Review

Advanced and Intensified Seawater Flue Gas Desulfurization Processes: Recent Developments and Improvements

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Abstract: Seawater flue gas desulfurization (SWFGD) is considered to be a viable solution for coastal and naval applications; however, this process has several drawbacks, including its corrosive absorbent; low vapor loading capacity since the solubility of sulfur oxides (SOx) in seawater is lower than that of limestone used in conventional methods; high seawater flowrate; and large equipment size. This has prompted process industries to search for possible advanced and intensified configurations to enhance the performance of SWFGD processes to attain a higher vapor loading capacity, lower seawater flowrate, and smaller equipment size. This paper presents an overview of new developments as well as advanced and intensified configurations of SWFGD processes via process modifications such as modification and optimization of operating conditions, improvement of spray and vapor distributors, adding internal columns, using square or rectangular shape, using a pre-scrubber, multiple scrubber feed; process integration such as combined treatment of SOx and other gases, and waste heat recovery; and process intensification such as the use of electrified sprays, swirling gas flow, and rotating packed beds. A summary of the industrial applications, engineering issues, environmental impacts, challenges, and perspectives on the research and development of advanced and intensified SWFGD processes is presented.

Keywords: marine seawater FGD process; process integration; process intensification; process modification; process improvement

1. Introduction

The global energy demand is increasing rapidly, leading to the construction of many power plants using fossil fuel [1]. Combustion of fossil fuel such as coal and/or oil in these plants increases the amount of sulfurous oxides (SOx, whereof the main constituent is sulfur dioxide (SO2)), which has a negative impact on human health and the environment [2]. Consequently, tight SOx emissions regulations have been promulgated in many countries [3].

Furthermore, marine shipping accounting for more than 90% of international trade [4] generates substantial SOx emissions [5]. To prevent the formation of SOx, the International Marine Organization (IMO) approved sulfur emissions regulations [6]. From 1 January 2015, equivalent sulfur emissions need to be lower (0.1% in weight) in some coastal regions termed as “Sulphur Emission Control Areas”
(SECAs). From 1 January 2020, sulfur emissions for ocean ships worldwide must be equivalent to that emitted by fuel with sulfur content lower than 0.5% in weight [7].

To effectively control SO$_2$ emissions, flue gas desulfurization (FGD), in which the flue gas interacts with an absorbent medium, is a viable solution [8], with wet processes occupying roughly 87% of the worldwide share [9]. Wet scrubbers can be classified as wet limestone FGD, wet lime and magnesium-lime FGD, seawater FGD (SWFGD), dual-alkali FGD, and ammonia FGD processes [10]. In all FGD processes (except the SWFGD process), large quantities of chemical sorbents (limestone, lime, magnesium-enhanced lime, calcium hydroxide, etc.) are needed. Therefore, significant capital is required to acquire and transport those chemical sorbents and to acquire space for storage. Furthermore, most of these processes generate solid waste, such as gypsum, which needs space for storage and is expensive to dispose of. Meanwhile, the high costs and the apparent excessive fertilizer use from industrialized countries restrict the use of the ammonia FGD system [8].

As large amounts of water are needed for cooling, many power plants prefer to be built in coastal areas. Furthermore, due to its natural alkalinity and high availability, seawater has been considered as a technically and economically reliable solvent for desulfurization processes in coastal and marine applications [11]. In this technique, the absorbed SO$_2$ is transformed into sulfate ions (SO$_4^{2−}$) and completely dissolved in seawater; therefore, no solid waste is generated and no storage space needed [12]. Thus, the FGD process using seawater as the sorbent is convenient and economical, and a large amount of research is being conducted to this end, especially in FGD improvement as shown in Figure 1. It was observed that the high salinity of seawater (mainly NaCl) further improved the SO$_2$ absorption [13]. In general, SWFGD systems may achieve a SO$_2$ removal efficiency of 85–98% [8].

![Figure 1. Percentage of articles mentioning the seawater flue gas desulfurization (SWFGD) process.](image_url)

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However, the SWFGD process has several drawbacks, such as its corrosive absorbent; low vapor loading capacity since SO$_2$ has a lower solubility in seawater as compared to that in limestone or lime in conventional processes; high seawater flowrate; and large equipment size. Furthermore, many constraints have to be considered when designing the marine SWFGD process. Thus, many solutions have been proposed to increase the efficiency, capacity, and output of SWFGD processes as well as to make this process more compact and lighter due to the restriction of space and weight for marine applications. This paper aims to produce a comprehensive review of the development of SWFGD, which has recently received significant consideration and is suitable for flue gas treatment for coastal and naval applications, as well as enhancement methodologies of this process by investigating both open literature and patents. This work also discusses commercially advanced and intensified SWFGD, engineering issues, environmental impacts, current barriers, and perspectives on the research and development of advanced and intensified SWFGD processes.
2. Land-Based SWFGD Systems

2.1. Process Description

The SO\textsubscript{2} composition in the flue gas from power plants burning coal is on an average between 210 and 1540 ppm\textsubscript{v} [11]. The typical pH of seawater varies from 7.6 to 8.4 with a temperature of between 5–15 °C [14]. The principle of SWFGD is the chemical absorption of SO\textsubscript{2} by using seawater as a solvent because SO\textsubscript{2} has much higher solubility as compared to other gases in flue gas. The reactions in the absorption of SO\textsubscript{2} into seawater are as follows [2,7]:

Absorption:

\[
\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+ \tag{1}
\]

Oxidation:

\[
\text{HSO}_3^- + \frac{1}{2}\text{O}_2 \leftrightarrow \text{SO}_2^- + \text{H}^+ \tag{2}
\]

Neutralization:

\[
\text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{3}
\]

\[
\text{CO}_3^{2-} + 2\text{H}^+ \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \tag{4}
\]

Figure 2 shows a simplified open-loop FGD process and a simplified closed-loop FGD process. In open-loop mode, as shown in Figure 2a, raw seawater is pumped through the scrubber system to absorb the SO\textsubscript{2} and neutralizes it with seawater’s natural carbonate ions (CO\textsubscript{3}\textsuperscript{2–}) and bicarbonate ions (HCO\textsubscript{3}–). The wash water is analyzed for turbidity, pH, nitrates, and polycyclic aromatic hydrocarbons (PAH) [15]. In closed-loop mode, as shown in Figure 2b, seawater or freshwater is recirculated through the scrubber with no discharge to the sea. A water cleaning unit is required to clean discharged water. A heat exchanger is used for cooling the wash water before recycling the scrubber. In both the open and closed loops, the scrubber gas passes through a demister or mist eliminator to avoid entrained liquid droplets before entering a stack.

2.2. New Developments

Since solubility or absorption equilibrium of SO\textsubscript{2} is essential and necessary to the design of scrubbers, several researchers measured the solubility of SO\textsubscript{2}. The solubility of SO\textsubscript{2} in seawater in the range 10 to 25 °C and 10\textsuperscript{−5} to 1 molal is predicted based on a simplified chemical model [16]. The predicted solubility of SO\textsubscript{2} in seawater is approximately two to three times higher than that in freshwater. Two thermodynamic models using Bromley’s model and Pitzer’s model for SO\textsubscript{2} solubility as a function of temperature (278.15–318.15 K) and pH were proposed [17].

In addition, the neutralization of seawater in the FGD process has been elucidated via experimental investigation and simulations [18]. To increase the pH, a NaOH solution can also be used in the traditional SWFGD process [19]. However, the use of NaOH is expensive, leading to the high operating cost of SWFGD. Back et al. [20] proposed the use of discharged fly ash from a coal power plant for the increase and restoration of pH to reduce the operating cost.
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Absorption:
\[
2\text{SO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_3 + \text{O}_2
\]  

Oxidation:
\[
2\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + \text{O}_2
\]  

Neutralization:
\[
2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{CO}_3
\]  

\[
2\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2
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Figure 2. Schematic diagram of the (a) open-loop FGD process, (b) closed-loop FGD process, and (c) hybrid mode.
3. Marine SWFGD Systems

As mentioned above, from 1 January 2020, all oceangoing vessels worldwide must comply with the SO\textsubscript{x} emission requirement of the IMO. There are several solutions including using low-sulfur fuel, replacing the existing engine system with new one using liquefied natural gas (LNG), and installing a desulfurization system. Burning low-sulfur fuel reduces SO\textsubscript{x} emissions directly, but it has a very large impact on operating costs and issues related to cylinder wear due to the lower viscosity [21]. Meanwhile, using LNG, which has very low sulfur content, is also attractive due to abundant reserve, cheap cost, and environmentally-friendly products [22]. However, this solution requires a high investment cost, and it is difficult to change the engine system using oil to one using LNG. The third option is using a scrubber, which can use a low oil price. The installation of scrubbers is attractive because cleaner fuels are more expensive, especially in long-distance marine transportation [23].

3.1. Characteristics of Marine SWFGD Process

In general, SO\textsubscript{2} in flue gas from existing ships has a typical range of concentrations of 80–1000 ppm\textsubscript{v} dry basis [23,24]. Table 1 lists the differences in system design conditions of desulfurization processes between land-based and marine SWFGD [7].

|                            | Thermal Power Plants | Large Ships |
|-----------------------------|----------------------|-------------|
| Flue gas flow rate (Nm\textsuperscript{3}/h) | 600,000 to 4,000,000 | 23,000 to 540,000 |
| Inlet SO\textsubscript{2} level (ppmd) | 100 to 1800 | 700 |
| Outlet SO\textsubscript{2} level (ppmd) | 10 to 220 | 20 |
| SO\textsubscript{2} removal efficiency (%) | 75 to 98 | 97.1 (3.5%S to 0.1%S): SECAs 85.7 (3.5%S to 0.5%S): global sea areas excluding SECAs |
| Regulatory items for seawater discharge | pH, dissolved oxygen (DO), temperature, etc. | pH, PAH, turbidity, nitrates |

The use of land-based scrubbers for marine applications has several challenges, such as the different legislative requirements, as mentioned above, and changing conditions when a ship sails through different waters [14]. Marine scrubbers have to be able to cope with changing seawater alkalinity (in case of seawater scrubbers), seawater temperature, and engine load. Furthermore, many constraints have to be considered when designing the marine SWFGD process. Besides constraints related to SO\textsubscript{2} outlet and operating conditions in terms of liquid to gas (L/G), due to restrictions of column height, weight, and space, the column should be short, light, and compact [25]. If the column internal is required to achieve higher efficiency, columns should be designed to withstand motion, limiting the column height and making the packed-type columns more suitable than tray columns [26].

3.2. Process Description

Either an open loop or closed loop can be used for marine applications. Furthermore, a flexible or hybrid process (Figure 2c), which can switch between the open and closed-loop systems, can be considered. In the global sea area, the open loop is applied to reduce the operating cost and the closed loop is applied in regulated areas to satisfy the regulation [27]. According to DNV GL, 2625 out of the 3266 scrubbers systems being installed, or 80.3%, are of the open-loop variety [28]. Hybrid systems account for 540 scrubber installations and closed-loop systems account for 65; the type of scrubber being fitted for 36 systems was unclear.

3.3. New Developments

Lamas et al. [29] numerically investigated the SO\textsubscript{2} absorption in a spray column using seawater via a CFD model. Via experiment, it was found that a 47% reduction in seawater flow rate can be achieved when using packed scrubber [30]. Ion Iliuta and Iliuta [31] modeled SO\textsubscript{2} seawater scrubbing
in countercurrent packed-bed columns via an integrated approach. Many new approaches were proposed for SWFGD, such as using electrified sprays [32], structured packings [33], or rectangular (square) shape scrubbers [7] for improving the special needs of new systems. This will be described with more details in Section 4.

4. Improvement of Water and SWFGD Systems

Available SWFGD systems in coastal and commercial marine scrubbers normally consist of spray towers fed with pure seawater or seawater doped with caustic soda [6]. Spray towers are favorable when the pressure drop is critical [34] and a high separation degree is not required [35]. Furthermore, they possess lightweight, simple construction and operation, low investment, operating, and maintenance costs, and are applicable for gases with solid particles and precipitating solvents [36,37]. Furthermore, scrubber wash-water is commonly warm and acidic, and especially in open-loop systems where seawater is adopted, it has appreciable corrosion potential [6] that leads to the preference of simpler spray scrubber to packed ones.

However, spray towers have several disadvantages, such as low mass transfer rates and high pumping costs [38,39]. These units are often bulky and heavy constructions [23]. Due to the typical constraints of marine applications, mass transfer rates, seawater consumption, and scrubber size should be considered to improve during process design [6]. Thus, new approaches were suggested for improving the performance of spray columns, including process modifications, such as modification and optimization of operating conditions, improvement of spray and vapor distributors, adding column internals, using a square or rectangular shape, using pre-scrubber, and using multiple scrubber feed; process integration, such as combining treatment of SO\(_x\) and other gases, and waste heat recovery; and process intensification, such as the use of electrified sprays, swirling gas flow, and rotating packed beds (shown in Figure 3).

Figure 3. Percentage of articles mentioning different solutions for improving SWFGD process.

4.1. Modification and Optimization of Operating Conditions

Operating pressure

SWFGD can be operated at atmospheric pressure due to the high solubility of SO\(_2\) in water, and even higher operating pressure is favorable for scrubber efficiency [40]. Additionally, due to
the turbocharger in engines, the flue gas already has atmospheric pressure leading to back pressure in the system. This back pressure may influence engine performance, leading to an increase in fuel consumption, particulate matter (PM) and CO emissions, and exhaust temperature [41]. An increase in NO\textsubscript{x} emissions is also possible due to the increase in engine load [42].

Operating temperature

Higher temperatures of absorption solution have negative desulfurization effects, i.e., lower operating temperature is theoretically favorable for enhancing the SO\textsubscript{2} removal efficiency. Nonetheless, the influence of absorption temperature within 20–40 °C is insignificant [43]. To enhance the absorption, the use of a venturi scrubber for quenching the flue gas and heat exchanger used for cooling seawater can be considered. As seawater with a temperature between 5–15 °C is used for cooling, the scrubber can be operated at 25–35 °C.

pH condition

The pH of seawater, which normally varies from 7.6 to 8.4, can be considered to enhance SO\textsubscript{2} removal efficiency. It is to be more useful to add NaOH to the same absorption seawater feed to support SO\textsubscript{2} removal while preserving a wash-water pH level close to neutral [11].

Effect of gas flow or gas velocity on desulfurization

Experimental results by Schmidt and Stichlmair [44] indicated that the gas velocity is of little importance for the transfer rate, at least in systems with high reaction rates or small liquid-side resistances (SO\textsubscript{2}/NaOH and air/water, respectively). It should be noted that quadrupling the gas velocity from 5 to 20 m/s and keeping the gas/liquid ratio (G/L) constant means a fourfold increased throughput. By investigating the gas velocity up to 5 m/s, Wang et al. [45] found that the removal efficiency and absorbent pH of SO\textsubscript{2} decreased with the increase in gas flow. More study is required to find the most efficient gas velocity for a SO\textsubscript{2} scrubber to minimize the scrubber size, which is required for off-shore scrubbers.

Effect of liquid-to-gas ratio on desulfurization

When the L/G increases at a fixed volume of gas, the volume of the liquid rises in the column, leading to a higher contact gas–liquid area [6,11]. As a result, higher SO\textsubscript{2} removal efficiency can be achieved, especially in the spray column [46]. Meanwhile, the pressure drop also increases with the increase of L/G [45].

Effect of seawater salinity and seawater alkalinity

Caiazzo et al. [47] indicated that seawater scrubbing SO\textsubscript{2} performed better than distilled water because of its inherent alkalinity. The absorption capacity of SO\textsubscript{2} reduces when both alkalinity and salinity decreases [18]. It was also observed that the high salinity of the seawater can improve SO\textsubscript{2} absorption [13]. Zhao et al. [48] claimed that at the same alkalinity, the effect of salinity is negligible, while the solubility of sulfur dioxide increases distinctly with the increasing alkalinity.

Effect of partial pressure of SO\textsubscript{2}

Zhang et al. [43] found that the strength of the factors arranged according to their influence on the removal efficiency of SO\textsubscript{2} is liquid–gas ratio > gas-flow rate > inlet concentration of SO\textsubscript{2} > temperature of absorption solution. Additionally, a lower inlet partial pressure of SO\textsubscript{2} leads to a higher removal efficiency of SO\textsubscript{2}. Ma et al. [49] pointed out that the pH of tailwater decreases and the desulfurization capacity of seawater increases upon increasing the partial pressure of SO\textsubscript{2}. 
Effect of use of additives

The addition of an additive is an important method to increase the removal efficiency of SO$_2$ [43,50]. Although many researchers have performed studies on the influence of additives on the limestone/lime-gypsum FGD [51–54], research on the effects of additives on seawater desulfurization is lacking [43]. Lower concentrations of inorganic additives (magnesium sulfate and sodium sulfate) increase the removal efficiency of SO$_2$ and have little effect on desulfurization seawater recovery [43,55]. Organic additives (acetic acid and hexanedioic acid) promote seawater desulfurization at lower pH, but they have negative effects on post-desulfurization seawater recovery. Additional research and development are needed to reduce the investment and operation costs for the process.

4.2. Improvement of Spray and Vapor Distributors

Spray and vapor distributors have to be considered to achieve adequate hydraulics in the inlet area. Failure to achieve this may result in low separation efficiency, premature flooding, and excessive entrainment [56]. Uniform vapor and liquid distribution allow maximum capacity and efficiency for a given tower design [57]. The quality of the spray distributor depends on several factors, such as the nozzle pattern, nozzle construction, spray angle, and height of the spray nozzles above the bed [56]. Uniformity of spray, small drop size with high velocity, and low atomization energy are the desired criteria for an atomizer [58,59].

The vapor distributor location is very important because if it is too low, it can be submerged in the bottom liquid, leading to turbulence on the liquid level, high pressure drop, and liquid entrainment into the rising vapor. The vapor distributor should not be close to the maximum liquid level; there should be space between them [56]. Note that a minimum liquid level at the bottom is also important because, if it is too low or the difference between column bottom edge and minimum liquid level is small, the vapor from a vapor distributor can partly release from the bottom of the column. Furthermore, the vapor flow from the distributor should not impinge on the bottom liquid surface, which can occur when an internal pipe is “elled” down, or if the column inlet pipe slopes downward at the entrance [56].

4.3. Adding Column Internals

Reconsidering structured packings, which can create a larger contact area for gas and liquid phases leading to higher separation efficiency, was suggested for improving marine scrubbers [60], provided that there are space-saving improvements of the scrubbers. Recently, findings were reported on the performance of two different SWFGD units including packed column and spray column [6]. The results indicated that the packed column can save 70% in terms of water requirement compared to spray towers. Recently, fourth-generation packing, which offers several advantages, such as high capacity, low pressure drop, and reduced costs [61], has been employed for marine SWFGD [31]. Systems with perforated plates benefit from extremely vigorous gas–liquid transfer, whereas packing uses a larger gas–liquid interfacial area. Recently, a combination of packings and perforated plates can achieve high SO$_2$ removal efficiency while reducing the absorber size and seawater consumption [2].

4.4. Square or Rectangular Shape

A cylinder shape is mostly used for small shop assembled columns and for pressurized columns, while a square shape could be considered when the absorber is operated at low pressure [35]. Square-based shapes have been widely used for coal boiler flue gas desulfurization systems, achieving a higher volumetric efficiency than that of existing cylindrical scrubbers [7]. The reason for this is because, with the same area, the diameter of the cylindrical scrubber is larger than the side of the square shape scrubber. With this shape, field erection and packing installation are simplified [35] and space can be reduced. However, it is difficult to obtain good flue gas distribution with this shape [62]. Note that other equipment and devices such as heat exchanger, pump, and tank are the same as those in
cylindrical desulfurization system. Recently, PacificGreen Technologies developed a compact, flexible rectangular shape that creates the smallest possible footprint without compromising on efficiency [63].

4.5. Using Pre-Scrubber

The outlet gas temperature is normally high, which is 120–130 °C from power plants utilizing coal [2] and from 385 to 490 °C from diesel engines [64,65]. Note that different exhaust temperatures correspond to different engine loads [66]. Low temperatures favor absorption, i.e., higher solubility is measured at low temperatures [67,68]. This reduces the solvent flow rate required to absorb a given amount of SO2. Thus, high-temperature flue gas must be cooled before entering the scrubbing gas. Reduced temperature is also used for system protection and allows the scrubber to be smaller since the volume flow rate of flue gas is smaller.

Hansen [14] invented a method using two scrubber sections for the removal of SO2 from the exhaust gas of a marine engine. The exhaust gas is quickly cooled from a temperature of approximately 180–250 °C to a temperature range of approximately 45–60 °C in the first scrubber section before entering the second scrubber section. Alfa Laval SOx scrubber combines a jet scrubber used to cool flue gas by using water and an absorber where the SOx is removed to the required level (as shown in Figure 4) [69].

![Figure 4](image-url)  
Figure 4. Schematic configuration combining a jet scrubber and an absorber [69].

The jet scrubber could be replaced by a venturi scrubber [70] to increase PM trapping, but this increases the pressure drop across the unit. Venturi scrubbers are also used as a cooler to quench hot flue gases (up to 1000 °C) [71]. Using a venturi scrubber for quenching (rapid cooling) leads to decreasing the volume flow rate because the volume is affected by temperature. This leads to a higher capacity of the scrubber. Furthermore, a venturi scrubber can remove SO2, leading to higher efficiency of the whole system in terms of SO2 removal.

4.6. Multiple Scrubber Feed

SO2 scrubbers also have a similar phenomenon for CO2 absorption: absorption mainly takes place in the bottom section, while very little absorption occurs in the upper section of the absorber [72]. In CO2 absorption, the lean amine stream can be split to achieve higher separation efficiency, with most
of the amine charged near the bottom of the column, where a large flow rate can carry large amounts of acid gas in the first few stages [73,74]. SO$_2$ absorption from flue gas also has a similar phenomenon; thus, this solution can be applied for improving SO$_2$ removal efficiency [45]. In particular, in a multiple feed configuration, (see Figure 5) there needs to be more than one solvent feed, with a large portion of seawater enters near the bottom of the scrubber to remove most of the SO$_2$ in that section as well as to reduce the flue gas temperature, leading to higher removal efficiency.

![Figure 5. Schematic diagram of a multiple scrubber feed.](image)

4.7. Simultaneous Treatment of SO$_x$ and Other Gases in a Single Process

NO$_x$, mainly produced from the combustion of N$_2$ and O$_2$ in air [75], can be removed using the two most popular methodologies, exhaust gas recirculation (EGR) and selective catalytic reduction (SCR). Meanwhile, for CO$_2$ removal or capture, chemical absorption using a solvent is one of the most popular technologies. Due to different removal methodology and mechanism, removal of SO$_2$ and other gases such as NO$_x$ or CO$_2$ is accomplished with high treatment efficiency in different independent equipment. Such a system has drawbacks, such as the requirement for a large installation area [76], a complex system [77], and high investment and operation costs [78]. Integrating the treatment of SO$_x$ with other gases is expected to be more compact and reduce investment and operating costs. Therefore, many studies have focused on the simultaneous removal of SO$_2$ with NO$_x$ and/or CO$_2$ in a single process via wet scrubbing [79–83]. Recently, a concept of simultaneous removal of SO$_x$ and NO$_x$ using seawater was developed by Yara Marine Technology [84].

4.8. Waste Heat Recovery

One of the drawbacks of wet scrubbers is that the heat contained in the exhaust gas is wasted [18]. Thus, a waste heat recovery system based on organic Rankine cycle (ORC), which vaporizes a working fluid expanding through a turbine in order to generate electricity, or Kalina cycle, which is an absorption power cycle, was proposed to improve overall energy efficiency onboard ships [85–88]. Figure 6 shows a schematic diagram of a simple ORC [85,89]. The first ORC onboard a ship is currently being tested on the newly built MV Figaro providing a maximum output power of 0.5 MW [90]. Note that the pressure drop needs to be checked carefully since the exhaust gas pressure is almost atmospheric pressure. Additional developments are required before the concept can be applied onboard marine ships.
4.9. Use of Electrified Sprays

Electrification is associated with an appreciable improvement of SO₂ absorption rate with low supplementary costs and can be a candidate for innovative spray tower absorbers [91]. Similar phenomena occur during thunderstorms when scavenging of gases and aerosols are enhanced by the electric charge of raindrops. Several researchers studied electrified water spray absorption of SO₂ to improve spray generation and droplet dispersion. Di Natale et al. [32] found that the mass transfer rate for charged droplets was 1.57 times higher than that of uncharged droplets. Recently, Di Natale et al. [92] tested a laboratory-scale wet electrostatic scrubber using distilled water sprays with flow rates from 2 to 6 mL/min, electrified by contact charging with a potential up to 5 kV.

4.10. Swirling Gas Flow

Mass transfer between the gas and liquid phases in spray towers can be enhanced using the concept of swirling gas flow [39]. With this solution, the flue gas also has a longer retention time in the scrubber, leading to longer contact time. Figure 7 shows the schematic diagram of a SOₓ scrubber system with swirling gas flow [93]. Schrauwen and Thoenes [94] studied mass transfer in a co-current spray tower with swirling gas flow by introducing the gas tangentially into the tower. More recently, Javed et al. [39] investigated the augmentation of mass transfer in a spray tower using swirling gas flow. Swirling gas flow leads to an increased retention time and compact scrubber, which is suitable for offshore applications.

Figure 6. Schematic diagram of a simple organic Rankine cycle.

Figure 7. Schematic diagram of a SOₓ scrubber system with swirling gas flow [93].
4.11. Rotating Packed Bed

A rotating packed bed (RPB) generating high acceleration via centrifugal force, leading to the formation of thin liquid films and tiny liquid droplets through a centrifugal acceleration, was invented to enhance the gas–liquid mass transfer [95]. Rao et al. [96] presented the potential of RPB for distillation and absorption, the most commonly applied separation unit operations. Substantial reduction in terms of volume or space can be achieved using Higee as compared to conventional packed beds [97]. The SO\(_2\) removal efficiency was improved using a RPB [98]. Recently, SO\(_2\) absorption intensification by an ionic liquid in a rotating packed bed was investigated [99]. Future investigations such as experiments on a wider range of SO\(_2\) concentrations and for seawater with different pH and alkalinity, development of model and design tool, and mitigation of liquid maldistribution [100] are necessary to make this solution more viable.

4.12. Membrane Contactor

Another advanced technology that can be considered is membrane contactor, which can realize gas–liquid contacting operation through the hollow fiber membrane. In this technology, the absorbent liquid flows on one side and the gas flows on the other side of the membrane [101]. Due to several advantages including high interfacial area per unit volume, absence of emulsion, no flooding at high flow rates, and high corrosion resistance [102], several studies investigated the application of membrane contactor for SO\(_2\) removal. Sun et al. [103] focused on a membrane contactor scrubber and showed that the mass transfer coefficient in seawater is about twice of the NaOH solution with pH 8.35. Recently, Liu et al. [104] introduced air bubbles to seawater to increase the fluid turbulence at the gas–liquid interface near the membrane surface, which could reduce the mass transfer resistance of the liquid film or improve the mass transfer. In particular, the overall mass transfer coefficient of SO\(_2\) could be increased from 1.15–1.5 \(\times\) 10\(^{-3}\) m/s without aeration to 1.35–1.85 \(\times\) 10\(^{-3}\) m/s with 5 L/min aeration flowrate.

5. Recently Commercialized Advanced and Intensified SWFGD Systems

The first scrubber in the world installed onboard a ship by Aalborg Industries A/S has been in operation since June 2010 [14]. This hybrid scrubber can operate in either a seawater mode or in a fresh water mode. From that time, much effort has been undertaken to improve the performance of SWFGD listed in Section 4. In this section, several recently commercialized advanced and intensified SWFGD systems, which simultaneously satisfy regulations, high efficiency, and low space requirement, were briefly surveyed. Mitsubishi Hitachi Power Systems, Ltd. has developed a rectangular FGD system, leading to improved installation layout [7]. In Korea, Hanbal Masstech Ltd. located in Gimhae has patented compact, flexible square-shaped FGD units creating the smallest possible footprint (as shown in Figure 8) as explained in Section 4.

Figure 8. Hanbal Masstech’s SO\(_2\) scrubber.
In addition, SO\textsubscript{x} scrubbers made by Fuji Electric uses cyclone technology in their internal structure. This can efficiently bring the seawater (or alkaline chemicals) and exhaust gas into contact by generating a vortex in the exhaust gas and spraying seawater from the pipes arranged spirally (as shown in Figure 9) [105]. It can be easily applied to existing ships with limited installation space, and the loss of loading space by mounting the system can also be reduced.

![Figure 9. SO\textsubscript{x} scrubber using cyclone technology [105].](image)

6. Engineering Issues

a. Scrubber has corrosion potential due to the acidic environment [6]; thus, selecting appropriate corrosion and wear-resistant material is crucial. Two-phase (duplex) stainless steel is mainly used for the scrubber tower [7] because it can perform well in corrosive environments [106].

b. Pressure drop related to the column auxiliaries (demister, gas distributor, piping, etc.) [6] should be low in scrubbers because flue gas has a similar pressure as the atmosphere. In case the excessive exhaust backpressure occurs, it can result in additional fuel consumption and other issues such as lower turbocharger efficiency, increased component temperatures, increased wear, and increased NO\textsubscript{x} emission [106].

c. Important factors such as droplet size, nozzle material, nozzle spray pattern and placement, nozzle connection size and type, required scrubbing fluid flow rates, and pressure drop need to be considered when selecting a marine scrubbing spray nozzle for proper absorption [107].

d. The scrubber on the ship should be flexible as a ship travels to different areas, which can have different regulations. Thus, a hybrid system should be considered.

e. Marine engines emit PM that has a complex nature, being composed of carbonaceous particles [23], especially the soot particles related to severe pathologies [108]. Electrostatic precipitator, wet scrubber, venturi scrubber, cyclone, in which the dust is collected, can be considered as a PM control device [109,110]. Further technologies can be referred to in Table 6 in the paper by Natale and Carotenuto [23].

f. In the closed-loop systems, salt and PM accumulation may need to be discharged, as crystallized solids may plug the pipe and pump. Bleeding off scrubber water from the system and adding seawater or fresh water to replace the lost volume can be considered [69]. The SO\textsubscript{4}\textsuperscript{2−} concentration in industrial effluents is set ranging from 250 to 500 mg/L in many countries [111,112]. The SO\textsubscript{4}\textsuperscript{2−} concentration in the waste and treated water tank needs to be checked and the discharge sulfate ion concentration needs to be calculated to remain in the allowable range. Depending on the SO\textsubscript{4}\textsuperscript{2−} concentration, SO\textsubscript{4}\textsuperscript{2−} may not need to be treated; alternatively, it can be treated using several technologies, such as biological or
chemical treatment [113–124]. In addition, in case a water cleaning unit is needed to clean bleed-off water, the addition of a coagulant can be considered [69].

g. The amount of oxygen from flue gas and seawater is generally not sufficient for complete oxidation of $\text{HSO}_3^-$ (and $\text{SO}_3^{2-}$) to $\text{SO}_4^{2-}$. This can be accomplished by using a blower to supply air into the bottom of the SWFGD [2].

h. Seawater can be added to the neutralization tank to dilute the mixture so that it can be discharged [2,19].

i. The seawater pH can decrease to a range of 2.5–3 after absorbing $\text{SO}_2$ from flue gas [18]. However, according to the 2015 IMO Guidelines, the effluent water should be no lower than 6.5 before it is discharged. To increase the pH, a NaOH solution can be employed in SWFGD [20].

7. Environmental Impacts

Despite the positive effect of the use of scrubbers to reduce atmospheric pollution, questions have been raised on their potential impacts on the marine environment [125]. The use of scrubbers results in a shift of the environmental impact of sulfur from emissions to the atmosphere toward a direct discharge into aquatic systems [126]. When the wash water from open-loop scrubbers is thrown back into the sea, the discharged $\text{SO}_4^2-$ is neutralized by the seawater alkalinity. This contributes to the acidification of the ocean and affects the marine carbonate cycle [127]. This process adds up to the ongoing ocean acidification resulting from the increase in atmospheric $\text{CO}_2$ injections to the sea related to the increase in $\text{CO}_2$ concentration in the atmosphere. Negative effects of ocean acidification on coral reefs and limestone-requiring organisms have already been observed and are well known [127]. Moreover, decreasing pH from around 8 to 6.5 will cause the desorption of massive amounts of carbon dioxide from the seawater, adding to the carbon dioxide emissions from the engine exhaust. This partly motivates IMO to initiate the approval process for the ship-based $\text{CO}_2$ capture.

Furthermore, together with high sulfur emissions, these scrubbers are known to result in higher emissions of other hazardous species including metals and PAHs [126]. In addition, the discharged water has a biochemical oxygen demand (BOD), leading to a reduction of oxygen in the local environment and a negative effect on the local marine environment [110].

8. Challenges and Future Perspectives

The equilibrium data at low $\text{SO}_2$ concentrations, needed to design SWFGD, are still scarce [11]. Furthermore, there is a need to explore additives enhancing the removal efficiency of $\text{SO}_2$. In addition, with many constraints to be considered when designing marine SWFGD processes and the trend for improving the process performance in terms of process compactness, reducing the scrubber weight, energy efficiency, lower seawater consumption, and process intensification can be an attractive solution. To achieve the development of solutions for process intensification for scrubbers, future investigations such as the development of models for the description of intensified scrubbers and the development of design tools are essential and necessary to support the implementation of intensified systems.

Research is still needed to find out the most efficient gas velocity for a $\text{SO}_2$ scrubber to minimize the scrubber size, which is essential for off-shore scrubbers. Due to limited space on a ship, methodologies for the simultaneous removal of $\text{SO}_2$ and other gases can be considered as a good future direction. Furthermore, to achieve better hydraulic performance for improving $\text{SO}_2$ removal efficiency, high-performance spray and vapor distributors need to be developed. In addition, techno-economic and life cycle analysis of marine SWFGD versus land-based SWFGD are needed for future works.

9. Conclusions

Considering the globally stricter IMO environmental regulations, in this paper, the current research and industrial applications of SWFGD were successfully investigated and analyzed. SWFGD can be considered as a technically and economically reliable unit operation for fossil fuel combustion
plants and marine applications, owing to its natural alkalinity and the large availability, simplicity of its process design and operation, no requirement of chemical sorbent, production of no solid waste, and relatively high removal efficiency. Many solutions using the concept of process modification, integration, and intensification to improve the performance of SWFGD were critically evaluated. It was found that several advanced and intensified scrubber systems have been commercialized, leading to many benefits, such as higher compactness, lower weight, higher energy efficiency, and lower seawater consumption. However, to achieve the smooth development of solutions for process enhancement and intensification for scrubbers, future investigations are necessary on the development of equilibrium data for a wider range of SO$_2$ concentrations, models for the description of advanced and intensified scrubbers, and the development of design tools.

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