Ship exhaust multi-pollutant control technology

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Abstract

With the continuous advancement of the"Sulfur Limitation"in 2020, it is extremely urgent to carry out the pollution control of ship exhaust. The pollutants emitted by the combustion of marine diesel engines are mainly sulfur dioxide, nitrogen oxides and particulate matter. The paper firstly lists the relatively mature pollutant control technologies on ships in recent years, summarizes the research progress of three pollutant control technologies in recent years, and analyzes the advantages and limitations of various control technologies. Then, for ships using high-sulfur oil, the ship pollutants coordinated control technology based on high-temperature particle removal is proposed. Finally, the system optimization of the collaborative control technology makes it characterized by high efficiency, stability and low energy consumption.

Keywords

Ship exhaust, Multi-pollutant control technology, High-sulfur oil.

1. Introduction

As the number of transport vessels increases continuously, the damages caused by pollutants emitted by ships to the atmosphere and water are becoming increasingly serious. The pollutants emitted by the combustion of marine diesel engines are mainly SO2, NOx and PM. Therefore, understanding the existing control technologies of three pollutants and the development status at home and abroad, and looking for a high-efficiency, stable and low-energy pollutant co-processing technology is the theme of the development of ship exhaust gas treatment.

2. Ship exhaust emission control technology

2.1 Particle Control Technology

The source and composition of PM are complex. The current research shows that the PM emitted by diesel engines mainly comes from three aspects [1] . The first is the insufficient combustion of fuel oil and lubricating oil and the accumulation of tiny particles produced by it. The size of particles is generally sub-micron; secondly, the fuel itself contains a certain amount of ash. After the oil is burned, the remaining ash is discharged to form PM, and its particle size is 200 nm to 10 microns; the third is secondary synthesis of gas pollutants generated by combustion, such as sulfuric acid/sulfate aerosols and nitric acid/nitrate aerosols, which are directly discharged as PM, and the particle size is generally on the order of micrometers. In terms of ship particle composition, 98% is PM10, 94% is PM2.5, and 92% is PM1. The third type of PM accounts for 78%-80% of the total PM; in terms of chemical composition, ship particles Contain a lot of black carbon, vanadium, nickel, sulfite, sulfate, etc [2]. Studies have shown that sulfur content in fuel has a significant impact on PM emissions. Currently, marine fuel oils are of poor quality and high sulfur content, so the amount of PM emitted by ships is significantly higher than vehicle emissions. The calculation shows that a large container ship using fuel oil with a sulfur content of 3.5%, the total amount of PM2.5 emitted by the ship is equivalent to one day's emissions of China's 500,000 National IV trucks [3].

Ship PM control technologies include Diesel Particulate Filter (DPF), Diesel Oxidation Catalyst (DOC), Continuous Regeneration Trap (CRT), cyclone particle removal, electrostatic precipitator, and wet scrubbing. Among the technologies that are suitable for high temperature sections and have a large competitive advantage are CRT, cyclone particle removal and electrostatic precipitator.

2.2 NOx control technology

The NOx in the gas emitted by marine diesel engines are mainly thermal NOx, which are formed by oxidation of nitrogen under high temperature conditions. In addition, the NOx produced by combustion account for more than 95% of the NO, the remaining major NO2 and a small amount of N2O [4]. At present, the relatively mature NOx control technologies on ships are SCR and EGR. Both technologies meet the emission standards of Tier III. However, EGR technology has made a big change to the overall structure of the ship. This paper only describes the development of SCR technology in detail.

2.3 SOx control technology

With the urgency of the“Sulfur Limitation”schedule in 2020, shipping companies are under tremendous pressure. Next, how to adopt the right investment and decision-making plan is a test for the entire shipping industry. There are currently three counter measures in the industry. The first way is to use low-sulfur fuel, which is the simplest response at the moment. The use of low-sulfur oils make less changes to the ship and only requires modifications to the relevant systems of the engine. However, because the price of low-sulfur oil is more than double that of heavy oil, the difference between low-sulfur oil and heavy oil exceeds $200/ton. If a ship consumes 100 tons of fuel per day, it will pay an additional 7.3 million dollars a year, and the cost increase will be more obvious, which will impose a heavy cost burden on shipping companies. In addition, the supply of low-sulfur fuels is difficult to meet market demand in the short term.

The second way is to use LNG as an alternative fuel. The use of LNG as a ship fuel can completely avoid sulfur emissions. However, the use of natural gas as fuel power will result in a large investment costs, expensive equipment and supporting systems and relatively large cost of modification, so LNG is generally used on newbuildings. In addition, the volume of the LNG fuel tank is much larger than that of the common fuel tank. Whether there is enough space to arrange a huge fuel tank is also a problem to be considered. Moreover, as a fuel for ocean-going ships, LNG also faces difficulties such as insufficient endurance. In addition, the filling facilities in port are not perfect at present [5].

The third way is the installation of a ship desulfurization unit. At present, the mainstream desulfurization system on ships is a wet desulfurization system, and the wet desulfurization system is divided into open, closed and mixed modes. The wet desulfurization device has high desulfurization efficiency and can meet the requirements of IMO regulations. However, the installation of the wet desulfurization system has a large modification to the ship, and the initial input cost is high.

3. Development status of ship pollutants control technology

3.1 High temperature particle removal technology

The high-temperature precipitator is arranged between the exhaust pipe and the SCR. Its long-term working temperature is up to 400 °C, it can withstand the corrosion of acid gases such as SO2 in the exhaust, and requires high particle removal efficiency. The method for removing the particles outside the machine, which suitable for the high-temperature section, can be summarized as the following three control technologies, namely, mechanical force particle removal method, electrostatic particle removal method, and filtration particle removal method.

3.1.1 Filtration method

The filtration method is a way in which exhaust gas is passed through a porous substance, and a gas flows to collect particulate contaminants to purify the exhaust gas, mainly including bag type particle removal method and DPF [6].

（1）Bag type particle removal method. The PM is captured on the surface of the filter material through the filtration effect of the fiber fabric and the filtration mechanism of screening, collision, diffusion, retention, static electricity, gravity sedimentation, etc. The main advantage of the bag type particle removal method is simple structure, convenient use and high efficiency; The main disadvantages are large floor space, large loss of filter material, and unsuitable for handling high temperature particulate gas.

（2）Diesel particulate trap (DPF). At present, it is generally believed that the DPF is the most effective and widely used diesel particulate emission technology. From the economic analysis, the DPF is the most advantageous among many PM emission reduction measures [7]. However, the DPF also have many disadvantages, such as Increased exhaust back pressure, correspondingly increased fuel consumption. Kazuki [8] proposed an asymmetric tunnel structure to reduce the back pressure of the diesel particulate trap, as shown in Fig. 1. Compared with the traditional square symmetrical structure SQ, the new octagonal asymmetric structure OS and VPL, have much lower back pressure, because the new pore structure can greatly increase the filtration area and improve the storage capacity of the particles.

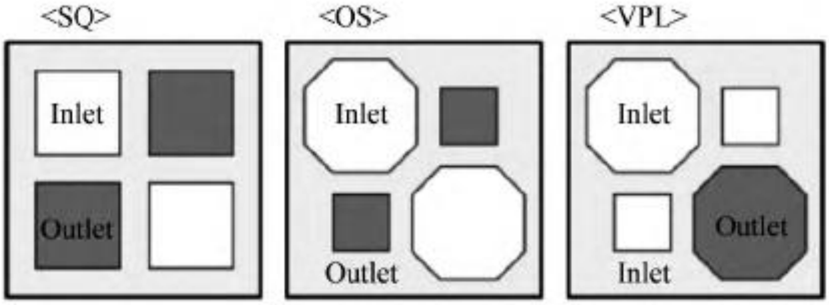

Fig. 1 The asymmetric channel structure of DPF

As the accumulation of the PM, the back pressure will become higher and higher, which will affect the performance of the diesel engine. Therefore, many researchers have studied the regeneration characteristics of the DPF. Kotrba [9] evaluated the influencing factors of passive regeneration of soot by oxidation of NO2. The study found that DPF coated with platinum group metal can significantly increase the rate of passive regeneration, but when the coating of platinum group metals reaches a certain level, the regeneration rate will no longer increase; the installation of DOC before the DPF without catalyst can improve the passive regeneration performance by about 5 times, but the effect is not obvious after the catalyst is continuously coated on the DPF; Improving the exhaust gas temperature from 300°C to 400°C can increase the soot burning rate by about 4 times in a steady state.

At present, the researchers are widely concerned about coating the SCR catalyst on the DPF, SCRF, as shown in Fig. 2. Blake-man [10] found that installing DOC before SCRF can be beneficial to the passive regeneration of soot and control the accumulation rate of soot. Kojima [11] compared the performance of SCR and SCRF under the same conditions. The results show that the NOx removal efficiency of SCRF is 10%~20% lower than that of SCR. In the experiment, a small SCR is added before SCRF. It can effectively improve the emission reduction performance at startup.

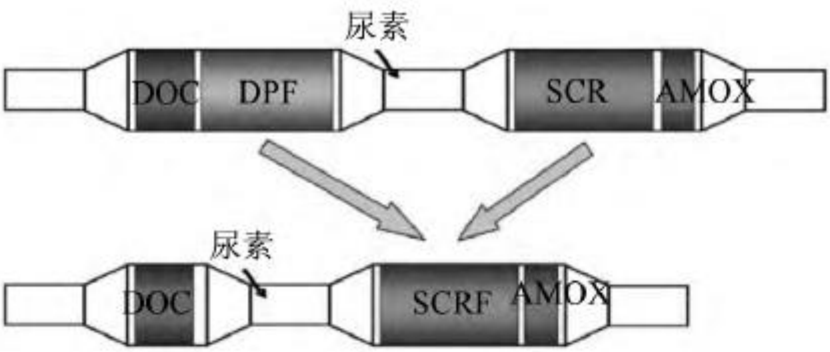

Fig. 2 SCRF device diagram

3.1.2 Mechanical particle removal method

The mechanical separation method is a way in which the exhaust gas is separated from the solid particles by gravity, inertial force or centrifugal force of the solid particles, and then the solid particles are captured and collected. Here we mainly introduce the inertial separation method and the centrifugal separation method.

The working principle of the inertial separation method is utilizing the inertial force of the solid particles in the airflow to separate the solid particles from the gas. When the airflow suddenly changes direction or hits the baffle and the steering is rapidly turned, the solid particles in the airflow will remain in the original motion due to the inertia, then particles deviate from gas route.

Among the centrifugal separation methods, the cyclone separator is the most efficient method. The cyclone separator separates the gas and the solid by centrifugal force generated by a high velocity gas containing particle. The structure of the cyclone separator is simple and there are no moving parts in it and the manufacturing and installation cost is low. However, the cyclone separator has a high pressure drop, and it is difficult to remove particles whose sizes are less than 10 microns in the gas. Especially for particle collection with a purity of less than 5 microns, the conventional cyclone particle collector is usually used as a pre-particling device (coarse separation), which is difficult to achieve final separation in accordance with ultra-low concentration requirements. Therefore, the development of new high-temperature and high-efficiency micro-particle cyclone particle collectors is particularly important. Liang Li, Xiang Zhang[12] designed the corresponding cyclone particle removal single tube and built a cold test platform according to the Leith design method. The results show that the cyclone particle removal single tube has a high particle removal efficiency for the particles size above 5 microns, and the 90% particle size of the entrained gas is less than 5.1 microns, and the particle removal efficiency of the 5 microns particles is as high as 98.52%. Bingtao Zhao [13] proposed a new integrated curved tube cyclone (ICTC) in order to improve particle separation performance. When the inlet velocity is 12 m / s, the efficiency of 180° ICTC particle removal is increased by 8.5%, and the particle removal efficiency of 360° ICTC is increased by 22.7%.

3.1.3 Electrostatic precipitator method

The electrostatic precipitator method is one of the methods for removing PM from marine diesel engines. The particle-containing gas is electrically separated when passing through a high-voltage electrostatic field, and after the negative combination of the particle particles and the negative ions, the surface of the anode is discharged and deposited. The electrostatic particle removal method has been widely used in the industry due to its technical advantages such as small pressure drop, stable operation and strong adaptability. How to achieve high-efficiency capture of particles under high temperature conditions and industrial application by electrostatic action is urgently needed. Zhijun Shen, Chenghang Zheng [14] designed and built a high-temperature electrostatic precipitator pilot plant in order to study the electrostatic trapping characteristics of particulate matter in high-flow flue gas flowing inside a wide-pitch electrostatic precipitator. It was found that the particle trapping efficiency rapidly decreased with an increase in temperature, which was related to an increase in the flow rate at a high temperature, a decrease in the discharge voltage, and an increase in the viscosity of the gas. Xi Xu, Dian Xu [15] established a high-temperature wire-plate electrostatic precipitator experimental system to study the law of corona discharge, particle migration and trapping of the exhaust gas in 400°C to 700°C. When the temperature rises from 400°C to 700°C, the maximum operating voltage drops from 21. 9 kV to 14.3 kV, and the particle capture efficiency drops from 98.1% to 68.2%.

In summary, among several particle removal technologies, cyclone separators have higher removal efficiency for large-particle soot, but the removal efficiency of soot below 1 micron is extremely unsatisfactory. The amount of PM, in which sizes in the exhaust gas is less than 1 micron, is as high as 95% or more, so the cyclone separator cannot meet the removal requirements and can only be used as a pretreatment device. The electrostatic precipitator method can remove 0.1 micron to 1 micron soot particles, but with the change of temperature, the removal efficiency changes greatly, and it needs to consume higher electric energy. The CRT can removes more than 95% of the PM and meets Tier IIII emission standards completely. It is also recyclable and can capture soot particles for long periods of time without downtime. After the implementation of the "Sulfur Limitation" after January 1, 2020, ships around the world will be forced to use low-sulfur fuel, and the effect of sulfur in the fuel on the DOC in the continuous regenerative trap will be minimized.

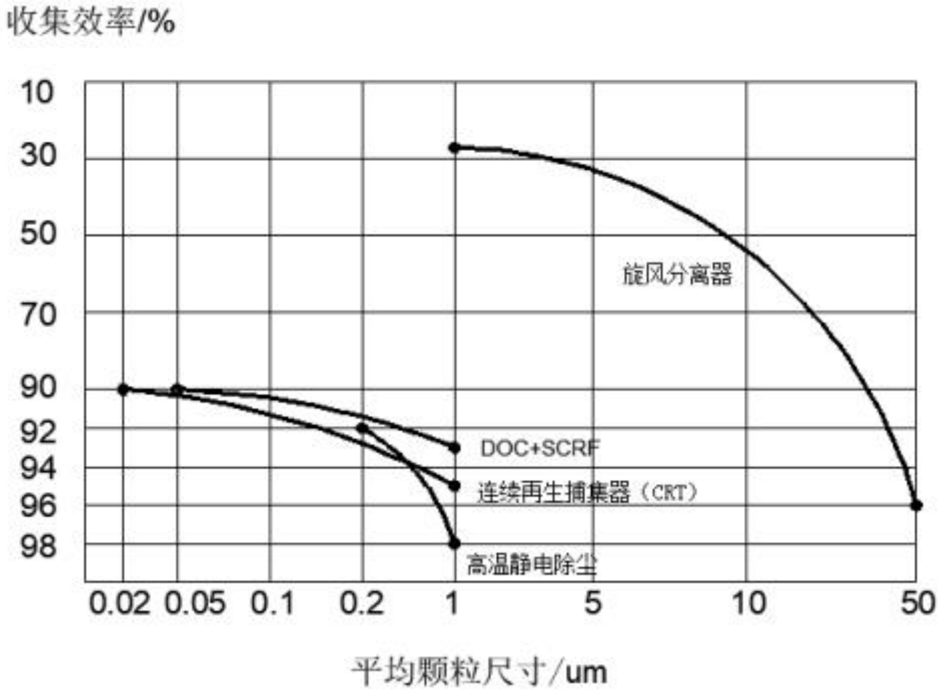

Fig. 3 Comparison of particle removal efficiency of high temperature particle removal technology

3.2 SCR denitration technology

SCR (Selective Catalytic Reduction) technology has the advantages of good economy, small modification to diesel engine, high NOx conversion rate, insensitivity to sulfur and wide application range. It is a technology with great application prospects for NOx emission control in the marine diesel engine [16]. According to the SCR reaction mechanism, the main factors affecting the SCR reaction are: the structure type of the catalyst, the reaction temperature, the space velocity, the ammonia excess coefficient and the mixing degree of the reducing agent. After the SCR structure design is completed, the structure type and space velocity of the catalyst have been determined. Under this circumstance, the optimization of the urea aqueous solution injection system, the optimization design of the mixer and the selection of the catalyst can effectively solve the operation problems of SCR in low temperature and improve conversion rates.

3.2.1 Optimization of urea aqueous solution injection system

In the urea aqueous solution injection system, the structure and diameter of the nozzle will directly determine the spray pattern and droplet size distribution, which in turn determines the denitrification performance of the SCR system [17]. Lidong Fu, Fengyang Yang [18] used the control variable method to analyze the influence of the number of nozzle holes, the length of the expansion section, and the distance of the nozzle from the first layer of catalyst on the SCR system. The test results show that when the diesel engine is in 75% load stable condition, exhaust temperature is 450, ammonia nitrogen ratio is 1.2, the optimal structural parameters are: nozzle hole number is 8 holes, expansion section length is 130 mm, nozzle distance from catalyst inlet The distance of the section is 6D (D is the diameter of the exhaust pipe). Lin Lu, Yue Chen [19] analyzed the internal flow of the nozzle and the development process of the spray by establishing a coupled model of the gas-liquid two-phase flow in the nozzle and the nozzle outlet flow field. The smaller the gas and hydraulic pressures, the slower the rate of droplet breakage and the larger the particle size within the same distance.

3.2.2 Optimization of the mixer

The criteria for measuring the performance of the mixer mainly include the mixing uniformity and the conversion efficiency of NOx. In addition, it is required to meet the requirements of small pressure loss, compact structure, high mechanical strength and avoidance of urea deposition. The mixer position is shown in Fig. 4. In general, the mixer and urea spray work together to optimize mixing. Yue Chen, Lin Lu[20]designed two different types of mixers and conducted experimental research. The results show that under the same catalyst volume and urea injection amount, the conversion efficiency of NOx increased by about 8% at the working point after installing the 8-bladed conical mixer, and the weighted specific emission of NOx decreased from 0.56g/(KW*h) to 0.37g/(KW*h). Yuanqing Zhu [21] showed that the combination of high pressure jet and static mixer can significantly improve the gas-liquid mixing uniformity of large Urea-SCR system, which is beneficial to the improvement of catalytic conversion efficiency.

Fig. 4 Schematic diagram of the SCR system

3.2.3 Selection of catalyst

Regarding the catalyst aspect of the SCR system, a carrier type catalyst mainly based on V2O5 is currently widely used. Gang Lu [22] prepared a V2O5 series screening catalyst by impregnation method, and investigated the catalytic performance of the above catalyst in the SCR reaction on a simulation evaluation device. The results show that the purification efficiency of NOx increases with the increase of reaction temperature, and there is a suitable reaction temperature window. As the reaction temperature increases, the ammonia leakage decreases gradually. Yan Gao [23] carried out simulation of catalyst denitration performance based on Lister Petter TR1 heavy-duty direct-injection single-cylinder diesel engine. Through simulation, it can be seen that the catalyst denitration activity decreases with the increase of load of diesel engine. Specifically, when the reaction temperature is 380C, space velocity is 20000/h, load is 25%, and ammonia-nitrogen ratio is 1.0, the denitration activity can achieve the maximum value at 1800r/min. The denitration activity up to 87.1%.

In summary, by increasing the mixing uniformity of NOx and NH3, the atomization capacity of the nozzle and the catalytic efficiency of the SCR catalyst, the denitration efficiency of the SCR can be improved to meet the increasingly stringent emission regulations.

3.3 Wet desulfurization technology

The wet scrubbing system includes open scrubbing system, closed scrubbing system, and mixing scrubbing system.

The schematic diagram of the open desulfurization system is shown in Fig. 5. The seawater enters the washing tower through the circulation pump, and acts as the detergent of the system, removes the SO2 in the exhaust gas, then enters the sewage treatment processor, finally it is discharged into the ocean after being treated. The seawater desulphurization technology is mature and reliable, and the process flow is simple. However, because it uses seawater as an absorbent and discharges it back to the ocean, it will inevitably have a certain impact on the environment of the ocean.

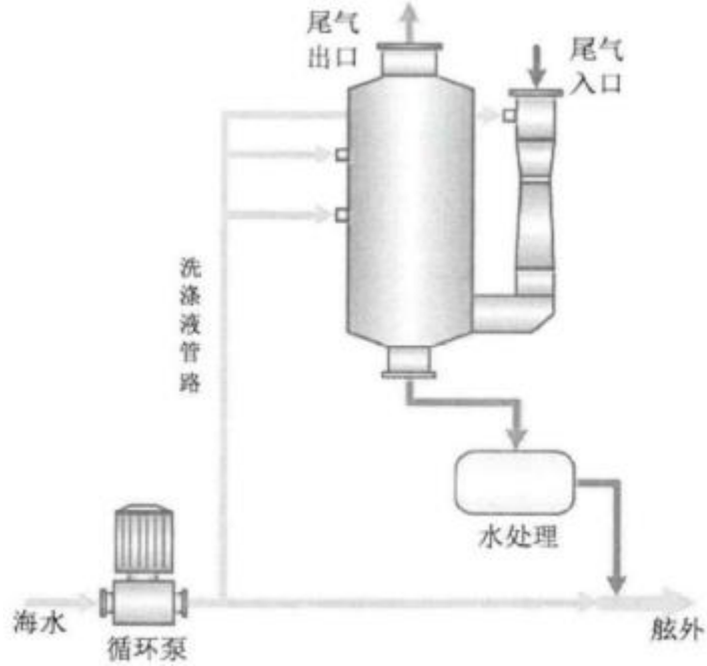

Fig. 5 open scrubbing system

Due to the limited solubility of seawater to SO2, it is necessary to continuously renew seawater using a circulating pump in order to ensure the efficiency of desulfurization[24]. In addition, the concentration of SO2 in the exhaust gas, the ratio of liquid to gas, gas flow rate, oxygen volume fraction, seawater alkalinity, water temperature, etc, all affect the desulfurization efficiency of seawater. However, most of the current research reports on small-scale data under the laboratory, and its data has certain limitations for engineering applications.

In order to provide more precise optimization parameters for the seawater desulfurization process, Fengju Lu, Xiaoqian Shen [25] studied the effects of various factors on the absorption of SO2 by spraying artificial seawater on the 1.08 million m3/h pilot platform. The results show that the main influencing factors of seawater desulfurization efficiency are liquid-gas ratio, alkalinity and temperature. When the optimum values are 16.51L/m3, 2.39 mmol/L and 293.15 K, respectively, the desulfurization efficiency is 99.8%. G. Caiazzo[26] built a ship's exhaust gas seawater washing rig and simulated the exhaust gas produced by burning heavy oil. The results show that the seawater is alkaline and the washing effect is better than that of fresh water. Increasing the washing liquid flow rate and exhaust gas retention time can increase the removal efficiency, up to 93%.

The closed system technical solution mainly includes the sodium alkali method and the magnesium method. The closed system uses the alkaline substance carried by itself as a detergent, absorbs the SO2 in the exhaust gas, both react to form sulfate, and the waste liquid generated after washing is processed and detected. After passing the test, it can be discharged into the ocean. The closed exhaust gas scrubbing system will not cause any adverse impact on the marine environment. Fig. 6 is a schematic diagram of the closed washing system.

The wet magnesium method desulfurization mostly adopts the countercurrent gas-liquid two-phase flow reaction mode, so the desulfurization efficiency is high, and the desulfurization efficiency can be as high as 98% or more, the technology is mature, and the operation reliability is high. The initial investment cost is low, the overall process system is simple, the equipment and structure specifications are small, and the corresponding power of each electrical equipment is small. Due to the shortage of fresh water resources on board, Xiaojia Tang [27] used seawater as a solvent for Mg(OH)2 to compare the desulfurization efficiency of seawater method, magnesium method and magnesium-based seawater method. The results show that the desulfurization efficiency of magnesium method and magnesium-based seawater method are almost the same, staying above 98.8%. It is indicated that the main role of desulfurization is Mg(OH)2, but the magnesium-based seawater method can effectively solve the problem of shortage of fresh water.

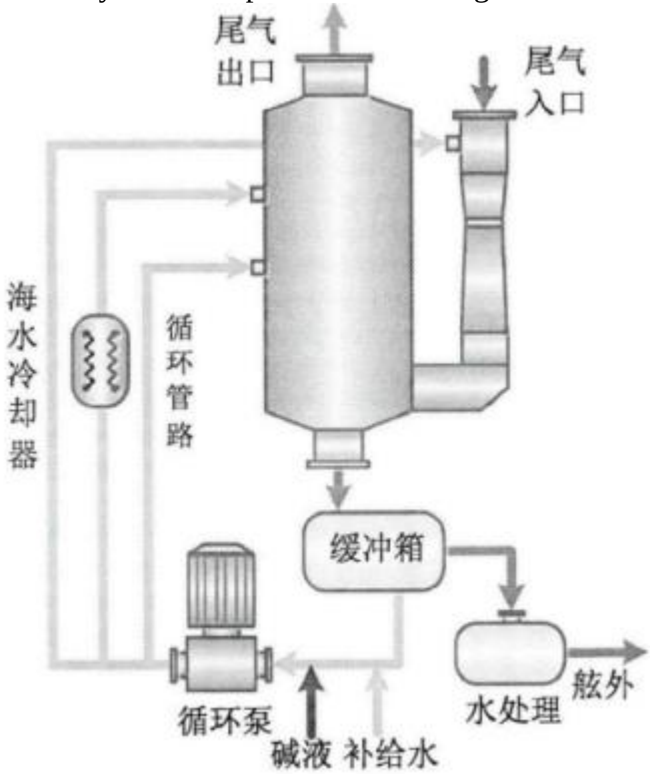

Fig. 6 the closed scrubbing system.

The biggest advantage of the wet sodium-alkali desulfurization technology is that its desulfurization effect is very good, and it is suitable for the exhaust gas generated after the combustion of heavy oil with a large sulfur content, and has wide applicability. Xue Liu [28] carried out a practical test of the washing tower according to the principle of equal gas volume by using the marine two-stroke MAN 5S50ME diesel engine. The washing effect of CO2, SO2, NOx and other components of exhaust gas was studied under full working conditions. The studies have shown that the desulfurization efficiency of the scrubbing system is higher, above 99%, and the desulfurization effect is better.

The mixing scrubbing system combines open scrubbing system with closed scrubbing system, using closed scrubbing in ports and areas where open loop washing is not available, and using open scrubbing systems in other areas to reduce alkaline consumption. Clean Marine Company has developed a hybrid scrubber desulfurization system. The system consists of two parts, seawater desulfurization and freshwater desulfurization, which can be switched to each other. Tests have shown that the system can reduce 98% of SO2 and 80% of PM, but fuel consumption is slightly increased.

In summary, the desulfurization efficiency of the open seawater system varies with the alkalinity of the seawater, and it is difficult to meet the emission standards. It is necessary to add a device for placing alkaline substances to cope with desulfurization of the exhaust gas in different waters. Not only increases the cost, but also increases the footprint of the open system. The closed desulfurization system has high desulfurization efficiency and stable operation, but the price of lye is relatively expensive. Now the main lye used on ships is NaOH and Mg(OH)2. Since the reserves of magnesium mine in China are extremely high, Mg(OH)2 solutions can reduce costs. At the same time, the use of seawater instead of fresh water as a solvent for lye does not have too much effect on the desulfurization effect, and can greatly reduce the amount of fresh water used in the ship. The hybrid desulfurization system has a high degree of flexibility, but At the same time, installing closed system and open system on the ship requires occupying a larger area and reducing the transportation volume of the ship. Only a small number of ships with special needs are available.

4. System optimization

The composition of exhaust pollutants is complex, such as PM, SOx, NOx, CO2, HC, CO, etc. Among them, PM, SOx and NOx are the main pollutants [29]. This paper summarizes the treatment technologies of three pollutants, and compares the removal efficiency and economy of various technologies to provide theoretical support for the next system optimization.

At present, there are three main methods for effectively controlling the emission of SOx from ships. The first one is to replace high-sulfur oil with low-sulfur oil. The second is to use LNG fuel. The last one is to retrofit the desulfurization equipment for existing ships. The biggest advantage of this method is the short cycle, low cost and high security [30].

Therefore, for ships using high-sulfur oil, this paper designs a system for synergistic removal of PM, NOx and SOx from ship's exhaust gas. The basic idea is shown in Fig. 7.

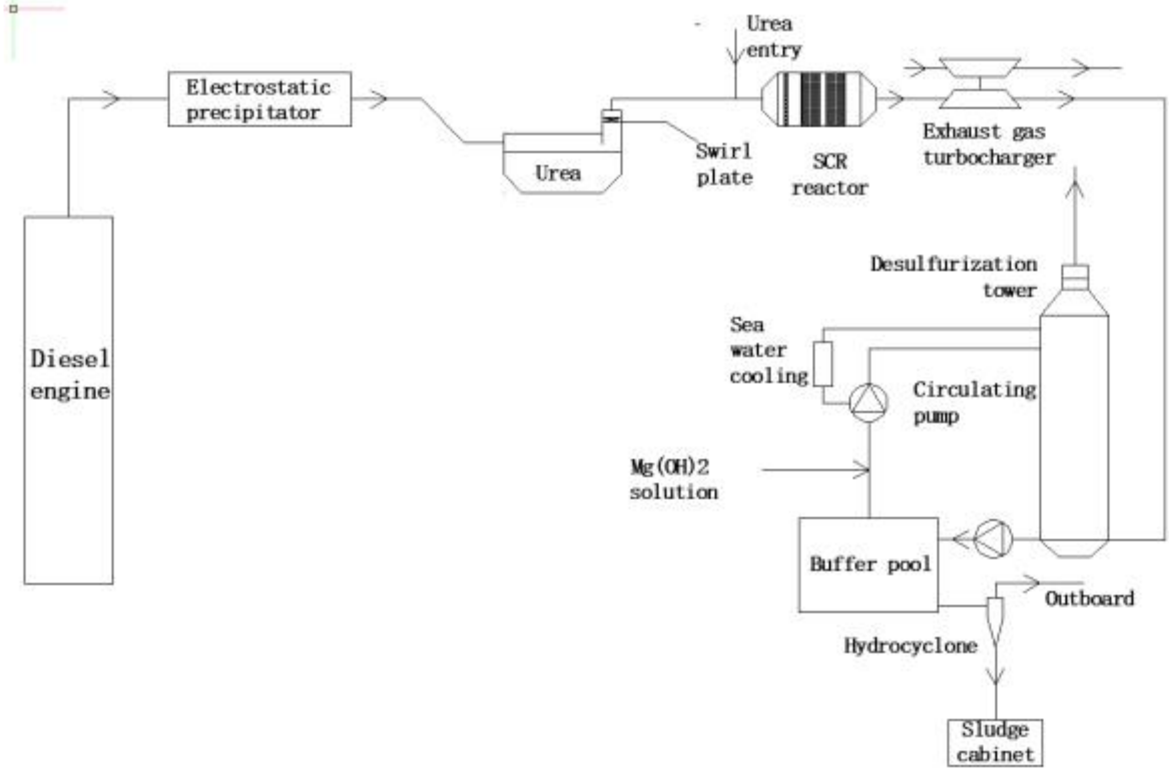

Fig. 7 High sulfur exhaust gas treatment system

In this scheme, a high-temperature electrostatic precipitator, a particle collection box, an SCR denitration catalytic reactor, and a closed desulfurization system using Mg(OH)2 as a desulfurizing agent are respectively arranged along the exhaust gas flow. The pollution control process is described as follows:

(1) After the exhaust gas passes through the high-temperature electrostatic precipitator, the PM particles are nearly completely captured, but the size of PM(0.2<dp<1) are difficult to capture (the particle removal rate of 0.2 to 1 micron is 90%, and the above 1 micron is 98%) [31]. This part of the particles will increase the wear of the SCR catalyst, inactivation of poisoning and the like. Therefore, a particle collection box has been added later to capture the particles of PM(0.2<dp<1) and reduce the concentration of heavy metals in the exhaust gas.

(2) The urea solution is contained in the particle collection box, and the exhaust gas enters the inner cavity of the cylinder and contacts the surface of the liquid to evaporate the liquid to generate droplets. At this time, some of the PM in the exhaust gas collides with the liquid surface due to the exhaust gas beats the liquid surface, and then PM is absorbed by the liquid; another part of the PM adsorbs on the evaporating liquid droplets to form a mixed particle, which causes the mass of the PM to increase, the speed decreases, and finally settles in the particulate collection box.[32]. The main function of the

particle collection box is to use the droplet adsorption method to adsorb large particles in the exhaust gas to form large particles, so that the particles with smaller particle size are separated from the exhaust gas. At the same time, the exhaust gas and NH3 are thoroughly mixed in advance to increase the denitration rate of the SCR reactor. Add a swirl plate at the exit to reduce the water vapor in the exhaust. Fig. 8 is a schematic view of a particle collection box.

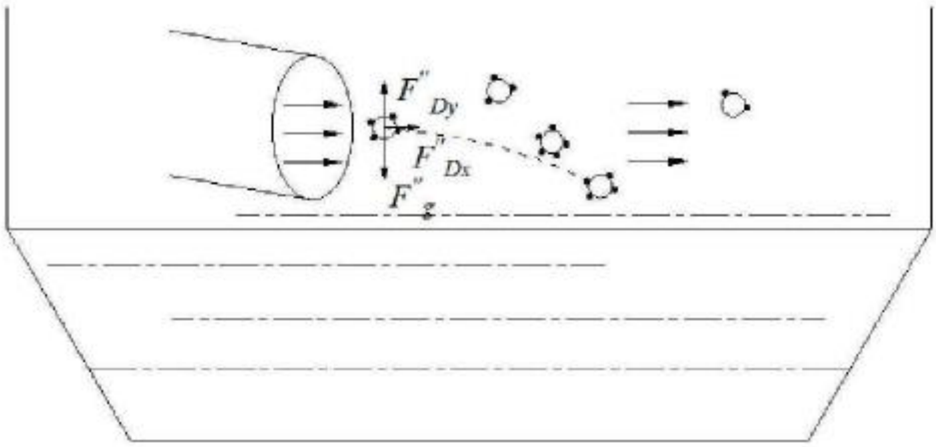

Fig. 8 particle collection box

(3) The exhaust gas enters the SCR reactor, removes about 90% of the NOx in the exhaust gas, and finally enters the closed desulfurization tower.

(4) Mg(OH)2 is added to seawater to prepare a magnesium-sea aqueous solution to reduce the fresh water consumption of the ship. The lye reacts with the SOx in the exhaust gas to achieve a desulfurization rate of 98%, and at the same time, removes heavy metals remaining in the exhaust gas.

5. Conclusion

In view of the increasingly prominent ship air pollution and the upcoming “sulphur limitation”, finding a technology that can synergistically remove a variety of pollutants is the only way for future ship exhaust emission control. In this paper, according to the sulphur content of fuel oil, one route for removing exhaust pollutants is designed to cope with the sulfur limitation issued by IMO. The exhaust gas treatment systems can remove pollutants in the exhaust gas efficiently and stably, so that the exhaust gas emissions reach the standard.

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