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Applying the Scrubber for Leaked NH3 and Derivation of Optimal Wash Water Management Measure

Basic research & advanced engineering - new concepts

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ABSTRACT

In the shipping industry, ammonia is a promising eco-friendly fuel that can conform to GHG regulations. Several studies have been conducted using ammonia for the propulsion and development of ships. Korean Register has been developing engines and related equipment that use ammonia with marine equipment manufacturers and has been operating an ammonia engine test bed. The pure fuel in piping generated during experiments can be treated with relative ease by recovering the fuel through a high-pressure nitrogen purge or using water seal treatment. However, in the case of ammonia leaking from an engine or double pipes inside a laboratory, a high flow rate at a relatively low concentration must be rapidly treated. It is expected that this treatment method can be applied to the operation of ammonia-related equipment in ships in the future, and a system was designed considering its application to ships. Thus, we developed and operated an absorption system that treats ammonia mixed in the atmosphere using the scrubber method. The system sprays cleaning water into the scrubber tower filled with packing and blows the atmosphere mixed with ammonia using forced draft fan to absorb ammonia using the water. Ammonia is highly water-soluble; however, the amount that can be dissolved in water is limited. In addition, scrubbing with ammonia water in which high-concentration ammonia is dissolved may cause low efficiency. Therefore, it is important to monitor and manage ammonia water to minimize ammonia leakage to the atmosphere. This study proposes an effective measurement method and presents optimal scrubber water supply conditions by comparing and analyzing two representative ammonia solution measurement methods, i.e., pH and electrical conductivity.

Mixed air with a constant ammonia concentration and cleaning water with a constant flow rate were supplied to the scrubber. The change in ammonia gas concentration behind the scrubber was observed while changing the pH of the supplied cleaning water.

A gas analyzer was installed in front of and behind the scrubber to measure the ammonia concentration in the supplied gas and the discharged ammonia concentration. To monitor the pH of the cleaning water supplied to the scrubber, the ammonia concentration of the solution was measured by installing water monitoring system and electro-conductive sensors.

The experiment results showed that the concentration of unionized ammonia gas increased behind the scrubber as the pH of the cleaning water increased. This indicated that cleaning water must be maintained at the optimal pH to meet the ammonia concentration behind the scrubber, which can be regulated in the future.

1 INTRODUCTION

Greenhouse gas (GHG) emissions from total shipping increased from 977 million tonnes in 2012 to 1,076 million tonnes in 2018, representing a 9.6% increase. This rise is primarily attributed to the continuous growth of global maritime trade. The share of shipping emissions in global anthropogenic GHG emissions also increased slightly, from 2.76% in 2012 to 2.89% in 2018. Without additional measures, shipping emissions are projected to rise further, reaching 90–130% of 2008 levels by 2050.[1]

At the 80th session of the Marine Environment Protection Committee (MEPC) in July 2023, the International Maritime Organization (IMO) adopted a significantly enhanced GHG reduction strategy. This strategy aims to achieve net-zero GHG emissions by 2050 and sets intermediate targets of at least a 20% reduction by 2030 and at least 70% by 2040, both compared to 2008 levels.[2]

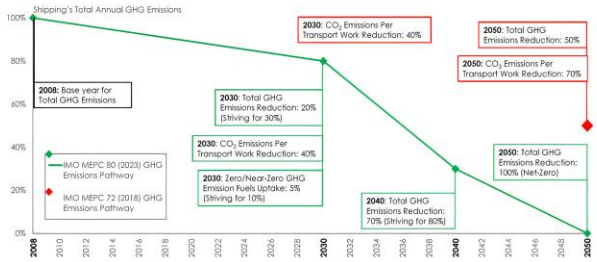

Figure 1. IMO's revised down shipping's GHG emissions reduction targets from 50% to 100% (Net-zero) by 2050

The International Maritime Organization (IMO) has implemented several regulations to reduce GHG emissions from ships. These include the Energy Efficiency Design Index (EEDI) and the Ship Energy Efficiency Management Plan (SEEMP), both introduced in 2013. Additionally, the Data Collection System (DCS) for monitoring fuel oil consumption has been in effect since 2019. The regulations for the Energy Efficiency Existing Ship (EEXI) and Carbon Intensity Indicator (CII) have been implemented since 2023. In addition, a development plan has been finalized to adopt measures combining technical and economic elements by 2025, with entry into force from 2027. [3]

In addition to global regulations, regional regulations are also being strengthened. The European Union (EU) announced the EU Fit for 55 package in 2021. The Fit for 55 package represents a series of legislative proposals aimed at achieving the revised mid-term emission reduction target of 55% by 2030, an increase from the previous target of 40%, compared to 1990 levels. Matters related to international shipping include the Emission Trading System (ETS) and the FuelEU Maritime.

FuelEU maritime gradually strengthens the GHG Intensity Limit for ships calling at EU ports by 2050, a regulation that aims to promote the transition to low-carbon and zero-carbon alternative fuel by tightening the regulation on the lifecycle emissions of fuels. [4]

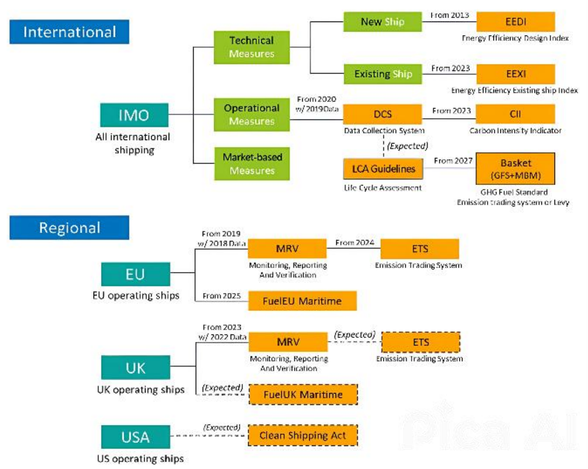

Figure 2. Major international and regional regulations to reduce GHG emissions from ships

The transition to low-carbon and zero-carbon alternative fuel is essential to meet IMO ship GHG regulations and regional regulations, including the EU. Among the various alternative fuels, ammonia is a zero-carbon fuel that does not emit carbon dioxide during combustion and can be used as a main fuel in engines. Therefore, many engine manufacturers are developing ammonia engines in preparation for orders for ammonia-fueled propulsion ships. Ammonia is the most efficient methods for hydrogen storage and transportation on a large scale because its hydrogen storage capacity per volume is greater than that of liquefied hydrogen, LOHC, and methanol, and it has the advantage that ammonia can be converted to hydrogen for use in fuel cells at the same time as it is transported.

Ammonia is a toxic substance and exposure to humans can cause skin irritation, breathing difficulties, eye irritation, and in severe cases, death from respiratory arrest. Ammonia is a toxic substance and exposure to humans can cause skin irritation, breathing difficulties, eye irritation, and in severe cases, death from respiratory arrest. In order to provide safety standards for ammonia-fueled ships, the IMO developed an interim safety guideline covering general and functional requirements for ammonia-fueled ships at CCC 10th, which was approved by MSC 109th. The guidelines limit the concentration of ammonia discharged from ammonia release mitigation systems to less than 110 ppm, with design requirements to prevent ammonia exceeding 220 ppm from reaching toxic spaces to non-toxic areas, etc. [5]

When ammonia fuel is applied to ships, a ventilation system to handle the ammonia and an ammonia release mitigation system are essential to ensure the safety of personnel on board. The ammonia reduction devices include a scrubber, gas absorption water tank, water mist system, and gas combustion unit. In gas combustion units, insufficient combustion of ammonia due to its low calorific value and low flame propagation velocity can result in the release of ammonia into the atmosphere [6], and the combustion of ammonia also produces nitrogen oxides. In addition, among the ammonia release mitigation systems that utilize the strong hydrophilicity of ammonia, scrubbers have low air resistance and can utilize the wide reaction surface of ammonia and water through spraying water, which is already widely used in other industries. [7]

Ammonia is absorbed through an ammonia scrubber as ammonium ions (NH_4) in an wash water(ammonia effluent), but there may be gaseous ammonia (NH_3) not absorbed by the wash water. When the dissolution limit of the wash water is exceeded, the ammonia can no longer be absorbed and is released into the atmosphere [8]. In order to prevent such ammonia release to the atmosphere, the management of wash water is essential. Therefore, This study analyzed the ammonia absorption efficiency according to changes in the wash water pH to determine whether the pH value of the wash water used in ammonia scrubbers can be applied as a factor for managing wash water.

2 METHOD

2.1 Test apparatus

The Green Ship Test & Certification Center of the Korean Register has been conducting research on the application of alternative fuels to ships in response to the International Maritime Organization's GHG regulations, and has recently established an ammonia fuel storage and supply system to conduct various research. Currently, TCC can supply both high-pressure liquid ammonia and low-pressure vapor ammonia through its ammonia fuel storage and supply system, and has built knockout drums and scrubbers to handle vent gas in ammonia piping. In addition, ammonia detection sensors were installed to detect ammonia leakage, and ventilation facilities and scrubbers were installed to measure ammonia leakage.

This study utilized the ammonia engine test facility established at TCC, and first simulated an ammonia leakage environment to examine the ammonia absorption efficiency according to the pH change of the wash water. The simulated conditions are based on a slight leak at the fitting/flange connection of a component inside the Fuel Preparation Room of an ammonia ship, which is a confined space where ammonia leaks can occur. The amount of ammonia leaked into the laboratory was constant using a Mass Flow Controller, and a forced draft fan in the ventilation system was utilized to flow the leaked ammonia into the scrubber. The scrubber is a close-loop type with a nozzle installed inside to spray the wash water through the nozzle, and the sprayed wash water is collected and recirculated in the wash water tank, and a packing is installed inside the scrubber to increase the contact area of the gas and liquid

The pH meter of the Water Monitoring System was used to monitor the pH of the wash water used in the ammonia scrubber in real time, and the ammonia detection sensor was used to monitor the ammonia that is not absorbed and discharged from scrubber's outlet in real time. The ammonia detection sensor is measured through the electrochemical measurement principle, and calibration tests have been performed by an accredited calibration organization to ensure the reliability of the measured value.

A schematic diagram of the laboratory equipment used in this experiment, including ventilation, scrubbers, and analyzers, is shown in Figure. 3.

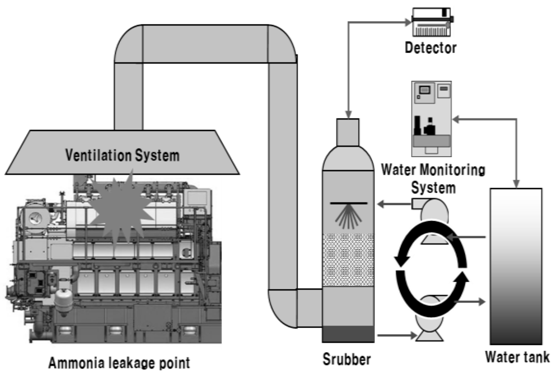

Figure 3. Schematics of the test apparatuses

2.2 Test conditions and method

In this study, a small leakage condition was assumed in the piping of the ammonia gas fuel supply system in the Fuel Preparation Room to supply fuel to the ammonia power generator engine(25 bore, about 1.7MW) through fittings and other leakage holes. To account for the different characteristics of land-based facilities than ships, a Mass Flow Controller was installed on the gas-phase ammonia supply piping from the sealed ammonia engine testbed and injected at 8 kg/h in the ammonia fuel preparation room. Considering the amount of ammonia sprayed inside the laboratory, the operation condition of the forced draft fan was set to 100 CCM(Cubic Centimeters Min), and the supply flow rate and temperature condition of the wash water were set to 20 m^3/h and 9 ~ 10 ℃.

The preliminary tests confirmed that the wash water completely absorbed the ammonia in the pH4 range. Therefore, in this test, the wash water was supplied at pH 4, the point at which ammonia is fully absorbed, and the test was conducted until 110 ppm, the limit concentration of ammonia discharged from the ammonia treatment unit in the Interim Safety Directive for Ammonia Fueled Ships, was discharged from the scrubber outlet. A dilute 99.5% solution of acetic acid was used to adjust the wash water to pH 4. The pH of the wash water was recorded in real time by the Water Monitoring System. To ensure the accuracy of the wash water pH measurement, calibration was performed using standard solutions (pH4., 7, 10) in advance, and the data of the ammonia detection sensor installed at scrubber's outlet was also acquired in real time at the same time as the pH data.

3 RESULT OF THE ABSORPTION CHARACTERISTICS OF AMMONIA AS A FUNCTION OF SCRUBBER SOLUTION PH

Figure 4. shows the analysis of ammonia absorption characteristics according to the change in the pH of the wash water. it was found that until pH 4 to pH 5 of the wash water, ammonia was sufficiently absorbed by the wash water and ammonia was not discharged from the outlet of the scrubber. At a pH of 5.3, the ammonia sensor installed at the scrubber outlet began detecting unprocessed ammonia, and it was found that the concentration of ammonia discharged increased as the pH of the wash water gradually increased. In addition, the pH of the wash water when the ammonia discharge limit of 110 ppm was reached was 8.7.

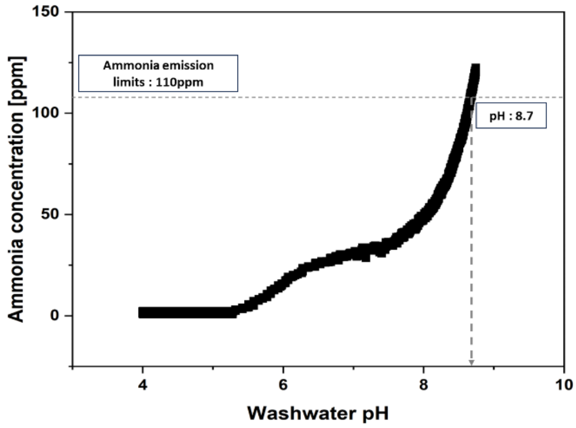

Figure 4. Ammonia concentration according to variation wash water pH

Also It can be seen that the concentration of ammonia discharged from the scrubber outlet increases rapidly from the point where the ammonia is not absorbed by the wash water. In addition, an exponential increase in the concentration of discharged ammonia was observed when the wash water pH exceeded 7.5. From that point, the pH of the wash water and the ammonia discharged concentration showed a similar pattern. The trend of ammonia discharge at pH above 7.5 is shown in Figure 5

The analysis results of ammonia discharged concentration over time showed that during the initial stage of the experiment, the wash water completely absorbed the ammonia However, once the absorption limit was reached ammonia discharged concentration rapidly increased within a short period. The changes in wash water pH and ammonia discharge concentration over time are shown in Figure 6

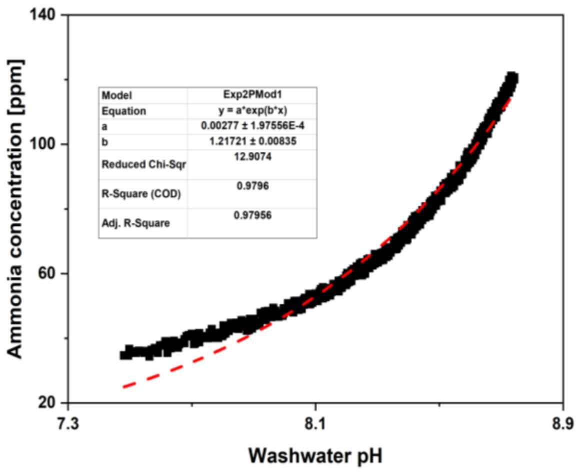

Figure 5. Trend of ammonia discharge at pH above 7.5

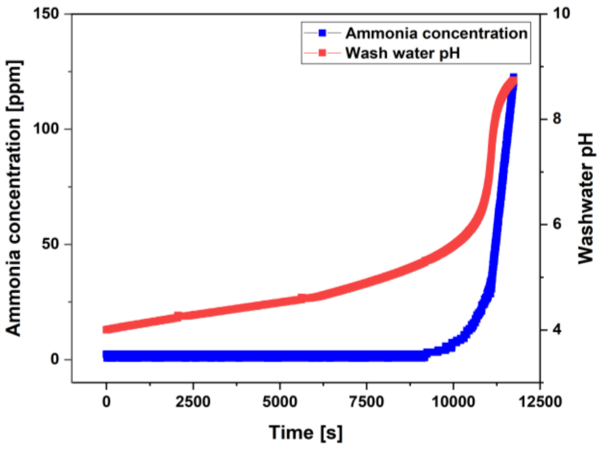

Figure 6. Wash water pH and ammonia discharge concentration changes over timeConclusion

In this study, the ammonia absorption characteristics in relation to variations in the pH of the ammonia scrubbing solution were examined and the following results were obtained.

• As the pH of the ammonia wash water increases, the concentration of ammonia discharged from the scrubber outlet also increases. This suggests that t he ammonia absorption efficiency decreases with an increase in the pH of the wash water.

• Based on the test results under the specified test conditions, an average of 36 ppm of ammonia was discharged from the scrubber outlet at a pH of app roximately 7. Therefore, maintaining the wash wat er an acidic condition is shown to be beneficial for enhancing ammonia absorption.

• The ammonia concentration increases rapidly on ce ammonia emissions begin. also at a wash wate r pH of 7.5, the ammonia discharge concentration i ncreases exponentially, indicating that the wash w ater should be proactively managed according to p H levels before ammonia is released from the scru bber's outlet.

In conclusion, it was confirmed that the ammonia absorption efficiency of the wash water increases as the pH decreases. Furthermore, The pH value of the wash water can be applied as a factor to manage the wash water and monitoring the wash water showed the potential to minimize ammonia emissions to the atmosphere. However, the absorption efficiency of the wash water is influenced by various factors, such as the temperature of the wash water and the supply flow rate. Therefore, experimental studies considering these factors are necessary to determine the optimal pH for effective management of the wash water.

4 ACKNOWLEDGEMENTS

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