The Role of Sodium-alkali Waste Gas Washing and Desulfurization Technology in the Exhaust Gas Treatment of Marine Diesel Engines

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Abstract. To reduce the concentration of sulfur oxide in the exhaust gas of marine diesel engines, the application of sodium-alkali waste gas washing and desulfurization technology in the exhaust gas treatment of marine diesel engines is explored. First, the reaction mechanism of sodium-alkali wet washing desulfurization technology is introduced, including the absorption process model of sulfur oxide, the absorption rate equation, the equation for absorbing sulfur oxide in aqueous solution, and the process of dissolving and absorbing sulfur oxide in sodium hydroxide solution. Then, a method to improve the absorption rate of sulfur oxides is proposed. Finally, the influence of load and pH of washing solution on desulfurization efficiency is discussed. The results show that the sodium-alkali waste gas washing and desulfurization technology has a good desulfurization efficiency. The desulfurization efficiency under different loads is more than 99%, and the maximum is 99.7%, which meets the desulfurization requirements of the national heavy oil exhaust gas treatment system. The higher the pH of washing solution, the more obvious the desulfurization efficiency. The results of this research provide a theoretical basis for the development of Chinese ships.

Keywords: Sodium-alkali method; marine diesel engine; exhaust gas desulfurization; exhaust gas washing and desulfurization technology.

1. Introduction
With the rapid development of the global economy, the scale of global trade has been expanding, and the trade volume between countries has been increasing year by year. In the rapid development of global trade, ship transportation is the most important way of trade transportation, and its annual transportation volume accounts for 80% of the world's trade volume. To speed up the development of trade, all countries in the world vigorously develop the shipping industry [1]. According to relevant statistics, the total tonnage of merchant ships in the world has exceeded 1 billion tons, among which the number of ships over 100 tons accounts for 85% of the total [2].

Although ships provide a good foundation for the development of trade economy because of their large cargo capacity, they also consume a huge amount of fuel during transportation. Ships are powered by diesel engines, which convert chemical energy into kinetic energy during operation, and the combustion products are discharged into the ocean atmosphere. There are a lot of hazardous substances
in these combustion products, among which the most serious pollution to the marine atmosphere is sulfur oxides and nitrogen oxides. After the sulfur oxide is discharged into the atmosphere, it will form acid rain, which seriously damages the atmospheric environment [3, 4]. Besides, acid rain will corrode crops and pollute groundwater, which will also have a serious impact on human life. To reduce pollution caused by marine diesel engine during operation, all countries around the world have made relevant restrictions on the emission of sulfur in the exhaust gas of marine diesel engine, and the control of marine exhaust gas will be more and more strict. At present, the research on desulfurization technology of marine diesel engine is mainly divided into two categories. One is to use low-sulfur fuels as required by law. The other is the post-treatment to the exhaust gas, that is, a washing device is installed at the exhaust gas outlet, and an alkaline liquid is put into the device to neutralize the sulfur oxides in the exhaust gas [5, 6].

In summary, in this research, the application of sodium-alkali waste gas washing and desulfurization technology in the exhaust gas treatment of marine diesel engines will be explored. First, the reaction mechanism of sodium-alkali wet washing desulfurization technology is introduced. Then, according to the reaction mechanism of desulfurization technology, an optimized method is proposed to improve the absorption rate of sulfur oxides. Finally, experiments are undertaken on the technology of washing and desulfurizing exhaust gas from marine diesel engines. This research aims to provide a certain direction for the development of China's shipping industry.

2. Methods

2.1. Reaction mechanism of sodium-alkali wet washing desulfurization technology

The most important key step for the sodium-alkali wet washing desulfurization technology is to explore the reaction mechanism for absorbing sulfur oxide. In this research, the double membrane theory is selected to construct the mass transfer model of sulfur oxides. In the process of absorbing sulfur dioxide by NaOH, the main form of mass transfer is convective diffusion by eddy diffusion, which includes molecular diffusion and convective mass transfer. The double membrane theory mainly simplifies the complex gas-liquid two-phase process into a simple gas-liquid interface on both sides of the gas film, so that all the force of mass transfer resistance can be concentrated in the retention membrane on both sides. Therefore, it can be inferred that the mass transfer rate of the gas-liquid phase is mainly affected by the diffusion rate of the gas film and the liquid film. According to the double membrane theory, the following assumptions exist in the process of washing sulfur oxide by sodium alkali method.

First, there is a phase interface between the gas phase and liquid phase, and two phases (gas film and liquid film) show turbulent flow.

Second, the absorption process is regarded as a diffusible process, in which the sulfur oxide molecules begin to move from the exhaust gas along the boundary of the gas film, then pass through the gas film and the phase interface, enter the liquid film region, and finally reach the boundary of the liquid film to be absorbed by the liquid phase.

Third, there is no concentration gradient between the gas and liquid phases, and there is no diffusion resistance.

Fourth, the molecules of sulfur oxides are in equilibrium at the phase interface, and there is no mass transfer resistance at the phase interface.

Fifth, the gas film and liquid film diffuse steadily during the absorption of sulfur oxides.

For gas, the equation of absorption rate of physical change can be expressed as follows.

\[
N_A = \frac{D_g}{\delta_g RT} \frac{P}{p_{BM}} (p_A - p_{Ad}) = \text{kg} (p_A - p_{Ad})
\]

(1)

In equation (1), \(D_g\) represents the molecular diffusion coefficient of the absorption component A in the gas phase; \(\delta_g\) represents the thickness of the gas film; \(P\) is the total pressure; \(p_{BM}\)
represents the logarithmic average partial pressure of other component B in the gas film; $k_g$ represents the mass transfer coefficient in the gas phase.

The mass transfer rate equation in the liquid phase can be expressed as follows.

$$N_A = \frac{D_i}{\delta_i}(c_{Ai} - c_i) = k_i(c_{Ai} - c_A)$$

In equation (2), $D_i$ represents the molecular diffusion coefficient of the absorption component A in the liquid phase; $\delta_i$ represents the thickness of the liquid film; $k_i$ represents the mass transfer coefficient in the liquid phase. Therefore, the total mass transfer rate equation can be expressed as follows.

$$N_A = k_i(c'^*_{Ai} - c_A)$$

$$N_A = k_g(p_A - p^*_A)$$

In equation (3), $p_A$ represents the concentration $c_A$ of component A in the main body of the liquid phase and the partial pressure of component A in the gas phase at equilibrium, $c'^*_{Ai}$ represents the molar concentration of component A in the liquid phase where the partial pressure $p_A$ of the component A in the main body of the gas phase is balanced, $k_i$ is the total mass transfer coefficient of the gas phase, and $k_g$ is the total mass transfer in the liquid phase.

The absorption rate equation of chemical reaction can be expressed as follows.

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{E \cdot H \cdot k_i}$$

$$\frac{1}{K_l} = \frac{1}{k_g} + \frac{1}{E \cdot k_i}$$

In equation (5) and equation (6), $K_l$ represents the total mass transfer coefficient of the liquid phase; $K_g$ represents the total mass transfer coefficient of the gas phase; $H$ is Henry’s constant.

In the process of washing sulfur oxides by sodium-alkali method, NaOH is the absorption liquid. Both NaOH and water in the solution can absorb sulfur oxides, so the steps of absorbing sulfur oxides can be divided into two steps: the absorption of sulfur oxides by NaOH solution and the absorption of sulfur oxides by water.

The equation of absorbing sulfur oxides by NaOH solution can be expressed as follows.

$$C_{so_{3-j}} = H \cdot p_{so_{3-j}}$$

$$C_{so_{3-j}}^* = \frac{N_{so_{3-j}} - k_{so_{3-j}} \cdot C_{so_{3-j}}}{\beta k_{so_{3-j}}}$$

$$N_{so_{3}} = \frac{p_{so_{3}} + \beta \cdot C_{so_{3-j}}^*}{H} + \frac{1}{k_{so_{3,g}} + \frac{1}{H \cdot k_{so_{3,j}}}}$$

In the above equations, $\frac{1}{k_{so_{3,g}}}$ represents the gas phase mass transfer resistance when sulfur oxides are absorbed by Na$_2$SO$_3$ solution, and $\frac{1}{H \cdot k_{so_{3,j}}}$ indicates the liquid phase mass transfer resistance when sulfur oxides are absorbed by Na$_2$SO$_3$ solution.
The expression of the absorption process of sulfur oxides by water is as follows.

\[ k_{so,g} \cdot a = 9.81 \times 10^{-4} W_G^{0.7} \cdot W_L^{0.28} \]  \hspace{1cm} (10)

\[ k_{so,l} \cdot a = \alpha \cdot W_L^{0.28} \]  \hspace{1cm} (11)

In the above equations, \( a \) represents the specific surface area of the filler; \( W_G^{0.7} \) represents the mass flow of gas phase; \( W_L^{0.28} \) represents the mass flow of the liquid phase; \( \alpha \) represents the constant that is temperature dependent.

According to the characteristics of the absorption of sulfur oxides by NaOH, there are many factors affecting the absorption rate, such as temperature, pressure, and solution concentration. Therefore, the absorption rate of sulfur oxides can be improved according to the influencing factors in the above equation: first, increase the force of mass transfer; second, increase the enhancement factor; third, improve the mass transfer coefficient of gas phase; fourth, increase the effective mass transfer area of component A between the gas and liquid phases; fifth, appropriately adjust the operating conditions.

2.2. Experimental conditions for washing and desulfurization of waste gas from marine diesel engines

By analyzing the reaction mechanism of sulfur oxides, it can be known that increasing the temperature of washing solution can accelerate the chemical reaction rate and the mass transfer rate between gas and liquids. Therefore, according to relevant studies, the NaOH solution should be kept below 50 °C in the experiment of absorbing sulfur oxides, otherwise the desulfurization efficiency will be seriously affected.

Na\(_2\)SO\(_3\) in the washing solution is the main substance that absorbs sulfur oxides, and the content of Na\(_2\)SO\(_3\) in the washing solution also has an important influence on the desulfurization efficiency. According to the solubility of Na\(_2\)SO\(_3\) at different temperatures, the solubility of Na\(_2\)SO\(_3\) in water is highest at 40 °C, and the solubility decreases at 60 °C; when the temperature drops to 0 °C, the maximum solubility drops by more than 50% [7].

In summary, the temperature of washing solution should be 20–40 °C.

3. Results

3.1. The influence of load on desulfurization efficiency

To verify the effectiveness of sodium-alkali waste gas desulfurization technology, the desulfurization efficiency is evaluated in this research. The desulfurization rate can be expressed as follows.

\[ \phi = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \]  \hspace{1cm} (12)

In equation (12), \( C_{in} \) represents the concentration of sulfur oxide before being washing, and \( C_{out} \) represents the concentration of sulfur oxide after being washing.

Figure 1 shows the change curve of sulfur oxide concentration before and after the waste gas is washed under different working conditions. As can be observed from the figure, the concentration of sulfur oxide produced by diesel engine increases with the increase of working condition load. Figure 2 shows the desulfurization efficiency under different working conditions. It can be observed from the figure that the desulfurization efficiency has been decreasing with the increasing working condition load, but the desulfurization efficiency has always been greater than 99%.
Figure 1. Concentration of sulfur oxide before and after the waste gas is washed under different working conditions

Figure 2. Desulfurization efficiency before and after the waste gas is washed under different working conditions

3.2. Effect of pH of washing solution on desulfurization efficiency

Figure 3 and figure 4 show the change relationship between the sulfur oxide concentration and the pH of the washing solution under 39% working condition. As can be observed in the figure, the concentration of the sulfur oxide after being washing has been decreasing with the increase of pH value, and the maximum dechlorination efficiency reaches 99.74%. Therefore, the pH value plays a very important role for the sodium-alkali method. It also shows that the greater the pH value, the better the desulfurization effect.
Figure 3. The relationship between concentration of sulfur oxides and pH of the washing solution under 39% working conditions

Figure 4. Desulfurization efficiency when the pH of the washing solution changes under 39% working conditions

4. Conclusion
To decrease the pollution of marine air environment from ship exhaust emissions in China, in this research, the application of sodium-alkali exhaust gas washing technology in the exhaust gas treatment of marine diesel engines is explored. First, the reaction mechanism of sodium-alkali waste gas washing desulfurization technology is analyzed, and then the method of improving desulfurization efficiency is put forward according to the reaction mechanism. Finally, the experimental conditions are set and the effects of different loads and pH values on desulfurization efficiency are discussed. The results show that the desulphurization efficiency decreases with the increase of load, but remains above 99%. The pH value of washing solution has a great influence on the desulfurization efficiency, and the desulfurization efficiency increases with the increase of pH value. The results of this study provide a certain theoretical
basis for China's shipping industry. However, there are still some limitations in this study, for example, only the influence of different loads and the pH value of washing solution on the desulfurization efficiency is studied. Therefore, to find more factors that affect the desulfurization efficiency is the focus of the next research.

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