

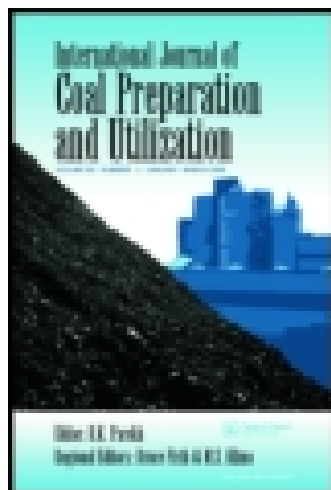
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Research on Mechanism of Enhanced Desulfurizing Flotation of High Sulfur Coal with Electrolytic Reduction

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Pretreatment of high sulfur coal by electrolytic reduction reduces the number of oxygen-functional groups on the coal surface and improves coal hydrophobicity, and reduces the initial oxidation products on the pyrite surface (e.g. polysulfide, free sulfur, etc.) increasing pyrite hydrophilicity. This improves the selectivity of the subsequent flotation process. The results indicate that the electrolytic reduction can significantly decrease the content of pyrite sulphur in the floatation concentrate. Using this method, 89% of pyrite in the Beisu coal could be rejected while only 54.5% of pyrite sulfur was rejected without the treatment.

Keywords Coal; Pyrite; Desulfurization; Electrolytic reduction; Modification

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Pyrite grains in coal appear in different shapes and different sizes. While coarse pyrite particles can easily be rejected from coal by gravity separation methods, pyritic sulfur reduction is very difficult if pyrite is finely disseminated and its liberation is poor.

Pyrite particles are known to exhibit high degree of natural floatability and in coal flotation commonly report to the clean product along with coal particles. The present study was undertaken to investigate the effect of electrolytic reduction on desulfurizing floatation of coal.

EXPERIMENTAL

Materials

Coal pyrite samples obtained from Zhongliangshan coal mine (Chongqing), which were crushed just prior to the experiments to avoid oxidation, were used. Bituminous coal samples from Chacheng coal mine (Jiangsu province), were utilized. Also, different coal-cleaning products were used in the tests, including samples from Xiaqiao coal mine (Jiangsu Province), Beisu coal mine (Shandong Province) and Datun coal preparation plant (Shanghai). Size grade of all the coal samples was less than 0.5 mm. Proximate analyzes of the tested coals are shown in Table 1.

Graphite anode and stainless steel cathode were utilized. Saturated calomel electrode was used as a reference electrode and platinum electrode as a working electrode.

30% H_2O_2 was used as oxidant, and HCl and NaOH to adjust pH. Kerosene was utilized in the floatation tests as a collector. Either octanol or GF commercial product was used as a frother.

Coal samples and pyrite samples were pretreated in a self-made electrolytic cell (Figure 1), powered by 10 A AC/DC stable power source.

The Design of Electrolysis Bath and the Experimental Apparatus

Electrolysis bath, also called “electrochemical substances producer,” is a kind of equipment in which certain electrochemical reactions took place

TABLE 1 Proximate analyses of different coal samples

	Mad, /%	Ad, /%	Vdaf, /%
Chacheng coal	2.05	9.58	34.50
Xiaqiao coal	1.58	20.29	25.87
Beisu coal	2.11	11.50	32.31
Datun coal	2.87	20.62	31.39

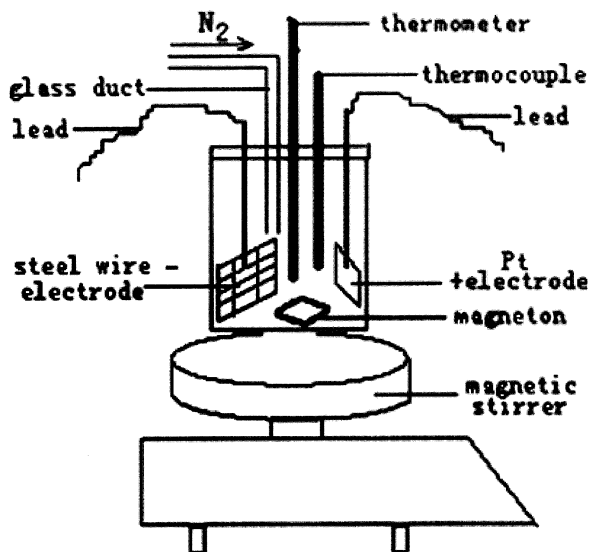


FIGURE 1. Electrolytic cell schematic diagram.

and new substances formed in the presence of outside power supply. When two electrodes with connection to a direct current are immersed in the electrolyte solution, the outside power will provide continuous current to the cell system, so oxidation reaction and reduction reaction can take place on the two electrodes to form new substances. Such a system, which converts electric power to chemical power, is called an electrolysis cell, or electrolysis bath. The electro bath used in our experiment is self-made. It is a single-cell bath in which the cathode is wire mesh gauze electrode and the anode is platinum electrode. This electro bath is excellent in conductivity, mass transfer, and current utilization, and it is easy to prepare.

1. Starting materials: beaker (200 ml), platinum sheet (anode), steel wire mesh gauze (cathode), harness, clamps, sponge sheet, thermometer, glass tube, thermoelectric couple.
2. Assembly:
 - I. Shear the sponge sheet into a lid with the same size of the beaker, drill into the lid some holes, and adapt to the diameters of thermometer, electrodes, thermoelectric couple, and glass tube.
 - II. Thick copper wires, connected to conductive wires, are welded to the platinum sheet.
 - III. Thick copper wires, connected to conductive wires, are welded to the steel wire mesh gauze sheared into a square of $3\text{ cm} \times 3\text{ cm}$.

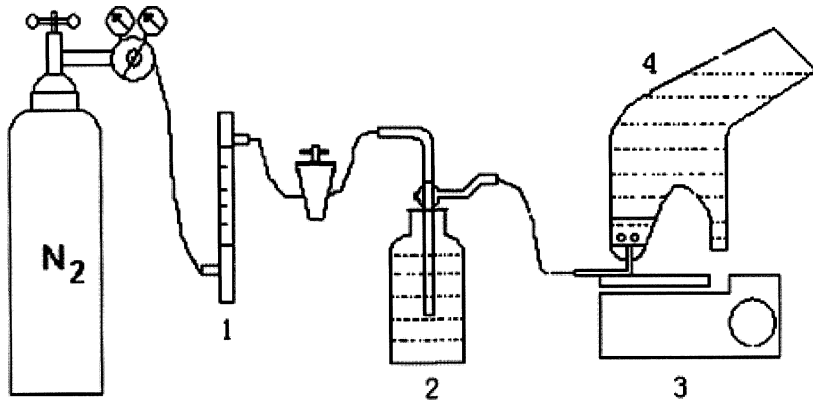


FIGURE 2. Flotation desulfurization experimental installation: 1, flowmeter; 2, washing bottle; 3, magnetic stirrer; 4, flotation tube.

- IV. Lead the conductive wires out of the holes in the sponge lid, then insert thermoelectric couple, thermometer, and glass pipe into corresponding holes.

Experimental Installation in Lab

Flotation experimental installation in lab is shown in Fig. 2.

Testing Instruments

X-ray diffraction (XRD): D/MAX-IIIB type, produced by Japanese Science Company, Cu target, K^α radiation, graphite corked crystal monochromator, 5 kV, 30 mA. The diffraction narrow crack is 1° , the receiving narrow crack is 0.3 mm, the prism narrow crack is 1° . Using continue scanning, the scanning speed is $2^\circ/\text{min}$. Sampling interval is 0.02° .

Raman Spectra: Renishaw Raman System Mki2000 type, produced by Britain, laser wavelength is 514.5 nm, 180° backscattering installment, 9 mW, 20-time len, continuous scanning lasts 10 s.

RESULT AND DISCUSSION

Experimental Results

Using the above electrolytic cell and flotation installation, Xiaqiao coal, Beisu coal, and Datun coal were treated in lab with a kerosene

dosage of 1.5 kg/t and a GF dosage of 0.6 kg/t. Experimental results are shown in Table 2.

It can be seen from Table 2 that the content of pyretic sulfur and the ash content of three cleanings decrease to various degrees after pre-treatment by electrolytic reduction. For example, using this method 89% of pyrite in the Beisu coal could be rejected, while only 54.5% of pyretic sulfur was rejected without the treatment. At the same time, ash content decreases by 0.7%. Recovery rates of cleanings are enhanced greatly (Datun coal increased by 10%). Electrolytic reduction is an effective method to enhance flotation desulfurization of high sulfur coal.

DISCUSSION

Pyrite [1–9]

Surface Natural Floatability

Natural floatability of coal pyrite tested without any collector is determined by hydrophobicity of pyrite surface. Fresh pyrite surfaces exhibit high natural floatability and float along with coal particles in flotation.

Preliminary tests show that particles freshly prepared by crushing are of poor floatability and good hydrophilicity. Tests with fresh pyrite particles under different pH show that only in acidic conditions was there a small amount of pyrite particles floating.

Pyrite surfaces, after initial oxidation, float excellently. When pulverized pyrite particles are placed in distilled water, the shorter the stirring time, the lower pyrite particles float; the fresh pyrite surfaces are

TABLE 2 Flotation results of different kinds of coal

Name	A_{ad}/S_p (%) in feedstock	Treat way	$r\%$ (clean coal)	$A_{ad}\%$ (clean coal)	S_p (%) in clean coal	Pyrite removing rate %	$\Delta r\%$
Xiaqiao Coal	20.29/1.77	1	64.02	7.39	1.07	61.30	13.41
		2	67.82	6.90	0.66	74.71	
Beisu Coal	11.50/1.62	1	77.53	5.96	0.94	54.51	35.44
		2	78.40	5.19	0.21	89.95	
Datun Coal	20.62/0.54	1	53.98	10.01	0.48	52.02	18.88
		2	62.86	9.64	0.25	70.90	

Notes: 1, conventional flotation; 2, enhancing flotation with electrolytic reduction.

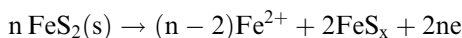
hydrophilic within the initial 30 min. With the prolonging of stirring time (> 30 min), the amount of pyrite particles floating increases sharply, with the peak floating content up to 85%.

Floataion experiments show that the floating content of pyrite remarkably decreases after deep oxidation in the H_2O_2 solution because floatability of pyrite surfaces is obviously decreased. The floatability-oxidation extent plot is shown in Figure 3.

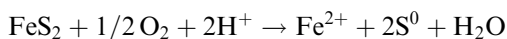
Surface oxidation

The main reason for oxidation to take place on pyrite surface is the redox potential and formation of different surface products depending on the redox conditions. The mechanisms may be as follows:

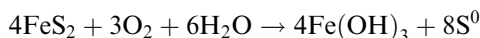
1. Fresh pyrite surface is thermodynamically unstable with a lot of polar groups, which are easily oxidized in the presence of oxygen and turn hydrophobic after initial oxidation, with oxidized products such as polysulfide FeS_x and free sulfur.



2. Further oxidation produces hydrophobic free sulfur in acid medium:



and in alkaline medium:



3. Deep oxidation produces hydrophilic match ion ($S_xO_y^{2-}$) on surface, which is of hydrophilicity in acid medium:

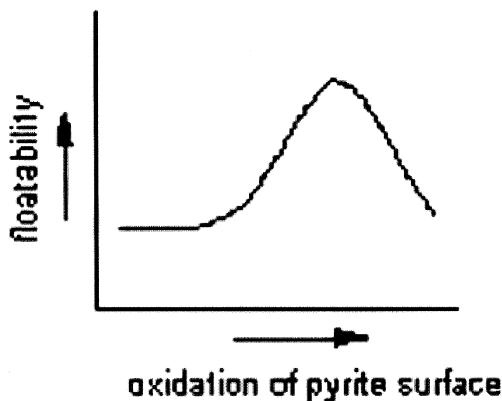
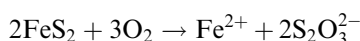
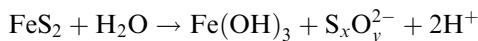
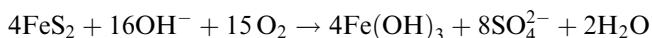
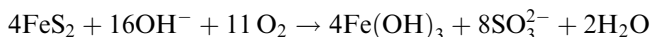
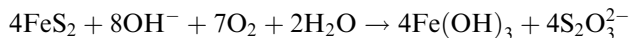


FIGURE 3. Change of floatability on pyrite surface along with oxidation.

and in alkaline medium:



In which $\text{S}_x\text{O}_y^{2-}$ is either $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , or SO_4^{2-} . Three reaction equations are as follows:



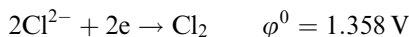
From practical operation in some coal preparation plants, it is known that flotation feeds stay for about 20–30 min before entering floatation circuit, i.e., pyrite particles are under their surface initial oxidized stages. In order to improve cleaning quality in floatation operation, current floatation flowsheet in coal preparation plants should be modified.

Surface Modification Mechanism

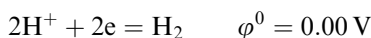
The purpose of pyrite surface modification is to prohibit surface oxidation from producing either free sulfur or polysulphide.

The following reactions were conducted in the above electrolytic cell. Anode and cathode reactions were as follows after NaCl dissolved in pulp:

Anode:



Cathode:



Corresponding Nernst equation:

$$\varphi_{\text{S}/\text{S}^{2-}} = \varphi_{\text{S}/\text{S}^{2-}}^0 + \frac{RT}{nF} \ln \frac{1}{a_{\text{S}^{2-}}}$$

$$\varphi_{\text{H}^+/\text{H}_2} = \varphi_{\text{H}^+/\text{H}_2}^0 + \frac{RT}{nF} \ln \frac{a_{\text{H}^+}^2}{P_{\text{H}_2}}$$

$$\varphi_{\text{Na}^+/\text{Na}} = \varphi_{\text{Na}^+/\text{Na}}^0 + \frac{RT}{nF} \ln a_{\text{Na}^+}$$

It can be seen from above three cathode reactions that S is easier to obtain electron than H^+ and Na^+ , so S is the first to gain electron on cathode.

XRD Spectra Analyses

Using XRD to analyze pyrite samples qualitatively before and after the treatment, the diffraction spectra are shown in Figure 4, in which 1 is the spectrum after electrolytic reduction and 2 is after initial oxidation.

The characteristic peaks of different valence sulfur are: the typical characteristic peaks of FeS_2 are three strong ones at 0.163 nm, 0.271 nm, and 0.242 nm, medium strong ones at 0.221 nm, 0.191 nm, and 0.312 nm, as well as other weak ones. The typical characteristic peaks of FeS are three strong ones at 0.313 nm, 0.191 nm, and 0.163 nm, medium strong ones at 0.124 nm, 0.161 nm, 0.191 nm, and 0.156 nm, as well as other weak ones. The typical characteristic peaks of FeS_x are a strong peak at 0.265 nm and other weak ones. The overlapping peaks of $FeS_2 + FeS$ are at 0.191 nm, 0.163 nm, and 0.313 nm.

It can be seen from Figure 4 that typical characteristic strong peak of spectra 2 is 0.271 nm, medium strong peaks are at 0.313 nm, 0.242 nm, 0.221 nm, 0.191 nm, and 0.163 nm, as well as other weak peaks at 0.156 nm and 0.124 nm. The diffraction peak at 0.265 nm of FeS_x appears

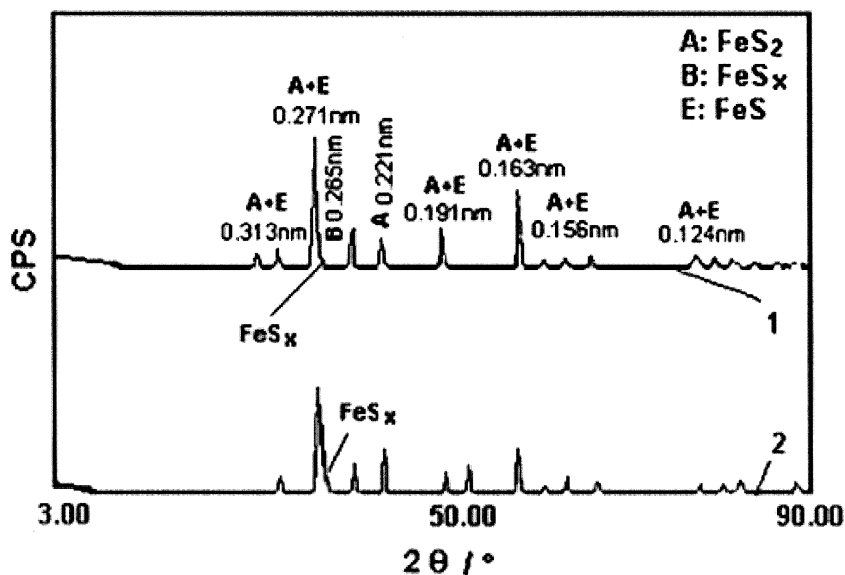


FIGURE 4. XRD spectra of pyrite surface before and after treatment.

on spectra 2. It may be conclude that oxidized products of spectra 2 surface are FeS_2 and FeS_x .

Compared from Figure 4, the diffraction peak at 0.221 nm of FeS_2 on spectra 1 decreases by 70.2%, that is, the content of FeS_2 in spectra 1 is reduced. The diffraction peaks at 0.313 nm, 0.191 nm, 0.163 nm, 0.156 nm, and 0.124 nm in spectra 1 enhance and inconsistent with the standard data of FeS_2 because of the overlapping of FeS . This may explain the existence of S^{2-} on spectra 1 surface. The diffraction peak at 0.265 nm of FeS_x on spectra 1 weakens obviously by 18.8%. It may be testified to by the following reactions: $\text{FeS}_x + ne \rightarrow \text{FeS} + \text{FeS}_2$ and $\text{S}^0 + 2e \rightarrow \text{S}^{2-}$.

Raman spectra analyses show that electrolytic reduction can modify pyrite surface property, reduce the number of oxygen-containing functional groups, and raise pyrite's floatability.

Coal [10–11]

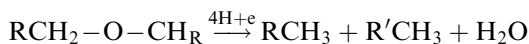
Surface Modification Mechanism

Coal is a complicated mixture made up of organic compound and inorganic substance. All kinds of coal at different degrees of metamorphism are of certain natural floatability. However, the number and type of oxygen-containing functional groups, such as $-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{OCH}_3$ are different in different coal kinds. Thus, coal's floatability differs. Oxygen-containing functional groups should be reduced in order to improve coal's hydrophobicity.

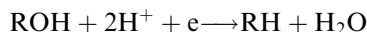
Using electrolytic reduction to pretreat 6 coals before floatation, the results show that all coal's floatabilities increase with the prolonging of reaction time. Their floatabilities reach the highest value after 10–15 min.

The following reactions may be reduced to explain modification mechanism on coal surface:

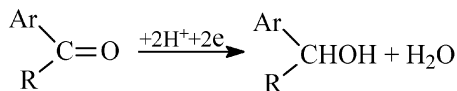
1. Ether-bond reduction:



2. Hydrocarbon group reduction:



3. Carbonyl group reduction:



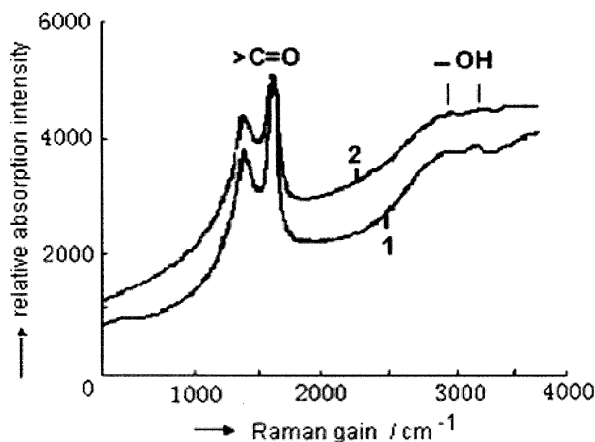
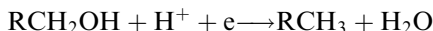
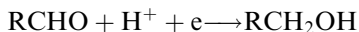
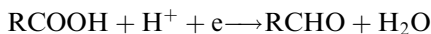


FIGURE 5. Raman spectra of gas coal before and after the treatment.

4. Carboxyl group reduction:



It can be seen from the above reactions that after pretreatment by electrolytic reduction some oxygen-containing functional groups in coal decrease, such as $-\text{C}=\text{O}$ and $-\text{COOH}$, which indicates that coal surface hydrophobicity has been improved.

Raman Spectra Analyses

Taking the above bituminous coal, for example, to analyze the changes of Raman spectra before and after the treatment with electrolytic reduction (shown in Figure 5), in which curve 2 is the spectra before and after treatment, respectively, it may be seen that some changes have taken place, indicated by peak intensity and peak width before and after the treatment. After the treatment, the $-\text{OH}$ peak intensity obviously weakens at 3400 cm^{-1} and the $-\text{CO}$ peak intensity also weakens at 1000 cm^{-1} .

CONCLUSIONS

1. The electrolytic reduction method can decrease the number of oxygen functional groups, such as $-\text{CO}$ and $-\text{OH}$, and increase

hydrophobicity of coal surface. At the same time, free sulfur and polysulphide on pyrite surface are reduced to hydrophilic substances on cathode, such as FeS and S^{2-} , which depresses floatability on pyrite particles.

2. In the same reduction atmosphere, the surface modification of coal and pyrite particle moves in opposite directions, which enhances flotation desulfurization of high sulfur coal.
3. Electrolytic reduction method can raise removal of pyrite in varying degrees. Flotation results of the Beisu coal show that above 89% of pyrite sulfur was removed. Ash contents of flotation clean coal decrease and recovery rates of clean coal increase.

With deep exploitation of coal and the improvement of mechanization, more and more coal fines and high sulphur coals will appear, so flotation action will become more important in coal preparation. Development of enhancing flotation desulfurization will have a vast range of prospects in making use of high sulphur coal.

ACKNOWLEDGMENT

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