Experimental Study on Optimization of Coal Electrochemical Desulfurization Process under Acidic Conditions

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Abstract. The feasibility of using added catalysts and organic solvents to improve the efficiency of coal electrolytic desulfurization was explored based on the study of the optimal electrolytic desulfurization conditions under acidic coal conditions using Shanxi Shigejie coal samples as raw materials.The effects of inorganic catalyst and organic solvent on inorganic and organic sulfur in coal were investigated under the condition of Hcl as the electrolyte, and the changes of sulfur content in coal before and after the experiment were analyzed by Coulometric titration, AAS, GB/T 215-2003, and total sulfur differential subtraction method, and the changes of surface functional groups of organic sulfur model compounds before and after desulfurization were analyzed using infrared spectroscopy to study the mechanism of electrolytic desulfurization of sulfur in coal.Nacl, $Mgcl_2$, $Fe(NO_3)_3$, $MnSO_4$ and $Fe_2(SO_4)_3$ were selected as inorganic catalysts, and DMF, CH_3OH and DMSO were used as organic solvents to compare the desulfurization rates of inorganic and organic sulfur in coal samples before and after immersion and before and after electrolysis, respectively.The experimental results show that under the best electrolytic desulfurization conditions, manganese sulfate can significantly improve the inorganic sulfur removal efficiency, DMF+CH_3OH, DMF organic solvent for immersion desulfurization is not obvious, but the organic sulfur removal efficiency is significant after electrolytic desulfurization.

Keywords: catalyst; organic solvent; desulfurization; mechanism.

1. Introduction

Coal is an important energy resource in China, and the characteristic of coal in China is high sulfur content, high sulfur coal with total sulfur over 2% accounts for 25% of the total coal reserves, among which organic sulfur content accounts for more than 40% of the total sulfur, and the sulfur content in some high sulfur coal even exceeds 70%. In order to reduce the pollutant emission during coal combustion, the desulfurization research of high sulfur coal has been widely concerned by scholars from various countries[1].In the 1970s, Coughglin and Farooque used electrochemistry to remove sulfur from coal. In the research process, it was found that the method of removing sulfur from coal by electrochemistry not only overcomes the disadvantages of traditional chemical desulfurization requiring high temperature and high pressure environment, but also can produce hydrogen at the cathode and reduce production costs. The sulfur in coal mainly includes pyrite sulfur and organic sulfur[2].In 1998, Li Dengxin et al.studied the electrochemical removal of pyrite sulfur from coal under acidic and alkaline conditions, and proposed the reaction mechanism of pyrite sulfur removal from coal under different conditions[3]. In 2002, Cui Ping and Wang Zhicai used Shanjialin washed clean coal as raw material to carry out experiments under acidic and alkaline systems respectively, and analyzed the characteristics of electrochemical desulfurization under different systems[4].

During the experiment, it was found that the addition of catalyst in the electrochemical desulfurization process can effectively improve the desulfurization efficiency. Therefore, the types of catalysts were compared and the mechanism of catalyst action in the electrochemical process was analyzed. In this study, the raw coal of Shanxi Shigejie Mine was used as the experimental sample, and the self-made diaphragmless electrolytic cell was used to carry out the catalyst and organic solvent enhanced electrolytic desulfurization experiment under the condition of acidic electrolyte[5]. The desulfurization efficiency changes before and after the use of the agent were compared, and the effects of different catalysts and organic solvents on the desulfurization efficiency were explored.

2. Experimental part

2.1 Experimental materials

This study is based on the raw coal of Shigejie Coal Mine of Lu'an Group as the research coal sample. Table 1 is the industrial analysis and sulfur analysis of raw coal with particle size less than 0.5mm.

Table 1 Industrial analysis and sulfur analysis of raw coal

Industrial analysis			Sulfur analysis			
Mad /%	Ad /%	Vdaf /%	St,d /%	Sp,d /%	Ss,d /%	So,d /%
1.29	45.01	14.67	4.01	2.79	0.53	0.69

2.2 Electrolytic desulfurization experiment

The effects of different electrolysis conditions on the total sulfur removal rate of high sulfur coal were investigated by using Hcl as electrolyte, Pt as electrode material and no diaphragm type electrolytic cell. In the process of electrochemical desulfurization, the desulfurization rate is affected by various electrolysis conditions, including coal slurry concentration, electrolyte concentration, electrolysis time, current density, electrolysis temperature and coal particle size[6]. The electrolysis conditions are used as independent variables to explain the change of desulfurization rate.The regression model of various factors (including coal slurry concentration, electrolyte concentration, electrolysis time, current density, electrolysis temperature, coal particle size) on the desulfurization rate was established. The regression model results showed that the coal slurry concentration, electrolysis temperature and coal particle size were negatively correlated with the desulfurization rate, and the electrolyte concentration, electrolysis time and current density were positively correlated with the desulfurization rate.The regression model shows that the current density has the greatest influence on the desulfurization rate, followed by the electrolyte concentration. After that, the orthogonal experiment analysis method was used to determine the optimal desulfurization conditions. The electrolyte concentration, electrolysis time, current density and coal slurry concentration were selected as the four factors of orthogonal experiment[7]. Then, three levels were selected according to the optimal desulfurization rate in the corresponding single factor experiment. The four-factor three-level orthogonal experiment $L_9(3^4)$ was listed. Finally, the current density was $0.044A \cdot cm^{-2}$, the coal slurry concentration was $20g \cdot L^{-1}$, the electrolysis time was 4h, and the electrolyte concentration was $0.75mol \cdot L^{-1}$.

In order to verify the optimal electrolysis conditions, experiments were conducted again. The morphological sulfur distributions of the raw coal before electrolytic desulfurization, the coal samples after 4h immersion at an electrolyte concentration of $0.75mol \cdot L^{-1}$ and a slurry concentration of $20g \cdot L^{-1}$, and the coal samples after electrolysis under optimal desulfurization conditions are shown in Table 2.

Table 2 Morphological sulfur distribution of soaked coal samples and electrolytic coal samples under Hcl system

Coal samples	Raw Coal	Coal sample after soaking	Coal sample after electrolysis
Quality/g	5	4.5	4.7
Full sulfur/%	4.01	3.43	0.953
FeS_2/%	2.79	2.66	0.579
SO_4^{2-}/%	0.53	0.16	0.095
Organic sulfur/%	0.69	0.61	0.279

The experimental results show that the organic sulfur and FeS_2 sulfur content of raw coal after soaking treatment are basically unchanged, and the SO_4^{2-} sulfur content has a large removal rate of 69.2%. After electrolytic treatment, FeS_2, $SO_4^{2-}$and organic sulfur have a large removal rate. After electrolysis, the sulfur content in coal samples is low, and the total sulfur removal rate is as high as 76.2%. The reason is that the sulfur in coal is mainly removed by electrochemical reaction in the process of electrolytic desulfurization, and soaking can only remove a small part of SO_4^{2-} sulfur in inorganic sulfur. Compared with the previous experiments, the desulfurization rate was the highest under the optimal electrolysis conditions, so the optimal electrolysis conditions were established[8].

2.3 Effect of inorganic catalyst on desulfurization rate

The sulfur in coal is mainly divided into inorganic sulfur and organic sulfur. It is necessary to carry out the experiment of catalyst enhanced electrolytic desulfurization. The catalyst can improve the desulfurization rate because the catalyst has the effect of oxidant, or can produce active oxides through electrolysis[9]. The catalyst can be oxidized to oxidized ions at the anode. These oxidizing ions oxidize sulfur-containing compounds in coal in the solution. The catalyst itself is reduced to reduced ions, and an redox cycle is formed between the electrolyte and the anode, which is reused and plays the role of electrocatalysis. In this experiment, Hcl was used as the electrolyte, the current density was $0.044A \cdot cm^{-2}$, the coal slurry concentration was $20g \cdot L^{-1}$, the electrolysis time was 4h, and the electrolyte concentration was $0.75mol \cdot L^{-1}$. Under the desulfurization conditions, $0.01mol \cdot L^{-1}$ Nacl, $0.01mol \cdot L^{-1}$ $Mgcl_2$, $0.01mol \cdot L^{-1}$ $Fe(NO_3)_3$, $0.01mol \cdot L^{-1}$ $MnSO_4$, $0.01mol \cdot L^{-1}$ $Fe_2(SO_4)_3$ were added. The effect of inorganic catalyst on electrolytic desulfurization was investigated. The results are shown in Table 3.

Table 3 Desulfurization rate of coal with inorganic catalyst

NO.	Catalyst species/mol·L^{-1}	Desulfurization rate/%
1	Hcl	76.21
2	Hcl+NaCl	76.33
3	Hcl+$MgCl_2$	76.85
4	Hcl+$Fe(NO_3)_3$	75.59
5	Hcl+$MnSO_4$	77.35
6	Hcl+$FeSO_4$	73.32

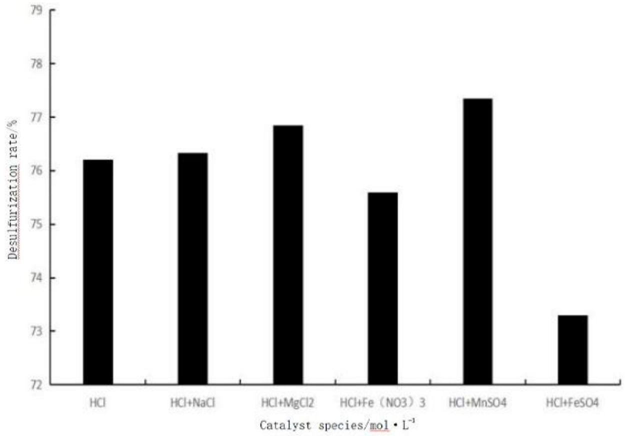


Fig. 1 Desulfurization rate of coal with inorganic catalyst

As shown in Figure 1, the desulfurization rate increased significantly after the addition of manganese sulfate, and the desulfurization rate of coal decreased after the addition of iron nitrate and iron sulfate. The reason was that the main component of inorganic sulfur was FeS_2.After the addition of iron nitrate and iron sulfate, the content of iron ions in the solution increased, which would react with the chemical substances in the electrolyte to affect the electrochemical desulfurization, resulting in the insignificant desulfurization effect after the addition of the catalyst[10].

2.4 Effect of organic solvents on desulfurization rate

In the process of electrochemical desulfurization of coal, the main chemical reaction is carried out on the electrode interface of coal particles, and the sulfur inside the coal particles is not fully removed by the electrolysis process. Although reducing the size of coal particles can improve the effect of electrolytic desulfurization, there are still some organic sulfur in coal particles, such as thioether, thiophenol and thiophene, which are not removed, resulting in a decrease in the removal rate of organic sulfur in coal. Domestic scholars have found that the addition of organic solvents such as methanol, ethanol and acetone, tetrachloroethylene in the process of coal electrolytic desulfurization can improve the desulfurization effect. Organic solvents can extract organic sulfur in coal and improve the desulfurization effect by reducing the chemical bond energy.

Different types of organic solvents were used for electrolytic desulfurization without soaking treatment, sulfur removal without electrolysis only after soaking treatment, and electrolytic desulfurization of coal samples after soaking treatment. The results were compared and plotted as Fig.2. The experimental process was carried out under the optimum desulfurization conditions of coal particle size less than 0.5mm, electrolyte concentration 0.75mol·L^{-1}, electrolysis time 4h, current density 0.044A·cm^{-2} and coal slurry concentration 20g·L^{-1}. The organic solvents used in the process were dimethylformamide (DMF), methanol (CH_3OH) and dimethyl sulfoxide(DMSO).

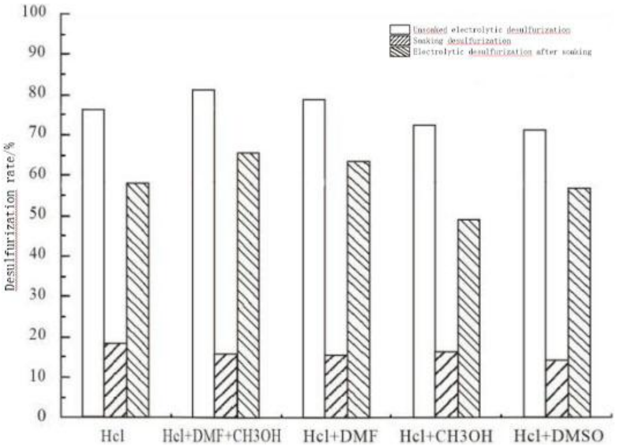


Fig. 2 Effect of organic solvents on desulfurization rate

It can be seen from Figure 2 that the electrolytic desulfurization rate without immersion and the electrolytic desulfurization rate after immersion in the organic solvent system with DMF+CH_3OH and DMF are significantly higher than those without organic solvent system. The reason is that the desulfurization of coal electrolysis is mainly caused by anodic oxidation. When Hcl is used as electrolyte, chlorine gas and hypochlorous acid with strong oxidation ability are produced by anodic electrolysis, so that inorganic sulfur and organic sulfur in coal are oxidized to sulfate ions. When the organic solvent is added, the organic solvent is extracted from the surface of the solid coal and the liquid sulfur dissolved in the solution to part of the sulfur, so that the extracted sulfur is more easily removed on the electrode surface to achieve high desulfurization rate. However, the effect of immersion desulfurization in DMF+CH_3OH and DMF systems is not obvious. The reason is that the soaking process mainly removes inorganic sulfur in coal. The acidic electrolyte can remove most of the SO_4^{2-}sulfur and pyrite by soaking. Although organic solvents can extract insoluble sulfur-containing functional groups in water, these sulfur-containing functional groups are not easily filtered and remain on the surface of coal. The experimental results show that the electrolytic desulfurization effect can be optimized under the DMF+CH_3OH and DMF systems, while the electrolytic desulfurization effect under the CH_3OH and DMSO systems is not good.

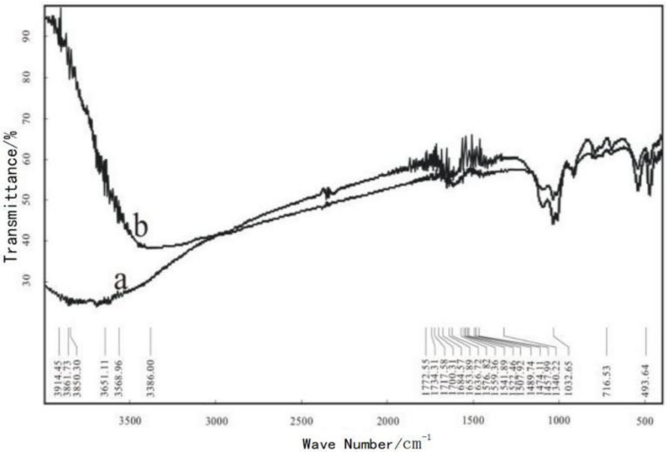
3. Result and discussion

3.1 Infrared spectroscopic analysis

In the experiment of electrolytic desulfurization optimized by organic solvent, the desulfurization rate of DMF+CH_3OH system was significantly improved. Table 4 verified that the organic sulfur content was significantly reduced after soaking and electrolysis. When adding DMF+CH_3OH to soak, it is mainly to remove SO_4^{2-},FeS_2 and organic sulfur are only slightly removed, and the removal rate of organic sulfur in DMF+CH_3OH system after electrolysis is higher than that without organic solvent.

Table 4 Sulphur content before and after electrolysis

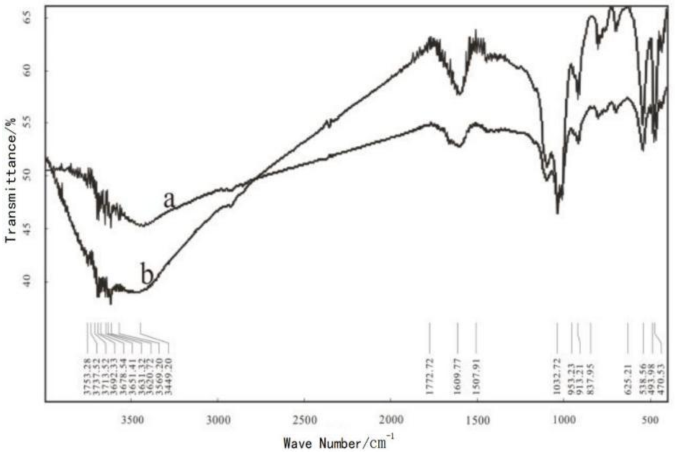
Coal samples	Raw Coal	Coal sample after soaking		Coal sample after electrolysis	
Electrolyte	——	Hcl	Hcl+ DMF+CH_3OH	Hcl	Hcl+ DMF+CH_3OH
Quality/g	5	4.5	4.5	14.7	14.4
Total sulfur/%	4.01	3.43	3.26	0.953	0.882
FeS2/%	2.79	2.66	2.62	0.579	0.588
SO42-/%	0.53	0.16	0.08	0.095	0.077
Organic sulfur/%	0.69	0.61	0.56	0.279	0.217



a-Adding organic solvents,b-No organic solvent added

Fig.3 Infrared spectrum analysis before and after soaking desulfurization

As shown in Figure 3, the infrared spectrum can visually see the difference between adding DMF+CH_3OH organic solvent and not adding organic solvent. The peak values of 1135 cm^{-1}(-SO_2), 1130cm^{-1}(-S=O), 539cm^{-1} and 476 cm^{-1}(-S-S-,-SH) did not change significantly with or without organic solvents. The reason is that organic solvents can extract water-insoluble sulfur-containing functional groups during the soaking desulfurization process, but these sulfur-containing functional groups are not easily filtered and remain on the surface of coal.



a-Adding organic solvents,b-No organic solvent added

Fig. 4 Infrared spectrum analysis before and after electrolytic desulfurization

As shown in Figure 4, the infrared spectrum analysis was carried out after adding DMF+CH_3OH organic solvent and without organic solvent electrolysis. From the diagram, the peak values at 684cm^{-1} and 771cm^{-1}((pyridine) were improved, and the analysis was caused by the decomposition of organic solvents during electrolysis. The peaks at474 cm^{-1}, 542cm^{-1}(-S-S-, -SH), 1610cm^{-1} and 1720cm^{-1} (-COOH) decreased with the addition of DMF+CH_3OH organic solvent, indicating that the addition of DMF+CH_3OH organic solvent can significantly improve the removal efficiency of organic sulfur and sulfur-containing functional groups.

3.2 Study on desulfurization mechanism

3.2.1 Mechanism of inorganic desulfurization

The inorganic sulfur in coal is mainly pyrite sulfur, and the oxidation reaction in the anodic solution is the reaction of removing pyrite sulfur. The pyrite in the coal is first oxidized to $FeSO_4$ and S on the anode surface, and then $FeSO_4$ continues to be oxidized to $Fe_2(SO_4)_3$. The sulfide in the coal is oxidized by Fe^{3+} and then reduced to Fe^{2+} again. Then it moves to the anode and is oxidized to Fe^{3+} again, reentering the sulfide in the oxidized coal in the coal slurry. In this way, Fe^{2+}-Fe^{3+}-Fe^{2+} ion circulation is formed, which can fully promote the electrolytic desulfurization reaction of coal.

In the electrolyte :

$$2Fe^{2+}+FeS_2 \rightarrow 3Fe^{3+}+2S$$

$$4H_2O+S+6Fe^{2+} \rightarrow 6Fe^{3+}+8H^{+}+SO_4^{2-}$$

On the cathode :

$$2H^{+}+2e^{-} \rightarrow H_2\uparrow$$

On the anode :

$$Fe^{2+}-e^{-} \rightarrow Fe^{3+}$$

Since the experiment was conducted under the electrolyte system of Hcl, Cl_2 was also generated during the electrolysis, and Cl_2 is very soluble in water to form HclO, which has strong oxidizing property and can oxidize pyrite sulfur in coal to achieve the effect of auxiliary electrochemical desulfurization. The reaction process is as follows：

$$2Cl^{-} \rightarrow Cl_2+2e^{-}$$

$$Cl_2+H_2O \rightarrow HclO+Hcl$$

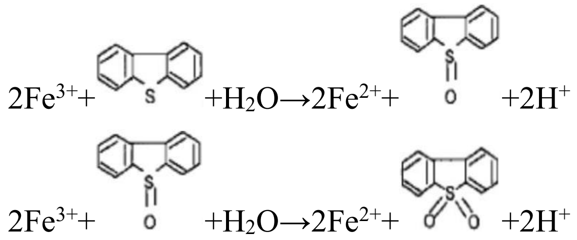
$$4HclO+FeS_2 \rightarrow FeSO_4+S+4Hcl$$

3.2.2 Organic desulfurization mechanism

Under the acidic system with Hcl as electrolyte, the possible reaction mechanism was proposed according to the change of surface morphology sulfur and the distribution of surface functional groups before and after electrochemical treatment of coal samples. Fe^{2+} is oxidized to Fe^{3+} on the surface of the electrode anode, and Fe^{3+} can oxidize organic sulfur such as thiophene in coal to sulfoxide, which is further oxidized to sulfone. At the same time, the desulfurization efficiency of pyrite sulfur can be promoted by adding $MnSO_4$ in the process of removing inorganic sulfur. $MnSO_4$ can not only be used as a catalyst for the removal of inorganic sulfur, but also has a catalytic effect on the removal of organic sulfur. The change process of Mn^{2+} is similar to that of Fe^{2+}, which is also oxidized on the anode surface to form Mn^{3+}. Mn^{3+} and organic sulfide react to form sulfoxide and sulfone. Sulfone is easily hydrolyzed in water to form water-soluble sulfonate or SO_4^{2-}. After adding DMF+CH_3OH organic solvent, the sulfur-containing functional groups in coal can be better extracted and the overall reaction process can be accelerated. The reaction process is as follows :

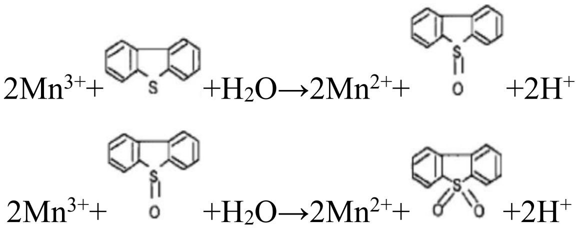
(1)The oxidation state of organic sulfur increased, but the carbon-sulfur bond did not break. Sulfur failed to break away from the molecular structure of coal to form sulfone or sulfoxide, and the desulfurization rate was zero or low.

The oxidation reaction process of organic sulfides:



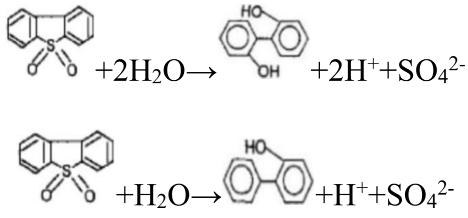
The catalyst promotes the oxidation reaction process of organic sulfides:

$$Mn^{2+}-e^- \rightarrow Mn^{3+}$$



(2)Under the long-term oxidation reaction process, the oxidation state in organic sulfur will further increase, and the carbon-sulfur bond will be broken, and sulfur will be oxidized from coal molecules to generate SO_2 or SO_4^{2-}, thereby further improving the degree of electrolytic desulfurization.

Hydrolysis of sulfone:



(3)In the process of deep desulfurization, some groups of coal molecules are oxidized, and some substitution reactions can also remove sulfur. If the electrolytic desulfurization conditions are strong, the carbon single bond will be broken, and the organic sulfur structure will be exposed and further oxidized.

4. Conclusion

(1)The optimum conditions for acid desulfurization in this experiment were current density of 0.044A·cm^{-2} , coal slurry concentration of 20g·L^{-1}, electrolysis time of 4h, and electrolyte concentration of 0.75mol·L^{-1}. The results show that the content of various forms of sulfur in coal samples after electrolysis is low, and the total sulfur removal rate is as high as 76.2%.

(2)Among the inorganic catalysts, manganese sulfate significantly improves the desulfurization efficiency, followed by magnesium chloride and sodium chloride, while iron nitrate and iron sulfate reduce the desulfurization efficiency. DMF+CH_3OH and DMF organic solvents have no obvious effect in the process of immersion desulfurization, but the removal efficiency of organic sulfur is significant after electrolytic desulfurization. The overall desulfurization effect of CH_3OH and DMSO organic solvents is not good.

(3)The inorganic sulfur in coal is mainly pyrite sulfur, and the reaction of removing pyrite sulfur is an oxidation reaction in the anodic solution. There will be a Fe^{2+}-Fe^{3+}-Fe^{2+} ion cycle near the electrolyte and anode, which can fully complete the removal process of pyrite sulfur.

(4)The organic sulfur in coal will be oxidized by Fe^{3+} and Mn^{3+}. Firstly, the oxidation state of organic sulfur increases, but the C-S bond does not break, and sulfur still exists in the molecular structure of coal to form sulfone or sulfoxide. After that, the oxidation state is further increased, the carbon-sulfur bond is broken, and the sulfur is separated from the molecular structure of the coal, forming SO_2 or SO_4^{2-} in the solution to achieve the effect of removing organic sulfur.

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