Study on oxidation desulfurization treatment of tail gas from large thermal power plants in Central Asia

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Abstract. In recent years, Kazakhstan's economic development has brought serious environmental problems. A large number of exhaust emissions are the important reasons for environmental pollution. Most of the tail gas emissions are due to coal combustion. In Kazakhstan, as many as 70% of large-scale thermal power plants will produce a lot of sulfur dioxide and other substances when burning coal, which will lead to acid rain and bring serious harm to the environment. On this basis, Kazakhstan continues to carry out research on desulfurization and denitrification technology of exhaust gas, so as to reduce the air pollution caused by exhaust gas. Combined with wind energy development technology, the oxidation desulfurization treatment method of power generation tail gas of large thermal power plants in Central Asia is studied in order to better purify the power generation tail gas and protect the environment.

1. Introduction
Kazakhstan has backward environmental protection facilities and frequent public demonstrations. Kazakhstan's large-scale thermal power plants use coal as the main fuel and produce a large number of sulfur dioxide and other substances during combustion, causing serious pollution to the environment and forming acid rain, seriously threatening human life and health[1]. In order to prevent tail gas pollution from thermal power plants, thermal power plants should strengthen the research on desulfurization and denitrification technology, steadily promote the application of integrated technology of exhaust gas denitrification, so as to better remove sulfur, nitrogen and other harmful elements in the exhaust gas, and reduce the environmental pollution caused by the exhaust gas [2-3]. Since the 1970s, developed countries began to explore the technology of flue gas desulfurization and denitrification, and on this basis, the industrial exhaust gas desulfurization and denitrification technology was studied. In recent years, Kazakhstan has made great progress in environmental protection.

Wind power is more suitable for the development of Kazakhstan than photovoltaic power generation. The integrated technology of catalytic oxidation desulfurization and denitrification not only has high desulfurization efficiency, but also can reach more than 80% at low temperature, and has good adaptability to the change of sulfur content[4]. The comprehensive activated carbon desulfurization and denitrification process mainly depends on the adsorption capacity of activated carbon, and secondary utilization is realized by desorption[5-6]. The sulfur and nitrogen in the exhaust
gas are removed by peak development technology based on the principle of physicochemical combination. Although the initial investment is huge, in the long run, its economic value is very high.

2. Treatment of tail gas oxidation desulfurization in thermal power plant

2.1 chemical composition analysis of power plant tail gas

The exhaust gas mainly contains organic sulfur compounds, such as oxygen, nitrogen, steam, oil and gas, mercaptan, thioether, dimethyl thiophene and so on. The content of organic sulfide gas is 10% ~ 40%, and the total mass fraction is more than 2000 mg/ m3. The specific results are shown in Table 1.

| Name            | Concentration | Name           | Concentration |
|-----------------|---------------|----------------|---------------|
| Low             | 1.24          | Methyl 2-butene| 1.46          |
| Bian            | 1.26          | 1-pentene      | 1.33          |
| Feng Ting       | 1.03          | 2-pentene      | 1.05          |
| 1-Cho           | 1.06          | Cyclopentene   | 1.24          |
| 2-Ch            | 2.64          | Isohexene      | 1.06          |
| Z 2 Cho         | 3.05          | 3-methylpentane| 1.13          |
| Yotsubo1        | 1.62          | 2-methyl + pen| 0.65          |
| Yotsubo2        | 1.43          | 2-methyl       | 0.42          |
| 2-Koki - 1 Cho  | 1.00          | 2-pentene      | 0.33          |
| Kogi no kenboku | 0.51          | 3 methyl+pentene| 0.12        |
| Gao Jinjun      | 0.62          | Hydroethyl     | 0.05          |
| Koh iwajun1     | 0.33          | Dimethyl disulfide| 0.12   |
| Koh iwajun2     | 0.11          | METHYLCYCLOPENTANE | 0.13 |

Based on the information in the above table, the desulfurization process is further optimized and divided into two steps: first oxidation, then liquid phase extraction or adsorption[7]. The obvious advantages of oxidative desulfurization are: low reaction temperature, low reaction pressure and no use of hydrogen. In oxidative desulfurization, sulfides difficult to remove in hydrodesulfurization are easily oxidized, which is another feature of oxidative desulfurization. Sulfur is oxidized by oxidants and more polar compounds are extracted from diesel oil. The specific evolution structure of the reaction of oxygen with benzophenone is as follows:

![Fig. 1 evolution of chemical structure of gases](image)

In the above algorithm, \( \alpha \) is the physical quantity needed to be solved for the emission of the power plant for a period of time; \( \Gamma \) shows that the diffusion coefficient of thermal power plant emission period; \( \text{div}(\alpha) \) is the environmental convection value; \( \text{div}(\text{grad}\alpha) \) is the diffusion term of emission period[9]; \( s \) is the original parameter. The contour distribution of exhaust gas flow field
in flue section of thermal power plant is analyzed by using FLUENT software. According to relevant specifications, the units are generally operated under 250 MW and 330 MW loads. The details are shown in the following figure:

![Fig. 2 contour distribution of flow field](image)

**Table 2 tail gas treatment equipment**

| Equipment name          | number | remarks                                      |
|-------------------------|--------|----------------------------------------------|
| Low temperature absorption tower | 1      | 304 stainless steel with internals, size 800m / 600mmx100000m |
| Rich oil pump           | 2      | The flow rate is 20m / h, the lift is 90m, the material is carbon steel, and the power is 15kw |
| Refrigeration unit      | 1      | Fusheng compressor, diesel oil flow passage parts are made of stainless steel |
| Lean / rich oil heat exchanger | 3      | Plate heat exchanger, heat exchange area 129m, 304 stainless steel |
| Deaerator               | 2      | 304 stainless steel, size 2200mmx2500mm |
| Desulfurizer pump       | 1      | Stainless steel, flow rate 10m / h, lift 50m, power 7.5kw, intermittent operation |

The above table includes plate heat exchanger with diesel oil as internal connecting point medium and stainless steel plate heat exchanger. The heat exchanger has the advantages of high heat exchange efficiency and small space occupation. The lean plate heat exchanger can recover about 85% of the cold energy of the system. Freezing device: it can cool and dilute the temperature of the oil absorber, the refrigerant is R22, the motor power of the unit is 37 kW, and the screw freezing compressor. 120 kW cooling capacity. Low absorption tower material: 304 stainless steel is used as low absorption tower material, the height of filler is 5 m, the thickness is 25 mm, and the stainless steel filler is annular bulk material. When the temperature is 6 ~ 10 ℃, the pressure difference of packed tower is 0.1 MPa. Rich oil pump: zhya40-250 pump, 90 m, flow rate 20 m³ / h. Desulfurizer: bubble type desulfurizer is used. There are many fillers in the desulfurizer, and the alkali liquid level in the desulfurizer is 2 ~ 3 m; desulfurization pump: magnetic pump is used for intermittent operation. After use, clean the pump body to avoid alkaline crystallization.

**2.2 Desulfurization algorithm of exhaust gas from thermal power plant**

Selective reduction with ammonia as reductant is the most effective method to remove NOx from exhaust gas. This method requires that the exhaust gas temperature should be the active temperature of
ammonia. Only in the utility boiler, the effective temperature of reducing agent can be reached, and other temperatures often can not reach this standard. On the basis of the above, the combined desulfurization optimization is carried out as follows:

![Fig. 3 optimization steps of combined desulfurization](image)

In this paper, SO2 and dust-free exhaust gas is oxidized by strong oxidant and sent to the absorption tower. Under the action of organic catalyst, it reacts with alkaline liquid, and SOx and NOx are removed at the same time. So dissolves in aqueous solution to form sulfite and forms stable compound with organic catalyst (LCO). Sulfuric acid was prepared by air oxidation method, the catalyst was separated, and ammonium sulfate was prepared from ammonia. By product ammonium sulfate fertilizer is produced by crystallization drying method. The special reaction equation is as follows:

\[
2NO + H_2O_2 \rightarrow N_2O_3 + H_2O \quad (2)
\]

\[
HNO_2 + 1CO \rightarrow ICO*HNO_2 \quad (3)
\]

\[
2LCO*HNO_2 + O_2 \rightarrow 2LCO + 2INO \quad (4)
\]

\[
HNO_2 + NH_4OH \rightarrow HN_4NO_3 + H_2O \quad (5)
\]

Under the action of catalyst, the activated carbon absorbs SO2 in the exhaust gas to the primary carbon bed and oxidizes to SO3, and then reacts with the water in the exhaust gas to form sulfuric acid. When N2 is reduced by activated carbon, the total nitrogen oxides account for 5% of the total nitrogen. The chemical equation is as follows:

\[
2NO_2 + 2C \rightarrow 2CO_2 + N_2 \quad (6)
\]

The exhaust gas contains no secondary carbon and is mixed with ammonia to react with no and ammonia

\[
6NO + 4NII_3 \rightarrow 5N_2 + 6dI_2O \quad (7)
\]

The adsorbents (NH4) 2SO4, NH4HSO4, H2SO4 and H2SO4 are desorbed and regenerated, and can be reused after cooling. SO2 reacts with strong reducing agents Co, CH4 and H2S to form S-element. SO3 is oxidized by catalyst, and then SO3 is dissolved in water to form sulfuric acid. Furthermore, the composition of pollutants in the tail gas of oxidative desulfurization alcohol is analyzed as follows:

| Pollution sources | Analysis project | Analysis of composition |
|------------------|------------------|------------------------|
| Catalytic oxidative desulfurization of gasoline | sulfide | hydrogen sulfide |
| | | Methyl mercaptan |
| | | Dimethyl disulfide and other sulfides |
| | Total | Total hydrocarbon |
| | hydrocarbon | hydrogen sulfide |
Catalytic oxidative甜ening of liquid hydrocarbons

| Methi mercaptan | Dimethyl disulfide and other sulfides
|------------------|-----------------------------
| Total sulfide    | Hydrogen sulfide
| Coking liquid hydrocarbon oxidation tax sulfur | Methyl mercaptan
| Total hydrocarbon | Total hydrocarbon of sulfide such as dimethyl disulfide

Through the above analysis, it can be seen that the use of advanced oxidants and catalysts to catalyze the oxidation of pollutants in the exhaust gas, and convert them into high value-added substances that are easy to absorb and remove, is a direct, simple and effective method to treat many kinds of pollutants in exhaust gas. The system can effectively solve the pollution problems of NO and Hg in the control of various pollutants.

2.3 Realization of desulfurization in power plant

In order to improve the effect of flue gas desulfurization and denitrification, the wind power exhaust catalyst was developed to improve the efficiency of flue gas desulfurization and denitrification. By adjusting the acidity and basicity of membrane surface, more genes with acid activity can be obtained, and the adsorption capacity of reducing agent on membrane surface can be improved. Moreover, wind power catalyst with higher activity can be developed by cooperating with materials with different activities, such as metal oxides (such as m, V, Mn). The catalytic changes were recorded, as shown in the figure below.

Fig. 4 catalytic change of oxidative desulfurization gas properties

The active coke method is adopted for desulfurization and denitrification of tail gas from thermal power plants. The lower part of desulfurization tower absorbs sulfur dioxide and enters into upper desulfurization tower. Under the catalysis of active coke, the nitrogen oxide in the exhaust gas is reduced by ammonia, and then converted into nitrogen to produce carbon dioxide and water. After adsorption, the activated coke is sent to the analysis tower of activated carbon analysis and regeneration cycle, and SO₂ is desorbed at about 400 °C. The separated activated coke is sent into the reaction tower, and then about 20% of the volume of sulfur dioxide is sent to the by-product recovery system to produce chemicals such as sulfuric acid and elemental sulfur. The linear relationship between differential pressure and tail gas flow rate can be obtained

\[ V = 23.96K \sqrt{\frac{\Delta p \cdot r}{b + p}} \]  

(8)

Among these variables, V is the flow rate of exhaust gas (M / s); K is the flow coefficient of exhaust gas; P is the output differential pressure of 1151 DP differential pressure flow transmitter (PA); R is the flue gas humidity in the flue gas (℃); B is the atmospheric pressure in the area where the
power plant is located (PA); P is the pressure of exhaust gas in the flue (PA). Other data show the following exhaust flow rates:

\[ T = 3600V \cdot M / div(\alpha) + V \]  

(9)

In the calculation formula, t is the flue discharge of the power plant (m³/h), M is the cross-sectional area of the flue (m²). According to the sulfur dioxide in the exhaust gas can be effectively recovered into sulfuric acid, sulfur and other emission values, the organic catalytic oxidation combined with desulfurization and denitrification of exhaust gas is carried out. By adding catalyst to the liquid phase, the sulfur dioxide is oxidized to nitrogen sulfate and nitrogen oxide under the action of oxygen, and ammonium sulfate and ammonium nitrate compound fertilizer are obtained under alkaline conditions.

3. Analysis of experimental results

In order to verify the actual effect of oxidation desulfurization treatment method for power generation tail gas of large-scale thermal power plant, the simulation exhaust gas generating unit, semi continuous bubbling reactor and exhaust gas detection unit constitute the exhaust gas denitrification experimental platform. The simulated exhaust gas system sends the set concentration and unit flow of exhaust gas into the reactor, and the treated or bypass exhaust gas is sent to the exhaust gas detection system (German mga5 type) through the dryer. The reactor was placed in a constant temperature water bath (Germany julabo model: f34-ed) to control the gas-liquid reaction temperature, which can be adjusted up to 60 °C. 14 μ m distribution hole and 16 w UV power are adjustable.

| Name                                | Parameter setting                      |
|-------------------------------------|----------------------------------------|
| Full pressure measurement range     | -30kPa~10KPa                            |
| Static pressure measurement range   | -30kPa~10KPa                            |
| Sampling flow                       | 10L/min~50L/min                         |
| Measurement range of smoke temperature | 0℃~500℃(expandable)                   |
| Power waste                         | ≤100W                                  |
| Working current                     | 50A~200A                                |
| Working voltage                     | AC220V±10%, 50Hz±1Hz                    |
| Air pump load                       | When the resistance is 30KPa,≥30L/min   |
| Range ratio                         | 100:1                                  |
| Relative working humidity           | 5℃~95℃                                 |

Based on the above table, the exhaust emission values of thermal power plants are further standardized. The SO₂ emission concentration is nearly 600 mg/m³, the NO₂ emission concentration is nearly 1500 mg/m³, and the SO₂ emission concentration is nearly 600 mg/m³ under the maximum power of continuous operation. Under the same conditions, the SO₂ emission concentration of a batch of low-speed diesel engines produced by German man company is 600 mg/m³ and 900 mg/m³, respectively. It is found that the sulfur content in the fuel oil is positively correlated with the SO₂ emission concentration. Based on the above environment, the treatment effect of the traditional method and the method in this paper is compared, and the specific results are shown in the figure.
Fig. 5 comparison test results

Based on the analysis of the above detection results, compared with the traditional gas oxidation desulfurization treatment method. The pollution gas emission of the large-scale thermal power plant tail gas oxidation desulfurization treatment method proposed in this paper has obviously decreased compared with the traditional treatment method in the actual application process, so as to confirm that the proposed wind power development method for thermal power plant tail gas. The effect of gas oxidation desulfurization treatment method in the actual application process is relatively better, which can achieve the requirements of pollution gas filtration more effectively and achieve the environmental protection goal.

4. Conclusion
In view of the current requirements and problems of flue gas desulfurization and denitrification in thermal power plants, this paper studies the method of using advanced wind power development technology to realize the efficient oxidation denitrification of pollutants in the exhaust gas. This method can effectively improve the efficiency of desulfurization and denitrification, and transform the process conditions for the control of multi pollutants in the exhaust gas of the existing wet desulfurization device, and analyzes the desulfurization and denitrification process of exhaust gas. Based on the environmental requirements of Kazakhstan and the actual situation of thermal power plants, the appropriate desulfurization and denitrification process is selected to analyze the desulfurization and denitrification methods of tail gas from thermal power plants and wind power generation. The research has proved that the application of desulfurization and denitrification technology for exhaust gas from thermal power plants is of great significance not only to improve the environmental problems in Kazakhstan, but also to promote the sustainable development of Kazakhstan's social economy.

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