Experimental Study on Electro Chemical Catalytic Oxidation Desulfurization of High Sulfur Coal Based on Computer

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Abstract. Coal and other fossil energy has a greater pollution, especially in the process of its combustion will bring a variety of environmental pollution problems, such as sulfur dioxide combustion, which produces more serious air pollution. Therefore, in order to reduce coal pollution, it is necessary to carry out desulfurization treatment before coal combustion. There are many shortcomings and problems in the traditional coal desulfurization methods, mainly in secondary pollution and harsh operating environment. As a mild desulfurization and purification technology, the research value of Electrochemical Catalytic Oxidation Desulfurization (ECOD) is highlighted. Based on this, this paper first analyses the process flow and desulfurization mechanism of high sulfur coal Electrochemical Catalytic Oxidation Desulfurization (EOD) technology, and then studies the ECOD technology of high sulfur coal, and verifies the influencing factors of ECOD of high sulfur coal.

Keywords: Electro Chemical Catalytic, Oxidation Desulfurization, High Sulfur Coal

1. Introduction
With the rapid development of social economy, the demand for energy in all walks of life is increasing, especially the consumption of fossil energy represented by coal[1]. However, coal and other fossil energy have great pollution, especially in the process of its combustion, which will bring various environmental pollution problems, such as air pollution and land pollution caused by coal cinder. Coal contains sulfur in its components, so sulfur dioxide is produced during combustion, which causes serious air pollution. Therefore, in order to reduce coal pollution, it is necessary to carry out desulfurization treatment before coal combustion. There are many methods of coal desulfurization, as shown in Figure 1 below. These different desulfurization methods have different characteristics and application scenarios, so it is necessary to make targeted selection and application based on their use environment.
There are many shortcomings and problems in the traditional coal desulfurization methods, mainly in the secondary pollution, so it is necessary to develop a relatively mild desulfurization and purification technology. With the rapid iterative development of information technology represented by computer, electrochemical catalytic oxidation desulfurization (Short for ECOD) method came into being. Compared with the coal desulfurization method, it has obvious application advantages, which embodies the following aspects. Firstly, ECOD of high sulfur coal can remove a variety of sulfur components, whether inorganic sulfur or organic sulfur can be removed. Secondly, the method has a wider range of application scenarios, such as can be used in less stringent environmental conditions, which can greatly expand its application scope and reduce the application cost, so it can be more and more widely studied. Therefore, it is necessary to further study and analyzes its desulfurization mechanism. At present, the main task is to analyze the mineral composition of coal, the change of mineral element content and electrolyte composition before and after electrochemical treatment, so as to clarify the desulfurization mechanism of high sulfur coal electrochemically catalytic oxidation. In addition, electrochemical desulfurization of high sulfur coal as a low-cost method, low-cost, easy to operate, no pollution, and strong effect, so it has a high practical research value.

2. ECOD of high sulfur coal

2.1. The birth background of electrochemical desulfurization process for high sulfur coal
In the traditional technology of controlling sulfur dioxide from coal combustion, physical desulfurization method is often used. Although the cost of this method is low, its desulfurization effect is poor. In addition, although the former chemical coal desulfurization method can achieve a more significant desulfurization effect, but its application scenarios are more limited, often need to use strong acid, strong alkali and other chemicals under high temperature and high pressure, which is not only high cost but also poor practicability. With the continuous improvement of electrochemical technology and the iterative development of computer technology, electrochemical desulfurization of high sulfur coal has become a relatively new process method, and can achieve relatively mild and low-cost desulfurization.

2.2. Process flow of electrochemical desulfurization of high sulfur coal
The operation environment of electrochemical desulfurization of high sulfur coal is carried out under the condition of mixing water, pulverized coal and additives. Firstly, high sulfur coal is crushed and mixed with water to form coal water slurry, and then it is mixed in the electrolytic cell for electrochemical catalytic oxidation reaction, so as to convert the organic sulfur in high sulfur coal into soluble sulfide. Secondly, the coal after electrochemical reaction is filtered to recover the sulfide in the coal to obtain clean coal. After that, the obtained clean coal is placed in the cathode chamber for electrolysis to produce high-purity hydrogen. The complete process flow of electro-chemical desulfurization of high sulfur coal is shown in Figure 2 below.

![Figure1. Different methods of coal desulfurization.](image-url)
2.3. Process flow of electro chemical desulfurization of high sulfur coal

The electro chemical catalytic oxidation desulfurization of high sulfur coal is based on the electrochemical oxidation reaction of coal slurry in electrolytic cell, so as to remove the organic sulfur in coal, and oxidize it into water-soluble sulfide, and remove these sulfides through filtration, so as to obtain clean coal without sulfur\[2\]. In the process of electro catalytic oxidation desulfurization of high sulfur coal, based on the difference of electrolytes used, the electrochemical oxidation catalytic methods can be further divided into two types: alkaline electrochemical method and acidic electrochemical method.

2.4. Desulfurization mechanism of inorganic sulfur in high sulfur coal

For the inorganic sulfur desulfurization of high sulfur coal by alkaline electrochemical catalytic oxidation, in alkaline medium, sulfur-containing pyrite in high sulfur coal will be oxidized by hydrogen oxygen radicals with high activity, and water-soluble sulfate will be formed, which can be further removed by washing. Figure 3 shows the alkaline electrolytic desulfurization process of pyrite from high sulfur coal.

\[
\begin{align*}
2H_2O & \rightarrow O_2 + 4H^+ + 4e \\
16OH^- + 4FeS_2 + 15O_2 & \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 2H_2O \\
8OH^- + 2FeS_2 + 7O_2 & \rightarrow 2Fe(OH)_2 + 4SO_4^{2-} + 2H_2O
\end{align*}
\]

The electrochemical reactions of the cathode are as follows:

\[
2H^+ + 2e \rightarrow H_2
\]

For the inorganic sulfur desulfurization of high sulfur coal by acid electrochemical catalytic oxidation method, the main desulfurization reaction in acidic medium is oxidation reaction in anode
solution with manganese ion as catalyst\[^3\]. Due to the difference of electrolytic potential, desulfurization reaction is different. The electrochemical reactions in anode solution are as follows:

\[
\begin{align*}
2\text{Mn}^{3+} + \text{FeS}_2 & \rightarrow \text{Fe}^{2+} + 2\text{S} + 2\text{Mn}^{2+} \\
4\text{H}_2\text{O} + \text{S} + 6\text{Mn}^{3+} & \rightarrow 8\text{H}^+ + \text{SO}_4^{2-} + 6\text{Mn}^{2+} \\
8\text{H}_2\text{O} + 15\text{Mn}^{2+} + \text{FeS}_2 & \rightarrow 16\text{H}^+ + \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 15\text{Mn}^{2+}
\end{align*}
\]

The electrochemical reactions on the anode surface are as follows:

\[
\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + e
\]

2.4.1. Desulfurization mechanism of organic sulfur in high sulfur coal

The removal of organic sulfur in high sulfur coal is mainly through oxidation of sulfur in coal by oxidant\[^4\]. Generally speaking, based on the desulfurization mechanism, it is mainly judged by the morphological changes of sulfur forms after electrocatalytic oxidation in acidic and alkaline media. Among them, in the treatment of organic sulfur desulfurization of high sulfur coal in acid medium, the oxidation reaction takes place on the anode surface firstly, which oxidizes the organic sulfur in coal to sulfoxide, and then further oxidizes to sulfone. Sulfone can be dissolved in hot water to form road salt. The whole process of catalytic oxidation can be divided into several stages and processes, such as the increase of oxidation state of sulfur, the shedding of sulfur from macromolecular structure, the oxidation of marginal groups of coal molecular structure and deep oxidation desulfurization. In this process, oxidation and desulfurization of high sulfur coal will occur alternately until complete desulfurization. The oxidation reaction of disulfide compounds of organic sulfur is as follows:

\[
\begin{align*}
8\text{Mn}^{3+} + \text{R} - \text{S} - \text{S} - \text{R} + 4\text{H}_2\text{O} & \rightarrow 8\text{Mn}^{2+} + \text{R} - \text{S(O}_2\text{)} - \text{S(O}_2\text{)}\text{R} + 8\text{H}^+ \\
\text{R} - \text{S(O}_2\text{)} - \text{S(O}_2\text{)}\text{R} + 6\text{H}_2\text{O} & \rightarrow \text{R} - \text{OH} + \text{R} - \text{OH} + 4\text{H}^+ + 2\text{SO}_4^{2-}
\end{align*}
\]

In the process of electrochemical oxidation of coal with high sulfur content, the electrochemical reaction at anode is as follows:

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}
\]

The electrochemical reaction at the cathode is as follows:

\[
4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2
\]

The total electrochemical reactions are as follows:

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2
\]

In the organic sulfur desulfurization reaction of high sulfur coal in alkaline condition, the active oxygen produced by electrolysis anode is used as oxidant to oxidize the organic sulfur in coal to sulfoxide and sulfone\[^5\]. The sulfone is hydrolyzed into sulfonic acid compounds or sulfate radicals which can be dissolved in water under alkaline conditions and hot water. The desulfurization reaction of other organic sulfur compounds in coal is similar to that of disulfide compounds.

2.5. Influencing factors of EOD of high sulfur coal

Generally speaking, the desulfurization rate of EOD of high sulfur coal can reach more than 75% in alkaline electrolytic medium, but it will produce deashing, while the desulfurization rate of inorganic sulfur in acid electrolytic medium is higher than that in alkaline medium, and there is no deashing\[^6\]. In addition, in the aspect of influencing factors of ECOD of high sulfur coal, the main influencing factors include but not limited to sulfur content, composition, particle size, coal slurry concentration,
potential and electrolyte types. In addition, the environmental conditions, such as temperature and time, also have a significant impact on the desulfurization efficiency.

3. Experiment on desulfurization of high sulfur coal by electrochemical catalytic oxidation

3.1. Selection of test samples, reagents and test equipment
The high sulfur coal from high sulfur coal mine is selected as the test sample. The test equipment includes DC stabilized power supply, crusher, mill prototype and vacuum pump. The electrolyzer for electrocatalytic oxidation of high sulfur coal is composed of base and cover. Graphite is used as anode and stainless steel as cathode without diaphragm.

3.2. Experimental process of ECOD of high sulfur coal
Take the coal sample and add it into the electrolytic cell, pour the prepared sodium hydroxide solution, stir it evenly with a mechanical mixer, put it in the water bath pot, turn on the power supply to adjust the temperature of coal slurry, turn on the power supply to adjust the current, and conduct electrolysis. After that, wash the electrode with deionized water repeatedly to neutral, and wash, filter and dry the coal sample after electrolysis for detection and analysis.

3.3. Analysis of experimental results of high sulfur coal desulfurization by electrocatalytic oxidation
Based on the experimental results of ECOD of high sulfur coal, it can be found that the electrolysis process of coal is affected by many factors, such as current, electrolyte concentration, time, coal slurry concentration, coal particle size, electrolysis temperature, etc. The desulfurization of high sulfur coal first increases with the increase of current, then decreases and tends to be stable. The reaction degree of coal on the electrode surface is determined by the electrolysis time, and the desulfurization rate increases with the increase of time, and then tends to be stable. In the aspect of electrolyte concentration, higher concentration can ensure the good conductivity of electrolyte and guarantee the desulfurization rate. In addition, in the coal slurry concentration level, too high concentration will lead to the reduction of stirring efficiency, which is not conducive to improving the desulfurization rate.

4. Conclusion
In summary, electro catalytic oxidation desulfurization of high sulfur coal can remove a variety of sulfur components, both inorganic sulfur and organic sulfur can be removed. Secondly, the method has a wider range of application scenarios, such as can be used in less stringent environmental conditions, which can greatly expand its application scope and reduce the application cost. In this paper, the ECOD technology of high sulfur coal was studied, and the process flow and reaction mechanism of electrochemical desulfurization of high sulfur coal were analyzed. Based on the computer-based ECOD test of high sulfur coal, the influencing factors of ECOD of high sulfur coal were analyzed, and the effects of coal composition, particle size, coal slurry concentration, potential and electrolyte on desulfurization rate were analyzed.

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