

Corrosion Prevention and Control for Marine Scrubbers

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Foreword

Regulations of diesel exhaust are limiting emissions of sulfur oxides and particulates from ships burning heavy fuel oil. In January 2020, the global 0.5 per cent sulfur cap was enforced and around 4,000 ships have been fitted with exhaust gas cleaning systems (scrubbers). There are over 94,000 vessels in the world, according to the United Nations Conference on Trade and Development (UNCTAD)⁽¹⁾ ranging from cruise ships to container carriers and oil tankers, military, and other smaller vessels. Although other options are available, the preferred compliance method is the installation of wet scrubber systems because they are more cost effective. Other options for compliance are low sulfur fuel oil (LSFO), most expensive, blended fuels, and alternative fuels (liquified natural gas [LNG], liquified propane gas [LPG], hydrogen, batteries).

This Technical Report provides sound technical information on the corrosion risk of exhaust gas scrubbers to ship owners, shipyards, marine engineers, scrubber designers and suppliers. Marine scrubbers used on ships are mainly wet scrubbers, which are open-loop, closed-loop, or hybrid types. Each system is discussed with respect to a description of each type of scrubber, washwater environments, materials of construction (metals and non-metals), pitfalls of inspection, fabrication, and welding of metals, service performance and applications history including descriptions of corrosion failures and successes, and repair and maintenance guidance.

The results of this study are remarkable. Marine (seawater) scrubber environments are not as corrosive as land-based limestone scrubber systems. This conclusion is based upon the fact that the supersaturation of seawater with calcium carbonate results in little, if any, insoluble sulfates forming. This means that the marine scrubber tower environments will be less aggressive than those found in land-based limestone scrubbers, where severe corrosion has been seen under calcium sulfate deposits. For this reason, duplex, superduplex, and 6% Mo superaustenitic stainless steels have been used extensively and successfully for the last 10 years. C-276 variant alloys are preferred for hot, inlet tower piping, and fiberglass reinforced plastic (FRP) for cooler washwater piping. 7% superaustenitic stainless steels, alloy C-type high Cr-Mo nickel alloys, and titanium alloys were identified as alternate materials of construction for marine scrubbers.

AMPP technical reports are intended to convey technical information or state-of-the-art knowledge regarding corrosion. In many cases, they discuss specific applications of corrosion mitigation technology, whether considered successful or not. Statements used to convey this information are factual and are provided to the reader as input and guidance for consideration when applying this technology in the future. However, these statements are not intended to be requirements or recommendations for general application of this technology, and must not be construed as such.

⁽¹⁾ United Nations Conference on Trade and Development (UNCTAD), Palais des Nations, 8-14, Av. de la Paix, 1211 Geneva 10, Switzerland, unctad.org.

Section 1: Introduction

AMPP continues to support the maritime industry by conducting a state-of-the-art survey on the corrosion of exhaust gas cleaning systems (EGCS) or scrubbers on ships. The ultimate objective of this study is to provide sound technical information on the corrosion risk of exhaust gas scrubbers to ship owners, shipyards, marine engineers, scrubber designers and suppliers. AMPP's objective was to gather information and data on existing materials of construction, service conditions, performance history, and corrosion failures and successes. With 40 years' worth of information in AMPP's technical literature, the lessons learned continue to be gleaned from land-based flue-gas desulfurization (FGD) systems. This knowledge base on scrubber corrosion will help to ensure that similar problems or failures do not happen at sea. To expand its knowledge base, AMPP produced this technical report on Corrosion Prevention and Control for Marine Scrubbers.

Section 2: Background

MARPOL Annex VI Regulation 14¹ places limits on the sulfur content of marine fuel oils to control sulfur oxides (SOx) and particulate matter emissions, which requires the sulfur content of any fuel oil used on board ships not to exceed 0.5% globally on and after 1 January 2020.² The maximum sulfur content was 3.5% before 1 January 2020. This affects around 52,000 merchant ships trading internationally as of January 2019. The worldwide average sulfur content of residual fuel oil supplied for use on board ships is monitored as required by guidelines in IMO⁽²⁾ Resolution MEPC.192(61),³ as amended by IMO resolution MEPC.273(69).⁴

After 1 January 2015, the sulfur content of fuel oil used by ships operating within an emission control area was not permitted to exceed 0.10% m/m. Emission control areas include the Baltic Sea area, the North American area (within 200 nautical miles of the coast of North America), the Caribbean Sea area and any other sea area, including any port area, designated by IMO criteria or by local regulations.

As an alternative to the sulfur-in-fuel limits shown above, approved Exhaust Gas Cleaning Systems (EGCS), such as SOx scrubbers, can be used, as permitted through MARPOL Annex VI Regulation 4 in association with any applicable IMO Guidelines for the use of EGCS.⁵ This is an alternative method of compliance with MARPOL Annex VI Regulation 14. The current applicable Guidelines for SOx EGCS are IMO Resolution MEPC.259(68), "2015 Guidelines for Exhaust Gas Cleaning Systems,"⁶ in which the exhaust gas emission testing, EGCS approval, survey and certification, are regulated. Acceptance of an EGCS installed onboard any vessel is subject to approval by the flag administration of the vessel.

Scrubbers or EGCS are to be installed onboard a ship to remove particulate matter and harmful components, such as sulfur oxides (SOx) and polycyclic aromatic hydrocarbons (PAH) from the exhaust gases generated by the combustion processes in marine engines. These scrubbing systems have been developed and employed to treat exhaust gas from engines and auxiliary engines onboard marine vessels, to reduce such harmful components for compliance with MARPOL Annex VI. Due to the large reduction of the sulfur content limit from 3.5% to 0.5% for fuel oil used on board of ships since 1 January 2020, the limit for SOx content for SOx scrubbers is also reduced accordingly. This requires much higher performance from the scrubbers used on board ships.

Scrubber performance depends on many factors and scrubber manufacturers have extensive databases regarding the performance of their commercial brands of scrubbers for removing pollutants from different types of industrial sources. For better corrosion prevention and control, this report provides detailed information on the types of scrubbers used, performance factors, considerations for materials of scrubber construction, operation service performance history, and information on scrubber's installation, maintenance, and inspection.

As of January 2019, the top five ship-owning economies combined accounted for 51 per cent of world fleet tonnage. Greece held a market share of 18%, followed by Japan (11%), China (11%), Singapore (6%), and Hong Kong SAR (5%). Almost half of the world's tonnage was owned by Asian companies. Owners from Europe accounted for 41% and from North America for 6%. Companies from Latin America and the Caribbean, Africa and Oceania had shares of 1% or less.

⁽²⁾ International Maritime Organization (IMO), 4, Albert Embankment, London, SE1 7SR, UK, www.imo.org.

The total number of world commercial ships of 1000 gross tons (GT) and above is about 52,000 according to the 2019 e-Handbook of Statistics from the United Nations Conference on Trade and Development (UNCTAD), which total 1,963 million deadweight tons (DWT).¹ General cargo ships are ranked as the most common type of ship in the global merchant fleet, accounting for about a third of the fleet. There were almost 17,000 such ships (around 116 million tons deadweight) in the merchant fleet as of the beginning of 2019. Bulk carriers, around 11,562, are ranked as the second most common type of ship in the world, accounting for over 20% of the global merchant fleet as of January 2019. Crude oil tankers and container ships are the third and fourth most common types, with about 14% and 10% of the share, respectively. There were about 7,400 crude oil tankers and about 5,150 container ships in the world at the beginning of 2019.

According to the Exhaust Gas Cleaning Systems Association (EGCSA),⁽³⁾ a May 2018 survey showed 983 ships with scrubber towers installed or on order.⁷ Open loop type systems were the most popular exhaust gas cleaning system specified. It is the simplest scrubbing system, easy to operate, and favored by ship crews. Many ships in the North Sea and Baltic areas were fitted with hybrid systems initially, but they are operated most of the time in an open loop configuration. Open loop scrubbing has also been used for years by coastal power plants, and by oil tanker inert gas (IG) systems when in port, without environmental issues. The EGCSA believes that although there has been a surge in demand, yard capacity is not an issue going forward, but other constraints, such as availability of experienced installation teams, mean that it may not be possible to pick and choose an installation slot or coordinate a scrubber installation with an already-scheduled drydocking. The majority of EGCSA members are still taking orders, with several now taking options through to 2023 to enable ship-owners to secure a position on the installation timetable.

During 2015, in readiness for the switch to 0.10% sulfur fuel, several RORO (Roll On Roll Off) ship and ferry operators led the way and successfully installed scrubbers as a means of compliance. The cruise industry came next. In 2018 – 2019, with 2020 looming, bulk carriers took over at the top of the ship types adopting exhaust gas cleaning, followed by tankers and container ships (Figure 2.1). In each of these ship types, retrofit open loop installations predominate.

The view of analysts is that over 4,000 scrubbers were installed by January 2020, which is approximately 11% of the global fleet by tonnage and 4.3% by vessel count.⁸ EGCSA estimates that 10,000 ships will have scrubbers installed by 2025. This construction schedule is obviously being impacted and delayed by the effects of the coronavirus pandemic.

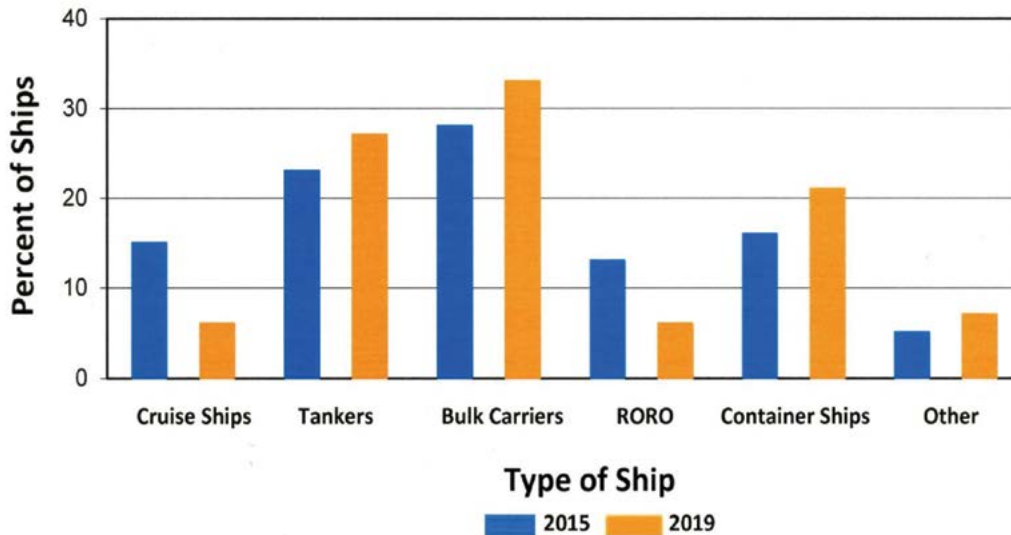


Figure 2.1: Types of Ships with Scrubbers Installed or On-Order

⁽³⁾ Exhaust Gas Cleaning Systems Association (EGCSA), Wraysbury, TW19 5AS, UK, www.egcsa.com.

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8. "Up to 6% of the Global Fleet Will Use Scrubbers by End of 2020 to Comply with IMO 2020," October 7, 2019, <https://intlreg.org/2019/10/07/up-to-6-of-the-global-fleet-will-use-scrubbers-by-end-of-2020-to-comply-with-imo-2020/> (July 2, 2021).

Section 3: Scrubber (Exhaust Gas Cleaning) Systems General Description

Marine scrubbers can be wet or dry scrubbers. Dry scrubbers use solid lime as the alkaline scrubbing material for removing sulfur dioxide from exhaust gases. Wet scrubbers use freshwater, seawater, or alkaline waters sprayed into the exhaust gas for removing the sulfur dioxide.

Marine scrubbers used shipboard are mainly wet scrubbers which are open-loop, closed-loop, or hybrid types. Open-loop or once-through scrubbers use seawater to remove sulfur oxides from the engine exhaust. The resulting waste is discharged back into the ocean. Because of its high temperatures and high content of chloride ions, the scrubber environment can be very corrosive. Closed-loop systems use seawater or freshwater mixed with chemicals, such as caustic soda, to provide the alkalinity of the scrubber liquor and neutralize the sulfur oxides. The scrubber liquor is re-circulated through the system. Closed-loop scrubbers are installed on ships sailing mainly in freshwater, e.g., the Great Lakes. Typical scrubber systems are shown in Figures 3.1 and 3.2. Hybrid systems operate in an open or closed loop configuration depending upon the discharge requirements of the area. They can operate as a once-through (open loop) system using seawater, or in the closed loop configuration using seawater, or freshwater mixed with chemicals. Hybrid or closed loop scrubbers may be required when ships are within an emission control area and operating with non-conforming high-sulfur fuels. These alternating environments complicate the problem of selecting corrosion-resistant alloys due to wide variations in pH, temperatures, and chlorides.

The exhaust/flue gases from the diesel engine enter the inlet duct or quench (precooling with seawater spray) section, at high temperatures, typically 250–450 °C (482–842 °F) (Figures 3.1 and 3.2). The exhaust/flue gases then enter the absorber chamber and are cooled to 80 °C (176 °F). Washwaters are seawater (18,000 – 20,000+ mg/L chloride; pH of 7.5 – 8.4), or freshwater ($\leq 5,000$ mg/L chlorides, pH > 7) containing alkali (either an addition of sodium hydroxide (NaOH), magnesium oxide (MgO), or sodium carbonate (Na₂CO₃) that is sprayed on the gases, absorbing the sulfur oxides, and creating an acidic liquid. The higher operating temperature can make the marine scrubbers more susceptible to pitting, crevice corrosion, and stress corrosion cracking. Marine scrubber exhaust/flue gas temperatures can reach 250–450 °C (482–842 °F) when operating in dry (bypass) mode. In the case of an in-line type scrubber, hot exhaust gas goes directly through the inside of the scrubber without bypass during dry operation. Therefore, there is a high risk of crevice corrosion in the connecting flange joint between the scrubber and piping due to excessive temperature of connected seawater and washwater. Such high operating temperatures eliminate coatings and plastics, impose limits on the materials that can be used for gaskets, and may increase the risk of embrittlement of duplex stainless steels.

The washwater is collected in treatment tanks. This area may be affected by water flow causing erosion corrosion. After cooling, the acidic washwater may be treated for neutralization and cleaning, and then onto the outlet transfer piping, which discharges it into the sea through an overboard valve. The environment in the transfer piping is generally less corrosive due to higher pH and lower temperatures, but the washwater can be very corrosive if its pH is acidic or if it sits stagnant during shutdowns.

The absorption area of the scrubber is where sulfur oxides and other pollutants are removed by reacting with the alkaline content of the washwater. Pump and piping systems may be exposed to cool or hot washwaters depending upon the scrubber design (open or closed loop). The mist eliminators section at the top of the EGCU (Exhaust Gas Cleaning Unit) removes much of the moisture from the gas before exiting out of the top of the absorber tower, where the cleaned and lower temperature gas goes out to the stack or funnel.

3.1 Scrubber Performance

Scrubber manufacturers have extensive databases regarding the performance of their products for removing pollutants from different types of industrial sources. Scrubber performance depends on many factors, including the following:

- Particle size distribution
- Mean and maximum gas flow rates
- Mean and maximum inlet gas temperatures
- Chemical composition of gas stream, including concentrations of corrosive materials present in the inlet gas stream
- Concentrations of potentially explosive materials present in the inlet gas stream
- Makeup water availability
- Purge liquid treatment and disposal requirements
- Process type, raw materials, and fuels

- i. Source operating schedule
- j. Area available for scrubber and washwater treatment
- k. Alkali supply requirements
- l. Emission test data

To promote maximum gas–liquid surface area and residence time, several wet scrubber designs have been used, including spray towers, venturis, plate towers, and mobile packed beds. Because of scale buildup, plugging, or erosion, which affect sulfur dioxide removal reliability and absorber efficiency, the trend is to use simple scrubbers such as spray towers instead of more complicated ones. The configuration of the tower may be vertical or horizontal, and flue gas can flow concurrently, counter-currently, or cross-currently with respect to the liquid. The chief drawback of spray towers is that they require a higher liquid-to-gas ratio for equivalent removal of sulfur dioxide than other absorber designs.

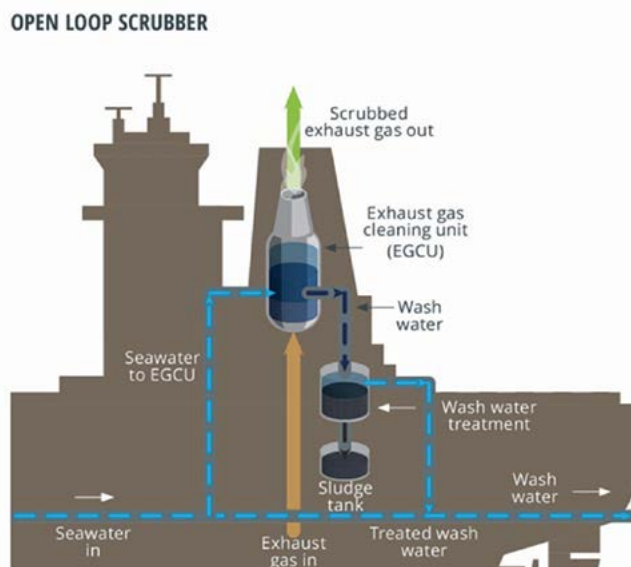


Figure 3.1: Typical Open Loop Scrubber System

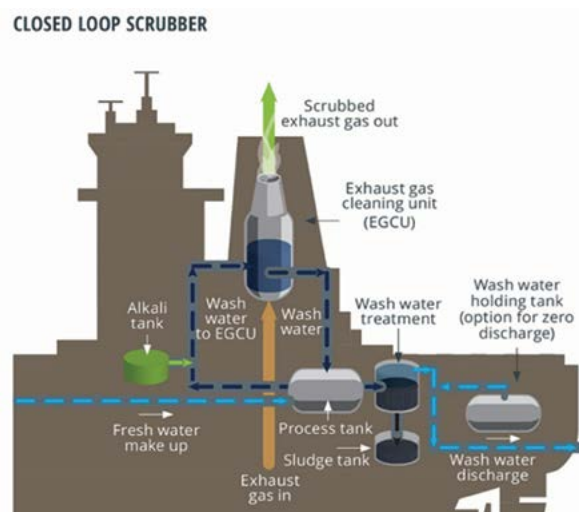


Figure 3.2: Typical Closed Loop Scrubber System

Section 4: Scrubber Environments (Washwaters)

4.1 Seawater

4.1.1 Composition and Properties

The main constituent of seawater is salt, i.e., sodium chloride, and this is one of the main causes of the corrosive nature of seawater. The concentration of seawater is often expressed as the salinity as shown in Equation (1):

$$\text{Salinity} = 0.03 + 1.805 (\text{chlorinity}) \quad (1)$$

where:

the chlorinity is the total halide content of seawater expressed as chloride, and salinity and chlorinity are in units of grams/kilogram (g/Kg) or parts per thousand (ppt).

The salinity of seawater varies considerably around the world, as shown in Table 4.1. The Atlantic is typical of the open oceans, all of which are similar in composition.¹ The Baltic and Black seas have a lower salinity due to restricted access to the open sea and their large influx of freshwater. The Caspian and Dead seas are landlocked and have been concentrated by evaporation and the presence of local salt deposits.

The composition of surface seawater in the open oceans is remarkably consistent and is shown in Table 4.2.² Where variations do occur, the elements are generally in the ratios shown in Table 4.2. If coastal water is diluted with freshwater, it is not necessary to do a full water analysis, but only for a few of elements; the rest can then be calculated. There is a variation in seawater composition with depth, but this is not discussed here because cooling water is usually taken from the surface or near-surface regions.

Besides its composition, seawater has other properties that can influence corrosion, e.g., pH, temperature, and dissolved oxygen. The bicarbonate content of clean seawater causes the pH to be well buffered to a typical pH of 8.2 ± 0.1 . An influx of freshwater usually lowers the pH, and values of 8 are not uncommon. Exceptionally large volumes of freshwater are required to lower the pH below 7.8, and lower values usually indicate the presence of acidic compounds, such as hydrogen sulfide.³

It is the bicarbonate in seawater that reacts with the acid from sulfur oxides in marine EGCS scrubbers. In waters with significant freshwater intake, such as the Baltic Sea, the efficiency of scrubbing will be reduced, and a higher injection rate of alkaline chemicals will be required to prevent unacceptably low pH values.

Seawater is very hard, not only because of the bicarbonate content, but also because of the substantial content of calcium and magnesium salts. When the seawater temperature or pH is increased, there is a tendency to form scales of calcium carbonate and magnesium hydroxide/carbonate. This is of major importance in plants where large quantities of seawater are heated. Scaling is prevented either by acidification or by the addition of anti-scaling compounds, such as polyphosphates. The acid from the EGCS scrubber will tend to lower the propensity for scaling. It is conceivable that excessive scaling might occur when shifting from high to low sulfur fuel if the EGCS is left on.

Seawater temperature is important for two reasons. Firstly, as the temperature increases, the kinetics of corrosion increase and some alloys become susceptible to localized corrosion, e.g., stainless steels. Secondly, as the temperature increases, the solubility of oxygen decreases. For materials undergoing general corrosion, such as carbon steel, there are two competing processes that change with temperature. The reduced oxygen also negatively influences re-passivation.

The temperature of surface seawater in the open ocean varies from -1°C close to the polar ice shelves to $\sim 28^\circ\text{C}$ in equatorial regions. Water temperatures can be higher in shallow coastal

regions, particularly where access to the open ocean is restricted. A good example of this is the Arabian Gulf, where temperatures can vary from around 18 °C in winter up to ~40 °C in shallow bays in summer. Seasonal variations can result in large temperature swings in some regions, while in others they are more modest. The temperature range of operation is critical for some materials in seawater. The average seawater temperatures for the three major oceans at various latitudes are shown in [Table 4.3](#).²

The most common cathodic reaction for corrosion in seawater is the reduction of dissolved oxygen. As seawater cooling systems usually take water from the surface or near the surface, it is usually saturated with oxygen. The change of oxygen solubility with temperature for a range of chloride concentrations is shown in [Figure 4.1](#). This shows that the solubility of oxygen in seawater is less than that of a salt solution of equivalent salinity. The reason for this is not only the presence of other ions in seawater, but also the presence of aerobic bacteria, which require the oxygen as part of their metabolic processes.

The chloride concentration also influences the corrosion of some metals. As the chloride concentration increases, so does the possibility of pitting or crevice corrosion of stainless steels. Increasing the alloy content of the stainless steels decreases this risk. Titanium (grades 1, 2 and 5) is very resistant to crevice corrosion in seawater up to around 70 to 80 °C and maintains this resistance down to pH 2.³ With alloys that undergo general corrosion in seawater, such as carbon steel, there is a gradual increase in corrosion rate as the chloride concentration increases. However, the increase is not very great for most metals.

4.1.2 Pollutants and Additions

Pollutants are mainly found in coastal waters and their presence in the open ocean will be at low concentrations, if present at all. The most common pollutant is hydrogen sulfide, and it can have a number of sources. One is from raw sewage discharged into the sea. Another source is from sulfate reducing bacteria (SRB), which reduce sulfate to sulfide as part of their metabolic process.⁴ SRB are only active under deaerated conditions, such as in bottom mud or under heavy fouling. When bottom mud is stirred up by tidal action or by passage of a ship, the sulfide can enter the cooling water system.

Sulfides may be present from 0.01 mg/L to tens of mg/L, in very severe polluting conditions. However, sulfide reacts with dissolved oxygen in aerated seawater with a half-life of ~ 15 minutes, so its concentration decreases rapidly in flowing seawater. Carbon steel⁵ and copper alloys⁶ can suffer severe acceleration of corrosion and pitting in the presence of sulfides, but high alloy stainless steels, Ni-Cr-Mo alloys and titanium are not significantly affected by sulfides.

Another pollutant that can be found in coastal waters is ammonia and this may have many sources.⁵ It can be present in discharges from fertilizer plants, for example, and can also be produced by the decomposition of organic material. Concentrations may vary from 0.1 to ~10 mg/L, but at these concentrations it does not affect the corrosion of carbon steel, stainless steels, Ni-Cr-Mo alloys or titanium.

A third pollutant that may be found in some coastal waters is silt and sand. Silt is defined as particles up to 50 µm diameter, while sand covers particles of greater diameter. Silt may be drawn down large rivers or it may be stirred up by strong tidal action, such as in the River Severn estuary in the UK, or the Bay of Fundy in Canada. Sand can also be stirred up by strong tidal action, or by local dredging operations.

Silt and sand are abrasive, and they increase the metal loss of most alloys. The aggressiveness increases with the sand/silt content and velocity, as well as particle diameter. Silt and sand have been seen to cause significant metal loss of carbon steel and copper alloys.^{4,5} Modest concentrations (<100 mg/L) for relatively short intervals do not significantly affect stainless steels, Ni-Cr-Mo alloys and titanium, and higher concentrations may be tolerated if the particle size is small.⁷ Non-metallic materials can also suffer severe erosion in the presence of suspended solids.

Chemicals can also be present in seawater as deliberate additions, and the most common is chlorine or hypochlorite. This is added to seawater to prevent fouling, and if it is properly controlled, it will not cause significant additional corrosion to the alloys discussed in Section 5. When added continuously, a chlorine residual at the discharge of 0.03 mg/L will prevent fouling.⁴ A maximum concentration of free chlorine of 0.5 mg/L in the system is safe for most materials.^{4,6} When chlorine/hypochlorite is added intermittently, dosing of 1 or 2 mg/L for ½ to 1 hour/day will not cause any corrosion problems.

Another way of preventing fouling is to use an electrically driven copper anode in the water box, sometimes with an aluminum anode as well. The dissolved copper will prevent fouling, provided it is maintained at a suitable concentration (tens of ppb), and this concentration will not affect the corrosion of the metals discussed in Section 5. Note that it is possible for this copper to be precipitated out in the sludge trap. It is not clear if this might affect corrosion in the sludge trap.

4.2 Brackish Water

Waters with significant chloride contents that are not seawater are termed brines or brackish water. Brines are waters with chloride concentrations significantly higher than that of seawater, such as the discharges from desalination plants. They would not normally form the water intake for any marine FGD scrubber. The definition of a brackish water is rather arbitrary but is typically used for waters from 5 to 15 g/L chloride. These can occur in large lakes that are not connected to the sea. Brackish waters can also occur where there is significant influx of freshwater to dilute seawater.

The Baltic Sea receives a large quantity of water from melting ice and snow, meaning that its salinity is about a quarter that of open ocean seawater. Because of its low bicarbonate content, its pH can be <7.8. The Baltic can be regarded as a brackish water.

Brackish waters that are produced by dilution of seawater contain the same species as shown in Table 4.2 in roughly the same proportions. Waters that are produced from surface sources other than seawater will tend to contain the same species as seawater, but the proportions can be very different. This may mean that the bicarbonate content could be much lower, in which case it will not neutralize the acid gases in the exhaust very efficiently. A brackish water with a higher bicarbonate content will be more efficient at neutralizing acid gases. The quantity of bicarbonate will control the pH of the water, but in conjunction with any dissolved carbon dioxide. As such, it is not possible to predict the pH of brackish waters, but they are typically in the range of 7.0 to 8.5.

The same pollutants and additions may be present in brackish waters as for seawater at roughly the same concentrations, and the same limits of use apply for different materials.

4.3 Freshwater

Freshwater can cover a range of compositions containing 0 to ~5,000 mg/L chloride. In practice, the large bodies of freshwater on which vessels requiring FGD scrubbers can operate typically have chloride contents from 10 to 2,000 mg/L. For example, the chloride content of the Great Lakes between Canada and the USA is ~20 mg/L.

With freshwaters, there are several terms that are important, and these are shown in Table 4.4 with their definitions. They relate to the hardness of a water and are usually expressed as the equivalent as CaCO₃. Thus, 40 mg/L calcium is 100 mg/L expressed as CaCO₃. Hardness is important because waters that are hard can deposit scale, which can be calcium carbonate, magnesium carbonate and/or magnesium hydroxide. Waters can be classed as soft or hard, and the approximate boundaries are:

Soft Waters–	Total hardness up to 50 mg/L
Moderately hard waters–	Total hardness 50 to 150 mg/L
Hard waters–	Total hardness >150 mg/L.

In a shipboard FGD scrubber, it is all the species expressed as total alkalinity that can neutralize the acid from the exhaust gases. The greater the total alkalinity, the greater is the water's ability to remove acid.

The hardness of a water depends on the type of rocks it has passed over or through prior to entering a lake or other water body. Limestone rocks will slowly dissolve in the water, giving rise to hardness. The concentrations of other species, such as chloride, sulfate, nitrate, etc. can be very variable. For instance, the chloride content of the water in the Great Lakes is ~20 mg/L, while that in the Caspian Sea is ~7,000 mg/L, and it classes as a brackish water. When designing an FGD scrubber system for a freshwater, it is important to consider the total alkalinity and the chloride content; the former for scrubbing efficiency and the latter for corrosivity.

The presence of sulfate in a water can increase the resistance of stainless steels to pitting and crevice corrosion,⁸ but this has not been properly quantified. However, most freshwaters will contain some sulfate.

4.4 Alkaline Additions

The acid gases in the exhaust will react with the bicarbonate in the cooling water, but bicarbonate is not present in sufficient quantities, so an alkaline reagent is typically injected into the scrubbing system to prevent the pH from going too low. The following section reviews the available chemicals, their commercial composition and availability, and what would be required for storage and dosing.

4.4.1 Caustic Soda

Caustic soda or sodium hydroxide is widely used commercially in a range of industrial processes. It is commercially available either as 50% solution or as pellets, which are known as "prills." Pellets (prills) would present several shipboard problems, as they require great care in handling and the reaction when they are dissolved in water is highly exothermic and generates a lot of heat. As a 50% solution, caustic soda is available either as 1,000 L totes or by the road or rail tanker load. In the quantities used in a scrubber, there are potential hazards loading numerous full totes, connecting them up, and then disconnecting and removing them when empty. Having a large on-board tank that can be filled from a dockside tanker is a simpler, lower risk alternative.

Caustic soda is made by two commercial processes, the diaphragm method and the membrane cell method. The caustic made by the diaphragm method typically contains at least 1 g/L chloride as an impurity and may contain as much as 6 g/L.⁹ In addition, it may also contain chlorate, which is a powerful oxidizer. Caustic produced by the membrane method contains low levels of impurities such as chloride. Caustic soda can cause stress corrosion cracking (SCC) of carbon steel, and the presence of chloride can cause SCC when it would not otherwise be expected, but it does not significantly affect the performance of stainless steels or nickel alloys in caustic soda.⁹ It may affect the performance of lower alloy stainless steels after the caustic is injected into the main scrubber water stream, if it is running on freshwater.

Caustic soda at a 50% concentration will freeze at about 5 °C, so vessels operating in cold climates should fit heaters to the caustic soda tank to prevent solidification. The heaters are usually either nickel alloy 200 (UNS N02200) or nickel alloy 201 (N02201) or alloy 600 (N06600), as these alloys are resistant to corrosion and SCC by caustic soda at high temperatures. It is important to ensure that the heater does not cause excessive heating of the caustic tank, because corrosion and possibly SCC could result.

When caustic soda reacts with sulfuric acid, it produces sodium sulfate, which is soluble and non-toxic. Materials for storing and handling caustic soda are discussed in [Sections 5 \(metals\)](#) and [6 \(polymers\)](#).

4.4.2 Magnesium Oxide

Another method of neutralizing acids in scrubber slurries is to dose with magnesium oxide slurry. Magnesium oxide is insoluble in water but reacts with sulfuric acid to produce magnesium sulfate, which is very soluble and non-toxic. Magnesium oxide powder is non-toxic and is relatively easy to handle. It would need to be added to water in a suitable tank, the material for which will depend on the composition of the water. As magnesium oxide is insoluble in water, the tank of slurry will require constant agitation to prevent settling of the oxide. Once it has formed a thick sludge in the bottom of the tank, it will take very vigorous agitation to restore the slurry to full strength.

For marine scrubbers, high reactivity magnesium oxide is required, and this is termed light-burned magnesia, or caustic calcined magnesia. The commercial product may contain some chloride as

an impurity. This might affect the corrosion of lower alloy stainless steels in a freshwater scrubber, if the chloride was present at g/L quantities.

4.4.3 Sodium Carbonate

Sodium carbonate (sometimes called soda ash) is not such a strong neutralizer of acid as caustic soda, but it is less hazardous. It is commonly supplied as powder and would need to be dissolved in an on-board tank with a suitable mixer/agitator. Powdered sodium carbonate requires some care in handling because it is still alkaline in nature. If the sodium carbonate were mixed in seawater, it would raise the pH significantly causing precipitation of calcium and magnesium scale. This might interfere with the dosing system. It would be better if the sodium carbonate solution were made up with a soft freshwater, or other water of low hardness.

Sodium carbonate is produced commercially by precipitation, so it should be low in impurities, such as chloride. Materials capable of handling caustic soda could also handle strong sodium carbonate solutions.

When sodium carbonate reacts with the acid in the scrubber, it will produce sodium sulfate, carbon dioxide and water. Sodium sulfate is very soluble and is non-toxic. The carbon dioxide would vent out of the scrubber with the treated exhaust gas.

4.5 Corrosion Products in the Absorber Tower

A marine FGD scrubber is quite different from a land-based unit where a limestone slurry is sprayed into the flue gases, producing a large quantity of calcium sulfate. In a marine scrubber, the exhaust gases contain a lot of carbon dioxide and a little SO_x. The sulfur gas concentration in marine diesel exhaust is low because of the increasingly restrictive regulations on the sulfur content of marine diesel fuel over the last few years.

Seawater is super saturated in calcium carbonate, and it is believed that it is the organic content of seawater that prevents the precipitation of calcium carbonate. In a marine scrubber, the organic content will quickly be destroyed, and the carbon dioxide will dissolve in the seawater, changing the CO₂/HCO₃ balance. This will cause the nucleation of calcium carbonate particles in the scrubber tower, probably initially as vaterite. This compound is unstable and will slowly convert to calcite. Because the calcium carbonate is nucleating in the center of the scrubber as the seawater and exhaust gases mix, there will be no protective calcium carbonate scale on the metal surfaces. The particles will be swept from the scrubber to the treatment tank and then to the sludge tank, along with any soot and other combustion products.

In recirculating mode, it is possible for the pH to decrease significantly, and this might reduce the production of calcium carbonate, in which case a little calcium sulfate might form. Reaction of the exhaust gases with any of the compounds used for pH control (see [Paragraph 4.4](#)) will mostly produce soluble compounds.

Because of the supersaturation of the seawater with calcium carbonate, there will be little, if any, insoluble sulfates formed. This means that the scrubber tower environment will be less aggressive than that found in land-based limestone scrubbers, where severe corrosion has been seen under calcium sulfate deposits.

In freshwaters, the calcium content will be lower than that in seawater, as will the bicarbonate content. This means that the scrubber will be operating in recirculating mode with chemical additions to control pH. Because of the low calcium content in the water, there will be little calcium sulfate, if any, and the products will mostly be soluble sulfates.

4.6 Corrosion in Closed Loop Mode

When operating in closed loop mode, using chemical additions to remove the SO_x, the water used to make up for evaporative losses may have a chloride content ranging from exceptionally low to several thousand mg/L. With extended operation in closed loop mode, the chloride concentration will increase, but the concentration will depend on that of the make-up water. For example, the water in the Great Lakes is ~20 mg/L chloride and even with five times concentration in closed loop mode, lower alloy stainless steels can be considered (see [Paragraph 5.2](#)). However, if the make-up water is brackish, say 7,000 mg/L chlorides, then a five-fold concen-

tration would increase this well beyond that of seawater. This would necessitate higher alloy stainless steels, nickel alloys or titanium for the absorber tower. There will be periodic blow down to reduce the chloride content in the recirculating water, but high concentrations of chloride can occur. It is important to consider the chloride content of the make-up water and concentration effects when selecting alloys for closed loop mode.

Table 4.1
The Salinity of Seawater around the World²

BODY OF WATER	TOTAL DISSOLVED SOLIDS (g/Kg)
Baltic Sea	8
Black Sea	22
Atlantic Ocean	37
Mediterranean Sea	41
Caspian Sea	130
Dead Sea	260
Irish Sea	32.5

Table 4.2
The Composition of Open Seawater²

SPECIES	ION	CONCENTRATION (g/Kg)
Chloride	Cl ⁻	18.979
Sodium	Na ⁺	10.556
Sulfate	SO ₄ ²⁻	2.649
Magnesium	Mg ²⁺	1.272
Calcium	Ca ²⁺	0.400
Potassium	K ⁺	0.380
Bicarbonate	HCO ₃ ⁻	0.140
Bromide	Br ⁻	0.065
Boric Acid	B(OH) ₃	0.026
Strontium	Sr ²⁺	0.013
Fluoride	F ⁻	0.001
TOTAL		34.481

Table 4.3
Average Surface Temperature of the Oceans at Various Latitudes²

LATITUDE	TEMPERATURE (°C)					
	NORTH LATITUDE			SOUTH LATITUDE		
	ATLANTIC OCEAN	INDIAN OCEAN	PACIFIC OCEAN	ATLANTIC OCEAN	INDIAN OCEAN	PACIFIC OCEAN
70° - 60°	5.60	-	-	-1.30	-1.50	-1.30
60° - 50°	8.66	-	5.74	1.76	1.63	5.00
50° - 40°	13.16	-	9.99	8.68	8.67	11.16
40° - 30°	20.40	-	18.62	16.90	17.00	16.98
30° - 20°	24.16	26.14	23.38	21.20	22.53	21.53
20° - 10°	25.81	27.23	26.42	23.16	25.85	25.11
10° - 0°	26.66	27.88	27.20	25.18	27.41	26.01

Table 4.4
Composition Factors for Freshwaters

TERM	FORMULA	UNITS
Total Hardness	Mg + Ca	mg/L as CaCO ₃
Calcium Hardness	Ca	mg/L as CaCO ₃
Total Alkalinity	OH ⁻ + CO ₃ ²⁻ + HCO ₃ ⁻	mg/L as CaCO ₃
Phenolphthalein Alkalinity	OH ⁻ + CO ₃ ²⁻	mg/L as CaCO ₃

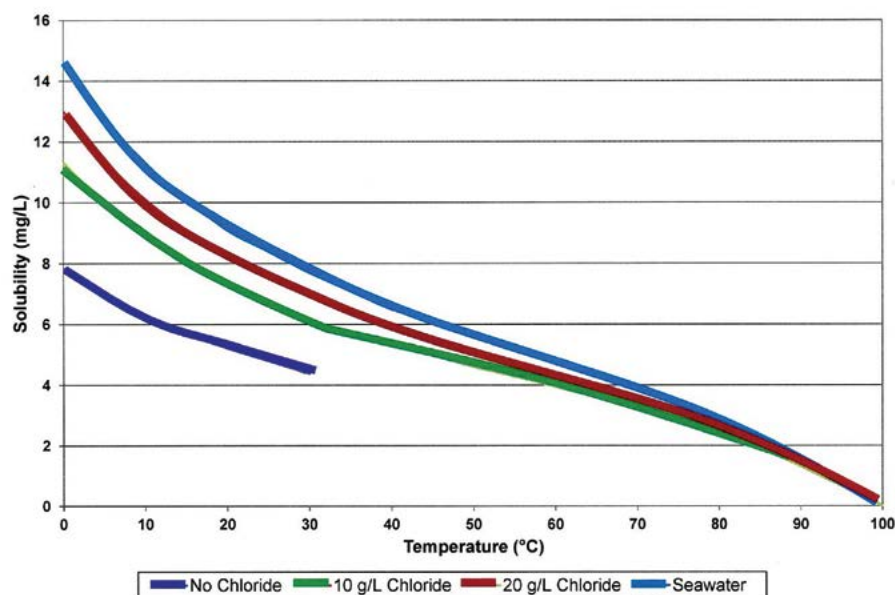


Figure 4.1: Effect of Temperature and Chloride on the Solubility of Oxygen at Normal Atmospheric Pressure

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Section 5: Basics of Corrosion of Metals¹

The resistance of metallic materials against corrosion is generally not just a material property but a property of the whole system. This corrosion system consists of the combination: material — medium - impurities – temperature – mode of operation – maintenance – deposits/incrustations and other factors that may influence corrosion ([Table 5.1](#) and [Figure 5.1](#)).

The term “land-based/marine scrubber” used in this paper refers to FGD (Flue Gas Desulfurization) systems at (mainly) coal fired power plants and marine scrubbers for diesel engines on ships.

Where the term “corrosion resistance” is used in this report, it always refers to an alloy in combination with the typical land-based/marine scrubber media. This medium is water with sulfur and chloride contents and other additions/impurities.

All stainless steels and nickel alloys discussed in this report gain their corrosion resistance by forming a thin, passive (chromium-rich) layer on the surface. In the same way, titanium is protected by forming a titanium dioxide layer. This layer protects the material from further corrosion attack. To form this protective layer, oxygen is needed. If the passive layer is destroyed chemically or mechanically, these alloys can repassivate in most oxygen-containing or oxidizing environments. For the repassivation, oxygen is needed.

In any system operating under real land-based/marine scrubber conditions, many other factors influence the corrosion potential on the surface of the material.

Any given composition of a medium in a scrubber must also consider further parameters and local conditions that are normally not given in any specification. The corrosive conditions on the surface of the material are often totally different from, like chlorides or sulfur content. Under deposits, for example, the chlorides will concentrate, and the pH value may drop to extremely low values.

Field tests and experience with comparable systems count much more than laboratory corrosion values!

5.1 Types of corrosion

In general, the following types of corrosion ([Figure 5.2](#)) can be distinguished in scrubbers for gas cleaning and other wet-corrosion applications.

5.1.1 General/uniform corrosion: The simplest form of corrosion is uniform or general corrosion. This type of corrosion is almost uniform across the entire surface and can be easily countered by an appropriate increase of sheet and plate thickness. General corrosion occurs mainly in the exhaust gas inlet.

5.1.2 Intergranular corrosion: Intergranular corrosion or attack is a form of corrosion which occurs in or adjacent to the grain boundaries of a metal. Some nickel alloys and stainless steels may become susceptible to intergranular corrosion because of their carbon content after heat treatment or after welding. Because titanium is a one phase system, it is not susceptible to intergranular corrosion in these systems.¹

A controlled heat input during welding and careful heat treatments are the best counteraction to minimize this effect.

5.1.3 Pitting and Crevice Corrosion: In any chloride-containing medium like land-based/marine scrubbers, pitting and crevice corrosion are always the most critical forms of corrosion. Pitting and crevice corrosion are described in detail later in this section ([Figure 5.3](#)).

5.1.4 Stress Corrosion Cracking (SCC): The susceptibility to stress corrosion cracking mainly depends on the nickel content ([Figure 5.4](#)). However, [Figure 5.4](#) shows the results in boiling 45% MgCl₂, which is more severe than seawater. Nonetheless, austenitic stainless steels with less than 20% Ni, such as Types 304L (UNS S30403) and 316L (S31603) may suffer SCC if mechanical

stress combines with a chloride-containing medium like seawater. The mechanical stress may result from residual stresses within the material (for example, from cold forming or welding) or from external stress like loads on fasteners. Nickel alloys and titanium are not attacked by SCC under land-based/marine scrubber conditions.¹ Duplex stainless steels and 6% Mo superaustenitic stainless steel are also very resistant to SCC.

- 5.1.5 Erosion:** Particles in the solution may continuously destroy the protective layer of oxides on the material surface and therefore accelerate corrosion. As this depends on many factors like quantity, size, hardness and velocity of the particles, no general recommendation can be given here. The differences between the alloys used in this application seem to be exceedingly small. Materials that can quickly repassivate by replacing any destroyed oxide layer are advantageous.
- 5.1.6 Corrosion Fatigue:** This is normally not encountered in land-based/marine scrubber systems, as it is mostly relevant for rotating parts. Pump shaft materials are selected by manufacturers to resist corrosion fatigue. Corrosion fatigue may be triggered by vibration caused by turbulent air flow.
- 5.1.7 Galvanic Corrosion:** Galvanic corrosion may happen when two or more metals with different electrochemical potentials are connected and exposed in an electrolyte. The potential differences of stainless steels and nickel alloys are so small that in practical land-based/marine scrubber applications, all these alloys can be combined without any problems. Only when using quite different materials, such as graphite, should countermeasures be considered.

- 5.2 Pitting and crevice corrosion:** Both these types of corrosion are based on similar electrochemical effects and become more critical with rising chloride concentration, increasing temperature, and decreasing pH value. The corrosion resistance of stainless steels and nickel alloys is a result of the spontaneous formation of a thin but very dense layer mainly consisting of chromium oxides. A local breakdown of this so-called passive layer and the presence of chlorides result in the typical pitting or pinhole corrosion. Crevice corrosion also refers to a breakdown of the passive layer in crevices due to lack of oxygen and the concentration of chlorides. This is followed by enhanced corrosion in this area. Such crevices can be formed by construction, e.g., under flanges, nuts, and bolts or under deposits ([Figure 5.2](#)).

Pitting and crevice corrosion are always the dominant form of attack if chlorides are present. This is the reason why all other types of corrosion can normally be neglected for FGD and marine scrubbers. Molybdenum confers increased resistance to chlorides and so is always present in chromium-bearing alloys intended for use in high-chloride environments, although SCC failures have recently been reported.

Therefore, in chloride-containing environments, any calculation of a corrosion rate or corrosion allowance and a resulting lifetime calculation does not make any sense. Pitting and crevice corrosion will always grow under the material surface without any significant general material loss, corrosion rate or thickness reduction ([Figure 5.1](#)).

The corrosion resistance of stainless steels and nickel alloys is of course determined by their composition. The main alloying element for most stainless steels and nickel alloys is chromium, which is necessary for a stable passive surface layer, upon which the corrosion resistance depends. Besides chromium, molybdenum is another important alloying element that increases the resistance to pitting and crevice corrosion. Tungsten is also helpful, but not as much as molybdenum. The combination of nickel, chromium, molybdenum, tungsten and nitrogen is decisive for the resistance of the alloy against localized corrosion. A common method of calculating the relative pitting and crevice corrosion resistance of alloys is by use of a Pitting Resistance Equivalent Number (PREN), which is determined from the alloy composition. The formula used in NACE MR0175/ISO⁽⁴⁾ 15156² and ISO 17781³ is shown in Equation (2):

$$\text{PREN} = \% \text{Cr} + 3.3(\% \text{Mo} + 0.5 \times \% \text{W}) + 16 \times \% \text{N} \quad (2)$$

Because of the high corrosion resistance of special stainless steels and the nickel alloys used in scrubbers, several overly aggressive tests have been established to compare and rank these materials. One of these tests is the determination of the so-called Critical Pitting Temperature (CPT) or Critical Crevice Temperature (CCT) as a function of the PREN, which is determined from the alloy composition. Of course, one should al-

⁽⁴⁾ International Organization for Standardization (ISO), Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, www.iso.org.