

Review

Selected Techniques for Cutting SO_x Emissions in Maritime Industry

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Abstract: Burning fuels with high sulfur content leads to SO_x emissions, especially SO₂, which leads to various environmental and health problems. The maritime sector is responsible for 13% of the global anthropogenic emissions of SO₂. Thus, the International Maritime Organization (IMO) has issued a protocol, known as MARPOL Annex VI, which aims to further limit SO₂ emissions derived from ships along with NO_x, particulate matter and volatile organic compound emissions. This has led ship owners and operators to choose between more expensive fuels with low sulfur content or to apply a DeSO_x solution, which still allows them to use the cheapest heavy fuel oil. The current work reviews the state-of-the-art DeSO_x solutions both for the maritime and land-based sector. Next, it proposes an alternative cheaper and environmentally friendly DeSO_x solution based on the selective reduction of SO₂ to elemental sulfur by utilizing a catalytic converter based on metal oxides, similar to the ones used in the automotive industry. Finally, it reviews the most promising metal oxide catalysts reported in the literature for the selective reduction of SO₂ towards elemental sulfur.

Keywords: sulfur; emissions; catalysis; reduction; marine; DeSO_x; ceria; copper; iron; MARPOL; IMO



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1. Introduction

Since the Industrial Revolution, fossil fuels such as coal, natural gas and oil have been almost exclusively covering the energy demands of our planet. Basic human needs such as transportation, communication and food production require large amounts of energy to be fulfilled, which keep increasing as the population rises. Unfortunately, however, the planet's pollution through air degradation resulting from the burning of fossil fuels had not been evident until recent decades. To that extent, several laws [1] and agreements [2] have been enforced, aiming for the decarbonization of our planet by 2050. Although this seems the right solution on paper, there are no mature technological solutions for carbon-free energy sources yet developed to be adopted in a worldwide scale. For the time being, energy derived from fossil fuels cannot be replaced for several technoeconomic reasons, driving the scientific interest towards the control and alleviation of pollution originating from carbon-based fuels. Indeed, most of the research interest has focused on carbon capture, storage [3] and CO₂ conversion [4] technologies, and although the majority of the scientific community is working on managing CO₂ emissions, there are still other equally severe pollutants that have not yet received adequate attention.

The following work focuses on summarizing all the developed and upcoming technologies to be utilized for the treatment of the SO_x emissions generated from maritime industry. The most efficient desulfurization methods and their pros and cons are being described and discussed under a technological perspective. The main disadvantages of the state-of-the-art method are being analyzed and catalytic systems are being introduced to replace them. Catalytic mechanisms and efficiency-affecting parameters for the desulfurization of flue gas streams have been analyzed and compared in detail, in order to conclude

and design the most promising and sustainable methods to decrease the sulfur content in the exhaust gas maritime streams.

Sulfur (S) is the most abundant heteroatom in crude oil, with varying content from 0.5 to 6 wt.%. Burning fuels with high sulfur content leads to sulfur oxide (SO_x) emissions, especially sulfur dioxide (SO_2), a colorless, odorless and corrosive gas, which is considered as a major environmental problem contributing to phenomena such as acid rain, the greenhouse effect, photochemical pollution and eutrophication [5–7]. In addition, SO_2 is a highly toxic gas responsible for premature human deaths caused by cardiovascular and respiratory diseases [8,9]. A study conducted by the marine environment protection committee (MEPC) predicted over 570,000 premature deaths due to SO_x emissions between the years 2020 and 2025 [10]. Another recent study showed that in 2014, with consideration to global fuel trade, the total global SO_2 emission from all sources (excluding natural sources such as volcanic eruptions) was estimated at 105.4 Tg/y (95.8–119.8 Tg/y), with a predominant contribution from anthropogenic sources at 98% [11]. Such anthropogenic emissions derive from the burning of coal and oil, rich in sulfur content, which are used at energy power plants, industrial combustion units (oil refinery and metal smelting), small combustion units in households and on road vehicles and ships. Most types of ships such as bulk carriers, tankers, containers and cruise ships are equipped with internal combustion engines (ICE) that utilize heavy fuel oil (HFO) with high sulfur content, about 3.5 wt.%. The maritime sector is estimated to contribute to around 13% of the global anthropogenic emissions of SO_2 [12]. According to IMO statistics [13], more than 90% of the world's trade is conducted through ocean transportation because of its strong transportation capacity and lower prices. Estimations dictate that up to 2024, international maritime transport trade will keep increasing annually at an average of 3.5%, faster than any other modes of transportation [14], also leading to an increase in SO_x emissions alongside other pollutants.

It is a fact that most developed countries have made progress in decreasing SO_2 pollution through different policies improving air quality over the last decades [15]. However, most developing countries such as China had failed, up until 2000, to impose strict regulations concerning SO_2 emissions to decrease the total amount of pollution per capita [16,17]. India, on the other hand, is the global leader in SO_2 emissions. In 2019, India emitted 21% of global anthropogenic (human-made) SO_2 emissions, nearly double that of the second-ranked global emitter, Russia. The total amount of pollution keep increasing annually [18], probably due to their increased energy demands, surpassing even China and the high population they exhibit and the lack of desulfurization units in the power plants [19]. In Europe, while land-based SO_2 emissions have started to decrease from the 1990s [20], emissions from international shipping in European waters have been increasing steadily [21], despite the fact that the maximum fuel sulfur limits have been greatly reduced over recent years. Specifically, from January 2020 the International Maritime Organization (IMO) has issued a new protocol, known as MARPOL Annex VI [10], which aims to limit NO_x , SO_2 , particulate matter (PM) and volatile organic compound (VOC) emissions. MARPOL was developed through the (IMO), a United Nations agency that deals with maritime safety and security, as well as the prevention of marine pollution from ships. MARPOL is the main international agreement covering all types of pollution from ships. More specifically, the latest protocol in force issues an upper limit of 0.50 wt.% sulfur content in the fuel oil used on ships operating outside designated emission control areas (ECAs). This limit was already stringent at the ECAs, at 0.1 wt.%. The Baltic Sea, the North Sea, the English Channel and the coasts of the US and Canada are considered such areas. By this measure, the reduction of SO_x emissions is expected to have major environmental and health benefits for the world, particularly for populations living close to ports and coasts.

However, such tighter regulations to counter SO_2 emissions have forced ship owners and operators to change their policy and choose between three different routes in order to comply with the new demands [22]:

- Switch to fuel oils with lower sulfur content than HFO, such marine gas oil (MGO) or very low-sulfur fuel oils (VLFO);

- Switch to alternative fuels such as renewable diesel, LNG, methanol (CH₃OH), ammonia (NH₃) and hydrogen (H₂);
- Consider a flue exhaust aftertreatment method that will reduce SO_x emissions, enabling them to still use the cheapest fuel (HFO).

Switching to fuels with low sulfur content sounds like the easiest and simplest DeSO_x solution. However, this might not be the most practical option for every ship due to the huge price gap between HFO and such oils. HFO is still the cheapest oil with a significantly lower cost around 300–400 USD/ton [23] compared to lower-sulfur fuel options. Taking into account that large cargo ships can burn more than 100 tonnes of fuel per day and cruise ships more than 200 tonnes of fuel per day, the price differential between high- and low-sulfur-content fuels is of prime economic importance. Lately, new carbon or/and sulfur-free alternative fuels have come into consideration, such as renewable diesel, methanol (CH₃OH), ammonia (NH₃) and hydrogen (H₂) [24–27]. The main conclusion of the above studies is that setting aside the need for modification of ships' systems and engines for the different storage necessities and requirements that these fuels have, the main problems such as premature commercial readiness, high toxicity, flammability or/and bunkering availability hinder these fuels to become widely accepted as a viable and sustainable solution in the near future [24–26].

The use of a neural-like structure of the successive geometric transformations model would facilitate the decision making for the appropriate integrated technical solution. The benefit of this method stems from the analysis of disadvantages of the known methods and missing data acquisition. Various simple and complex algorithms are enabled, among which are the arithmetic mean algorithm and regression modeling. It has been proven that the above-mentioned imputation techniques in data monitoring and processing of air pollution would allow for reliable results to be obtained due to high prediction accuracy. An example of filling data by forecasting CO, NO and NO₂ missed parameters in data monitoring of air pollution would be applied and the most suitable technology would be incorporated. The accuracy of this method is based on calculated evaluation criteria, advantages and disadvantages of the methods [28].

Until this method is applied, commercial solutions for the reduction of SO₂ emissions of engines using HFO have been developed, such as scrubbers [29,30]. Scrubbers utilize seawater by spraying it into the exhaust and discharging it overboard, often without treatment. Many research studies and organizations [30–32] have reported that in this way, the problem of air pollution is transferred to the oceans by polluting them with sulfuric acid and other pollutants such as polycyclic aromatic hydrocarbons and nitrates, which increase the temperature and lower the pH of the oceans. Due to the large volume of solid waste produced from such systems along with their high cost, large installation size and complex operation, scrubbers have not yet received adequate acceptance.

The aim of this review is firstly to give a brief picture of the current state-of-the-art DeSO_x technologies both for land-based applications and for ships. Secondly, the authors would like to highlight the potential role that heterogenous catalysis could have on countering SO₂ pollution, as it already has on NO_x emissions. Recently, much research has been conducted in developing selective catalytic reduction (SCR) catalysts for the reduction of NO_x, present in flue gasses, to N₂ [33–36]. In recent years, the selective reduction of SO₂ to solid elemental sulfur, a chemical with considerable economic value finding uses in the sulfuric acid and fertilizer production industries, has gained more attention but has not yet been widely adopted as a possible state-of-the-art solution for countering SO₂ emissions. Major challenges include the development of an active catalyst with high selectivity towards elemental sulfur, able to catalyze the SO₂ reduction reaction under conditions that coexist with flue gases streams such as temperature and reducing agents. We will try to address these challenges and review the most promising heterogenous catalysts that could be efficient for the reduction of SO₂ under such conditions.

2. Industrial Flue Gas State-of-the-Art DeSO_x Processes

The most notable wet technologies include:

- Wet desulfurization;
- Dry or semi-dry desulfurization;
- Bio-desulfurization.

Wet desulfurization technologies can achieve up to 99% desulfurization efficiency [37] and are applied at a wide scale, not only because of their effectiveness but also due to their technological maturity compared to the dry/semi-dry methods. On the other hand, they demand larger installation sites and have very high capital and operational cost. In wet process technologies, the first step is the interaction of flue gases with an absorbent in a vessel, usually called scrubber. Then, SO₂ reacts with the absorbent and dissolves into the solution, producing a slurry or liquid that contains sulfur compounds in a dissolved or solidified state. The most notable wet technologies include:

- Limestone (CaCO₃) or lime (CaO) sludge desulfurization process through gypsum (CaSO₄·2H₂O) production;
- Magnesium oxide (MgO) desulfurization through SO₂ adsorption and production of MgSO₄;
- Zinc oxide (ZnO) desulfurization process;
- Dual-alkali desulfurization process;
- Ammonia (NH₃) desulfurization process.

Wet limestone technology was the primary flue gas desulfurization process used in power plants, accounting for 83% of flue gas desulfurization systems in 1998 (Figure 1) [38]. The mechanism of this process can be summarized by the following steps: (i) Absorption of gas SO₂ to the liquid phase with subsequent hydrolysis to H₂SO₃, (ii) dissolution of CaCO₃. The above side reactions lead to the following overall chemical reaction [39]:

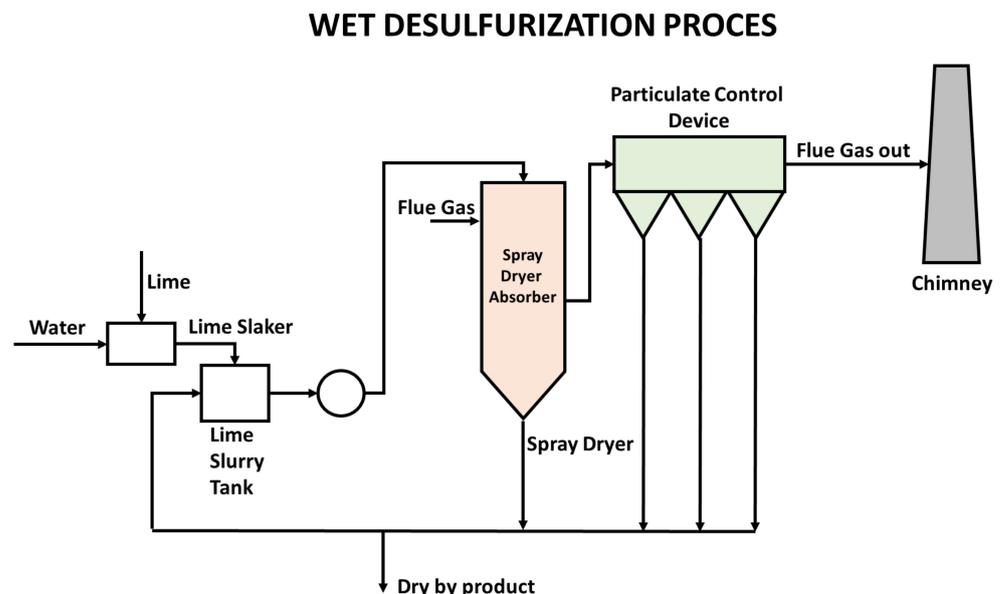


Figure 1. Wet flue gas desulfurization process.

Finally, the calcium sulfite (CaSO₃·2H₂O) is oxidized under forced oxidation conditions for the production of gypsum:



Oxidation might also occur under natural conditions, but in this case, there is a lower yield of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, with $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ being the main product and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ mostly being a side product. Under forced oxidation conditions, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the main product with a yield over 90%. The oxidation conditions depend on the pH of the limestone slurry, the concentration of SO_2 and the concentration of O_2 in the flue gas [39,40]. Gypsum is collected in the form of fine crystals after removing excess water of the suspension by a gypsum separator and through centrifuge [41].

The sulfur-removal efficiency of this method can be higher than 95% [42], which depends on the scrubber design (contact time between flue gases and sorbent suspension) that governs the absorbance efficiency of SO_2 . This method can be applied to any boiler and the capital cost varies depending on the flow volume of flue gases. Retrofitting a boiler with this kind of installation increases capital costs by 16%, while operating costs are influenced by the annual full-load operating hours as well as by the total flue gas flow rate [41]. Similar to wet limestone technology are lime systems. **Lime technology** uses lime (CaO) instead of limestone as a sorbent material for SO_2 , which is more reactive but more expensive because it is produced from limestone through calcination [43].

In the **magnesium oxide desulfurization process**, magnesium oxide (MgO) is hydrolyzed to magnesium hydroxide ($\text{Mg}(\text{OH})_2$) which acts as the sorbent for the SO_2 present in the flue gases. Through this process, the main products that are produced are magnesium sulfite ($\text{Mg}(\text{SO}_3)$) and magnesium sulfate ($\text{Mg}(\text{SO}_4)$). Depending on the process selected, there are two different routes to recover the formed sulfur solids. If the oxidation of $\text{Mg}(\text{SO}_3)$ is promoted, the main product formed is $\text{Mg}(\text{SO}_4)$ but if the oxidation is inhibited, $\text{Mg}(\text{SO}_3)$ is decomposed to MgO and SO_2 through calcination [44]. The efficiency of this process mainly depends on the hydrolysis rate of MgO and the dissolution rate of the subsequent formed magnesium hydroxide [45]. A variation of this technology is the **zinc oxide (ZnO) desulfurization process** which mainly finds application in zinc smelting plants, because ZnO is produced during the zinc smelting process. In this case, a slurry with the oxide form of zinc acts as the sorbent to produce zinc sulfite ($\text{Zn}(\text{SO}_3)$) as the main product and small amounts of zinc sulfate $\text{Zn}(\text{SO}_4)$ and zinc bisulfate. The desulfurized product, zinc sulfite, is recovered through thermal decomposition or through acid decomposition, producing zinc sulfate and other products [44]. The best way to treat sulfite byproducts in industrial applications is by producing zinc sulfate through oxidation, which can be used again in zinc smelting [44].

The **dual-alkali scrubbing method** utilizes two alkaline solutions: a sodium-based one for scrubbing and a lime-based one for the treatment of the scrubbed solution. The sodium-based alkali solution consists mainly of NaOH and Na_2CO_3 , which react with the SO_2 in the flue gases to produce Na_2SO_3 and NaHSO_3 . Next, the alkali solution and the produced slurry with the absorbed SO_2 is regenerated with CaO or CaCO_3 . Finally, CaSO_3 or CaSO_4 are precipitated and discarded as sludge, whereas the regenerated sodium solution can be reused as a sorbent. This method can reach a desulfurization efficiency up to 98% [39]. This technology can be suitable for boilers of small and medium size but it is not yet technologically mature enough to be applied at a larger scale [44].

Finally, the **ammonia-based scrubbing technology** is considered a simple process with a high desulfurization efficiency, but gathers a lot of disadvantages due to its volatility, toxicity and high cost because of its market potential in various industries [46,47]. The process is similar to those previous discussed, where NH_3 acts as the sorbent for the SO_2 , producing $(\text{NH}_4)_2\text{SO}_4$, which has a marketable value, as it can be used as a fertilizer [47].

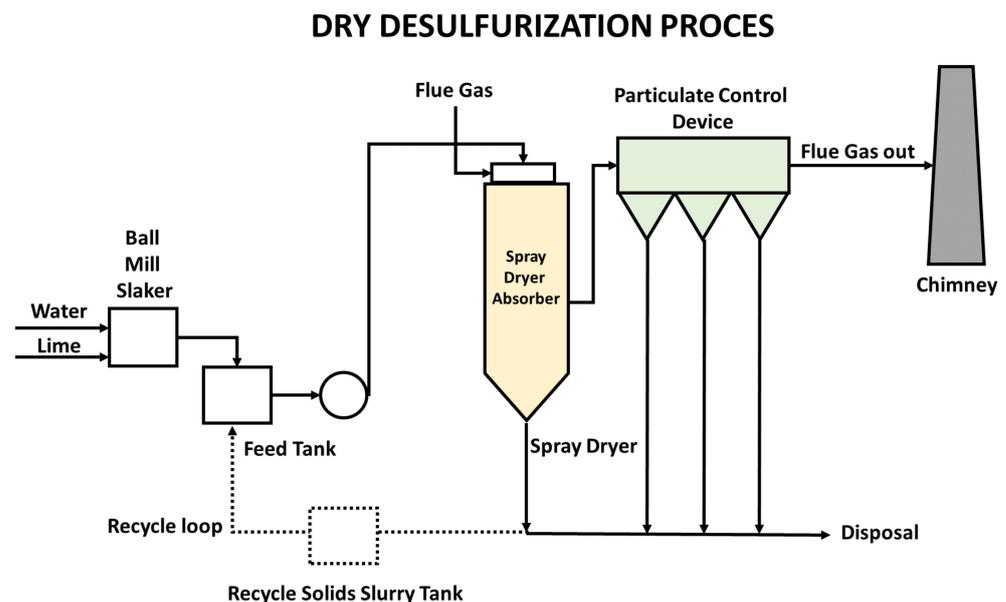
Table 1 summarizes the different methods described above, including the main advantage and disadvantage of each wet desulfurization technology.

Table 1. Comparison of wet desulfurization technologies [38–47].

Method/Sorbent	Main Product	Main Advantage	Main Disadvantage
Wet limestone (CaCO_3)	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	High efficiency (>95%)	High cost
Lime (CaO)	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	High efficiency (>95%)	High cost
Magnesium oxide (MgO)	$\text{Mg}(\text{SO}_4)$	Cheaper	Efficiency varies greatly
Zinc oxide (ZnO)	$\text{Zn}(\text{SO}_3)$	Suitable for zinc smelting plants	Limited applications
Dual alkali (NaOH , Na_2CO_3)	CaSO_3 , CaSO_4	High efficiency up to 98%	Not mature and applicable at large scale
Ammonia (NH_3)	$(\text{NH}_4)_2\text{SO}_4$	Very high efficiency	NH_3 is toxic

The *dry or semi-dry desulfurization* technologies achieve lower desulfurization efficiencies compared to the wet technologies (Figure 2). The main advantage that these methods have is that the sorbent and the waste produced are in a dry state, making them more manageable and easier to dispose compared to the sorbents and products of wet processes. Moreover, they demand installation sites that need fewer space. The main dry or semi-dry desulfurization technologies include:

- Sorbent injection method;
- Active carbon adsorption;
- Circulating fluidized bed desulfurization;
- Spray dry method.

**Figure 2.** Dry flue gas desulfurization process.

At the **sorbent injection method**, a dry sorbent is injected at the upper part of a furnace, which reacts with the SO_2 present in the flue gas. The calcium injection method is based on the calcination of limestone powder into a furnace at high temperatures (500–800 °C) for the decomposition of limestone to CaO . The produced CaO reacts with SO_2 of the flue gases to produce CaSO_4 . Although this method has low capital and operational cost, with no production of wastewater, it is not widely applied because of the low desulfurization efficiency (20–50%), low utilization rate of limestone (10%) and the uncertainty around the selection of the best sorbent suitable for each operating condition [48]. However in China, in recent years, the state emission standard becomes more stringent, so that the environmental protection authorities even forced the owners of CFB to install the wet FGD for CFB boiler. For example, Shandong Huasheng Power Plant, with the help

of Xian TPRI, selected the most active limestone and optimized the limestone technical characteristics and improved the limestone feeding system for a 135 MW CFB boiler. The average SO_x emission over one month of operation was 104 mg/Nm^3 when $\text{Ca/S} = 2.2$, burning a coal with sulfur content of 2.11%. They compared the operational cost of de- SO_x in a CFB boiler and a wet FGD used in a PC boiler with the same capacity. It was found that the cost for a CFB boiler is 0.008 CNY/kWh and that for the FGD is 1.5 times higher, while the compensation for de SO_x from the power grid is 0.015 CNY/kWh. Many Chinese CFB boiler power plants with efficiency of more than 85–90% are encouraged by the above example to take action to implement in-furnace de SO_x [49–51].

The **active carbon adsorption** process is considered a physical-chemical method as it is based on the physical absorption of SO_2 into the pores of active carbon or into another carbonaceous agent with high specific surface area. The absorption of SO_2 occurs at around 100°C and the regeneration of the carbonaceous agent is achieved at a higher temperature (400°C) where sulfur compounds are desorbed and the agent can be reused for further adsorption desulfurization. The disadvantages of this method are the high cost and the low desulfurization efficiency [44].

In the **dry circulating fluidized bed** desulfurization process, the flue gas is injected from the bottom of a vertical fluidized bed reactor along with a calcium-based desulfurization agent, which reacts with the SO_2 present in the flue gas. Through this method, a long contact time is achieved between the desulfurization agent and the SO_2 , since they pass through the fluidized bed several times, leading to high desulfurization efficiency. The purified gas is released through the top part of the reactor and the solid–gas phases are separated using separation devices, such as cyclone separators. Due to the high particulate matter formed through this method, a particulate control device must be also used [38]. In the semi-dry form of this technique, the desulfurization efficiency is higher because the contact time between the flue gases and the lime adsorbent is increased.

The **spray dry method** is the second most applied desulfurization technology (11%) finding uses in smaller or medium boilers in size. Larger-size boilers require several modifications to deal with higher gas flow rates. The efficiency of this technology can achieve desulfurization efficiency up to 90% and it is suitable for fuels with sulfur content up to 3.5 wt.% [41]. For this method, lime (CaO or $\text{Ca}(\text{OH})_2$) slurry is used, which is in the form of fine droplets. The droplets are sprayed into the absorption tower where the flue gases flow and react with SO_2 . Because of the high temperature that the flue gases have, excess water is evaporated and no wastewater is formed. The final dry mixture is collected by a particulate-collecting device, downwards of the absorption tower, and consists of CaSO_4 , CaSO_3 , fly ash and unreacted lime [39].

The comparison of the different dry/semi-dry desulphurization methods is presented in Table 2.

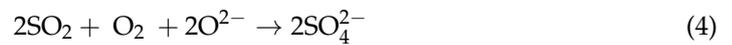
Table 2. Comparison of dry desulfurization technologies [38–48].

Method	Main Advantage	Main Disadvantage
Sorbent injection	Low cost, no wastewater	Low efficiency (20–50%)
Active carbon	Easy to apply	High cost, low efficiency
Dry circulating fluidized bed	High efficiency	Particulate matter production
Spray dry	90% efficiency	Difficult to apply at large-size boilers

The **bio-desulfurization technology** is another cutting-edge technique for reducing SO_x emissions, which is one of the precombustion desulfurization processes. This method is in principle based on the biological sulfur-cycle theory and consists of three steps. Initially, SO_2 that derives from flue gases is dissolved into water, where sulfates are formed. Then, sulfates are reduced to S^{2-} ions under the anaerobic environment through attached bacteria consuming sulfates, and finally to S in the aerobic environment [50].

In this process, the extensive use of alkali absorption and biotechnology results in the conversion of SO_2 to S. The process decreases the raw material addition, but there are

financial advantages attained from the sulfur products. Moreover, this process is beneficial to the safety of the environment because there are no secondary contaminants or emissions. The combustion of sulfur-containing coal produces SO_2 , which can be dissolved readily in water and converted to SO_4^{2-} or SO_3^{2-} .



The most significant advantage of biodesulfurization processes is the ability to work under atmospheric pressure and ambient temperatures, resulting in relatively low energy consumption. Although this process appears to be environmentally feasible, its competitiveness with conventional sulfur-removal techniques is under discussion and investigation. This process has not yet been applied on an industrial scale. The major difficulty in implementing biological processes in industry is their low solid ratio, which significantly decreases the process efficiency. Despite their successful lab-scale applications, these processes cannot be shifted to industry because of their very high capital and operational costs.

3. State-of-the-Art DeSO_x Processes for Marine Diesel Engines

Judging by the latest IMO regulations, if a ship chooses to rely exclusively on HFO, an exhaust aftertreatment retrofit solution must be established in order to treat the increased SO_2 emissions and comply with the IMO rules. Currently, the only commercial exhaust aftertreatment solution available is scrubbers. Scrubbers are basically a wet desulfurization method that mainly utilizes seawater to treat sulfur emissions. Scrubbers produce a large volume of solid waste, and for this reason, along with their high cost, large installation size, complex operation and maintenance, they have not yet been widely embraced by many ships. Scrubbers are divided into three categories regarding their operating principle. The numbers in brackets dictate the percentage of each scrubber type currently installed in the global market [51]:

- Open-loop (81%);
- Closed-loop (2%);
- Hybrid (17%).

The flow chart of scrubbers operation is presented in Figure 3, while the main characteristics of the three types of scrubbers are summarized below:

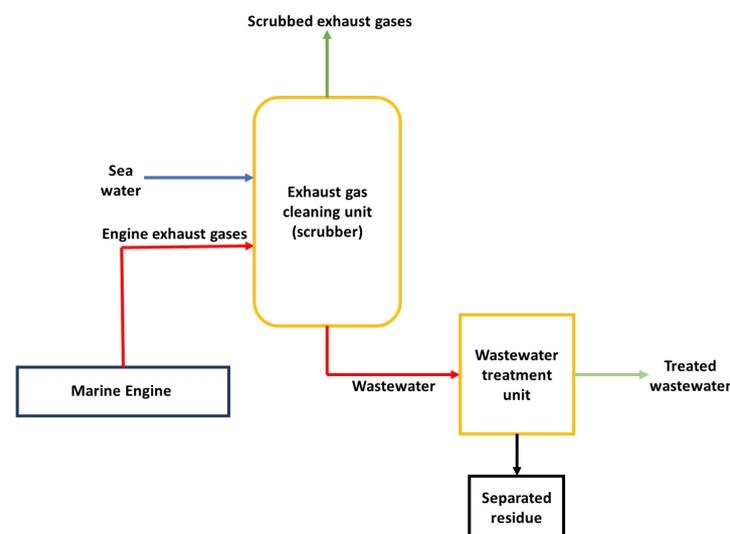


Figure 3. Flow chart of a scrubber operation. In an open-loop scrubber, there is no wastewater-treatment unit.

Open-loop: The operating principle of such systems depends on sucking seawater by a dedicated pump and spraying it into the exhaust to treat SO₂ in the flue gases. The seawater is discharged overboard, often without treatment, along with the formed sulfurous acid and other pollutants present in the flue gases such as polycyclic aromatic hydrocarbons and nitrates. These discharges are often blamed to cause severe pollution problems at the maritime ecosystem [30–32]. Nevertheless, by this procedure, ships comply to the IMO regulations reducing air pollution [52].

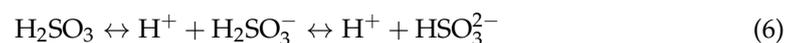
Open-loop scrubbers utilize only seawater, which has low alkalinity, which is why they have poorer desulfurization efficiency compared to other types of scrubbers where a strong alkaline solution is used, as is described below. Despite the above disadvantages, open-loop scrubbers still remain the most popular among other types of scrubbers due to their lower installation and operational cost.

The chemistry involved in the DeSO_x process using seawater is summarized in the following chemical reactions:

During the first step, SO₂ dissolves in water and forms sulfurous acid (H₂SO₃).



Next, sulfurous acid is ionized, acidifying seawater to a pH = 2–3.



Because of the oxygen present in seawater, sulfurous anions are oxidized.



Finally, acidic water is neutralized by the natural alkalinity of seawater due to the presence of HCO₃[−] anions. Large amounts of fresh seawater are used to neutralize the acidic solution.



Closed-loop: Instead of using seawater, closed-loop scrubbers keep a tank of alkaline-dosed freshwater onboard to neutralize the pH of the wastewater. After it is sprayed into the exhaust, the water is filtered to remove solid particles and then recirculated, with a small amount of “bleed-off” water discharged overboard. These are the most expensive type of scrubbers, and unlike open-loop systems, continuously collect and store scrubber sludge that has to be removed ashore from the recirculating washwater. In this case, an alkaline chemical, usually sodium hydroxide (NaOH), is used to control the water’s alkalinity. Manufacturers claim that compared to the open-loop scrubber, the closed-loop requires far less of the seawater flow to achieve the same scrubbing efficiency because of the direct control of the pH level using the alkaline chemical injection process.

Hybrid: Such scrubbers can be operated both in open- or closed-loop mode. Such a type of scrubber provides some insurance against local restrictions on scrubber discharges, as they can be switched to closed-loop or zero-discharge mode. Later, in open sea, they can switch back to open-loop operation. Their main disadvantages are their high complexity, high capital cost and large occupation space.

The advantages and the disadvantages of the three types of scrubbers are summarized in Table 3.

Table 3. Brief comparison between the 3 types of scrubbers.

Type	Advantages	Disadvantages
Open-Loop	<ul style="list-style-type: none"> • Only seawater required for scrubbing • Simpler system compared to the others • Smaller installation site • Lowest capital and operational cost 	<ul style="list-style-type: none"> • The most ocean-polluting option • Lower efficiency when seawater of lower alkalinity is used • Prohibited in many ports • Large amounts of seawater required
Closed-Loop	<ul style="list-style-type: none"> • Can be used at every port with no restrictions • Seawater of low alkalinity also suitable 	<ul style="list-style-type: none"> • More complex operation • Larger installation site/more equipment • Safety protocols for handling the hazardous NaOH solution • Operation duration depends on the effluent's tank volume • Higher operational and capital cost
Hybrid	<ul style="list-style-type: none"> • Used in every condition regardless of local restrictions and seawater alkalinity • Can work in closed-loop mode and store the effluent where restrictions are in effect and discharge in the ocean where no restrictions are applied 	<ul style="list-style-type: none"> • The most complicated systems, with a lot of equipment demanding a lot of space • Safety measures and protocols for handling NaOH solution and effluents when in closed-loop mode • The highest capital and operational cost

In order to counter the sea pollution problem, some ports and coastal states have issued local regulations with stringent requirements regarding scrubbers, which completely prohibit the use of open-loop scrubbers or restrict the discharge of washwater [52,53]. A list of ports and states have been summarized in a report conducted by the International Council on Clean Transportation [52], and are presented in the following table (Table 4):

Table 4. Ports around the world with scrubber restrictions—data taken from [52].

Country	Prohibited Scrubber Use
Bahrain	at port or at anchor
Belgium	within 3 nautical miles of the coast
Brazil	territorial seas
China	in domestic emission control areas
Egypt	in all ports and Suez canals
Gibraltar	in Gibraltar waters
Ireland	in Dublin and Waterford ports
Malaysia	in territorial seas (12 nautical miles)
Norway	in the World Heritage Fjords Sea areas of Geirangerfjord and Nærøysfjord
Pakistan	in the ports of Karachi and Bin Qasim
Panama	in the Panama Canal
Portugal	in any port or at berth
Singapore	in any port
Spain	in the ports of Algeciras, Cartagena and Huelva
United States	California, Connecticut and Hawaii ports or waters
United Arab Emirates	in the port of Fujairah

The list of countries that are turning against the usage of scrubbers is still growing, with the latest country issuing regulations being Canada, where from March of 2022 the Port of Vancouver prohibits ships from dumping contaminated scrubber washwater while at berth or at anchor [54]. From Phase I of this regulation, it is expected that around 88% of in-port scrubber discharges will be eliminated [55,56]. According to a 2017 study focused on Canada's Pacific coast [32], 30 scrubber-equipped ships dumped 35 million tonnes of contaminated washwater near British Columbia, including 3.3 million tonnes within the

designated critical habitat for threatened and endangered killer whales. Cruise ships were responsible for 90% of these discharges. Since 2017, the government of Canada has doubled the size of the resident killer whale critical habitat. Under the revised definition, 5.1 million tonnes of washwater were dumped inside these areas. It is hard to overstate the positive effect that this new regulation will have on the endangered marine ecosystem. Before these restrictions, the Port of Vancouver was the fourth most impacted port in the world in terms of washwater discharges, and now after the new regulations it will hardly make it to the top 100 of that list [56].

Despite the IMO's scrubber discharge guidelines for pH, temperature, polycyclic aromatic hydrocarbons, turbidity and nitrates, studies are showing that scrubber washwater damages ecosystems and harms wildlife [30–32,57]. A recent study [57] estimates that if 15–35% of the fleet operating in the English Channel and the southern North Sea were equipped with open-loop or hybrid scrubbers, each year the pH would drop by between 0.004 and 0.010 pH units, about as much as the ocean acidifies in two to four years due to climate change. Near Rotterdam, the pH decrease was estimated at up to 0.088 pH units per year, which would normally take between 30 and 50 years from climate change.

There are no doubts that open- and closed-loop scrubbers are highly effective in treating SO_x and PM emissions, leading to almost 100% SO_x reduction. Moreover, scrubbers can be regarded as the only currently available aftertreatment solution for ensuring compliance with the IMO global sulfur cap, in case the marine industry continues to rely on conventional high-sulfur fuel oils [58].

However, there are significant delays for shipping companies and governments to respond to new SO_x regulation. For example, according to a survey on Korean shipping companies, the owners do not seem to deeply understand the necessity and the function of the scrubber technology; thus, they postpone the retrofit of their ships until they determine the alternatives, and make prompt adjustments to execute their response strategies. The main criteria to meet for a technology to be adapted are operating costs, government/port support, fuel consumption costs and price volatility, and reliability of fuel supply. In addition, the results of the survey indicate that most Korean shipping companies decide their response according to cost factors such as investment and operating costs [59].

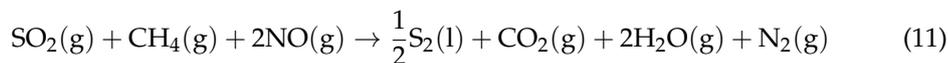
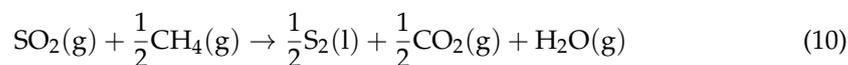
4. Beyond the State of the Art

On the other hand, it is clear from the above that scrubbers as a DeSO_x solution for ships have three main disadvantages:

- High cost, which varies between EUR 2–6 million [60], depending on the power of the engine and the type of scrubber used;
- Even more countries issuing regulations that disband the use of scrubbers or scrubber discharges at their ports or coast;
- The environmental problem shifting to the oceans, even though the released emissions comply with regulations.

To that extend, Monolithos Catalysts & Recycling Ltd. has been awarded with a European patent [61] that proposes a novel method, device and process for the abatement of SO₂ emissions from internal combustion engines that utilize HFO with high sulfur content. The proposed apparatus relies on the development of a catalytic system for the selective catalytic reduction of SO₂ to elemental sulfur, similar to the currently available marine SCR systems for the reduction of NO_x [62,63] emissions that use urea as the reducing agent. The proposed solution aims to overcome the aforementioned scrubber problems in a low-cost and environmentally friendly way. In brief, a catalytic converter, similar to the ones used in the automotive industry for the treatment of gasoline engine exhaust gases, will selectively catalyze the chemical reduction reaction of SO₂ to elemental sulfur by utilizing carbon monoxide (CO), hydrocarbons and nitrogen oxides (NO_x) as reducing agents, which are already present in the flue gases of the marine internal combustion engine. The main products of these reactions will be CO₂, H₂O and N₂. The catalytic converter should be

highly active and stable at a wide temperature range of 100 to 700 °C. The corresponding chemical reactions that can occur for the reduction of SO₂ are summarized below:



The catalytic converter will consist of a ceramic monolithic matrix, which will be sprayed with the appropriate metal oxide heterogeneous catalyst. The elemental sulfur produced will be stored onboard in solid form in a dedicated vessel and serve as a marketable product. The above-described apparatus could be installed in the engine exhaust stream at an appropriate temperature in line with a catalytic microparticle filter (catalyzed diesel particulate filter, C-DPF), which will also treat particulate matter and other toxic gaseous pollutants present in the engine's exhaust gases (Figure 4). Finally, a SCR system could also be installed in-line, after the SO₂ catalytic converter, which would treat NO_x emissions. The above-described system could serve as a retrofit solution for eliminating SO_x emissions for any kind of vessel, new or old.

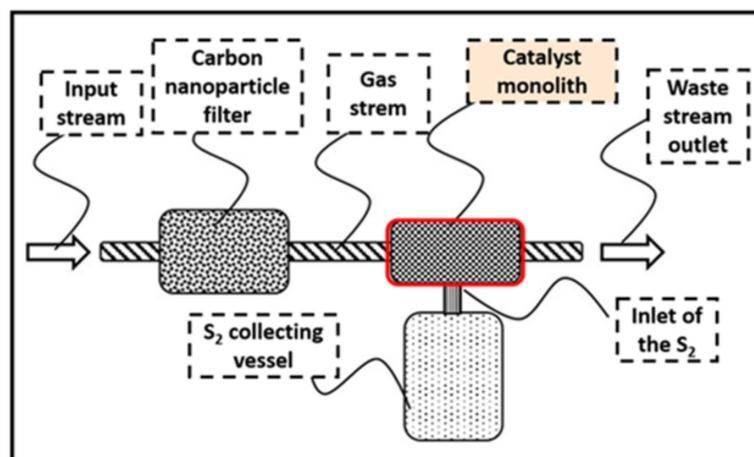


Figure 4. Graphical illustration of the above-described DeSO_x apparatus.

The metal oxide heterogeneous catalyst, which will be installed in the above system must be highly active for the conversion of SO₂, but at the same time has to be very selective towards elemental sulfur production, with minimum or no production of harmful byproducts such as COS or CS₂. In the following chapter, the most promising metal oxide catalysts suitable for that kind of application that are proposed through the literature are reviewed.

5. Metal Oxide Catalysts for the Reduction of SO₂ to Elemental Sulfur

Happel et al. [64] were one of the first groups that studied the catalytic reduction of SO₂ with CO to elemental sulfur with a binary coprecipitated lanthanum titanate catalyst. Their study focused on the formation of the toxic byproduct carbonyl sulfide (COS), proving that the tendency towards the formation of COS increases with the increase in the molar ratio [CO]/[SO₂] in the gas reactant stream. In the case of the studied catalyst, the production of COS is not significant until the ratio [CO]/[SO₂] is close and lower than 2 (stoichiometric ratio). The group continued their study further [65] to determine the optimal catalytic composition of this system, proving that catalysts with high wt.% of lanthanum (i.e., 50% and 97%) and titanium as promoter are the most effective for the reduction of SO₂. The catalytic activity of such systems was attributed to their structure, which is fluorite with anion defects that act as chemisorption sites for carbon monoxide. Finally, they pointed out

the importance of the pretreatment of these catalysts with a gas mixture containing all the reactants SO_2 , CO and CO_2 .

In the following years, research has focused on determining the most promising support, active phase and mechanism that this reaction follows. By the review of the following works, most of the researchers agree that a presulfidation step is required for the catalysts to be highly active with high stability. Furthermore, it has been proven that this reaction can be carried out through two different mechanisms or a combination of the two, i.e., a redox mechanism or a mechanism through the production of an intermediate, which depends on the reducing agent used.

The group of Flytzani-Stephanopoulos was the first to extensively study the reduction of SO_2 to elemental sulfur using carbon monoxide as the reducing agent. On one of their first works [66], a series of CeO_2 -supported transition-metal catalysts were tested, proving that copper- and nickel-supported ones were the most active. The temperatures, where SO_2 conversion exceeded 90%, had the following trend: 500 °C for Cu/CeO_2 and Ni/CeO_2 ; 550 °C for Pd/CeO_2 ; 600 °C for Co/CeO_2 and Mn/CeO_2 ; and >600 °C for Cr/CeO_2 catalysts. The group further tested the Cu/CeO_2 catalyst, showing that copper loading does not influence the catalytic activity but influences sulfur selectivity, which decreases as the copper loading increases. Moreover, with the presence of 2% water in the gas stream, hydrogen sulfide (H_2S) becomes the major byproduct instead of carbonyl sulfide (COS), reducing the elemental sulfur yield from 95% to 70%. The $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalyst exhibits a slightly higher activity than the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$, but they are both less active than the Cu-Ce-O catalysts. Furthermore, in contrast to the Cu-Ce-O system, the copper/alumina catalyst favors the formation of COS during the presence of water. The group emphasized the role of the crystal structure, suggesting that catalysts with a fluorite-type oxide support with high oxygen vacancy concentration and mobility properties, such as CeO_2 and ZrO_2 , are highly active and selective for the SO_2 reduction reaction to elemental sulfur, as they tend to follow the redox reaction mechanism with lower production of intermediate byproducts such as COS . The mechanism that the reaction of SO_2 with CO follows in the Cu-Ce-O system was further elucidated [67], suggesting that the cerium oxide support serves as the oxygen vacancy reservoir, while copper promotes the reducibility of cerium oxide, providing surface sites for CO adsorption. SO_2 has a strong affinity to cerium oxide, such that an active Cu-Ce-O catalyst comprises partially sulfated and partially reduced cerium oxide.

The potential of ceria as a support was studied further from the group of Flytzani-Stephanopoulos. The group tried to improve the catalytic activity of ceria [68] by doping it with La through the urea gelation/coprecipitation preparation method and by calcination in static air at 650 °C for 3 h. The catalyst was highly active for the SO_2 reduction by methane at temperatures higher than 550 °C. The addition of transition metals such as Cu and Ni influenced the selectivity of elemental sulfur. Copper catalysts were more selective towards sulfur production by catalyzing the complete oxidation of CH_4 by SO_2 , which leads to elemental sulfur. Furthermore, in the presence of water vapor at the gas stream, the copper-promoted catalyst retained its high catalytic activity and selectivity, compared to the bare support. Their research continued [69] using the lanthanum-promoted ceria support for the preparation of nickel or copper catalysts with 2.5 wt.%, proving that the metal doping significantly improved the low-temperature reactivity of the pure support along with its resistance to water vapor poisoning for the reaction of SO_2 with CO . Furthermore, the catalysts were studied for the combined reduction of SO_2 and NO by CO . In dilute gas mixtures containing 0.1–1.0 mol% SO_2 and NO , a stoichiometric amount of CO and with the presence of 40% H_2O , the presence of NO enhanced both the SO_2 conversion and the elemental sulfur yield. The Ni-CeO_x appears to be the most active catalyst for the combined reduction reaction. This is an important result for NO_x reduction, because most NO reduction catalysts are susceptible to sulfur poisoning [69].

It seems from the previous works that CeO_2 and fluorite oxides with anion defects in general are promising supports for an active catalyst for the reduction of SO_2 . On the other hand, the following works have focused on $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts, a support

with amphoteric nature with both acidic and basic sites, with researchers pointing out the importance of the Lewis and Brønsted acid sites. The researchers also aimed to increase both acidic and basic sites of the supports through various techniques such as pretreatment or promotion with other elements.

Yu et al. [70] studied different supports, such as SiO₂, a 5A molecular sieve, a 13X molecular sieve and γ -Al₂O₃ for the preparation of cobalt catalysts. The authors tested the catalysts at the temperature range of 740–820 °C, proving the superiority of the γ -Al₂O₃ support where the SO₂ conversion efficiency and the sulfur yield exhibited the following order: γ -Al₂O₃ > SiO₂ > 13X molecular sieve > 5A molecular sieve. Mitchell et al. [71] compared pure γ -alumina with promoted γ -alumina impregnated with different amounts of sodium ions. Through extensive DRIFTS measurements they proved that after impregnation, the number of both the basic and acidic sites increased as a function to sodium loading. This was demonstrated by the increase in both physisorption and chemisorption of SO₂. Another group [72] highlighted the role of the activation of lanthanum oxide for the SO₂ reduction with CO. Lanthanum oxide is rehydrated to the corresponding hydroxide, prompting the creation of Lewis and Brønsted sites in the subsequent dehydroxylation of the hydroxide. These sites can chemisorb SO₂ and CO simultaneously, promoting the formation of reactive SO species and lattice oxygen vacancies that readily accept sulfur. The oxide is then sulfidized using the reaction gas mixture in order to form the active phase of lanthanum oxysulfide, La₂O₂S.

A series of modified γ -Al₂O₃-supported Fe-based catalysts promoted with Ni, Co or Ce were developed and tested for the reduction of SO₂ using CO, H₂ or CO-H₂ gas mixture as the reducing agent and GHSV = 5000 h⁻¹ [73]. When CO was used as the reducing agent, the 14 wt.% Fe–2 wt.% Co/ γ -Al₂O₃-supported catalyst achieved the best catalytic performance with 99% SO₂ conversion and 99% sulfur selectivity at 400 °C. The authors claim that the catalyst does not require a presulfidation step but only a short period of in situ prereaction to achieve high catalytic activity. When H₂ was used compared to CO, the catalytic activity was reduced significantly, and concerning the gas mixture of CO and H₂, the group proved that they act completely independently of each other, showing no signs of synergism or competition. Finally, the catalyst proved very stable for over 200 h under reaction conditions, with no signs of reduced catalytic activity. The reaction proceeded through a redox mechanism with the production of an intermediate (H₂S or COS depending on the reactant) which reacted with SO₂ over the support to produce elemental sulfur. The group continued their work [74], preparing a series of three component catalysts with γ -Al₂O₃ as a support. The presulfided La-Co-Cu/ γ -Al₂O₃ promoted with 1 wt.% La catalyst was the most active, achieving a 99% conversion of SO₂ and sulfur selectivity at 400 °C. The addition of 1% La improved the activity and stability of the catalyst, which remained highly active for over 200 h under reaction conditions. La promotion altered the surface state of γ -Al₂O₃, increasing the effective surface area of the sulfide active component. The group also studied the effect of the duration of presulfidation, proving that 2 h is the optimal time for the corresponding reactions to reach chemical equilibrium.

H. Zhao et al. [75] prepared a series of sulfided CoMo/ γ -Al₂O₃ catalysts using a combination of incipient wetness impregnation and sulfur chemical vapor deposition methods. The catalysts were tested for the reduction of SO₂ with CO using a total reactant gas flow rate = 1200 mL/min. For every catalyst, it was shown that SO₂ conversion efficiency and selectivity to elemental sulfur increase with the increase in temperature (200–450 °C) while the selectivity of COS formation decreases. The catalyst with the highest activity was the one with 9 wt.% Co and 20 wt.% Mo loading, achieving almost 100% SO₂ conversion efficiency and selectivity to elemental sulfur at temperatures above 300 °C. The high activity of these catalysts was attributed to the formation of MoS₂ in the shape of trigonal prisms, while Co atoms acted as promoters localized at the edges of MoS₂, forming a well-dispersed Co–Mo–S structure, which serves as the active center.

SC. Paik et al. [76] prepared a series of various transition-metal catalysts supported on γ -Al₂O₃ which were presulfided in a flow of H₂S-containing gas (10 vol.% H₂S in H₂

balance) at 400 °C for 2 h. The catalysts were evaluated for the reduction of SO₂ with a H₂/SO₂ feed ratio of 2.0 (5% SO₂, gas hourly space velocity = 3600 h⁻¹). For every catalyst, the maximum point of elemental sulfur yield was found at around 300 °C and the conversion of SO₂ had the following trend: (Fe, Co, Ni) > (Cr, Mo, W) > Cu, Zn > V, Mn with a very low conversion observed for Cu and Zn, and almost zero for V and Mn. During the reaction, the metal sulfide phase was transformed from a sulfur-deficient form to a sulfur-rich form of disulfide (FeS₂, CoS₂, NiS₂). Finally, sulfur vacancies in the metal sulfide form were considered as the active sites for the SO₂ hydrogenation, and the most active catalyst was considered to be able to regenerate sulfur vacancies more easily. The group also studied [77] the reduction of SO₂ with H₂ or CO using 10 wt.% cobalt-supported catalysts on γ-Al₂O₃ or TiO₂. Prior to the reaction, the catalysts were presulfided in a gas flow of H₂S (10 vol.% H₂S in H₂ balance) at 400 °C for 2 h. In the case of H₂ as reductant, the reaction occurred via two individual steps on two different sites: first, SO₂ was fully hydrogenated to H₂S on the CoS₂ site and then elemental sulfur was produced on the Al₂O₃ site through the reaction of H₂S with SO₂. In the case of CO, COS was generated by the reaction between CO and CoS₂, which reacted with SO₂ on TiO₂ for the production of elemental sulfur through a redox mechanism. Therefore, they proved that the reduction of SO₂ is achieved via two individual reaction steps through the production of an intermediate associated with the reducing agent.

Wang et al. [78] performed an extensive screening of catalysts in terms of active metal, support, pretreatment method and optimal feed ratio of [CO]/SO₂, supporting their results via CO-TPD, CO-TPR and SO₂-TPD experiments. First, they used γ-Al₂O₃ as a support and they impregnated it with eight different metals (i.e., Fe, Ni, Mo, Mn, Mo, Cr, Co, Pd, Pt). The most active catalyst proved to be the one with Fe₂O₃ exhibiting 100% conversion of SO₂ and almost 95% sulfur yield at 380 °C. The catalyst with NiO had similar conversion of SO₂ but lower sulfur yield, close to 70%. It should be noted that Pt and Pd γ-Al₂O₃-supported catalysts exhibited a very poor performance, possibly due to the tendency that these metals have to sulfur poisoning [79,80] or because of the low interaction that they exhibit with SO₂ [81]. Finally, the group impregnated various supports (γ-Al₂O₃, SiO₂, TiO₂, CeO₂, La₂O₃, V₂O₅ and zeolite Y) with Fe₂O₃, proving that CeO₂ is the best support (100% SO₂ conversion and sulfur yield at 340 °C), followed by γ-Al₂O₃. The group pointed out that presulfidization of the catalyst is necessary, proving that catalysts pretreated with CO + SO₂ exhibit higher activity and stability than those pretreated with CO, H₂ or He. The group continued their research [82], proving that also in the case where C₂H₄ ([C₂H₄]/[SO₂]) is 1:1) is used as reducing agent, the catalyst Fe₂O₃/CeO₂ was still the best-performing, with 10 wt.%, optimal Fe loading, and was presulfided by H₂ + H₂S. They also note that CO is the best-performing reducing agent, followed by C₂H₄ and finally H₂, which does not yield good results.

It seems that iron/alumina-supported catalysts have drawn scientific attention, with this study [83] focusing on iron oxides supported on several supports (γ-Al₂O₃, HZSM-5, SiO₂, and MgO) for the catalytic reduction of SO₂ by CO. The catalytic activity of those catalysts followed the order Fe₂O₃/γ-Al₂O₃ > Fe₂O₃/HZSM-5 > Fe₂O₃/SiO₂ > Fe₂O₃/MgO. Presulfidation was again proven necessary with the reaction's gas mixture at 500 °C for 2 h for the formation of the active-phase FeS₂. The catalyst Fe₂O₃/γ-Al₂O₃ with 20 wt.% Fe loading, presulfided at 500 °C for 2 h yields a 99.31% SO₂ conversion and 99.17% sulfur yield at 380 °C under a [CO]/[SO₂] ratio of 2:1. It should be noted that this group did not select CeO₂ for their studies, which proved the most effective support elsewhere [66,78,82]. Finally, Mousavi et al. [84] prepared a series of alumina-supported catalysts with Ni or Cu 5 and 10 wt.% and tested them for the reduction reaction of SO₂ with CH₄. At temperatures lower than 700 °C, Al₂O₃-Cu (10%) catalysts exhibited the best catalytic activity. At 750 °C, complete conversion of SO₂ and sulfur selectivity higher than 99.5% was achieved by both 10 wt.% catalysts.

Han et al. [85] conducted a mechanistic study to investigate the pathway of the SO₂ reduction by CO over a ZrO₂ catalyst prepared through the precipitation method and by

calcination in air 600 °C for 6 h. The catalyst was tested at fixed-temperature conditions of 490 °C with a $[\text{CO}]/[\text{SO}_2]$ molar ratio of 2.0 and a variable space velocity between 5000 and 20,000 mL/g_{cat} h. The optimal space velocity was at 10,000 mL/g_{cat} h, at which point SO₂ conversion and the selectivity of sulfur and COS reached about 100, 86 and 14%, respectively. The sulfur selectivity increased and COS selectivity decreased with rising space velocity, respectively. It was proven that contact time plays a major role not only in the conversion of SO₂, but also in S₂ and COS selectivity. Finally, they proved that the ZrO₂ catalyst was sulfated in the process of SO₂ reduction by CO, and that the Lewis and Brønsted acid sites were improved by the formation of the sulfate group. Lewis and Brønsted acid sites favor the COS intermediate mechanism as in the case of $\gamma\text{-Al}_2\text{O}_3$. The same group also studied the SO₂ reduction by CO over an SnO₂ catalyst, which achieved an SO₂ conversion and sulfur selectivity about 78% and 68%, respectively, at 550 °C with a molar ratio $[\text{CO}]/[\text{SO}_2] = 2$ and GHSV = 8000 h⁻¹ [86]. The high COS selectivity of this catalyst was explained through both the red ox and COS intermediate mechanisms, where the reaction was initialized by the redox mechanism and followed by the COS mechanism, which seems to be predominant.

An interesting study concerning gold catalysts was conducted by Ngwenya et al. [87], who developed three 1 wt.% Au-supported catalysts at three different metal oxide supports (TiO₂, ZnO and Al₂O₃), through the deposition precipitation method. The group proved that the Au/TiO₂ exhibited the best catalytic performance for SO₂ reduction, with CO achieving an 86.4% conversion and 100% sulfur selectivity at 300 °C with a feed ratio $[\text{CO}]/\text{SO}_2 = 2$ and GHSV = 3600 mL g⁻¹ h⁻¹. Moreover, the activity of the catalyst remained unchanged for over 144 h under reaction conditions at 300 °C. The other two catalysts exhibited poor performance due to sulfur poisoning, as SO₂ is adsorbed dissociatively on the surface of their surface, preventing CO adsorption and the subsequent reduction of SO₂. The high activity of the TiO₂ was attributed to Au nanoparticles, which seem to increase the mobility of oxygen vacancies present in the TiO₂ support.

None of the above studies have explored the influence of O₂ present in the gas feed stream. Possibly the only study that explored the presence of O₂ at high concentrations [88] developed a series of 0–20 wt.% copper-promoted catalysts using a mixed SnO₂ and ZrO₂ support to study the reduction reaction of SO₂ to elemental sulfur. The catalysts were prepared through the coprecipitation method and the final form of the catalysts was received through calcination in air at 600 °C for 4 h. The gas reactant mixture consisted of 5 vol.% SO₂ and 0 or 4 vol.% O₂ with N₂ as the balance. The molar ratio of CO/(SO₂ + O₂) was equal to 2 and the reaction was carried out from 200–550 °C. The bare support and the catalyst with 5 wt.% of copper were the most active, achieving a SO₂ conversion and S₂ selectivity over 95% at 330 °C, under oxygen-free conditions. The copper oxide catalyst performed better than the bare support in oxygen rich conditions (4 vol.%), but its activity was significantly reduced, achieving 80% of SO₂ conversion at 450 °C. Finally, the group examined the catalytic activity of a presulfidated catalyst proving that the formation of CuS onto the catalyst's surface led towards the COS intermediate mechanism improving the catalytic activity.

Judging from the above studies, the authors claim that the reduction reaction of SO₂ can proceed mainly via two different mechanistic routes. The first step, common for both mechanisms, is the chemisorption of SO₂ onto the catalyst surface. It is pointed out that catalysts with a large number of Lewis acidic sites are suitable for the interaction of the electron-rich SO₂ molecule. Many researchers have tried to improve the number of Lewis and Brønsted sites through various pretreatment modifications or via alkali promotion of the support [71,72]. On the other hand, supports with high surface energy might not be suitable as they tend to adsorb SO₂ dissociatively, leading to irreversible sulfur poisoning, preventing CO from adsorbing on their surface and from proceeding with the subsequent reduction of SO₂ [87]. For the next step, there are two different mechanisms proposed, depending on the catalyst used. The redox mechanism firstly involves the adsorption of the reducing agent onto the catalyst's surface, and secondly involves the desorption of the

reducing agent in its oxygenated form, utilizing an oxygen atom from the catalyst's support. Finally, the structural oxygen vacancy that is formed is filled with an oxygen atom of the preadsorbed SO₂ molecule, leading to the formation of less-oxygenated sulfur species. It is clear from the above that defective supports with large number of oxygens vacancies and high oxygen storage capacity, such as ceria or zirconium oxide [67,68], are suitable to carry out the reaction through the redox mechanism. Research has also focused on tuning these properties to achieve better catalytic activities, mainly through doping with trivalent cations such as La⁺³ [68,89,90]. Finally, doping these supports with transition-metal cations such as copper or nickel improve their redox properties.

The selectivity of such catalysts towards elemental sulfur production might be impaired through the production of major pollutants as side products (COS, CS₂ or H₂S), which depend on the reducing agent that is employed. It is believed that the production of such byproducts might be initiated through the sulfidation of the catalyst during the reaction or before, through a presulfidation step with the gas reactant stream or with a different reducing gas stream. The second mechanism that is proposed through the literature relies on the production of such byproducts through the formation of a highly active sulfided form of the active metal (MS₂) [75,76]. It is also believed that that the sulfidation of the catalyst increases the number of Lewis and Brønsted acid sites [85]. Nevertheless, even sulfided catalysts can be highly selective as the intermediate byproduct can react with SO₂ for the production of elemental sulfur. In addition, it has been reported that contact time [85], molar ratio of the reactants [64] and presence of water vapor in the gas feed stream [66] can influence the formation of such byproducts.

6. Conclusions and Suggestions for the Future

- Results obtained in this paper: It seems from the above that highly active and selective catalysts have been developed for the selective reduction of SO₂ towards elemental sulfur. Most authors emphasize on the role of ceria and γ -Al₂O₃, attributing the high catalytic activity that these supports exhibit to their oxygen defective fluorite structure and to the high concentration of acidic sites, respectively. Impregnating these supports with transition metals such as Fe, Cu, Ni and Co greatly promote their catalytic activity, selectivity and stability. Most of the studies that emphasized screening a wide range of active metals for this reaction proved that Fe might be the most active compared to the others.
- Limitations on the conducted review: On the other hand, there are very few studies focusing on noble metals, possibly because of their susceptibility to sulfur poisoning. The literature lacks studies that emphasize on the role of oxygen in the gas feed stream, which is an important topic to consider if these catalysts are developed for commercial DeSO_x solutions. Monolithos Catalysts & Recycling Ltd. has proposed a very promising DeSO_x solution that can be easily applied both for land based and marine applications. Compared to the other solutions proposed in the literature, a SO_x selective catalytic reduction system can overcome problems that current state-of-the-art solutions exhibit, such as secondary environmental pollution, high operational and capital cost, low DeSO_x efficiency and/or waste management.
- Prospects for future research: The research in the near future should focus mainly on supported catalytic systems to treat SO_x emissions, simultaneously to NO_x and hydrocarbon emissions, taking advantage of the compositions and the concentration of the flue gas streams that are formed from the HFO fuel, which is used on marine sector. Additionally, significant improvement steps should be performed on the particulate matter treatment, assisted with catalytic supported phases in order to enhance the catalytic efficiency and meet the strict environmental criteria of the IMO MARPOL regulations. Byproducts of the flue gas treatment should be taken under serious consideration to avoid side pollution by the desulfurization catalytic system, in order to obtain an integrated, environmental and economically feasible solution requiring the least maintenance and expertise. Finally, a prediction method for probable recovery

of partially missing or completely lost data based on the improvement of the combined gas treatment technologies should also be considered and should take place to enhance the evolution, development and demonstration of these systems.

7. Patents

Iakovos YAKOUMIS, Konstantinos Miltiadis SAKKAS, Anastasia Maria MOSCHOVI, Monolithos Catalysts & Recycling Ltd., Method, device and process for the abatement of SO₂ emissions from internal combustion engines, EP3939690A1, 19 January 2022.

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Conflicts of Interest: The authors declare no conflict of interest.

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