

Marine Exhaust Gas Treatment Systems

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Contributor: Theodoros Zannis, Elias Yfantis, Roussos Papagiannakis, Efthimios Pariotis, Dimitrios Rakopoulos, Constantine Rakopoulos, Athanasios Vallis

Two basic types of treatment systems of exhaust gases generated from marine compression ignition engines and from marine combustion systems, e.g., exhaust gas boilers, exist. These two basic exhaust gas treatment systems are used for SO_x and particulate matter (PM) mitigation. Marine aqueous exhaust gas treatment and mainly SO_x reduction systems have been commercially dominant. Since 2011, dry exhaust gas treatment and SO_x mitigation systems have been commercially available from only one manufacturer. As can be realized, the main objective of both aqueous and dry exhaust gas treatment systems is the sorption and the rejection of SO_x emissions from exhaust gases generated from marine combustion systems. One additional virtue of these systems is the sorption of particulate emissions of marine-generated exhaust gases, thus reducing the heavy metals, the soot, the polyaromatic hydrocarbons (PAH) and the sulfur contained in the particulate matter.

Keywords: exhaust gas treatment systems ; IMO 2020 global sulfur cap: IMO NO_x Tier II/III limits ; scrubbers ; selective catalytic reduction (SCR)

1. Introduction

The main gaseous constituents of exhaust gases generated by marine diesel engines are carbon dioxide (CO₂), water vapor (H₂O), nitrogen (N₂) and oxygen (O₂) [1]. As known, in-cylinder available nitrogen and oxygen react at high temperatures in the reaction zone of combustion flame, generating nitrogen oxides (NO_x) which are primarily a mixture of nitrogen monoxide (NO) and nitrogen dioxide (NO₂) with the latter in small quantities [1]. In addition, marine diesel engines burning sulfur-containing fuels such as heavy-fuel oil (HFO) emit sulfur oxides (SO_x). Marine diesel engines are also significant emitters of carbon monoxide (CO), total unburned hydrocarbons (THC) and particulate matter (PM) [2]. Hence, marine diesel-emitted CO₂, NO_x, CO, THC and SO_x are the main gaseous species in conjunction with particulate emissions (PM) that have the highest negative impact on the environment and on human health [3]. For this reason and with concern for maritime SO_x emissions, the International Maritime Organization (IMO) has issued specific limits for marine fuel sulfur content to control marine diesel-emitted SO_x values. The IMO fuel sulfur limits are higher on a global level compared to the ones specified for SO_x Emission Controlled Areas (SECAs) [3]. According to IMO Regulation 2.9 [3], sulfur oxides and PM emission controls apply to all fuels, on-board combustion systems, including main and auxiliary engines with boilers and inert gas generators. Previously mentioned controls include those that are implemented inside Emission Control Areas (ECAs), which are targeted to curtail SO_x and PM emissions, and those that are implemented globally outside ECAs and are attained by controlling the maritime fuel sulfur percentage as it is bunkered and used on-board. As evidenced from IMO Regulations 14.1 and 14.4 [3], fuel sulfur limits, which are provided as %m/m, have undergone specific modifications during recent years. The chronological evolution of the sulfur content of maritime fuels, both globally and in SECAs, is given in **Table 1** [2].

Table 1. Marine fuel sulfur contents that have been legislated by the International Maritime Organization (IMO) according to the MARPOL Annex VI and are effective in both SO_x Emission Control Areas (SECAs) and globally. (Table was genuinely generated using data from ref. [3]).

Year of Issue	Permitted Fuel Sulfur Content (% m/m)	
	SECAs	Worldwide
2000	1.5%	4.5%
2010.07	1.0%	
2012		3.5%
2015	0.1%	
2020		0.5%

The establishment of the IMO Global Sulfur Cap of 0.5% on 1 January 2020 changed the scenery of fuel supply and availability ^[3]. Though the technological solutions to comply with the IMO Global Sulfur Cap are numerous, the selection of a certain solution is quite difficult because it is based on various technical, environmental and economic criteria ^[3]. In addition to the maritime fuel sulfur limit of 0.5% which is implemented globally, there is an additional requirement by the IMO for a 0.1% maritime fuel sulfur limit in SECAs such as the North American coastline, the Caribbean Sea, the North Sea and the Baltic Sea ^[3]. It is also worth mentioning that maritime vessels using exhaust after-treatment systems are allowed to use high sulfur fuel oil (HSFO) ^[4].

To fulfill the limitations of fuel sulfur content as dictated by the IMO ^[3] both inside and outside SECAs, ships can operate with low sulfur conventional fuels that comply with the IMO fuel sulfur regulations. Alternatively, ships can operate with alternative fuels that contain extremely low sulfur or do not contain sulfur ^[5]. Such alternative fuels that have been used in the maritime industry are liquefied natural gas (LNG), biofuels, dimethyl ether (DME), methanol and ethanol, ammonia and hydrogen, which are fuels that do not contain sulfur ^[5]. However, the use of these alternative fuels in ships, though contributing significantly to the minimization of SO_x emissions, is accompanied by many drawbacks such as their bunkering availability, high production cost, variable on-board storage capacity and others. Hence, taking into consideration that the use of high sulfur fuel will be continued because it is compliant with existing marine diesel engines and existing bunkering and on-board infrastructure and also taking into consideration the IMO's fuel sulfur limits inside and outside SECAs, one of the most prominent ways to ensure that existing and future vessels comply with the IMO's SO_x and PM emission regulations is for them to use exhaust gas treatment systems (EGTS) ^[6].

The main exhaust after-treatment systems that are utilized nowadays in maritime vessels are comprised of wet scrubbers operating either as open-loop systems with seawater as the scrubbing medium or as closed-loop systems with aqueous solution of NaOH as the scrubbing medium ^[7]. The careful examination of the literature has shown that various solutions have been suggested to curtail NO_x emissions generated from marine engines and combustion systems and to comply with the IMO Tier II limits that are effective globally. According to a recent study, the available marine NO_x reduction technologies for compliance with Tier III NO_x limits were amended. Furthermore, this study examined the operational principles and progress of various NO_x reduction technologies and thoroughly assessed and criticized the advantages and the disadvantages of these technologies. As witnessed, the implementation of exhaust gas recirculation (EGR) technology can lead to marine engine operation compliant with Tier III NO_x limits without taking into consideration the increased engine fuel consumption. EGR is one of the most promising and well-proven NO_x-controlling technologies, which has proven quite effective over the years in curtailing in-cylinder NO_x formation in marine internal combustion engines. Though EGR is highly effective in reducing NO_x formation inside the cylinders of marine engines, it results in a significant deterioration of brake-specific fuel oil consumption (SFOC) and of soot emissions. For this reason, a detailed examination of the impact of various EGR percentages on NO_x, SFOC and soot emissions is required prior to its implementation in marine diesel engines. In addition, it was shown that the application of SCR systems in the exhaust of marine engines and combustion systems is the most effective way to achieve the IMO NO_x Tier III values. However, despite the continuous optimization of SCR units, the problem of catalyst progressive pollution seriously narrows their broad implementation. Another important issue for the in-cylinder control of pollutant emissions from marine engines is the successful turbo matching with the engine because it allows the feeding of the engine with adequate amounts of intake air at all engine loads. Successful turbo matching is a crucial factor that affects the selection of either a high pressure or a low-pressure

SCR system. Significant NO_x reduction rates can be attained with natural gas marine engines, but additional technologies are required for natural gas engines to comply with NO_x Tier III limits. Other technologies such as variable valve timing and Miller cycle, two-stage turbocharging and fuel/water emulsion can contribute significantly to the control of NO_x values emitted from marine engines, but these technologies are scarcely used independently, almost always being used in conjunction with other technologies instead. These technologies can be used in combination with EGR, SCR and natural gas technologies for the optimization of marine engine fuel economy and polluting behavior. Hence, the most effective and promising technology for the direct compliance of marine engines with NO_x Tier III standards is the exhaust gas treatment using SCR technology [8]. Recently, Lion et al. [9] examined the operational principles, the effectiveness and the advantages and disadvantages of internal measures for NO_x reduction from marine engines and exhaust gas cleaning technologies such as SO_x scrubbers and SCR systems. They found that scrubbers are highly effective in reducing SO_x emissions from marine combustion systems, especially in the case of alkali dosage control, and the SCR system is the most effective NO_x reduction technology for commercial vessels. Similar conclusions were drawn in the recent review studies for marine emission reduction strategies published by Ni et al. [10] and Deng et al. [11].

2. Operational Principles and Key Characteristics of Marine Exhaust Gas Treatment Systems

2.1. General Description

According to the literature [12], two basic types of treatment systems of exhaust gases generated from marine compression ignition engines and from marine combustion systems, e.g., exhaust gas boilers, exist. These two basic exhaust gas treatment systems are used for SO_x and particulate matter (PM) mitigation. Details about both are listed below:

- Aqueous—wet exhaust gas treatment and SO_x and PM curtailment systems, or wet scrubbers.
- Dry flue gas treatment and SO_x mainly reduction systems (dry scrubbers).
- The aqueous SO_x and PM mitigation systems are divided into three categories [13]:
- Open circuit or open-loop aqueous scrubbing systems, usually based on the use of seawater as flue gas scrubbing and SO_x and PM mitigating medium in specially designed counterflow heat exchangers that are called scrubbers [14].
- Closed circuit or closed-loop aqueous scrubbing systems usually based on the use of an aqueous solution of fresh water and alkaline medium (usually sodium hydroxide (caustic soda), NaOH) as exhaust gas scrubbing, and SO_x and PM mitigation medium in specially designed counterflow heat exchangers [15].
- Aqueous hybrid scrubbing systems which can function as either open-loop systems with seawater or closed-loop systems with aqueous solution of NaOH [16].

Moreover, exhaust gas treatment systems exist that are modified versions or applications of the previously mentioned SO_x and PM mitigation systems:

- The aqueous exhaust gas treatment and scrubbing systems (scrubbers) that operate as sub-systems of exhaust gas recirculation (EGR) installations in marine engines. As known, EGR is used in marine engines for the reduction of the in-cylinder NO_x formation rate. Hence, the integrated EGR systems equipped with wet scrubbers are primarily used to mitigate NO_x formation inside the cylinders through exhaust gas recirculation, and they employ wet scrubbers to curtail SO_x and PM emissions. The employment of the aqueous gas treatment systems of this category, besides SO_x and PM mitigation, result in the curtailment of the fouling and corrosion phenomena of the marine diesel due to aqueous exhaust gas cleaning [17][18].
- Inert gas aqueous systems that use small-size aqueous SO_x and PM mitigation systems to clean and convert exhaust gas to inert gas can further be used for tanker evacuation [19].

Marine aqueous exhaust gas treatment and mainly SO_x reduction systems have been commercially dominant. Since 2011, dry exhaust gas treatment and SO_x mitigation systems have been commercially available from only one manufacturer. As can be realized, the main objective of both aqueous and dry exhaust gas treatment systems is the sorption and the rejection of SO_x emissions from exhaust gases generated from marine combustion systems. One additional virtue of these systems is the sorption of particulate emissions of marine-generated exhaust gases, thus reducing the heavy metals, the soot, the polyaromatic hydrocarbons (PAH) and the sulfur contained in the particulate matter [20].

The main exhaust gas treatment technology implemented in marine diesel engine exhaust to reduce NO_x emissions, is the selective catalytic reduction (SCR). SCR technology operates by combining the use of ammonia (NH₃), which is

typically produced from a urea solution, with one catalyst that is placed on a ceramic monolith to convert nitrogen oxides (NO_x) to nitrogen (N₂) and water (H₂O).

2.2. Wet Exhaust Gas Cleaning and SO_x Reduction Systems with Seawater or with Caustic Soda (SO_x Scrubbers)

Before describing the operation principles and the constructional peculiarities of aqueous SO_x mitigation after-treatment systems, it is very important to delineate the chemistry of aqueous sorption of sulfur oxides from marine-generated exhaust gases. SO_x containment chemistry is almost the same for all aqueous flue gas treatment systems, and it can be described from the following chemical reactions [21]:



The sulfurous acid will be ionized in the presence of water with regular acidity, formulating bisulfite and sulfite ions according to the following reactions [22]:



Inside seawater, which contains oxygen, the sulfite ions will be oxidized and provide sulfate roots:



In addition, the sulfuric acid which is produced from the SO₃ fraction that exists in exhaust gases will undergo pertinent chemical reactions with the previous ones, providing sulfate roots and additional acidity (H⁺ ions) [23]:



The reduction of pH (acidity increase) that results from the previously mentioned chemical reactions which are conducted during the scrubbing process of exhaust gases, is inactivated mainly by the physical alkalinity of the seawater providing satisfactory freshwater quantities. The natural alkalinity of the seawater is mainly the result of the presence of the natural bicarbonate root (HCO₃⁻) [24].

The basic scrubbing chemistry of SO_x emissions from aqueous exhaust gas treatment systems that are using fresh water is almost the same as the one of the seawater wet scrubbers. However, in this case, the absence of a natural alkaline medium in the water should be compensated for by the addition of a proper alkaline medium. Most commercially available wet scrubbers use sodium hydroxide, NaOH (or caustic soda), as an alkaline SO_x capture medium.

The sodium hydroxide appears with the form of ions in an aqueous solution as described by the following chemical reaction:



Similar to the seawater exhaust gas treatment, the exhaust gas treatment with fresh water (depending on the solution pH) will oxidize exhaust gas containing SO₂ and SO₃ ions and convert them into sulfate ions, generating in parallel additional acidity (H⁺ ions). In the presence of caustic soda, the roots of sulfuric, bisulfite and sulfite salt will create a mixture of sodium sulfate, sodium bicarbonate and sodium sulfite [19]:



The hydroxide ions will inactivate the produced acidity by reacting with H⁺ ions and produce fresh water:

An aqueous exhaust gas treatment installation is basically comprised of the wet scrubber which is placed in the exhaust of one or more marine internal combustion engines, and which is followed, in the majority of the cases, by an effluent water treatment unit and by an effluent water discharge unit.

The aqueous exhaust gas treatment and mainly the SO_x mitigation system or the SO_x scrubber is a specially designed heat exchanger with extended exchange area of mass, momentum and heat between the flue gas stream and the aqueous scrubbing medium. After extensive and detailed experimental studies, numerous manufacturers have concluded that marine SO_x scrubbers are the optimum solution for the treatment of exhaust gases and the dramatic curtailment of SO_x emissions from marine combustion systems [19].

Gregory and West [15] who provided information about the constructional specifications and the operational data of seven aqueous SO_x mitigation systems have found that three out of the seven systems have the ability to change operating mode from open-loop systems with seawater as scrubbing medium to closed-loop systems with fresh water, and with the addition of SO_x, they can capture chemicals. (At least one of these systems uses a small amount of NaOH during its open-loop operation with seawater to avoid extensive corrosion of the mechanical equipment). Two aqueous SO_x scrubbing systems manufacturers use exclusively closed-loop systems, and two corresponding manufacturers use only seawater during the exhaust gas scrubbing process. Extremely detailed technical specifications for SO_x mitigation scrubbers are not available in the literature since scrubber manufacturers are reluctant to provide all the technical details. However, there is a variation from systems that guide the exhaust gas stream through an inlet duct to a swallow water tank to cyclonic scrubbing systems, which achieve SO_x mitigation through centrifugation and scrubbing of exhaust gases [19]. Despite that, the SO_x capture rate appears to be similar between different constructional layout scrubbers, although the mitigation rate of PM emissions varies significantly with the configuration of the SO_x and PM scrubber. This fact motivated specific scrubber manufacturers to examine various pre-processing exhaust gas treatment systems [15]. These pre-processing initiatives comprise injection nozzles and venturi-type adjustable nozzles. The use of venturi nozzles results in flow strangulation, leading to lower outlet pressure and higher outlet exhaust gas velocities. These parameters on a combinatory basis result in the increase of turbulence levels and significantly enhance the SO_x and PM emissions capture rate [19]. However, the increased pressure strangulation in venturi nozzles can lead to high values of back pressure at the marine engine exhaust; hence, it can disrupt the critical balance of pollutant mitigation degree at optimum levels with a parallel compromise of the operational efficiency and fuel consumption of marine diesel engines. The contemporary technical challenges that SO_x and PM scrubbers face are the following according to the MEPC 56/INF. 5/Annex 1 2007 [19]:

- The preservation of exhaust gas buoyancy phenomenon (i.e., the avoidance of excess temperature reduction of exhaust gases during their scrubbing process by the aqueous medium).
- The simultaneous minimization of the space captured and the weight and the energy consumption by the SO_x and PM mitigation aqueous gas treatment system.
- The minimization of the pressure drop of the exhaust gas stream.
- Hot corrosion avoidance of the SO_x scrubber constructional elements from exhaust gases that contain sulfur and possibly acid sulfate roots.
- The avoidance of exhaust gas vapor condensation and appearance of water droplets at the SO_x and PM scrubber outlet.

The on-board aqueous SO_x scrubbers have three different waste fluid streams [25]:

- The effluent water from the scrubber which is either ejected to the sea or guided to an on-board wastewater treatment plant.
- The heavy residues that are rejected from the on-board wastewater treatment plant or from the freshwater recirculation process.
- The flue gases that contain the remaining pollutant species which were not captured from the aqueous flue gas treatment process.

One of the most critical questions regarding the aqueous exhaust gas scrubbing process and SO_x capture is the rejection of the effluent water from the scrubbing process. Gregory and West [15] tried to address this question and suggested that the aqueous exhaust gas treatment systems with seawater or caustic soda are not highly effective regarding SO_x capture. However, they are effective in capturing particulate emissions and lubricant oil with capture rates more than 80%. Hence, the on-board existence of an effluent water treatment installation is essential. This effluent water treatment installation will

have the ability to capture and reject the particulate matter and lubricant oil that are carried in processed exhaust gases [26]. Effluent water flows from seawater scrubbers and scrubbers operating with an aqueous solution of NaOH are quite different, both in their composition and quantity. A seawater scrubber will reject the total amount of effluent water in all cases, except for a small quantity of water that is drawn from the residue stream in operational wastewater process installations. The caustic soda scrubber under normal conditions could reject a small amount of impure water to counterbalance the pollutant species that are contained in the scrubbing process water. The impure water rejection rates in both types of scrubbers, i.e., open-loop and closed-loop, will vary depending on the design of the exhaust gas scrubber. However, for simplicity reasons, generally accepted values of impure water rejection rates can be found in MEPC 58/23 Annex 16 of 2008 [27]:

- The impure water rejection rate from a SO_x scrubber with seawater as the scrubbing medium is 45 m³/MWh.
- The impure water rejection rate from a SO_x scrubber with caustic soda varies from 0.1 to 0.3 m³/MWh (The indicative recirculation rate is 20 m³/MWh).

According to the MEPC 56/INF.5/Annex 1 of 2007, three different fluids are present in SO_x scrubbers [28]:

- Exhaust gases that are generated from marine diesel engines (Exhaust gases are produced from the combustion of intake air with fuel. Lubricant oil can also be present in exhaust gases depending on the engine status and the operational conditions).
- Seawater or fresh water with NaOH which are used for scrubbing exhaust gases.
- Impure water which may contain combustion products and chemical additives.

In addition to the previously mentioned sources, there will be contributions to the impure water of the exhaust gas scrubbing process from the wear of engine metal parts and possibly from corrosion products, e.g., seawater corrosion products. In cases where the marine SO_x scrubbers are equipped with impure water processing units, a stream of heavy residues will be produced in parallel with the discharge of processed water. This includes SO_x scrubbers with seawater where the effluent water stream should be processed and systems where the small stream of impure water discharged from a freshwater scrubber will be processed by any processing installation [29]. Heavy residue process technologies indicate a considerable degree of differentiation, and for seawater scrubbers, the challenge is the effective processing of large quantities of effluent water (almost 45 m³/MWh). In the present situation, cyclonic systems and flocculation systems for exhaust gas processing are under testing. The same processing technologies are used in exhaust gas processing units with caustic soda, but in this case, the quantities of impure water are considerably lower compared to the previously mentioned case (0.1 to 0.3 m³/MWh). Moreover, the concentration of pollutants in the small stream of impure water in freshwater scrubbers is considerably higher compared to the corresponding concentration of the impure water discharged stream from seawater scrubbers, thus resulting in the production of a higher residue fraction [30]. The on-board incineration of heavy residue is not allowed. Thus, the existence of a specially designed unit for the on-board storage of scrubbing process discharged residues is required. The generated quantities of heavy residues and their composition are not often found in the literature, as it appears that most of the published studies concentrate on the operational effectiveness of the exhaust gas scrubbers and on the composition of the process discharged water. However, a large marine engine manufacturer [31] reported that the quantity of heavy residues produced from its own aqueous SO_x scrubber is almost 0.1 to 0.4 kg/MWh, whereas Ritchie et al. [29] reported heavy residue production of 0.2 kg/MWh from a seawater SO_x scrubber installed on the coastal ship "Pride of Kent" [32].

Undoubtedly, aqueous SO_x scrubbers significantly reduce the negative environmental footprint of the vessels on which they are installed by removing sulfur constituents, particulate matter and some metallic constituents from flue gases that are generated from vessel combustion systems. However, there is relative uncertainty about the size distribution of the particulate emissions captured in an aqueous scrubber. Though the higher size particulates contribute to the "optical gaseous pollution" because they are visible as black smoke, the smaller size particulates (PM_{2.5} which refer to particulates with size smaller than 2.5 µm) have considerably more detrimental repercussions on the human population.

The amount of CO₂ emitted from a vessel equipped with SO_x scrubber will be higher compared to a conventional vessel due to the higher fuel consumption of about 2% in diesel engines, which is the outcome of the back pressure that the SO_x after-treatment system imposes on the main and auxiliary engines. This has been reported from large aqueous scrubber manufacturers [20]. One of these manufacturers has estimated an additional fuel consumption of about 2% compared to the previously mentioned percentage. Since in most of the cases NaOH is a by-product of the chlorine production, the CO₂ environmental footprint that involves chlorine production and NaOH production is another important variable to the general calculation of CO₂ emissions. The broader image of CO₂ emissions, related to the use of SO_x scrubbers should be assessed in combination with increased CO₂ emissions from refinery fuel-desulfurization installations [33]. This issue

has thoroughly been examined by a large scrubber system manufacturer [20], and it was shown that the following contributions in CO₂ emissions can be traced when a flue gas scrubber is used:

- A total of 2 kg CO₂/GJ of fuel heating energy can be produced from the neutralization/inactivation process.
- A total of 1.6 kg CO₂/GJ of fuel heating energy can be generated from the flue gases scrubbing process in the aqueous scrubber.

The two previously mentioned CO₂ emissions cumulatively remain lower from CO₂ emissions generated from an oil refinery that produces distillation fuel with low sulfur content. The corresponding value of CO₂ emissions for the refinery production process of low sulfur fuel is almost 10 kg CO₂/GJ of fuel energy consumption [31].

2.3. SO_x and PM Mitigation Wet Scrubbers Integrated in EGR Systems

As observed from practical applications, there are no important restrictions regarding the size of the marine diesel engine suitable for the installation or the retrofit of aqueous SO_x scrubbers. Marine SO_x scrubber manufacturers offer commercially available systems suitable for values of marine diesel engine which start from 20 MW and have no upper limit [15]. One of the scrubber manufacturers has proposed the installation of SO_x and PM scrubbers as parallel units to make the configuration compatible with any size of marine engine. In vessel retrofits, the volume and weight of the exhaust gas scrubber plays an especially important role, whereas in new ships the scrubbing unit can easily be adapted to the design of the vessel. The exhaust treatment gas system should be installed downstream not only of the main and the auxiliary engines, but also of any exhaust gas boiler and economizer. In addition, specific types of SO_x scrubbers can replace the silencer in the exhaust of the main and auxiliary engines, leaving available space free for other applications. The most usual arrangement is the SO_x and PM scrubber unit placed next to the vessel chimneys and not inside or after the exhaust duct [32].

Some of the scrubber manufacturers have chosen the installation of an additional impure water process unit before this impure water is discharged into the marine environment to control the pollutant species that are accumulated in the scrubbing process impure water. The technologies that are used for the treatment of the scrubbing process impure water can either be flocculation systems or centrifugal cyclonic systems. The size of the impure water process unit depends on the size of the marine diesel engine [16].

However, during the development of the aqueous SO_x scrubbers, the impure water treatment units demanded 1.5 to 4.5 m² of processing area, depending on the type of exhaust gas treatment technology and the size of the marine diesel engine. The impure water processing unit generates two streams of fluids. The first one contains clear water either discharged to the marine environment or stored in tanks, and the second one contains solid residues that should be stored on-board and should be transferred safely to the shore during the approach of the vessel. Hence, the vessel should be equipped with proper means for on-board residue storage [16].

In aqueous SO_x scrubbers that use freshwater recirculation as the main or complementary operational medium, a water storage tank should be available in the installation. According to SO_x and PM scrubber manufacturer data, the volume of the water storage unit should be varied from 10 to 40 m³ depending on the size of the marine compression ignition engine. If the vessel does not have freshwater processing equipment, the limitations imposed from the number of the vessel's approaches to freshwater shore supply installations can further increase the freshwater tank volume requirements. In addition, for the periodic vessel operation without pollutant emissions, an additional process water tank should be installed in closed-loop scrubbers with fresh water and NaOH.

Freshwater consumption from the exhaust gas treatment system demands the on-board freshwater production or the periodic vessel supply with fresh water from pertinent shore installations. The installation of an on-board freshwater production system obviously increases the overall energy consumption of the vessel due to, for example, the power consumption of the recirculation pumps, whereas the periodic vessel supply with fresh water explicitly affects the capacity of the freshwater tank. The solution that should be selected depends mainly on the operational profile of the vessel, especially if a large part of it is in SO_x Emission Control Areas (SECAs) and on the on-board space availability. The addition of alkaline chemicals in the exhaust gas treatment process requires the availability of a corresponding on-board storage tank [33][34]. The capacity of this storage tank will mainly depend on the vessel routes, the potentiality for connection to shore supply stations and the required desulfurization levels. However, most of the manufacturers recommend the use of storage tanks with capacity of 10 m³ or higher for this purpose [32].

In the specific system, part of the exhaust gases after the engine turbocharger are guided to a pre-scrubber fed with an aqueous solution of fresh water and NaOH. Afterwards, the gases are guided into the main scrubbing unit or to the

exhaust gas scrubber, where exhaust gases are treated and pollutant species such as SO_x, PM and potentially heavy metals are mitigated [35]. After this process, the quantity of cooled exhaust gas that has been treated in the scrubber and cleaned from pollutant constituents and species that are hazardous for the engine are guided to the EGR cooler where they are further cooled [36][37]. After the EGR cooler, the exhaust gases are guided through a water mist catcher (WMC) where they are dried. Next, they are guided through a blower to the engine intake system to be mixed with the intake charged air and through in-cylinder combustion of the intake mixture with the injected fuel to achieve an in-cylinder curtailment of the NO_x formation rate. Recirculated exhaust gas flow to the diesel engine intake system is adjusted by a proper valve [38][39]. The impure water and the heavy residues produced from the scrubbing process in the main scrubber are collected and guided to a storage tank where they are mixed with an aqueous solution of NaOH. The impure water with the residues and the NaOH aqueous solution are guided through a pump to an impure fluid processing unit where the heavy residues are collected and stored in a specially designed on-board tank [40]. After this process, the impure water with the NaOH aqueous solution passes through a second unit which filters the water and collects it in clean form. The clean water is transferred through a three-way valve; one part of the clean water quantity is stored in the heavy residue tank, while the other part is discharged to the sea. After the previously mentioned filtering, the aqueous solution of NaOH is transferred to the pre-scrubber unit and to the main scrubber unit for capturing the SO_x and PM emissions contained in the exhaust gases [17][18].

The intake pressure of exhaust gases to the SO_x and PM mitigation scrubber is almost 4 bar(a), whereas the corresponding intake temperature is expected to be about 400 °C. The higher exhaust gas pressure due to their recirculation before the turbine of the turbocharger in conjunction with the fact that only a fraction of engine exhaust gases is recirculated (typically EGR rate varies from 20 to 40% of the total generated exhaust gas flow rate) allows the EGR scrubber to have a significantly smaller size compared to the conventional exhaust gas scrubber used in marine engines without EGR [19].

The impure discharged water from EGR scrubbers should comply with the IMO criteria for the quality of the water that is discharged to the sea. As it happens in the case of a conventional scrubbing and SO_x mitigation system, an EGR scrubber will capture considerable quantities of particulate matter that will be accumulated in the discharged water. One of the best known pilot installations with an EGR system is equipped with a scrubbing process impure water cleaning unit. Specific water quantities after cleaning are discharged to the sea in accordance with the IMO regulations for water quality, whereas the residues are guided to the on-board residue tank [19].

NO_x and SO_x emissions after EGR and scrubbing will be lower compared to the ones of the conventional engine operation. However, there will be an increase of gaseous emissions due to the power consumption of the EGR installation. Additionally, Gregory and West [15] have reported an increase of specific fuel oil consumption (SFOC) and CO emissions when the EGR installation operated to achieve the maximum NO_x reduction. In this case, the modification of engine settings can counterbalance a part of the previously negative effect on SFOC [19].

2.4. Inert Gas SO_x Scrubbers

Inert gas scrubbers are designed to remove sulfur and PM emissions from gases used to replace inert gas in tanks and pipes during unloading of a gas or liquid shipment. Inert gas scrubbers are aqueous scrubbers and are like exhaust gas scrubbers regarding their operational principle, but they are smaller in size due to the management of lower gas volumes and consume seawater at a relatively higher level compared to the exhaust gas scrubbers. This can be attributed to the high requirement for gas cooling because the peak temperature at the tankers' decks is 37 °C. In most of the cases, the inert gas scrubbers are seawater scrubbers, but an alternative technical solution will be the use of scrubbers with recirculated fresh water where the seawater would additionally be used for cooling [19].

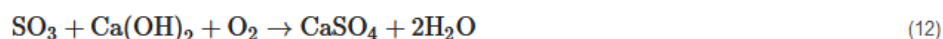
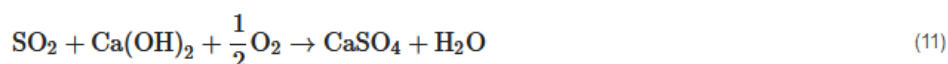
Inert gas scrubbers clean mainly the flue gases that are generated from on-board exhaust gas boilers since the maximum O₂ limit in the inert gas is 8%. Flue gases from exhaust gas boilers usually contain 3% to 5% O₂, whereas diesel engine exhaust gases usually contain oxygen that varies from 7% to 15%. As a result, they do not cover the requirements of inert gases. The inert gas scrubbers are used mainly in crude oil tankers and in chemical tankers.

As the inert gas generators and hence the inert gas scrubbers are considered safe systems and are operational only for certain time periods during the unloading process of the vessel, the quality of the processed impure water does not fall under the limits of the IMO. There is limited effluent water analysis for inert gas scrubbers. In inert gas scrubbers, high water quantities (0.015 m³/Nm³ gas) are used. For this reason, the requirements of temperature should be satisfied, and the concentrations of the effluent species including particulate matter should be exceedingly small. The commercially available flue gas treatment systems with scrubbers operate with only one pass of flue gases from the scrubber. There are

no impure water processing units; hence, there is no heavy residue quantity that should be removed later from the ship. The produced particulate matter is directly dispatched to the sea.

2.5. Dry Exhaust Gas Treatment and SO_x Capture Systems

Dry exhaust gas treatment and SO_x capture systems are used extensively in shore installations for the desulfurization of industrial flue gases. The operation of all dry exhaust gas cleaning systems is based on the use of limestone or hydrated lime to clean SO_x from the flue gases. Even though the dry exhaust gas treatment process is a proven SO_x reduction method, it has certain disadvantages such as the supply and the storage of lime products and the storage and the shore disposal of the used reactants. Dry exhaust gas treatment systems used for marine applications are based on a packing material bed from hydrated lime (calcium hydroxide). The maximization of the area of the dry exhaust gas cleaning system and the conservation for long time of the exhaust gases in contact with the packing material optimizes the removal of sulfur and particulate matter from the exhaust gas stream. The dry capture of sulfur oxides is based on the following chemical reactions ^[19]:



The previously mentioned reactions are exothermic, i.e., they release heat allowing the exhaust gas treatment system to thermally contribute to the efficiency of the exhaust gas boiler through proper installation. Dry exhaust gas cleaning systems do not reject impure substances to the maritime environment such as the aqueous exhaust gas treatment systems do. The used packing material is discharged to specific shore installations. According to one dry exhaust gas cleaning systems manufacturer, the residues of these units can be used in shore industrial installations for high temperature desulfurization based on the remaining capacity of the packing material for SO_x capture. Dry exhaust gas cleaning systems have relatively lower energy consumption requirements compared to the conventional aqueous exhaust gas treatment systems (1.5–2 kW/MW of diesel engine power output). Therefore, the additional CO₂ emissions from a vessel that operates with a dry exhaust gas treatment system are correspondingly low. However, the industrial process of production and distribution of packing material for dry exhaust gas treatment systems is anticipated to contribute to the total CO₂ emissions, and this is a negative contribution of the dry exhaust gas cleaning systems ^[13].

2.6. Marine Selective Catalytic Reduction (SCR) Systems

Marine diesel engine exhaust gases pass through a selective catalytic reduction reactor supplied with an aqueous solution of ammonia (urea). Nitrogen oxides are a mixture of nitric oxide (NO) and nitrogen dioxide (NO₂). As the aqueous solution of ammonia is supplied to the exhaust gas stream, the water of the solution is vaporized. The high temperature of the exhaust gas stream results in the thermal decomposition of urea (NH₂)₂CO into ammonia (NH₃) and carbon dioxide (CO₂) based on the following chemical reaction ^{[17][18]}:



The chemical reactions that take place inside the selective catalytic reduction reactor are the following:



As can be concluded from the above two chemical reactions, the nitric oxide (NO) reacts with ammonia (NH₃) and is converted to nitrogen (N₂) and water (H₂O), whereas the nitrogen dioxide (NO₂) reacts with ammonia (NH₃) and is converted to nitrogen (N₂) and water (H₂O). It is obvious that both nitrogen (N₂) and water (H₂O) are chemical species without negative repercussions on human health and the environment. The SCR reactor is manufactured from a ceramic monolith which operates as a chemical catalyst to facilitate the chemical reactions of NO and NO₂ conversion to harmless N₂ and H₂O ^{[17][18]}.

The marine diesel engine exhaust gases from the exhaust gas receiver are guided to the duct where the vaporization of the injected urea solution and its mixing with the exhaust gas stream is conducted. Afterwards, the gaseous mixture is supplied to the SCR system reactor, where the mixture of NO and NO₂ is converted to N₂ and H₂O. As known, large two-

stroke marine diesel engines are characterized by high brake efficiency and low trapping efficiency; so, the exhaust gas temperature exiting the turbocharger is relatively low and varies from 230 to 260 °C depending on engine load and ambient conditions. These low exhaust gas temperatures are problematic for the operation of the SCR system when heavy fuel oil (HFO), which contains high sulfur content, is used. Thus, with respect to the highest fuel flexibility, it has been a priority that marine diesel engines generate an exhaust gas stream with the proper temperature for the optimal operation of the SCR system. The inlet exhaust gas temperature to the SCR system should ideally vary from 330 to 350 °C when the marine diesel engine operates with HFO ^{[17][18]}.

3. Applications of Marine Exhaust Gas Treatment Systems

3.1. Wet Closed-Loop and Open-Loop SO_x Scrubbers

Many manufacturers of marine aqueous exhaust gas treatment systems have significant experience from similar shore applications (mainly as desulfurization units of flue gases that are generated from industrial installations and oil refineries). Other manufacturers of marine aqueous exhaust gas cleaning systems transfer their experience from the construction and installation of corresponding exhaust gas treatment and inert gas production systems for the maritime industry.

It should be clarified that starting in 2011 and after 20 years from the first testing installation, the aqueous exhaust gas scrubbers have shown considerable technological evolution. It should be noted that for more than 30 years the aqueous exhaust gas treatment systems have operated as exhaust gas treatment and inert gas production systems ^[19].

The first prototype aqueous exhaust gas treatment system with seawater was installed in a ship in 1991. Specifically, the installation was made in the passenger ferry *Kronprins Harald* of the Color Line Company ^[19]. In 1993, an aqueous exhaust gas treatment system with seawater was installed in the oil tanker *MT Fjordshell*. Another company processed a part of the exhaust gas stream of the icebreaker *Louis S. St-Laurent* in 1998, and in cooperation with a large marine engine manufacturer installed a prototype exhaust gas treatment unit to mitigate mainly SO_x emissions in the Ro/Pax Ferry *Leif Ericson* in 2001 ^[19].

In recent years, many manufacturers of aqueous exhaust gas processing systems have installed exhaust gas cleaning systems in ships. These installations include the systems installed in the Ro-Ro *Ficaria* Seaways, the Ro-Ro *Pride of Kent*, in the cruise ship *Zaandam* and in the chemical tankers *Baru* and *Suula* ^[19].

One SO_x scrubber manufacturer has its own systems placed on a barge. Inside the harbor, the barge can come close to the ship in which the exhaust gas processing will take place, and the exhaust gas cleaning systems of the barge can capture unwanted gaseous emissions emitted from the diesel engines and exhaust gas boilers of the ship ^[12].

The main challenge that the on-board installation of a SO_x scrubber must face concerns the purchasing and the transfer of the consumables (mainly caustic soda) that are required for the operation of the exhaust gas treatment systems. Caustic soda is consumed with a rate ranging between 1 and 15 L per hour and per MW of engine power. The higher the consumption of caustic soda is, the higher the SO_x capture from exhaust gases in the scrubber ^[12].

The consumed quantity of caustic soda required for the achievement of specific SO_x reductions in diesel engine gaseous emissions in comparison to those achieved by specific fuel sulfur content are the following:

- Quantity of 11 L caustic soda with 50% w/w NaOH/MWh achieves SO_x emissions equivalent to 2.9% sulfur in fuel oil.
- Quantity of 8 L caustic soda with 50% w/w NaOH/MWh achieves SO_x emissions equivalent to 2.4% sulfur in fuel oil.
- Quantity of 4 L caustic soda with 50% w/w NaOH/MWh achieves SO_x emissions equivalent to 1.4% sulfur in fuel oil.
- Quantity of 1 L caustic soda with 50% w/w NaOH/MWh achieves SO_x emissions equivalent to 0.9% sulfur in fuel oil.

3.2. Wet SO_x and PM Scrubbers Integrated in Marine EGR Systems

One of the best known applications of a “dual” NO_x and SO_x mitigation system is the wet SO_x and PM scrubber integrated in an EGR system installed in the containership *Alexander Maersk*. The on-board space requirements for the EGR installation are expected to be reduced as the experimental prototype installations are progressively converted to commercially available units. Preliminary estimations report that 15 to 20 m³ of on-board captured space are required for the EGR installation per 10 MW of diesel engine power ^[19].

3.3. Inert Gas Wet SO_x Scrubbers

Inert gas scrubbers as parts of gas treatment systems are widely recognized as effective means of deactivating oil and chemical cargo, especially where higher grades of inert gases are not required (since the source is the flue gas boiler exhaust). Typical operational parameters in the case of inert gas scrubbers are the cooling requirements and the subsequent high seawater consumption demands which range from 0.010 to 0.020 m³/Nm³ of inert gas [19].

3.4. Dry SO_x Scrubbers

In the present situation, only one manufacturer has commercially available dry exhaust gas cleaning and SO_x mitigation systems for marine applications. This manufacturer has installed a testing dry SO_x scrubber in the cargo ship MV *Timbus* which carried cellulose from Sweden to Holland [13]. The specific system was approved by class in April 2010. The dry SO_x scrubber in the present phase of development has significant on-board space requirements. Both the dry exhaust gas processing unit and the storage facilities of the unprocessed and the processed packing material have considerable on-board space requirements [19]. The on-board space requirement for the packing material depends obviously on the operational profile of the ship and the availability of the unprocessed and processed packing material. A scrubber system manufacturer [41] guarantees the supply of new packing material when this is required and plans the construction of a packing material supply system in significant harbors around the world. Although the limestone is a directly available commercial product, its supply can set limitations to the number of ships in which its installation is suitable [13].

3.5. Marine Selective Catalytic Reduction (SCR) Systems

The selective catalytic reduction, which uses ammonia as reductive mean, was patented in the USA in 1957. From this year and on, thousands of SCR systems have been manufactured and installed in shore applications from industrial installations and electric power generation units to trains and cars. The maritime sector has more than two decades of technological experience with SCR systems. The first marine applications of SCR systems were conducted by large marine engine manufacturers [42]. Between 1989 and 1992, a well-known engine manufacturer tested the viability of SCR systems through their installation in four vessels in San Francisco Bay and received a certificate of acceptable operation of these system regarding their achieved NO_x reduction from the corresponding maritime transport management body in the San Francisco Bay (Bay Area Air Quality Management District (BAAQMD)). In addition, between 1999 and 2000, another large engine manufacturer installed SCR systems in three two-stroke main diesel engines of Ro-Ro vessels attaining NO_x emissions of 2 g/kWh that were lower than Tier III values for 10 years of continuous operation. The use of SCR systems was expanded in 2000 and 2001 in LPG carriers. Today, SCR technology is widely accepted and is a highly effective NO_x reduction technology with more than 500 examples of applications in the maritime sector until 2013 [42].

An important study was published in 2013 in which shipowners and operators gathered data for a significant number of vessels, engines, fuel types, and equipment manufacturers that they used to develop SCR technologies. Almost 1250 SCR systems have been installed in ships during the last decade. These ships have assembled more than 80,000 h of technological experience from the use of SCR systems during the last two decades. SCR technology has been implemented in different types of ships and marine engines with various types of fuels.

Although SCR technology was first installed in the exhaust of main marine diesel engines, SCR systems have been used for NO_x mitigation in the exhaust of auxiliary engines and exhaust gas boilers. According to the study of IACCSEA [43], 67% of the ships that were examined in this study were equipped with SCR systems in their main marine engines, 23% of the examined ships had SCR systems installed in their auxiliary engines, and 9% of the examined ships used SCR systems for NO_x mitigation in the flue gases generated from gas boilers [42][43]. In addition, SCR technology has successfully been operated in both engines and boilers with a variety of fuels, including low sulfur and high sulfur fuels. Almost half of the ships that were examined in the study of IACCSEA [43], used marine gas oil (MGO) or heavy fuel oil (HFO) almost at the same levels, whereas 22% of the examined cases in the specific study used light diesel oil, and 14% used marine diesel oil (MDO). In the specific study, a smaller number of engines operated with combinations of the previously mentioned fuels. According to the data of the study [43] and in combination with the conclusions of other studies [42], it is proven beyond doubt that SCR technology can be implemented in various types of ships with different fuel requirements which cannot be considered as limiting factors for the application of SCR technology. Many manufacturers have invested in SCR technology in the last 25 years from the first application of this technology to the maritime industry. A significant number of companies in Europe, the USA and Asia possess SCR technologies that are capable of satisfying current and future limits of NO_x emissions from ships [42].

In SCR system applications, a variety of catalysts is used. The most suitable catalysts for marine applications appear to be vanadium catalysts due to their low cost and low sensitivity to the fuel sulfur content [31][32]. SCR catalysts should be

replaced periodically to ensure the effective operation of SCR systems. SCR systems require intermediate inspections every 2.5 years and full inspections every 5 years. The used catalysts should be processed due to heavy metals that can be deposited after a period on the SCR catalysts. For this reason, one company has moved on to the regeneration of the used catalysts and to their reinstatement for commercial use. The effective lifetime of a marine SCR catalyst can be in the order of 5 to 6 years, whereas SCR catalyst manufacturers guarantee their continuous operation for almost 16,000 h [42]. For ships that operate for a small percentage of their lifetime inside NO_x emission areas (NECAs), the lifetime of SCR catalysts can be extended, especially in the case of use of maritime fuel with 0.1% sulfur [32][42].

Today, there are various technologies for the extension of the marine diesel engine operational conditions to engine loads, where the SCR system operates effectively, under development. Marine diesel engine exhaust gas temperatures can be increased to be suitable for the exhaust gas processing from SCR systems under various techniques which include the reduction of intake air mass and the use of exhaust gas preheating before their entrance to the SCR unit. In addition, these techniques include the adjustment of fuel injection timing or the bypass of part of the generated exhaust gas mass flow rate through a heated hydrolysis catalyst which allows the urea injection at low exhaust gas temperatures of about 150 °C. They also include the heating of the urea quantity adjustment system before its injection into the exhaust gas stream for maximization of the effectiveness of the catalytic reduction system. For ships with more than one diesel engine, the interruption of the operation of one or more engines and the operation of a smaller number of engines at higher power output has been proposed. Under another strategy, at low engine loads, a part of the SCR catalyst can be bypassed through the condensation of the exhaust gas volume and its transportation into a smaller catalyst volume by sustaining at the same time the turbulent flow of the exhaust gases and the catalyst temperature. In 2011 a successful sea trial of a SCR system that managed to operate effectively for diesel engine operation at extremely low load (10% of full engine load) was completed [18][42].

In addition, the type of operation of the marine diesel engine (two-stroke or four-stroke) can allow the implementation of different control techniques of the SCR–engine system. Specifically, in four-stroke diesel engines, the SCR catalyst can be placed after the turbocharger. It has been observed that SCR systems coupled to four-stroke diesel engines can be operated efficiently at extremely low loads of 10% to 15% of full engine load. In two-stroke diesel engines, the catalyst is placed before the entrance of the exhaust gases to the turbine of the turbocharger, where the values of exhaust gas temperature and pressure are high. This technique has the advantage of allowing the SCR system to operate efficiently using a smaller reactor size. For two-stroke diesel engines, the placement of the SCR catalyst upstream of the turbocharger turbine can ensure the reduction of NO_x emissions to 25% of the corresponding NO_x emissions of the conventional diesel operation. In some cases, it can offer even higher NO_x reductions. A SCR system placement technique before the turbocharger turbine has successfully been used for more than a decade in ships equipped with two-stroke diesel engines which required the control of NO_x emissions when they operated at low engine loads close to the shore. In 2011, a diesel engine was approved, which used a small volume SCR system with high exhaust gas pressure and temperature and satisfied the IMO Tier III limits for NO_x emissions for diesel engine operation at 10% of full engine load, whereas it generated extremely low CO₂ emissions [42].

Overall, it can be stated that the requirement of urea supply of marine SCR systems is expected to be low compared to other applications of those systems. The application of SCR technology in vehicles is estimated to lead to a total urea consumption of 6 million tons. The existing maritime sector requires urea consumption less than 1% of all installed SCR systems at all applications. The Environmental Protection Agency (EPA) in the USA estimates that the total urea consumption in NO_x emission areas in North America will be close to 454,000 tons in 2020, or it will be smaller than 10% of the total urea consumption in vehicle applications in 2015. Since SCR applications in vehicles are expected to consume no more than 5% of the global needs in urea production, this denotes that the total urea consumption for marine applications in 2020 will be significantly lower than 1% of the global needs [42].

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