"NaClO₂-Sea Water" Wet Denitrification Technology Using NOx Treatment Technology in the Desulfurization and Denitrification of Ship Exhaust Gas

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Abstract. To minimize the emission pollution of nitrogen oxides (NOx) in marine diesel engine exhaust, based on the existing NOx treatment technology, the "NaClO₂-sea water" wet denitrification technology was further proposed. The denitrification performance of NaClO₂ solution in seawater and NaClO₂ solution in fresh water was analyzed by self-designed and built experimental platform. Moreover, the effects of the temperature of the absorption solution, the initial concentration of NaClO₂ and the concentration of NO in diesel exhaust gas on the denitrification performance of NaClO₂ sea water solution were studied. The experimental results showed that the denitrification rate of NaClO₂ solution with seawater as solvent was slightly lower than that of NaClO₂ solution with fresh water, but the denitrification duration of seawater solution had obvious advantages over that of fresh water solution. In addition, by increasing the temperature of the absorption solution and the initial concentration of NaClO₂ and decreasing the concentration of NO, the denitrification rate of NaClO₂ sea water solution was increased. Whereas, if the temperature exceeded a certain limit, the continuous denitrification time of the solution would be decreased. Therefore, "NaClO₂-sea water" wet denitrification technology has the advantages of cheap raw materials and long continuous denitrification time. High denitrification efficiency can be achieved by optimizing reaction conditions, so it can be used for denitrification of marine diesel engine exhaust gas.

Keywords: Wet denitrification; NOx treatment; NaClO₂; sea water.

1. Introduction

With the development of global economy, the trade exchange between countries becomes more frequent. Because of the characteristics of large cargo capacity and low cost, sea transportation takes on many transportation tasks. However, due to the rising price of international crude oil, many companies began to use a lot of inferior residual oil in order to save costs, resulting in the increasingly serious emissions of marine diesel engine exhaust. The pollutants in diesel engine exhaust gas mainly include sulfur oxide (SOx), nitrogen oxide (NOx), and particulate matter. Among them, the emission of NOx is the most, and most of the NOx is toxic gas NO. As it is difficult to dissolve in water, the absorption of NO is very difficult [1].
Experts and scholars in foreign countries have carried out many studies on the denitrification of exhaust gas. The main research directions are internal purification and post-treatment. Because the internal purification technology needs to transform the existing diesel engine, the cost is high, and the purification degree is limited, it cannot be popularized [2]. The post-treatment technology includes dry denitrification and wet denitrification. The catalytic method in dry denitrification has been applied at the end of the last century, but its cost is still high and the catalyst sometimes fails. The plasma method oxidizes NOx by accelerating the generation of electron beam, but the accelerator is expensive and not practical [3]. Wet denitrification includes liquid-phase reduction and liquid-phase oxidation absorption. The former realizes denitrification through urea reduction, and the process is relatively mature; the latter oxidizes NO into water-soluble NO2 by using oxidants H2O2, NaClO, NaClO2, and KMnO4, and then further absorbs it. This method has been applied to different degrees through extensive research by experts [4]. Among these oxidants, H2O2 is unstable and easy to decompose, and it is easy to generate toxic gas Cl2 at high temperature. Compared with other oxidants, NaClO2 has certain advantages in solution stability and denitrification, and is the most effective oxidant confirmed in recent years [5].

Based on NaClO2 selected as the oxidant, the NaClO2 solution is prepared by using sea water as solvent, and the "NaClO2-sea water" wet denitrification technology is proposed. At present, the studies mainly focus on the preparation of NaClO2 solution with fresh water as the solvent. However, for ships, it is very convenient to use sea water. The "NaClO2-sea water" wet denitrification technology proposed in this paper is more feasible in ship navigation, and has significant advantages in cost saving. By using the method of comparative experiment and control variable, the denitrification performance of NaClO2 seawater solution and NaClO2 fresh water solution is compared, and the difference in denitrification performance between them is studied. The effect of different conditions on the denitrification performance of NaClO2 sea water solution is further discussed by further changing the parameter conditions, thereby finding the best application conditions of denitrification performance.

2. Method
Due to the difference of exhaust emission components of various diesel engines, and the different time components of natural sea water in different places, the simulated exhaust gas and simulated seawater are used to replace the marine diesel engine exhaust gas and natural sea water in this experiment. The simulated flue gas is mixed with N2, O2, NO, SO2 and other gases, and the concentration of each gas is calculated with N2 as the standard using the calculation equation of gas mass flow conversion coefficient [6]:

\[
C = \frac{0.2106[N_1(\omega_1/\omega_0) + N_2(\omega_2/\omega_0) + L N_n(\omega_n/\omega_0)]}{\rho_1 C_{p1}(\omega_1/\omega_0) + \rho_2 C_{p2}(\omega_2/\omega_0) + L \rho_n C_{pn}(\omega_n/\omega_0)}
\]

(1)

\(N_1...N_n\) is the molecular composition coefficient of the gas, \(\omega_1...\omega_n\) is the flow rate of the corresponding gas, \(\omega_0\) is the density of the gas under the standard condition, \(C_{p1}...C_{pn}\) is the specific heat of gas at constant pressure.

The solvent of the absorption solution is fresh water and sea water, respectively, in which the fresh water is deionized water prepared by ultra-pure water preparation mechanism, and the sea water chooses simulated sea water. The simulated sea water used in this study is made up of MgCl2, CaCl2, KCl, NaHCO3, NaCl and Na2SO4 in strict accordance with the national standard of the United States. After the configuration, the weighed NaClO2 and the simulated sea water are mutually dissolved in a certain proportion, to obtain the required NaClO2 sea water solution for this experiment [7].

The experimental platform is composed of gas distribution module, reaction module, and detection module. The gas distribution module provides stable and continuous simulated exhaust gas for this experiment. In this experiment, the mass flow controller is used as the core device to precisely control the feed gas flow [8]. The core of the reaction module is the spray tower reactor, where the simulated exhaust gas enters the reactor, where NOx is absorbed by NaClO2 solution, and other gases continue to be discharged. The detection module mainly uses the flue gas analyzer to carry out real-time detection and analysis of various components in the discharged gas to observe the denitrification results of NaClO2 solution.
The prepared simulated waste gas and NaClO$_2$ solution are introduced into the spray tower reactor. The two flows in two directions, and NOx in the waste gas is absorbed. The gas concentration of each component in the flue gas at the inlet and outlet is measured by the flue gas analyzer, and the absorption rate of NO is calculated according to Eq. 2 [9]:

$$E_{NO} = 1 - \frac{C_{NO, out}}{C_{NO, in}} \times 100\%$$  

$E_{NO}$ is the absorption rate of NO, $C_{NO, in}$ and $C_{NO, out}$ are the concentrations of NO at the inlet and outlet of spray tower, respectively.

3. Results and discussion

3.1. Comparative analysis of denitrification performance of NaClO$_2$ sea water solution and NaClO$_2$ fresh water solution

Figure 1 shows the comparison of NO absorption rate between NaClO$_2$ sea water solution and NaClO$_2$ fresh water solution.

![Figure 1. Comparison of NO removal between NaClO$_2$ sea water solution and NaClO$_2$ fresh water solution](image)

Figure 1 showed that, at the beginning of the reaction, the absorption of NO by NaClO$_2$ sea water solution and NaClO$_2$ fresh water solution had an obvious growth trend, and the growth rate of NaClO$_2$ fresh water solution was slightly faster than that of sea water solution. At the 8th minute and when the NO absorption rate reaches about 80%, the NO absorption rate of NaClO$_2$ solution decreased slightly, but then increased rapidly, reaching 100% at about 13min, and remained at about 45min. After that, the absorption rate decreased rapidly to zero at 58min, and then NaClO$_2$ solution lost its absorption of NO. There were two peaks in the whole detection process of NaClO$_2$ sea water solution, and the highest absorption rate was only about 90%, which did not achieve the complete elimination of NO. However, the absorption rate of the solution did not drop to zero until 100min, and the whole absorption process lasted about 1.7 times that of NaClO$_2$ fresh water solution.

3.2. Effect of temperature of absorption solution on denitrification performance of NaClO$_2$ sea water solution

Temperature is an important factor affecting the chemical reaction rate. Generally, the higher the temperature is, the faster the chemical reaction rate will be. The influence of the temperature of the absorption solution on the absorption of NO is studied. Select 30°C, 50°C and 70°C, respectively, and the results are shown in Figure 2:
Figure 2. Effect of temperature of absorption solution on NO absorption rate

Figure 2 suggested that at the beginning of the reaction, with the increase of the temperature of the absorption solution, the absorption rate of NO became larger. When the temperature was 70°C, the absorption rate could be 100%. However, it can also be seen that the effective denitrification time of the solution was shorter with the increase of temperature, especially when the temperature was 70°C. The denitrification time of the solution was shortened by nearly half, which greatly affected the denitrification effect. The analysis of experimental results indicated that the increase of temperature would lead to the faster movement of molecules and the increase of the number of collisions between molecules, thereby increasing the activation energy of reaction and making the oxidation performance of NaClO$_2$ better. However, too high temperature would affect the activity of the molecule, making the effect of NaClO$_2$ shorter. In addition, when the temperature was moderate, it was found that there were two peaks of NO absorption rate, which might be due to the buffering effect of sea water. It could maintain a high pH value in the beginning period, so that NO absorption was inhibited in a short period. After about 60 minutes of action, the pH of the solution decreased and the NO absorption rate increased again, which could also explain the reason why the denitrification time of seawater solution was longer than that of fresh water solution.

3.3. Effect of initial concentration of NaClO$_2$ on denitrification performance of NaClO$_2$ sea water solution

The concentration of reactants also affects the rate of chemical reaction. In this paper, the initial concentrations of 0, 5, 10, 20mmol of NaClO$_2$ seawater solution were selected to determine its absorption rate of NO. The experimental results are shown in Figure 3:
Figure 3. Effect of initial concentration of NaClO₂ on NO absorption rate

Figure 3 showed that the initial concentration of NaClO₂ had a great influence on the NO absorption rate. The initial concentration was zero, namely, the natural sea water without adding NaClO₂ had little absorption effect on NO. With the increase of the initial concentration of NaClO₂, the absorption rate of the absorption solution to NO increased gradually. When the initial concentration was 5mmol, the highest absorption rate was about 65%; when the initial concentration was 10mmol, the highest absorption rate rose to 85%; when the initial concentration was 20mmol, the absorption rate could reach 100%, realizing the complete absorption of NO. In addition, with the increase of the initial concentration of NaClO₂, the time of continuous denitrification of the absorption solution was also increasing. When the initial concentration was 20mmol, the denitrification time could be extended to about 115min. It was found that when the initial concentration was large, there would be two peaks of NO absorption rate.

3.4. Effect of NO concentration on denitrification performance of NaClO₂ seawater solution

The effect on denitrification performance of NaClO₂ sea water solution was tested by changing the concentration of NO. The NO gas with concentration of 250, 400, 550 and 700ppm was selected, respectively. The experimental results are shown in Figure 4:

Figure 4. Effect of NO concentration on NO absorption rate
Figure 4 suggested that when other parameters were fixed, with the increase of NO concentration in the exhaust gas, the continuous denitrification time of the absorption solution decreases, and the absorption rate of NO also correspondingly decreased. The main reason was that the concentration of NO was too high and NaClO$_2$ was too much consumed in the solution. When the concentration of NO exceeded 550ppm, there were two peaks of NO absorption. Although with the increase of NO concentration, the absorption rate of NO decreased correspondingly, but not obvious. The absorption rate remained above 90%, indicating that NO concentration had little effect on the absorption rate of NO. Therefore, when the concentration of NO in the exhaust gas was too high in practical application, it only needed to change the NaClO$_2$ sea water solution in time.

4. Conclusion
The denitrification performance of NaClO$_2$ seawater solution and NaClO$_2$ fresh water solution is compared by designing the experimental platform of marine exhaust gas and preparing simulated flue gas and simulated seawater. On this basis, the influence of various factors on the denitrification performance of NaClO$_2$ seawater solution is studied by changing various parameters. The results show that the absorption rate of NO in NaClO$_2$ solution is slightly lower than that in NaClO$_2$ solution, but the denitrification duration is almost twice as long as that in NaClO$_2$ solution. Considering the comprehensive economic factors, the extraction of sea water is much easier than that of fresh water, so NaClO$_2$ sea water solution can be completely used for the denitrification of marine diesel engine exhaust gas with low cost. By increasing the temperature of absorption solution and the initial concentration of NaClO$_2$ and reducing the concentration of NO, the denitrification rate of NaClO$_2$ sea water solution can be increased. However, when the temperature is too high, the continuous denitrification time will be greatly reduced. The "NaClO$_2$-sea water" wet denitrification technology designed in this paper has the advantages of convenient access to raw materials, good economy, good denitrification performance, and obvious denitrification time, but there are still problems to be further discussed in the practical application process. This study only discusses the denitrification of waste gas, while further research is needed for the desulfurization of waste gas. The solution treated in this study contains Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and other ions, easy to cause secondary pollution, so it is necessary to further study the treatment of waste liquid.

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