MSc Thesis

Study on Microbial Desulfurization of High Sulfur Coal in Shanxi Province

Author: Mengmeng Gou

Supervisor: Professor Yuegang Tang

Date(10/062020)

College of Geological and Surveying Engineering
China University of Mining and Technology (Beijing)

Beijing Haidian district Xueyuan Rd,Ding 11.
Zonghe Building 537

Declaration of Authorship

“I declare in lieu of oath that this thesis is entirely my own work except where otherwise indicated. The presence of quoted or paraphrased material has been clearly signaled and all sources have been referred. The thesis has not been submitted for a degree at any other institution and has not been published yet.”

Abstract

This paper comprehensively uses coal petrology, coal chemistry, biology and other research methods to carry out microbial flotation desulfurization experiments on typical high sulfur coals in Shanxi, China. In order to study the best desulfurization effect under certain conditions, also to make evaluation and analysis. The results show that microbial pretreatment has an effect on the desulfurization rate of coal samples, but it has different effects on different coal samples. The microbial flotation desulfurization rate of high-sulfur coal is affected by various factors, including pretreatment time, particle size of coal samples, morphological sulfur occurrence characteristics, morphological sulfur distribution characteristics, coal ash content, etc. Overall, most samples reach the maximum desulfurization rate when the pretreatment time is 20 minutes. The smaller the particle size of the coal sample, the better the desulfurization effect. There is no significant correlation between the degree of coal metamorphism and the microbial flotation desulfurization rate. The occurrence characteristics of morphological sulfur and the ash content have a great influence on the desulfurization rate. The total sulfur removal rate is positively correlated with the total sulfur content in the coal and the proportion of pyrite sulfur in the coal to the total sulfur content. The ash removal rate and the desulfurization rate are also significantly positively correlated.

Keywords: high sulfur coal, desulfurization, microorganisms, flotation

Contents

1 Introduction

1.1 Background and significance of this research

The basic characteristic of China's energy structure is "rich coal, poor oil, and low gas". Coal is the cornerstone of China's energy. Due to the important position of coal in primary energy, coal will still be China's main energy source and will remain unchanged for a long time. In order to meet the needs of social development, high-quality, low-sulfur coal resources have gradually decreased with mining over the years, and the quality of coal has continued to decline. Sulfur is one of the main harmful elements in coal, and the presence of sulfur in coal severely restricts the use of coal. The sulfur element in coal can also cause many environmental and production problems. For example, sulfur-containing gas such as SO_2 released by coal combustion causes acid rain, and sulfur dioxide gas causes corrosion of experimental equipment, causing poisoning of laboratory technicians, etc., which seriously affects the efficiency of production (gasification and coking). The classification standard for high-sulfur coal in China is that the sulfur content in coal is higher than 3%. At present, the proven reserves of high-sulfur coal are 62 billion tons, and the total forecast is 426 billion tons. China's high-sulfur coal resources account for a relatively large amount, accounting for about one-third of total reserves and one-sixth of total mining. High sulfur coal is a kind of coal with special properties, which has huge potential development value. The distribution of sulfur in China's coal generally shows a trend of "low from north to south", and the sulfur content in coal increases from north to south and from west to east. The average sulfur content in coal in North China and East China is relatively high, while the average sulfur content in coal in South China is relatively low. In order to increase the recoverable quantity of coal, the clean utilization technology of high-sulfur coal should be developed.

There are many types of coal desulfurization methods currently used, including physical, chemical, and biological methods. The method of microbial desulfurization comes from the history of biological beneficiation, and its application in the field of coal desulfurization is also being studied by scholars from all walks of life. Coal microbial desulfurization technology has the general advantages of clean, environmentally friendly and sustainable biological methods. The process is simple, low energy consumption, mild reaction conditions. This method also can remove organic sulfur and pyrite sulfur in coal, and does not affect the calorific value of coal, which is not achieved by many methods.

Coal desulfurization is a very important research topic, and solving it has great practical significance. Coal microbial desulfurization reaction is mild, will not reduce the calorific value of coal, and can also remove organic sulfur in coal. It is a promising method of coal desulfurization, which has economic and research significance.

1.2 Overview of high sulfur coal desulfurization research

1.2.1 China’s high-sulfur coal resources and properties

The distribution of sulfur in China's coal generally shows a trend of "North is low and South is high". The sulfur content in coal varies greatly, with a minimum of 0.04% and a maximum of 9.62%. The overall coal types are mainly low-sulfur coal and ultra-low-sulfur coal, which are mainly distributed in Northeast, Northwest and North China. Overall, the sulfur content of coal in China increases from north to south and from east to west. The average sulfur content in coal in southern and eastern China is higher, while the average sulfur content in coal in northern regions (northwest, northeast, and north China) is lower. High-sulfur coal occupies a certain proportion in Chinese coal, mainly in southern and eastern provinces, and a small amount of high-sulfur coal appears in parts of North and Northwest China [1]. Among them, Shanxi, Guizhou, Inner Mongolia, Sichuan, Chongqing, Shaanxi and Shandong are the provinces with the main medium-high sulfur coal and ultra-high sulfur coal distribution in China [2].

China's high-sulfur coal ranks vary widely, including lignite, bituminous coal, and anthracite. High-sulfur coal is widely distributed, mainly in Sichuan, Guizhou, Shaanxi, Shandong, Shanxi and other provinces. There are also a small amount of high-sulfur coal in parts of North China and Northwest China [3]. Among different coal types, gas and fat coal have the highest average sulfur content, followed by lean coal, fat coal and coking coal. Lignite, long-flame coal, non-stick coal and weakly sticky coal have lower average sulfur content. Overall, the average sulfur content of coking coal is higher than that of thermal coal.

1.2.2 Occurrence of sulfur in coal

Sulfur in coal is divided into inorganic sulfur and organic sulfur. Elemental sulfur is also present in coal, but the content is very small [4]. In most of the mining areas in China, the sulfur form in high-sulfur coal is mainly inorganic sulfur, and only a small number of small mining areas are mainly organic sulfur [5].

Inorganic sulfur in coal is generally divided into sulfate sulfur and pyrite sulfur, and a small amount of elemental sulfur. Sulphate sulfur appears in the coal in the form of sulfate, such as barium sulfate ($BaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), etc. Among them, the appearance form of pyrite sulfur is mainly pyrite sulfur, and the structure of pyrite sulfur is square crystal. The pyrite sulfur in coal mostly appears in the form of nodules, dissemination, clumps, and lenses. In addition, pyrite sulfur also includes a small amount of orthorhombic crystal pyrite sulfur, which is mostly radial. In addition to pyrite sulfur, there are other inorganic sulfides, such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), arsenite pyrite ($FeS_2 \cdot FeAS_2$) and galena (PbS), etc[6]. Sulphate sulfur dissolves in water and has little content in coal, usually less than 0.2%. In general, the research on the desulfurization of inorganic sulfur in coal mainly focuses on pyrite sulfur. The formation of pyrite should generally have the following conditions: sulfur source, organic matter and iron supply, suitable for the growth of sulfur-reducing bacteria (anaerobic, neutral pH)[7].

The organic sulfur in coal is mainly bonded to the coal macromolecular framework by C—S bonds, and is stored in the coal macromolecular structure. There are many types of organic sulfur macromolecular skeletons in coal, and the structure is complicated, mainly including thienyl (C4H4S—) and sulfur groups (—S—). Studies[8] suggest that dibenzothiophene (DBT) is used as a model compound of organic sulfur in coal, in organic sulfur of coal The content is high. The sources of organic sulfur in coal are generally considered to be the following: (1) from the original coal-forming parent material; (2) secondary organic sulfur, produced by the interaction of organic matter and inorganic sulfur. Low-sulfur coal is based on the organic Sulfur is dominant, while high sulfur coal is dominated by secondary organic sulfur. Similar to inorganic sulfur, the coal-forming environment determines the enrichment characteristics of organic sulfur in coal [9].

1.2.3 Method and principle of removing sulfur from coal

Industrial desulfurization methods of coal can be generally divided into: desulfurization before combustion, desulfurization during combustion and desulfurization after combustion.

Methods of desulfurization before coal combustion can be divided into chemical desulfurization, physical desulfurization, and biological desulfurization.

Coal physical desulfurization methods include gravity separation, flotation, magnetic separation, oil reunion, etc[10, 11]. Generally, the physical properties of coal and pyrite are used to separate. The properties used by the physical method include electromagnetic properties, density, surface properties, etc. The physical process is simpler and more effective for the removal of pyrite. It cannot remove the organic sulfur in coal. Generally, more than 50% of pyrite can be removed, but the physical method is not high in the removal efficiency of all forms of pyrite, for example, it is not effective for dispersed pyrite.

(1) Desulfurization by flotation: Flotation desulfurization is often used for fine coal desulfurization. Flotation is the separation of coal and pyrite due to the difference in the hydrophilic properties of coal and pyrite with the help of flotation reagents (collector, foaming agent). When this method is applied, the carbon content will affect the flotation results, because carbon particles and pyrite coexist, the effect of high carbon content is better. In addition, sulfur element is hydrophobic, it is enriched on the surface of coal pyrite, carbon particles and pyrite easily enter the foam product at the same time, which makes the separation more difficult. For this reason, the research and development of flotation reagents is an important direction of flotation desulfurization [12].

(2) Gravity desulfurization method: This method is widely used in coal preparation plants, which can achieve the purpose of ash reduction and desulfurization, and generally has high efficiency. Commonly used instruments include jig, shaker, water medium cyclone, heavy medium cyclone, etc. Each machine has its own scope of application and optimal effect.

(3) Magnetoelectric desulfurization method: This method is to use the difference in magnetic properties to further desulfurize, which can effectively reduce sulfur and ash on fine coal. Different materials in coal have different magnetic properties and organic materials are diamagnetic, but pyrite is paramagnetic. Clay and iron-bearing minerals are also paramagnetic. Contrary to organic materials, magnetoelectric methods can be used to achieve effective separation. Mainly include high gradient magnetic separation desulfurization technology, electrostatic method, etc. High gradient magnetic separation desulfurization technology uses magnetic difference, and electrostatic method uses electrical difference.

The biological desulfurization method of coal is a desulfurization method different from the physical method and the chemical method, and its application is not yet widespread. It is usually desulfurized under the conditions of moderate temperature and normal pressure, using the principle of oxidation-reduction reaction. The microbial method has low energy consumption, does not change the calorific value of coal, and can also remove organic sulfur from coal. It is a very clean and environmentally friendly desulfurization method.

There are three main types of coal microbial desulfurization methods, which are microbial flotation, microbial leaching and microbial flocculation.

(1) Microbial flotation

Microbial flotation is a combination of microbial and physical flotation, and its principle is the selective adsorption of bacteria. When microbial bacteria and coal slurry are mixed, the hydrophilicity of pyrite changes due to the selective adsorption of bacteria. However, the adsorption of bacteria and coal particles will not occur, and the surface properties of the coal particles in the mixed coal slurry will not change. After the pyrite and coal with large surface properties are obtained, the flotation method can be used to separate the pyrite and coal particles. The physical properties of the two are quite different, and the flotation method is also more efficient. At present, the most used microorganisms in microbial flotation are Thiobacillus thiooxidans and Thiobacillus ferrooxidans. In the current research field, microbial flotation desulfurization research has several directions: first, on the premise of domesticating the original strain, select and explore new bacterial species, change their characteristics or find new characteristics, and apply them to production practice; second It is to combine with actual production, find out the best technological conditions, meet the requirements of industrial production, and reduce economic costs.

(2) Microbial leaching method

The principle of the biological leaching method is to oxidize pyrite through the reaction of bacterial microorganisms with pyrite. The microorganisms can convert the sulfur in the coal to sulfur dissolved in water, and then discharge it from the solution. The experimental process of this method is not complicated, the point is only to contact the two, and fully react to convert the sulfur in the coal into water-soluble sulfur, and then eliminate it. In addition, the sulfuric acid generated under the coal pile must be collected to avoid polluting the environment. However, the microbial leaching method also has unique shortcomings: (1) long processing time, about 30 days to effectively remove sulfur from a pile of coal samples, which is slower and less efficient than other methods; (2) may pollute the environment due to the acidity of the waste liquid Stronger, it is necessary to deal with the reaction solution in time, otherwise it may pollute the environment.

(3) Microbial flocculation method

The microbial flocculation method mainly uses the surface properties of special microbial strains, combined with the selective adsorption of bacteria. During the test, the bacterial species and coal particles are mixed, and the surface properties of the coal particles will change due to the adsorption of bacteria. The changed coal particles will flocculate with bacteria and be suspended in the coal slurry, but the other components in the coal slurry are still in their original state and will not flocculate and resuspend, so that the two can be separated.

In addition to the above desulfurization technology before coal combustion, desulfurization in coal combustion is also a method. The desulfurization in coal combustion mainly converts the sulfur in the coal into sulfate, which is left in the slag and discharged after the end. The method is to add sulfur-fixing agent to the furnace when coal is burned in the low-temperature boiling bed. The general temperature condition of the desulfurization method in coal combustion is 800~850℃ The sulfur fixing agent is generally $CaCO_3$, CaO or MgO powder. This method can remove 50% to 60% of the sulfur in coal.

Desulfurization after coal combustion is to desulfurize the gas after coal combustion. The desulfurization of coal after combustion can be divided in various ways, according to whether the product is recovered, the wet and dry nature of the desulfurization process, the use of desulfurization agent, etc. According to whether the product is recovered, it can be divided into abandonment method and recovery method; according to the use of desulfurization agent, it can be divided into regeneration method and non-regeneration method; according to dry and wet properties, it can be divided into dry desulfurization, semi-dry desulfurization and wet desulfurization. After the coal is burned, the desulfurization and desulfurization rate can be as high as 90%, but there are also shortcomings, the process is complicated, the operating cost is high, and there are many by-products that are difficult to handle.

In summary, the pre-combustion desulfurization technology has many characteristics, such as desulfurization while reducing ash, low transportation costs, low sulfur content in flue gas, and less corrosion of boilers and flues. In addition, it has the advantages of low tailings disposal and equipment maintenance costs, good environmental protection effects and economic benefits, and is also most suitable for application. Among them, microbial desulfurization not only requires low energy consumption, does not change the calorific value of coal, but also can remove organic sulfur in coal. It is a very clean and environmentally friendly desulfurization method.

1.3 Overview of coal biological desulfurization

1.3.1 Research progress of coal microbial desulfurization

Coal microbial desulfurization started earlier. At the beginning of the 20th century, people began to understand the oxidation of microbial strains, which is the basis of microbial desulfurization. In 1922, Rudolf. W et al. [13, 14] pioneered the leaching experiment of pyrite with microbial bacteria. In 1947, Clomer and Hinkle [15] discovered the presence of Thiobacillus ferrooxidans (T.f bacteria) in acid mine water, and experiments proved that the strain could promote oxidation and dissolve pyrite in coal. This discovery is considered to be the beginning of microbial metallurgy research. Based on this research, research on microbial desulfurization was carried out in the 1950s. In the next few decades, microbial leaching technology has attracted the attention of scholars at home and abroad, and has conducted many experiments and production knowledge. At present, the use of microbial ore leaching technology is becoming mature, and the fields of industrialization include gold mine, copper mine, uranium mine and so on. However, the technology of coal microbial desulfurization is not mature. It is currently in laboratory tests, and a few are in the stage of semi-industrial application, which has not yet been applied on a large scale.

In the history of coal microbial desulfurization, T.f bacteria was first used to desulfurize pyrite in coal in 1958. Leathen et al. [16] obtained groundbreaking research results. Sliverman studied the oxidation mechanism and growth characteristics of pyrite by T.f bacteria and found that T.f bacteria had an accelerated effect on the oxidation of pyrite [17]. Since then, Kargi et al. [18,19] are not limited to the current research direction and began to explore the possibility of applying microbial leaching method to coal desulfurization. Kargi et al. [20] studied Sulfolobus acidocaldatius and found that it can remove pyrite and organic sulfur, which can remove most pyrite and some organic sulfur. Bhattacharyya et al. [21] used T.f bacteria and Thiobacillus thiooxidans (T.t bacteria) for research, which not only confirmed the removal of inorganic sulfur in coal, but also found that it can remove organic sulfur in coal. Lu et al. [22] proposed the mechanism of microbial coal desulfurization through experiments. It is believed that the oxidation of pyrite (FeS_2) to $Fe_2(SO_4)_3$ is the reason for the removal of inorganic sulfur, and the trivalent iron ions produced by the reaction are used as catalysts. It helps the subsequent oxidation reaction. In addition, two mechanisms for the removal of organic sulfur are also proposed. One is the removal by oxidation and decomposition, and the other is the direct absorption and utilization by microorganisms.

Stevens[23] selected bituminous coal from Illinois in the United States for a microbial desulfurization experiment, using T.f bacteria, and obtained a pyrite removal rate of 87% with a recovery rate of 95%. Tsuji et al. [24] selected Turkish lignite as the research object, and also carried out a desulfurization test using T.f. bacteria, resulting in a 50% organic sulfur removal rate and a 90% pyrite removal rate. Klein et al. [25] made innovations, not limited to the coal field. They applied the idea of microbial desulfurization to petroleum and achieved remarkable results. In addition, scholars have used Sulfolobus acidocaldarius[26], Acidthiobacillus ferrooxidans (Af bacteria)[27,28], Acidianus brierleyi[29 , 30] and other different bacteria, desulfurization experiments on high-sulfur coal in different regions, using biological pretreatment flotation[31], leaching desulfurization, etc.[32], all of which achieved a high desulfurization rate. In addition to common strains, Anger et al. [33] used microorganisms enriched locally in Spain (mainly Acidithiocacillus sp. and Leptospirillum sp.) to study different coal types such as lignite, bituminous coal, and anthracite, and the results showed that the desulfurization rate can reach 70% to 90%. L. Gonsalvesh et al. [34] used Phanerochaeta chryosporium and Sulfolobus solfataricus to carry out the desulfurization orthogonal test, and obtained good results, proving that microorganisms can improve the desulfurization effect. After this, L. Gonsalvesh[34,35] conducted a study on Bulgarian lignite and innovatively selected Pseudomonas putida, which obtained a total sulfur removal rate of 71% and 90.6% yellow iron Mine sulfur removal rate, 49.4% organic sulfur removal rate.

The overall research on microbial desulfurization technology in China is later than abroad. In 1992, Li Lei [36] and others used A.f bacteria and Acidthiobacillus thiooxidans to conduct microbial desulfurization studies on Zaozhuang high-sulfur coal. The experimental results were good, and the maximum desulfurization rate in 12 days could reach 44.1%. Subsequently, Hou Chun [37], Li Xikun[38], Fu Jianhua[39], Zhang Lifang[40,41] and other scholars used A.f bacteria against Shenyang[42, 43], Yunnan[44], Inner Mongolia[45] , Chongqing[46] and other high-sulfur coal desulfurization studies in different regions, the desulfurization rate is above 45%, and some can reach 90%. In addition to A.f bacteria, scholars have also used Phanerochate chrysosporium[47,48], Escherichia coli[49], Pseudomonas sphaeroides[50,51] to desulfurize high-sulfur coal Experiments have achieved a higher desulfurization rate. In 2009, Xie Zuohuang [52] pioneered the use of silicate bacteria for high-sulfur coal desulfurization experiments, with a total sulfur removal rate of up to 35.78%. The bacteria are used in biological fertilizers [53,54], mineral bioprocessing, and sewage There has been a lot of research and application in processing[55,56] and other aspects. In addition, some scholars have also used other methods to study coal desulfurization. Wang Deqiang et al. [57] conducted a desulfurization experiment on high-sulfur coal in southern Anhui, using colored bacteria in a continuous stirring (CSTR) reactor. The experimental results showed that the desulfurization rate in 35 days could reach about 50%. Zhang Dongchen et al. [58,59] used microbial magnetization technology to study the role of various bacteria in coal flotation desulfurization. Tao Xiuxiang et al. [60] attempted to quote the electrochemical method, which is an innovative method that makes the A.f bacteria and coal more tightly combined, resulting in a better desulfurization effect. Wang Rui[61] provided a theoretical basis for the basic principles of biological desulfurization through systematic research. Mainly through the study of different bacterial physiological indicators, analysis of its mineral metabolism pathways, so as to obtain the basic principles of sulfur sulfur bacteria metabolizing sulfur in coal[62].

In summary, China's research on microbial desulfurization of high-sulfur coal has not been interrupted from the beginning to the present, but there has been no major breakthrough. Most of the actual results are not ideal enough to be extended to the industrial stage, and are still in the laboratory research stage. The main research form is the desulfurization effect of a single strain laboratory, and the research focus is also on the removal of inorganic sulfur. Because the energy structure abroad is different from China, it is mainly based on oil and natural gas, and there are few studies on coal microbial desulfurization.

1.3.2 Desulfurization microorganisms

The basis of coal biological desulfurization is desulfurization microbial strain resources. The key to coal microbial desulfurization technology is to select well-cultivated and suitable desulfurization microbe strains. Microbial experiments are generally more targeted, and different desulfurization microorganisms are also needed to treat the morphological sulfur.

Combined with previous research, Thiobacillus ferrooxidans (T.f) and Thiobacillus thiooxidans (T.t) are two types of bacteria that are widely used in desulfurization and have good effects. These two microorganisms have the best effect on removing pyrite sulfur in coal, but the effect on removing organic sulfur is not obvious. The most effective strains for removing organic sulfur are CB1, R. rhodochrous of Pseudomonas and S. acidocaldarius of Sulfolobus. There are few bacterial species that can effectively remove inorganic sulfur and organic sulfur from coal at the same time.

At present, the common microorganisms used to remove pyrite sulfur in coal include Thiobacillus ferrooxidans, Thiobacillus ferrooxidans, Leptospirillium ferrooxidans, Thiobacillus acidophilus, etc. The principles of the above-mentioned microbial desulfurization are similar, all of which oxidize the sulfide minerals in the coal, thereby removing sulfur from the coal.

In addition to inorganic sulfur in coal, the removal of organic sulfur is also of great concern. The research on the technology of desulfurization is a hotspot of related research in the field of geology and mining. Due to the limited knowledge of organic sulfur, there is no universal and efficient model material as a representative, and the structure of organic sulfur is very complex and there are many types, so it is difficult to breed bacteria for organic sulfur desulfurization. The commonly used organic sulfur model substances are DBT (dibenzothiophene) and BT (phenylpropylthiophene). After years of research by scholars at home and abroad, some microorganisms with organic sulfur metabolic capacity have been found, represented by Rhodococcus, Gordonella, Arthrobacter, and Sulfolobus acidophilus. The following table shows common microorganisms that are effective in removing organic sulfur.

Tab. 1.1 Common desulphurization bacteria for sulfide minerals and elemental sulfur

Strain name	Form	Taxonomy	Physiological and biochemical characteristics
Acidthiobacillus thiooxidans	Short rod		Obligatory autotrophic, growth temperature 20~40℃, pH1.5~4, oxidized elemental sulfur and reduced sulfide
Thiobacillus ferrooxidans	Short rod, G-	Acidthiobacillus	Obligatory autotrophic, growth temperature 20~40℃, pH1.2-3.0, ferrous oxide and elemental sulfur
Acidthiobacillus caldus	Short rod, G-, Flagella		Obligatory autotrophic, growth temperature 30~55℃, pH1~5, oxidized elemental sulfur and reduced sulfide
Ferroplasma themophilum	Archaea, no cell wall, no flagella	Ferrobacter	Facultative autotrophic, 23~46℃, pH0.2~2.5, capable of oxidizing ferrous sulfur

Continued Tab. 1.1

Strain name	Form	Taxonomy	Physiological and biochemical characteristics
Ferroplasma curpicumulans			Facultative autotrophic, 22~63℃, pH1.0~1.2, oxidize ferrous sulfur
Ferroplasma acidiphilum			Facultative autotrophic, pH2.4~3.5, oxidize ferrous sulfur
Ferroplasma acidarmanus			Facultative autotrophic, 35~42℃, pH1.0~1.7, Ferrous oxide, sulfur oxide, need growth factors
Leptospirillum ferriphilum	Spiral, G-, Flagella	Leptospira	Obligatory autotrophic, 20~45℃, pH1.2~3.0

There are many factors that affect microbial growth activities and desulfurization effects, mainly including the following seven points:

(1) Coal particle size: Coal particle size has a great influence on the oxidation activity and leaching effect of bacteria. Generally speaking, the smaller the particle size of coal, the larger the surface area and the greater the porosity, the easier the pyrite leaches.

(2) Temperature: The suitable temperature of the strain should conform to the physiological characteristics of the strain. In addition, consideration should be given to the need for heat dissipation, and cooling equipment should be prepared to avoid the temperature rise of the exothermic reaction of biological leaching ore, and to ensure that the temperature is basically stable. For example, 30°C is the optimal growth temperature for Thiobacillus thiooxidans.

(3) Coal slurry concentration: If the concentration of coal slurry is too high, it will hinder the growth and activity of microorganisms, and a lower concentration is better. For the effect, the coal slurry concentration cannot exceed 20%.

(4) pH: Environmental pH is an important indicator of microbial growth activity. For most microorganisms, the environmental pH for growth is 5 to 9, but for desulfurized microorganisms, the optimal pH for desulfurization is generally low. For T.f bacteria, the optimal pH value for desulfurization test is 2~3.

(5) Redox potential value: The redox potential has a great influence on the growth activities of microorganisms. Most of the desulfurized microorganisms are aerobic autotrophic bacteria, and it is necessary to ensure an appropriate amount of dissolved oxygen in the water.

(6) Inoculation concentration: The cell concentration is the same as the slurry concentration, and the higher the better, there is an optimal value. For the T.f bacteria desulfurization experiment, the optimal inoculum is 106~1013 cells per g of pyrite.

(7) Desulfurization time: the growth and reproduction of microorganisms is slow, and the general cycle is more than 5~7 days. Similarly, the desulfurization of microorganisms generally takes a long time, and there is also an optimal time. The optimal action time of each strain is different, which is related to the characteristics of the strain and the reaction conditions.

1.3.3 Microbial desulfurization mechanism

Sulfur in coal is generally divided into inorganic sulfur and organic sulfur. Inorganic sulfur mainly includes pyrite sulfur and sulfate sulfur. There are many types of organic sulfur and complex structure. When describing the microbial removal mechanism of organic sulfur in coal, DBT is usually used as the model compound. In characterizing the removal mechanism of inorganic sulfur, the oxidation process of pyrite sulfur in coal is described by microorganisms. The removal mechanism of pyrite sulfur by microorganisms is divided into two categories: direct mechanism and indirect mechanism. The direct mechanism is that microorganisms directly oxidize the sulfur in FeS_2. The indirect mechanism is to oxidize the ferric iron ions to ferric iron ions first, and then the ferric ions oxidize the sulfur in FeS_2 indirectly. In addition, the removal of organic sulfur is also divided into two types: 4-S mechanism and Kodama mechanism. When the sulfur in DBT is selectively oxidized by microorganisms, the calorific value of the coal is not reduced, and the coal structure is not destroyed, which is the 4-S mechanism. The carbon source of microorganisms in the Kodama mechanism comes from the carbon in the DBT and does not oxidize or partially oxidize the sulfur in the DBT. Microorganisms degrade the aromatic ring structure in coal, and finally generate sulfur-containing compounds, which are water-soluble, and the coal calorific value of Kodama mechanism is lost. At present, scholars do not know much about the mechanism of microbial cells on the metabolism of sulfur-containing compounds, but the microbial metabolism and intermediate products are well understood, and they also have a deep understanding of the conversion of sulfides in the reaction.

(1) Inorganic sulfur removal mechanism

Pyrite can be oxidized to SO_4^{2-} and Fe^{2+} in the presence of water and oxygen. This process is very slow under natural conditions. But this process can be accelerated by certain species of bacteria, such as acidophilic thiobacillus. There are two ways to accelerate the strains: First, pyrite is directly oxidized by microorganisms:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \tag{1.1}$$

The second is that Thiobacillus quickly oxidizes the ferric iron ions into ferric iron ions, which act as catalysts and strong oxidants to react with metal sulfides to oxidize pyrite sulfur:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{1.2}$$

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S \tag{1.3}$$

Although direct mechanisms are more valued, indirect mechanisms are also very useful. For example, sometimes microbial cells cannot physically contact pyrite, and the ability of ferric iron ions to penetrate becomes the key to pyrite oxidation [63].

When pyrite is dispersed very finely in coal, there is a lot of room for indirect mechanisms. The indirect mechanism requires the introduction of sulfur-oxidizing bacteria, which are oxidized to SO_4^{2-} by the following reaction, resulting in the deposition and removal of elemental sulfur.

$$S + \frac{3}{2}O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \tag{1.4}$$

Organic sulfur in coal is mainly present in the coal's macromolecular structure, in the form of thiophene (C4H4S-), mercapto (-SH), sulfide (-S-), and polysulfide chain $(\text{-S-})_x$. The desulfurization mechanism using DBT as a model compound is as follows: (1) 4-S route[64], mainly for metabolizing sulfur; (2) Kodama pathway, mainly for carbon metabolism, the reaction is shown in Fig. 1.1. The above-mentioned forms of existence are mostly dispersed at the molecular level, which is difficult to remove by ordinary physical methods.

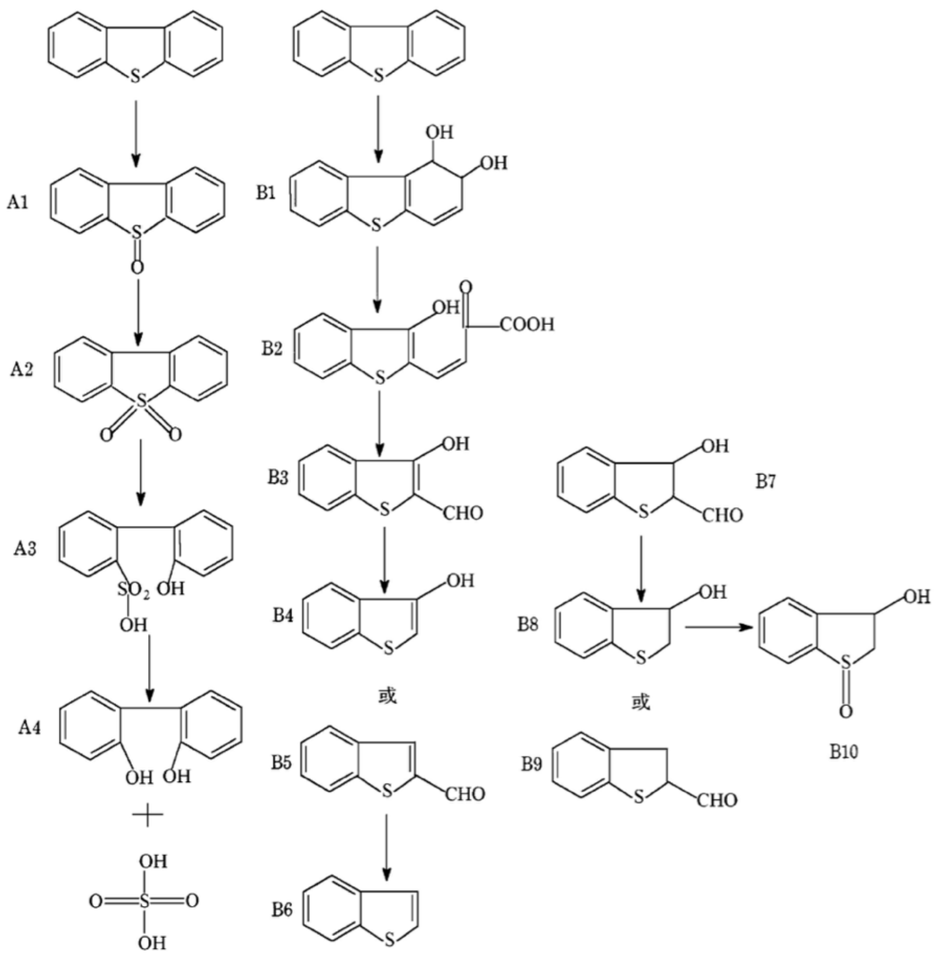


Fig. 1.1 Decomposition mechanism of DBT by microorganisms

1.3.4 Microbial desulfurization process

The current basic process of microbial desulfurization is shown in Fig. 1.2.

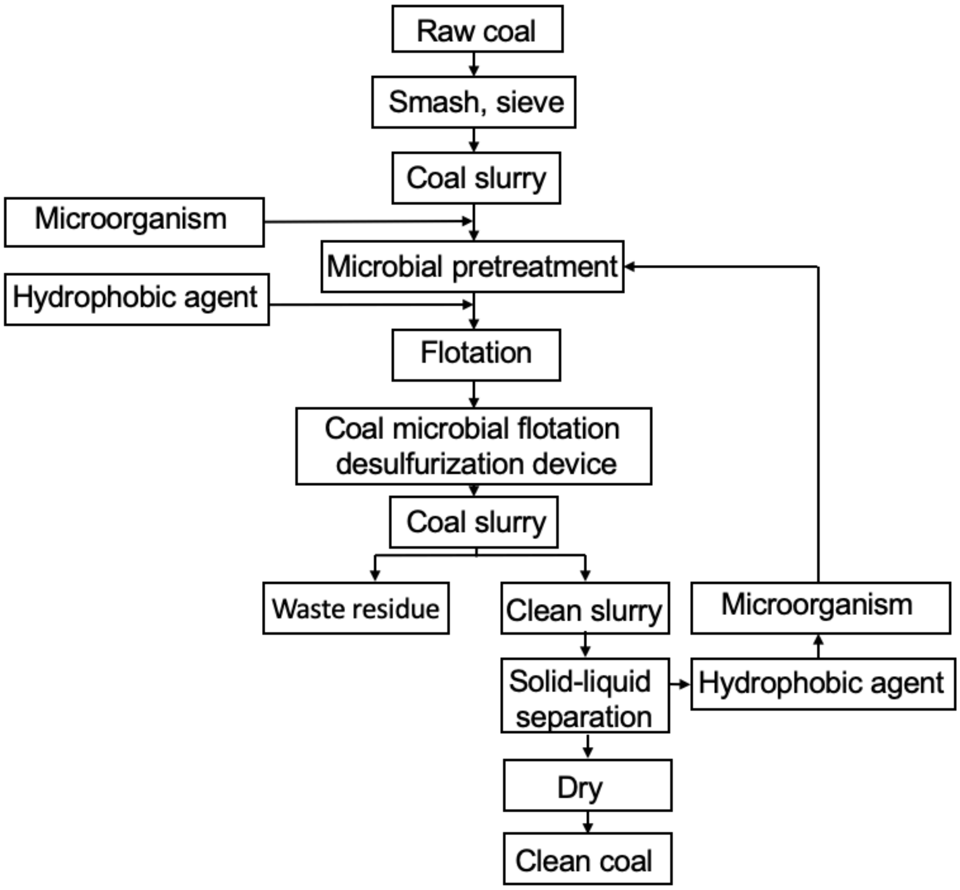


Fig. 1.2 Basic process of microbial desulfurization

1.4 Research content and technical route

1.4.1 Main research content

The purpose of this study is to use microbial technology to conduct desulfurization experiments on Shanxi high-sulfur coal, select suitable desulfurization microorganisms, and study the best desulfurization effect that can be achieved in a certain period. Based on the full collection of existing research results at home and abroad, select typical high-sulfur coal samples in Shanxi, comprehensively use geochemical, coal petrology, mineralogy methods and experimental simulation, statistical analysis and other methods to study the characteristics of coal and coal, coal The nature of medium sulfur, and select the appropriate desulfurization microorganisms according to this, to study the best desulfurization effect that can be achieved in a certain period. Finally, combined with the desulfurization effect of other desulfurization technologies, evaluation and analysis are made to provide more options for coal desulfurization technology and help the next development of coal microbial desulfurization technology.

(1) Analysis of coal and rock quality of high sulfur coal in Shanxi

Use optical microscope and other experimental instruments to quantify the microscopic components of the coal samples used, and analyze the characteristics of the microscopic components in the raw coal and washed samples. Analyze the coal phase type, coal rock component characteristics, coal chemical characteristics, etc. of high-sulfur coal samples from the perspectives of coal rock coal quality and coal geology, and determine the occurrence of total sulfur, various forms of sulfur, and sulfur in coal samples Parameters such as state.

(2) Preliminary research on microbial desulfurization experiment

The typical desulfurization microorganisms were used to conduct desulfurization studies on Shanxi high-sulfur coal samples to determine the desulfurization effect of each bacterial species, and to conduct comparative analysis.

(3) Microbial desulfurization experiment

Based on the results obtained from the preliminary experimental research, the coal desulfurization conditions of the optimal strains were optimized to determine the optimal coal desulfurization conditions for the strain, and the desulfurization experiments were carried out on the high-sulfur coal samples.

(4) Mechanism and evaluation of microbial coal desulfurization

A preliminary study on the desulfurization mechanism of the selected microbial coal is carried out from the change of sulfur content in the coal sample before and after treatment and the change of the treatment liquid element, combined with the coal rock quality of the high-sulfur coal sample, the occurrence state of sulfur in the sample, and common desulfurization methods Compare the results and make an evaluation.

1.4.2 Research methods

Extensive investigation of domestic and foreign research materials, comprehensive use of coal petrology, coal chemistry, geochemistry, statistical analysis and other methods to study Shanxi high sulfur coal samples. Use typical desulfurization microorganisms to conduct desulfurization research on the collected high-sulfur coal samples, conduct preliminary experiments, select the best strains to carry out in-depth experiments, and finally select the microbial coal from the changes in the sulfur content of the coal samples before and after treatment and the changes in the treatment liquid elements. A preliminary study on the mechanism of desulfurization was conducted, combining the coal rock quality of the high-sulfur coal sample and the occurrence state of sulfur in the sample, and compared with the results of common desulfurization methods and making an evaluation.

(1) Coal petrology method: Under the oil-immersed reflected light, the coal powder composition of the sample powder coal is quantified, and the mineral composition of the micro component is observed and quantified under the microscope.

(2) Coal chemistry method: perform industrial analysis and elemental analysis on raw coal and washed coal samples, and compare the changes of industrial indexes in coal of various washed products, especially before and after the sulfur element experiment.

(3) Biological method: apply the redox reaction in the process of microbial metabolism, perform desulfurization experiments on the sample, record the desulfurization rate, and make analysis and interpretation.

(4) Statistical methods: The regression analysis method and the orthogonal method of multivariate statistics are used to analyze and analyze the analyzed data, and the correlation between the sulfur content in the sample and related factors is investigated.

1.4.3 Technical route

The main technical route of this research is shown in the following figure:

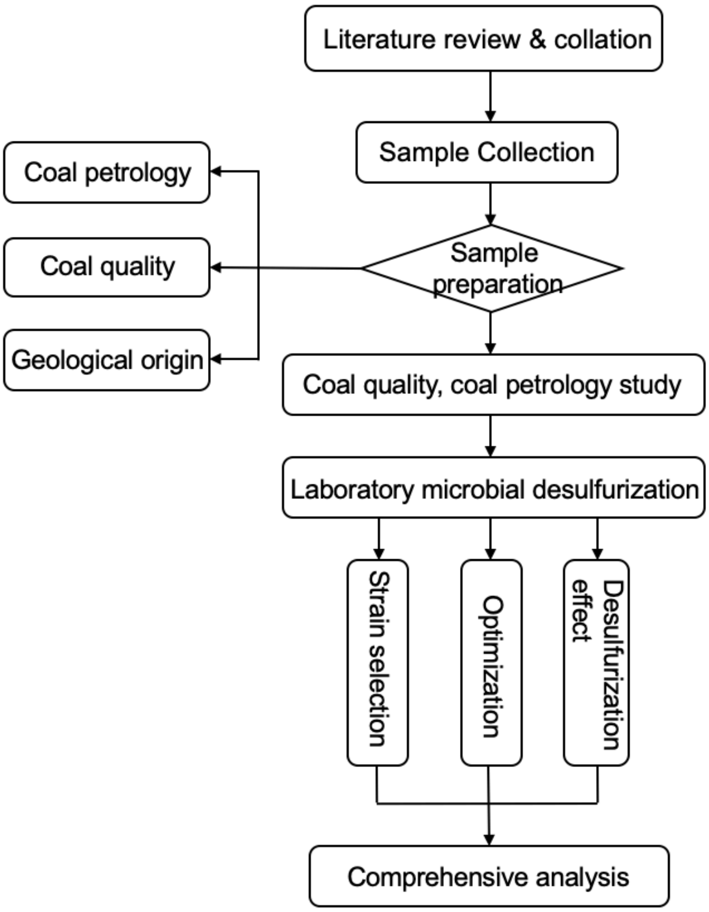


Fig. 1.3 Technology roadmap

1.5 Chapter summary

This chapter elaborates the research background and significance of this subject. Through a comprehensive analysis of the research status of high sulfur coal desulfurization at home and abroad:

(1) There are many types of coal desulfurization methods currently used, including physical, chemical, and biological methods. The method of microbial desulfurization comes from the history of biological beneficiation, and its application in the field of coal desulfurization production is also a research hotspot. Coal microbial desulfurization technology not only has the general advantages of biological methods, such as clean and environmentally friendly, simple process flow, low energy consumption, mild reaction conditions, but also microbial desulfurization method can remove organic sulfur and pyrite sulfur in coal, and does not Affecting the calorific value of coal, this is not achieved by many methods.

(2) China's research on high-sulfur coal microbial desulfurization has not been interrupted from the beginning to the present, but there has been no major breakthrough. Most of the actual results are not ideal enough to be extended to the industrial stage, and are still in the laboratory research stage. The main form of research is the study of the desulfurization effect of a single strain laboratory, and the focus of the research is also the removal of inorganic sulfur. The energy structure abroad is different from China, mainly oil and natural gas, and there are few studies on coal microbial desulfurization.

(3) At present, the most effective desulfurization strains for pyrite sulfur present in coal are Thiobacillus ferrooxidans (T.f) and Thiobacillus thiooxidans (T.t), which also have a certain removal effect on organic sulfur. Selecting different coal samples for microbial flotation experiments and exploring the desulfurization effect of microorganisms on high-sulfur coal samples are of great significance for the development of microbial flotation desulfurization methods.

Coal desulfurization is a very important research topic. Based on the above literature survey, the research content of this topic has been determined. Shanxi is a major coal province in China, with rich coal resources. Shanxi's high-sulfur coal is widely distributed and the degree of metamorphism changes greatly, which is conducive to the study of the adaptability of high-sulfur coal to microbial surface flotation. In this experimental study, Shanxi typical high organic sulfur coal was selected as the research object, and microbial desulfurization treatment was carried out to study the best desulfurization effect that can be achieved in a certain period. Finally, combined with the desulfurization effect of other desulfurization technologies, evaluation and analysis were made for coal. The desulfurization technology provides more options, and also helps the next development of coal microbial desulfurization technology.

2 Sample selection and analysis method

2.1 Sample selection

Shanxi is a major coal province in China, with rich coal resources. Shanxi's high-sulfur coal is widely distributed and the degree of metamorphism changes greatly, which is conducive to the study of the adaptability of high-sulfur coal to microbial surface flotation. In this experimental study, three coal samples with significant differences in coal and coal quality were collected in Shanxi Province. Thiobacillus ferrooxidans were used to carry out microbial flotation desulfurization experiments to explore different particle sizes, pretreatment time and coal samples. The influence of its own characteristics on the desulfurization effect of microbial flotation.

Yunquan YQ 15-2 is low ash, extra low volatile anthracite; Xinyu XY10-4 is extra low ash, medium volatile bituminous coal; East Open DLT11-10 is low, medium ash, high volatile long flame coal. The total sulfur content of YQ, XY, and DLT coals is 4.65%, 3.24%, and 5.90% respectively, all of which are greater than 3%. They are all high-sulfur coals. The organic sulfur content of coals is relatively high, accounting for more than 50% of the total sulfur.

2.2 Geological background of the study area

The Yunquan mining area is located in Mishan Town, Gaoping City, Shanxi Province. This field is an irregular polygon with a width of 2.80km from east to west and a maximum length of 4.35km from north to south. The mine field is located in the south of Qinshui coal field. The valleys in the minefields are developed and the terrain is complex, which belongs to the middle and low hilly landforms. The highest elevation of the terrain in the Yunquan mining area is 1167.03m, which is located on the mountain beam in the central and southern parts of the mine field. The lowest elevation of the terrain is 873.95m, and it is located in the northwest of the mine field. The maximum relative height difference is 293.08m. This area belongs to the Dan River tributary of the Qinhe River system in the Yellow River Basin. The Dadongcang River, a tributary of the Dan River, flows 7km away from the western boundary of the well field. There is no perennial surface runoff and large surface water bodies in this field. The main water source is atmospheric precipitation. The gully is naturally discharged to the Dan River in the west.

East Open Pit Coal Mine is under the jurisdiction of Pinglu District, Shuozhou City, Shanxi Province, and is located at the northern end of Pingshuo Mining Area. The whole area is mostly covered by loess, with sparse vegetation, which is a typical loess hilly landform. The coal seams in the area are mostly black, brown-black, and the streaks are brown-black; weak glass gloss or asphalt gloss; strip-shaped, uniform structure, massive structure. Staggered and irregular fractures; endogenous fissures developed, filled with calcite veins; No. 9 and 11 coal see pyrite nodules or thin films.

The Xinyu mining area is located in Xiaoyi City, Shanxi Province. The mining area is about 8.4km long from north to south, 7.1km wide from east to west, and the mining area is 57.02km^2. The total thickness of the coal-bearing rock series is 144.8m. The Taiyuan Formation has an average thickness of 102.6m and 7 coal-bearing layers. The Shanxi group has an average thickness of 42.2m and contains 4 layers of coal.

2.3 Analysis method

(1) Coal petrology method: quantify the microscopic coal rock composition of the pulverized coal light sheet of the sample under oil-immersed reflected light, and observe and quantify the microscopic mineral composition under the microscope.

(2) Coal chemistry method: perform industrial analysis and elemental analysis on raw coal and microbial treated samples, and analyze the changes of industrial indicators in each coal sample, especially the changes before and after the sulfur element experiment.

(3) Biological method: Select Thiobacillus ferrooxidans, apply the redox reaction in the process of microbial metabolism, perform desulfurization experiments on the samples, record the desulfurization rate before and after the experiment, and make analysis and explanation.

2.4 Chapter summary

This study selects high-sulfur coal in three typical mining areas in Shanxi Province as the research object. The distribution is more comprehensive, the degree of metamorphism varies greatly, and it is representative. Using a combination of coal petrology, coal chemistry and biological methods to carry out experimental research on microbial flotation desulfurization of different types of high-sulfur coal.

The three high-sulfur coal samples used in the experiment were taken from Yunquan Mine in the southeast of Shanxi Qinshui Coalfield, East Opencast Mine in the northwest of Shanxi, and Xinyu Mine in Xiaoyi, Shanxi. YQ 15-2 is low ash and extra low volatile anthracite; XY10-4 is extra low ash and medium volatile bituminous coal; DLT11-10 is low and medium ash and high volatile long flame coal. The total sulfur content of YQ, XY, and DLT coals is 4.65%, 3.24%, and 5.90% respectively, all of which are greater than 3%. They are all high-sulfur coals. The organic sulfur content of coals is relatively high, accounting for more than 50% of the total sulfur.

3 Coal rock and coal quality characteristics of high organic sulfur samples

3.1 Coal rock characteristics

The analysis of coal rock characteristics of Shanxi's high-sulfur coal samples mainly includes the production of pulverized coal flakes, the determination of vitrinite reflectance, and quantitative analysis of microscopic components. The microscopic coal rock characteristic data of this experiment sample are shown in Tab. 3.1.

3.1.1 Macrolithtype coal characteristics

According to the macro coal type of bituminous coal, YQ15-2 is bright coal, XY10-4 is semi-bright coal, DLT11-10 is semi-dark coal, and each sample belongs to three different macro coals Rock type.

3.1.2 Micro coal characteristics

The degree of deterioration of the test samples is quite different. The range of the maximum reflectance of the vitrinite group of each sample is 0.70%~2.59%. Among all the samples, the vitrinite reflectance of the YQ15-2 is 2.59, which belongs to high-rank coal I; the reflectance of the XY10-4 is 1.15, which belongs to medium-rank coal; and DLT11-10 is 0.70, which belongs to medium coal rank coal. Identify the microscopic coal and rock characteristics of the sample, and then classify the microscopic components of the sample. The quantitative results of the microscopic coal and rock of the sample are shown in Tab. 3.1.

Overall, the microscopic coal rock components of each coal sample are mainly in the vitrinite group, the lipid group is the lowest, and the inert group is in the middle. The vitrinite content of the whole sample is 66.2%~78.0%, of which the vitrinite content is the highest in DLT11-10, 78.0%; the vitrinite content in YQ15-2 is the lowest, 66.2%. In addition, the gel structure vitrinite content of DLT11-10 coal sample is relatively high, reaching 51.8%. XY10-4 and YQ15-2 have a higher content of gel debris and structural vitrinite. In addition, the mineral content of YQ15-2 was the highest at 11.2%, and the mineral content of XY10-4 was the lowest at

3.8%. Among the minerals, the clay content is the highest, followed by quartz and pyrite.

Tab.3.1 Maceral content and macrolithtype of coal samples

Location	No.	Macrolithotype of coal	Vitrinite (%)				V	Inernite (%)						I	Liptinite (/%)	Minerals (%)				M
			T	CD	CT	VD		F	SF	Ma	ID	Fu	Mi			Py	Qu	Ca	Cl	
Yunquan	YQ15-2	Bright coal	10.0	20.8	25	10.4	66.2	5.6	5.2	7.2	4.6	-	-	22.6	-	2.0	5.6	-	3.6	11.2
Xinyu	XY 10-4	Semi-bright coal	15.6	36.0	17.6	3.4	72.6	13.8	6.6	2.2	0.8	0.2	--	23.6	-	0.6	0.4	1.4	1.4	3.8
East Open Pit	DLT11-10	Semi-dark coal	9.2	15.0	51.8	2.0	78.0	0.6	2.0	0.2	3.2	-	6.2	12.4	-	5.2	0.2	0.8	3.4	9.6

Note: T-telinite, CD-collodetrinite, CT-collotelinite, VD-vitrodetrinite, V-virtrinite, F-fusinite, SF-semifusinite, Ma-macrinite, ID-inertodetrinite, Fu-funginite, Mi-micrinite, Py-pyrite, Qu-quartz, Ca-calcite, Cl-clay, M-mineral, -not detected.

3.2 Coal quality characteristics

The industrial analysis, elemental analysis and total sulfur and morphological sulfur analysis of the coal samples in this test are based on national standards and were measured at the Shanxi Institute of Geology. The experimental data is shown in Tab. 3.2.

3.2.1 Industrial analysis

Water (M_{ad}): The water in coal can be divided into free water and combined water according to the combined state. The measured moisture in industrial analysis is the "air-dry moisture" or internal moisture. The internal moisture of coal is adsorbed in the capillary pores inside the coal particles. In addition to the surface area, the internal moisture content is also related to the adsorption capacity of coal. DLT11-10 has the highest moisture content of 2.09%. YQ15-2 has the lowest moisture content of 0.64%. Overall, the moisture content of each experimental sample is not much different, ranging from 0.64% to 2.09%.

Ash (A_d): Ash in coal generally indicates the content of minerals in coal, which is the residue left after coal is completely burned. The ash content of coal is divided into internal ash content and external ash content. The ash yield of the selected samples this time is from 4.59% to 12.46%, which are not high, and all belong to low ash coal. Among them, XY10-4 has the lowest ash content of 4.59%, which is an ultra-low ash coal; YQ15-2 ash content is in the middle, 6.18%, which is a low ash coal; DLT11-10 ash content is the highest, 12.46% , low and medium ash coal.

Volatile matter (V_{daf}): The fraction of volatile matter in the mass of coal sample is called volatile matter. The higher the volatile content, the lower the calorific value. The selected samples have a volatile yield ranging from 8.71% to 47.74%, with a large variation range, ranging from low-volatile coal to high-volatile coal. The volatile content has a strong correlation with the degree of coalification. The lower the degree of coalification, the higher the volatile yield. Among them, DLT11-10 has the highest volatile yield, at 47.74%, which belongs to high volatile coal; YQ15-2 has the lowest volatile yield, at 8.71%, belongs to ultra-low volatile coal; XY10 -4 The yield of volatile matter is 22.12%, which belongs to medium volatile coal.

Tab.3.2 Industrial analysis, elemental analysis and morphological sulfur determination of samples

Location	No.	Industrial analysis (%)			Element analysis (%)					H/C	O/C	Morphological sulfur analysis (%)				$S_{o,d}/S_{t,d}$
		M_{ad}	A_d	V_{daf}	C_{daf}	H_{daf}	N_{daf}	O_{daf}	$S_{o,daf}$	(atom)	(atom)	$S_{t,d}$	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$	
Yunquan	YQ15-2	0.64	6.18	8.71	88.57	3.39	1.23	0.46	3.69	0.46	0.03	4.65	1.18	0.01	3.46	0.74
Xinyu	XY10-4	0.76	4.59	22.12	82.98	4.40	1.20	3.33	3.16	0.64	0.03	3.24	0.2	0.02	3.02	0.93
East open pit	DLT11-10	2.09	12.46	47.74	79.20	5.47	1.17	7.43	3.46	0.83	0.07	5.90	2.85	0.02	3.03	0.51

Note: M_{ad}-moisture, A_d-ash, V_{daf}-volatile, C_{daf}-carbon content, H_{daf}-hydrogen content, N_{daf}-nitrogen content, O_{daf}-oxygen content, $S_{o, daf}$-organic sulfur content (dry ash-free), H /C-hydrogen-carbon atomic ratio, O/C-oxygen-carbon atomic ratio, $S_{t, d}$-total sulfur content, $S_{p, d}$-pyrite sulfur content, $S_{s, d}$-sulfate sulfur content, $S_{o, d}$-organic sulfur Content, $S_{o, d}/S_{t, d}$-organic sulfur accounts for the proportion of total sulfur.

3.2.2 Elemental analysis

The content of each element in coal is mainly determined by the combustion method. Common elements in coal include carbon, hydrogen, oxygen, nitrogen and so on. The tested high sulfur coal sample carbon content (C_{daf}) ranged from 79.2% to 88.57%, and the hydrogen content (H_{daf}) ranged from 3.39% to 5.47%. Among them, the anthracite YQ15-2 carbon content is 88.59%, which is the highest in all samples, and the Yunquan coal sample hydrogen content is 3.39%, which is also the lowest. In addition, the maximum vitrinite reflectance of Yunquan is also the highest, at 2.59. The DLT11-10 sample of Changyan Coal has the lowest metamorphism, with the lowest carbon content of 79.20% and the highest hydrogen content of 5.47%. Studies have shown that the carbon, hydrogen, and oxygen content of coal increases with the degree of coalification. The H/C atomic ratio changes positively with the degree of metamorphism of coal. The higher the degree of metamorphosis, the greater the H/C atomic ratio.

3.2.3 Analysis of total sulfur and morphological sulfur of coal samples

The coal samples in this experiment were all high-sulfur coal samples, and the total sulfur content in the samples was greater than 3%. The overall total sulfur content ($S_{t,d}$) ranged from 3.24% to 5.90%. The total sulfur content of each coal sample is: YQ15-2 ($S_{t,d}$=4.65%), XY10-4 ($S_{t,d}$=3.24%), DLT11-10 ($S_{t,d}$=5.90%) .

It can be seen from the percentage of sulfur in coal samples (Fig. 3.1) that the organic sulfur in each coal sample accounts for a high percentage of total sulfur, followed by pyrite sulfur, and sulfate sulfate is almost absent. Overall, organic sulfur accounts for more than 50% of total sulfur, and XY10-4 organic sulfur accounts for 93.21% of total sulfur.

3.3 Chapter summary

Among the test samples, Yunquan YQ15-2 is bright coal, Xinyu XY10-4 is semi-bright coal, and East Open DLT11-10 is semi-dark coal. Each sample belongs to three different macro coal types.

Yunquan YQ15-2 is low ash and extra low volatile anthracite; Xinyu XY10-4 is extra low ash and medium volatile bituminous coal; East Open DLT11-10 is low, medium ash and high volatile long flame coal. The total sulfur content in YQ, XY, and DLT coals is 4.65%, 3.24%, and 5.90%, all of which are greater than 3%. They are all high-sulfur coal. The organic sulfur content in coal is relatively high, accounting for more than 50% of the total sulfur.

The maximum reflectivity of the vitreous group ranges from 0.70% to 2.59%. The microscopic coal rock components of the three samples are mainly in the vitreous group, the lipid group is the lowest, and the inert group is in the middle. Open-air DLT11-10 has the highest moisture content of 2.09%. Yunquan YQ15-2 has the lowest moisture content of 0.64%. Overall, the moisture content of each experimental sample is not much different, ranging from 0.64% to 2.09%. The ash content of each coal sample ranges from 4.59% to 12.46%, and the volatile content ranges from 8.71% to 47.74%.

The carbon content (Cdaf) of each coal sample varied from 79.20% to 88.57%, the hydrogen content (Hdaf) was between 3.39% and 5.47%, and the oxygen content (Odaf) and nitrogen content (Ndaf) were 0.46% to 7.43, respectively. % And 1.17%~1.23%.

The total sulfur content (St,d) of each coal sample varies from 3.24% to 5.90%. According to national standards, all three coal samples are high-sulfur coals, and all of them are mainly organic sulfur, which accounts for the proportion of total sulfur. All are above 50%. In addition to organic sulfur, the sulfur content in the sample is followed by pyrite sulfur, and the sulfate sulfur content is very low. The organic sulfur content (So, daf) of coal samples ranges from 3.02% to 3.46%, and the organic sulfur of XY10-4 accounts for 93.21% of the total sulfur.

4 Experimental study on microbial flotation desulfurization of different types of high-sulfur coal

China is a large coal resource country with abundant coal resources, a large part of which is high-sulfur coal. The clean and environmentally friendly use of high-sulfur coal is a subject of great economic benefit and significance. Microbial flotation using the selective adsorption of sulfide minerals by microorganisms is a new way to desulfurize high-sulfur coal, which can change the surface properties of particles and improve the desulfurization effect of flotation.

Shanxi's high-sulfur coal is widely distributed, and the coal's metamorphic degree varies widely, covering all coal types. It is very suitable for exploring the adaptability of microbial flotation.In order to explore the microbial desulfurization effect of Thiobacillus ferrooxidans on high sulfur coal in Shanxi, three coal samples with significant differences in coal quality in Shanxi Province were collected, and the coal petrological characteristics, coal chemical process characteristics, sulfur content of each high sulfur coal sample were analyzed. Thiobacillus ferrooxidans was selected for microbial flotation experiments to explore the adaptability of different high-sulfur coals to the experimental conditions and the factors that affect the desulfurization rate.

4.1 Experimental materials

4.1.1 Coal sample preparation

The three high-sulfur coal samples used in the experiment were taken from Yunquan Mine in the southeast of Shanxi Qinshui Coalfield, East Opencast Mine in the northwest of Shanxi, and Xinyu Mine in Xiaoyi, Shanxi. The collected raw coal is crushed and sent to industrial analysis and coal rock analysis, and then the part is ground to 80~200 mesh and below 200 mesh. According to the preliminary investigation and analysis, it was determined that the experiment selected Thiobacillus ferrooxidans (T.f), which came from the School of Chemical Environment, China University of Mining and Technology (Beijing).

Coal samples vary greatly in coal quality. The industrial analysis results are shown in Tab. 3.2. YQ15-2 is low ash and extra low volatile anthracite; XY10-4 is extra low ash and medium volatile bituminous coal; DLT11-10 is low medium ash, high volatile long flame coal. The total sulfur content in YQ, XY, and DLT coals is 4.65%, 3.24%, and 5.90%, all of which are greater than 3%. They are all high-sulfur coal. The organic sulfur content in coal is relatively high, accounting for more than 50% of the total sulfur.

The results of coal sample micro-component analysis are shown in Tab. 4.1. YQ15-2's coal rock micro-components are dominated by the vitrinite group, followed by the inert group, not determined to the lipid group, and the maximum reflectance of the vitrinite group 2.59, the coal has a high degree of metamorphism and belongs to anthracite. The vitrinite group of Xinyu XY10-4 accounts for more than 70%, followed by the inert group, which has a high degree of coal metamorphism and belongs to bituminous coal. East open-air DLT11-10 has the largest proportion of vitreous group, and the coal metamorphism is not high, which belongs to long-flame coal.

Tab. 4.1 Maceral content of coal samples

No.	Vitrinite %	Inertinite (%)	Liptinite (%)	Clay (%)	Carbon-ates(%)	Sulfide (%)	Oxides (%)	R_{max} (%)
YQ15-2	66.2	22.6	-	3.6	2.0	-	5.6	2.59
XY10-4	72.6	23.6	-	1.4	0.6	1.4	0.4	1.15
DLT11-10	78.0	12.4	-	3.4	5.2	0.8	0.2	0.70

4.1.2 Strains and culture medium

Thiobacillus ferrooxidans used in this experimental institute comes from China University of Mining and Technology (Beijing) College of Chemical Environment. Refer to Gong Guanqun's (2006) medium formula, using modified 9K medium, and the composition is shown in Tab. 4.2.

Tab. 4.2 Compositions of 9K culture medium

Medium composition	Volume (g/L)
$FeSO_4 \cdot 7H_2O$	44.78
$(NH_4)_2SO_4$	2.5
$MgSO_4 \cdot 7H_2O$	0.5
KCl	0.1
K_2HPO_4	0.5
KNO_3	0.04
$CaCO_3$	0.02

4.2 Test procedure

The test process combined with previous studies, which is mainly divided into three steps: bacterial inoculation and activation, microbial flotation experiment pretreatment, and flotation experiment.

The selected experimental instruments and reagents are: XFDIV-0.5L single tank flotation machine, diesel as collector, and secondary octanol as foaming agent.

4.2.1 Bacterial inoculation and activation

Reagents other than $FeSO_4 \cdot 7H_2O$ in 9K medium are formulated into solvents and sterilized at high temperature, and then UV-sterilized $FeSO_4 \cdot 7H_2O$ solid is added to prepare 9K medium and inoculated with Thiobacillus ferrooxidans. The bacteria were activated and cultured at a temperature of 30°C, a pH of 2, and a shaker speed of 150 r/min. Use this bacterial liquid to carry out microbial pretreatment on coal slurry.

4.2.2 Pretreatment of microbial flotation experiment

Add 20g of coal to 200ml of Thiobacillus ferrooxidans bacterial solution and shake to make a suspension with 10% solids content. Set the temperature of the shaker to 30°C, place the mixed bacterial liquid of bacterial liquid and coal particles, and perform pretreatment for 10, 20, and 30 minutes respectively. After the pretreatment, suction filtration is performed to separate the bacterial liquid and coal particles. The separated coal particles are then dried and weighed in preparation for the flotation experiment.

4.2.3 Flotation experiment

Adjust the pretreated coal sample into coal slurry and put it into a flotation machine (XFDIV-0.5L single tank flotation machine). After adding water and stirring for 1min, add an appropriate amount of collector diesel (300g/t) and stir for 3 minutes. Then add the foaming agent secondary octanol (100g/t) in proportion, then open the valve to ventilate and scrape the coal for 3 minutes. After the scraping of coal, the cleaned and tailed coal after flotation are filtered separately, dried and weighed, and then sent to Shanxi Geological Research Institute for laboratory analysis.

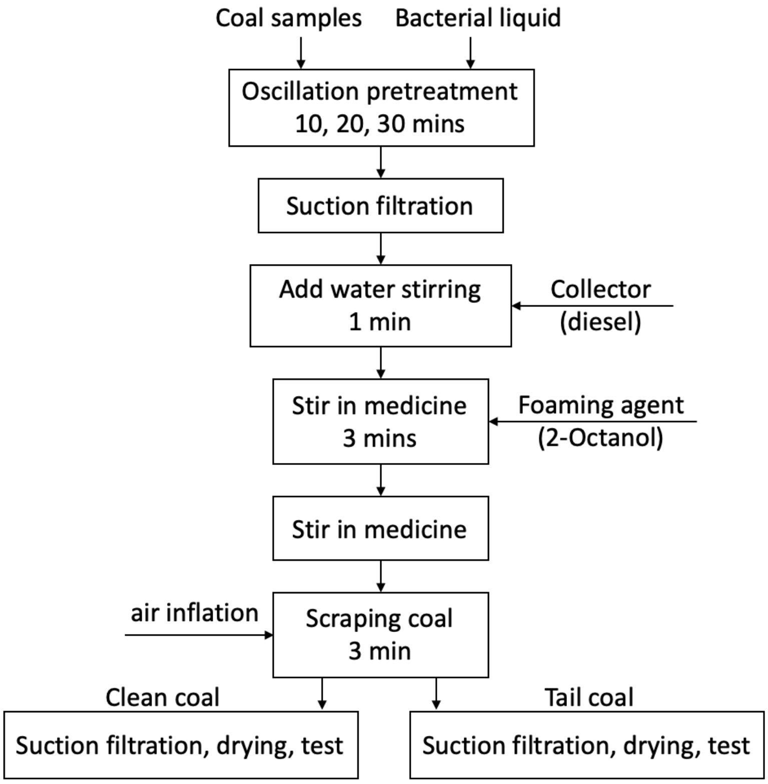


Fig. 4.1 Microbial flotation experiment flows

4.3 Analytical method

The coal samples are sent to Shanxi Coal Geological Research Institute for coal rock analysis, industrial analysis, and morphological sulfur analysis in coal. The analysis method is in accordance with the national standard. The desulfurization rate is calculated as follows

$$\text{The desulfurization rate} = \frac{S_y - \gamma_j \times S_j}{S_y} \tag{4.1}$$

In the formula: S_y is the sulfur content of raw coal, %; S_j is the sulfur content of clean coal, %; γ is the yield of clean coal, %.

4.4 Analysis of the effect of microbial flotation desulfurization

After YQ15-2, XY10-4, DLT11-10 coal samples were crushed to 200 mesh (⩽0.075 mm), 80 mesh (0.075~0.180mm) two particle sizes, they were respectively activated with ferrous sulfide after activation culture The bacterium solution is mixed, pre-treated for 10, 20, 30 minutes, and a blank group without pre-treatment is set for comparison. After the pre-treated coal sample is filtered and re-slurryed, the flotation experiment is carried out. The clean coal and tail coal are dried and weighed, the clean coal yield is calculated, and then the industrial analysis and morphological sulfur analysis are carried out. According to formula 4.1, the desulfurization rate is calculated to obtain the total sulfur desulfurization rate and sulfur of the sample. Iron ore sulfur desulfurization rate and organic sulfur desulfurization rate. Tab. 4.3 is the experimental data of sample microbial flotation desulfurization rate. The original experimental data is shown in Addendum Tab. 1.

Tab. 4.3 Desulphurization rate of sample microorganism flotation

No.	Time (min)	Total sulfur desulfurization rate (%)		Pyrite desulfurization rate (%)		Organic sulfur desulfurization rate (%)	
		80 目	200 目	80 目	200 目	80 目	200 目
YQ 15-2	0	29.09	14.54	62.63	8.08	17.72	20.55
	10	42.78	36.79	73.60	22.32	32.10	41.76
	20	44.55	48.92	96.30	54.66	26.75	47.01
	30	36.91	40.42	81.24	50.41	21.61	36.84
XY 10-4	0	14.89	29.09	85.64	52.32	9.64	27.08
	10	28.78	45.92	73.38	89.73	25.36	42.66
	20	12.02	47.96	15.64	83.79	18.85	45.24
	30	5.95	40.03	38.87	77.32	9.06	37.17
DLT 11-10	0	71.10	46.33	76.14	49.12	50.13	44.49
	10	36.04	59.49	49.40	66.19	30.13	53.63
	20	53.13	79.49	65.49	79.35	42.15	79.65
	30	48.92	69.95	56.02	75.18	42.12	65.13

According to the analysis of the data, the total sulfur desulfurization rate of the sample ranges from 5.95% to 79.49%, the pyrite desulfurization rate is 8.08% to 96.30%, and the organic sulfur desulfurization rate is 9.06% to 79.65%. Among them, the 80 mesh sample has a total sulfur removal rate of 5.95% to 71.10%, a pyrite desulfurization rate of 15.64% to 96.30%, and an organic sulfur desulfurization rate of 9.06% to 50.13%. The total sulfur removal rate of the 200 mesh sample is 14.54%~79.49%, the pyrite desulfurization rate is 8.08%~89.73%, and the organic sulfur desulfurization rate is 20.55%~79.65%.

Microbial pretreatment has an effect on the desulfurization rate of coal samples, but it has different effects on different coal samples and different particle sizes. For the YQ15-2 coal sample, after microbial pretreatment, the total sulfur desulfurization rate, pyrite desulfurization rate, and organic sulfur desulfurization rate are higher than direct flotation. For 200 mesh coal samples of XY10-4, the desulfurization effect of microbial pretreatment is higher than that of the flotation control group without treatment, but the desulfurization rate of 80 mesh coal samples when the microbial treatment time is 20 or 30 minutes is lower than that of direct flotation. . DLT11-10 coal samples are similar to XY coal samples. For 200 mesh samples, microbial flotation improves the desulfurization rate, but for 80 mesh samples, microbial flotation reduces the desulfurization rate instead. In addition, the organic sulfur removal rate of the DLT11-10 sample is 30.13~79.65%, and the overall organic sulfur removal effect is better. Therefore, it can be seen that the effect of microbial treatment on coal desulfurization is both positive and negative, and needs comprehensive analysis.

4.5 Influencing factors of desulfurization rate of microbial flotation

Coal microbial flotation desulfurization rate is affected by a variety of factors, mainly divided into two parts, experimental conditions and the characteristics of coal itself. The experimental conditions include pretreatment time, coal sample size, reaction system pH, bacterial species, bacterial species concentration, culture medium type, slurry concentration, etc. The characteristics of coal itself include the degree of coal metamorphism, the occurrence characteristics of morphological sulfur in coal, the distribution characteristics of morphological sulfur, and the ash content in coal.

After preliminary investigation and experiment, it is clear that Thiobacillus ferrooxidans is currently one of the best bacteria for coal desulfurization. Under the condition of selecting 9K medium, the system pH value is 1~2, and the temperature is 30℃. The optimal environment can achieve the best desulfurization effect. Under the condition that other conditions are consistent, this experiment sets the pretreatment time and coal sample size as variables, and examines the effect of different experimental conditions on the desulfurization rate of Shanxi's high sulfur coal.

4.5.1 Pretreatment time

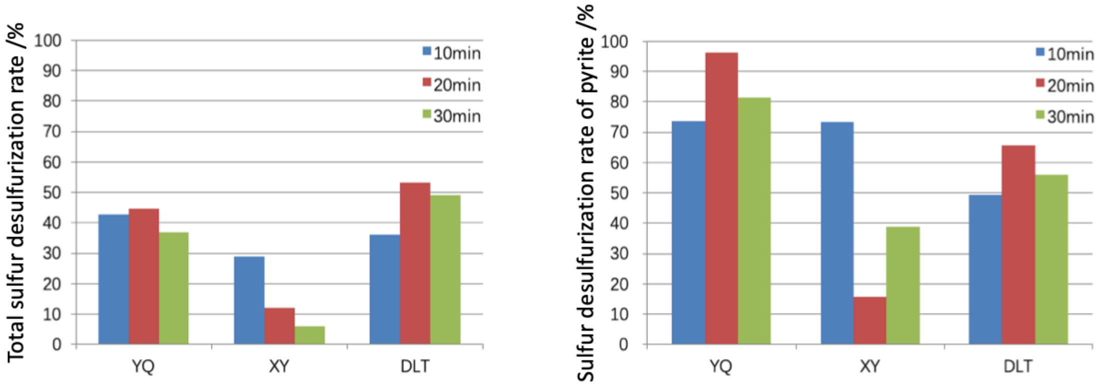
It can be seen from the experimental results shown in Fig. 4.2, Fig. 4.3, and Fig. 4.4 that in this experiment, the effect of pretreatment time on the desulfurization rate of the three coal samples is not the same.

When the particle size of the sample is 80 mesh, the pretreatment time is from 10min, 20min to 30min, the total sulfur desulfurization rate and pyrite desulfurization rate of YQ15-2 coal sample and DLT11-10 coal sample increase first and then decrease. When the treatment time reaches 20min, the desulfurization rate of total sulfur and pyrite reaches the maximum. The trend of XY10-4 is different from the former two. As the pretreatment time increases, the total sulfur removal rate gradually decreases, and the maximum value is when the pretreatment time is 10 minutes; the pyrite removal rate decreases first and then increases. It reached the minimum at 20min.

When the sample size is 200 mesh, the YQ15-2 coal sample and the DLT11-10 coal sample show the same trend as the 80 mesh. The total sulfur desulfurization rate and pyrite desulfurization rate increase first and then decrease, reaching the maximum desulfurization rate at 20 minutes. value. The total sulfur desulfurization rate of the XY10-4 coal sample is the same as the first two. It rises first and then decreases, and reaches the maximum value at 20 minutes. However, the desulfurization rate of pyrite gradually decreases with time, and the maximum value is at the pretreatment time of 10 minutes. achieve.

It is worth mentioning that, at a particle size of 200 mesh, the organic sulfur desulfurization rate of each sample reached the maximum value at 20 min, and it increased first and then decreased with time. Among them, the organic sulfur desulfurization rate of DLT11-10 coal sample was as high as 79.65%. At 80 mesh particle size, the organic sulfur desulfurization rates of YQ and XY decrease with the increase of the treatment time. DLT11-10 and 200 mesh have the same trend, first rising and then decreasing, reaching the maximum value at 20min.

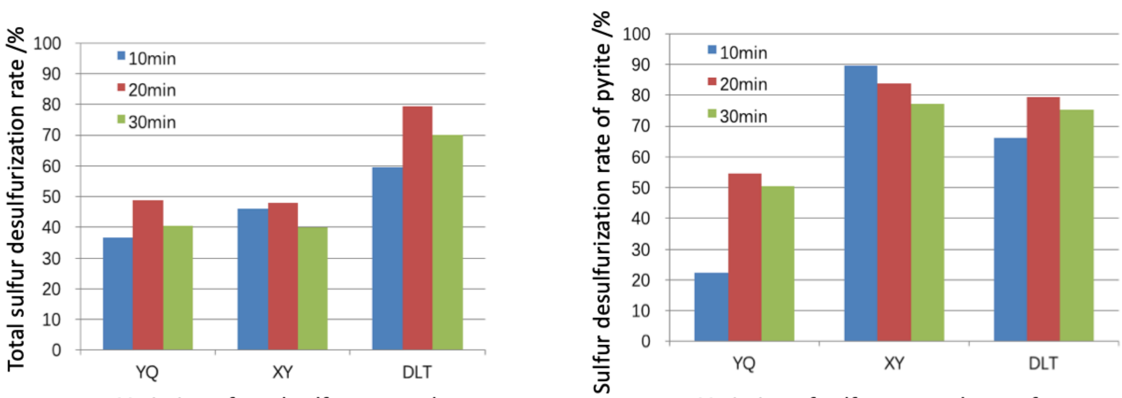
Overall, the removal rate of each coal sample in this experiment varies greatly with the pretreatment time. The total sulfur removal rate is between 1.77% and 22.83%, and the pyrite removal rate is between 4.17% and 57.74. The removal rate of organic sulfur is between 0.03% and 26.02%. Among them, the total sulfur removal rate of YQ15-2 coal samples varies from 1.77% to 12.13%, the pyrite removal rate is from 4.25% to 32.34%, and the organic sulfur removal rate is from 4.92% to 10.49% between. The total sulfur removal rate of XY10-4 coal samples varies from 2.04% to 22.83%, the pyrite removal rate is from 5.94% to 57.74%, and the organic sulfur removal rate is from 2.59% to 16.29% . The DLT11-10 coal sample has a total sulfur removal rate ranging from 4.21% to 20.00%, a pyrite removal rate from 4.17% to 16.09%, and an organic sulfur removal rate from 0.03% to 26.02%.



Variation of total sulfur removal rate with pretreatment time

Variation of sulfur removal rate of pyrite with pretreatment time

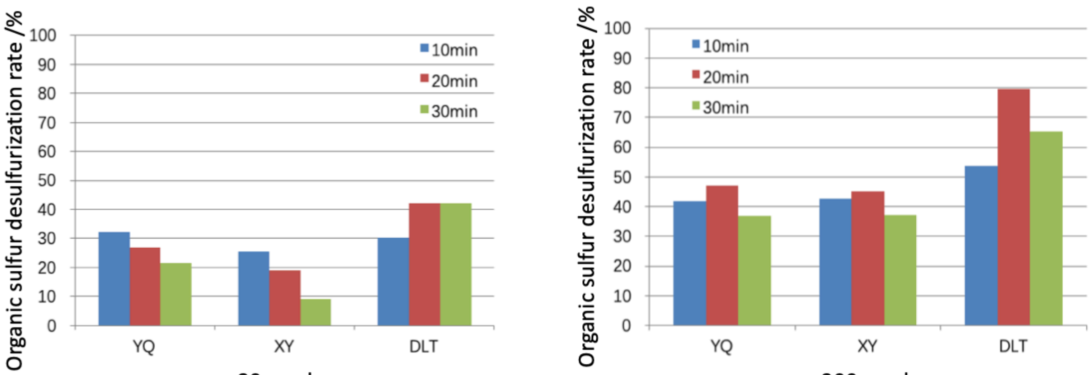
Fig. 4.2 Relationship between pretreatment time and total sulfur and pyrite sulfur desulfurization rate at 80 mesh particle size



Variation of total sulfur removal rate with pretreatment time

Variation of sulfur removal rate of pyrite with pretreatment time

Fig. 4.3 Relationship between pretreatment time and total sulfur and pyrite sulfur desulfurization rate at 200 mesh particle size



80 mesh

200 mesh

Fig. 4.4 Relationship between sample pretreatment time and organic sulfur desulfurization rate of coal samples

4.5.2 Particle size

It can be seen from the experimental results shown in Fig. 4.5, Fig. 4.6 and Fig. 4.7 that for different coal samples, the effect of particle size on them is also different.

For the XY10-4 and DLT11-10 coal samples, after pretreatment at the same time, the total sulfur desulfurization rate of the 200 mesh sample is higher than that of the same treatment time of 80 mesh, as is the desulfurization rate of pyrite sulfur and organic sulfur. But for the YQ15-2 sample, the total sulfur desulfurization rate of the 200 mesh sample is lower than 80 mesh at 10 minutes, and it is higher than 80 mesh with time to 20min and 30min. The 200-mesh sample pyrite desulfurization rate of the coal sample is always lower than the 80-mesh sample, but the organic sulfur desulfurization rate is the opposite. The 200-mesh sample is higher than the 80-mesh sample. The analysis should be due to the low sulfur content of pyrite in the YQ sample. The 80 mesh sample contains more pyrite, which is more conducive to the removal of pyrite sulfur.

The results show that the smaller the particle size of the coal sample, the more complete the crushing, the larger the area of the fungus and the coal sample, the better the desulfurization effect. The organic sulfur removal rate of the three samples showed a good correlation with the particle size. The smaller the particle size, the higher the organic sulfur removal rate. The removal rate of each coal sample of 200 mesh samples was better than 80 mesh.

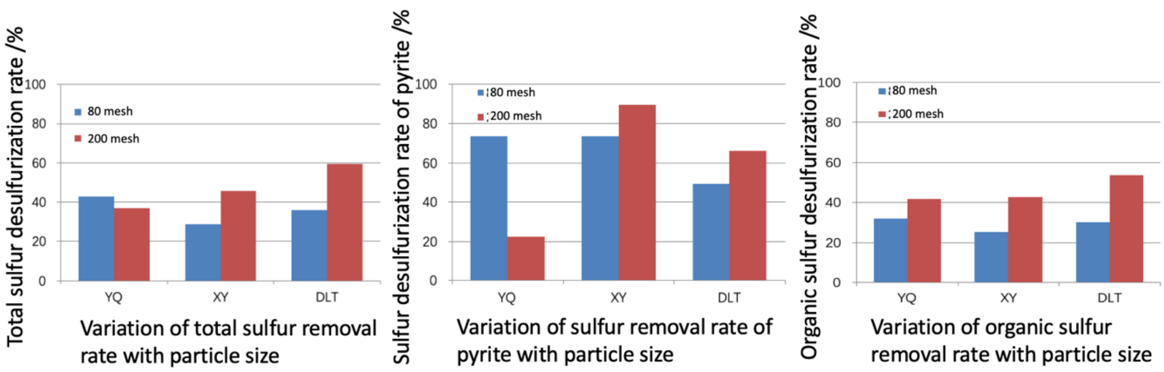


Fig. 4.5 Relationship between coal particle size and desulfurization rate after 10 min pretreatment

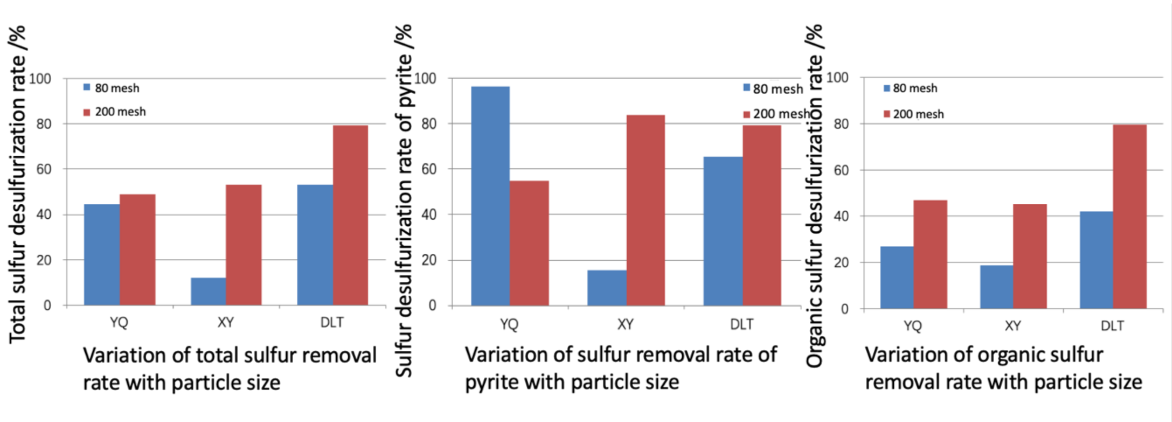


Fig. 4.6 Relationship between coal particle size and desulfurization rate after 20 min pretreatment

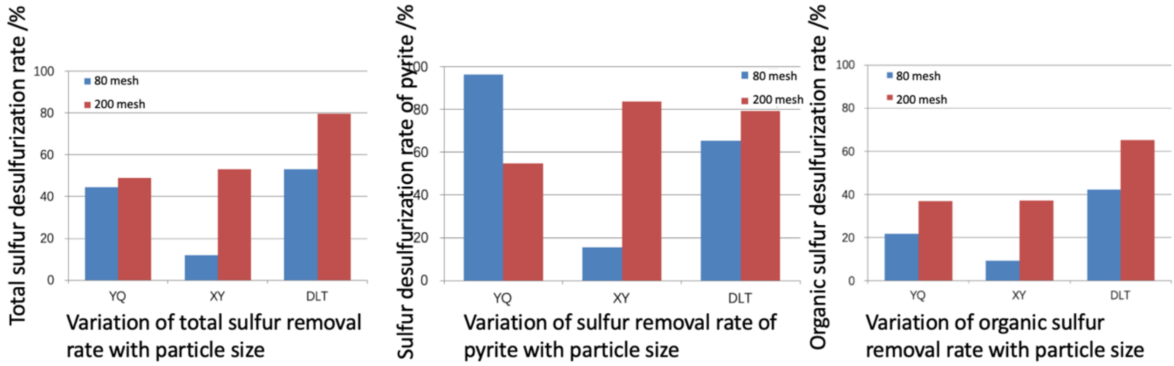


Fig. 4.7 Relationship between coal particle size and desulfurization rate after 30 min pretreatment

4.5.3 Coal metamorphism

Previous studies have shown that the coal structure contains a certain amount of minerals, which makes the coal surface polar. The degree of coal metamorphism determines the surface properties of coal and coal minerals. As the degree of coal metamorphism increases, the carbon content in the coal increases, the oxygen content decreases, the oxygen-containing functional groups decrease, and the hydrophobicity of the coal surface increases, which is more conducive to The separation of coal and pyrite has a great influence on the flotation desulfurization rate of coal, as well as the selective adsorption of Thiobacillus ferrooxidans.

It can be seen from the experimental results Tab. 4.4 and Fig. 4.8 that the anthracite YQ15-2 with the highest degree of metamorphism is not the best in desulfurization, and the long flame coal DLT11-10 with the lowest degree of metamorphism is also not the worst. Overall, the total sulfur, pyrite, and organic sulfur desulfurization effects of the DLT11-10 sample are the best, followed by the YQ sample, and the XY sample is the worst.

The experimental results show that there is no obvious correlation between the degree of coal deterioration and the desulfurization rate of microbial treatment flotation, and the absolute value of the correlation coefficient between the two is 0.57. It can be seen that although the degree of coal metamorphism determines the surface properties of coal and coal minerals, it is not the only factor that affects the desulfurization rate. The desulfurization effect of different coal samples is also controlled by other factors. These factors include pretreatment time, coal sample size, morphological sulfur occurrence and distribution characteristics in coal, coal ash content, etc.

The flotation desulfurization effect of coal is closely related to the clean coal yield. The essence of the reduction of organic sulfur content in the coal in this experiment is the change in clean coal yield. After microbial treatment, the floatability of organic matter and minerals in the coal changes, resulting in changes in the yield of clean coal. The lower the yield of clean coal, the higher the desulfurization rate (Fig. 4.8).

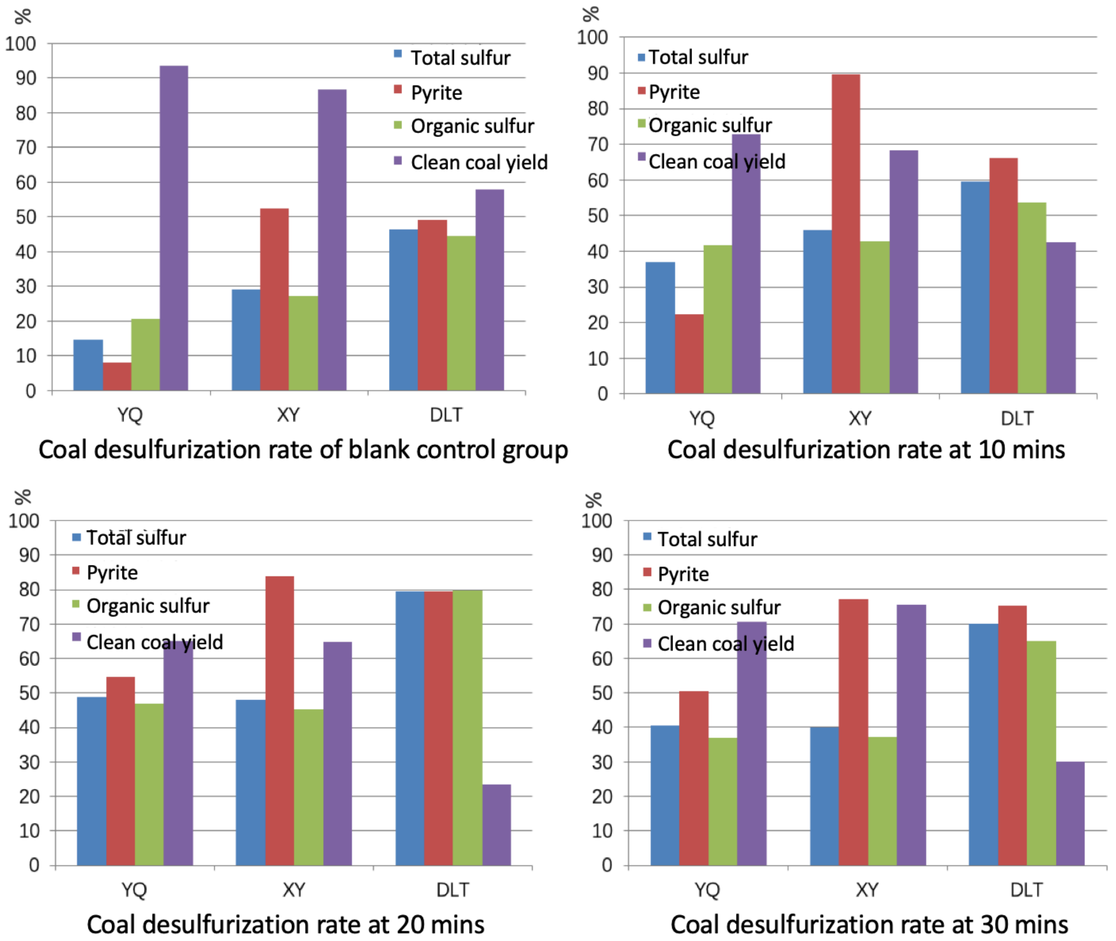


Fig. 4.8 Desulfurization effect before and after modification of 200 mesh coal samples

4.5.4 Occurrence characteristics of morphological sulfur in coal

The occurrence forms of sulfur in coal are divided into inorganic sulfur and organic sulfur. Inorganic sulfur mainly includes pyrite sulfur and sulfate sulfur. The content and distribution of sulfur in various forms have an important influence on the desulfurization rate.

The results of this experiment show that the desulfurization effect of Shanxi's high-sulfur coal has a strong correlation with the morphological sulfur content and occurrence status in coal (Fig. 4.9). When the confidence level is 0.95 and n=3, the standard r=0.9877. Compared with the standard data, the desulfurization rate is positively correlated with total sulfur content (r=0.91), and is also positively correlated with the proportion of pyrite sulfur in coal to total sulfur content (r=0.80), and organic sulfur accounts for total sulfur content Has a negative correlation (r=0.95).

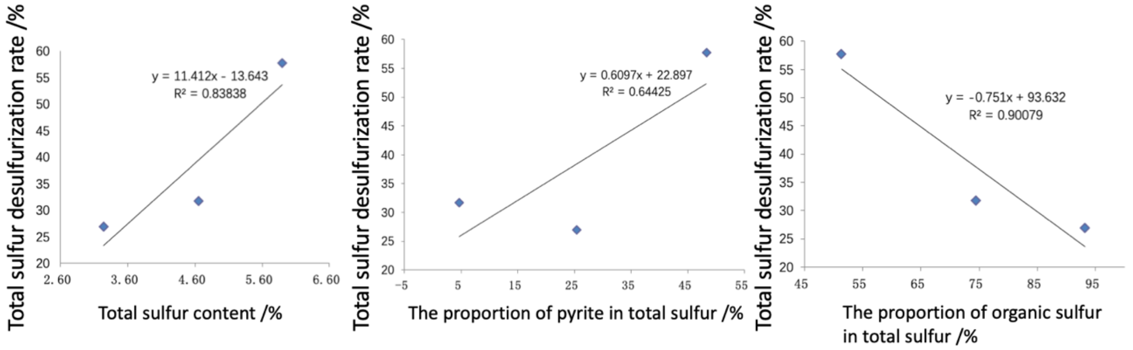


Fig. 4.9 Relation between desulfurization rate and total sulfur content, pyrite sulfur to total sulfur ratio, and organic sulfur to total sulfur ratio

As shown in Tab. 4.5, the pyrite sulfur in the DLT11-10 coal sample with the best desulfurization effect accounts for 48.31% of the total sulfur content, while the YQ15-2 and XY10-4 coal samples account for 4.65% and 25.38%, respectively. It can be inferred that the higher the proportion of pyrite sulfur, the better the microbial flotation effect.

In addition, the desulfurization rate of organic sulfur in coal samples is consistent with the trend of total sulfur desulfurization rate, which is also the best desulfurization effect of DLT11-10 coal samples, followed by YQ15-2, and XY10-4 is the worst.

Tab. 4.5 The relationship between the sulfur content of various samples and the desulfurization rate

No.	Total sulfur (%)	Pyrite percentage of total sulfur %	Organic sulfur percentage of total sulfur (%)	Total sulfur desulfurization rate (%)
YQ15-2	4.65	25.38	74.41	31.73
XY10-4	3.24	6.17	93.21	26.95
DLT11-10	5.90	48.31	51.36	57.77

4.5.5 Ash in coal

The ash content in coal is closely related to the mineral composition and also affects the properties of coal. Common minerals in coal include pyrite, quartz, calcite and clay. Yunquan YQ15-2 is low-ash and extra-low volatile coal with an ash content of 6.18%; Xinyu XY10-4 is an extra-low ash and medium volatile coal with an ash content of 4.59%; East Open DLT11-10 coal is Low-medium ash, high volatile coal, ash content is 12.46%. The quantitative results of microscopic coal rock samples (Tab. 3.4) are consistent with the coal industry analysis.

When the confidence level is 0.95 and n=8, the standard r=0.5493. Comparing standard data, after microbial flotation (Fig. 4.10), the deliming rate and total sulfur removal rate of the DLT11-10 sample (r=0.86), pyrite desulfurization rate (r=0.97), and organic sulfur removal rate (r=0.84) were positively correlated. The ash reduction rate of YQ15-2 was also positively correlated with total sulfur removal rate (r=0.86) and pyrite desulfurization rate (0.85). The correlation between the ash reduction rate and desulfurization rate of the XY10-4 sample is poor.

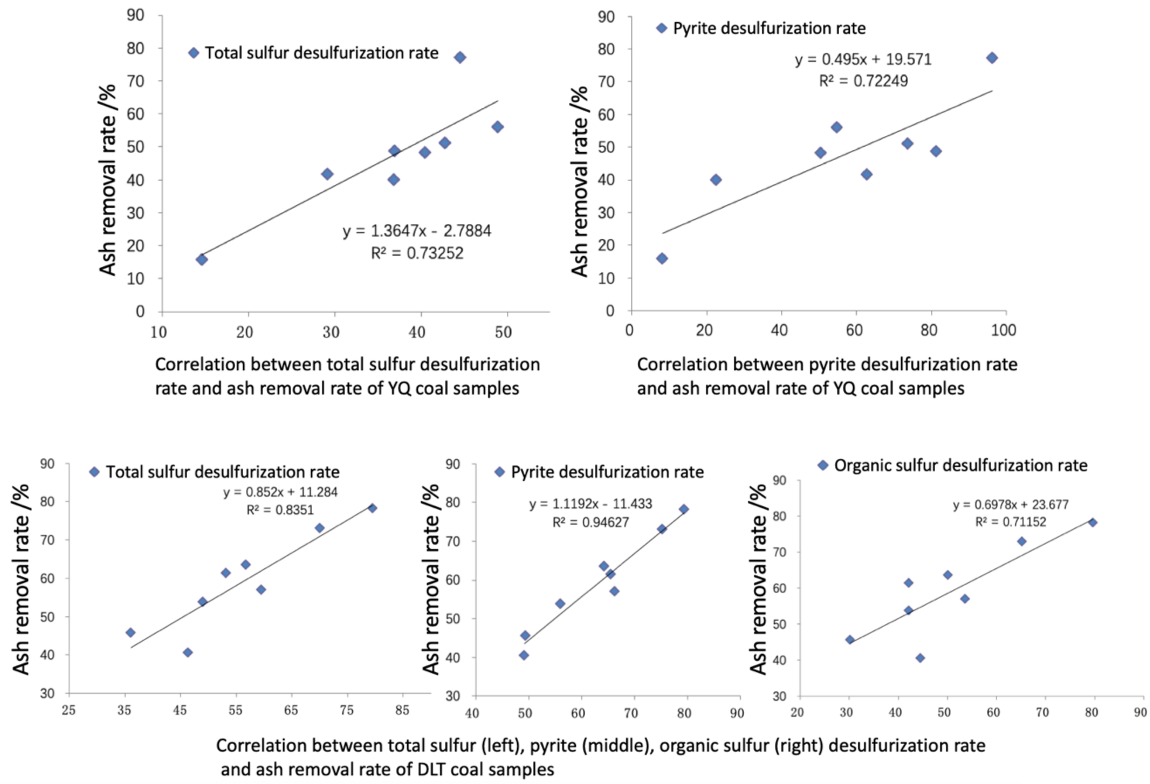


Fig. 4.10 Correlation between ash removal rate and desulfurization rate

It can be deduced from this that when the ash and sulfur in the coal are both high, it is conducive to the microbial flotation desulfurization of coal, and when the clay minerals in the coal are few, it is not conducive to the microbial flotation desulfurization of coal.

4.6 Chapter summary

This experiment conducted microbial flotation experiments on three high-sulfur coal samples YQ15-2, XY10-4, and DLT11-10 with significant differences in coal quality in Shanxi Province. Thiobacillus ferrooxidans was selected to explore different high-sulfur coal samples for The adaptability of experimental conditions and the factors that affect the desulfurization rate.

According to the analysis of the experimental results, the total sulfur desulfurization rate of the sample ranges from 5.95% to 79.49%, the pyrite desulfurization rate is 8.08% to 96.30%, and the organic sulfur desulfurization rate is 9.06% to 79.65%. Among them, the 80 mesh sample has a total sulfur removal rate of 5.95% to 71.10%, a pyrite desulfurization rate of 15.64% to 96.30%, and an organic sulfur desulfurization rate of 9.06% to 50.13%. The total sulfur removal rate of the 200 mesh sample is 14.54%~79.49%, the pyrite desulfurization rate is 8.08%~89.73%, and the organic sulfur desulfurization rate is 20.55%~79.65%.

Microbial pretreatment has an effect on the desulfurization rate of coal samples, but it has different effects on different coal samples and different particle sizes. Microbial treatment has both positive and negative effects on coal desulfurization, which requires comprehensive analysis.

The microbial flotation desulfurization rate of high-sulfur coal is affected by various factors, which are mainly divided into two parts: experimental conditions and the characteristics of the coal sample itself. The experimental conditions include pretreatment time, coal sample size, reaction system pH, bacterial species, bacterial species concentration, culture medium type, slurry concentration, etc. The characteristics of coal itself include the degree of coal metamorphism, the occurrence characteristics of morphological sulfur in coal, the distribution characteristics of morphological sulfur, and the ash content in coal. This experiment mainly analyzed the influence of pretreatment time, coal sample size, coal metamorphism degree, morphological sulfur occurrence characteristics in coal and coal ash content on desulfurization rate.

Coal samples of different coal quality and different particle sizes have different adaptability to the pretreatment time, and the variation trend is also different. Overall, most samples reach the maximum desulfurization rate when the pretreatment time is 20 minutes. The desulfurization rate of each coal sample varies greatly with the pretreatment time, and the overall range is between 1.77% and 22.83%.

The overall trend of the effect of particle size on different coal samples is consistent, with only slight differences. The desulfurization rate of XY and DLT is higher under

200 mesh, while the desulfurization rate of 80 mesh sample is higher when YQ has a shorter pretreatment time. The organic sulfur removal rate of each sample showed a good correlation with the particle size. The smaller the particle size, the higher the organic sulfur removal rate. The removal rate of 200-mesh samples was better than 80 mesh. The experimental results show that the smaller the particle size of the coal sample, the more thorough the crushing, the larger the area of the fungus and the coal sample, the better the desulfurization effect.

There is no obvious correlation between the coal metamorphism degree and the desulfurization rate of microbial treatment flotation. The anthracite YQ15-2 with the highest metamorphism degree is not the best desulfurization effect, and the long flame coal DLT11-10 with the lowest metamorphism degree is not the worst effect. Although the degree of coal metamorphism determines the surface properties of coal and coal minerals, it is not the only factor affecting the desulfurization rate, and the desulfurization effect is also controlled by other factors.

The flotation desulfurization effect of coal is closely related to the clean coal yield. The essence of the reduction of organic sulfur content in the coal in this experiment is the change in clean coal yield. After microbes and treatment, the floatability of organic matter and minerals in the coal changes, resulting in changes in the yield of clean coal. The lower the yield of clean coal, the higher the desulfurization rate.

The occurrence state of morphological sulfur in coal greatly affects the desulfurization rate. The total sulfur removal rate is positively correlated with the total sulfur content in the coal. It is also positively correlated with the proportion of pyrite sulfur in the coal to the total sulfur content, and negatively correlated with the proportion of organic sulfur to the total sulfur content. The higher the pyrite sulfur content in the sample, the better the microbial flotation desulfurization effect.

The ash content and the ash removal rate in coal also have a great influence on the desulfurization rate. The ash removal rate of the samples is significantly positively correlated with the total sulfur removal rate, pyrite desulfurization rate, and organic sulfur removal rate. When the ash content and sulfur content in the coal are both high, it is beneficial to the microbial flotation desulfurization of coal, and when the clay minerals in the coal are few, it is not conducive to the microbial flotation desulfurization of coal.

5 Conclusion and Outlook

On the basis of fully investigating the current status of coal microbial desulfurization research at home and abroad, three representative high-sulfur coal samples of different coal rocks and coal quality in Shanxi Province were selected. Thiobacillus ferrooxidans bacteria was selected as the experimental strain to comprehensively use coal petrology, geochemistry, statistical analysis and other research methods to carried out detailed coal and coal quality analysis of coal samples, and microbial flotation desulfurization experiments under multiple sets of different experimental variables. By studying the adaptability of different high-sulfur coals in Shanxi to microbial flotation desulfurization experiments, the best desulfurization effect and experimental parameters that can be achieved in a certain period of time. The main factors that affect the desulfurization rate of coal samples are discussed and evaluated and analyzed.

(1) After preliminary investigation and experiment, it is clear that Thiobacillus ferrooxidans is one of the best bacteria for coal desulfurization. Under the condition of 9K medium, when system pH is 1~2 and the temperature is 30℃ can achieve the best desulfurization effect. This is the optimal environment for bacterial growth and reproduction.

(2) The total sulfur desulfurization rate of the sample ranges from 5.95% to 79.49%, the pyrite desulfurization rate is 8.08% to 96.30%, and the organic sulfur desulfurization rate is 9.06% to 79.65%. Among them, the 80 mesh sample has a total sulfur removal rate of 5.95% to 71.10%, a pyrite desulfurization rate of 15.64% to 96.30%, and an organic sulfur desulfurization rate of 9.06% to 50.13%. The total sulfur removal rate of the 200 mesh sample is 14.54%~79.49%, the pyrite desulfurization rate is 8.08%~89.73%, and the organic sulfur desulfurization rate is 20.55%~79.65%.

Microbial pretreatment has an effect on the desulfurization rate of coal samples, but for different coal samples and different particle sizes, the effect is different. Microbial treatment has both positive and negative effects on coal desulfurization.

The microbial flotation desulfurization rate of high-sulfur coal is affected by various factors, which are mainly divided into two parts: experimental conditions and the coal sample's characteristics. The experimental conditions include pretreatment time, coal sample size, reaction system pH, bacterial species, bacterial species concentration, culture medium type, slurry concentration, etc. The coal sample's characteristics include the degree of coal metamorphism, the occurrence characteristics of morphological sulfur in coal, the distribution characteristics of morphological sulfur, and the ash content in coal.

(3) Coal samples with different coal quality and different particle sizes have different adaptability to the pretreatment time, and the change trend is also different.

Overall, most samples reach the maximum desulfurization rate when the pretreatment time is 20 minutes. The desulfurization rate of each coal sample varies with the pretreatment time from 1.77% to 22.83%. The overall trend of the effect of particle size on different coal samples is consistent, with only slight differences.

The smaller the particle size of the coal sample, the more thorough the crushing, the larger the area of the fungus and the coal sample, the better the desulfurization effect. The removal rate of organic sulfur has a good correlation with the particle size. The smaller the particle size, the higher the removal rate of organic sulfur. The removal rate of 200 mesh samples is better than 80 mesh.

(4) There is no obvious correlation between the degree of coal metamorphism and the desulfurization rate of microbial treatment flotation. Although the degree of coal metamorphism determines the surface properties of coal and coal minerals, it is not the only factor that affects the desulfurization rate, and the desulfurization effect is also controlled by other factors.

The flotation desulfurization effect of coal is closely related to the clean coal yield. The essence of the reduction of organic sulfur content in the coal in this experiment is the change in clean coal yield. After microbes and treatment, the floatability of organic matter and minerals in the coal changes, resulting in changes in the yield of clean coal. The lower the yield of clean coal, the higher the desulfurization rate.

The occurrence state of morphological sulfur in coal greatly affects the desulfurization rate. The total sulfur removal rate is positively correlated with the total sulfur content in the coal. It is also positively correlated with the proportion of pyrite sulfur in the coal to the total sulfur content, and negatively correlated with the proportion of organic sulfur to the total sulfur content. The higher the pyrite sulfur content in the sample, the better the microbial flotation desulfurization effect.

The ash content and the ash removal rate in coal also have a great influence on the desulfurization rate. The ash removal rate of the samples is significantly positively correlated with the total sulfur removal rate, pyrite desulfurization rate, and organic sulfur removal rate. When the ash content and sulfur content in the coal are both high, it is beneficial to the microbial flotation desulfurization of coal, and when the clay minerals in the coal are few, it is not conducive to the microbial flotation desulfurization of coal.

Addendum

Tab.1 Microbiological pretreatment sample data

No.	Time (min)	Sulphur content of clean coal (%)				Clean coal yield (%)	Total sulfur desulfurization rate (%)	Pyrite desulfurization rate (%)	Organic sulfur desulfurization rate (%)
		$S_{t,d}$	$S_{p,d}$	$S_{s,d}$	$S_{o,d}$				
YQ 15-2	0	3.44	0.46	-	2.97	95.85	29.09	62.63	17.72
	0	4.25	1.16	-	2.94	93.5	14.54	8.08	20.55
	10	3.16	0.37	-	2.79	84.2	42.78	73.60	32.10
	10	4.04	1.26	0.01	2.77	72.75	36.79	22.32	41.76
	20	2.95	0.05	-	2.9	87.4	44.55	96.30	26.75
	20	3.64	0.82	-	2.81	65.25	48.92	54.66	47.01
	30	3.18	0.24	-	2.94	92.25	36.91	81.24	21.61
	30	3.93	0.83	-	3.1	70.5	40.42	50.41	36.84
XY 10-4	0	2.88	0.03	-	2.85	95.75	14.89	85.64	9.64
	0	2.65	0.11	-	2.54	86.7	29.09	52.32	27.08
	10	2.6	0.06	-	2.54	88.75	28.78	73.38	25.36
	10	2.56	0.03	-	2.53	68.45	45.92	89.73	42.66
	20	3.21	0.19	-	2.76	88.8	12.02	15.64	18.85
	20	2.6	0.05	-	2.55	64.85	47.96	83.79	45.24
	30	3.24	0.13	0.02	2.92	94.05	5.95	38.87	9.06
	30	2.57	0.06	-	2.51	75.6	40.03	77.32	37.17
DLT 11-10	0	5.09	2.03	0.05	3.01	50.2	56.69	64.24	50.13
	0	5.46	2.5	0.06	2.9	58	46.33	49.12	44.49
	10	4.92	1.88	0.04	2.76	76.7	36.04	49.40	30.13
	10	5.63	2.27	0.05	3.31	42.45	59.49	66.19	53.63
	20	4.78	1.7	0.04	3.03	57.85	53.13	65.49	42.15
	20	5.16	2.51	0.02	2.63	23.45	79.49	79.35	79.65
	30	4.64	1.93	0.01	2.7	64.95	48.92	56.02	42.12
	30	5.89	2.35	0.03	3.51	30.1	69.95	75.18	65.13

Reference

1. Luo Mefei. Research on the distribution characteristics of sulfur in Chinese coal [J]. Coal Conversion, 2005, 28(3):14-18.

2. Yang Qi, Han Dexin. China Coalfield Geology [M]. Coal Industry Press, 1979.

3. Zhang Weiguo, Zhu Yong. China High Sulfur Coal Resources Research [J]. Guangzhou Chemical Industry, 2014, 42(2):24-25.

4. Shu Xinqian, Xu Xuchang. Microbial leaching method to remove pyrite in coal [J]. Coal conversion , 1996(4):24-30.

5. Li Rui. Distribution of sulfur in coal in China [J]. Clean Coal Technology, 1998, 4(1): 44-47.

6. Chen Peng. The occurrence characteristics and desulfurization of sulfur in coal in China [J]. Coal Conversion, 1994(2): 1-9.

7. Zi Jianwei, Yang Hongying, Gong Enpu. Sulfur in coal Existing characteristics and microbial desulfurization [J]. Coal Preparation Technology, 2004(1): 4-8.

8. Hu Xudong, Zang Liang, Cui Shumao, et al. Chemical properties of organic sulfur in coal And structure [J]. Journal of East China University of Science and Technology, 1994(3):321-326.

9. Tang Yuegang, Zhang Huiyong, Peng Suping, et al. Coal in China Study on the occurrence state and geological origin of organic sulfur[J]. Journal of Shandong University of Science and Technology: Natural Science Edition, 2002, 21(4):1-4.

10. Abdollahy M, Moghaddam A Z, Rami K. Desulfurization of mezino coal using combination of ‘flotation’ and ‘leaching with potassium hydroxide/methanol’ [J]. Fuel, 2006, 85(7):1117-1124.

11. Ayhan F D , Abakay H , Saydut A . Desulfurization and Deashing of Hazro Coal via a Flotation Method[J]. Energy & Fuels, 2005, 19(3):1003-1007.

12. Jing Guodong. Talking about coal desulfurization technology [J]. Coal Mine Modernization, 2004(1): 58-59.

13. Rudolf W．Oxidation of pyrites by microorganisms and their use for making mineral phosphates available[J]．Soil Science，1922，14：135-147．

14. Rudolf W．Helbronner A.Oxidation of zinc sulfides by microorganisms[J]．Soil Science，1922，14：459-464．

15. Clomer A R，Hinkle M E．The role of microorganisms in acid mine drainage：a preliminary report[J]．Science，1947，106：253-256．

16. Leathen W W , Sr S A B , Mcintyre L D . The role of bacteria in the formation of acid from certain sulfuritic constituents associated with bituminous coal. I. Thiobacillus thiooxidans.[J]. Applied Microbiology, 1953, 1(2):61.

17. Silverman M P , Rogoff M H , Wender I . Bacterial Oxidation of Pyritic Materials in Coal.[J]. Applied microbiology, 1961, 9(6):491-496.

18. Kargi F. Enhancement of microbial removal of pyritic sulfur from coal using concentrated cell suspension of A.ferrooxidans and an external carbon dioxide supply[J]. Bioengineering，1982，24：749-752.

19. Monticella D J . Finnerty W R.Microbial desulfurization of fossil fuels[J]. Microbiology，1985，37：371-389.

20. Kargi F. Microbial methods for desulfurization of coal[J]. Trends in Biotechnology, 1986, 4(11):293-297.

21. Bhattacharyya D, Hsieh M, Francis H, et al. Biological desulfurization of coal by mesophilic and thermophilic microorganisms.[J]. Resources Conservation & Recycling, 1990, 3(2):81-96.

22. Lu-KwangJu. MICROBIAL DESULFURIZATION OF COAL[J]. Liquid Fuels Technology, 1992, 10(8):40.

23. Andrews G F, Stevens C J, Leeper S A. Heaps as bioreactors for coal bioprocessing[J]. Applied Biochemistry & Biotechnology, 1993, 39-40(1):427-443.

24. Tsuji M , Funahashi S , Takigawa M , et al. Biodesulfurization of Turkish lignites - 1. Optimization of the growth parameters of Rhodococcus rhodochrous, a sulfur-removing bacterium[J]. Fuel, 1996, 75(13):1596-1600.

25. Klein J, Afferden M V, Pfeifer F, et al. Microbial desulfurization of coal and oil[J]. Fuel Processing Technology, 1994, 40(2-3):297-310.

26. Kargi F , Robinson J M . Removal of organic sulphur from bituminous coal: Use of the thermophilic organism Sulfolobus acidocaldarius[J]. Fuel, 1986, 65(3):397-399.

27. Miller K W , Risatti J B . Microbial oxidation of pyrrhotites in coal chars[J]. Fuel, 1988, 67(8):1150-1154.

28. Weerasekara N S , F.J. García Frutos, Cara J , et al. Mathematical modelling of demineralisation of high sulphur coal by bioleaching[J]. Minerals Engineering, 2008, 21(3):234-240.

29. Dadkhah F , Amini E , Lashay A , et al. UP-1.115: Comparison of the Predictive Accuracy of Serum Prostate Specific Antigen Levels (PSA), Free PSA and PSA Density in the Detection of Prostate Cancer[J]. Urology, 2009, 74(4):S206-S206.

30. Cara J , Antonio Morán, Carballo T , et al. The biodesulphurization of a semianthracite coal in a packed-bed system[J]. Fuel, 2003, 82(15):2065-2068.

31. Marinov S P, Stefanova M, Gonsalvesh L, et al. Biodesulphurized low rank coals appraisal: Initial, treated, their bitumens and solid residues[J]. Fuel Processing Technology, 2011, 92(12):2328-2334.

32. Pandey R A , Raman V K , Bodkhe S Y , et al. Microbial desulphurization of coal containing pyritic sulphur in a continuously operated bench scale coal slurry reactor[J]. Fuel, 2005, 84(1):81-87.

33. Ángel Aller, MartíNez O, Linaje J A D, et al. Biodesulphurisation of coal by microorganisms isolated from the coal itself[J]. Fuel Processing Technology, 2001, 69(1):45-57.

34. Gonsalvesh L, Marinov S P, Stefanova M, et al. Organic sulphur alterations in biodesulphurized low rank coals[J]. Fuel, 2012, 97(7):489-503.

35. L. Gonsalvesh, S.P. Marinov, M. Stefanova, et al. Biodesulphurized low rank coal: Maritza east lignite and its “humus-like” byproduct[J]. Fuel, 2013, 103:1039-1050.

36. Li Lei, Zhang Xing. The influence of coal particle size and coal slurry concentration on coal desulfurization by microbial method [J]. Environmental Science, 1992, 28(1):32-36.

37. Hou Chun, Li Jun, Zhu Haitao, et al. Study on removal of sulfur in coal from Yangzonghai Power Plant by microorganisms Ⅰ. Screening of strains [J]. Journal of Yunnan University: Natural Science Edition, 1998(S4):505 -506.

38. Li Xikun, Lin Yongbo. Research on coal biological leaching desulfurization in Hongyang No.3 Mine[J]. Nonferrous Mining and Metallurgy, 2001, 17(2):11-13.

39. Fu Jianhua. The role of Thiobacillus ferrooxidans extracellular polymer in biological leaching [J]. Journal of Laser Biology, 2004, 13: 62-66.

40. Zhang Lifang, Wang Qian, Sun Yufeng. Study on the removal of sulfur from coal by Thiobacillus ferrooxidans [J]. Journal of Shenyang University of Science and Technology, 2004, 23(1):81-84.

41. Zhang Chenggui, Xia Jinlan, Qiu Guanzhou. Research progress of ferrous oxidation system of Thiobacillus ferrooxidans [J]. Chinese Journal of Nonferrous Metals, 2006, 16(7): 1239-1249.

42. Ma Aixia, Zhu Yimin, Liu Wengang, et al. Desulfurization test of Thiobacillus ferrooxidans by column leaching [J]. Nonferrous Mining and Metallurgy, 2006, 22(4):47-49.

43. He Dewen, Chai Liyuan, Song Weifeng. Experimental factors and laws of fungal coal desulfurization [J]. Environmental Science and Technology, 2004, 27(1): 5-6.

44. Yang Yu, Shi Wuyang, Zhang Yanfei, et al. Study on the effect of Thiobacillus ferrooxidans on coal desulfurization[J]. Journal of Eco-Environmental Sciences, 2006, 15(2):261-264.

45. Gong Guanqun, Tao Xiuxiang, Zhang Xing, et al. Study on optimized culture and desulfurization of Thiobacillus ferrooxidans[J]. Journal of China University of Mining & Technology, 2006, 35(4):510-514.

46. Ma Aixia, Lu Ning, Yi Jun, et al. Thiobacillus ferrooxidans heap leaching to remove sulfur from coal[J]. Coal Science and Technology, 2008, 36(7):110-112.

47. Deng Enjian. Application of microorganisms in coal biological desulfurization [D]. Hunan University, 2006.

48. Zhang Dongmin, Xie Qinglin, Zhang Ping, et al. Experimental research on coal desulfurization of white rot fungus [J]. Energy Technology and Management, 2008(1):67-69.

49. Sun Jianfeng, Zhang Mingxu, Liu Xiaoyan. Study on the use of E. coli to remove sulfur from coal[J]. Coal Processing and Comprehensive Utilization, 2007(1):52-53.

50. Zhang Mingxu, Sun Jianfeng. Research on Pseudomonas sphaeroides used in coal biological leaching and desulfurization [J]. Coal Preparation Technology, 2009(4): 6-11.

51. Zhou Changchun, Tao Xiuxiang, Liu Jiongtian. Research on influencing factors of flotation desulfurization of Rhodopseudomonas [J]. Coal Conversion, 2005, 28(3): 35-38.

52. Xie Zuohuang. Experimental study on coal desulfurization by silicate bacteria [J]. Journal of Rock Mineralogy, 2009, 28(6):587-592.

53. Lian Bin. Potassium-releasing effect of silicate bacteria GY92 on illite[J]. Journal of Mineralogy, 1998(2):234-238.

54. Li Dingxu. Application effect of silicate bacteria on apples[J]. Journal of Fruit Trees, 2003, 20(1):64-66.

55. Sun Desi, Zhang Xianzhen, Zhang Qiang. Study on the leaching effect of metabolites of silicate bacteria on silicate minerals[J]. Mining and Metallurgical Engineering, 2006, 26(3):27-29.

56. Lian Bin, Chen Ye, Yuan Sheng, et al. Flocculation characteristics of silicate bacteria GY03 strain [J]. Journal of Mineralogy, 2003, 23(4):303-307.

57. Wang Deqiang, Zheng Mingdong, Huang Jiping. Cultivation of coloring bacteria in CSTR reactor and its effect on coal desulfurization[J]. Coal Chemical Industry, 2003, 31(1):28-30.

58. Zhang Dongchen, Zhang Mingxu, Chen Qingru, Li Qing, Wu Xuefeng. Study on the selective flocculation of Mycobacterium phlei to remove pyrite sulfur from coal [J]. Journal of China Coal Society, 2004, 29(5): 585-589.

59. Zhang Dongchen. Breeding of coal desulfurization microbial strains and removal of pyrite sulfur in coal [D]. Xuzhou: Doctoral Dissertation of China University of Mining and Technology, 2004.

60. Tao Xiuxiang, Gong Guanqun, Wen Yangming, et al. Electrochemical regulation of the growth and metabolism of coal desulfurization microorganisms [J]. Journal of China University of Mining and Technology, 2005, 34(6):698-702.

61. Wang Rui. Preliminary study on microbial desulfurization of Shanxi's high-sulfur coal [D]. Central South University, 2013.

62. Qiu Guan Zhou, Fu Bo, Zhou Hong Bo. Isolation of a strain of Acidithiobacillus caldus and its role in bioleaching of chalcopyrite[J]. World Journal of Microbiology and Biotechnology, 2007, 23: 1217-1225.

63. Tributsch H, Bennett J C, J. Ch em . Techn ol. Biotechn ol., 1981, 31, 627.

64. Kodam a K, Nak atani K, Um eh ara K, Sh im izu K, Minoda I, Yam ada K, Agr ic. Biol. Chem., 1973, 37, 45-50.

Thesis Grade

Thesis: Study on Microbial Desulfurization of High Sulfur Coal in Shanxi Province

Author: Mengmeng Gou

Supervisor: Yuegang Tang ______ **Grade:** 91 ______ **Signature:** Yuegang Tang

Co-Supervisor: ______________ **Grade:** ______ **Signature:** ________________