, It is proved through the ignition temperature experiment of coal and rock components that due to the large specific surface area, silk carbon can adsorb more oxygen at low temperature and react most fully with oxygen, so it has a high spontaneous ignition tendency. At the same time, the large holes in the silk charcoal can also provide oxygen channels, which is helpful for the combustion of other components in the coal. It is also found that pyrite is usually included in the silk carbon, which further promotes the oxidation heat release of coal[30].

(8) Influence of ash content

The spontaneous combustion tendency of coal would first

increase and then decrease with the increase of ash content, and the critical ash content was 40%[31].

(9) The effect of volatile matter

The relationship between the quality of coal samples and the production amount of carbon oxides, and found that there were two sources of carbon oxides, namely, the oxygen-containing functional groups in coal and the reaction with coal oxygen.

The number of active functional groups in coal was in positive proportion to the difficulty of coal spontaneous combustion. The spontaneous combustion tendency of coal was related to the content of aryl hydrocarbon C=C-, and when the content of aryl hydrocarbon increased, the spontaneous combustion tendency of coal became weaker. When the relative content of oxygen-containing functional groups -COOH and -OH decreases, the spontaneous combustion tendency of coal becomes weaker[32].

5. Conclusion

There are many influencing factors of coal spontaneous combustion. The results obtained by studying coal spontaneous combustion with a single factor are not comprehensive nor objective.The progress of science and technology and the improvement of the detection level of instruments and equipment provide a guarantee for the in-depth study of the influencing factors and correlation of coal spontaneous combustion tendency. By analyzing different metamorphic degree of coal structure and composition of the basic data itself, probing into the cause of the coal spontaneous combustion propensity to show differences, and analyzes the influence factors on the spontaneous combustion tendency of "contribution value" and the effect of the impact, explore the mechanism of spontaneous combustion, can provide reference for the study of the coal spontaneous combustion and the theory support.

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