Effect of Wet Scrubbing Oxidation Denitration Technology Combined with Ultraviolet Online Irradiation on the Efficiency of Desulfurization and Denitrification of Ship Exhaust Gas

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Abstract. In order to alleviate the air pollution caused by nitrogen and sulfur oxides discharged from ships, the efficient method of deoxidization and desulfurization of marine diesel engine exhaust gas has been explored. In this study, at present, the mainstream technology of ship exhaust gas removal at home and abroad, wet scrubbing oxidation denitration technology is taken as the research object. Ultraviolet (UV) online irradiation is introduced into the process of wet scrubbing oxidation denitration of NaClO\textsubscript{2} solution. The effects of different parameters, such as the concentration of NaClO\textsubscript{2}, the temperature of washing solution, the concentration of O\textsubscript{2} and SO\textsubscript{2}, on the removal of No are studied. The reaction mechanism is further analyzed. The results show that photochemical reaction will take place between UV online irradiation and NaClO\textsubscript{2} solution, resulting in a large number of active radicals with strong oxidation, which can obviously enhance the effect of No removal by wet scrubbing of NaClO\textsubscript{2} solution. It can be seen that the wet scrubbing oxidation denitration technology combined with UV online irradiation can greatly improve the efficiency of desulfurization and denitrification of ship's exhaust gas. It is an efficient method of deoxidization and desulfurization of ship's diesel engine exhaust gas, which is of great help to alleviate exhaust gas pollution.

Keywords: ship exhaust gas; wet scrubbing; UV online; deoxidation and desulfurization.

1. Introduction

Since entering the 21st century, the degree of economic globalization has been deepening, China's foreign trade has developed rapidly, and the volume of foreign trade has increased year by year. As an important means of foreign trade goods transport, maritime transport bears more than 90% of China's foreign trade volume [1]. According to the data released by the Ministry of transport, in 2017, the foreign trade cargo throughput of ports above Designated Size reached 4.01 billion tons, an increase of 5.7% compared with the same period in 2016. Among them, the container throughput reached 240 million TEU (standard container), an increase of 8.3% year on year.

At present, large-scale diesel engine with its comprehensive advantages of good economy, high thermal efficiency, flexible power operation, good mobility and high reliability gradually occupies the
leading position in the modern transport ship's main power device. Ship transportation is generally recognized as one of the relatively green and environmentally friendly modes of transportation. However, the power of large diesel engines is generally large, and heavy oil with poor oil quality and high sulfur content is generally used in ships, which discharge a large number of pollutants [2, 3]. In addition, compared with motor vehicles and non-road mobile machinery, the emission control policies and measures of ships are still in the initial stage, making the problem of ship emissions more prominent [4]. According to statistics, at present, No emissions from ships account for about 15% of all fossil fuel sources in the world, and SO$_2$ emissions account for 4% ~ 9% of all human sources [5]. Due to the low water solubility of No, conventional treatment methods are difficult to remove it efficiently, so how to remove no from ship exhaust gas efficiently is the research hotspot and difficulty in the field of ship exhaust gas emission reduction [6, 7].

In this study, buffer is used to prepare NaClO$_2$ washing solution for denitration experiment. The effects of different parameters on the removal of No are compared under the condition of UV online irradiation or not. The mechanism of NaClO$_2$ wet denitrification is explored, which provides a theoretical basis for the application of NaClO$_2$ wet denitrification in the treatment of diesel engine exhaust gas.

2. Method

2.1. Simulated flue gas configuration

The composition of marine diesel engine exhaust gas is complex and difficult to obtain, and the concentration of various gases cannot be changed independently. Therefore, in order to study the influence of a single factor on the wet denitrification performance of NaClO$_2$ solution irradiated by UV online, the simulated flue gas is used in this study. In the study of the influence of SO$_2$ concentration at the reactor inlet, CO$_2$ concentration at the reactor inlet and O$_2$ concentration at the reactor inlet on the wet denitrification performance of NaClO$_2$ solution irradiated by UV online, the simulated flue gas used in this study is composed of N$_2$ and No mixed first in the pipeline, then in the pipeline with SO$_2$, CO$_2$ and O$_2$ [8, 9].

In this study, all mass flow controllers are calibrated with N$_2$ at the factory, and the product of solenoid valve opening and mass flow controller range is N$_2$ flow. In actual use, when regulating the flow of other gases, N$_2$ flow needs to be converted, and N$_2$ flow needs to be multiplied by the mass flow conversion coefficient A of the actual regulated gas.

When the actual regulated gas is a single component gas, the calculation equation of mass flow conversion coefficient A is:

$$A = \frac{0.1306 \times N}{\rho \times C_p}$$

(1)

In the equation,

- $N$ - molecular composition coefficient of gas;
- $\rho$ - density of gas in standard state;
- $C_p$ - specific heat of gas at constant pressure;

When the actual regulated gas is a single component gas, the gas molecular composition coefficients of single atom molecule (such as He), double atom molecule (such as N$_2$), three atom molecule (such as SO$_2$) and multi atom molecule (such as NH$_3$) are respectively 1.01, 1.00, 0.94 and 0.885. When the actual regulated gas is a multi-component gas, the calculation equation of its molecular composition coefficient N is:

$$N = N_1 \times \frac{Q_1}{Q} + N_2 \times \frac{Q_2}{Q} + \cdots + N_p \times \frac{Q_p}{Q}$$

(2)

In the equation,
The calculation formula of mass flow conversion coefficient A is:

\[
A = \frac{0.1306 \times N}{\rho_1 \times C_{p_1} \times \frac{Q_1}{Q_r} + \rho_2 \times C_{p_2} \times \frac{Q_2}{Q_r} + \rho_n \times C_{p_n} \times \frac{Q_n}{Q_r}}
\]  

(3)

In the equation,
\[\rho_1, \rho_2\] - density of gas in standard state;
\[C_{p_1}, C_{p_2}, C_{p_n}\] - specific heat at constant pressure of each gas.

The density and specific heat at constant pressure at standard state are shown in Table 1.

**Table 1. Density and specific heat at constant pressure of some gases in standard state**

| Gases | Density (g/L) | Specific heat at constant pressure (KJ/Kg) |
|-------|--------------|------------------------------------------|
| N₂    | 1.25         | 0.1045                                  |
| NO    | 1.339        | 0.0999                                  |
| SO₂   | 2.858        | 0.0625                                  |
| CO₂   | 1.964        | 0.0849                                  |
| O₂    | 1.427        | 0.0923                                  |

According to equations 1, 2 and 3, it can be obtained that:

\[
A_{NO} = \frac{0.136 \times (N_{NO} \times 10\% + N_{N₂} \times 90\%)}{\rho_{NO} \times C_{p_{NO}} \times 10\% + \rho_{N₂} \times C_{p_{N₂}} \times 90\%} = 0.9971
\]  

Also,
\[A_{SO₂} = 0.9582, \ A_{CO₂} = 0.7370, \ A_{O₂} = 0.9920, \ A_{N₂} = 1.0000\]

The total simulated flue gas flow \(Q_G\) is:

\[
Q_G = Q_{N₂} + Q_{NO} + Q_{SO₂} + Q_{CO₂} + Q_{O₂}
\]  

(5)

In the equation,
\[Q_{N₂}\] - nitrogen gas flow, ml/min;
\[Q_{NO}\] - NO gas flow, ml/min;
\[Q_{SO₂}\] - SO₂ gas flow, ml/min;
\[Q_{CO₂}\] - CO₂ gas flow, ml/min;
\[Q_{O₂}\] - O₂ gas flow, ml/min;

The concentration of NO in the simulated flue gas is:

\[
C_{NO} = \frac{Q_{NO}}{Q_G} \times 1000000
\]  

(6)

In the equation,
\[C_{NO}\] - concentration of nitric oxide, ppm.

The relationship between NO gas flow and NO mass flow controller opening is as follows:

\[
Q_{NO} = B_{NO} \times D_{NO} \times A_{NO} \times E_{NO}
\]  

(7)
In the equation,
\[ B_{NO} \] - opening of No mass flow controller, \%;
\[ D_{NO} \] - range of No mass flow controller, ml / min;
\[ E_{NO} \] - purity of No gas, \%.

According to the required gas flow rate, gas concentration and equations 5, 6 and 7, the opening of No mass flow controller can be calculated. Similarly, the opening of other gas mass flow controllers can be obtained. Finally, according to the gas concentration measured by the flue gas analyzer, the opening of each mass flow controller is properly corrected.

2.2. The experimental procedure of denitrification of NaClO\(_2\) solution by UV online irradiation

Hydrochloric acid solution with a concentration of 1mol / L and sodium hydroxide solution with a concentration of 2mol/L are prepared. According to the experimental conditions, a certain concentration of NaClO\(_2\) solution 5L is prepared. According to the experimental conditions, 1mol / L hydrochloric acid solution or 2mol / L sodium hydroxide solution is used to adjust the pH value of NaClO\(_2\) solution to a certain value. pH meter and ORP meter are used to measure the pH value and ORP value of solution respectively. When the concentration of each component of flue gas and the temperature of deionized water reach a stable value, the spray denitration is carried out without UV irradiation. After 10 minutes, the stable concentration of each gas is recorded. After a small amount of spray solution is taken out, the pH value and ORP value of the solution are measured and recorded. Meanwhile, the UV light is turned on. Under the condition of online UV irradiation, the spray denitration is carried out. After 10 minutes, the stable concentration of each gas is recorded. A small amount of spray solution is taken out for pH value and ORP value measurement and recording. Each experimental condition is repeated three times. The average value is taken for subsequent discussion and analysis.

2.3. Experimental analysis method

The No removal rate can be calculated by the ratio of the difference between the NO concentration at the reactor inlet and the NO concentration at the reactor outlet to the NO concentration at the reactor inlet. No is almost insoluble in water, so the concentration of No at the outlet of the reactor is the same as that at the inlet of the reactor. SO\(_2\) is very soluble in water, so when measuring the SO\(_2\) concentration at the reactor inlet, it is necessary to connect the simulated flue gas directly to the gas sampling inlet of the flue gas analyzer to avoid the influence of the liquid inside the reactor on the measurement results. The flue gas analyzer samples every 10s. After the gas concentration is stable, it needs to measure continuously for 2.5min, and the average value is taken as the calculated concentration. The desulfurization and denitrification efficiency of wet scrubbing of NaClO\(_2\) solution can be calculated by equation 8:

\[ \eta_1 = \frac{C_1 - C_2}{C_1} \times 100\% \] (8)

The desulfurization and denitrification efficiency of wet scrubbing of UV irradiated NaClO\(_2\) solution can be calculated by equation 9:

\[ \eta_2 = \frac{C_1 - C_3}{C_1} \times 100\% \] (9)

In the equation,
\[ \eta_1 \] - Desulfurization and denitrification efficiency of wet scrubbing of NaClO\(_2\) solution, \%;
\[ \eta_2 \] - UV online irradiation of NaClO\(_2\) solution wet scrubbing desulfurization and denitrification efficiency, \%;
\[ C_1 \] - concentration of NO, NO\(_x\) and SO\(_2\) at the reactor inlet, ppm;
\[ C_2 \] - concentration of NO, NO\(_x\) and SO\(_2\) at outlet of reactor after oxidation reaction, ppm;
$C_3$ - concentration of NO, NOx and SO$_2$ at the outlet of reactor after photocatalytic oxidation, ppm.

3. Experimental results and analysis

3.1. Effect of initial concentration of NaClO$_2$ on denitration performance

It can be seen from Figure 1 that with the increase of initial concentration of NaClO$_2$, the NO removal rate shows an obvious upward trend. With the increase of the initial concentration of NaClO$_2$ from 2.5mmol/l to 12.5mmol/l, the removal rate of NO increases from 24% to 83% without UV irradiation. When UV irradiation is used, the removal rate of NO increases from 39% to 99%. Under the condition of NO UV irradiation online, the increase of initial concentration of NaClO$_2$ will promote the gas-liquid mass transfer, thus significantly improving the NO removal rate.

![Figure 1. Relationship between removal rate and initial concentration of NaClO$_2$](image)

3.2. Effect of washing solution temperature on denitrification performance

It can be seen from Figure 2 that with the increase of washing solution temperature, the NO removal rate shows an obvious upward trend. With the temperature of washing solution increasing from 20°C to 60°C, the removal rate of NO increases from 70% to 80% without UV irradiation. When UV irradiation is used, the removal rate of NO increases from 84% to 97%. The solubility of NO is $4.68 \times 10^{-5}$g at normal temperature and pressure. Therefore, the effect of temperature change of washing solution on NO solubility is negligible. From the point of view of chemical reaction, the increase of washing solution temperature can improve the activation energy required by chemical reaction, and then improve the chemical reaction rate, which is conducive to the removal of NO. The increase of washing solution temperature may also promote the decomposition of NaClO$_2$ to produce more oxidizing ClO$_2$ gas. ClO$_2$ is easy to dissolve in NaClO$_2$ solution, so as to improve the oxidation capacity of the solution.
3.3. Effect of $O_2$ concentration at reactor inlet on denitrification performance

It can be seen from Figure 3 that when there is no UV online irradiation and the $O_2$ concentration at the reactor inlet is in the range of 0-15%, the NO removal rate does not change with the $O_2$ concentration at the reactor inlet, and the NO removal rate is basically stable at 76%. Although $O_2$ also has certain oxidizability, which can oxidize part of NO to NO$_2$, the oxidizability of NaClO$_2$ is much stronger than that of $O_2$. Therefore, when there is no UV online irradiation, the $O_2$ concentration at the reactor inlet has little effect on the NO removal rate. When the concentration of $O_2$ at the reactor inlet is in the range of 0-15%, the NO removal rate slightly increases with the increase of $O_2$ concentration at the reactor inlet. With the increase of $O_2$ concentration from 0% to 15%, the removal rate of NO increases from 88% to 92%. When the concentration of $O_2$ at the reactor inlet is 0%, the NO removal rate of NaClO$_2$ solution under UV online irradiation is 12% higher than that without UV online irradiation. When the concentration of $O_2$ at the reactor inlet is 15%, the NO removal rate of NaClO$_2$ solution under UV online irradiation is 15% higher than that without UV online irradiation.

3.4. Effect of SO$_2$ concentration at reactor inlet on denitrification performance

It can be seen from Figure 3 that when there is no UV online irradiation, NO removal rate increases with the increase of SO$_2$ concentration at the reactor inlet. With the increase of SO$_2$ concentration from 0 ppm to 600 ppm, no removal efficiency increases from 73% to 93%. Under the condition of no UV
online irradiation, the oxidation of solution is an important factor affecting the removal efficiency of nitrogen oxides. The activation energy required for the reaction of SO$_2$ with NaClO$_2$ is less than that required for the reaction of No with NaClO$_2$, that is, the reaction rate of SO$_2$ with NaClO$_2$ is higher than that of No with NaClO$_2$. Therefore, with the increase of SO$_2$ concentration at the inlet of the reactor, the pH value of the solution decreases continuously, and ClO$_2$ is generated in the solution, which enhances the oxidation and denitrification rate. On the other hand, NO$_2$ is the main intermediate product in the denitrification process, and NO$_2$ is prone to disproportionation to produce No.

![Figure 4. Relationship between removal rate and SO$_2$ concentration at reactor inlet](image)

**4. Conclusion**

In this study, based on the study of the existing technology of denitrification of marine diesel engine exhaust gas, a new method of denitrification by UV online irradiation combined with NaClO$_2$ wet scrubbing is proposed for the first time. UV online irradiation is combined with wet scrubbing of NaClO$_2$ solution. A certain number of active radicals are produced by photochemical reaction between UV light and NaClO$_2$ solution. Due to the characteristics of active free radicals with short existence time and strong oxidation, UV online irradiation can obviously enhance the denitrification performance of NaClO$_2$ solution by wet scrubbing, which provides a new idea and method for alleviating the environmental pollution caused by the exhaust emissions of marine diesel engines. However, other components in marine diesel engine exhaust gas, such as particulate matter and volatile organic compounds, may have a certain impact on UV online irradiation combined with NaClO$_2$ wet scrubbing denitrification, and the experiment needs further study.

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