

Review

Marine Exhaust Gas Treatment Systems for Compliance with the IMO 2020 Global Sulfur Cap and Tier III NO_x Limits: A Review

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Abstract: In the present work, the contemporary exhaust gas treatment systems (EGTS) used for SO_x, PM, and NO_x emission mitigation from shipping are reviewed. Specifically, after-treatment technologies such as wet scrubbers with seawater and freshwater solution with NaOH, hybrid wet scrubbers, wet scrubbers integrated in exhaust gas recirculation (EGR) installations, dry scrubbers, inert gas wet scrubbers and selective catalytic reduction (SCR) systems are analyzed. The operational principles and the construction specifications, the performance characteristics and the investment and operation of the reviewed shipping EGTS are thoroughly elaborated. The SCR technology is comparatively evaluated with alternative techniques such as LNG, internal engine modifications (IEM), direct water injection (DWI) and humid air motor (HAM) to assess the individual NO_x emission reduction potential of each technology. Detailed real data for the time several cargo vessels spent in shipyards for seawater scrubber installation, and actual data for the purchase cost and the installation cost of seawater scrubbers in shipyards are demonstrated. From the examination of the constructional, operational, environmental and economic parameters of the examined EGTS, it can be concluded that the most effective SO_x emission abatement system is the closed-loop wet scrubbers with NaOH solution which can practically eliminate ship SO_x emissions, whereas the most effective NO_x emission mitigation system is the SCR which cannot only offer compliance of a vessel with the IMO Tier III limits but can also practically eliminate ship NO_x emissions.

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

1. Introduction

1.1. General Concepts

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	0.1%	3.5%
2015		0.5%
2020		

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].

In addition to maritime SO_x emissions, the IMO, with increasing concern about maritime NO_x emissions, has issued specific NO_x emission limits from marine engines both inside and outside NO_x Emission Control Areas (NECAs) [5]. NO_x emission limits in g/kWh that have been issued by IMO inside and outside NECAs are given in Table 2.

Table 2. NO_x emission limits from marine engines that have issued by IMO according to MARPOL Annex VI. (Table was genuinely generated using data from ref. [5]).

Tier	Year of Issue	Nitrogen Oxides Concentration Limit, g/kWh		
		RPM ** < 130	130 ≤ RPM < 2000	RPM ≥ 2000
Tier I	2000	17.0	45 * RPM ^{−0.2}	9.8
Tier II	2011	14.4	44 * RPM ^{−0.23}	7.7
Tier III	2016 *	3.4	9 * RPM ^{−0.2}	1.96

* In Nitrogen Oxides Emission Control Areas (Tier II limits are effective outside NE-CAs); ** Engine speed in rotations per minute.

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 [6]. 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 [6]. 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) [7].

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 [8]. 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 [9]. Recently, Lion et al. [10] 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. [11] and Deng et al. [12].

1.2. Literature Review

Numerous theoretical, experimental and review studies have thoroughly examined various marine exhaust gas treatment technologies used for compliance with the IMO's sulfur content standards and NO_x emission limits. The results of 16 of these studies are listed in Table 3. The main objectives of these studies were the examination of the performance characteristics and the efficiency of open-loop and closed-loop scrubbers and SCR catalysts, the investigation of the influence of exhaust gas recirculation (EGR) technology for NO_x reduction in conjunction with seawater scrubbers for SO_x curtailment and the assessment of the impact of low sulfur fuels and LNG conversion on SO_x reduction in contrast to the use of marine EGTS. The main findings of the reviewed studies listed in Table 3 are that marine scrubbers are highly effective in reducing SO_x and PM emissions. SCR catalysts are also highly effective in curtailing NO_x emissions, and in the case of low-sulfur fuels, the investment cost of the marine EGTS is associated with low-sulfur fuel price scenarios.

Table 3. Consolidation of the results of the literature review on marine exhaust gas treatment systems. For each study examined in the literature and listed in this table its type (experimental, theoretical or review), its main objectives and its main conclusions are shown along with its reference.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
1	Experimental	The polluting behavior of low-pressure an EGR system operating in combination with a seawater scrubber on a LPG carrier, which operated with HSFO.	(1) Increased back pressure due to the scrubber operation and small fuel penalty due combustion efficiency worsening from the use of EGR were evidenced. (2) A 70% NO_x reduction and simultaneous dramatic reduction (98%) of SO_x emissions, which was interpreted as compliance with NO_x Tier III values and maritime fuel sulfur limits in ECAs were observed. (3) It was witnessed Adequate performance of the water wash treatment unit resulting in the receipt of good quality water samples compared to all measured compounds was witnessed.	[13]

Table 3. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
2	Theoretical/Case Study	The environmental and economic repercussions from the implementation of fuel sulfur directive in the Scandinavian industry, i.e., transition from heavy fuel oil (HFO) to marine diesel oil (MDO).	It was found that before the decision of the industry and the owners, there was a profound requirement for extensive feasibility studies and elaborative research relevant to the upcoming environmental decisions for SO _x ECAs and their repercussions on maritime logistics, economy, and environment.	[14]
3	Theoretical/Case Study	The economic burden and pollutant emissions as functions of the reduction choices in pollutant Emission Control Areas were thoroughly investigated.	(1) It was evidenced that the optimum solution is a function of the engine size, the engine fuel consumption inside ECAs and the projected future fuel prices. (2) It was found that the investment cost for the sulfur reduction technologies must be fully covered from fuel saving inside ECAs, which favors MGO or LFO compared to scrubbing systems or LNG.	[15]
4	Theoretical/Case Study	(1) Two different SO _x emission reduction technologies, namely, the use of low sulfur fuel oil and scrubbers, were comparatively evaluated from an economic and environmental perspective. (2) The effectiveness of the investments of SO _x scrubbing system installations for compliance with the requirements of VI MARPOL 73/78 was analyzed.	It was found that the investments in exhaust gas scrubbing systems are effective under any fuel price option examined.	[16]
5	Experimental	(1) Construction of a selective catalytic reduction (SCR) system. (2) The on-board NO _x reduction effectiveness of the investigated SCR module was examined.	The proposed SCR system is highly effective in reducing NO _x emissions from the marine engines of the maritime vessel under examination.	[17]
6	Experimental	The relative influence of fuel sulfur content and water on the performance indicators and the effectiveness of a SCR system was investigated. The impact of fuel sulfur percentage on the NO _x reduction potential of a commercial SCR catalyst fed with urea at low temperatures was analyzed.	(1) It was shown that the addition of SO ₂ in the absence of water enhances NO _x reduction rates and promotes the conversion of NH ₃ with an increased N ₂ O formation (This effect appeared to be independent from temperature). (2) It was found that the addition of H ₂ O in the absence of SO ₂ results in NO _x reduction and in the curtailment of N ₂ O formation. (3) It was witnessed that in the presence of SO ₂ and water, NO _x reduction potential is curtailed.	[18]
7	Experimental	The influence of the KCl poisoning on the performance indicators of MnO _x catalyst, which is a key component of the SCR system, was investigated.	(1) It was shown that at low temperatures, MnO ₂ -based catalysts indicate superior performance compared to conventional catalysts. (2) It was found that SCR catalytic performance was related directly to the oxygen availability of MnO _x catalyst. (3) It was witnessed that the presence of KCl negatively affected the performance of SCR catalyst at low temperatures mainly due to oxygen mobility of MnO _x species.	[19]

Table 3. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
8	Experimental	The PM and SO ₂ emission reduction potential from a marine engine equipped with an open-loop seawater scrubber was examined.	(1) It was shown that a seawater scrubber effectively reduced SO₂ emissions at levels like the ones corresponding to <0.1% fuel sulfur content (0.1% is the allowed fuel sulfur percentage in SECAs since 2015). (2) It was realized that the use of a seawater scrubber resulted in the reduction of PM emissions by 75% compared to conventional marine engine operation. (3) The use of a seawater scrubbing system also results in a significant reduction of polycyclic aromatic hydrocarbons (PAHs). (4) It was also found that the captured SO₂ resulted in the reduction of pH and in a high sulfuric acids concentration in the water effluent. (5) PM emission reduction with a seawater scrubber is the same as with the one attained with a fuel transition from HFO to marine gas oil (MGO).	[20]
9	Experimental	The following three methodologies complying with both ECA regulations for sulfur and Tier III for NO _x were evaluated: (a) heavy fuel oil (HFO) in combination with SCR and an open-loop seawater purifier, (b) marine gas oil (MGO) in combination with SCR, (c) liquefied natural gas (LNG).	(1) All methodologies reduce the impact on particles, photochemical ozone formation, acidification, and terrestrial eutrophication potential in the life cycle. (2) It was necessary to adjust the slip of ammonia from the use of SCR and the slip of methane from the LNG engine. (3) Methane slip could possibly be reduced by engine modifications or oxidation catalysts.	[21]
10	Theoretical/Case Study	The environmental impacts of the following exhaust gas reduction methodologies were compared: (a) selective catalytic reduction (SCR), (b) seawater treatment (SWS), (c) MGO, (d) LNG conversion.	(1) The use of LNG conversion or a combined system (SCR + SWS) or (SCR + MGO) can be applied to the ship. (2) High NO_x and SO_x emission reduction rates can be achieved using a combined system (SCR + SWS). (3) The LNG conversion process achieves the greatest reduction of PM emissions, while it is the only method that reduces CO₂ emissions. (4) LNG conversion can economically achieve the required emission levels according to international regulations.	[22]
11	Theoretical/Case Study	Various ship emission reduction strategies were compared for compliance with the IMO SO _x and NO _x emission standards.	(1) The use of SCR and seawater purification seemed to be the best on-board reduction technologies. (2) LNG appears to be the most efficient type of fuel. (3) The type of ship and the operation area play an important role in choosing the appropriate strategy.	[23]
12	Theoretical/Literature review	The effects of maritime emissions (i.e., particulate matter, gaseous pollutants, etc.) on urban air quality in Europe's coastal areas were examined.	(1) Emissions from shipping contribute to 1–7% of ambient air. (2) Contributions to environmental NO₂ levels range between 7% and 24%.	[24]

Table 3. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
13	Theoretical/Simulation Model	(1) It was estimated the incremental cost of reducing NO_x and SO_x from maritime vessels working in Emission Control Areas (ECAs). (2) It was comparatively evaluated the following five emission abatement methods: (a) SCR, (b) Humid Air Motor and Internal Engine Modification (HAM/IEM), (c) scrubbers, (d) marine gas oil (MGO), and (e) wet scrubbers and LNG.	(1) Increased sensitivity of NO_x reduction methods to functional behavior, with the HAM/IEM combination performing well for exclusive circulation. (2) A Tier-III HAM / IEM combination can prove to be a worthwhile investment for technology vendors. (3) SO_x reduction methods are generally independent of functional behavior. (4) MGO is the most expensive solution but simple to operate. (5) The scrubbing system is economical and relatively insensitive to operating behavior. (6) LNG successfully competes with MGO and scrubber. (7) LNG performs better in terms of cost.	[25]
14	Experimental	The abatement potential of a combined system comprised of catalyst and seawater scrubber was examined.	(1) A significant reduction in emissions was achieved. (2) The proposed emission abatement system can be used with sulfur fuel content up to 0.4%, whereas problems occurred when 2% fuel sulfur percentage was used. (3) Manipulation of scrubber operation is necessary to improve NO_x reduction through the catalyst.	[26]
15	Theoretical/Simulation Model	The requirements for the reduction of harmful emissions in ports and coastal areas without investigating the overall cooling effect of maritime transport were investigated.	(1) The use of 2.7% sulfur HFO outside the ECA in combination with clean fuels within the ECA is appropriate both to maintain the global cooling effect of shipping and to reduce harmful emissions near land. (2) Combustion of low-grade fuels on the high seas offers cooling benefits. (3) Hybrid power settings have a lower environmental impact than standard engine solutions and a lower annual fuel bill.	[27]
16	Theoretical/Simulation Model + Literature Review	How changes in CO ₂ taxation may affect the time schedule and routing of maritime vessels was examined.	The increase of the carbon tax can substantially change the planning of ship services, incur additional costs for route services and improve environmental sustainability.	[28]

1.3. Motivation, Methodology and Innovative Aspects of the Present Work

From the elaborative investigation of existing literature in the field of gaseous and particulate emissions from shipping and the NO_x, SO_x, and PM emission abatement technologies, it can be concluded that there is a lack of consolidated information about the operational principles and the construction specifications of modern exhaust gas treatment systems used for SO_x, PM, and NO_x emission mitigation. Moreover, there is no detailed analysis or direct comparison between exhaust gas treatment technologies and other alternative techniques used to curtail SO_x, PM, and NO_x emissions from shipping. In addition, until now no single study has detailed results about the performance characteristics and the investment and operation cost of the most important contemporary exhaust gas treatment technologies used for SO_x and NO_x emission mitigation in ships. Finally, and most importantly, its actual data about the time required for seawater scrubber installation in a vessel and the actual purchase and the installation cost of seawater scrubbers on various cargo vessels has never before been published.

For this reason, the primary goal of the present review study is the detailed analysis and evaluation of the literature about the operational principles and the construction specifications of the major modern exhaust gas treatment systems used for SO_x, PM and NO_x emission mitigation in ships. These SO_x after-treatment technologies include wet scrubbers with seawater, caustic soda and hybrid scrubbers, wet scrubbers integrated in EGR installations, dry SO_x abatement scrubbers with packing material and inert gas wet scrubbers. The main NO_x after-treatment technology that is reviewed in the present study is the SCR technology. In addition, in the present study the SCR technology is directly compared with alternative NO_x reduction technologies such as EGR, direct water injection (DWI), HAM and the use of LNG and internal engine modifications (IEM) to prioritize the optimal solution for existing and future vessels. Details are also provided about the performance characteristics and the investment and operational cost of SO_x, PM, and NO_x after-treatment shipping technologies. Unlike the existing literature, the present study provides realistic data about the time several vessels spent in a shipyard for seawater scrubber installation. Moreover, another virtue of this investigation that differentiates the present article from the existing literature is that detailed real data about the purchase cost and the installation of seawater open-loop scrubbers in cargo vessels at shipyards in East Asia are presented. The facts about the operational behavior, the performance characteristics and the investment and operational cost of the reviewed EGTS are comparatively evaluated, and the optimal EGTS is proposed for both SO_x and PM emission mitigation and NO_x emission mitigation in ships.

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

2.1. General Description

According to the literature [29], 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 [30]:
- 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 [31].
- 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 [32].
- Aqueous hybrid scrubbing systems which can function as either open-loop systems with seawater or closed-loop systems with aqueous solution of NaOH [33].

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 [34,35].

- 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 [36].

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 [37].

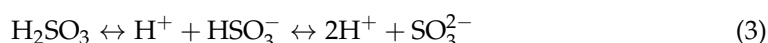
The main exhaust gas treatment technology implemented in marine diesel engine exhaust to reduce NO_x emissions, is the selective catalytic reduction (SCR). SCR technology operates by combining the use of ammonia (NH₃), which is typically produced from a urea solution, with one catalyst that is placed on a ceramic monolith to convert nitrogen oxides (NO_x) to nitrogen (N₂) and water (H₂O). In the next paragraphs of this section, we thoroughly analyze the operational principles and the constructional peculiarities of aqueous and dry SO_x, PM, and NO_x mitigation systems [38].

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 [39]:



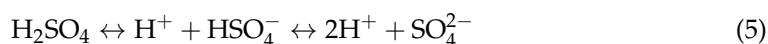
The sulfurous acid will be ionized in the presence of water with regular acidity, formulating bisulfite and sulfite ions according to the following reactions [40]:



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) [41]:

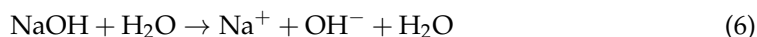


The reduction of pH (acidity increase) that results from the previously mentioned chemical reactions which are conducted during the scrubbing process of exhaust gases, is inactivated mainly by the physical alkalinity of the seawater providing satisfactory freshwater quantities. The natural alkalinity of the seawater is mainly the result of the presence of the natural bicarbonate root (HCO₃[−]) [42].

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 [36]:



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. A schematic view of the operation principle of the on-board installation of an aqueous exhaust gas treatment system with seawater (seawater scrubber) is shown in Figure 1 [29].

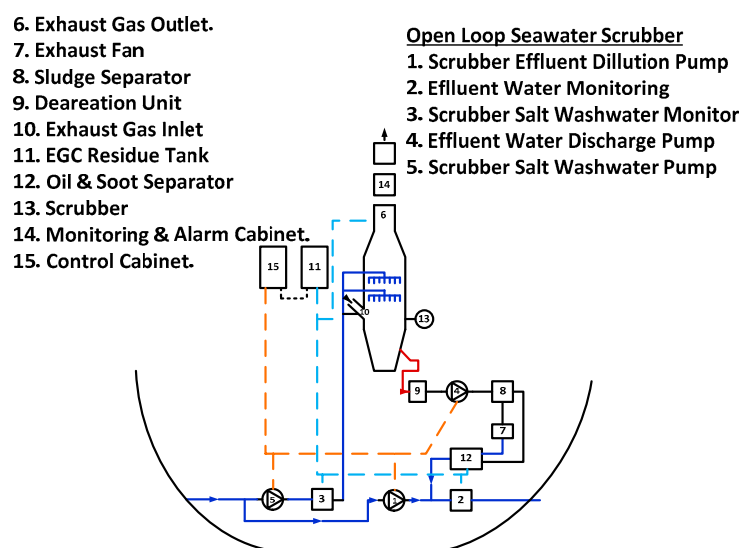


Figure 1. Schematic view of the on-board installation of an open-loop wet SO_x scrubbing system operating with seawater. (Figure was genuinely generated using data from ref. [29]).

A closed-loop SO_x capture installation with a freshwater solution of NaOH as scrubbing medium is shown in Figure 2 [29], while in Figure 3 a hybrid SO_x mitigation scrubber which can operate as either an open-loop or a closed-loop installation [29] is shown.

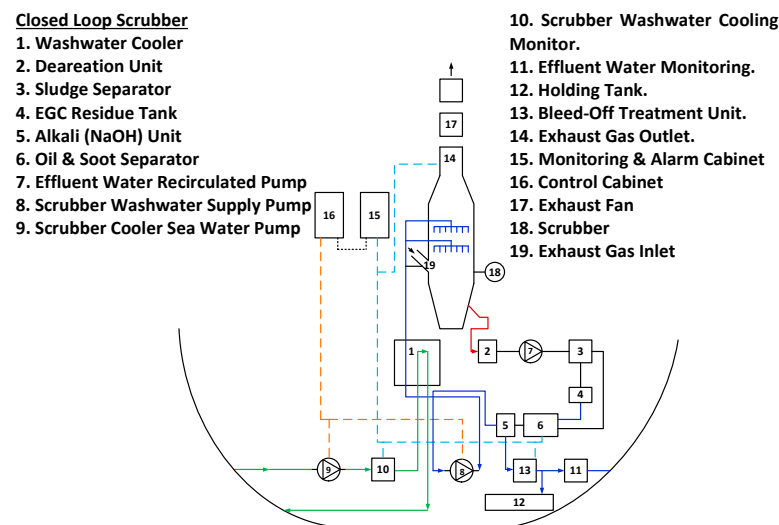


Figure 2. Schematic view of the on-board installation of a closed-loop wet SO_x scrubbing system operating with a freshwater solution of NaOH. (Figure was genuinely generated using data from ref. [29]).

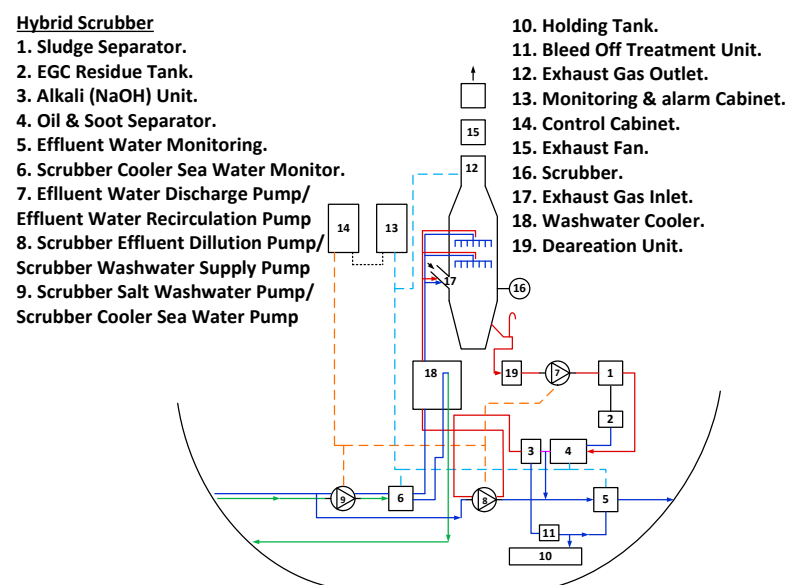


Figure 3. Schematic view of the on-board installation of a hybrid wet SO_x scrubbing system operating with seawater (open-loop operation) or with an aqueous solution of NaOH (closed-loop operation). (Figure was genuinely generated using data from ref. [29]).

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 [36].

Gregory and West [32] 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 [36]. 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 [32]. 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 [36]. 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 [36]:

- 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 [43]:

- 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 [32] 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 [44]. 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 [45]:

- 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 [46]:

- 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 [47]. 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 [48]. 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 [49] 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. [47] reported heavy residue production of 0.2 kg/MWh from a seawater SO_x scrubber installed on the coastal ship "Pride of Kent" [50].

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 [37]. 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 [51]. This issue has thoroughly been examined by a large scrubber system manufacturer [37], 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 [49].

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 [32]. 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 [50].

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 [33].

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 [33].

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 [51,52]. 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 [50].

As evidenced from Figure 4, 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 [53]. 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 [54,55]. 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 [56,57]. 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 [58]. 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 [34,35].

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 [36].

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 [36].

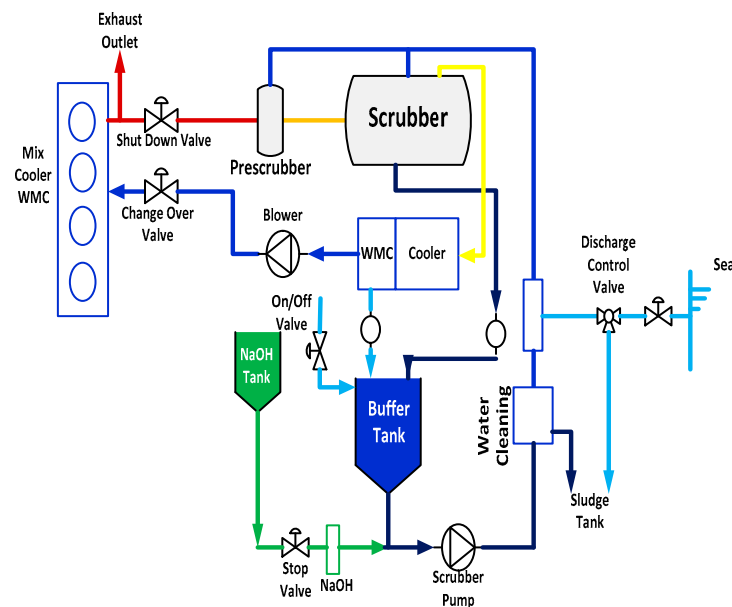


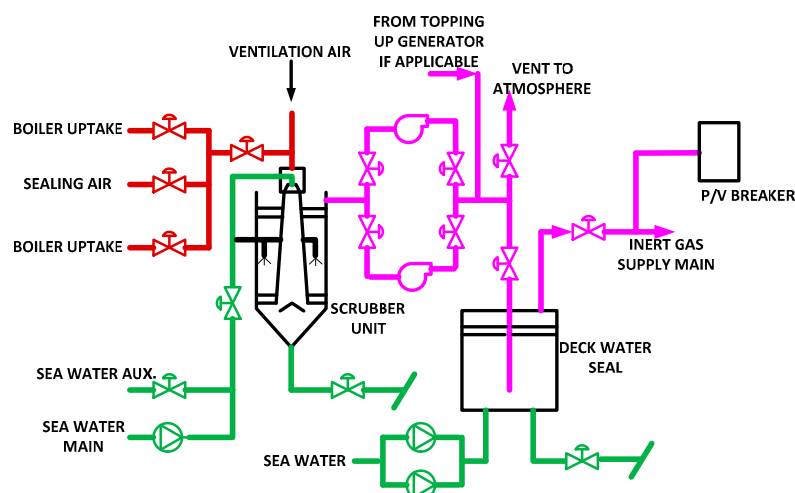
Figure 4. Graphical representation of an EGR system installed on a marine diesel engine for NO_x emissions reduction. The specific installation incorporates a closed-loop system with scrubbers operating with fresh water and NaOH for the reduction of marine diesel engine emitted SO_x and PM. (Figure was genuinely generated using data from refs. [34,35]).

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 [32] 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 [36].

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 [36].

Inert gas scrubbers clean mainly the flue gases that are generated from on-board exhaust gas boilers since the maximum O_2 limit in the inert gas is 8%. Flue gases from exhaust gas boilers usually contain 3% to 5% O_2 , 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. A typical inert gas treatment installation for SO_x and PM capture is shown in Figure 5. The specific gas treatment unit operates with seawater as the SO_x capture medium [38].



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 CO_2 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 CO_2 emissions, and this is a negative contribution of the dry exhaust gas cleaning systems [30].

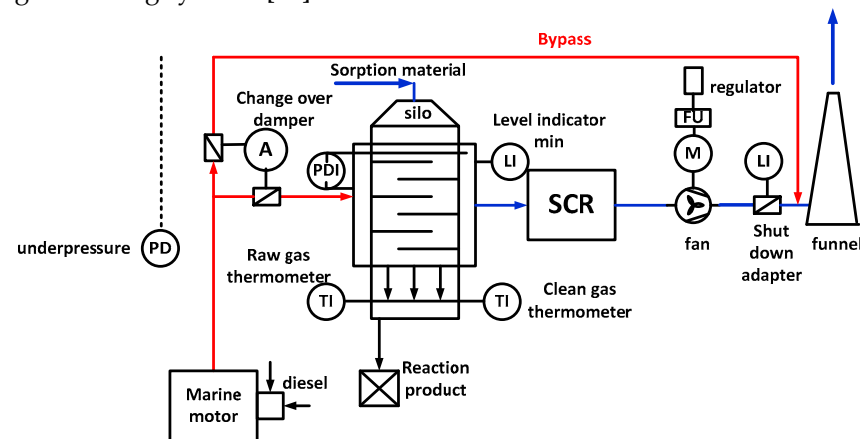


Figure 6. Schematic view of a dry exhaust gas treatment system for SO_x reduction and a SCR unit for NO_x mitigation. (Figure was genuinely generated using data from ref. [30]).

2.6. Marine Selective Catalytic Reduction (SCR) Systems

The operational principle of the selective catalytic reduction system proposed by a large marine engine manufacturer is shown in Figure 7 [34,35]. According to Figure 7, exhaust gases come out from a marine diesel engine with high temperature, containing high levels of NO_x emissions. 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 (NO_2). 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 (NH_2) $_2\text{CO}$ into ammonia (NH_3) and carbon dioxide (CO_2) based on the following chemical reaction [34,35]:

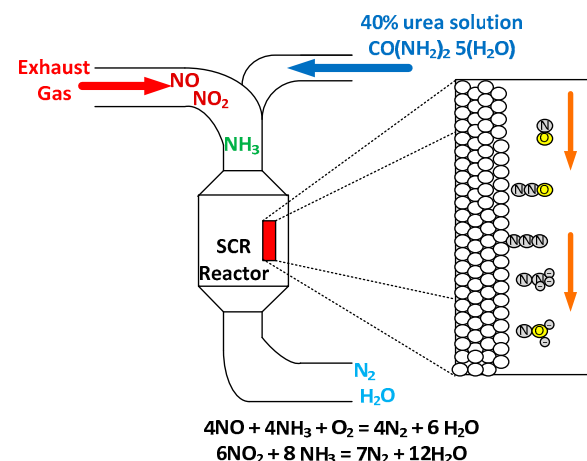
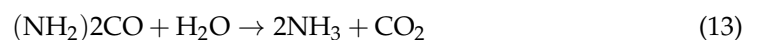
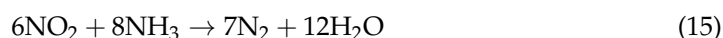
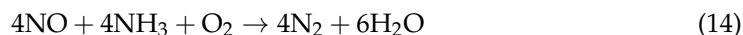


Figure 7. Characteristic view of the operational principle of the selective catalytic reduction (SCR) process. (Figure was genuinely generated using data from refs. [34,35]).

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 [34,35].

As observed from Figure 7, 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 [34,35].

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 [36].

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 [36]. 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 [36].

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* [36].

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 [29].

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 [29].

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 [36].

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 [36].

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 [30]. 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 [36]. 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 [59] 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 [30].

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 [60]. 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 (see Figure 8) [60].

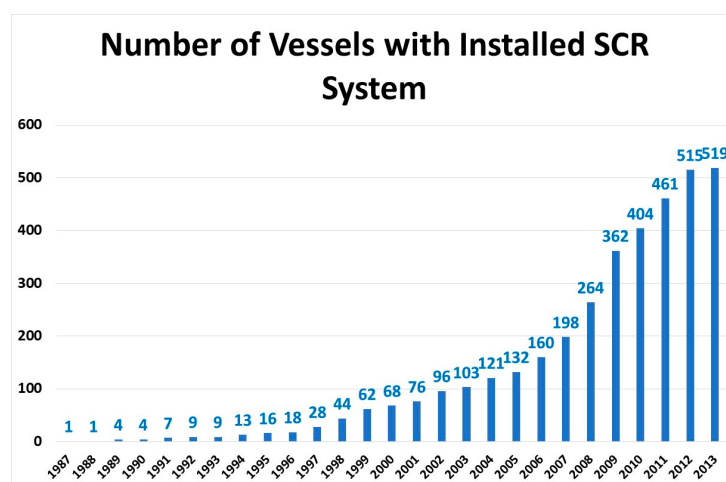


Figure 8. Number of vessels with installed SCR system from 1987 to 2013 (Figure was genuinely generated using numerical data from ref. [60]).

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. Figure 9 shows the various types of ships that today use SCR systems including ferries, oil tankers, container ships, icebreakers, cargo ships, work boats, cruise ships and warships. Almost half of the ships that use SCR systems are ships that carry people and products, including RoPax, RoRo, cargo ships, ferries, high speed catamarans, container ships, RoRo cargo ships, cruise ships, tankers, LPG carriers and chemical tankers. Patrol boats (15%) and supply vessels (14%) are the second and the third most dominant ship type equipped with SCR system [60].

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 [61], 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 [60,61]. 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 [61], 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 [61] and in combination with the conclusions of other studies [60], 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 [60].

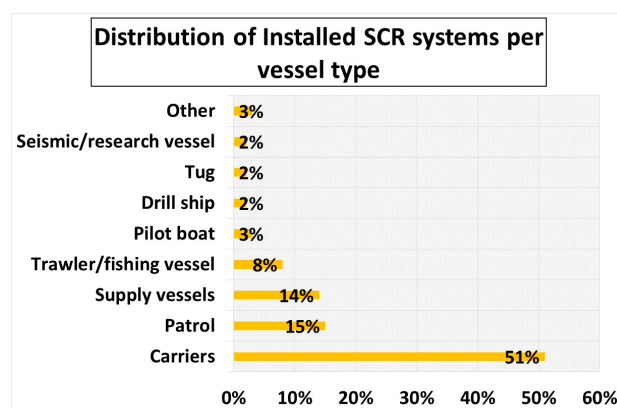


Figure 9. Distribution of installed SCR systems per vessel type. (Figure was genuinely generated using data from ref. [60]).

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 [49,50]. 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 [60]. 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 [50,60].

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 [35,60].

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 [60].

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 [60].

4. Performance Characteristics of Marine Exhaust Gas Treatment Systems

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

The sulfur capture rates from the exhaust gas stream depend on the aqueous mean flow rate in the SO_x and PM capture scrubber. According to Ritchie et al. [47], a series of experimental tests in a SO_x scrubber showed that the sulfur capture rate from exhaust gases varied from 65% to 94%. The only varying parameter in these tests was the water mass flow rate, which was reduced in the case of the sulfur capture rate being 65%, whereas it was increased in the case of the SO_x capture rate being maximized and reached the limit of 94% [30].

In general, the manufacturers of SO_x capture aqueous systems report extremely high capture rates of sulfur from the exhaust gas stream which vary from 90% to 99% with favorable operating conditions of the SO_x scrubbing system. Of more importance is the study of the exhaust gas cleaning rate from SO_x emissions of the commercially available aqueous mitigation systems by comparing the maximum fuel sulfur content that these systems can process and to provide gaseous emissions equivalent to the emissions that are generated from the combustion of maritime fuel with 0.1% sulfur. The capture rates that are described below are based on information obtained from SO_x capture aqueous scrubbing systems, and they are not confirmed in all cases from independent reports. As shown below, the aqueous systems with fresh water and alkaline and the hybrid systems demonstrate the highest SO_x capture effectiveness. The closed-loop systems and the hybrid systems can manage high fuel sulfur contents under specific conditions [30]. Hence, the following conclusions can be derived for the effectiveness of SO_x aqueous scrubbing systems:

- The effectiveness of the aqueous hybrid SO_x scrubber is 3% sulfur in fuel without limit. This value is confirmed by three major manufacturers. The effectiveness without limit demands overestimated the liquid cleaning system, the free water flow rate, and the high SO_x capturing chemical consumption.
- The effectiveness of the seawater SO_x scrubber is 3.5% sulfur in fuel. This value is confirmed by two major manufacturers. Both manufacturers declare 3.5% sulfur in fuel as maximum percentage.
- The effectiveness of the caustic soda SO_x scrubber is 3.5% up to 5% sulfur in fuel. This value is confirmed by two major manufacturers.

The corresponding capture rates of PM, NO_x and CO₂ emissions are described below in Table 4. The facts that will be presented below in Table 4 have been obtained from manufacturers of aqueous pollutant mitigation systems from marine diesel engines. There are indications from ongoing investigations that the facts to be presented below are rather optimistic, and for this reason, under a risk assessment analysis it can be more logical if a 50% efficiency is considered.

Table 4. PM, NO_x and CO₂ capture rates from aqueous exhaust gas processing systems coupled to marine diesel engines. The classification of the capture rates is conducted according to the type of aqueous exhaust gas processing system. (All values have been derived from available data of manufacturers of corresponding systems, and the table was genuinely generated using data from ref. [32]).

Pollutant	Aqueous Exhaust Gas Processing System	Capture Rate (%)
PM	Hybrid system	60 to >90
	Seawater scrubber	70 to 90
	Freshwater scrubber	65 to 95
NO _x	Hybrid system	0 up to “less than 10”
	Seawater scrubber	0 to 2.5
	Freshwater scrubber	7
CO ₂	Hybrid system	0 to 15
	Seawater scrubber	0
	Freshwater scrubber	0

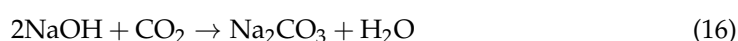
The aqueous scrubber has the capacity to capture particulate emissions (PM); thus, it is expected to find other pollutant species to the impure water that is rejected from an aqueous scrubber. The amount and the composition of the particulate matter that is emitted from marine diesel engines was affected by the combustion process and the type of fuel used. The composition of the particulate matter emitted from marine diesel engines, can be divided into three basic groups according to the IMO MEPC 56/INF.5/Annex 1 2007 [32]:

- Metal oxides and sulfates: These are generated mainly from the fuel type that is used, but also in the quantity of these emissions, which will appear in the effluent water discharge from an aqueous SO_x scrubber and can contribute the engine lubricant oil or the engine and scrubber corrosion products. In aqueous scrubbers, the scrubbing water of the exhaust gases can contain specific species that contribute to the production of metal oxides and sulfates. This phenomenon is not considered to be another source of pollution, and the specific subject is generally not expected to be especially important. However, the background values should be taken into consideration when the concentration of dangerous species in the effluent discharged water is monitored.
- Carbon (Soot): Soot and carbon particles are considered as stable species of the exhaust gases. The smaller soot particles (with diameter smaller than 2.5 µm) cause serious respiratory problems in humans. A previous study showed that the carbonaceous soot

was comprised mainly of soot particles of intermediate and high diameter which are not easily inhaled by humans. However, more studies are required for the determination of the soot particle size distribution that can be captured from aqueous exhaust gas scrubbers.

- Other organic species: These typically contain polyaromatic hydrocarbons (PAHs) and PAHs products, aldehydes, alkanes, alkenes and a small quantity of unburned fuel or unburned fuel constituents. Many species of the PAHs and of their products, especially the nitric PAHs, has been verified as responsible for genetic mutations and carcinogenesis. Hence, the monitoring of the concentrations of the PAHs and their products in the scrubber-discharged impure water is necessary.

Theoretically, there is the potentiality of CO₂ removal that exists in the exhaust gases of marine diesel engines with the use of aqueous exhaust gas scrubbers that operate with the addition of an aqueous NaOH solution. This observation is theoretically based on the following chemical reaction [36]:



However, the preferred chemical reaction in the aqueous scrubber is the sulfur capture. Therefore, there is a need for high amounts of NaOH which can be used not only for sulfur capture but also for the removal of CO₂. The production of NaOH has a direct effect on the formulation of the CO₂ environmental footprint (carbon footprint). The sodium hydroxide is basically a byproduct of the chlorine production through the seawater electrolysis. Depending on the environmental footprint expressed as CO₂ emissions, which is required for the electric power generation that is necessary for the seawater electrolysis, the aqueous CO₂ capture from marine diesel engine exhaust gases in corresponding scrubbers in the presence of NaOH can be proven unprofitable based on the total lifecycle carbon footprint expressed in CO₂ emissions [30].

In the past, interesting numerical and experimental studies, which thoroughly examined the operational performance of various types of open-loop and closed-loop wet scrubbers have been performed. The type of each study (i.e., theoretical, or experimental), its main objectives and its main conclusions along with its citation are listed in Table 5. Specifically, Table 5 contains 28 reviewed studies extracted from the literature. The main objective of the studies listed in Table 5 is the investigation (either numerically or experimentally) of the effect of various scrubbing mediums either under open-loop or closed-loop installations on the performance characteristics and the efficiency of SO_x and PM emission reduction. The main findings of these studies are that the marine closed-loop scrubbers are more effective compared to marine open-loop scrubbers in significantly reducing SO_x and PM emissions because they facilitate the adjustment of the scrubbing medium dose, and the closed scrubbing systems noticeably lower the risk of negatively affecting the surrounding seawater environment.

Table 5. Consolidation of the results of the literature review on scrubber systems. For each study listed in this table its type (theoretical, experimental or review study), its main objectives and its main conclusions along with its citation is mentioned.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
1	Theoretical/Simulation Model	The effect of (a) using sodium persulfate aqueous scrubbing, (b) temperature and (c) Na ₂ S ₂ O ₈ , FeSO ₄ and H ₂ O ₂ concentrations on NO and SO ₂ emission concentrations was examined.	(1) Increased persulfate concentration leads to an increase in NO removal at various temperatures. (2) SO ₂ was almost completely eliminated in the range of 55–85 °C. (3) NO removal of 93.5–99% with the addition of Na ₂ S ₂ O ₈ and Fe ²⁺ . (4) SO ₂ removal was as high as 98.4% both at 35 °C and at 80 °C.	[62]

Table 5. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
2	Theoretical/Case Study	An extensive and detailed report providing information on various methods for compliance with the IMO sulfur content standards, including alternative fuels such as LNG, LPG, CNG, biofuels, ammonia, and hydrogen and EGTS.	Provides detailed information on how the specific class can support owners and operators during the decision-making process of the suitable SO _x abatement technique.	[63]
3	Experimental	The operational behavior and the SO ₂ capture efficiency of a seawater scrubber located on a marine application was examined.	(1) Seawater indicated superior performance compared to distilled water. (2) The efficiency of the scrubber was enhanced by increasing the liquid flow rate and the gas residence time, (3) SO ₂ capture efficiencies up to 93% were realized.	[64]
4	Experimental/Detailed Report	The effect of fuel sulfur content on marine engine lubrication was investigated, and it specific suggestions concerning the most suitable lubricant oils that should be used were provided.	(1) Fuels with lower than 0.50% sulfur content will drive demand towards lower base number (BN) cylinder oils. (2) The use of HSFO with sulfur content potentially higher than 3.5% coupled with the use of scrubber technology will drive the demand towards higher BN cylinder oils.	[65]
5	Theoretical/Simulation Model	The environmental policy constraints for acidic exhaust gas of open-loop marine scrubbers' discharges from ships was examined. The focus was on the underlying phenomena that primarily affect the disposal of acidic discharges in seawater.	Significant jet deflection was observed during an open-loop scrubber discharge.	[66]
6	Experimental & Theoretical/Simulation Model	The ability of an open-loop seawater scrubber for sulfur dioxide removal from exhaust gas was investigated. The investigation was focused on the examination of the following three absorbing methodologies: (a) seawater; (b) NaOH addition to seawater; and (c) by using distilled water as benchmark.	(1) The seawater was able to absorb a limited quantity of SO ₂ at very low equilibrium partial pressure. (2) The addition of NaOH allowed slightly higher solubility levels compared with only seawater. (3) For SO ₂ concentration up to 500 ppmv, an absorption efficiency above 98% can be achieved.	[67]
7	Theoretical/Case Study-Stochastic Model	How the existing fleet can be adapted to the new emission regulations was explored. The following techniques were considered: (a) the use of low-sulfur marine diesel oils and (b) the installation of scrubbers.	(1) The net present value of the scrubbers' investment and the investment in the change of fuel types for different assumptions depends on the mode of operation of the vessels. (2) Significant data were provided on the relationship between increases in fuel consumption and CO ₂ emissions due to the use of scrubbing systems and how these affect the financial analysis of whether these incremental emissions are to be compensated under a CO ₂ pricing mechanism.	[68]

Table 5. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
8	Theoretical & Experimental Report	An extensive and detailed report providing information about the decisions taken during the recent IMO committee meetings.	(1) The 0.5% fuel sulfur limit is a significant reduction from the current global limit of 3.50% m/m which has been established since 2012. (2) The only regular exception to the use of 0.50% fuel sulfur will be for the relatively small number of ships that choose to use the ‘equivalent’ compliance mechanisms in accordance with Regulation 4 of MARPOL Annex VI such as LNG fuel or the fitting of an exhaust gas treatment system.	[69]
9	Theoretical/Case Study	The impact of the “global sulfur cap” on the tribological behavior of two-stroke marine diesel engines was examined.	(1) The operation with high-sulfur residual fuels allows a smooth transition for marine diesel engines in 2020 and beyond. (2) Cylinder lubrication systems might be optimized by new parameter settings for the extended residence time of the lubricant instead of aiming at constantly feeding fresh lubricant for acid neutralization onto the cylinder liner running surface. (3) Reduced addition needed for acid neutralization in cylinder lubricants is providing potential to focus on higher oxidation stability, deposit control, and lubricity for difficult operating conditions.	[70]
10	Theoretical/Simulation Model	The fluid dynamics and SO ₂ absorption in an open spray tower desulfurization reactor was investigated.	The proposed model is a powerful tool for designing and optimizing an open spray desulfurization tower, e.g., enabling the numerical evaluation of the best position of the spray nozzles, the distance between the spray plumes, the size of the wall rings, the number of operating spray jets and other critical parameters.	[71]
11	Theoretical/Simulation Model	The operational performance of a SO ₂ scrubber was examined and optimized. The results of the specific study represent a preliminary work for SO ₂ removal based on different nozzle designs.	(1) The slurry injection quantity considerably affects the improvement of the scrubber efficiency. (2) The high inlet velocity of the slurry flow positively affects the SO ₂ removal efficiency.	[72]
12	Theoretical/Simulation Model	The desulfurization efficiency of an integrated magnesium-based seawater scrubber was investigated. Various parameters were considered such as: (a) the ratio of liquid to gas (VL/VG), (b) the pH and (c) the velocity of the empty container.	(1) The VL/VG and pH parameters are the most effective factors influencing the desulfurization performance. (2) The desulfurization efficiency is greater than 90% under optimized conditions VL/VG = 10.39 L/m ³ and pH = 7.66.	[73]

Table 5. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
13	Theoretical/Case Study	The effect of the following alternatives used to reduce sulfur emissions on the investment and operating costs of a ship and a shipping company was investigated financially. Solutions: (a) switch to higher quality and lower sulfur fuels (referred to as distillates), (b) install flue gas cleaning facilities (referred to as scrubbers) and (c) retrofit of an existing LNG engine.	(1) There is a difference in the direction of recognition and response regarding SO _x regulation between LC and SMC shipping companies. (2) SO _x regulations affect the activities of a shipping company. (3) Governments and related bodies may lead active investment in shipping companies through reasonable political incentives such as the Green Shipping Award, the Green Award Certification and the NO _x Fund.	[74]
14	Theoretical/Simulation Model	The lifetime cost of a scrubbing system and a fuel change approach were compared.	(1) The scrubber system seems to be more attractive to shipping companies that have a higher ECA port call density on their commercial lines, while the fuel change approach is more suitable for ships operating in loops with fewer ECA port calls. (2) There is a knowledge gap in the literature, namely that a ship's sailing plan should be included in the evaluation of sulfur emission control methods for the ECA regulation and different methods of compliance.	[75]
15	Theoretical/Case Study	(1) The study examined the link between innovation policy and environmental legislation. (2) The study applied technological and legal material that illustrates the context of marine laundry systems as technological responses to more rigid environmental regulations, examining their impact on market potential and change.	(1) Demand for environmental innovation has gradually increased as the date for the IMO regulations expired due to the need and government support for the adoption of this technology. (2) Environmental regulations can lead to innovation, and for this reason government support in R&D to produce innovative products is extremely important, as market demand alone may not be enough—before environmental regulations—to persuade manufacturers to develop new environmentally sound technologies. (3) In cases where innovation is driven by environmental regulations, government support is also required for its adoption and implementation, as higher initial market prices usually complicate the assessment of the economic feasibility of environmental innovation compared to established technologies, leading to a resistance to adopt or implement them.	[76]
16	Theoretical/Financial Simulation Models	The limitations of the financial evaluation of technologies assisting compliance with the sulfur regulations in MARPOL Annex VI were identified.	The proposed methodology could improve the understanding of the problem and support decisions and could help operators select the necessary technical alternatives in a better way.	[77]

Table 5. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
17	Experimental & Theoretical/Simulation Model	The following were investigated: (1) the removal of SO ₂ from seawater in a spray tower, (2) the effect of: (a) the flow rate of liquid to gas, (b) the initial concentration of SO ₂ in the gaseous phase, (c) the initial gas temperature and (d) the nozzle type, relative to the SO ₂ removal efficiency.	(1) The effective factors in order of importance are: (a) the liquid flow, (b) the gas flow, (c) the SO ₂ concentration in gas phase and (d) the inlet gas temperature. (2) At high gas temperatures, an increase in evaporation rate leads to an increase in resistance against SO ₂ transfer from gas to liquid phase up to a distinctive temperature. (3) The suitability of seawater for SO ₂ absorption in spray towers was revealed.	[78]
18	Theoretical/Cost-benefit analysis.	The costs and benefits of the two SO _x reduction methodologies were examined: (a) SO _x scrubbers and (b) use of MGO.	(1) Investing in MGO on a container ship tends to be more attractive than SWS. (2) The SWS installed on a new ship is generally more attractive than on an ex-post. (3) An old ship is not suitable for scrubber installation when its remaining life is less than 4 years.	[79]
19	Theoretical/Cost-benefit analysis.	The main goal of the study was to identify the best options, i.e., the lowest reduction costs depending on its type, size and functional model.	(1) For ships with high fuel consumption, on-board cleaning and continuous HFO use provide the lowest cost. (2) In a case with crude oil prices below USD 50 per barrel, diesel is an interesting reduction option for smaller vessels currently using HFO. (3) The desulfurized HFO has production costs which make it a competitive reduction option for all ships except the largest fuel consumers. (4) With scrubber systems, it encourages the operation of vessels at higher speeds. Fuel consumption and CO ₂ emissions per ton increase as higher speeds require more power input in proportion to the transport work performed.	[80]
20	Theoretical/Literature Review	The environmental impacts of exhaust gas scrubber discharge were investigated.	(1) It is not clear whether scrubbers will become the standard way to reduce air pollution from shipping for decades to come. (2) It is not clear whether scrubbing systems are currently the most environmentally friendly technology. (3) Important information is provided on policy recommendations and on removing operational and investment uncertainty for the shipping industry.	[81]
21	Theoretical/Case Study	Two technologies used for reduction SO _x emissions, i.e., (a) low sulfur fuel and (b) scrubber were elaboratively examined.	Comparing the technologies, it is observed that: (1) the technology chosen does not matter because each will require additional costs, i.e., capital cost and operating cost, loss of profits due to reduced load capacity; (2) the evaluation of the return on investment should be carried out by comparing the different technologies (in this case scrubber and low sulfur fuel) that meet the requirements of MARPOL 73/78; (3) the effectiveness of the investment in technology was assessed by cash flow modeling during the invoicing period covering the period from the introduction of the technology to the completion of the fiscal year.	[82]

Table 5. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
22	Theoretical/Case Study	The repercussions of smokestack and scrubber release of acidic oxides in the Baltic Sea were thoroughly examined.	(1) As shipping is projected to become a major source of strong acid deposition in the Baltic Sea, the long-term effects on pH and alkalinity have been shown to be significantly lower than estimated from previous scope studies. (2) An important contribution to this difference is the effective extraction of acidification of surface waters.	[83]
23	Theoretical/Case Study	The well-to-wake energy consumption and GHG emissions of several major SO _x abatement solutions used in marine transportation were investigated.	(1) An HFO scrubbing system has the potential to reduce SO _x emissions with lower energy consumption and greenhouse gas emissions compared to the transition to low sulfur fuel production at the refinery. (2) A sensitivity analysis covering a number of system parameters revealed that fluctuations in the intensity of greenhouse gas emissions from the tank and the energy efficiency of the main engine have the highest effects on emissions.	[84]
24	Theoretical/Report	All available restrictions on the process of selecting fuels and propulsion equipment for maritime compliance with the IMO regulations on SO _x emissions were examined.	The specific study: (a) provides various alternatives for compliance with “global sulfur cap 2020”, and (b) the advantages and disadvantages of each method were highlighted.	[85]
25	Experimental	The following methodologies used to control exhaust emissions in marine diesel engines were examined, i.e., (a) using only seawater, (b) electrolysis with electrolyzed alkaline seawater.	(1) With a seawater scrubber system. SO _x removal could be achieved nearly perfectly leading to a sufficient reduction of PM. (2) Seawater electrolysis is more suitable for absorption of NO _x and CO ₂ .	[86]
26	Theoretical/Simulation Model	The mechanism of SO ₂ seawater absorption was investigated.	(1) The absorption capacity of typical seawater is about twice that of brackish water with almost zero salinity. (2) The absorption capacity decreases with both salinity and alkalinity. (3) The cleaning efficiency of 66%, which corresponds to compliance with the limits of the SO _x emission control zones (SECA) when operating on fuel containing 4.5% <i>w/w</i> sulfur, requires a minimum water flow rate of 40–63 kg/(kWh depending on the composition of the seawater in terms of salinity and alkalinity.	[87]
27	Experimental	(1) A comparative study between seawater and distilled water was carried out to examine the effect of seawater alkalinity. (2) The liquid phase was analyzed for alkalinity, pH and sulfate content before and after the tests. (3) The spray droplet size distribution was measured as a function of fluid flow rate.	(1) Seawater performed better than distilled water, taking advantage of its inherent alkalinity. (2) The desulfurization efficiency was improved by increasing the liquid flow rate and gas residence time and by decreasing the SO ₂ concentration.	[88]

Table 5. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
28	Theoretical/Simulation Model	The heat and mass transfer process occurring in a seawater scrubber for marine application was comparatively investigated.	(1) A DPM (discrete phase model) was chosen for this case to simulate a real scrubber prototype. (2) Important information was given concerning the droplets trajectory, the velocity and the temperature inside the scrubber system.	[89]

4.2. Wet Scrubbers Integrated in Marine EGR Systems

As already mentioned, the main objective of the exhaust gas recirculation is the reduction of NO_x values emitted from marine compression ignition engines. During engine tests with the EGR system by a large engine manufacturer [34,35], reductions of NO_x emissions higher than 85% compared to the conventional diesel operation were observed but with simultaneous significant deteriorations of specific fuel oil consumption and CO emissions [90]. The operation of a marine diesel engine at low engine loads, though that it can be a problem for the effectiveness of other NO_x mitigation technologies such as SCR, appears not to cause major problems in the case of EGR [91,92]. The installation of an EGR system with the integrated closed-loop scrubber contributes not only to the reduction of NO_x emissions but also to the reduction of SO_x emissions [93,94]. It also contributes to the avoidance of wear and corrosion of the engine metallic parts from exhaust gases [95,96]. However, in this case the closed-loop NaOH scrubber mitigates SO_x emissions only from the recirculated exhaust gas stream, and as a result, the contribution of the SO_x scrubber to the reduction of the total emitted SO_x amount is limited (typical EGR rate for marine applications: 20% to 40% of the total exhaust gas quantity at each operating condition of the marine diesel engine) [97–99].

4.3. Inert Gas Wet Scrubbers

Inert gas scrubbers are designed to process high quantities of satisfactorily cooled inert gas (typically the available designs of corresponding scrubbers vary from 2000 to 30,000 Nm^3/h). The scrubbing part of inert gases has a high degree of sulfur and particulates capture due to the consumption of large quantities of alkaline water. The SO_2 percentage of inert gas is typically less than 100 ppm, and it has resulted from a flue gas concentration of 3000 ppm. The relative reduction of SO_2 depends on the fuel that is used on the exhaust gas boiler. The efficiency of inert gas scrubbers regarding soot removal is higher or equal to 99% for soot particles higher than 1 μm . O_2 , CO_2 and NO_x percentages are like the ones that come out from diesel exhaust gas scrubbers and are not seriously affected from the scrubbing process of the inert gases [36].

4.4. Dry SO_x Scrubbers

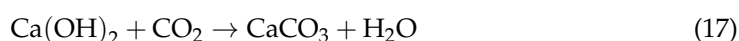
According to published data [36], in experimental tests of dry exhaust gas cleaning systems, the SO_x capture rate reaches almost 99%. Specifically, these tests have shown that fuel with 4.5% sulfur after a dry exhaust gas treatment had SO_x emissions equal to the ones of fuel with 0.1% sulfur content. The removal percentage of particulate matter in the previously mentioned tests reached almost 80%. The packing material bed and the packing material porosity operated as soot particles filters. In the specific tests, only the capture of higher size soot particles was assessed [30,36].

An advantage of dry exhaust gas treatment systems is their ability for installation and operation in combination with an SCR system used for NO_x emissions mitigation. As the exhaust gas treatment process in the packing material bed releases heat, the exhaust gas stream is removed from the dry gas processing bed with an ideal temperature for optimized exhaust gas processing in the SCR unit. In these integrated dry SO_x capture system and SCR system for NO_x removal from exhaust gases, the SO_x emissions will be

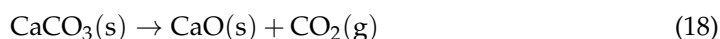
cleaned before they enter the SCR unit. This results in the reduction of SCR unit size and the higher anticipated lifetime of the SCR unit catalyst [30,36].

The most toxic substance for the operation of the SCR unit is SO_3 . SO_3 reacts with ammonia (NH_3), and this leads to the production of ammonium sulfate which can cause fouling of the SCR unit catalyst. The lower the sulfur percentage in the exhaust gases that enter the SCR unit is, the higher the anticipated lifetime of the SCR catalyst. The SCR unit can also operate at lower temperatures without the risk of fouling when the sulfur percentage in exhaust gases is low. A SCR unit can remove 80% to 95% of NO_x emissions from the exhaust gas stream practically making the strictest IMO NO_x limits (Tier III) at least at high engine loads, which are required for the optimized operational performance of the SCR unit [30,36], achievable.

Theoretically, the dry exhaust gas treatment unit also has the capacity for CO_2 removal. This can be attained based on the following chemical reaction:



However, this will result in higher CO_2 emissions at the end because the limestone is produced with limestone calcification at 900°C , as follows:



The produced calcium oxide (CaO) undergoes cooling and hydrogenation.

4.5. Selective Catalytic Reduction—SCR

It is quite interesting to compare the NO_x reduction potential of SCR to other NO_x reduction technologies, which can either be implemented inside marine diesel engines or in the exhaust of marine diesel engines [100–102]. Such a comparison will facilitate the assessment of the comparative effectiveness of SCR compared to other alternative NO_x reduction technologies [103–105]. For this reason, in Figure 10 the NO_x reduction potentials of different NO_x mitigation technologies are shown. These are implemented either inside diesel engines (called “internal measures”), or outside diesel engines in their exhaust line (called “external measures”). Figure 10 shows the lower and the higher limit of the NO_x reduction potential variation of each technology [60].

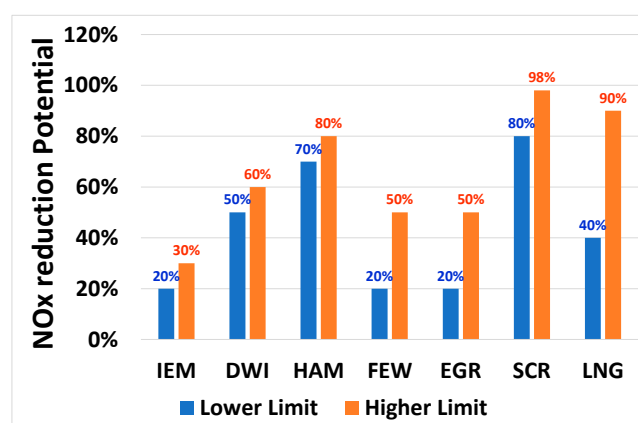


Figure 10. Comparison of the NO_x reduction potential of various technologies that are implemented inside diesel engines (internal measures) and outside diesel engines at their exhaust (external measures). IEM means internal engine modification. All other abbreviated NO_x reduction technologies have already been explained in the main text. (Figure was genuinely generated using data from ref. [60]).

At this point it is important to review several important theoretical and experimental studies that have been performed to assess the operational behavior of marine SCR

systems and to quantify their performance characteristics. The results of this targeted literature review are consolidated in Table 6, which contains 15 already published studies. In Table 6 for each study, its type is shown (theoretical, experimental or review study) along with its main objectives, and its main conclusions and its citation. As evidenced from the examination of Table 6, the key objectives of these studies were the examination of the impact of marine SCR catalysts on NO_x emission reduction in contrast with other NO_x reduction technologies that can be implemented inside marine engines (i.e., internal measures) and the assessment of the performance characteristics and the NO_x reduction efficiency of marine SCR catalysts. The most important findings of the studies shown in Table 6 are that marine SCR catalysts are highly effective in curtailing NO_x emissions that are generated from combustion systems installed in various types of vessels, and their NO_x reduction efficiency is considerably higher compared to all available NO_x reduction measures that can be implemented inside marine engines and marine combustion systems such as EGR, humid air motor or conversion of conventional combustion systems to operate with LNG. Hence, a SCR catalyst is proven to be the most effective means for reducing NO_x species generated from marine engines and marine combustion systems with, however, considerations about its investment and operational cost.

Table 6. Consolidation of the review results for marine SCR systems. For each published study listed in this table is shown by type (theoretical, experimental or review study), its main objectives and its main conclusions along with its reference.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
1	Experimental	The performance indicators of a marine SCR catalyst was investigated.	(1) Substrates must be durable to: (a) survive the high sulfur content of marine fuels and (b) provide cost and pressure drop benefits. (2) Extruded honeycomb substrates offer advantages in system volume and provide increased catalyst surface (in direct compensation with increased pressure drop). (3) Higher cell densities can be more easily clogged by the deposition of soot and/or sulfate particles on the inlet surface of the monolithic converter as well as on the channel walls and catalyst coating, ultimately leading to unacceptable flow restriction or catalytic flow suppression.	[106]
2	Theoretical/Simulation Model	The control rules in an SCR-DeNO _x installation for a marine diesel engine working at full load conditions were elaborated.	The velocity distribution at the inlet of the catalyst layers, which can be affected by the position, size and angle of the gate leaves, plays an important role in the NO _x removal efficiency of SCR systems.	[107]
3	Theoretical/Simulation Model	The operational performance of a compact diesel after-treatment system combining an SCR system with a reactive muffler was investigated.	(1) The system is capable of increasing NH ₃ homogeneity and improving NO _x reduction efficiency. (2) In the integrated SCR—muffler, the pressure loss was significantly increased compared to a simple SCR system.	[108]

Table 6. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
4	Theoretical/Assessment Study	The effects of the main important characteristics (i.e., composition, temperature, etc.) of the exhaust gases from a low-speed marine diesel engine on the performance characteristics of a SCR system were investigated.	(1) The weighted average NO_x value of the low sulfur exhaust gas complied with the requirements of the IMO Tier III regulations when the low speed diesel engine was mated to the high pressure SCR system. (2) The weighted average NO_x value under the high sulfur exhaust was slightly higher than that required by the IMO Tier III. (3) For both strategies, the engine exhaust performance meets the requirements of the IMO Tier III. (4) The cleaning bypass configuration design appears to have less impact on the initial performance of the engine.	[109]
5	Theoretical/Simulation Model	For marine SCR applications, the effect of static mixer geometry on flow mixing and pressure drop was investigated.	(1) Regardless of the type, the presence of a mixer leads to an improvement of the mixing efficiency by about 20%. (2) There was a compensatory relationship between uniformity and pressure drop. (3) In terms of mixing efficiency and pressure drop, the vortex type stirrer seems to be more suitable than the line type mixer.	[110]
6	Experimental and Theoretical/Simulation Model	The operational impact of a marine SCR-urea system on the reduction of NO _x emissions was examined.	(1) The increase of the catalyst length leads to an increased total denitrification rate. (2) The increased length of the catalyst negatively affects the oxidation reaction rate of ammonia.	[111]
7	Experimental	The operating principles (a) and the behavior concerning the NO _x reduction, of a scrubber system (components: exhaust heat exchangers, catalyzed particulate filter (CPF), diesel oxidation catalyst (DOC), packed bed wet scrubber), working on the principle of absorption of NO _x species into water (b) were examined.	(1) NO_x emissions absorption ranged from 4–66%. (2) The average NO_x absorption of the cycle ranged from 15–58%. (3) NO_x absorption varies depending on: (a) the residence time of the gas, (b) the absorption surface, (c) the temperature and (d) the NO_x concentration.	[112]
8	Theoretical/Simulation Model	The control strategy of a marine SCR system was examined.	Nitrogen oxide slip function control requires a massive pre-study of the catalyst NO _x reduction capacity to set an appropriate control target for each operating condition.	[113]
9	Theoretical/Simulation Model	The transient thermal response of a high pressure SCR system for a Tier III two-stroke marine diesel engine was investigated.	(1) It is possible to predict the thermal response of a marine SCR after-treatment system under transient engine loading conditions. (2) It is possible to predict the transient inertial response of the SCR during acceleration, deceleration, and operating conditions of the low load engine.	[114]

Table 6. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
10	Experimental	The effect of the use of $\text{Na}_2\text{S}_2\text{O}_8$ -urea on NO removal from diesel engine exhaust gas was experimentally elaborated.	(1) NO removal efficiency increased with increasing reaction temperature and increasing $\text{Na}_2\text{S}_2\text{O}_8$ concentration. (2) NO removal efficiency increased with increasing urea concentration. (3) The NO removal efficiency increased with the increase of the initial pH value, while the proposed solution also has a positive effect (reduction) on the nitrate concentration in the effluent.	[115]
11	Theoretical/Simulation Model	The impact of the use of $\text{Na}_2\text{S}_2\text{O}_8$ -urea on NO removal from diesel engine exhaust gas was numerically examined.	(1) The increased level of turbulence intensity in combination with the increased residence time in the chamber positively affect (increase) the rate of urea decomposition reaction. (2) The increased level of turbulence intensity increases the NH_3 conversion rate leading to improved NO_x reduction efficiency of the system. (3) It is possible to reduce the length of the chamber by 55% without significantly reducing the NO_x reduction efficiency.	[116]
12	Theoretical/Simulation Model	(a) The structural optimization and the design evaluation of a high pressure SCR system and (b) The influence of the structural configuration and dimension parameters of the flow-guiding devices to the exhaust flow were studied.	(1) Pressure losses between the front and rear of the flow guide device were the predominant source of total pressure loss. (2) The vaporizer/mixer installed with irregular animal plates was good for the NH_3 mixing effect. (3) It is necessary to optimize the shape and configuration of the flow guide device.	[117]
13	Theoretical/Simulation Model	After the optimization of a high-pressure SCR system the following elements of the catalytic process were taken into consideration: (a) the concentration uniformity, (b) the linear velocity, (c) the total pressure loss, (d) the concentration distribution of NH_3 , NO and NO_2 and (e) the catalytic kinetics of the NO_x reduction reaction.	For the optimized high-pressure SCR system: (1) the concentration of NH_3 and the flow uniformity of the catalyst section against the wind met the design requirements of the HP-SCR system. (2) the pressure loss of the SCR catalyst layer accounted for about 40% of the total pressure loss. (3) The weighted average NO_x emission value behind the HP-SCR system was found to be 2.67 g/kWh, which meets the IMO Tier III NO_x limits.	[118]
14	Experimental	The operational performance of a diesel oxidation catalyst (DOC) installed upstream to the SCR coated DPF (SDPF) in a compact exhaust after-treatment system (EATS was elaborated).	(1) The combination of vanadium-based coatings and DPF substrates leads to a significant degradation of SCR performance. (2) The combination of DPF, consisting of silicon and vanadium carbide coatings, reveals sufficient NO_x reduction and sufficient sulfur resistance. (3) In the SDPF system, a remarkable production of NO_2 was recorded, which allows the passive regeneration of soot.	[119]

Table 6. Cont.

No.	Type of the Study	Main Objectives of the Study	Main Conclusions of the Study	Reference
15	Experimental	The operating performance of an electrostatic water spray cleaner was studied to evaluate its efficiency for the simultaneous removal of NO _x and diesel particles (DPM).	Overall, the electrostatic water spray purifier seems to be a promising alternative method for controlling DPM emissions by both mass and number. Especially: (1) For a given gas flow rate, the removal of the DPM is enhanced by increasing the applied voltage. (2) The overall DPM removal efficiency was higher than 97% due to electrostatic attraction. (3) The removal of NO _x emissions depends on the chlorine concentration in the seawater and the engine loads.	[120]

5. Economic Evaluation of Marine Exhaust Gas Treatment Systems

5.1. Wet Open-Loop and Closed-Loop Scrubbers

The capital cost of the installation of a SO_x scrubber on a vessel depends heavily on the size of the main and the auxiliary engines, the type of fuel, and the investment cost of the on-board constructional modifications that are required for the installation of the SO_x capture system [121]. According to the literature, the capital cost of an aqueous SO_x scrubber used for the exhaust gas treatment from 1 MW power diesel engine, can be close to USD 1 million, whereas the corresponding cost for an aqueous SO_x scrubber that can be installed in the exhaust of a 20 MW power diesel engine range from USD 3 to 5 million [122]. Additional economic data are related to the energy consumption of the exhaust gas treatment system. This energy consumption cost obviously will mainly depend on the size of the main and the auxiliary engines and so from the size of the SO_x scrubber. Indicative results for the power consumption (in kW/MW of engine power) of a hybrid aqueous SO_x scrubber, a seawater SO_x scrubber, and a freshwater scrubber are provided in Table 7 [36].

Table 7. Power consumption of three types of SO_x scrubbers. (Table was genuinely generated using data from ref. [36]).

SO _x Scrubber Type	Power Consumption (kW/MW of Engine Power)
Hybrid scrubber	10–23
Seawater scrubber	10–30
Freshwater scrubber	6–110

Indicative results for the operation cost of a hybrid SO_x scrubber, a seawater scrubber, and a freshwater scrubber that have been collected by Gregory and West [32] considering combustion of heavy fuel oil with 2.7% sulfur content for 300 days/year, are shown in Table 8 [36].

The exhaust gas treatment system and its mechanical devices (pumps, pipelines, valves etc.) are exposed to a corrosive environment, especially in the case of seawater use in the SO_x scrubber, which can corrode equipment from gray steel and stainless steel, e.g., SS316 steel. The manufacturers of scrubbing equipment faced with the corrosive effect of the SO_x capture chemical substances in different ways. Some use nickel alloys, whereas others use titanium or nonmetallic material such as epoxy material and composites. The gradual degradation of the constructional quality and the potential replacement of the exhaust gas treatment installation will raise the total cost of the construction materials further burdening the carbon footprint of the exhaust gas treatment system [32].

Table 8. Operation cost of three types of SO_x scrubbers. The classification has been made based on the operational principle of each system. The values have been obtained from corresponding manufacturers of these systems. (Table was genuinely generated using data from refs. [32,36]).

SO _x Scrubber Type	Operation Cost
Hybrid scrubber	Not available
Seawater scrubber	3% of the investment cost
Freshwater scrubber	5 USD/MWh
	≈0.5 to 2.5 × 10 ⁶ USD

In a previous study [47], an effort was made to estimate the cost per emission ton, which is reduced with SO₂ reduction techniques in the engine exhaust compared to the change from a high sulfur fuel to a low sulfur fuel. The alternative scenarios that were examined in this study are the following [47]:

- Use of a seawater SO_x scrubber.
- Change from heavy fuel oil with 2.7% sulfur to marine fuel with 1.5% sulfur.
- Change from heavy fuel oil with 2.7% sulfur to marine fuel with 0.5% sulfur.

In the specific study [47], the previously mentioned SO₂ emission reduction scenarios were examined by considering the following SO₂ capture percentages:

- Use of a seawater SO_x scrubber: 75%.
- Change from heavy fuel oil with 2.7% sulfur to marine fuel with 1.5% sulfur: 44%.
- Change from heavy fuel oil with 2.7% sulfur to marine fuel with 0.5% sulfur: 81%.

The results of the previously mentioned study [47] are presented in Table 9.

Table 9. Cost per ton of emitted pollutants reduced from the use of seawater scrubbers and from the change to low sulfur fuel. (Table was generated using data from refs. [36,47]).

SO _x Reduction Measure	Vessel Type	Small Size Vessel (€/ton SO ₂)	Medium Size Vessel (€/ton SO ₂)	Large Size Vessel (€/ton SO ₂)
Seawater scrubber	New building	390	351	320
Seawater scrubber	Retrofit	576	535	504
Fuel change from 2.7% sulfur to 1.5% sulfur	New building/Retrofit	2053 (1230)	2050 (1230)	2045 (1230)
Fuel change from 2.7% sulfur to 0.5% sulfur	New building/Retrofit	1439 (1690)	1438 (1690)	1434 (1690)

The previously mentioned calculations [36,47] fall with further uncertainties such as:

- Intrinsic variations of the retrofit cost due to the special characteristics of each vessel.
- The maintenance levels of the mechanical equipment.
- The operating conditions and the loading factors of each vessel.
- Variations in the sulfur contents of all examined fuels.

Reynolds [46] in a second study examined the cost advantage of the exhaust gas treatment systems compared to the change from a fuel with high sulfur content to a fuel with low sulfur content, and he concluded that with 2015 as a starting year, the vessels that are consuming at least 4000 metric tons of fuel per year inside Emission Control Areas (ECAs) should use an exhaust gas treatment system. The specific study [46] further reports that a key turning point in the differences of the fuel costs is when the fuel sulfur contents become so small that their removal from the marine fuels is either impossible or has extremely high cost. It is considered that fuel sulfur contents equal to or lower

than 0.5% require oil refinery products with extremely high production cost, or the use of alternative technologies such as exhaust gas treatment systems or LNG. The critical part in any calculation of this cost advantage heavily depends on the predictions and assumptions of the fuel prices and on the gap between the alternatives of the high and low fuel sulfur content. Ship operators are encouraged according to the study of Reynolds [46] to utilize their predictions for the fuel cost differences because the cost analysis is significantly sensitive to the variations of the fuel cost.

Of interest are the statistical data for the installation schedule, management, and cost of seawater scrubbers in a fleet of commercial vessels, which were made available to us by a Greek maritime company [123]. Table 10 lists data for scrubber delivery date, the vessel estimated time of arrival (ETA) in Shipyard 1 and the corresponding Shipyard 1 indicated cost for nine different vessels of a Greek maritime company [123]. Here, it should be noted that the names of the vessels and the names of shipyards are classified and cannot directly be released due to confidentiality reasons. Therefore, they are named with numbers, e.g., VSL 1, VSL 2 or Shipyard 1, S Shipyard 2, etc. As evidenced from Table 10, the indicative yard installation cost ranges from USD 540,000 to USD 635,000 depending on the vessel capacity. Data for seawater scrubber purchase cost, scrubber maker, and scrubber indicative installation cost for 16 different vessels of a Greek maritime company [123] are listed in Table 11. As evidenced from Table 11, the scrubber purchase cost ranges from USD 980,000 to USD 1,091,475 and can be considered relatively high, whereas the scrubber installation cost is close to USD 600,000. Thus, the total scrubber purchase and installation cost is estimated to be close to USD 1,600,000 for the examined vessels [123]. Hence, it can be concluded that the installation of seawater SO_x scrubbers in a fleet of vessels is a time-consuming and costly procedure which requires significant management and coordination of skills and effort.

Table 10. Data for scrubber delivery date, Shipyard 1 vessel estimated time of arrival (ETA) and Shipyard 1 indicative cost for nine different vessels of a Greek maritime company. (Table was genuinely generated using data from ref. [123]).

	VSL Name	DWT	Scrubber Delivery Date	Scrubber Delivery Location	Scrubber Arriving China	VSL-ETA	Yard 1—VSL-E TA	Yard 1 Indicated Cost \$
1	VSL#1	92K	30 June 2019	EUROPE	30 August 2019	25 August 2019	25 August 2019	635.K PLUS
2	VSL#2	82K	15 July 2019	EUROPE	15 September 2019	10 September 2019	10 September 2019	590.K PLUS
3	VSL#3	82K	31 July 2019	EUROPE	30 September 2019	26 September 2019	30 November 2019	540.K PLUS
4	VSL#4	82K	31 July 2019	EUROPE	30 September 2019	26 September 2019	30 November 2019	540.K PLUS
5	VSL#5	82K	31 July 2019	EUROPE	30 September 2019	27 September 2019	07 October 2019	540.K PLUS
6	VSL#6	82K	31 July 2019	EUROPE	30 September 2019	28 September 2019	15 December 2019	540.K PLUS
7	VSL#7	92K	15 October 2019	CHINA	20 October 2019	20 September 2019	15 October 2019	635.K PLUS
8	VSL#8	92K	22 September 2019	CHINA	27 September 2019	22 September 2019	22 September 2019	635.K PLUS
9	VSL#9	92K	30 September 2019	CHINA	5 October 2019	29 September 2019	29 October 2019	635.K PLUS

Table 11. Seawater scrubber purchase cost, scrubber maker and scrubber indicative installation cost for 16 different vessels of a Greek maritime company. (Table was generated using data from ref. [123]).

	VSL Name	Scrubber Cost	Scrubber Installation Cost
1	VSL#1	\$1,149,225	\$580,000
2	VSL#2	\$1,091,475	\$580,000
3	VSL#3	\$1,091,475	\$580,000
4	VSL#4	\$1,091,475	\$580,000
5	VSL#5	\$1,085,700	\$580,000
6	VSL#6	\$1,027,950	\$580,000
7	VSL#7	\$1,027,950	\$580,000
8	VSL#8	\$1,027,950	\$580,000
9	VSL#9	\$1,027,950	\$580,000
10	VSL#10	\$1,027,950	N/A YET
11	VSL#11	\$1,027,950	N/A YET
12	VSL#12	\$1,200,000	\$600,000
13	VSL#13	\$1,200,000	\$600,000
14	VSL#14	\$980,000	\$580,000
15	VSL#15	\$980,000	N/A YET
16	VSL#16	\$980,000	N/A YET

5.2. Wet SO_x Scrubbers Integrated in EGR Systems

The stage of development of EGR technology does not yet allow its detailed economic assessment. One crucial factor that will affect the rate of development of EGR systems and possibly their future market price is whether the EGR technology will succeed in providing NO_x emissions from large two-stroke marine diesel engines, which will satisfy the strictest IMO standards (Tier III) for ships operating inside Emission Control Areas. Up to now, the ER technology is considered a most promising technology regarding the achievement of Tier III standard [124,125].

5.3. Wet Inert Gas Scrubbers

There are no available specific economic data in the literature for the market prices and the operation cost of inert gas scrubbers. However, the power consumption of these systems is reported to be 0.01 kW per Nm³/h of gas, and it depends on the special power consumption requirements of the pumps of each installation.

5.4. Dry SO_x Scrubbers

The commercially available dry exhaust gas treatment systems have the following indicative investment cost values [36,126]:

- For 1 MW power engine, the investment cost is USD 0.5 million.
- For 20 MW power engine, the investment cost is USD 4 million.

Taking into consideration the relatively low values of investment cost compared to the available information for the dry SO_x scrubbers, the most important conclusion is that these prices vary almost at the same levels with the pertinent investment costs of the aqueous SO_x scrubbers.

In addition, the corresponding annual operation costs of the dry exhaust gas treatment and SO_x capture systems according to published data [36,127] are the following:

- For 1 MW power engine, the annual operation cost is USD 43,500.
- For 20 MW power engine, the annual operation cost is USD 477,200.

These operation costs include power consumption cost, packing material cost, maintenance cost, and labor cost. It appears from the accumulated information for the dry exhaust gas treatment systems that one significant advantage of these systems is power consumption. A general picture about the power consumption of the dry SO_x capture systems is that it reaches up to 10% of the corresponding power consumption of an aqueous SO_x mitigation system for similar diesel engine power (1.5–2 kW/MW of engine power) [128,129]. The previously mentioned prices do not include energy consumption for production, transport, and distribution of the packing materials that the dry exhaust gas cleaning systems require to be efficient [36,130,131].

The preferred handling process of the used packing material is the removal of the packing material from the dry exhaust gas treatment system with a remaining pollutant capture activity. This residue can be an attractive product for the desulfurization of high temperature flue gases generated from land-based industrial installations. Therefore, the used packing material in most of the cases will not contribute negatively to the total lifetime cost of the dry exhaust gas cleaning and SO_x mitigation systems [132].

5.5. SCR Systems

The continuous development of SCR technology and its increasing market share has led to a reduction of its investment cost. In addition, the stabilization of the materials cost with the parallel increase of the market demand denotes an increase of the SCR system installations, which creates competition in the market and reductions in the investment cost of these systems. This led to higher availability of SCR systems at more reasonable purchasing prices [60].

The International Association for Catalytic Control of Ship Emissions to Air (IACC-SEA) developed an estimation model for the installation and operation cost of SCR systems. The application of this model provides an indicative calculation of the investment cost and of the operation cost, as well as of the benefits that are expected from the SCR marine applications [60]. Using as example a 10 MW power diesel engine, which provides propulsion to a 20,000 DWT vessel, uses HFO and operates 1500 h annually in NECAs, the total investment cost (including the installation cost of the system) will be approximately USD 725,000. The highest portion of the operation cost required for the fulfillment of the IMO Tier III standards initiating from a higher level of NO_x emissions equal to the IMO Tier I standards, will vary from USD 3 to 5 million depending on the urea cost, whereas the recharging of the catalyst will require USD 500,000. In addition, there will be a deterioration of the fuel consumption due to the increased back pressure to the engine exhaust from the operation of the SCR system, and there will also be a potential efficiency improvement of the engine when the cooperative operation of the engine and the SCR system is optimized [60].

Without taking into consideration that the deterioration of the specific fuel oil consumption due to the back pressure from the SCR system operation will be approximately 2%, the improvement of the specific fuel consumption by 4% due to the optimized operation of the marine diesel engine and SCR system combined installation will lead to a fuel cost saving of approximately USD 625,000. This is equal to a total (without discounts) operation cost that varies from USD 104,000 to USD 224,000 dollars per year or approximately 900 to 2000 per ton of reduced NO_x emissions [60].

It is expected that the operation cost of marine SCR systems will continue to decrease. This conclusion is drawn because there is a reduction tendency of the operation of SCR systems used in land applications. Taking into consideration a small degree of uncertainty, the cost for the ammonia-based reagents has stayed relatively constant during the last few years, whereas the catalyst unit cost has decreased in the USA by almost five times between 1980 and 2005. It is estimated that it will stay almost constant until 2015 for new catalysts and will slightly be decreased for the regenerated catalysts. The expected lifetime has been increased from 1 to 10 years, contributing to the realistic reduction of the operation and maintenance cost of the SCR systems [60].

The operational efficiency of SCR systems that are used for NO_x mitigation in land-based coal-fired electric power stations from the mid-1980s until 2000 has been increased, the investment cost has been decreased by 86%, and the operation and management cost has been reduced by 58% compared to the initial values. The future estimates for the continuous regeneration of SCR systems predict an additional investment cost reduction of 7.4%, and a corresponding operation and maintenance cost reduction by 15.8% until 2020. The variations of the SCR technology cost that have been evaluated in these analyses reflect the effect of the technological developments, and the competition on the investment cost and on the operation cost of the SCR systems, which are linked with the continuous stringent environmental limits that motivate the technological development and evolution. This phenomenon has appeared in the SO_x reduction technologies, also denoting that the application of the continuous stringent environmental regulations and limits will lead to further investment cost and operation cost reductions of the exhaust gas treatment systems soon ahead [60].

In addition, to the already thoroughly described technologies considered for fulfillment of the global sulfur cap and the IMO NO_x Tier III limits, there are additional technologies already proposed in the literature, which can be used for seriously reducing NO_x values emitted from marine combustion systems. One of these technologies is the utilization of non-thermal plasma (NTP) in combustion-emitted exhaust gases for significantly reducing NO_x and SO_x emissions. According to Deng et al. [12], NTP technology can reduce NO_x and SO_x emissions by 60% and 80%, respectively. NTP technology can effectively oxidize nitrogen oxide to nitrogen dioxide in a SCR system and perform a fast reaction. Cho et al. [133] performed an experimental study for the reduction of NO_x emissions from a diesel engine with NTP in combination with a high pressure SCR system, and they observed that NTP technology can effectively improve the NO_x conversion efficiency of a SCR system at low temperature.

At this point, it is worth emphasizing that the broad use of either seawater scrubbers or closed-loop scrubbers with fresh water and NaOH and the broad use of SCR technology will drastically contribute to the elimination of the serious polluting issue of maritime vessels in all coastal countries of the world because it has been proven that maritime pollution can seriously impair nutrition and degrade the quality of air and waters. Characteristic is the example of China where, according to Liu et al. [134] and Zhang et al. [135], the detrimental effects of maritime pollution on local air and water quality can seriously be mitigated with the implementation of various shipping-related emission control measures such as marine EGTS such as the ones examined in the present review study.

6. Overall Comparative Assessment, Advantages, and Disadvantages

In the present review study, the operational principles and the construction specifications, the performance characteristics and the economic facts of modern marine exhaust gas treatment systems used for SO_x, PM, and NO_x mitigation, were thoroughly analyzed. The detailed analysis of the gaseous and particulate emission marine after-treatment systems resulted in the following conclusions for each pollutant mitigation system:

- Seawater scrubbers or open-loop scrubbers: These are heavy and bulky heat, mass, and momentum exchange systems between the exhaust gas stream and the seawater stream. Due to its alkalinity, the seawater stream can capture large quantities of SO_x, PM, and heavy metals from the stream of exhaust gases that are generated from the on-board combustion systems. The SO_x and PM mitigation efficiency depend heavily on the alkalinity of the local seawater, considering also that seawater alkalinity varies significantly around the world. The on-board installation of seawater scrubbers requires the existence of an impure scrubber-discharged water processing unit for the capture and on-board storage of the heavy residues and of the processed effluent water. Marine seawater scrubbers are bulky installations characterized by high complexity and parasitic losses due to the operation of their auxiliary equipment. Moreover, their operation is associated with significant corrosion to the engines and, in general, to

the machinery equipment in case of seawater leakages due to scrubber cracks. Hence, caution is required during their installation and their operation with continuous monitoring of the exhaust gas stream and of the seawater stream to avoid potential operational problems or heavy seawater leakage.

- Freshwater scrubbers or closed-loop scrubbers: These marine exhaust gas treatment systems operate under the same principle as seawater scrubbers. In this case, the variable alkalinity of the seawater is replaced by the almost constant alkalinity of the NaOH aqueous solution that circulates in the installation in a closed-loop. These systems require transport and on-board storage of fresh water and NaOH, and they indicate higher auxiliary requirements and thus parasitic losses compared to the open-loop seawater scrubbers. Closed-loop freshwater scrubbers have lower discharged impure water processing requirements compared to the open-loop systems because the quantity of effluent water discharged from the closed-loop scrubbers is lower compared to seawater scrubbers. Another virtue of a caustic soda scrubber is that the alkalinity of the scrubbing medium can be adjusted through the adjustment of the NaOH dosage unlike the open-loop scrubbers where their efficiency is exposed to the variable seawater alkalinity. Thus, closed-loop scrubbers can achieve higher SO_x capture rates compared to open-loop scrubbers, and they can also be highly effective in reducing SO_x emissions, even in the case of high sulfur marine fuels. Moreover, open-loop and closed-loop scrubbers require continuous monitoring of the pressure and temperature of the exhaust gas stream and the scrubbing medium stream to ensure reliable operation and to avoid leakage or excessive fouling of the scrubbers, which can create serious back-pressure issues and significant deterioration of the specific fuel oil consumption of the on-board engines.
- Hybrid scrubbers: These systems can operate as either open-loop or closed-loop scrubbers; they are large, heavy, and bulky installations, where the exhaust gas stream exchanges heat, mass, and momentum with the alkaline medium, which depending on the mode of hybrid scrubber operation can be seawater or caustic soda. Owing to their high complexity, high parasitic losses and high investment and operation cost, hybrid scrubbers have more limited application compared to open-loop and to closed-loop scrubbers.
- Aqueous SO_x and PM mitigation scrubbers that are integrated in EGR installations: These aqueous scrubbers are mainly used by one major marine engine manufacturer as heat exchangers to reduce the temperature of the recirculated exhaust gases before they are introduced back to the engine intake for curtailing in-cylinder NO_x formation rate. These integrated scrubbers cause not only a reduction of recirculated gas temperature but also manage to capture significant quantities of SO_x and PM emissions carried in the recirculated gas stream. For this reason, they are proposed by a large marine engine manufacturer as a technology capable of mitigating not only NO_x emissions but also SO_x and PM emissions. It should be emphasized, however, that the total SO_x emissions that are captured with the integrated scrubber, is considerably lower compared to a closed-loop or an open-loop scrubber because in the EGR scrubber the scrubbing medium interacts only with a portion ranging from 20% to 40% of the total exhaust gases generated from a marine engine at each operating point.
- Aqueous inert gas scrubbers: These scrubbers can process and capture SO_x and PM emissions from inert gases generated from the evacuation of oil tankers or chemical tankers, and for this reason they are suitable only for these limited applications.
- Dry scrubbers: The operation of these systems is based on the processing of the exhaust gas stream from a large dry surface SO_x and PM capture medium (usually, limestone). Dry exhaust gas treatment systems are used extensively for the processing of industrial flue gases in land-based installations, but their use in the maritime industry (if any) is very limited due to the problems associated with the supply and on-board storage of the limestone and the packing material.

- **SCR systems:** The efficiency of SCR systems is based on reaching the proper exhaust gas temperature at the entrance of the SCR reactor because the chemical reactions on the catalyst are optimized for a specific temperature frame. The control of exhaust gas temperature for optimized SCR system operation requires the installation and operation of exhaust gas temperature control devices in case the exhaust gas temperature is not suitable for optimized SCR operation such as in the case of low engine loads of a main marine two-stroke diesel engine. Today, marine SCR systems are highly effective in mitigating NO_x emissions, and in many cases, they can practically eliminate NO_x emissions, thus providing the opportunity for a vessel to comply with the strictest IMO NO_x Tier III limits. The main drawbacks of the marine SCR systems are their relatively high installation and operation cost, which is burdened by the installation of exhaust gas temperature control devices and by the supply and on-board handling cost of the urea.

In general, it can be stated that the modern aqueous SO_x scrubbers can attain SO_x capture rates that vary from 90% to 99% and hence can practically eliminate SO_x emissions from ships. As a conclusive remark, the SO_x capture rates per exhaust gas treatment and SO_x mitigation system are provided in Table 12. Specifically, Table 12 gives the sulfur contents that a maritime fuel should have after exhaust gas processing from an aqueous or dry exhaust gas treatment systems. The SO_x emissions should be equivalent to the ones generated from the combustion of a marine fuel with 0.1% sulfur content. From Table 12, it can be concluded that higher SO_x mitigation percentages appear in the case of a closed-loop freshwater scrubber and in the case of a dry scrubber [36].

Table 12. Consolidation of data for SO_x capture rate per type of exhaust gas treatment system. (Table was genuinely generated using data from ref. [36]).

SO _x Mitigation System	Maximum Fuel Sulfur Content for Which SO _x Emissions Are Attained, Which Are Equivalent to the Ones of Fuel with 0.1% Sulfur Content.
Hybrid SO _x scrubber	3–3.5%
Seawater SO _x scrubber	3.5%
Freshwater SO _x scrubber	3.5–5%
Dry SO _x capture system	4.5%

The continuous technological development, the competition in marine SO_x mitigation systems, and the high production cost of very low or ultra-low sulfur fuels from oil refineries around the world, the incapacity of efficient on-board mixing low-sulfur fuels with high sulfur fuels for fuel mixture sulfur content adjustment and the potential generation of residues from the on-board use of very low or ultra-low sulfur fuels, is anticipated to result in the broadening of the market share of marine exhaust gas treatments and SO_x and PM mitigation systems.

The increasing focus of the IMO for dramatic suppression or even elimination of marine NO_x emissions in combination with the continuous technological advancement and the intense commercial competition between SCR systems manufacturers is expected to lead to a significant reduction of costs of marine SCR systems soon.

7. Conclusions

In this investigation, the operational principles, the constructional specifications, the main performance characteristics, and the economic facts of marine EGTS were thoroughly described and discussed. The main conclusions of the present review study are summarized as follows:

- SO_x and PM scrubbers are the only possible current solution for complying with the IMO global sulfur cap in the maritime industry in case conventional high-sulfur fuels continue to be needed for marine combustion systems.
- Contemporary open-loop and closed-loop scrubbers are high effective in reducing SO_x and PM emissions, and they can practically eliminate SO_x emissions.
- In most vessel applications, open-loop seawater scrubbers are used because they are most cost-effective compared to closed-loop scrubbers, but their effectiveness varies with seawater salinity. On the other hand, closed-loop scrubbers are the most effective systems in reducing SO_x emissions mainly due to alkali dosage adjustment, but they have high operational cost compared to seawater scrubbers.
- SCR is the most effective EGTS for practically eliminating NO_x emissions generated from marine combustion systems. SCR systems are more effective in reducing NO_x emissions compared to all other engine “internal measures”. The operation of modern SCR systems in commercial vessels can lead to marine engines’ operation with output NO_x values considerably lower compared to the strictest IMO NO_x Tier III limits.

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