Research on Desulfurization and Denitrification Technologies of Ship Exhaust

Peng Chen
College of Marine Engineering, Jiangsu Maritime Institute, Nanjing Jiangsu 211170, China

Abstract. Ship exhaust is one of the main sources of air pollution, at present; there are three methods for treating ship exhaust, including desulfurization, denitrification, and desulfurization-denitrification integration. This paper introduces the mainstream desulfurization and denitrification technologies, and the desulfurization-denitrification integration technology can achieve the simultaneous removal of multiple pollutants, which will become the main method of ship exhaust treatment in the future and has broad development prospects. This paper introduces some treatment methods and advantages and disadvantages of ship exhaust, and hopes to provide some references for the treatment of ship exhaust.

Keywords: ship exhaust; desulfurization; denitrification.

1. Introduction
Modern socio-economic development is rapid, and trade links among countries are becoming closer and closer, the advantages of convenient and efficient maritime transportation make it become the main mode of international transportation. Compared with motor vehicle exhaust, marine fuel is mainly diesel and heavy oil, higher concentrations NO\textsubscript{X} and SO\textsubscript{X} are contained in in the ship exhaust, which are transferred, transformed, and deposited through atmospheric and water cycles, as a result, ocean acidification and the degradation of terrestrial ecosystems have severely affected global climate change.

2. Ship Exhaust Pollutant
The composition of ship exhaust pollutants is complex, including NO\textsubscript{X}, SO\textsubscript{X}, CO, CO\textsubscript{2}, HC, and PM, among them, NO\textsubscript{X} and SO\textsubscript{X} are the main pollutants, and International Maritime Organization lists them as the primary ship exhaust pollutants need to be controlled. SO\textsubscript{2} is completely converted from the sulfur in the fuel, so the SO\textsubscript{2} in the exhaust is only related to the sulfur content of the fuel, and has nothing to do with the engine power and type; it has severely harmful effects on human health and also damages the ecological environment. NO\textsubscript{X} mainly comes from the oxidation of nitrogen in the air, which is further promoted by combustion and high-pressure environments. NO\textsubscript{X} has a toxic effect on the human respiratory system and also affects the contents of troposphere O\textsubscript{3} and OH free radical. Therefore, the control of ship exhaust pollution must first remove SO\textsubscript{2} and NO from the exhaust.
3. Desulfurization Technologies of Ship Exhaust

The control technology of SO$_2$ can be basically divided into three categories: desulfurization before combustion, desulfurization during combustion, and flue gas desulfurization after combustion, at present, the most effective method for controlling SO$_2$ is flue gas desulfurization. There are many flue gas desulfurization methods, the main desulfurization technologies are: limestone-gypsum desulfurization, circulating fluidized bed method, magnesium desulfurization, seawater desulfurization, and ammonia desulfurization. In addition, there are plasma method and double alkali method, etc., the principle of each method is shown in the Fig.1.

Fig.1 Principle of desulfurization technology of ship exhaust

Each method has its advantages and disadvantages. The equipment of seawater desulfurization and gypsum desulfurization occupies a large area, and the efficiency of seawater desulfurization is related to the salinity of the seawater, the gypsum desulfurization method has low desulfurization efficiency, pipelines are easily blocked, and the desulfurization equipment is easily corroded and worn. Magnesium sulfate, a by-product of the magnesium desulfurization process, needs to be pressed into a filter cake and stored on the ship, which requires a certain floor area and cannot be unloaded until the port. The ammonia desulfurization equipment covers small area, but the price of ammonia is high, and the cost of this method is high. Rotating spray dryer-flue gas desulfurization the advantages of wet desulfurization and dry desulfurization, it has fast reaction speed, high desulfurization efficiency, and no sewage and waste acid products.

3.1. Limestone-gypsum desulfurization

The limestone-gypsum method is a wet flue gas desulfurization technology, it uses limestone or quicklime as the absorbent absorb and separate SO$_2$ and convert it into a stable substance, gypsum. Its working principle is: the absorbent is made of water and limestone powder, and it is in full contact with
the flue gas in the absorption tower, \( \text{CaCO}_3 \) in the slurry reacts with \( \text{SO}_2 \) to form \( \text{CaSO}_4 \), which is oxidized by the added air to form \( \text{CaSO}_4 \cdot \text{H}_{2}\text{O} \), and finally dihydrate gypsum. Although this technology is quite mature, and has high desulfurization efficiency, reliable operation, and easy to obtain absorbent, the limestone-gypsum desulfurization requires a large amount of water, it is difficult to handle the absorbent, the production of by-products is large, a large amount of sulfur resources is wasted, and fresh water consumption is large. In the cold north, this method can easily lead to pipeline blockage, needs to consider the storage and handling of absorbents and by-products, the operation space on ships is limited, and the method is difficult to run.

3.2. Magnesium desulfurization

Compared with calcium desulfurization, the desulfurization principle of magnesium desulfurization is similar desulfurization tower, its principle is to use magnesium oxide as an absorbent, the saturated solution of magnesium hydroxide is made through the pulping system, and makes full contact with the flue gas in the desulfurization tower, after the magnesium sulfate is discharged, it can be processed by dehydration and other methods to achieve comprehensive utilization in the end. The system of the magnesium oxide desulfurization process has a smaller area than the limestone-gypsum desulfurization, the main investment of desulfurization equipment is low, the desulfurizer resource is abundant and the amount is small, and the required residence time is short. This process runs stably and reliably, is not easy to plug, and the final reaction product is easily soluble in water, related laws stipulate that \( \text{MgSO}_4 \) can be used as a pollution-free discharge in large water bodies or sea areas without requiring more complicated or difficult subsequent treatment. The application of calcium desulfurization and magnesium desulfurization should be adapted to local conditions, and selected based on the actual situation of raw material supply and by-product processing. In ship exhaust treatment, magnesium sulfate can be directly discharged into seawater as a harmless product, so magnesium desulfurization has a better application prospect.

3.3. Seawater desulfurization

The seawater desulfurization process is a method to use the alkalinity of natural seawater to remove sulfur dioxide from flue gas. Sea water is alkaline; usually its natural alkalinity is 1.2-2.5 mmol/L, its main components are chlorides, sulfates, soluble carbonates, etc., a large amount of \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) in seawater is main reason why seawater can absorb sulfur dioxide. Compared with other processes, seawater desulfurization has obvious advantages. Seawater is used as an absorbent to effectively save fresh water resources; the absorbed sulfur dioxide is converted into sulfate and can be directly discharged into the seawater without the problem of waste disposal; the desulfurization efficiency is high, which can reach more than 90%; it will not foul and block equipment; construction and operating costs are very low. Although seawater desulfurization has many advantages mentioned above, its equipment volume and floor area are relatively large, and it is limited to regional factors, so it is only suitable for coastal areas. However, the limited natural buffering capacity of seawater makes it only suitable for exhaust with low sulfur content, when the sulfur content is higher, the removal efficiency is lower.

4. Denitrification Technologies of Ship Exhaust

The main nitrogen oxide component of ship exhaust is NO, which is chemically stable and has a low solubility in water, so it is not applicable to remove NO by direct absorption. Traditional exhaust denitrification methods include selective catalytic reduction technology (SCR) and selective non-catalytic reduction technology (SNCR). At present, the SCR denitrification technology has been quite mature and is widely used in flue gas denitrification in land facilities such as thermal power plants, however, the problems of catalysts being easily deactivated, expensive catalysts, and storage and leakage of ammonia have limited the development of this technology, these problems must be solved in order to be better applied in ships.
4.1. Selective catalytic reduction (SCR) technology

The principle of selective catalytic reduction technology is: the organic matter contained in the exhaust gas is used as reducing agent or adding reducing agent, under the condition that the concentration of oxygen is higher than the concentration of nitrogen oxide (more than two orders of magnitude). The nitrogen oxides contained in the engine exhaust are preferentially reduced to nitrogen, therefore, the nitrogen oxides in the exhaust are removed very effectively, and the pollution to the environment is controlled.

The SCR technology is a practical technology with stable operation and high denitration efficiency, but it also has some problems. First, catalyst poisoning or blockage reduces the working efficiency of SCR. Because of the high sulfur content in diesel, a part of the SO$_2$ produced after combustion is oxidized to SO$_3$ and reacts with the original SO$_2$ and NH$_3$ in the flue gas to produce ammonium salts, which easily block the catalyst or poison it; second, there is a limit to the proportion of NO$_2$ in NO$_X$.

The reaction process needs NO$_2$ to participate, and the volume ratio of NO$_2$ to NO should be 1:1 according to the reaction mechanism. At present, a large number of research experiments show that the maximum conversion rate of nitrogen oxides reaches maximum when temperature higher than is 185°C and the volume ratio of nitrogen dioxide and nitrogen oxides is 0.5.

![Fig.2 Schematic diagram of SCR system](image)

4.2. Selective non-catalytic reduction (SNCR) technology

The principle of selective non-catalytic reduction technology for removing NO: in the absence of catalyst, the reducing agent is sprayed into the furnace cavity, and the temperature in the furnace cavity is about 850 to 1,100 °C, which is suitable for the occurrence of denitration reaction, the reducing agent is rapidly pyrolyzed in the high-temperature furnace cavity to form ammonia gas, which reduces nitrogen oxides in the flue gas to nitrogen and water vapor. The reducing agent can be ammonia, urea, etc., and the reducing agent only reacts with NOX in the flue gas, and O$_2$ does not participate in the reaction. The desulfurization efficiency of SNCR is generally 30% to 80%, because it uses the furnace cavity as a reactor, the efficiency is greatly affected by the boiler structure, the technical equipment is
large-scale, covers a small area, has no secondary pollution of by-products, and the system operates stably and reliably.

5. Desulfurization-denitration Integration Technology of Ship Exhaust

It can be seen from the above contents that the mainstream SCR method and the seawater washing method have some problems in removing NO\textsubscript{X} and SO\textsubscript{X} from the ship exhaust, respectively, desulfurization technology or denitration technology process or equipment is more complicated, separate desulfurization and denitration equipment for the desulfurization and denitration of ship exhaust gas will inevitably greatly increase the manufacturing cost of the equipment, and the stepwise desulfurization and denitration technology has problems such as complicated processes and high operating costs. Therefore, internationally, they are committed to the development of technologies that are simple in technology, low in operating costs, and more efficient in desulfurization and denitration. At present, desulfurization-denitration integration technologies of ship exhaust include oxidation absorption method, modified seawater method and low temperature plasma method.

5.1. Oxidative absorption method

The oxidative absorption method can treat component in the exhaust gas that are difficult to be removed by the absorbent, it is mainly NO. This method is to oxidize NO to NO\textsubscript{2} and then absorb it by absorbent. The oxidant can be hydrogen peroxide, chlorine dioxide, ozone, etc., the absorbents are mainly the alkaline solution and sulfite solution. Some people have studied using chlorine dioxide and hydrogen peroxide as oxidants, when using chlorine dioxide, the desulfurization rate and denitration rate can reach 90% and 80%, and the simultaneous removal of SO\textsubscript{2} and NO two pollutants has been achieved. The capacity of hydrogen peroxide is limited, after combining with ultraviolet for improving its oxidation performance, the desulfurization and denitration rate can reach 95%. Compared with the above two, O\textsubscript{3} is strongly oxidizing. Studies have shown that simultaneous desulfurization and denitration take O\textsubscript{3} as oxidant feasible, although the existence of sulfur dioxide reduces the ability to oxidize O\textsubscript{3}, the O\textsubscript{3} oxidation rate can still reach more than 90%. Researchers believe that the combination of ozone oxidation and wet washing is a relatively economical and effective method.

5.2. Modified seawater method

The seawater washing method is only applicable to the case where the SO\textsubscript{2} concentration in the flue gas is low, when the SO\textsubscript{2} concentration is high, the removal efficiency is significantly reduced, and the removal effect for the water-insoluble NO is very little, so more and more scholars are studying the modified seawater method to improve the removal efficiency. For example, the electrolytic method is used to modify seawater to generate sodium hydroxide solution to increase the pH value of seawater, which not only saves the amount of seawater, but also reduces the volume of the absorption tower. However, the electricity on the ship is limited, the electrolytic seawater consumes a large amount of electricity, and the operating cost is high. Some scholars have studied that the magnesium-seawater method can effectively improve the removal efficiency; magnesium hydroxide slurry is added to seawater to increase the alkalinity of natural seawater, this method not only improves the removal efficiency of gas pollutants, but also the slurry is not easy to block the nozzle. However, ship space is limited, and magnesium hydroxide is not a standing material in ports, which limits its widespread promotion.

It can be seen that the modified seawater method can effectively improve the removal rate of pollutants in comparison with the seawater method, but it still faces many problems and needs further study of scholars.

6. Conclusion

The problem of air pollution caused by ship exhaust has attracted increasing public attention; countries around the world have begun to take action to study more effective methods to reduce the pollution of ship exhaust to the environment. Source reduction is still the most ideal pollution control measure, but
finding cost-effective marine fuels is still difficult to achieve. At present, relatively mature treatment technologies can only remove a single pollutant and cannot achieve the simultaneous and efficient removal of multiple pollutants. Therefore, research on efficient, economical and environmentally friendly ship exhaust treatment technology will be the development direction of ship exhaust treatment.

Acknowledgments
Project on Natural Science Research of Jiangsu University in 2019 (Research on Desulfurization and Denitrification Technology of Ship Exhaust Gas Based on Plasma Coupling Method, No. 2019-151), Project of Science and Technology Innovation Fund of Jiangsu Maritime Vocational and Technical College in 2019 (Integrated Technology and Experimental Research on Desulfurization and Denitrification of Ship Exhaust Gas, No. 2019-01) In 2017, the outstanding backbone teachers of the "Blue Project" in Jiangsu Province and the training object of the "333 Project" in the fifth phase of Jiangsu Province in 2018 were funded.

References
[1] Wang Haifeng, Zhang Chunxia, Qi Yuanhong. Status of Research on Desulfurization by Ammonia Method[J]. Environmental Engineering, 2010, 28(6), 55-58, 62.
[2] Hao Jiankuan. Application of Sea-water Desulfurization Technology to Coastal Power Plant[J]. Northeast Electric Power Technology, 2007, 28(5), 11-13.
[3] Li Songmei, Dong Yaohua, Zhang Chenglei, Zhang Li, Dong Lihua. Development of Domestic and International Marine Exhaust Gas Treatment[J]. Mechanical Engineer, 2013, (5), 1-5.
[4] Guo Lugang, Wang Haizeng, Zhu Peiyi, Deng Peichang, Xing Kun. Application of Seawater FGD Process, Ocean Technology, 2006, 25(3), 10-14.
[5] Zhang Zhiyou, An Shijie, Wei Yukun. Analysis of EGR Research Status[J], Internal Combustion Engines, 2014, (4), 24-27,30.