Application study of Bio-FGD based on environmental safety during the coal combustion

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Abstract. Coal combustion produces a large amount of acidic gas, which is the main cause of acid rain and other natural disasters. Flue Gas Desulfurization (FGD) is a necessary requirement for clean coal combustion. Compared with the traditional chemical desulfurization technology, biological desulfurization has the advantages of low operating cost, without secondary pollution, low carbon emission and the additional economic benefits. The process and structure of BioDeSOx which as one of Bio-FGD technology is introduced. The major factors that influent BioDeSOx Bio-FGD system is the pH, oxidation reduction potential (about -300 MV to -400 MV), electrical conductivity, the adding amount of nutrient and temperature (30ºC-40ºC). Taking the Bio-FGD project of Yixing xielian thermal power plant as an example, the BioDeSOx technology was applied in this project. The environmental and economic benefits of the project were greater than the traditional desulfurization technology. With the continuous improvement of environmental safety standards, Bio-FGD technology will have broad application prospects.

1. Introduction
Since 2000, China’s rapid economic development has brought a growing demand for energy. Coal mining technology made considerable progress in the past 15 years by the exploitation of shallow and low sulfur coal seam turn to deep and high sulfur coal seam, especially in the southern areas of China where there is a coal shortage, a larger proportion of high sulfur coals have been mining [1]. Due to combustion temperature, the sulfur (S) content of coal starts to oxidize, and SOx /H2S gasses are released to the atmosphere through a chimney. Although SOx gasses are made up of sulfur dioxide(SO2), and sulfur trioxide(SO3), the SO3 content is rather low[2]. Fossil fuels are the main cause of the SO2 emissions in the world, measuring roughly 80% [3]. From the environmental perspective, acidic gas, particularly SO2 and H2S, has serious negative effects on the environment (air pollution). This is because combustion of SO2 and H2S produces highly toxic byproducts, such as sulfur dioxide, sulfuric acid, sulfurous acid, carbon monoxide [5]. These byproducts affect air quality and also considered as major sources of acidic precipitation, see Kohl and Nielson [4]. Sulfur compounds in the chemical industry and hydrocarbon fueled vehicles also cause corrosion to parts of refineries and combustion engines because of the formation of oxy-acids of sulfur from combustion products [5]. Ma Yuzhen et al [6] considered that the safety critical content of SO2 was 0.036%, and the amount of SO2 generated during coal combustion is higher than the safety levels. “The most serious environmental protection law in China history” was implemented since 2015. The new environmental law put forward has higher requirements for FGD. With the development of gas...
purification technology, organizations have been looking for FGD technology which is more efficient, safe, economical and easy to operate.

2. The desulfurization technology based on environmental safety
The formation of sulfur and its compounds cycle changed through oxidation or reduction reaction in nature. In the course of the development of desulfurization technology, people through chemical or biological methods promote the process of oxidation or reduction reaction, changing gaseous sulfide into liquid, solid sulfides or elemental sulfur and separated, reducing sulfur content in the flue gas. The FGD technology based on the environmental safety is established in sustainable development concept, in the process of reducing the sulfur content of the flue gas, there is no secondary pollution to the environment, no need to deal with the desulfurization slag, liquid, etc., and least carbon emission. Although the removal rate of using conventional technology such as NaOH or CaO to reduce sulfur content in the flue gas is high, the two processes are continuously adding the massive lyes, belonging to the transfer of waste rather than efficient treatment. Biological oxidation desulphurization technology [7] is through the metabolism of sulfur bacteria to convert sulfide into sulfur, such microorganisms include: photosynthetic bacteria, denitrifying bacteria, colorless sulfur bacteria [8].

2.1. Traditional desulfurization technology
The traditional desulfurization technology mainly refers to chemical oxidation method, by adding chemical oxidant to convert sulfide into sulfur. The chemical oxidation widely used in engineering field for a hundred years, the initial process including Burkheiser, Ferrox, Clund and Manchester, Alkali washing method [9], these traditional processes are used less and less because oxidant need to be add constantly, which result in high cost for running. Iron chelate oxidation desulfurization technology is one of chemical oxidation methods widely used. Fe$^{3+}$ has a higher oxidation -reduction potential for turning sulfide to Sulfur. Sulfur can be recycled by coagulation and gravity separation, Fe$^{3+}$ will be regeneration and cyclic utilization [10]. The following shows the chemical process:

$$\text{H}_2\text{S}_{\text{fluid}} + 2\text{Fe}^{2+} + L^n → 2\text{Fe}^{2+} + L^n + 2\text{H}^+ + S$$
$$\text{O}_2\text{fluid} + 4\text{Fe}^{2+} + L^n + 2\text{H}_2\text{O} → 4\text{Fe}^{3+} + L^n + 4\text{OH}^- (L \text{ as ligand})$$

In this process, although oxidizer can achieve recycling, the energy consumption is large, the byproduct is more complex, there will be lots of constraints when used in agriculture, such as soil PH, excess soluble salts, aluminum toxicity, sulfite toxicity and etc. [11]. It is also easier to introduce second pollution to the environment.

2.2. Bio-desulfurization technology
The sulfur and its compounds gain or lose electrons by oxidation or reduction reaction, and the morphology of the compound of sulfur can be changed by the cycle. Sulfur of the biological cycle includes the following parts [12], in anaerobic environment conditions and under the action of sulfate reduction bacteria, sulfate is reduced to sulfide. The sulfide is oxidized to elemental sulfur and sulfate under the action of aerobic thiobacillus, which is called the process of biological oxidation. Sulfate is converted to organic sulfur under the action of bacteria, which is called the assimilation and reduction process of sulfur. The biological cycle of these sulfur and the physical and chemical processes are shown in Figure 1. Sulfur circulation is mainly through the biological cycler. Bio-FGD technology based on biological sulfur cycle theory, it can be divided into three steps. The first step is sulfur dioxide in the flue gas is dissolved by water or absorption tower and converted to sulfite or sulfate, the second step is to use sulfate reducing bacteria to reduce the sulfite and sulfate to sulfide under anaerobic conditions and external carbon sources. The third step is to use the role of sulfur bacteria in aerobic reactor to convert sulfide into sulfur. BioDeSOx process is one of Bio-FGD technologies.

Several companies jointly developed a new bio-desulfurization technology, which was called BioDeSOx process. In this process, comprehensive utilization of alkali absorption and biotechnology
can convert SO₂ to sulfur, alkali also can be regenerated. This not only reduces the raw material adding but also can produce sulfur products to achieve economic benefits [13]. There are no secondary pollutants and emissions produced, therefore it is conducive to the security environment.

SO₂ will be generated in the combustion process of sulfur in coal, which is easy soluble in water and transfer to SO₄²⁻ or SO₃²⁻ [14].

\[
\begin{align*}
SO_2 + O_2 & \rightarrow SO_3^{2-} \\
2SO_2 + O_2 + 2O_2 & \rightarrow 2SO_4^{2-}
\end{align*}
\]

**Figure 1. Schematic diagram of sulfur cycle in nature**

Liquid phase under anaerobic conditions, the sulfur ion of sulfate and sulfite can gain or lose electrons to form S²⁻, then the process requires sufficient electron donor to provide electron. Generally, the electron donor can be hydrogen or alcohols (methanol, ethanol), it can also be a high concentration of organic wastewater that the reductive substances COD react with sulfate and sulfite to general S²⁻.

\[
SO_3^{2-} \text{ and } SO_4^{2-} \rightarrow S^{2-}
\]

Liquid phase under aerobic conditions, colorless sulfur bacteria transfer S²⁻ to sulfur(S).

\[
S^{2-} \rightarrow S
\]

3. **Biodeso, bio-fgd technology**

In the 1990s, the company Paques began to research and develop the biological desulfurization technology - Thiopaq technology, is mainly used in the removal of H₂S. This has been applied in more than 100 desulfurization projects all over the world, the industrial application has proven that Thiopaq technology is an environmentally friendly and efficient method. Subsequently, this technology created large company’s attention in companies such as Shell and UOP [15]. These companies used this technology for removal H₂S in the petroleum and chemical industry. On this basis, the two other big energy companies Hoogovens and Nuon with Paques jointly researched and developed the BioDeSOx technology for removing SO₂ in flue gas. Firstly, SO₂ in the gas will be adsorbed by lye and converted to sulfate, the reduction reaction of sulfate occurs under anaerobic conditions and H₂S would be formed, which is then uses the Thiopaq technology to convert H₂S to S. The application of BioDeSOx technology greatly reduces the running cost and reduces the risk of the secondary environmental pollution. Biological sulfur produced by biological desulfurization has no harmful chemical components, even though it has not pass through purification treatment process can also be widely used in agriculture, which will result in economic benefits [16].

3.1. **The process flow**

The BioDeSOx technology process as shown in Figure 2 [17].
3.1.1. Washing system. In the washing system, gas is pumped into the bottom of the washing tower and discharged from the upper part of the tower. There is a sprinkler system at the top of the tower. When gas goes through washing liquid spray at the top, sulfur oxides, halides and dust are removed from flue gas by the washing liquid and the purified gas is discharged from the top of the tower. The washing liquid that adsorb the sulfur oxides and others by products is discharged from the bottom of the tower to the anaerobic system.

In order to achieve high SO₂ removal efficiency, lye such as NaOH, Na₂CO₃, and Ca (OH)₂ was widely used as a washing liquid because of the effective reaction between SO₂ and alkaline substances. In the traditional way of desulfurization, the price of sodium salt (Na⁺) is high, companies usual make use of calcium salt (Ca²⁺), which is cheaper but may easier cause blockage problems. The lye of BioDeSOx biological systems can be renewable and restore the alkaline of washing liquid, the method of sodium salt can be used economically in this system to avoid the blockage problem.

The coal combustion cycle not only contains SO₂, but also contains a large number of CO₂. CO₂ is easily soluble in alkali solution, which can make the circulation system rapidly form a NaHCO₃ buffer. The buffer system has a very strong resistance to the fluctuations of the concentration of SO₂ in the flue gas and maintains a stable and low concentration of SO₂ in the final exhaust gas [9].

\[
\text{SO}_2 + \text{NaHCO}_3 \rightarrow \text{NaHSO}_3 + \text{CO}_2 \\
\text{SO}_3 + 2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{CO}_2 + \text{H}_2\text{O}
\]

The concentration of NaHCO₃ in flue gas is balanced with the concentration of CO₂, and maintains the PH at an optimum range required by the biological reaction. There are no need to add NaOH unless the consumption of the washing liquid to remove sulfur is too large.

3.1.2. Biological reactor system. The core patent of the BioDeSOx technology is the biological reactor [18], which is divided into anaerobic system and aerobic system. The anaerobic system is using an IC reactor whereas the aerobic system is using CIRCOX reactor [19].

The detergent containing sulfite and sulfate is pumped into the anaerobic system after a simple precipitation. In the anaerobic system, sulfite and sulfate are converted into sulfides through a microbial process and then pumped into the aerobic reaction system. The aerobic microbial convert the sulfides to elemental sulfur and re-used lye [20].

In the anaerobic system, sulfite and sulfate are converted to sulfide required a donor element to provide electrons. The CODcr concentration of wastewater from coal (generally above 5000mg
/ L), it is a very economical way to use the high concentration organic wastewater as the reducing agent. Considerable testing and analysis must be completed to understand the wastewater characteristics whether it can use reasonable, then it can greatly reduce the operational cost of the FGD in coal chemical industry [21].

\[
\begin{align*}
\text{NaHSO}_3 + 0.75 \text{HAc} & \rightarrow \text{NaHS} + 1.5 \text{H}_2\text{O} + 1.5 \text{CO}_2 \\
\text{Na}_2\text{SO}_4 + \text{HAc} & \rightarrow \text{NaHS} + \text{H}_2\text{O} + \text{CO}_2 + \text{NaHCO}_3
\end{align*}
\]

In the aerobic system, sodium sulfide was oxidized to sulfur by colorless sulfur bacteria, as follows:

\[
\text{NaHS} + 0.5 \text{O}_2 \rightarrow \text{S} + \text{NaOH}
\]

The CIRCOX reactor is a sleeve structure tower where microorganisms in the reactor will form granular sludge and have good separation and settlement properties. Both the wastewater containing sulfide and compressed air enter into reactor from the bottom. The compressed air enters into the inner cylinder to raise the granular sludge in to air where it mixes with the wastewater resulting in aerobic micro-organisms reaction with wastewater. At the top of reactor, compressed air is discharged through the exhaust holes and slurry containing sulfur overflow into the separator. Because there is no disruption airflow, granular sludge with good settlement performance will settle in the bottom of outer cylinder and participate in the next cycle of reaction. Liquid overflow into the solid-liquid separation system, after separating the sulfur, the high pH value of the liquid is returned to the washing tower to realize the lye regeneration. The structure of CIRCOX reactor as shown in Figure 3.

![CIRCOX reactor structure diagram](image)

**Figure 3.** CIRCOX reactor structure diagram

3.1.3. *Solid-liquid separation system.* Sulfur generated in the aerobic biological reactor and separated by solid-liquid separator. A small portion of sulfur slurry is returned to bioreactor for controlling the concentration of sulfur/ microbial, the vast majority of sulfur removed as the slurry where the solid content is 5-10%. The purity of sulfur is 90%, and the remainder is organic matter and trace amounts of salts. The picture of sulfur separated by solid-liquid separator is shown in Figure 4 [22].

3.1.4. *Features.* Compared with the traditional desulfurization technology, the characteristics of BioDeSOx technology is obvious:

1) Biological desulfurization technology is simple, reliable, easy to operate and can meet the requirements of desulfurization.

2) Can directly use the local high concentration organic waste water or waste residue as an electron donor, not only meeting the requirements of desulfurization, but also can achieve the aim of treatment and utilization of waste as the circular efficient process.
3) Have good adaptability to the high CO2/SO2 concentration of gas, will consume less lye, low energy consumption.

4) Biological sulfur has good hydrophilicity and mobility, to avoid the phenomenon of sulfur blocking and equipment corrosion, biological sulfur can be directly used as raw material for agricultural or compound fertilizer, which increase the economic efficiency.

5) Lye can regenerate and recycling, thus reducing the operational cost of desulfurization process.

6) There is no waste liquid and waste residue discharged, has no the risk of secondary pollution, carbon emissions are low.

The concentration of the SO2 in the process of coal combustion is low, the fractional volume will generally not exceed 25%. The high ratio of gas CO2/SO2(this kind of gas is not suitable for using traditional sulfur treatment) is an excellent choice for the BioDeSOx desulfurization technology.

3.2. Influence factor
BioDeSOx technology is simple and stable operation, but as a biological system, microorganism survival still requires certain conditions, the main factors are the following.
1) Washing tower requires a certain pH buffer range. Microorganism have a fixed range of sulfur processing load, the sulfur components in intake-air are larger, the washing liquid sulfate fluctuation is then bigger, that will have an impact to the subsequent biological treatment system and thus reducing the processing efficiency. If the CO2 of the intake-air is within a certain pH value, the formation of HCO3- solution with the role of buffer.

2) Oxidation reduction potential in aerobic system. Oxidation reduction potential is decided by the oxygen quantity. If the redox potential is too high, the sulfide is oxidized to sulfate. If it is too low, this will cause the low removal of sulfide, decrease the absorption efficiency of lye and reduce the removal rate of the gas SO2 and H2S. The redox potential is an important parameter with an ideal control range of -300mV to -400mV, which can be adjusted by controlling the frequency of the conversion blower.

3) Electrical conductivity. The electrical conductivity reflect the concentration of salt in the reactor. The conductivity is higher, the salinity of liquid in the reactor is higher, which will resulting in the death of microorganisms. The lower the conductivity and lower liquid salinity is not conducive to the growth of microorganisms. The electrical conductivity of the reactor can be controlled by discharging the reactor liquid and adding the softened water.

4) Nutrient additions. Microbial growth requires adding quantitative nutrient salts. The amount of nutrients can be determined according to the amount of sulfur removal. If nutrient additions are too few, microorganisms do not grow and adding too much can cause poisoning. Microbial biomass determines desulfurization effect.
5) Temperature. Microbial growth requires an appropriate temperature. If the temperature is too high, it will cause the death of microorganisms; if the temperature is too low, it will lead to a decrease in microbial activity. Desulfurizing bacteria suitable temperature range is between 30 degrees to 40 degrees.

3.3. Benefits analysis
By comparing the traditional alkaline cleaning method, iron chelate and BioDeSOx desulfurization technology, one can clearly see the advantages of biological desulfurization technology.

Table 1. Advantages Comparative Analysis of Desulfurization Technology

|                          | Alkaline cleaning method | Iron chelate method | BioDeSOx method |
|--------------------------|--------------------------|---------------------|-----------------|
| Chemical cost            | RMB20000 yuan/tS         | RMB5000 yuan/tS     | RMB2000 yuan/tS |
| Operation time           | 12h/d                    | 12h/d               | 1h/d            |
| Desulfurization efficiency | >90%                    | >90%                | >98%            |
| External emission        | Waste chemicals          | Waste chemicals     | Non toxic salt  |
| Failure rate             | Easy to jam, high failure rate | Easy to jam, high failure rate | Not easy to jam, low failure rate |
| Economic performance     | N/A                      | N/A                 | Produce biological sulfur with economic benefits |

4. Case analysis

4.1. Project profile
Yixing xielian heat and power plant is a Sino Thai joint venture, located in the Yixing City which is "township of Chinese environmental protection". This city is in the Taihu Lake Basin, which belongs to the key environmental protection area. In 2003 - 2005, the boiler flue gas desulfurization came into operation with the implementation of the 2 x 125MW coal-fired thermal power unit expansion project. BioDeSOx desulfurization technology [23] was chosen for this project. Design of flue gas emissions 1.1×10^6 m^3/h, SO2 content of the gas is 0.037%. The Yixing xielian company also had a citric acid plant beside the heat and power plant. This is a great amount of reducing agent will be needed in the anaerobic systems of the flue gas desulfurization. The citric acid plant produces a large quantity of high concentration wastewater can be as electron donors providing microbiological and eventually convert the SO2 in flue gas to sulfur. The process as shown in Figure 5 mainly includes washing, cooling and precipitation, anaerobic treatment, aerobic treatment system, solid-liquid separation system, etc.

4.2. Benefits Operation Analysis
After the completion of the project, there will be 3 million high methane concentration gas directly into the biogas generating units and the rate of flue gas desulfurization up to 98%, emissions concentration of SO2 < 100mg / m^3, and removal dust. Because there is no addition of limestone, there is no chemical waste, which avoids the secondary pollution; microorganisms in the reaction exist in nature and do not impact the environment. At the same time, sulfur with high application value is produced. The annual production is estimated at 5000 tons, resulting in good economic benefit to offset costs. When compared with the traditional flue gas desulphurization technology, the initial one-time investment is larger for BioDeSOx technology, the economic benefits is significantly once in operations, Also, in view of the life
cycle of this technology, the running cost, the effect of energy saving and emission reduction is undoubtedly better than the traditional desulfurization technology.

![Diagram of BioDeSOx technology process of Yixing xielian thermal power plant](image)

**Figure 5.** BioDeSOx technology process of Yixing xielian thermal power plant

5. **Conclusion**

With higher environmental protection standards being striven for, acidic gas generated in the process of coal combustion and coal chemical industry is constantly being improved through energy saving and emission reduction requirements. Bio-desulfurization technology used to convert SO$_2$ to elemental sulfur with the utilization of recycled high concentration organic wastewater, obviously realizes the lowest environmental pollution and best environmental benefit. The regeneration of alkali liquid will reduce the operational cost. There is no waste gas discharge and energy-saving emission reduction effect is good as well as sulfur resources are produced to realize the additional economic value resulting in good application for the foreseeable future.

6. **References**

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