

Mechanism of coal electrochemistry desulfurization under alkaline conditions

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Abstract: To study the desulfurization mechanism of coal-derived pyrite and organic sulfur in coal, the experiment used the solution of NaOH whose concentration is 2.0mol/L as electrolyte to dispose high sulfur coal samples whose content is 3.08% with the H type undivided electrolytic cell, and analyzed the before and after desulfurization of coal samples by scanning electron microscope, XRF and IR spectrum and the filtrate is from after electrolyzing coal sample by ion chromatograph. The results showed that the inorganic sulfur of coal sample mainly in the form of Pyrite that is a fine granular distribution in the coal and disseminates on the coal particle, then pyrite is removed by generating sulfate at the anode oxidation reaction, and finally, organic sulfur in coal samples mainly is removed by electrochemical reaction that can convert into the form of sulfate radicals.

1. Introduction

Coal chemical desulfurization technology is a new kind of chemical purification technology developed by Coughin and Farooque in the 1960s^[1-3]. This technology overcomes the shortcomings of traditional physical desulfurization technology that cannot remove organic sulfur and the defects of biological desulfurization technology which has a long period of process. Liu Xuguang^[4] conducted a study on the electrochemical desulfurization of Xiaoyi coal, and the results were obtained from the aspects of electrochemical desulfurization behavior, desulfurization rule in alkaline system, electrolysis system and so on; Cuiping^[5] studied the influence of electrolytic condition on the efficiency of desulfurization and the optimum technological condition of desulfurization to Shanxi Linfen clean coal in the system of acid and alkalinity. However, the mechanism of electrochemical desulfurization of coal, especially in the alkaline environment, is still not fully understood^[6]. In this paper, the author selected a typical high sulfur coal sample in Shanxi Shigejie, with NaOH solution as the electrolyte in electrochemical desulfurization experiment, and using the instruments such as scanning electron microscopy (SEM), X-ray fluorescence spectrum analyzed and characterized the composition and structure of coal samples before and after desulfurization, and exploring the mechanism of electrochemical desulfurization of pyrite and organic sulfur in coal in alkaline environment.

2. The experiment

2.1 Coal sample analysis and reagents

In this experiment, the coal sample comes from Shanxi Lu'an Shigejie Coal Mine. Electrolyte is NaOH Solution, NaOH reagent comes from Tianjin Pengkun chemical LTD., Coal sample industrial analysis and various forms of sulfur see also in Table 1.



Table 1. Coal sample analysis %

M_a d	A_d	V_{daf}	w			
			$S_{t,d}$	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$
1.1	42.	15.	3.0	1.9	0.5	0.5
3	10	27	8	4	8	6

As can be seen from table 1, the total sulfur content of coal sample is 3.08%, which is high sulfur coal. The sulfur in coal mainly exists in the form of inorganic sulfur, and the mass fraction of pyrite sulfur is 1.94%, and the mass fraction of sulfate sulfur is about 0.58%; the mass fraction of organic sulfur is about 0.56%. At the same time, the coal sample was used to study the removal of organic sulfur and inorganic sulfur.

2.2 equipments

The electrolysis experiment uses the H type no diaphragm electrolytic cell that the electrolytic cathode and anode are all platinum electrodes. The current meter is the rxn-3003A type produced by the Zhaoxin electronic technology company. The analytical representation instruments are: The thermal field emission scanning electron microscope (MX2600) produced by Camscan company of England, whose working voltage is 0~25V, with a resolution of 1.5nm; Bruker S4 X-ray fluorescence spectrometer, test conditions for Cu target is 1.5406Å, continuous scanning with speed of 7.2°/min, step 0.02°, 2θ is 10°~65°, operating voltage is 40kV and electric current is 40mA; High pressure ion chromatography (Thermo Scientific Dionex ICS-5000+) the maximum operating pressure is 0.7 MPa (100 psi), precision of velocity error < 0.1%, the largest flow < 0.1%, detector resolution is 0.00238 nS/cm; The infrared spectrum analyzer MB104 is produced by Nicolet company of America, its electromagnetic wave with a wavelength range of 0.76~500.00μm; Sulfur analyzer is used in Taizhou Han Tang automation equipment Co., Ltd. HTC LS-800B.

2.3 Method

2.3.1 Electrolytic experiment

Put 6g coal samples into the electrolytic cell, and then pour the configured 300mL solution of 2mol/L NaOH into it. Mix coal and solution evenly with mechanical blender, and put it into water bath pot. Adjust the temperature to 70 °C, connect the power supply, adjust the current to 2.0A. Electrolytic will be finished after four hours. The coal samples were washed, filtered and dried after electrolysis for testing and analysis.

2.3.2 Filtrate and blending

In the experiment, 100 mL filtrate of the electrolytic experiment and 100 mL filtrate of the check experiment were collected. Diluting 20 mL soaked filtrate 100 times and take it as sample 1 for on detection; Diluting 10 mL electrolyzed filtrate 1000 times and take it as sample 2 for ion detection

2.3.3 Determination of sulfur content

All sulfur in coal are measured by automatic sulfur meter, SO_4^{2-} and FeS_2 are measured by titration method, and the organic sulfur is calculated by differential subtractive method.

3. Results and analysis

3.1 The sulfur content in different forms

The various forms of sulfur content of raw coal, electrolytic coal, Soaked coal samples is shown in table 2.

Table 2. Each form sulfur content in coal samples

Coal samples	m/g	w/%			
		Total sulfur	FeS ₂	SO ₄ ²⁻	Organic sulfur
Raw coal	6.0	3.08	1.94	0.56	0.58
Soaked coal	5.7	2.89	1.90	0.43	0.56
Electrolytic coal	5.2	1.34	0.92	0.17	0.36

The above sulfur content is based on dry basis

As can be seen from table 2, After the raw coal samples were soaked, the sulfur content of organic sulfur and pyrite was not changed, and sulfates were partially re-moved. However, through electrolysis treatment, pyrite sulfur, sulfate sulfur and organic sulfur have a greater removal rate, the sulfur content in the samples is lower, and the total sulfur removal rate is as high as 56.49%. The analysis shows that the coal in the electrolysis process mainly relies on the electrolysis reaction to remove the sulfur in the coal, and the soaking can only remove the small parts of the sulfates of the inorganic sulfur^[7].

3.2 XRF analysis

The elements qualitative and quantitative analysis of the coal samples before and after the process of electrolytic desulfurization were analyzed by X-ray fluorescence technology, and the coal samples were dry coal samples. The results of the XRF analysis of the coal samples before and after the electrolytic desulfurization are shown in table 3.

Table 3. Before and after desulfurization XRF analysis of coal samples

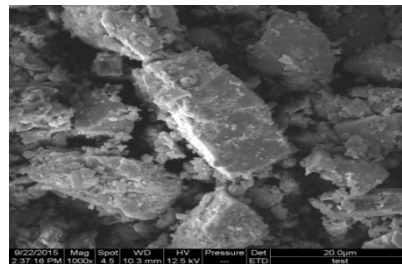
The element	(W/%)	
	Raw coal	Desuphurization coal
Fe	7.745 0	8.130 0
Si	1.190 0	1.020 0
Al	0.766 0	0.574 0
Ca	0.380 0	0.499 0
S	0.429 0	0.258 0
Sr	0.112 0	0.092 1
Zn	0.056 8	0.083 9
Ti	0.041 8	0.052 9
Mn	0.035 1	0.048 1
K	0.049 5	0.046 8

As you can see from table 3, after the coal is electrolyzed in the alkaline electrolyte, the content of Fe and Ca element has been increased. This is because pyrite produces F^{3+} in the process of electrolysis,

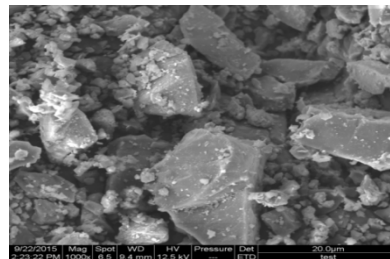
and because coal samples react in an alkaline environment, they are prone to precipitate and cannot be filtered. As a result of the electrolysis reaction, the recovery rate of coal is reduced, leading to the enrichment of Fe element, which is finally shown as the increase of Fe element content. As a result of electrochemical reaction, pyrite in coal is oxidized to soluble sulfates. Then, the soluble sulfates were separated from coal by washing and filtration, and the content of S element was decreased.

3.3 SEM analysis

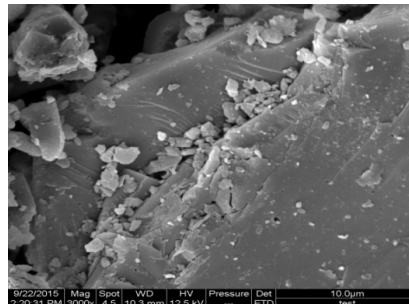
The distribution and morphology of pyrite on coal surface were studied by SEM technique. The results of SEM analysis of coal samples before and after electrolysis were shown in figure 1.



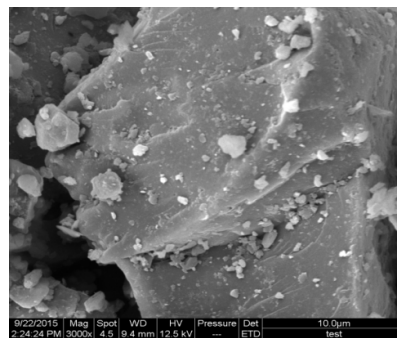
a. Raw coal sample(1 000×)



b. Coal sample after desulfurization(1 000×)



c. Raw coal sample(3 000×)



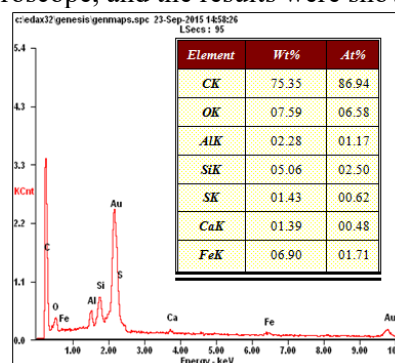
d.Coal sample after desulfurization(3 000×)

Fig . 1. SEM images of coal samples before and after desulfurization

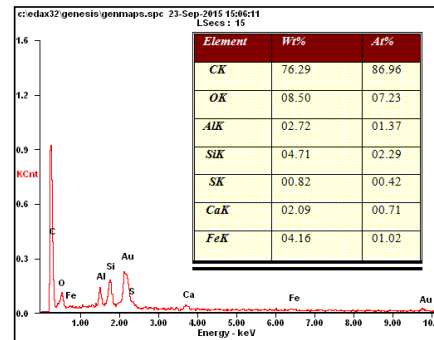
By observing figure 1a, figure 1c and figure 1b, figure 1d can be found, the surface morphology of coal particles was changed before and after electrolysis, before electrolysis, the surface of the coal particles is smooth and shiny, After electrolysis, the surface of the coal particles is denuded and emerge dent.

3.4 Energy spectrum analysis

In order to further analyze the change of sulfur content in the coal before and after the electrolytic desulfurization, the energy spectrum analysis of the coal samples before and after electrolysis was carried out by scanning electron microscope, and the results were shown in figure 2.



a. Raw coal sample



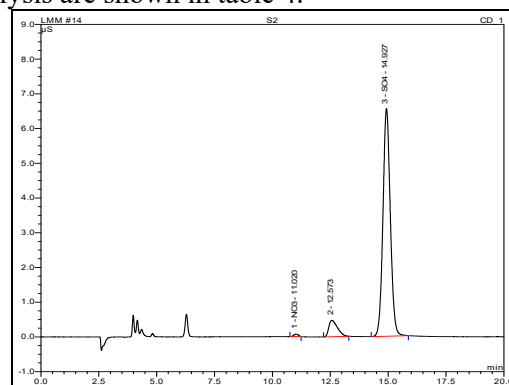
b. Coal sample after desulfurization

Fig.2.Coal samples before and after desulfurization energy spectrum analysis

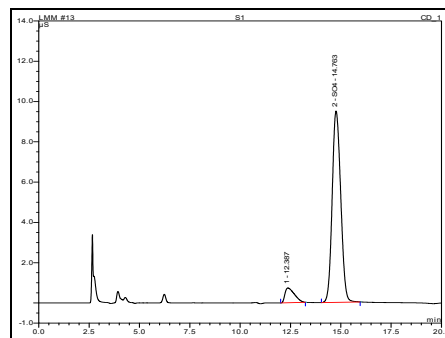
As can be seen from figure 2, The mass fraction of O increased after electrolysis, This shows that the oxidation-reduction reaction occurred in the electrolysis process, and some of the S in the sulfur perssard was replaced by O, due to the relative atomic mass of O is lower than S, leading to the mass fraction of C increases, and the increase of C can improve the combustion performance of coal, So the electrolysis reaction improved the combustion performance of coal. Compared with the mass fraction of S before and after the electrolysis, the mass fraction of S decreased obviously after electrolysis, which indicates that the electrolytic reaction indeed removing S in coal.

3.5 Filtrate ion analysis

In order to further study the mechanism of electrochemical desulfurization, the filtrate ion is analyzed. Considering that the main reaction of the electrochemical desulfurization is that the sulfur in coal can be converted into sulfuric acid by electrochemical oxidation-reduction reaction, therefore, the main purpose of the experiment is to detect the orientation and quantification of sulfate in the filtrate. The ion chromatogram of the soaked and electrolytic coal sample filtrate and is shown in figure 3, and the results of filtrate analysis are shown in table 4.



a. Coal sample filtrate after soaking



b. Coal sample filtrate after electrolysis

Fig.3. Soaking coal and electrolytic coal filtrate Ion chromatography analysis

Table 4. Analysis of soaking coal and electrolytic coal filtrate

Coal sample filtrate	time	Peak's area	Peak's height	Test concentration	Actual concentration
	<i>min</i>	$\mu S \cdot min$	μS	$\mu g/ml$	$\mu g/ml$
Soaked coal	14.93	2.417	6.562	13.3879	66.94
Coal after electrolysis	14.76	4.664	9.494	24.7226	2472.26

As can be seen from Figure 3, No matter the filtrate obtained from the soaking or the electrolytic coal sample, the peak is near 14.9 min, they all had peaks near 14.9 min, Compared to the standard comparison card, the peak is defined as the peak of sulfate.

As can be seen from Figure 3, according to the calculation of sulfate ion concentration given by ion chromatograph, it is found that the content of sulfate radical in the filtrate is very small and can be neglected, but the content of sulfate radical in the filtrate of electrolytic coal samples was increased to 2472.26 g/ml, it can be seen from the analysis that the increase of sulfate radical in solution is caused by electrolysis.

3.6 Infrared spectrum analysis

Organic sulfur is the sulfide group in the structure of the coal molecule, in order to study the change rule of organic group in the process of electrolysis, the infrared spectrometer was used to detect the coal samples before and after electrolysis, infrared spectrum analysis results are shown in Figure 4, and infrared vibrational characteristics of main groups in coal sample structure are shown in Figure 5.

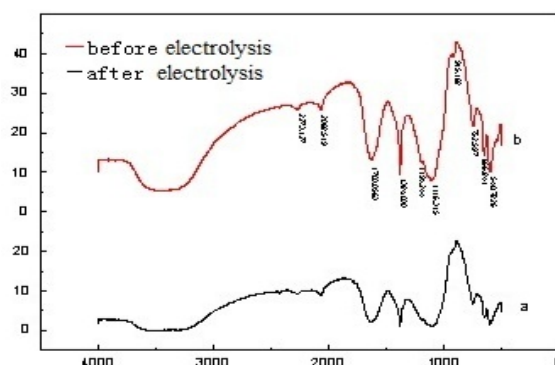


Fig. 4. Infrared spectra of coal samples before and after electrolysis

Table 5. Infrared vibrational characteristics of major groups in coal sample structure

Wave number/cm ⁻¹	Corresponding groups
>5 000	Frequency doubling or group frequency of vibration peaks (weak)
3 300	-OH (-NH) ;Phenols
3 030	-CH
2 930~2 860	-CH ₃
2 780~2 350	Hydroxyl
1 900	Aromatic hydrocarbon, 1,2(1,2,4)-substituted aromatics -CH
1 780	Aromatic hydrocarbon, 1,2(1,2,4) substituted aromatics -CH
1 700	Carbonyl
15 90~1 470	Most aromatic hydrocarbons
1 460	-CH ₂ -CH ₃ or inorganic carbonate
1 375	-CH ₃
1 040~910	Ash content, such as kaolin
860	1,2,4-;1,2,4,5-,(1,2,3,4,5) substituted aromatics -CH
833	1, 4-substituted aromatics -CH
815	1,2,4-(1,2,3,4) substituted aromatics -CH
750	1, 2 replace arenes

700	Monosubstituted or 1, 3- substituted aromatics -CH, ash content
540	Aromatic disulfide-S-S

The absorption peak at 1700 cm^{-1} is the carbonyl group's, compared with the absorption peak before and after desulfurization, it can be seen that the absorption peak of carbonyl is obviously weakened after electrolysis, which shows that the carbonyl on the surface of coal particles react in the electrolysis reaction, because hydrogen is produced in the process of electrolysis, it may be that the carbon oxygen bond breaks, and the hydrogenation reaction occurs, which helps to reduce the carbon oxygen ratio, which in turn improves coal quality^[8]. The absorption peak of $1,040\sim 910\text{ cm}^{-1}$ is attenuated before and after desulfurization, which may be the absorption peak of kaolin, which indicates that electrolytic desulfurization is good for reducing ash^[9]. There is no significant change in the absorption peak of 750 cm^{-1} , at which 1,2 replaces arenes. The results showed that the electrolytic desulfurization reaction had no effect on the molecular composition of coal. Appear absorption peak at 540 cm^{-1} , which is the characteristic peak of aromatic disulfide group, and the absorption peak is obviously weakened after electrochemical desulfurization reaction, the results show that electrochemical method can remove organic sulfur from coal.

4. Conclusion

In the process of electrolytic desulfurization, coal is mainly dependent on electrolytic reaction to remove the sulfur in coal, and Soaking can only remove the small amount of sulfate sulfur from inorganic sulfur.

The pyritic sulfur in coal is mainly embedded in the coal surface by fine particle shape and it was oxidized by electrochemical reactions to the soluble sulfates.

Organic sulfur is sulfur-bearing perssard in the molecular structure of coal, which can be partially removed by electrochemical reaction.

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