Design and experimental study on desulphurization process of ship exhaust

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Abstract. This desulfurization process involves removing sulfur oxides with seawater or alkaline aqueous solutions and then treating the effluent by aeration and pH adjustment before discharging it into the ocean. In the desulfurization system, the spray tower is the key equipment and the venturi tubes are the pretreatment device. The two stages of plates are designed to fully absorb sulfur oxides in exhaust gases. The spiral nozzles atomize and evenly spray the desulfurizers into the tower. This study experimentally investigated the effectiveness of this desulfurization process and the factors influencing it under laboratory conditions, with a diesel engine exhaust used to represent ship exhaust. The experimental results show that this process can effectively absorb the SO$_2$ in the exhaust. When the exhaust flow rate was 25 m$^3$/h and the desulfurizer flow rate was 4 L/min, the sulfur removal efficiency (SRE) reached 99.7%. The flow rate, alkalinity, and temperature of seawater were found to have significant effects on the SRE. Adjusting seawater flow rate (SWR) and alkalinity within certain ranges can substantially improve the SRE.

1. Introduction
Diesel engines that power ships mainly use heavy fuel oils with high sulfur content (> 1.5%). Large ocean-going vessels usually use low-grade oils that contain up to 2.7% sulfur[1]. Therefore, exhaust gases from marine diesel engines contain very high levels of sulfides. The pollutants in ship exhausts currently account for about 10% of the world's total pollutant emissions[2]. According to figures from a Norwegian statistical agency, the annual sulfur emissions from marine diesel engines amount to over 6 million tons, 4% of the global total[3]. To reduce the sulfur emissions from ship exhausts to levels below international or local limits, Marine Environment Protection Committee and International Maritime Organization (IMO) require ships to take the following three measures: using low-sulfur fuel oils or liquefied natural gas, or installing and using exhaust desulfurization systems approved by classification societies[4]. As using low-sulfur fuel oils or liquefied natural gas is still technologically and economically difficult, exhaust desulfurization systems applicable to ships are widely adopted. At present, famous foreign companies like Wärtsilä, Alfa Laval Aalborg, and Clean Marine provide a desulfurization process that sprays circulating seawater or alkali solutions to scrub exhaust gases and desulfurization equipment such as primary scrubbers and spray towers. This process is efficient, cost-effective and highly practical. China is still in the initial stage of researching technologies for cleaning ship exhausts. Previous research and experiments were mostly based on the principles of the conventional land-based flue-gas desulfurization, but failed to make any breakthrough. The authors developed an exhaust desulfurization process and relevant equipment applicable to ships, in order to achieve localization of ship exhaust desulfurization technologies.
2. Design and equipment development of ship exhaust desulphurization technology

2.1. Design of seawater desulfurization technology

Figure 1 shows the flow diagram of the desulfurization process using seawater. The detailed operations are as follows: First, the diesel engine exhaust passes through an exhaust boiler for waste heat recovery and is then impelled by a blower into the desulfurization tower. The exhaust goes through cooling and primary scrubbing by the venturi scrubber in the desulfurization tower in order to remove part of the SO\textsubscript{2} and particles in the exhaust. After that, the exhaust enters the main part of the desulfurization tower and flows countercurrently with respect to the atomized seawater (or alkaline desulfurizers such as NaOH solutions) in contact with it. The contact time between the exhaust and seawater is increased in order to ensure complete mass transfer between them. Next, the purified exhaust passes through filters to remove fine droplets and is then discharged from the tower top as long as its sulfur content meets the standard. After the scrubbing, the waste seawater is aerated in an aeration device in order to oxidize the sulfites in it to sulfates (the used alkaline desulfurizers can be recycled after separation treatment in a scrubbing liquid treatment tank). The aerated seawater is then pumped into a hydrocyclone for solid-liquid separation. After the separation is completed, the particles removed from the seawater are sent into a sludge tank and the remaining seawater is mixed with unused seawater in pipeline to adjust its pH. After the pH reaches an acceptable level, it can be discharged into the sea. During actual ship assembly, this desulfurization system is equipped with an automatic control system. It consists of sensors for monitoring exhaust temperature, SO\textsubscript{2} concentration, and seawater’s pH, temperature and COD as well as a computer control system for receiving feedbacks from the sensors and implementing adjustments. The main chemical reactions involved in the desulfurization system are as follows:

\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HSO}_3^- \quad (1) \]
\[ \text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (2) \]
\[ \text{HSO}_3^- + \text{HCO}_3^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{CO}_2 \quad (3) \]
\[ \text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-} \]  \hspace{1cm} (4)

2.2. Development of seawater desulfurization equipment

The \( \text{SO}_2 \) absorption subsystem is the very core of the whole desulfurization system. Its condition directly determines the whole system’s effectiveness in desulfurization. The main part of the \( \text{SO}_2 \) absorption subsystem is the desulfurization tower, whose structure has a critical influence on SRE. Spray tower is the most common tower type used in industrial flue-gas desulfurization. Based on a comprehensive evaluation, a spray tower was designed for the desulfurization system proposed in this study[5]. Its basic structure is shown in Figure 2. This spray tower consists of two parts: a venturi primary scrubber and a cylindrical main tower, which is divided into a primary desulfurization zone and a secondary desulfurization zone. The venturi primary scrubber is made up of venturi tubes and spray nozzles. The main tower has two plates inside it and nozzles above the plates. The diesel engine exhaust first enters the venturi primary scrubber connected to the main tower for cooling, humidification and primary desulfurization. After that, it flows along an elbow into the bottom of the main tower and then moves up to the desulfurization zones. The seawater is atomized by spiral nozzles and reacts with the exhaust from the bottom to remove the \( \text{SO}_2 \) in it.

3. Experimental study on seawater desulfurization of exhaust gas

3.1. Determination of seawater desulfurization parameters

3.1.1. Seawater configuration and experimental conditions. As it is difficult to gather natural seawater, artificial seawater was prepared using Mocledon’s formulation and used as an alternative to natural seawater[6,7]. Desalination tests were carried out at room temperature (30°C) and atmospheric pressure (101kPa).

3.1.2. Flue gas flow and \( \text{SO}_2 \) concentration setting. It has been found that the \( \text{SO}_2 \) concentration in diesel engine exhaust tends to remain unchanged as long as the fuel oils used are similar. In the experiment, the exhaust flow rate at the inlet was 32 m\(^3\)·h\(^{-1}\) and the \( \text{SO}_2 \) concentration was 2200 mg·m\(^{-3}\)
3 (approximately 840 ppm when the inlet exhaust temperature was 30 °C; the corresponding fuel sulfur content was 2.42% m/m).

3.2. Test equipment for desulphurization of seawater

Figure 3. shows the desulfurization test setup used in the experiment. It consisted mainly of an exhaust supply system, desulfurization equipment, detection devices, and seawater supply system. The exhaust supply system, composed primarily of a R180 diesel engine produced by Changchai Co., Ltd., a draft fan, and delivery pipes, served to provide inlet gas to the desulfurization equipment. A spray tower was used as the desulfurization tower, the key part of the whole setup. It was divided into two parts: a venturi primary scrubber and a main tower. The detection devices included rotor flow meters, thermometers, pH meters, a salinometer, a gas analyzer, etc. The seawater supply system is composed of seawater, pump and conveying pipeline, which provides desulfurizer for the whole desulfurization unit.

![Figure 3. seawater desulfurization test device.](image)

3.3. Test method for desulfurization of seawater

The experimental exhaust gas generated by the R180 diesel engine was piped into the spray tower from its bottom. The experimental seawater was conveyed by the seawater supply system to the top of the spray tower and the sprayed down. The seawater absorbed SO₂ in the exhaust by reacting with it. During the experiment, sulfur content, and SFR and alkalinity were variables. The diesel’s sulfur content was changed by adding dimethyl sulfide. The SWR was adjusted using the valves in the seawater supply system. The seawater alkalinity was altered by adding NaOH. These quantities were changed to examine their influences on the effectiveness of the proposed process.

3.4. Test analysis for desulfurization of seawater

(1) Effects of Venturi initial washing device, Primary Desulfurization Zone, Secondary Desulfurization Zone and Mixed Desulfurization on Desulfurization Efficiency

Figure 4 illustrates the relationship between SRE and SWR spray obtained when the primary scrubber, primary desulfurization zone, and secondary desulfurization zone worked independently and when they worked together. The initial SO₂ concentration at the inlet was 1410 mg·m⁻³ (approximately 538 ppm when the inlet exhaust temperature was 30 °C; the corresponding fuel sulfur content was 1.55% m/m) and the exhaust flow rate was 32 m³·h⁻¹.

It can be seen from figure 4, for a given SWR, the desulfurization system exhibited the highest SRE in the mixed mode, followed by the SRE of the secondary desulfurization zone. The SRE values of the primary desulfurization zone and primary scrubber were similar. In the mixed mode, when the SWR was 4L·min⁻¹, the SRE peaked at 99.7% and the SO₂ concentration at the outlet was 4.23 mg·m⁻³,
which corresponds to a fuel sulfur content of 0.047%. This concentration is far below the emission limit: 0.047% fuel sulfur content[8]. The primary scrubber removed around 52% of the SO$_2$ in the exhaust when the SWR was 4L·min$^{-1}$. It was more effective than the primary desulfurization zone at certain SWRs, possibly because when the SWR was high enough, the stronger turbulence in the scrubbing zone promoted more sufficient contact between the exhaust and seawater and thereby improved the SWR. This suggests that the primary scrubber can not only remove dust and other particles, but also can absorb large quantities of SO$_2$ and thus reduce the main tower size. Figure 4 reveals that the seawater allocation among the nozzles in the primary scrubbing, primary desulfurization, and secondary desulfurization zones affected SRE. The optimal flow rate for each nozzle was determined through multiple experimental runs. As shown in Table 1.

![Figure 4](image1.png)

**Figure 4.** Concentration and desulfurization efficiency changing of different work ways along with flow changes.

| The initial wash zone flow / L·min$^{-1}$ | Secondary desulfurization zone flow / L·min$^{-1}$ | Total flow / L·min$^{-1}$ |
|-----------------------------------------|-------------------------------------------------|--------------------------|
| 0                                       | 1                                               | 1                        |
| 1                                       | 1                                               | 2                        |
| 1                                       | 2                                               | 3                        |
| 2                                       | 2                                               | 4                        |
| 2                                       | 3                                               | 5                        |

**Table 1.** The nozzle flow distribution

![Figure 5](image2.png)

**Figure 5.** Desulfurization efficiency changing of different pH along with flow changes.

![Figure 6](image3.png)

**Figure 6.** Effect of SO$_2$ concentration on desulfurization efficiency
(2) Seawater alkalinity or pH

Figure 5 illustrates how SRE varied with seawater pH when the initial SO₂ concentration was 1590 mg·m⁻³ (about 607 ppm when the inlet exhaust temperature was 30 °C; the corresponding fuel sulfur content was 1.75% m/m) and the exhaust flow rate was 32 m³·h⁻¹. As shown in this figure, the SRE increased with increasing seawater pH when other conditions did not change and high pH values can ensure relatively high SRE for a wide range of liquid-gas ratio. The influence of pH on SRE was significant when the SFR was low and tended to decrease with increasing SFR. Therefore, for a large liquid-gas ratio, increasing the amount of seawater can promote SO₂ absorption and reduce the influence of PH influence on SRE.

(3) Influence of ship’s tail gas properties on desulfurization efficiency

The relationship between SO₂ concentration in the inlet exhaust and SRE was derived for a seawater flow rate of 4 L·min⁻¹ (the secondary desulfurization zone: 2 L·min⁻¹; and the primary scrubbing zone: 2 L·min⁻¹) and an exhaust flow rate of 32 m³·h⁻¹ under certain external conditions. As shown in Figure 6.

The results show that the SO₂ in the exhaust can be fully absorbed by the seawater and the SRE did not vary when the SO₂ concentration in the inlet exhaust was low and the SFR was high enough. As the SO₂ concentration further increased, the SRE declined markedly, even though the resulting increase in the partial pressure of SO₂ promoted its physical absorption by the seawater. This is because SO₂ is removed primarily by neutralization with HCO₃⁻ and CO₃²⁻ in the seawater, and thus the seawater with limited amount of HCO₃⁻ and CO₃²⁻ cannot absorb excess SO₂.

4. Conclusions

(1) In this desulfurization process, seawater or alkaline aqueous solutions are used as desulfurizers and sulfur oxides are removed in a spray tower that consists of a venturi primary a main tower with two desulfurization zones and spray nozzles. This design significantly improves the SRE for exhausts. According to the experimental results, the SRE was as high as 99.7% when the exhaust and seawater flow rates were 25 m³/h and 4 L·min⁻¹, respectively.

(2) The study suggests that the flow rate and alkalinity (pH) of seawater were the major factors influencing sulfur removal efficiency and adjusting them within certain ranges can substantially improve sulfur removal efficiency.

References

[1] Anders A and Stefan M 2007 Use of seawater scrubbing for SO₂ removal from marine engine exhaust gas J. Energy & Fuels 21(6) 3274-79
[2] Yao Lingyu, Zhang Li and Dong Lihua 2012 Investigation on Technology of Desulfurization Performance From Ship Emissions J. Science & Technology Information 11 196-97+192
[3] Eyring V, Köhler H W, Aardenne J V and Lauer A 2005 Emissions from International Shipping: 1. The last 50 Years J. Journal of Geophysical Research Atmospheres 110(2005) D17305
[4] Sun Huadong 2012 Emission control of sulfur oxides in ships J. World Shipping 8 51-54
[5] Gai Guosheng 2012 Numerical Simulation and Experiment Research about Seawater Desulphurization of Ship D. Harbin Engineering University
[6] Lu Yanhai, Xie Peixuan and Xin Liang 2008 Artificial Seawater Preparation Agents: Seawater Crystals J. Chines Journal of Chemical Education 29(4) 1-2
[7] Xu Yiru 2013 Research of An Artificial Seawater Preparation Device D. Wuhan Institute of Technology
[8] China MSA 2011 s. MARPOL 73/78 annex VI 2008/2011 amendment