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# **CORROSION OF CRUISE VESSEL OUT-FITTING PARTS**

Faculty of Engineering and Natural Sciences  
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# ABSTRACT

Liisa Ojaniittu: Corrosion of cruise vessel outfitting parts  
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Corrosion causes huge costs for ship industry. Marine environment is very corrosive and the presence of marine salts accelerate corrosion and may cause local corrosion. High humidity of marine environment also has an influence on corrosion. Materials that are used in marine environment should have high corrosion resistance, or they should be protected against corrosion by coatings. Corrosion resistance in marine atmosphere of materials is important to know in ship building. It is also important to know how materials behave together due to galvanic effects. Surface preparation before coating is important since great part of coating failures are results of poor surface preparation.

The aim of this thesis was to study marine corrosion and to determine the causes of corrosion on Meyer Turku ships. Corrosion related claims on pool decks and on life boat decks are investigated in the case studies. Claims are processed by Jira software which is used in Warranty section of Meyer Turku. The main causes of corrosion are divided in five groups which are flying metallic dust and other impurities, coating failure, material selection, maintenance and design. Dividing has been done by photos, by comments of warranty engineers and by other documents.

Keywords: Corrosion, Marine corrosion, Marine environment, Shipbuilding, Corrosion prevention

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# TIIVISTELMÄ

Liisa Ojaniittu: Risteilyalusten ulkokansien varustelujen korroosio

Diplomityö

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Meri-ilmastossa tapahtuva korroosio aiheuttaa suuria kuluja laivanrakennuksessa. Meri-ilmaston sisältämät suolat kiihdyttävät korroosiota ja aiheuttavat paikallista korroosiota. Lisäksi meri-ilmaston kosteus vaikuttaa korroosioon. Tämän takia materiaaleilta vaaditaan hyvää korroosionkestävyyttä tai materiaalit on päällystettävä pinnoitteilla korroosion estämiseksi. Materiaalien korroosionkesto on tärkeää tietää, kun valitaan materiaaleja laivanrakennukseen. Tärkeää on myös tietää miten materiaalit toimivat galvaanisessa kontaktissa toisiinsa. Ennen pinnoitusta on tehtävä kunnolliset esikäsittelyt, kuten puhdistus, sillä esikäsittelyn puutteesta johtuvat monet pinnoitteisiin liittyvät korroosio-ongelmat.

Tämän diplomityön tavoite oli selvittää korroosiota meri-ilmastossa sekä määrittää mistä korroosio-ongelmat Meyer Turun laivoilla johtuvat. Tutkimus osiossa tarkastellaan korroosioon liittyviä korvausasioita uima-allas kansilla sekä pelastusvene kannella, jotka ovat ongelma-alueita korroosion suhteen. Korvausasiat on käyty läpi Jira-ohjelman avulla, jota käytetään korvausasioiden selvittelyyn Meyer Turun telakalla. Korroosiota aiheuttavat tekijät on jaettu viiteen eri ryhmään ja korvausasiat on jaoteltu näihin ryhmiin. Nämä viisi ryhmää, jotka ovat irtoruosteen ja muiden epäpuhtauksien aiheuttama korroosio, viallisen pinnoitteen aiheuttama korroosio, väärästä materiaalivalinnasta aiheutunut korroosio, huollon puutteesta johtuva korroosio sekä huonosta suunnittelusta johtuva korroosio. Tämä on tehty valokuvien, takuuiinsinöörien kommenttien ja muiden dokumentaatioiden perusteella. Näiden perusteella yleisimmät korroosio-ongelmien syyt kartoitettiin.

Avainsanat: Korroosio, korroosionesto, laivanrakennus, meri-ilmast

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## **PREFACE**

This master's thesis was carried out at Meyer Turku Oy and was part of Master of Science degree at Tampere University in Faculty of Engineering and Natural Sciences. I want to thank Meyer Turku for this opportunity to study marine corrosion and ship building.

I want to thank Jari Valtonen, my instructor at Meyer Turku, for instructions and comments during this project. I also want to thank Warranty department for helping me.

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Turku, 15.05.2019

Liisa Ojaniittu

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# 1. INTRODUCTION

The subject of this thesis is to investigate marine corrosion, materials and corrosion protection used in marine environment and to determine the causes of corrosion in Meyer Turku cruise vessels. This thesis was done in Meyer Turku shipyard.

Corrosion causes huge costs in ship building industry. These costs consist for example of material wastage, corrosion protection, maintenance and repairing costs. Marine environment is highly corrosive due to high humidity and the presence of corrosive agents, such as sodium chloride. There are also many other factors which vary by location and time of the year. Materials selection for marine environment is difficult since marine environment is highly corrosive for most of the materials. Materials with excellent corrosion resistance may not have other required properties, or they may have high cost. Cheaper materials can be used with protective coatings. However, the protective coatings may fail, due to demanding circumstances of marine environment.

Chapters 2-5 constitute literature survey of this work. Theoretical part of this work goes through the basics of marine corrosion, the most general types of corrosion in marine environment, corrosion of different materials used in marine environment and corrosion prevention in marine environment. Basics of marine corrosion include the cost of marine corrosion and factors affecting to the marine corrosion and in the most general types of corrosion is presented theory of the most general types of corrosion in marine environment. Corrosion of different materials includes the most used materials in ship building and the corrosion prevention in marine environment includes the most used corrosion prevention methods used in ships.

Case studies include dividing of corrosion claims into five category and examples of some corrosion claims in Meyer Turku ships. Corrosion claims are from five Mein Schiff cruise vessels. The purpose of dividing was to determine the most general causes of corrosion in Meyer Turku cruise vessels.

## 2. MARINE CORROSION

Marine environment is very corrosive and corrosion cause huge costs to ship industry. [1][2] Factors affecting to the marine corrosion can be divided to chemical, physical and biological factors. [3]

### 2.1 Corrosion cost in marine environment

It has been evaluated that 25 – 30 % of steel produced in one year is destroyed by corrosion. [4] Direct costs, caused by corrosion, were evaluated to be staggering \$276 billion which is approximately 3.1 percent of the nation's Gross Domestic Product (GDP) in the United States, due to a study called "Corrosion Cost and Preventive Strategies in the United States". These costs are composed not only of repair and inspection of corroded surfaces and structures and disposal hazardous corrosion waste materials but also of the application of protective coatings such as paintings and surface treatments. According to British Hoar committee report, corrosion costs are 3% of British Gross National Product (GNP) and 23% of this could be prevented. There are estimations that of an industrialized nation's income or its GNP, 3.5 - 5% is spent on corrosion lost, replacements, maintenance and prevention. There are also many costs associated to corrosion, such as lost in production due to shutdowns and leakages, contamination of products and maintenance costs. [5]

The main costs of corrosion in ships are indirect costs, such as increased mass, increasing workload in design and building, decreased performance and costs of repairing. [2] The costs of corrosion and corrosion protection in the shipbuilding industry was 21% according to a survey of ten different industries in the U.K. With better design and better protective coatings, 1/5 of this amount could be saved. [6] In Table 1 can be seen that the corrosion cost, which includes corrosion prevention and actual corrosion, are 350 USD millions for new cruise vessels. In Table 2 can be seen that the annual repair and maintenance cost for cruise vessels are 337 USD millions. [2]

**Table 1.** *Average expenses associated with corrosion in new ship structures. [2]*

Ship type	Amount	Structure ex- penses due to corrosion (%)	Average ship expenses (USD millions)	Average corrosion expenses per year (USD millions)
Oil tankers	6920	13	50	1799
Chemical tankers	2471	30	50	1483
Bulkers	6252	10	20	500
RoRo	18611	10	15	1117
Fishing vessels	23711	10	5	474
Tugs	12954	10	11	570
Refrigeting vessels	1441	10	6	35
Cruise vessels	337	13	200	350
Passanger vessels	5386	10	24	517
Others	7724	10	20	618
World total				7463

**Table 2.** *Average expenses associated with corrosion in ship operation and refit. [2]*

Ship type	Amount	Refit ex- penses due corrosion (USD mil- lions)	Annual refit expenses (USD mil- lions)	Average corro- sion expenses per year (USD millions)	Total an- nual ex- penses (USD mil- lions)
Oil tankers	6920	0,2	1283	0,1	969
Chemical tanekrs	2471	0,3	741	0,1	346
Bulkers	6252	0,05	313	0,06	350
RoRo	18611	0,05	931	0,07	1303
Fishing vessels	23711	0,025	593	0,02	474
Tugs	12954	0,05	648	0,05	648
Refrigeting vessels	1441	0,05	72	0,05	72
Cruise vessels	337	0,2	67	1,0	337
Passanger vessels	5386	0,05	269	0,6	302
Others	7724	0,05	386	0,6	433
World total			5404		5234

## 2.2 Marine environment

Marine environment is very corrosive due to high chlorine content. [1] Factors affecting on the marine environment can be divided on physical, chemical and biological factors. The major factors affecting to the atmospheric corrosion in the marine environment are time of wetness, thickness of the electrolyte layer on the metal surface, chloride deposition and temperature. [3] Factors affecting to the corrosively of seawater are high conductivity of seawater, temperature, pH and dissolved oxygen content. [1]

According to the ISO standard 9223 atmospheres can be divided to five groups classified by their corrosivity. The key factors of atmospheric corrosion are airborne salinity, temperature-humidity complex and pollution by sulphur dioxide, according to this international standard. According to this standard corrosivity of atmosphere can be divided to six groups: C1, C2, C3, C4, C5 and CX. Marine environments belong to the group C5 or CX. [7]

In marine atmosphere there is constant exposure to sun light, seawater, abrasion and living organism. Wind and waves cause stresses and abrasion. The salt is carried on the deck by wind, sprays and waves. Surface temperatures on the deck can vary from 0°C to as high as 75°C depending on the sun. Cold water and rain may cause thermal shock due to alternating exposure to warm and cold. [8] Atmospheric corrosion in marine environments occurs by the electrolyte layer on the metal surface. This surface may be a very thin solution layer which is invisible for naked eye, layer of hygroscopic and wet corrosion products or solution layer visible for naked eye. [3]

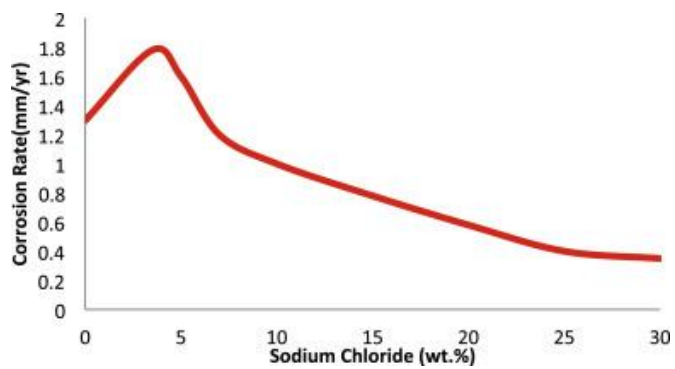
### **2.2.1 Chemical factors**

Concentration of airborne particles is influenced by location, atmospheric conditions, time of day or year and altitude, wind velocity. Deposited salts decrease protection properties of protective oxide layer and increase the water vapor condensation on the metal surface. [3]

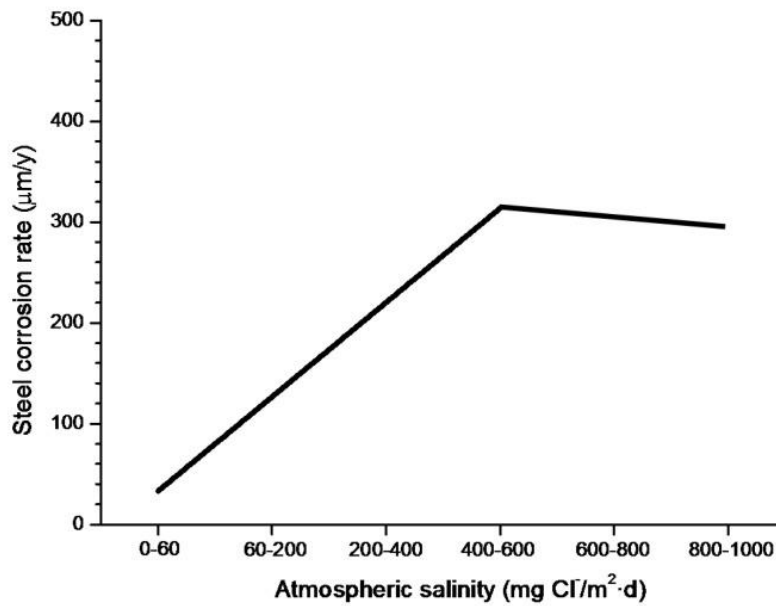
Chlorides cause local corrosion such as pitting on passivating metals by preventing passivation. [1] Dissolved chlorides in moisture layer on the metal surface increase conductivity of electrolyte film and destroy the protective oxide film. Corrosion rate is a function of the activity of  $\text{Cl}^-$  ions. [9] Chlorine is hygroscopic and it promotes condensation on the metal surface. [3] Chloride species, such as  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , promote the electrochemical corrosion process by decreasing relative humidity values needed for corrosion to start and by changing the solubility of the forming corrosion products. [9] Cleaning of metal surface out of the salt is important since chlorides of sea salt attracts moisture and thus the corrosion rate is higher. [10] The time during which the metal surface is covered with thin electrolyte film is called time of wetness. [3] Concentration and precipitation of chlorides in the atmosphere increases corrosion rate due to its influence to the time of wetness, corrosion products,  $\text{O}_2$  transportation on the surface and by direct influence on electrode reactions. [10] Salinity of seawaters in different seas is presented in Table 3. The corrosivity of  $\text{NaCl}$  in seawater is presented in Figure 1 and the variation in the corrosion rate of mild steel with atmospheric salinity is presented in Figure 2.

**Table 3.** *Salinity of Sea waters.* [11]

Body of water	Total dissolved solids, ppm
Baltic Sea	8
Black Sea	22
Atlantic Ocean	37
Mediterranean Sea	41
Caspian Sea	13
Dead Sea	260
Irish Sea	33
Red Sea	41
Persian Gulf	39-42



**Figure 1.** *The rate of corrosion versus the concentration of Sodium Chloride (NaCl) in seawater.* [12]

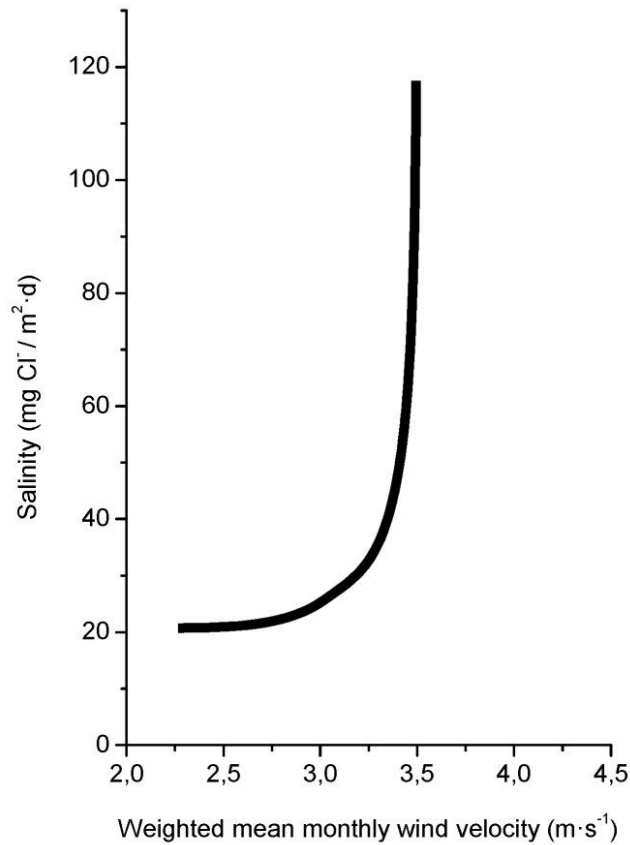


**Figure 2.** Variation in the corrosion rate of mild steel with atmospheric salinity. [13]

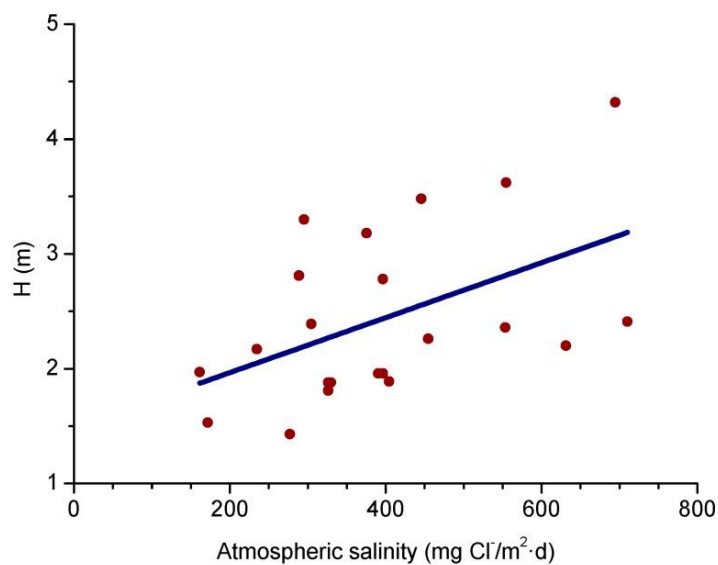
Sulfur dioxide,  $\text{SO}_2$ , originates from the combustion of fuels which contain sulfur, such as diesel, gasoline, coal and natural gas.  $\text{SO}_2$  is especially born when burning is not properly controlled. [14]  $\text{SO}_2$  is one of the most important air pollutants contributing to atmospheric corrosion of metals and alloys. [15] The presence of  $\text{SO}_2$  in marine atmosphere decreases the critical relative humidity, increase the aggressiveness of the environment and increase the thickness of the electrolyte film on the surface. [14] In water  $\text{SO}_2$  will oxidize to sulfate ion  $\text{SO}_4^{2-}$ . This process produce hydrogen ions  $\text{H}^+$  which increases corrosion rate due to rising of acidity of the electrolyte. [16]

### 2.2.2 Physical factors

Wind is the most important factor leading to the salinity of marine atmosphere. Breaking of waves leads to the formation of marine aerosols. The amount of marine aerosols increase while the height of waves increase. Breaking of waves on high seas depend on of the wind speed. The effect of wind speed to atmosphere salinity is presented in Figure 3 and the effect of wave height to the salinity of atmosphere is presented in Figure 4. In surf zone, the forming of aerosols is depended more on the width of the surf zone and the type of sea floor, since waves can break without the action of the wind. [17] Wind may also remove the protective oxide layer from metal surface. [18]



**Figure 3.** Relation between atmosphere salinity and weighted mean monthly wind velocity for marine winds. [13]



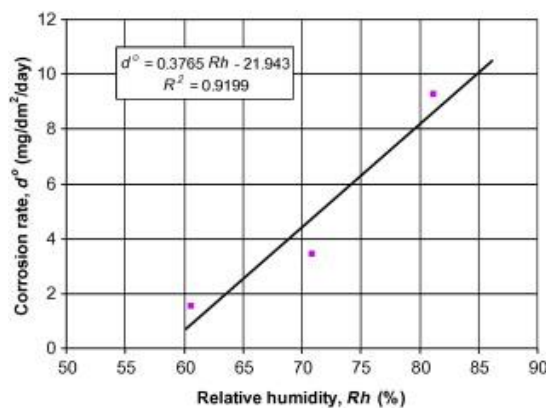
**Figure 4.** Variation of monthly average salinity with monthly average spectral wave height values ( $H$ ). [13]

Increasing salt content increases the conductivity of seawater. Due to high salt content conductivity of seawater is about 250 times higher than in fresh water. High conductivity

leads more aggressive corrosion. In higher temperatures the conductivity is even higher. [1]

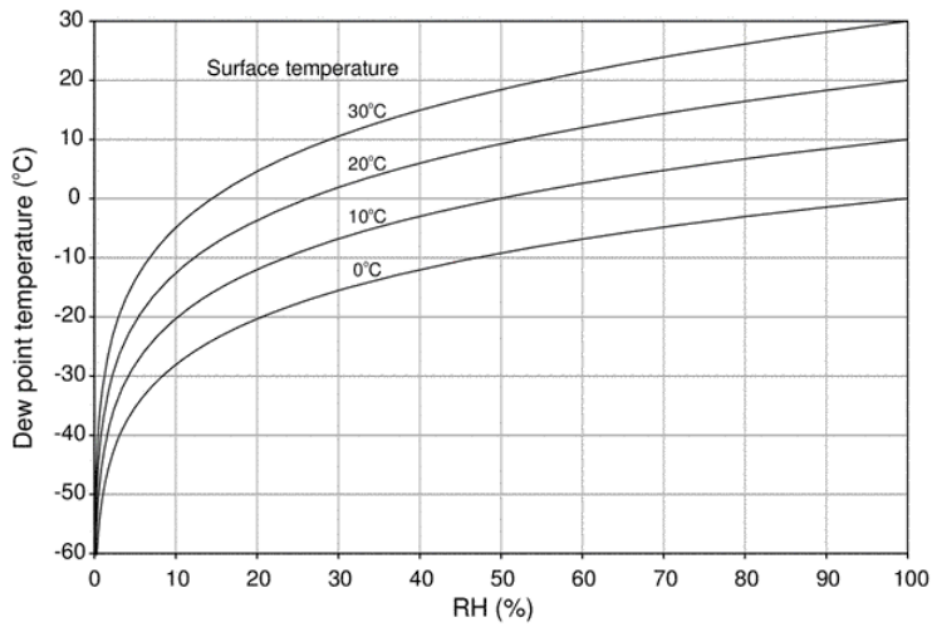
Duration of corrosion process is determined by time of wetness. Time of wetness is influenced by many environmental factors such as air temperature, relative humidity, impurities on the metal surface, sun radiation, rain, wind and the angle of surface. [3] When temperature increases the adsorption of water decreases. The time of wetness is also affected by surface properties, such as porosity, degree of oxidation, grain boundaries and the nature of surface. Water adsorption increases when the number of voids and grain boundaries increase. Water adsorption increase when surface roughness increase. Increasing of oxidation decrease water adsorption. [18]

For corrosion to occur is needed only a thin layer of deposited water. This thin layer can be formed when the relative humidity is between 80% and 90 %. Many metals have a critical value of relative humidity over which corrosion rate increase. This critical value can vary with metal or alloy, corrosion products and impurities in air. Dependence of corrosion rate of steel on relative humidity is presented in Figure 5. Critical humidity is defined as a humidity where wet corrosion or the electrochemical corrosion does not occur any more since water does not form a thin layer any more on the clean metal surface due to low humidity. [19] The main promoter of atmospheric corrosion are humidity condensation due to temperature and aqueous precipitation such as rain and fog. [9] Temperature affects to relative humidity by affecting to evaporation and condensation of water vapor. [16] In Figure 6 is presented relationship between dew point temperature and critical relative humidity for selected surface temperatures. Critical relative humidity decreases in the presence of chlorides, for example steel may corrode even in 40 % of relative humidity. [20]



**Figure 5.** Dependence of corrosion rate of steel on relative humidity. [21]





**Figure 6.** Relationship between dew point temperature and critical relative humidity for selected surface temperatures. [15]

Hygroscopic salts on the metal surface decrease the critical relative humidity value. [3] In Table 4 is presented the critical relative humidity in the case of some hygroscopic salts. [22] The surface of the metal may wetted even in 34% relative humidity under the presence of magnesium chloride hexahydrate while 77% relative humidity is needed if there is sodium chloride on the surface of metal. [16]

**Table 4.** Relative humidity producing condensation on salt contaminated surfaces. [22]

Salt	Critical Relative Humidity (%)
$\text{Na}_2\text{SO}_4$	93
$(\text{NH}_4)_2\text{SO}_4$	81
$\text{NaCl}$	78
$\text{CaCl}_2$	35
$\text{FeCl}_3 \cdot 12\text{H}_2\text{O}$	10

While temperature of air is 10°C, an air pressure is 1.013 hPa and 60 % of relative humidity, the water content is around 5.7 g/m<sup>3</sup>. When the temperature of air is 30°C, relative humidity is 100%, the water content is 31.4 g/m<sup>3</sup>. [23] Clean metal surface does not corrode in temperatures below 0°C, but if the metal surface has some corrosive impurities, metal surface can corrode even in below 0°C. Critical relative humidity generally decreases when temperature increases. At higher temperatures water evaporates from the metal surface. [20]

Rate of corrosion generally increases when temperature increases. Increasing temperature decreases the solubility of oxygen. Biological activity increases with increasing temperature. [1] Temperature affects to the atmospheric corrosion in marine environments by two aspects: influencing to electrolyte film formation and directly to the corrosion reaction rate. [16] Temperature has also an effect on relative humidity, dew point, kinetics of the corrosion process and to the time of wetness. [14]

Sun light influences to the time of wetness, to the biological activity and to the performance of protective coatings. Sun light also promotes photosensitive corrosion reactions [14] Solar radiation influences to the wet-dry cycles on the metal surface by electrolyte evaporation. [3] North and west sides are more susceptible to corrosion than east and south sides since due to the solar radiation they dry more slowly in the sun. [24] In tropical areas the effect of the radiation of sun is more intense than in northern areas. [25]

Rain can either increase or decrease the corrosion rate. The frequency of rain affects to the corrosion by flushing harmful salts and pollutants from the metal surface. [3] Due to the high solubility of chlorine ions to the water they are easily removed by water. [9] Fog and dew instead wet the metal surfaces without the beneficial flushing effect of rain. [14]

In tropical climate areas there are two main seasons, rainy season and dry season. In Table 5 can be seen that corrosion rate is higher in the winter time which is dry season. In winter the chloride deposition is double and the corrosion almost four times compared to summer season. This behavior can be explained by cleaning effect of rain and higher deposition of airborne salinity. [26] Climate areas can be divided to different zones. In the temperate zones the values of time of wetness are 100-2700 h/year when as in the tropic-humid the values are usually higher, 3000-5000 h/year. [18]

**Table 5.** *Average corrosion rate of steel, standard deviation, average chloride deposition rate and standard deviation for 6 months exposure periods at Viriato.* [26]

Climatic season	Average corrosion rate of steel (g/m <sup>2</sup> )	Standard deviation	Average chloride deposition rate (mg/m <sup>2</sup> d)	Standard deviation	TOW-ISO (h)
Summer (May to October)	569	168	225	108	2112
Winter (November to April)	2116	893	486	174	2000
Winter/Summer	4	-	2	-	1

### 2.2.3 Biological factors

Fouling is characterized as settlement and growing of living organism, such as bacteria, barnacles, oysters, tube worms and mussels. Marine fouling can cause corrosion as well as it increases weight and resistance to flow. Increased weight and resistance to flow affects to fuel consumption and decrease speed. [8]

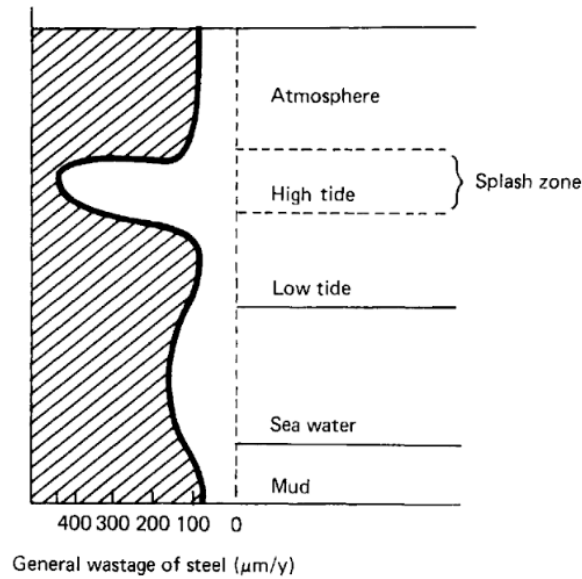
Bacteria have an effect on corrosion by several ways, such as by using oxygen on the surface, changing pH and by producing metabolic products. [27] Some micro-organism, such as sulfate reducing bacteria, produces acids that are corrosive to metals. Hydrogen sulfide is very corrosive for steels and exposes the steel surface to local corrosion and pitting. [28] In marine environments where sulfate abundance is high, sulfate reducing bacteria are an important factor influencing corrosion. Sulfate reducing bacteria form a biofilm by attaching on the metal or alloy surface. Cathodic and anodic areas are formed on the surface of metal or alloy due to this biofilm. [29]

#### **2.2.4 Surface properties**

Increasing surface roughness decrease pitting potential of metal. [30] Rougher surface reduces the number of sites capable of being activated into metastable pit growth and thus incidence of metastable pitting. The smoother surface is, the more rapidly growing pits are eliminated. [31]

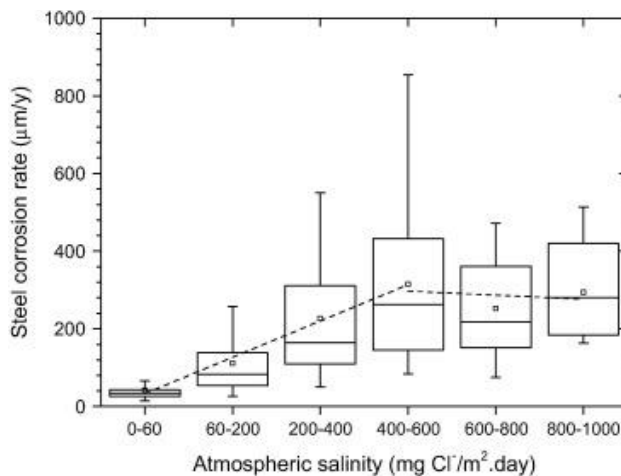
#### **2.2.5 Marine zones**

Usually marine environment is divided to atmospheric zone, splash zone, tidal zone, shallow water zone, deep ocean zone and mud zone. [32] The corrosivity of different marine zones is presented in Figure 7. A thin electrolyte layer is needed to atmospheric corrosion to occur. This layer is formed by the humidity and impurities of the air. [21] In the atmosphere there is always a plenty of oxygen available and thus electrolyte on the metal surface is the controlling factor of corrosion. [33] The main parameters affecting to atmospheric corrosion are humidity, temperature and airborne contaminants. [34] In marine environments, chlorides of salt spray are the principally responsible for metal corrosion. [21] The amount of salt particles has the greatest influence on intensity of corrosion attack in the atmospheric zone. Wind and wave conditions as well as height above the sea and exposure influence on the amount of salt. Due to hygroscopic behavior of some sea salts a liquid film is formed on the metal surface. [32] The atmosphere may contain carbon dioxide, hydrogen sulphide, sulphur dioxide and sulphur trioxide. These agents activate the thin electrolyte layer and accelerate corrosion since the oxygen rich atmosphere. [21]



**Figure 7.** Marine zones and their corrosion. [35]

Marine atmospheric corrosion is affected by many factors such as high temperatures, sunshine, relatively high humidity and high NaCl precipitation. The corrosion rate of steel in atmospheres with different salinity is presented in Figure 8. The marine atmosphere has unique feature where the formation of a deposited salt layer aggravates corrosion. [36] Solar radiation stimulates photosensitive corrosion on metals such as copper and steel. Rain may prevent corrosion in atmospheric zone since it washes salts away from metal surface. Climatic factors that have an influence on corrosion in atmospheric zone are dew cycle, temperature, dust, season and pollution. Tropical marine environments are generally more corrosive than Arctic marine environments. Temperature is a major factor, but others corrosion factors also vary with geographical location. [32]



**Figure 8.** Variation in the corrosion rate of mild steel with salinity over broad spectrum of atmospheric salinities. The graph shows a trend (broken line). Information obtained in an exhaustive bibliographic search. [9]

Surface of material is almost continuously wet with well aerated seawater in the splash zone. [32] Increasing height above the sea decreases the corrosivity of splash zone since surface of material is not wet as often. [14] High wind may increase the corrosion by the seawater impinging on the metal surface. For many materials, such as steel, splash zone tends to be the most aggressive of all marine zones as seen in Figure 7. Splash zone may be beneficial for metals which form a protective oxide layer since the atmosphere is well aerated. An example of this kind of metals are titanium and stainless steel. Splash zone is especially hazardous for protective coatings such as paint films, which usually deteriorate more rapidly. Air bubbles in the seawater may remove protective coating mechanically. Protective coatings are more difficult to maintain in splash zone. [32]

Corrosion rate is affected by salinity, pH, velocity, chemical composition, oxygen content and temperature in the shallow water zone. These factors vary by the location and water depth. [32] In immersed parts the amount of dissolved oxygen is controlling factor. [33] Shallow water zone has high oxygen content and it is at or close to saturation. There is a lot of biological activity, including both animal and plant life. Painting and cathodic protection are used as corrosion protection methods in the shallow water zone. In tidal zone metal and alloy surfaces are part of the day in contact with well aerated seawater. Marine fouling may occur in the tidal zone. [32]

### **2.2.6 Corrosion in different geographical areas**

The most important properties of cold brackish water in the Baltic Sea are low concentration of dissolved solids, low conductivity and high concentration of dissolved oxygen. Temperature of water varies from 0 °C in January to approximately 15-16 °C in summer. [37] In Canary Islands the salinity of the atmosphere is generally high due to constantly blowing trade winds. [38] Caribbean area is influenced by different weather conditions in winter and in summer. In winter the weather conditions are influenced by Arctic and polar masses and in summer by Atlantic anticyclone and tropical waves. [39] Northern Caribbean coastal area the corrosion rates are much higher than the rates in southern coast. In the winter period there is tendency for high salinity in the coastal areas in the Caribbean area. Salinity is lower in the southern coastal areas. [40] In the northern coastal areas of Cuba are influenced by breeze reinforces trade winds which cause the stronger penetration and higher salinity. [9] Corvo et al. [40] proposed the new introduction of category (C<sub>6</sub>) for ISO 9223, since the tropical zones are locating on northern coasts in Caribbean area have extreme corrosion values that do not fall within the classification established in ISO 9223.

## **2.3 Galvanic series in seawater**

Galvanic series is based on the potentials of different metals and alloys in a specific electrolyte. In galvanic series metals and alloys are arranged due to their potentials from less

noble to more noble. Galvanic series in seawater is presented in Appendix A. [41] Galvanic series is a good tool to estimate the risk of the galvanic corrosion when coupling metals and alloys. The risk of galvanic corrosion should be considered when the two metals have a great difference in galvanic series table. It is generally assumed that larger the difference is in table of galvanic series the risk of galvanic corrosion is higher. The more noble material acts as a cathode and less noble as an anode. Corrosion occurs on the anode. [42]

### **3. TYPICAL FORMS OF CORROSION IN MARINE ENVIRONMENT**

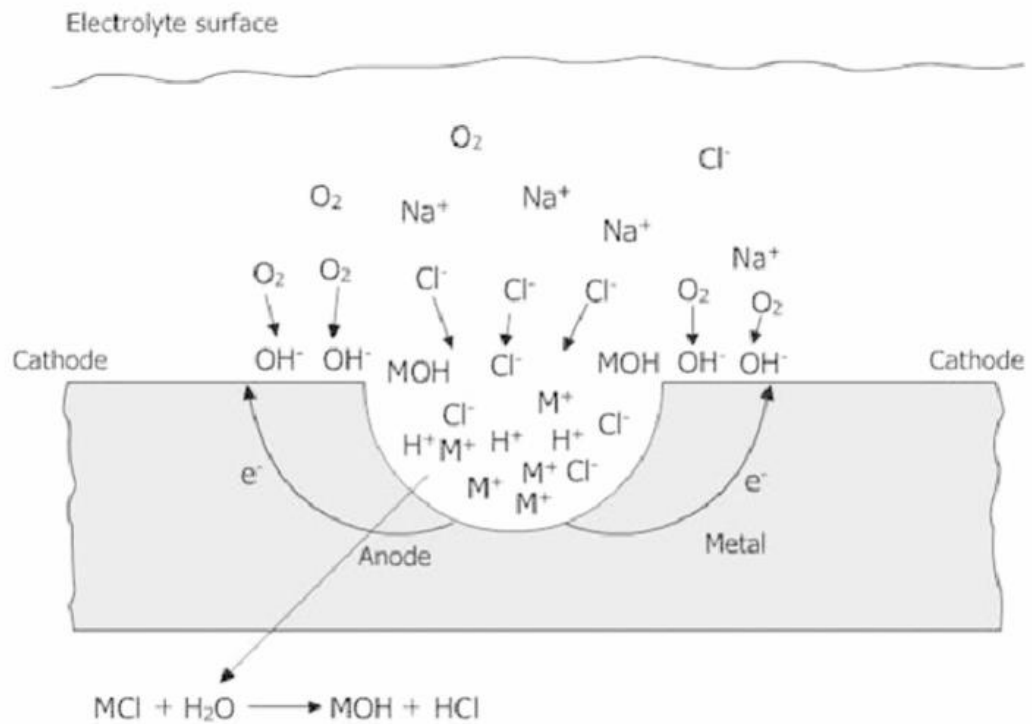
When metal structures are exposed to certain types of environments some forms of corrosion are more common than other forms. The most common forms of corrosion in marine environment are galvanic corrosion, pitting and crevice corrosion. [43]

#### **3.1 Uniform corrosion**

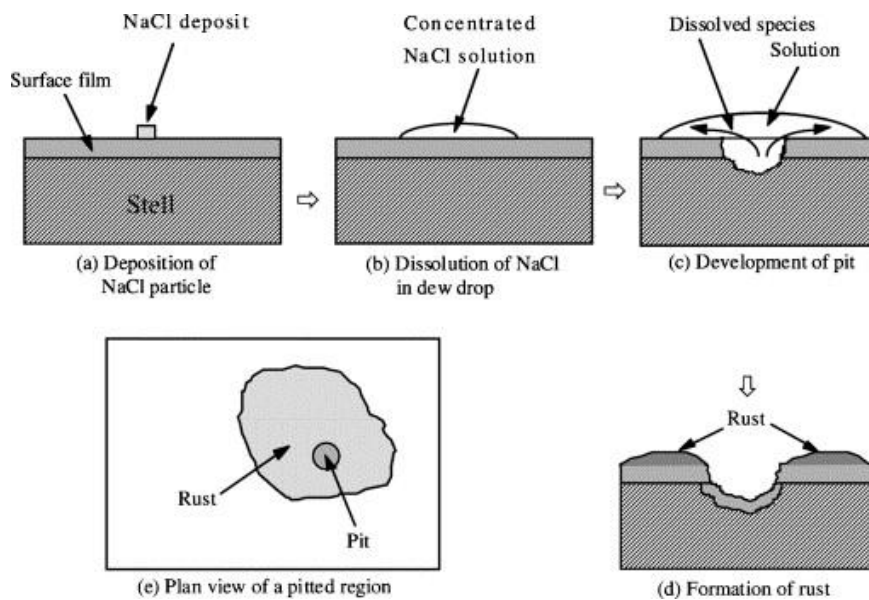
In uniform corrosion the reduction of thickness occurs uniformly on the metal surface. Metals which do not form protective passive layer are susceptible to uniform corrosion. [24] Steel rust uniformly in the presence of air. Uniform corrosion requires a thin electrolyte layer on the metal surface. Corrosion products which forms on the surface may slow down the corrosion rate. Uniform corrosion is not usually as dangerous as localized attack since the penetration of uniform corrosion is not usually very deep. [44]

#### **3.2 Pitting**

Pitting is a form of localized corrosion where small areas corrode and forms cavities or pits. Pitting is typical for metals and alloys which passivates. Pitting is result of passive film breakdown. Pitting occurs when small area of the surface undergoes a rapid attack while the surrounding surface area remains unaffected. The formation of a pit is presented in Figure 9 and in Figure 10. The forming of a pit starts of damage in the passive film. Pit starts growing when there are conditions where the repassivation does not occur any more. After this the dissolution of the substrate starts. Eventually pit can be seen by naked eye and there are corrosion products around the mouth of the pit. The growth of pit consists of various stages, which are passive film breakdown, pit initiation, metastable pitting and pit propagation. Pitting initiates by factors, such as localized or chemical or mechanical damage in passive film, damage in protective coating, low dissolved oxygen concentrations and high chloride concentrations. [12]



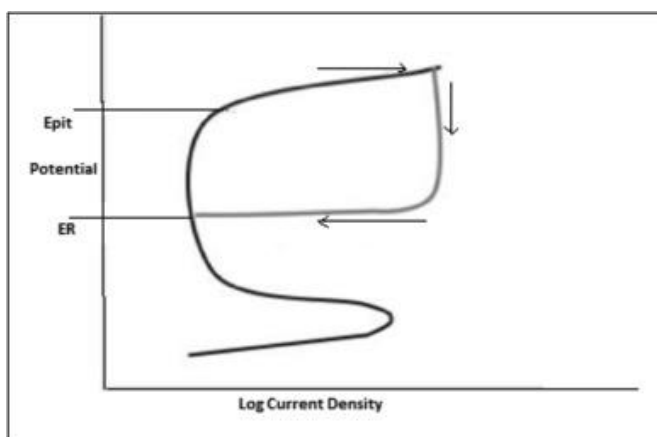
**Figure 9.** Schematic of an active corrosion pit on a metal in a chloride solution. [43, pp. 151]



**Figure 10.** Pit formation on stainless steel by atmospheric exposure. [45]



For pitting corrosion has been characterized three critical potentials. These critical potentials are pitting potential  $E_p$ , repassivation potential  $E_r$  and pitting inhibition potential  $E_i$ . The most important of these is pitting potential. Pitting potential is the potential in a potentiostatic polarization curve, where below it, the surface remain passive and above it pitting corrosion occurs. [46] In pitting potential  $E_p$  stable pits start to grow. Below repassivation potential the already growing pits are repassivated and the growth stops. Pitting potential and repassivation potential are presented in anodic curve in Figure 11. [47]



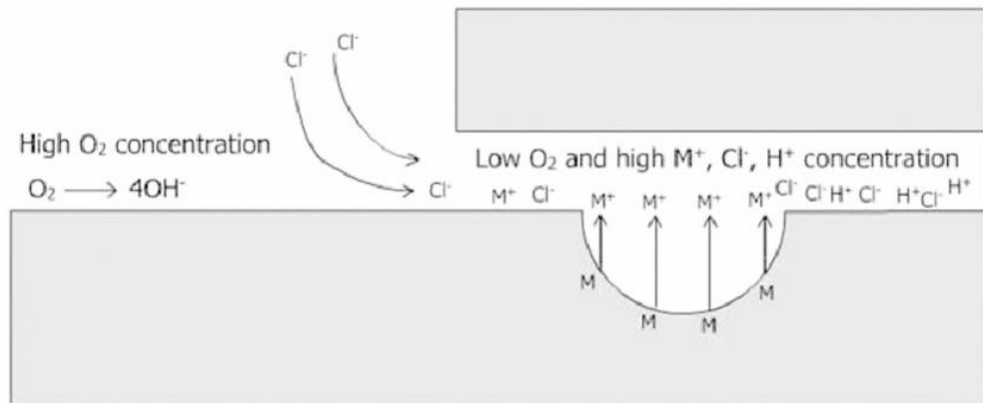
**Figure 11.** Schematic of anodic curve for a metal immersed in a solution containing aggressive ions. [12]

Surface of the metal is in big role in prevention of pitting corrosion. By providing uniform surface through proper cleaning, heat treating and surface finishing the resistance to pitting corrosion reduces. Susceptibility to pitting reduces by making smooth and shiny surface and not allowing impurities on the surface. By use of coatings and inhibitors, risk of pitting can be avoided. [44]

### 3.3 Crevice corrosion

Metals whose corrosion resistance is result of passivation, such as stainless steels and aluminum, are susceptible to crevice corrosion. Reasons of crevice corrosion are narrow gaps between two metals or between metal and non-metal, presence of cracks and other defects on the metal surface, deposition of biofouling organism and bacteria, deposition of dirt. The crevice becomes a permanent anode while the surrounding area become a permanent cathode. [44] Figure 12 illustrates mechanism of crevice corrosion. The crevice becomes oxygen starved, compared to surrounding area. This leads to formation of differential oxygen cells and to the initiation of corrosion in crevice. [48] The growth of crevice causes lower pH and increased chloride content in the gap, thus the growth of the crevice becomes autocatalytic. [49] Crevice corrosion typically indicates beneath O-rings, threaded connection, in flange faces under gaskets, in tube to tube sheet rolled joints, in non-metallic connectors, under adhesive tape and in oxide scale. Aggressivity

of the crevice corrosion depends on the deep and tightness of the crevice. The most aggressive to crevice corrosion are deep and thigh crevices. [50]



**Figure 12.** Mechanism of crevice corrosion. [43, pp. 144]

Risk of crevice corrosion can be decreased with right material choices, right coatings and good design. Risk of crevice corrosion can be reduced by using alloys resistant to crevice corrosion such as titanium and Inconel, or by reducing susceptibility to crevice corrosion of metal by alloying. Use of molybdenum as alloying element decreases the probability to crevice corrosion. Crevice corrosion can be prevented with right designing. Risk of crevice corrosion can minimize by avoiding of sharp corners, edges and pockets, by sealing crevices by non-corrosive materials and by avoiding contact with hygroscopic materials. [44] To avoid crevice corrosion, fastening should do by welded joints instead of flange, bolted or riveted joints. [48]

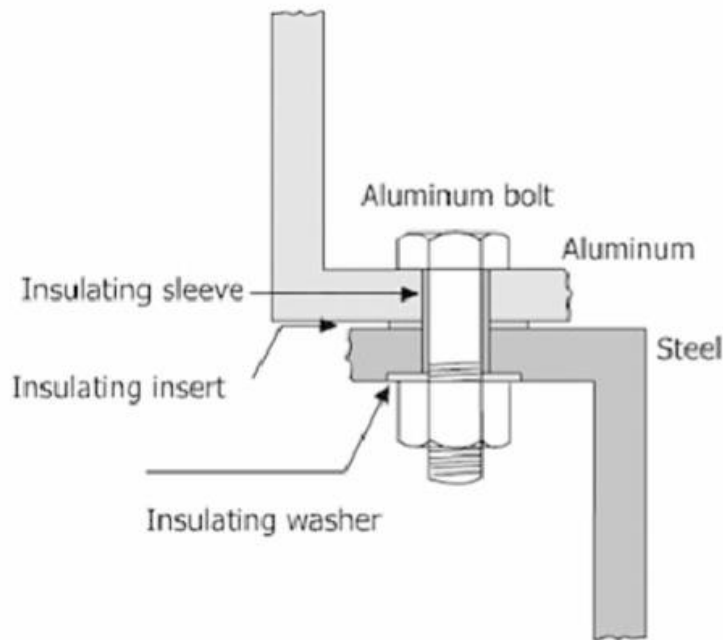
### 3.4 Galvanic corrosion

Galvanic corrosion occurs when two metals or alloys are coupled in the same electrolyte. Materials processing different surface potential, a common electrolyte and a common electrical path are needed to galvanic corrosion to occur. Electron flow between the dissimilar metal or alloy occurs due to the potential difference. More active metal or alloy becomes anode and more noble metal or alloy becomes cathode. [51]

Rates of galvanic corrosion vary with the potential difference between metals and alloys, polarization behavior of metals or alloys and electrochemical properties of materials. Area ratios, distance and geometry have also an effect to the galvanic corrosion behavior. [51] Galvanic corrosion rates also depend on the environmental variables such as temperature, oxygen content, salinity and flow rates. [42] Small amounts of alloying elements generally do not change the potential of metal, but may change the kinetics of galvanic corrosion. [52]

To prevent galvanic corrosion, metals and alloys should select as near each other in galvanic series as possible. If metals and alloys are far away each other in galvanic series,

they should be insulated. In Figure 13 is an example how the galvanic corrosion can be avoided by insulating. The area of anode should be bigger than the one of cathode if possible. Both the anode and cathode should be coated or just the cathode. An aggressive corrosion occurs if the anode is coated only. Components should be designed in that way that it is possible to replace only the corroded area instead of the whole component. [44]



**Figure 13.** *Avoidance of galvanic corrosion.* [47, pp. 130]

Magnesium is highly susceptible to galvanic corrosion, due to an extremely active position. Pure aluminum is quite compatible due to it acts as a polarizable cathode. However, in marine environment aluminum alloys which contain small percentages of copper may cause serious galvanic corrosion. The dual position of stainless steel in galvanic series in chloride containing environments, makes the prediction of corrosion difficult. Galvanic corrosion may occur in chloride containing environments when coupling stainless steel with copper or nickel or their alloys. [53] Zinc is used to protect iron and steel from corrosion since it is anodic to iron and steel. However, in the temperatures over 70°C zinc becomes cathodic to iron and steel. [54]

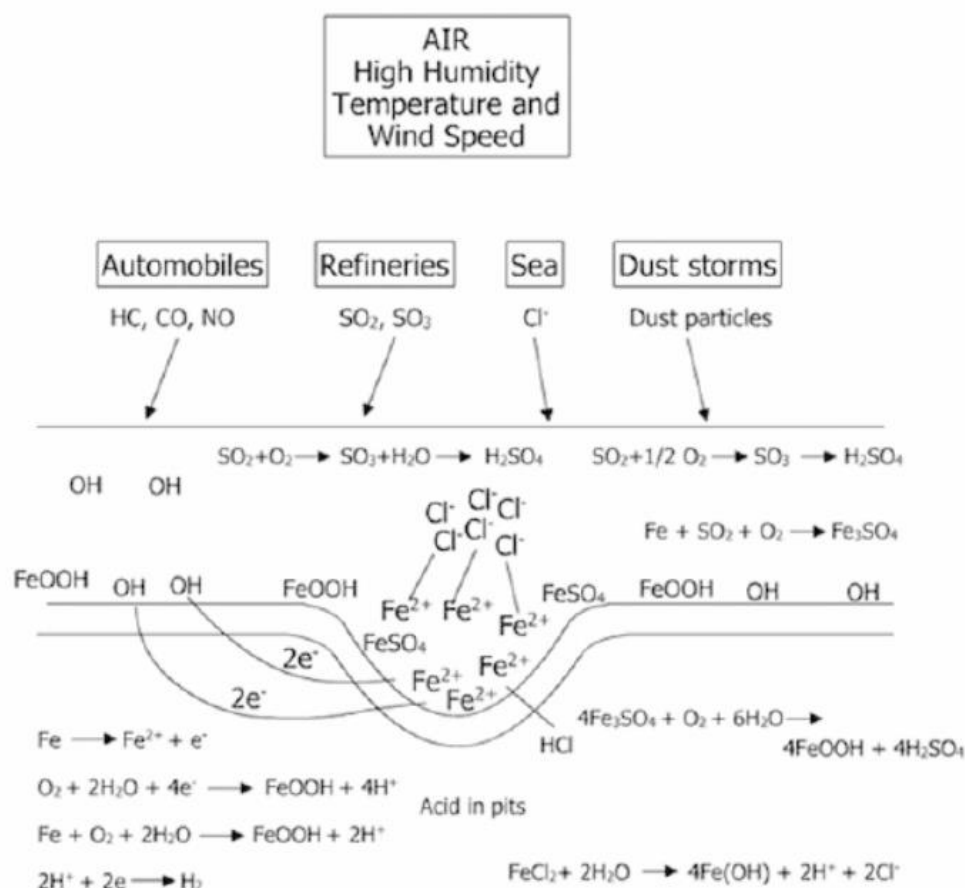
## **4. CORROSION OF DIFFERENT MATERIALS IN MARINE ENVIRONMENT**

Steels, stainless steels, aluminum and their alloys, are the most used metals in marine industry. Many other metals and alloys, such as titanium, zinc and nickel, are also widely used in marine industry. Plain carbon steel is the most important metal in marine industry. Stainless steel has good corrosion resistance in marine atmospheres due to its ability to passivate. Aluminum is widely used in marine atmospheres and some of its alloys have excellent resistance to corrosion. Titanium and its alloys are among the most resistant to marine environments. Nickel has good corrosion resistance in marine atmospheres. [43]

### **4.1 Corrosion of cast iron and steels in marine environment**

Iron corrodes faster than any other engineering material in an industrial and marine atmospheres. [44] If the relative humidity is over 60-80% the steel starts to corrode. The presence of chlorides and other impurities may decrease the critical relative humidity. Usually cast irons and low-alloy steels need corrosion protection. Generally applied protection methods are organic and inorganic coatings, electrical protection and inhibitors. [55] Uniform corrosion of iron in marine environment is presented in Figure 14. Factors affecting the corrosion of iron are also presented in Figure 14.

Both wrought iron and carbon steel are rapidly attacked by exposure to marine atmosphere when being unprotected. [43] Usually pitting of steel structures in marine environments occurs due to ineffectiveness of protective measures such as paint coating, galvanizing or cathodic protection. [12]



**Figure 14.** Atmospheric corrosion of iron. [43, pp. 122]

## 4.2 Corrosion of stainless steel in marine environment

Low corrosion rate of stainless steel is predominantly based on protective chromium oxide film which form when the surface of stainless steel exposures to oxygen. If the protective oxygen layer breaks it will repair itself when there is enough oxygen. In sea water oxygen content is usually high enough for this repairing reaction. In chlorine containing environments, such as marine environments, the protective film can break locally and cause local corrosion such as pitting, crevice corrosion and chloride stress corrosion cracking. Resistance for pitting and crevice corrosion can be increased with alloying stainless steel with additions of molybdenum, nitrogen and chromium. Resistance to chloride stress corrosion cracking can be improved with additions of nickel. [50]

Chloride is the most general initiation agent for pitting corrosion. Other halides such as bromide also cause pitting corrosion on stainless steel. [56] Pitting and crevice corrosion may appear when chloride ions migrate, pH is lowered or the amount of oxygen reduces. Resistance to pitting and crevice corrosion can be improved with higher alloying. [50]

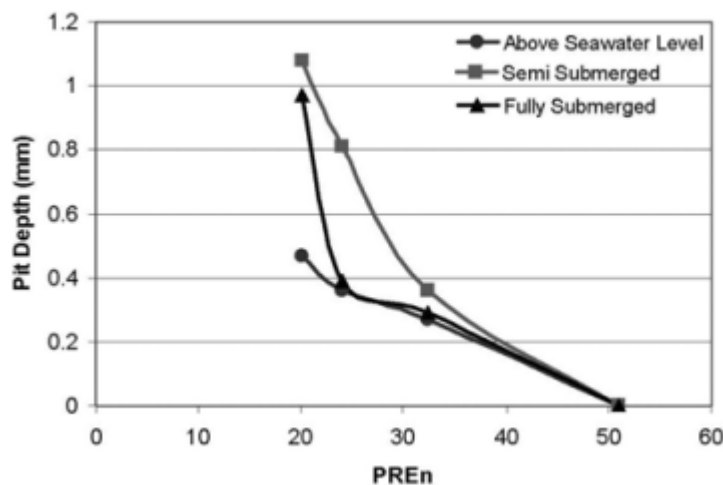
Behavior of stainless steel depends on state of it. Stainless steel may be in passive state or in active state. Stainless steel in passive state is more noble. [41] When selecting stainless

steel for special environment it must be determined whether the environment causes passive state or active state for selected stainless steel. [44] If passive stainless steel is connected with more noble metal it usually not produce significant corrosion, but when connecting active stainless steel with more noble metal, stainless steel will corrode rapidly without repassivation. [56] This may have influence on material design in marine environments. For example, in applications where stainless steel is coupled with copper and its alloys, since stainless steel is more noble in active state, but copper is more noble when stainless steel is in active state. Passivity of the stainless steel in seawater depends on many factors such as chlorination, dissolved oxygen, velocity and biological activities. [41] Knowledge of galvanic corrosion is important when selecting weldment or fasteners since of the large cathodic area of stainless steel. For example there can be appeared aggressive corrosion in steel bolts if they are placed to more noble stainless steel. [56] Gaskets, packing and lubricants containing graphite should not be used in seawater with stainless steels since they can cause serious galvanic corrosion. [50]

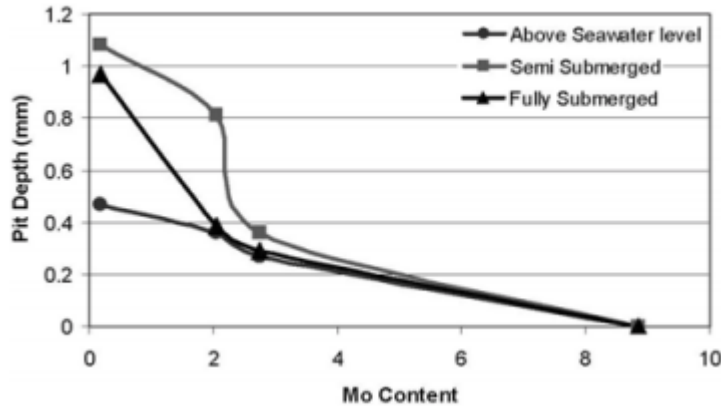
Pitting resistance of austenitic and duplex steels can be rated with pitting resistance equivalent number PREN. PREN is based on the experimental results. PREN is calculated from the contents of molybdenum, chromium and nitrogen in the alloy. [57] The higher the PREN is, the more resistant stainless steel is to pitting. [58] PREN is calculated by next formula: [57]

$$PREN = \%Cr + 3.3 * (\%Mo) + 16 * (\%N) \quad [57]$$

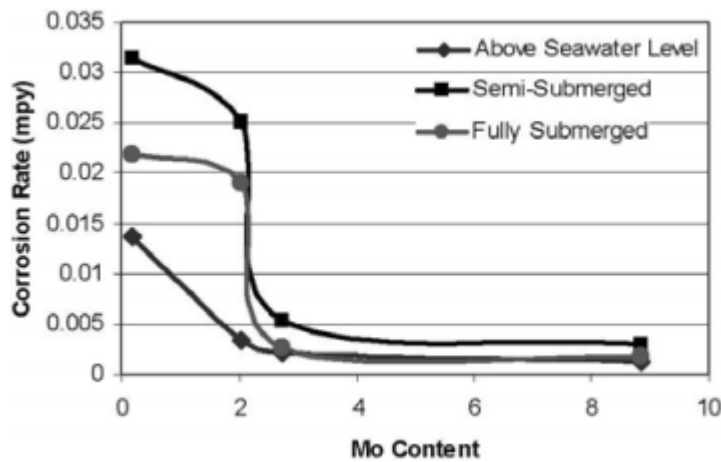
The effect of PREN and molybdenum content of stainless steel are presented in Figure 15, Figure 16 and Figure 17. The graphs show that the higher PREN is the lower is corrosion rate and the lower pith depth is. [59]



**Figure 15.** Effect of PREN content on pit depth of stainless steel. [59]



**Figure 16.** Effect of molybdenum content on pitting depth of stainless steel. [59]



**Figure 17.** Effect of molybdenum content on corrosion rate of stainless steel. [59]

Austenitic and duplex stainless steels are the most commonly used stainless steels in marine environments. Even if ferritic and martensitic have not such sea water corrosion resistance as austenitic and duplex stainless steels, most have better resistance to atmospheric marine corrosion resistance compared to carbon and low alloy steels. Superferritic alloys containing high levels of chromium, molybdenum and nickel have good resistance to marine atmospheric corrosion. [50]

The most used stainless steel in marine environments is 316L alloy which contains 17% Cr, 12% Ni and 2.5% Mo. Stainless steel 316 have adequate corrosion resistance in marine atmospheres. Molybdenum in stainless steel 316 increases the resistance to localized corrosion such as pitting and crevice corrosion. [57] 316L has limited resistance to local corrosion and might need cathodic protection or galvanic protection from surrounding components in the presence of crevices or quiescent exposure conditions. [50] The cold rolling is harmful for corrosion protection potential of 316L stainless steels. [60] The content of molybdenum in stainless steel 316 may vary from 2% to 3%. [57]

PREN number of stainless steel 316 when the molybdenum content is 2%:

$$\text{PREN} = 185 + 3,3 * 2 + 16 * 0,1 = 26,7$$

PREN number of stainless steel 316 when the molybdenum content is 3%:

$$\text{PREN} = 18,5 + 3,3 * 3 + 16 * 0,1 = 30$$

Pitting and crevice corrosion resistance increase with increasing molybdenum content. AISI 316 with only 2% molybdenum may not give required corrosion resistance. Steel producers encourages low molybdenum content due to high price of molybdenum. [57] As seen in Figure 15, stainless steels with 2% and 3% of molybdenum have a difference in pith depth.

Recently developed super austenitic stainless steels have 5-7% molybdenum and some nitrogen. These stainless steel grades have higher resistance to corrosion than usual austenitic stainless steels. [50]

Duplex stainless steels consist both ferrite and austenite structures in roughly 50/50 proportions. Duplex stainless steels have almost same local corrosion resistance as 316L grade, but better resistance to stress corrosion. Super duplex alloys have higher chromium, molybdenum and nitrogen content and sometimes additives such as copper and tungsten. These have high corrosion resistance and high proof stress. [50]

Chromium, nickel and molybdenum increases local and general corrosion resistance of stainless steel. Chromium is the most important alloying element to increase the corrosion resistance. Chromium considerably increase the resistance to both pitting and local corrosion of stainless steel when the content of chromium is above ~13 %. [58] After chromium, molybdenum is the most important alloying element in stainless steel to prevent corrosion. Molybdenum is effective at minor constitutes of 2-6 wt. %, but only if alloy consist chromium. Molybdenum improves passive properties and resistance to pitting in chloride containing environments to austenitic and ferritic stainless steels. [47] Molybdenum improves resistance to local corrosion of nickel-based alloys. Critical current density for passivation and passive current density decrease by adding molybdenum. [58] Whereas silicon, sulfur nitrogen and carbon decrease the resistance to pitting. [44]



**Table 6.** *Austenitic Stainless Steel Chemical Compositions (W%). [61]*

Austenitic Stainless Steels									
Name	UNS No.	C	Cr	Ni	Mo	N	Mn	Cu	Other
201	S20100	0,15	16-18	3,5-5,5	-	0,25	5,5-7,5	-	-
301	S30100	0,15	16-18	6-8	-	0,1	2	-	-
304L	S30403	0,03	17,5-19,5	8-12	-	0,1	2	-	-
305	S30500	0,12	17-19	10,5-13	-	-	2	-	-
321	S32100	0,08	17-19	9-12	-	0,1	2	-	Ti 5x(C+N)
347	S34700	0,08	17-19	9-13	-	-	2	-	Cb 10xC to 1
309S	S30908	0,08	22-24	12-15	-	-	2	-	-
310S	S31008	0,08	24-26	19-22	-	-	2	-	-
316L	S31603	0,03	16-18	10-14	2-3	0,1	2	-	-
317L	S31703	0,03	18-20	11-15	3-4	0,1	2	-	-
317LMN	S31726	0,03	17-20	13,5-17,5	4-5	0,1-0,2	2	-	-
904L	N08904	0,02	19-23	23-28	4-5	0,1	2	1-2	-

AISI 304 stainless steels have austenitic microstructure. They have very good corrosion resistance, but they are prone to pitting and crevice corrosion in chloride containing environments. [62] AISI 316 stainless steels have better resistance to pitting and crevice corrosion than AISI 304 stainless steels, especially in chloride containing environments, due to molybdenum. PREN number of AISI 304 stainless steel is 20,1 which is lower than PREN number of AISI 316 stainless steels. Stainless steel 316 grades are austenitic. AISI 316 stainless steels have good resistance to pitting, crevice corrosion and stress corrosion cracking in warm chloride containing environments. They are not fully resistance to seawater and in many marine environments they are prone to pitting and crevice corrosion. Also, corrosion may appear in rough surface finishes. AISI 317L stainless steels has higher corrosion resistance in chloride containing environments than AISI 316 stainless steels. [62] AISI 316 may present unacceptable corrosion behavior in swimming pool atmospheres where water temperatures are higher than 30 °C and the water is treated with chlorine. [22]

AISI 904 stainless steel is austenitic and has very high corrosion resistance. They have high resistance to sulphuric acids. PREN number of AISI 904L is 35. They have higher corrosion resistance to pitting, crevice corrosion and stress corrosion cracking than AISI 316 stainless steels. 6Mo and super duplex steels have even higher resistance to pitting and crevice corrosion. [62] AISI 404 stainless steels have martensitic microstructure and thus they are magnetic. They have very high strength and very high hardness. Their corrosion resistance is close to the resistance of AISI 304 stainless steels in many environments. [62] Chemical compositions of stainless steels are presented in Table 6.

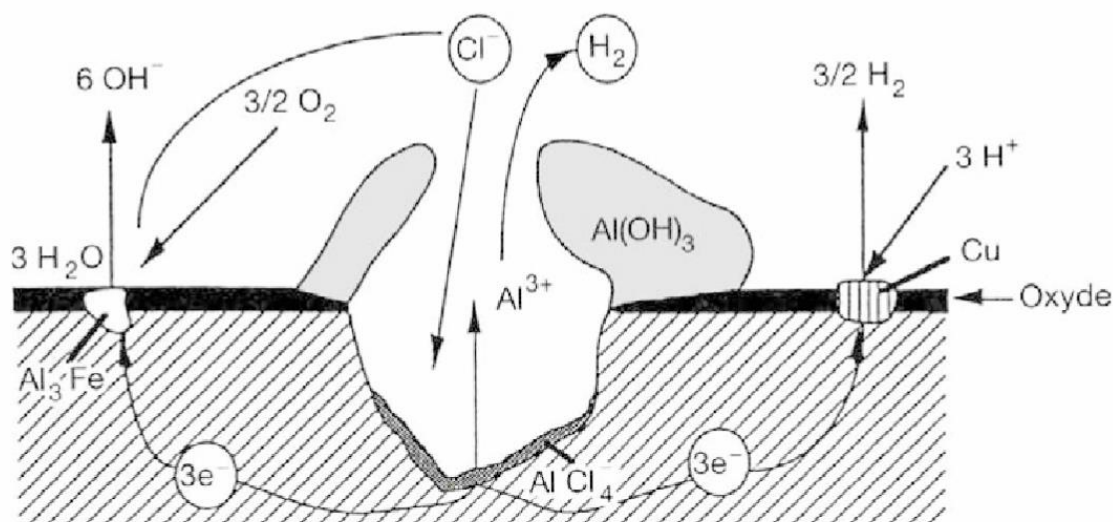
### 4.3 Corrosion of aluminum in marine environment

Aluminum is greatly used in marine environments due to its high corrosion resistance, high strength and lightweight, recyclability, weldability and design flexibility. If aluminum is used in upper decks of cruise vessels the more cabins can be accommodated above the water line. Maintenance of these areas is also reduced. By choosing right aluminum alloy and right corrosion resistance can be optimized. [63] In seawater pure aluminum and aluminum alloy with magnesium, manganese and silicon are the most corrosion resistant. [64]

Aluminum is naturally passive metal and it forms a protective oxide layer. [65] Corrosion is more intensive if the metal component is immersed and emerged in repeated cycles than if the component is permanently immersed for aluminum and other metals. Climate has a major effect on the influence of dryness and dampness. When climate is humid and cold, the effect is less pronounced than in hot and dry climate. Pitting corrosion of aluminum is more common in hot and dry climate due to the higher frequency of dryness and wetness. [66]

Thickness of colorless protective oxide layer of aluminum is between 4 nm and 10 nm and it consists of two superimposed layers. The first film is called barrier layer since its dielectric properties. Corrosion product of alumina is aluminum hydroxide  $Al(OH)_3$ , which is also called alumina. Alumina precipitates as gelatinous white gel, which will come white powder when a part of water will evaporate. Alumina is hard to clean since it is not soluble in water and it adheres well in the metal surface. Corrosion of aluminum can be seen with naked eye since corrosion pits are covered with white, plentiful and gelatinous pustules of alumina gel. The alumina pustules are much larger than the actual corrosion cavity. [65]

Pitting corrosion is the most common form of corrosion of aluminum. It starts at defects in protective oxide layer. [67] The main cause of pitting corrosion of aluminum is the presence of chloride ions. [26] Aluminum is prone to pitting corrosion in environments with pH close to neutral. Chromium and magnesium have a beneficial influence on pitting resistance in seawater. Copper and iron increases the susceptibility to pitting corrosion. [44] In Figure 18 the mechanism of pitting corrosion of aluminum is presented. [67]



**Figure 18.** Mechanism of pitting corrosion of aluminum. [67, pp. 116]

General uniform corrosion is not common with aluminum and non-heat-treatable alloys of aluminum. Uniform corrosion can occur for aluminum in salt waters. The intensity of galvanic corrosion depends on the conductivity of the water. The amount of salt increases the conductivity of sea water. Thus, galvanic corrosion is more intensive in seawater. Both metals should be painted or at least the cathode. Surface should be repainted regularly, to avoid galvanic corrosion. Galvanic corrosion of aluminum with steel, can be prevented by coating steel with cadmium or by galvanizing the steel. [68]

Corrosion of aluminum can be prevented in several ways. Anodizing is used to enhance the resistance of protective oxide film. Protective painting provides long term additional protection for aluminum and aluminum alloys in marine environments. Repainting of aluminum structures is needed half as often as would be for steel structures. [43]

All aluminum alloys belong to one of eight alloy series, alloys of these series offer a wide range of compositions, properties and uses. Alloys which belong to the same series have a set of common properties such as castability, mechanical properties, extrudability and corrosion resistance. Common basic properties of alloys, belonging to the same series, are determined by alloying elements. [69]

Unalloyed aluminum belongs to the series 1xxx. Alloys which has copper as a main alloying element belong to the series 2xxx. Alloys with manganese as main alloying element belong to the series 3xxx. Alloys where silicon is main alloying element belong to the series 4xxx. Alloys which contain magnesium as main alloying element belong to the series 5xxx. Alloys which contain magnesium and silicon as main alloying elements belong to the series 6xxx. Alloys which contain zinc as a main element belong to the series 7xxx. Alloys in 8xxx series have miscellaneous compositions, containing tin, lithium and/or iron. [70]

The 1xxx alloys have the highest resistance for general corrosion. [68] Typical alloys for marine environments are 5052, 5454, 5083, 5086, 6061, 6063 and 6082. Due to lower corrosion resistance aluminum-copper and high strength aluminum-zinc, magnesium-copper alloys should not be used in seawater without protection. [63] The most used aluminum alloy in marine environment is 6061. Alloy 6061 has good strength and good resistance to seawater. Like other aluminum alloys, alloy 6061 is susceptible to pitting corrosion. [63] Anodized AlMg alloys are widely used in structural purposes such as lifeboats and fittings. [6] 2000 series, 4000 series and 7000 series have relatively poor corrosion resistance in marine environments. [43]

#### **4.4 Corrosion of titanium in marine environment**

In marine environments titanium and titanium alloys are the most resistant to corrosion of metals used in marine industry. [43] The cost of titanium is approximately four times that as high as the one of stainless steel and this is why it is not generally used. [71] They are immune to pitting, crevice and uniform corrosion in ambient temperatures. Titanium is cathodic to copper, steel and aluminum, but for steel the galvanic effect is minimal. [43] While temperature is low, titanium does not corrode in seawater or in chloride solutions. Titanium forms a protective oxide layer automatically protective oxide layer if there is even a small amount of oxygen or water. This oxide layer is more stabilized and stronger than one with stainless steel. Pitting or intergranular corrosion are rare in titanium and titanium alloys. Titanium generally corrodes uniformly. Pitting can appear in titanium in high temperatures above 132 °C. [72]

#### **4.5 Corrosion other metals in marine environment**

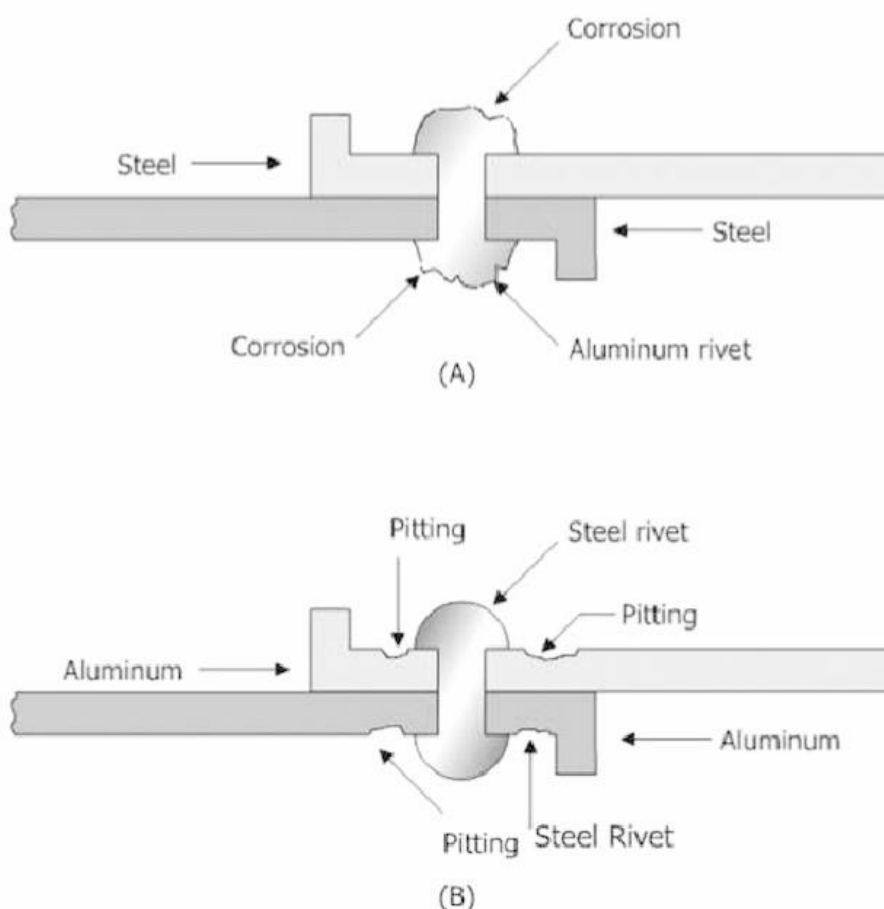
Corrosion product of zinc is formed on the surface of the zinc as a white rust. In marine environments zinc hydroxyl carbonate  $3Zn(OH)_2 \cdot ZnCO_3 \cdot H_2O$  is the most general form of zinc corrosion. [56] The rusting of zinc looks worse than it really is due to the volume of white rust of zinc is 500 times bigger than corroded zinc. [73]

In marine atmospheres all nickel alloys have excellent resistance to corrosion. Nickel alloys form a thin and tightly adherent nickel oxide layer or chromium oxide layer depending on alloy content. These protective oxide layers give the high corrosion resistance to nickel alloys. [57] In the quiet seawater nickel may lose its passive film at local sites and pitting may occur. [32]

## 4.6 Corrosion of weldments and joining materials in marine environment

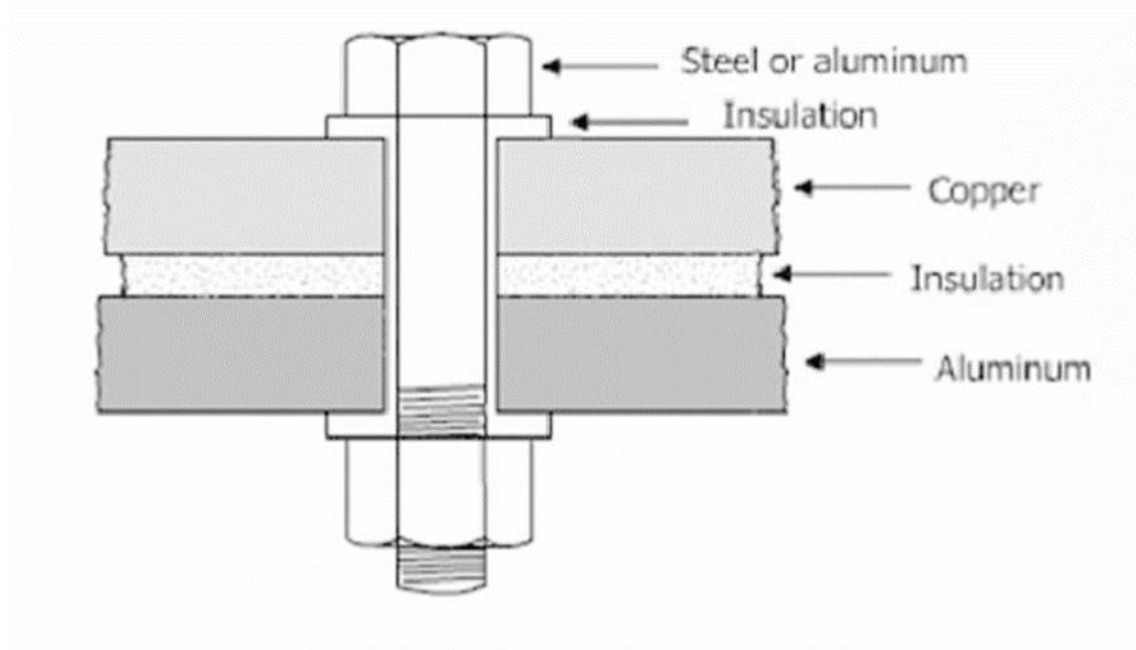
Factors influencing to the corrosion of weldments are weldment design, fabrication technique, welding practice, welding sequence, moisture contamination, organic and inorganic chemical species, oxide film and scale, weld slag and spatter, incomplete weld penetration or fusion, high residual stresses, improper choice of filler metal, final surface finish, porosity and cracks. There are several methods to minimize weld corrosion, such as careful selection of material and welding consumable, preparation of surface, welding design, surface coating, post treatments and avoidance of forming crevices. [74]

Corrosion related failures of joints are generally caused by galvanic corrosion, crevice corrosion and hydrogen interactions. [75] To avoid galvanic corrosion different materials should be insulated when joining them together. [48] For stainless steel structures should only use stainless steel fasteners. For example galvanized steel fasteners cause rusty marks on the stainless steel surface and will fail eventually since it is less noble metal. [76] To avoid the formation of crevices the two metals should be shielded by sealing or other methods. [48]



**Figure 19.** (A) and (B) have a bad design approach with no insulation. [47, pp. 450]

In Figure 19 there are two examples of bad joining. In figure A an aluminum bolt is used to join two steel plates. Steel is cathodic to steel and therefore aluminum bolt undergoes galvanic corrosion. Due to the great difference in size of anodic aluminum rivet would corrode at greatly increased rate. In figure B aluminum still corrode in preference of steel. In Figure 20 two metals with different potentials are joined together without the risk of galvanic corrosion, due to inserting insulation sleeves and washers. [48]



**Figure 20.** *Illustration of a good bolted joint.* [47, pp. 450]

## 5. CORROSION PREVENTION IN MARINE ENVIRONMENTS

The selection of corrosion prevention technology depends on many factors, such as environment where the ship is used, materials that are used, wanted appearance, availability of raw materials, price and subcontractors. Usually the target is to get structure which is as long-lasting as possible with a minimal price. [77]

Corrosion prevention coatings can be divided into four categories due to their prevention habit. These categories are barrier coatings, conversion coatings, cathodic coatings and anodic coatings. Barrier coatings can be divided to four types. These types are anodic oxides, inhibitive coatings, anodic oxides and organic coatings. [78]

### 5.1 Materials selection for marine usage

Materials with the highest possible corrosion resistance may not always be the best choice. These materials may not have other needed properties such as suitable strength and ductility. Also, the selection of material with the highest possible corrosion resistance is not always most economically viable. The costs of maintenance while designed service life and initial costs should compare when the material is selected. There are two extremes when selecting materials economically for corrosion selection. These are minimum investment and minimum maintenance. In minimum investment will use the cheapest material, but the maintenance and replacing is required. In the minimum maintenance are used material with higher costs, but there is no need for replacements or and the maintenance costs are low. [79]

### 5.2 Organic coatings

Main principle of anticorrosive coatings is to act as a physical barrier by preventing the electrolyte to touch the surface of the metal. [8] Corrosion prevention paints should have intrinsic durability, adequate flexibility, adhesion to the surface and adequate toughness to withstand impacts and cracking. Paint should maintain its appearance when subjected to weathering, stress, mechanical abuse and swell. There are many factors that affects to the durability of anticorrosive coating system, such as environmental properties, base material properties and coating properties. Environmental properties contain factors such as the type of exposure, temperature, water, salts, chemicals, bacteria, UV-radiation and time. Factors affected of base material are base material type and surface conditions such as cleaning, surface preparation, pretreatments and surface roughness. [80] Coatings for the ship deck should have excellent corrosion resistance and resistance to influences of weather. Other important properties are resistance to UV-radiation, scratching, impact,

abrasion, seawater, cleaning agents, and they should be non-slip and non-toxic. [77] Epoxy coatings are used in cosmetic topcoats due to their good resistance to sunlight. [8]

Corrosion prevention mechanism of anticorrosive coatings may be either inhibitive, barrier or galvanic. Barrier coatings prevent the access of water, oxygen and hazardous chemicals to the base material. Barrier coatings can be used as primer, intermediate coating or topcoat. Usually the thicker barrier coating is the more effective it is, but too thick coating may fail. The effectiveness of coating increase when the number of protective layers increase. [80]

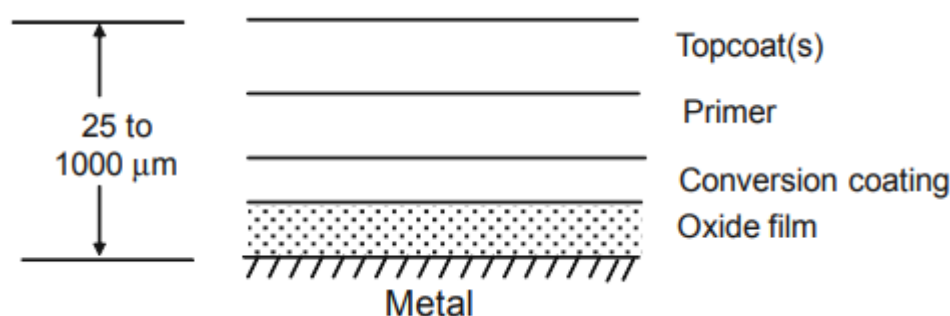
Applying of paint coating on the surface usually consist of four steps, which are surface preparation, primer application, intermediate coat application and top coat application. Absence of any of these may steps decrease the performance of coating and reduce service life.[81] Rust converter is also used in some cases. Structure of the coating layers are shown in Figure 21. [82] Anticorrosive coatings usually consist of multiple coating layers with different properties and purposes. For marine environment is usually used a primer, one or several intermediate coatings and topcoat. Primer protects the surface from corrosion and ensure a good adhesion to surface. In the marine atmosphere and splash zone, zinc or inhibitive pigments are often used in primers. Intermediate layers prevent the transportation of corrosive ions and to builds up the thickness of the coating. Intermediate layers should ensure a good adhesion between the primer and the topcoat. [80]

Rust converter is a substance that convert rust, such as iron oxides that are hard to remove, to a harmless adherent protective layer on which painting is feasible. Rust converters provides further corrosion prevention, decrease the necessity for extensive surface cleaning, such as sandblasting and improves the adhesion of paint, with low cost. The affectivity of rust conversion treatment depends on the properties of the rust layer, such as film thickness, rust structure and composition, and properties of rust converter such as structure, solubility, pH and concentration. The effectiveness of paint layer depends on the synergism and compatibility of rust converter with different constituents of paint. The most used rust converters are based on phosphoric acid or tannic acid. [83]

The main function of the primer is to provide a proper adhesion to the surface. Adhesion can be either physical or chemical. Physical adhesion is based the pulling forces of two surfaces which are close to each other. Chemical adhesion is based on the chemical reaction between the base material surface and coating surface and it is stronger than physical adhesion. Good adhesion between base material surface and the coating is obtained when the distance of these two surfaces is shorter than 5 Å. Good adhesion requires a clean surface of base material since impurities reduce the adhesion between primer and base material surface. Primers have also several other functions, such as providing a corrosion resistant barrier, to create adequate rough surface, improve the wetting properties of the surface, passivate the surface and to provide cathodic protection. [84] The most used primers for corrosion protection are zinc-based. There are two types of zinc coatings which



are organic zinc-rich coatings and inorganic zinc silicate coatings. Intermediate coat provides the main barrier protection. Depending on the environment, there might be one or more intermediate coats. [81] Topcoats give shine and desired color to the surface. They also prevent the access of oxygen, water and impurities to the intermediate layers and primers. Topcoats should withstand environmental impacts and should be compatible with primer and intermediate layers. [84] In the cruise ships the aesthetic properties of paint, such as the color durability, are also important. Epoxy coatings provides excellent adhesion, good mechanical properties and have resistance to deterioration for many chemicals. [86] Applications for alkyd coatings in vessels are habitability spaces, equipment finishes, storerooms and as decorative and marking coatings. [8]

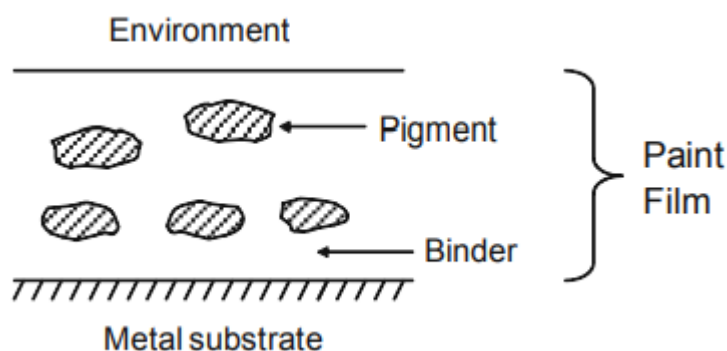


**Figure 21.** *Figure of various layers which may be present in a paint film.* [82, pp. 405]

### 5.2.1 Composition of paints

Paints consist of three major elements which are pigment, solvents and binder. [84] Figure 22 presents structure of the paint after evaporation of solvent. [82] Paint may also consist vehicles, additives and extenders. [78] Adhesive is the most important component in paint. [84] Durability of corrosion prevention paints depends on many parameters, such as composition of paint, surface, pretreatments, curing, thickness of the coating, adhesion between paint and surface, and environment. [80] Pigments may act as a corrosion inhibitor, provide cathodic protection, provide paints with a different colors or reinforce the paint. [82] Filling pigments make the coating tighter. Generally used filling pigments for corrosion prevention are barite, calcite, talc and micaceous iron oxide. [84] Inhibiting pigments passivate the metal surface, consume oxygen or increase pH. Generally used inhibiting pigments are chromates and lead based pigments. Corrosion prevention pigments are divided in three groups based on their corrosion prevention properties. Pigments usually consist of metallic oxides, such as  $\text{TiO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  or other compounds, such as  $\text{ZnCrO}_4$ ,  $\text{BaSO}_4$ ,  $\text{PbCO}_3$  and clays. Inert pigments protect paint physically against external factors such as sun light, UV radiation and humidity. Generally used inert pigments are aluminum scales and micaceous iron oxide. [85] Zinc can be used either in inorganic coatings or as pigment in organic coatings. [8] Binder forms a film which adheres on the surface. Inside this film are the pigments, which are tied by binder. Binder determines the properties of the paint film, such as strength of the film, adhesion to the

surface, chemical properties, drying of paint and type of paint. [84] Binders are organic compounds that are mostly synthetic polymers. [85] Binder can be polymer or paint resin which is formed to polymer in film forming stage. [86] Solvents dissolve solid binder or decrease the viscosity of liquid binder. [84] This enables a form of paint which can physically apply on the surface. [85] Solvents usually evaporate completely from the paint. [84]



**Figure 22.** *Structure of paint after solvent has evaporated.* [82, pp. 404]

Due to Diamond, C. [8] two coating systems for freeboard areas and other exterior surfaces above the waterline are recommend. First system is epoxy with silicone alkyd, this system contains three coats epoxy (50–100 $\mu\text{m}$  dry film thickness (DFT) per coat, 250–300 $\mu\text{m}$  DFT total) and two coats silicone alkyd (50–75 $\mu\text{m}$  DFT). Second system is zinc-rich (inorganic or organic)/epoxy/alkyd, which contains one coat zinc-rich (50–100 $\mu\text{m}$  DFT) and three coats epoxy (50–100 $\mu\text{m}$  DFT per coat, 250–300 $\mu\text{m}$  DFT total) and two coat silicone alkyd (50–75 $\mu\text{m}$  DFT).

### 5.2.2 Painting ships

Corrosion of the ship structures depends on different painting factors such as cleanliness of metal surface before painting, type of paint, thickness and durability of the paint. [85] Poor surface preparation cause many paint failures. Surface preparation is the major factor that influence to the life of paints. [87]

Surface preparation consists of two main steps which are cleaning of impurities such as dirt, greases and oils, from the metal surface and removal of rust and mill scale. Cleaning is done with solvents or by alkaline solutions. Solvents are mineral spirits such as alcohols and ethers, which can be applied by dipping, brushing or spraying. Alkaline solutions are used to remove oily surface contaminations from the metal surface. Cleaning by alkaline solutions can be applied by immersing in the hot solution, spraying or electrolytic cleaning. The use of alkaline solutions is usually more efficient, cheaper and less hazardous than the use of solvents. On the other hand, solvents are more effective to remove heavy or carbonized oils. Removal of rust and mill scale can be done either with pickling or

blasting. The aim of these is to removal of upper  $\text{Fe}_3\text{O}_4$  scale from the oxide layer. Pickling is done by dipping the metal piece into an acid containing a pickling inhibitor for approximately 5-20 min at a temperature of 65-90 °C. Blasting is done with high speed particles, such as sand, by air blast or by high-velocity wheel. [87]

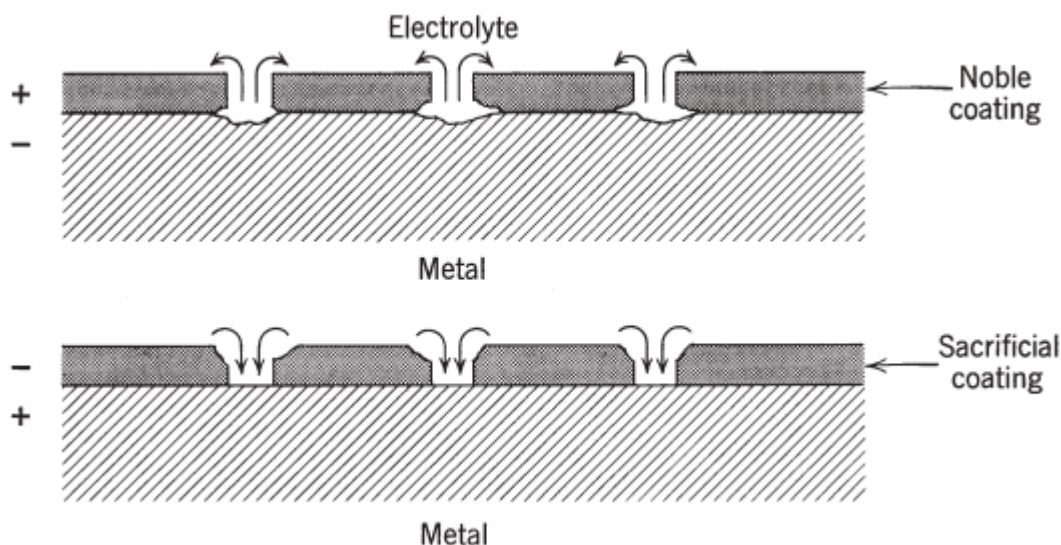
Rust scale, mill scale and corrosion products should remove before painting since they may cause corrosion under the paint. [88] Surface temperature and air humidity should consider when epoxy paints are applied on the metal surface. Epoxy paints should apply when the steel surface is 3 °C warmer than surrounding air. [89] All paints do not suit to use together. Wrong top coat may dissolve primer, when it became soft. When applying maintenance painting or replacing painting, paint should be the same as original or it should suit to use with original paints. [89]

### 5.3 Inhibitors and passivators

Inhibitors are chemical substances that effectively decrease corrosion rate when they are added in small concentrations to corrosive environment. Inhibitors act differently with different metals. For some metal inhibitor can prevent corrosion and to other metal it can cause corrosion. [90] Generally inhibitor influences to corrosion prevention either by interaction or reaction between the metal surface and inhibitor or by making the environment less corrosive. [91] Inhibitors can be divided to anodic and cathodic inhibitors by their ability to polarize either cathodic or anodic reaction. [92] Anodic inhibitors or passivating inhibitors act by preventing adsorption of aggressive anions or by repassivating or stabilizing damaged passive film. Anodic inhibitors can be divided into two groups by their ability to passivate the metal surface directly or indirectly. Direct passivating inhibitors are oxidizers and indirect passivating inhibitors need oxygen. Cathodic inhibitors act by reducing the rate of cathodic reaction and thus slow down the corrosion. [93] Inhibitive coatings are generally used as primers since they react with the base material to protect the base material. Inhibitors can be divided to three groups which are passivators, organic inhibitors and vapor phase inhibitors. Inhibitive pigments are inorganic salts, which are slightly soluble in water. Phosphates are most used inhibitor pigments in Europe. In the presence of moisture, the inhibitive pigments partly dissolved. Dissolved ions react with the base metal and passivates the surface of base metal. [80]

### 5.4 Metal coatings

Metal coatings are usually porous, and they can get damaged in shipment and in use. Therefore, metal coatings also protect the base metal by galvanic actions. Metal coatings can be divided into two classes: to noble coatings and to sacrificial coatings. Noble coatings only provide barrier protection whereas sacrificial coatings also provide cathodic protection in addition to barrier protection. In Figure 23 can be seen the difference in current flow at defects in noble and sacrificial coatings. [94]



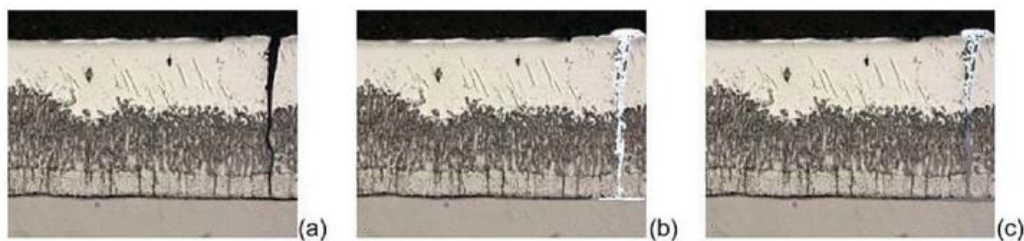
**Figure 23.** Sketch of current flow at defects in noble and sacrificial coatings. [94, pp. 271]

Metal coating can be applied on the metal surface several ways, such as by hot dipping, electroplating, metal spraying, metal cladding or cementation. [85] In hot dipping the base material is immersed into molten metal. [94] Hot dipping is mostly used for zinc, but also aluminum, aluminum alloys, tin and lead. Hot dipping which is done by molten zinc, is called galvanizing. [85] In electroplating, the coated metal is dipped into salt solution where the coating is deposited on the surface. Electroplating is used to achieve corrosion resistance and for decorative purposes. Thermal spraying of metal coatings is a technique where molten metal is sprayed into the surface of base metal. There are several thermal spray techniques which can varies of the temperature of the flame, the velocity of the sprayed particles and nature of the materials which forms the coating. Thermal spraying is not used for large surfaces. [94] Thermal spraying is used for aluminum and zinc coatings. [85] Thermal spray coatings may be porous and therefore pores are sometimes filled with a thermoplastic resin. [94] Cladding is a method where thick film of protective metal is pressed or hot rolled on the base metal. Cladding material is usually aluminum. [85] Cladding techniques are hot-roll bonding, cold-roll bonding, explosive bonding and weld cladding which includes laser cladding. [95] Cementation is a process where metal powder and the base metal below it, are heated when metal powder is diffused on the base metal. Cementation is used for zinc, aluminum and chromium. [85] By anodizing the formed oxide layer of aluminum have a greater resistance to corrosion. Properties of the oxide film depend on both anodizing parameters, such as potential and electrolyte type, and composition of electrode. For corrosion protection is used barrier anodic film type. These films can be formed in boric acid, ammonium borate and ammonium tetra borate in ethylene glycol. [94]

Applying zinc coatings on the metal surface is called galvanizing. [96] Galvanizing may extend the lifetime of steel by several decades. [97] During the hot dip galvanizing process, molten zinc forms different zinc and iron phases. [98] Adhesion of galvanize coatings is good by a very strong metallurgical bond between two phases. [99]

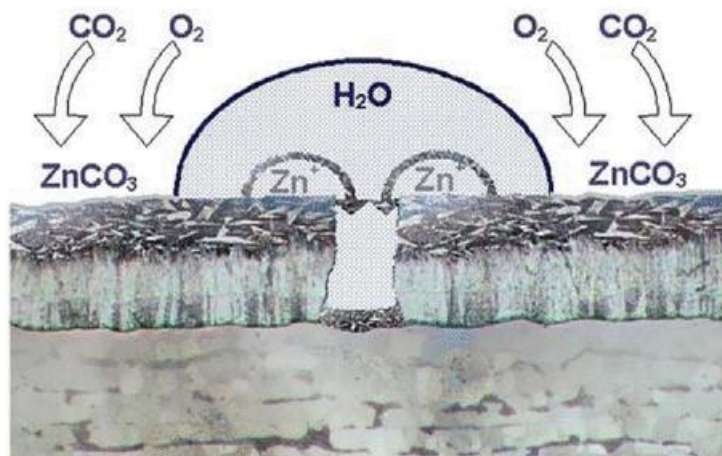
Galvanizing provides durable and maintenance free corrosion protection. [98] Painted galvanized steel has better corrosion resistance than only galvanized or only painted steel. [100] Corrosion rate of zinc and galvanized steel are almost similar. [101] Corrosion resistance of galvanized coatings can be improved with certain alloying elements. [99] Galvannealing is process where galvanized steel is annealed at 490 – 540 °C. [102]

When zinc coating get contact with air it will be covered with a layer of zinc oxide  $\text{ZnO}$ . When this layer is reacted with water in the air, for example during dew or rainfall, it will form zinc hydroxide  $\text{Zn(OH)}_2$  layer, which is porous and gelatinous. When this layer dries it reacts with carbon dioxide  $\text{CO}_2$  and forms layer which mainly composed of basic zinc carbonate  $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ . This layer is thin, compact, tightly adherent and have good corrosion resistance. This layer can be recognized by the loss of brightness of the coating. [99] Figure 24 illustrates sacrificial protection of zinc coating.



**Figure 24.** Coating defect zinc coating a. Pore in zinc coating, b. water capillary elevation into a pore, c. pore closed by zinc corrosion products. [103]

When galvanized coating is exposed in a corrosive environment, such as marine environment, it will cover by protective patina which mostly consist of zinc carbonate. Zinc carbonate is grey an insoluble in water. [103] Service life of galvanized steel is shortened in the presence of chlorides. In the presence of chlorides, zinc carbonate layer dissolves more rapidly by rain and moisture due to its ability to modify the composition of carbonate layer and increasing the solubility of zinc carbonate layer. Barrier protection ability of galvanized coating is the result of weathering. Unfavourable weathering may cause failure of galvanized coating due to occurrence of pitting corrosion. Failure may occur due to improper storage which may disturb the formation of zinc carbonate layer. [99] Figure 25 illustrates barrier and cathodic protection of zinc coating and passivation of zinc coating. Tropical marine atmosphere may lead to the pitting of galvanized coatings. [97]



**Figure 25.** Barrier formed by zinc coating, cathodic protection in a pore and passivation of zinc on the coating surface. [103]

## 5.5 Electrochemical protection

The principle of cathodic reaction is that electric current, which is caused by corrosion reactions, is subverted with opposite electric current and thus corrosion does not occur. [104] Cathodic protection can only be applied in electrolyte such as seawater, above the waterline cathodic protection has no effect. [105] Sacrificial-anode systems and impressed-current systems are the two types of cathodic corrosion protection. [106]

Corrosion protection by sacrificial anodes is based on the exploitation of galvanic corrosion. [104] The main principle of sacrificial anode is that the more active sacrificial anode will corrode instead of protected metal structure. Completely consumed anode is replaced with new sacrificial anode. [85] The most used sacrificial anode materials are zinc, aluminum and magnesium alloys. Steel anodes are used in some seawater applications to prevent pitting and crevice corrosion of stainless steel or titanium. [104] Sacrificial anodes are used places where the use of external electric power is not economical or convenient. [105] Sacrificial anodes are used as a corrosion protection method in ships and boats. [85] Impressed current cathodic protection system uses an external direct current power to convert the corroding metal from anode to cathode. The negative terminal of the external power source is connected to the protected metal and the other terminal is connected to the inert anode. [85] Anode is generally fabricated from relatively noble material such as graphite or platinated titanium. [85] [104] When using both organic coating and cathodic protection in the same time, the needed current is reduced. Approximately the needed current for unprotected metal structure is 110 mA/m<sup>2</sup> where it is only 5 mA/m<sup>2</sup> for coated structure. Usually the most economical and practical corrosion protection outcome is combination of cathodic protection and coating. [77]

In anodic protection the object to be protected is anode. The principle of anodic protection is to form and maintain passive layer. Materials for anodic protection should be able to



form passive layer affected by electric current in operating conditions. The direction of used electric current is opposite to the one in cathodic protection. Anode is mildly corroded to produce protective oxide layer to the metal surface. The need of electric current decreases due to poorly electric current permeability of protective layer when passive layer is formed. Furthermore, the electric current is carried to the places where the protective layer is thin or damaged. [104]

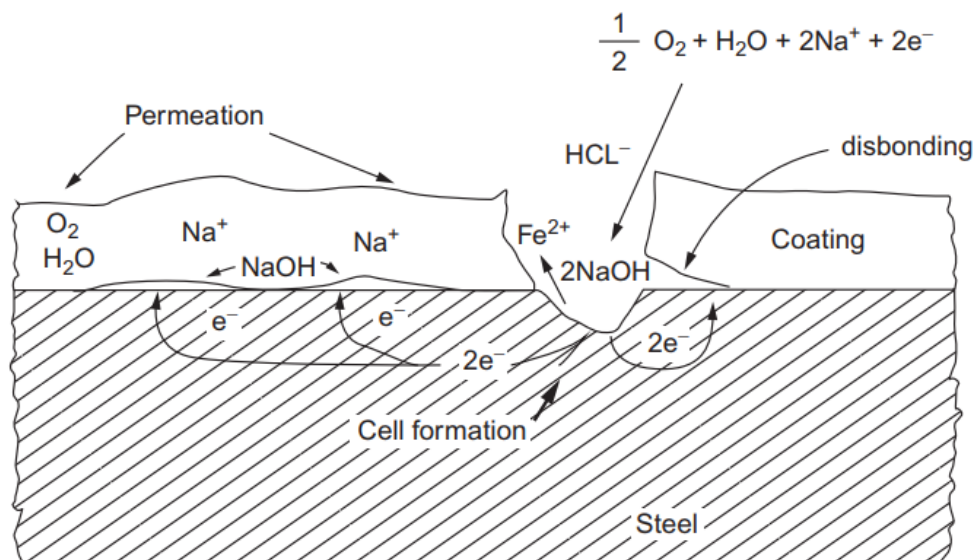
## **5.6 Corrosion prevention by design**

Probability to corrosion may be reduced by right design. Design should allow easy washing and easy exit of water so that water do not accumulate on the surface. [85] Design should allow easy repairing and maintenance of surfaces. Design should allow uniformly application of paint on the surface. [48]

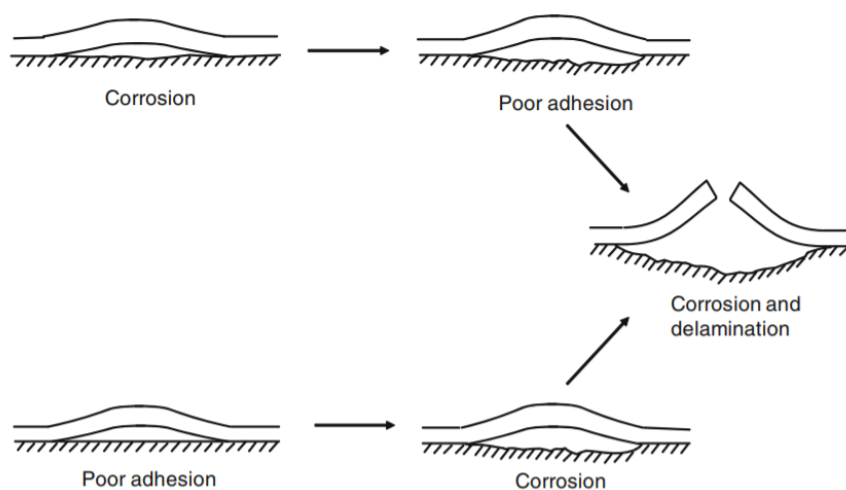
Narrow gaps should be avoided. All joints should design to be watertight by sealing or shielding the crevice from environment. Sharp corners, edges and packets should be avoided. Materials that are galvanically very different should not be used together, or they should be properly isolated. Joining components, such as screws should be made of the same or more noble material. [48]

## **5.7 Coating failures**

The background information such as coating type, application procedure, service history and environment and physical evidence of failed coating are needed to investigate why, how, when and where the failure of the coating may have occurred. [107] Cost of coating failures not only involve the cost of lost paint but also involve the repairing costs of base material and lost in production time. [108] Six primary causes accrue the majority part of paint and coating related failures. These causes are improper surface preparation, improper coating selection, improper application, improper times in drying and curing, lack of protection against water and aqueous systems and mechanical damage. [107] Typical failure of organic coating is presented in Figure 26. Corrosion which is caused by poor adhesion and coating failure due to corrosion under coating are presented in Figure 27.



**Figure 26.** Typical coating failure. [109, pp. 413]



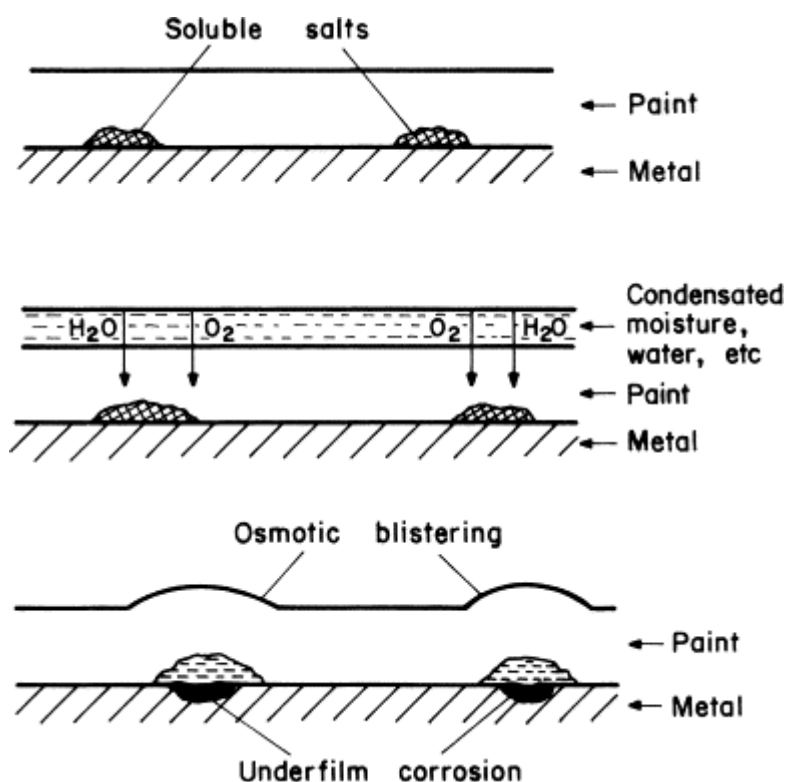
**Figure 27.** Relationship between poor adhesion and poor corrosion resistance of an organic coating. [82]

Coating failure may occur when coating is too thin or too thick. Too thin coatings may lead to reduced barrier properties due to higher permeability, corrosion at the edges of component due to inadequate permeability and susceptibility to blistering and coating failures. Too thick coatings dry slowly and may have stress cracking and adhesion related failures. [112]

Corrosion under the coatings only occurs while electrolyte exists in the interface of coating. Defects in the coating or mechanical or chemical rupture of the coating may cause corrosion under the coating. [82] Corrosion protection ability of polymer coatings is depended on water and oxygen permeability apart from other factors such as wet adhesion, pigment volume and presence of other additives. [110]



Deterioration of paint may occur in the presence of hydro soluble salts at the interface of metal and paint. This may cause underfilm corrosion and osmotic blistering. In Figure 28 principle of osmotic blistering is presented. The most common mechanism for blisters is osmotic blistering. Osmotic blistering occurs when there are contaminants, such as chlorides, in interface of metal surface and paint. Soluble salts on the metal surfaces during the painting may cause cathodic disbandment, scribe creep, loss of adhesion and decreasing of adhesion and cohesion strength. Osmotic migration of water through organic coating depends on the coating properties such as thickness and type of binder, filler, pigment and other additives. [111]



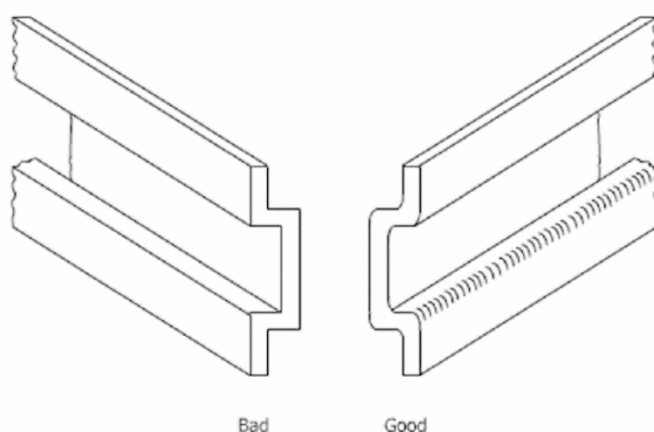
**Figure 28.** Osmotic blistering of the paint coating and underfilm corrosion of the metal substrate induced by the presence of soluble salts at the metal/paint interface. [111]

Any contaminant on the metal surface increases the separation between metal and paint decreases adhesion of paint film. Removal of contaminants, such as oxides, dirt, dust, grease, oil, old paint, corrosion products, rust, moisture, mill scale or hygroscopic salts, from metal surface may increase the amount of surface area where adhesion may occur. These contaminants not only promote the corrosion by interfering to mechanical and chemical adhesion of paint film but also attract water or water vapor through paint film. This may cause blistering, delamination and acceleration of corrosion on underlying metal surface. [112]

Basically, all organic coatings are permeable to water to some degree. Permeability to water depends on thickness and how cross-linked the coating is. [113] Crosslinking of polymer makes diffusion process of water slower. Extent and type of crosslinking have

also effect to permeability of coating. [110] Thick coatings and coatings that are highly cross-linked are more impermeable to water than thin coatings which are less cross-linked. Water penetration is more rapid in warm or hot environments. Oxide underneath the paint have a great influence on the cathodic delamination. Oxygen may penetrate to organic coating through cracks, molecular pathways or when diffused to water. [113] Osmosis occurs due to solute concentration gradient. Contaminants in the metal coating interface may also chemically destroy the binder. [114] UV-radiation may cause decomposition of binder which may has an influence to aesthetic properties. [80]

Corrosion generally originate in sharp edges and exterior corners since sharp edges are more subject to damage, coating is generally thinner in these areas and edges may provide a sharp break in the coating. Sharp edges should grind and apply with an extra paint coat on the surface. [48] [115] Coating may also fail in interior corners where the failure occurs generally by two different ways. The first is the shrinkage of the coating away from the interior corner, which causes the failure of paint. Second type is accumulation of dirt in the corner which causes corrosion. [115]

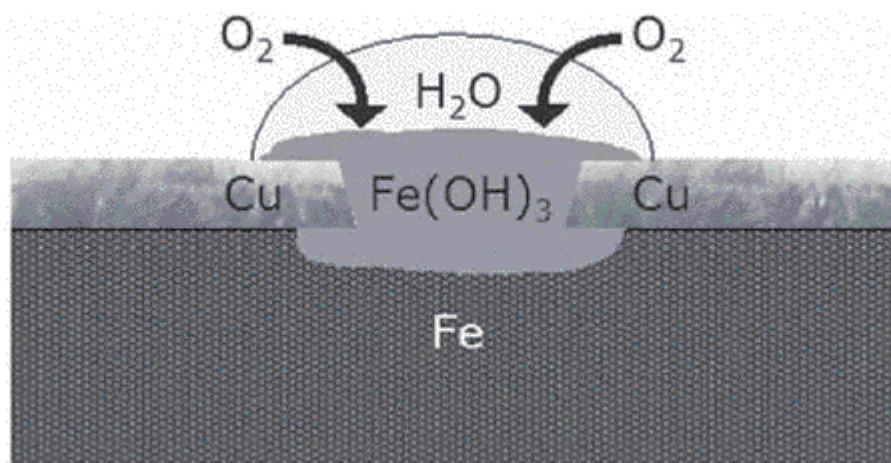


**Figure 29.** *An example of good and bad edge for painting.* [48]

Filiform corrosion is one type of corrosion under the protective coating. Filiform corrosion occurs when water and oxygen enter beneath the coating from the weak point of the surface. [82] Filiform corrosion generally occurs in coated aluminum, but it also may occur on coated steel and magnesium. Filiform corrosion is generally only an aesthetic problem since the corrosion attack is usually shallow. Filiform consist of the head and tail where anodic reaction occurs in the head and cathodic reaction in the tail. Filiform corrosion spreads due to differential aeration cell between the head and tail. Filiform corrosion generally occurs in the marine environment since the presence of chlorides and high humidity are essential for filiform corrosion to occur. [116]

Failure type of metal coating depends on nobleness of coating. If metallic coating is more noble than metal to be coated, coating becomes cathode and substrate becomes the anode when coating is damaged. This leads to the corrosion of substrate material. The failure in

noble coating is presented in Figure 30. In the case of less noble coating, it provides cathodic protection to substrate even it is damaged as long as it is present on the surface. [103]



**Figure 30.** Failure in noble metal coating. [103]

## 5.8 Maintenance

Even if stainless steel with adequate grade is selected, it still may have corrosion due to contaminants on the surface. Thus, the surface of stainless steel needs regular maintenance. [76] Contaminants on the surface of stainless steel, may be particles of iron, rust particles from other stainless steel from nearby or atmospheric contaminants such as salt deposits. Particles of iron or steel may lead to localized corrosion on the surface of stainless steel. Surfaces need regular washing to flush away these impurities. [117] Above-mentioned particles may come from the grinding, cutting or welding of steel nearby. [76] Aggressive environments increase corrosion rate and thus stainless steel surfaces requires more frequent maintenance in marine environments. Since rain effectively flushes contaminants from surfaces, the surfaces that are exposed to the rain do not require as frequent cleaning as the surfaces that are not flushed by rain. [117]

The frequency of cleaning depends on both the aesthetic requirements of the surface and the corrosivity of atmosphere. Corrosive contaminants flush easier by rain from the smooth surface than from rough surface. Cleanability is depended on the features of stainless steel component such as the geometry of component, the grade of stainless steels and the surface finish. [76]

## 6. EXPERIMENTAL METHODS

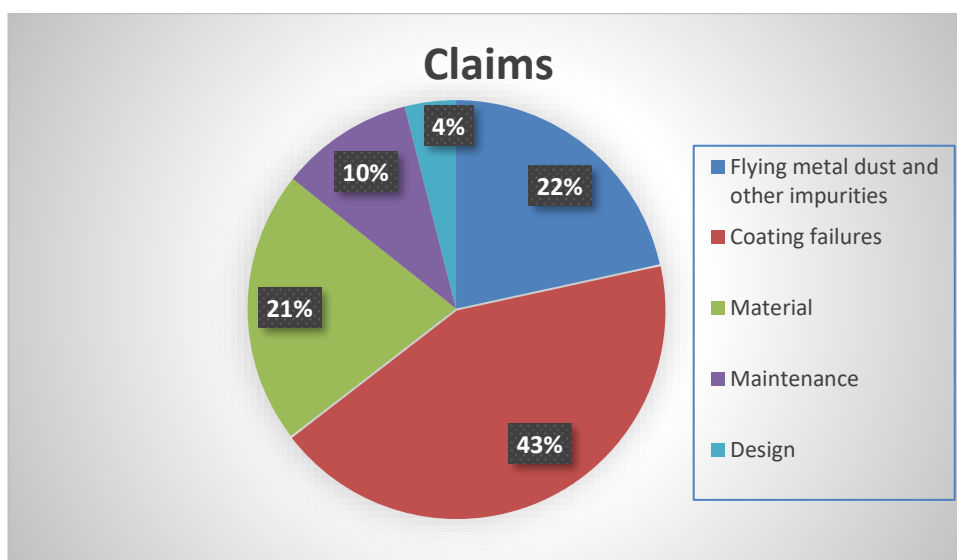
Warranty section of Meyer Turku uses software called Jira as a tool to handle claims from ships. Warranty engineers on the ship open the claims and put a description of claim to Jira. As attachments there are photos from corrosion affected area, work plan and other documents, such as order and product descriptions. The cause of corrosion should be determined by these attachments and decide corrective actions. The cause of corrosion may determine the warranty actions. Jira also act as a discussion platform between warranty engineers and warranty section of Meyer Turku.

I went through 387 corrosion related claims from life boat deck and exterior pool decks of five ships by using Jira. These areas were selected since they are ones of the most problematic areas regarding corrosion since these areas are susceptible to marine atmosphere and splashes from sea water. I distributed the 387 claims into five main categories on account of the cause of corrosion. I used excel as a working tool in distribution of claims. The main causes of corrosion were flying metallic dust and other impurities, such as sea salts, rust scale, mill scale and corrosion products; coating failures, wrong material selection, lack of maintenance and design related problems. Some claims belong to two or more corrosion cause groups. For example, the corrosion by flying metallic dust can be prevented by right design or by good maintenance. I took some examples of claims from each category.

## 7. RESULTS

Ships of Meyer Turku are sailing in many different areas such as in Baltic Sea, in Norwegian Sea in North Atlantic, in Mediterranean, in Arabic sea, in Indian Ocean, in South China Sea and in Caribbean Sea. In these areas the corrosivity has great differences due to different environments with variable by climate, temperatures and salinity. Usually shipyards have high humidity throughout the year and therefore corrosion protection is important during the construction of a ship. Serious corrosion due to atmospheric corrosion may occur where the relative humidity is above about 70%. Corrosion rate, even in humid atmospheres, is mainly determined by the impurities in the air such as sea salts. [33]

Deck fittings are influenced by rain, high humidity and aggressive marine atmosphere. Aggressive marine atmosphere has many corrosive properties such as high chloride content, high relative humidity, high content of other corrosive minerals and high oxygen content. Salts are also detected due to salt spray blown by wind. Pool decks are also exposed to high temperature and UV-radiation due to sun. [21] Life boat decks are located in between spray and atmospheric zone. Life boat materials should resist highly corrosive environment caused by salt spray from waves and highly corrosive atmosphere.



**Figure 31.** Fractionation of corrosion causes in the five Meyer Turku ships.

Results are presented in Figure 31. Figures of claims have been taken from Jira. The greatest part of the corrosion related claims are coating failures. Painting of ship is challenging due to chlorides, moisture and flying metal dust. Under the coating these impurities cause rusting and other coating failures.

The cost of these failures usually includes new materials and equipment, working hours, preparation of the area, such as building of scaffolds and cost which come from closing some area from passengers. For example, when paint failures in the swimming pools are painted, the pool needs to empty.

## **7.1 Flying metallic dust and other impurities**

There are many impurities in ship building environment, these include sea salts, rust scale, mill scale and corrosion products. These particles may come from the grinding, cutting or welding of steel nearby. While building the ship, there are many overlapping construction stages. This leads to metal dust which will deposit to surfaces which lead to the corrosion of metal dust in crevices, inside and below coatings and coverings and on stainless steel surfaces. Metallic dust is hard to remove, especially from crevices and corners. In this chapter I go through some examples of claims, related to flying metallic dust and other impurities, from Meyer Turku ships.

### **7.1.1 Deck 14 Ausenalster - corrosion through grouting**

In this claim there is notable amount of corrosion on the grouting as seen in Figure 32. Corrosion has occurred through cracks on the grouting. Flying rust and metallic dust during building and use has probably caused this corrosion. Water and sea salts have accumulated through cracks and thus the corrosion have occurred. Even this does not affect usability, it is an aesthetic problem. Work plan for this claim was removing of old grouting, cleaning the grouting seams and removing of the rust. After this the area was primed and new grouting was applied.



*Figure 32. Corrosion through grouting.*

#### **7.1.2 Deck 5 champagne turf sliding door to open deck - corrosion at edge and deck 14 scupper - corrosion between Bolidt and stainless steel**

Bolidt is a trade name for deck covering used on these ships. In many areas there are flying rust and other impurities between stainless steel profiles and Bolidt covering. Many scuppers suffer from corrosion between Bolidt covering and stainless steel profile as seen in Figure 33 and Figure 34. If there is a crevice between stainless steel profile and Bolidt covering it may gather impurities which may cause corrosion. Work plan for this claim was sanding or polishing the stainless steel profile from corrosion.





*Figure 33. Corrosion between stainless steel and Bolidt covering.*



*Figure 34. Corrosion between Bolidt covering and stainless steel profile.*

### **7.1.3 Deck 12 Ice bar - corrosion next to stainless steel profile**

Rust has been developed between stainless steel profile and Bolidt covering as seen in Figure 35. There can be seen a clear crevice between stainless steel profile and Bolidt covering. Crevices are hard to clean from impurities and thus corrosion generally occurs in crevices. Actions on this claim were that Bolidt edge was smoothed to avoid dirt and water accumulation which may cause corrosion in crevices.





*Figure 35. Corrosion next to stainless steel profile.*

## **7.2 Coating failures**

Coating failure may be result of impurities under the paint, inappropriate paint, the lack of paint coats or carelessness in paint work. Coating failures may cause corrosion problems. In this chapter there are some examples of coating failures from Meyer Turku ships.

### **7.2.1 Main pool area – rust**

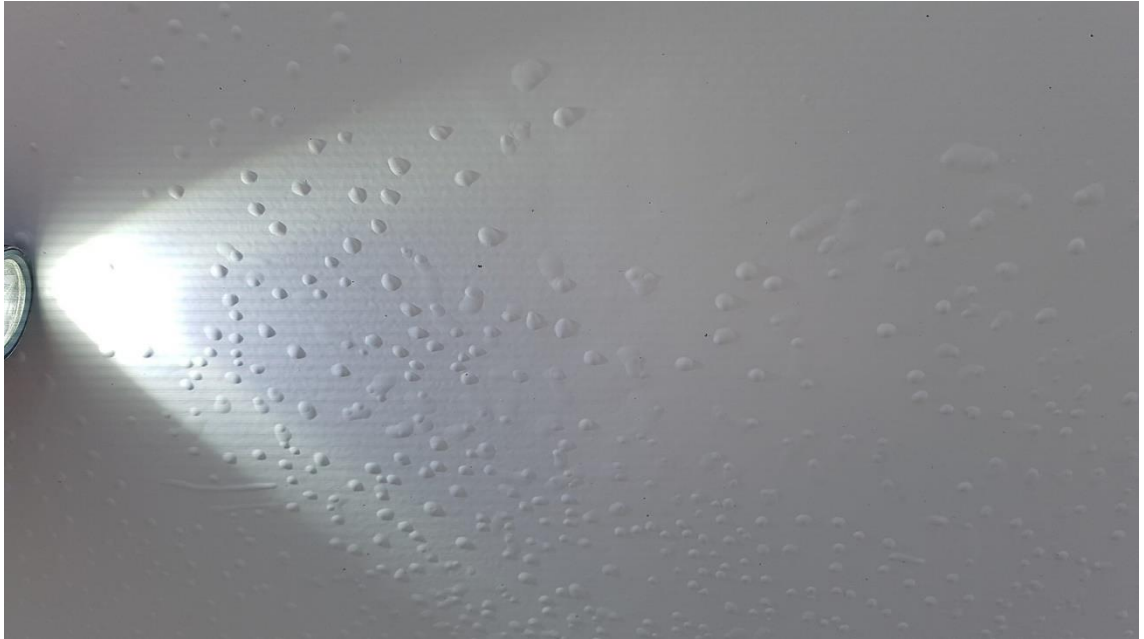
Corrosion occurs in the crevice and in the sharp edge as seen in Figure 36. These are very susceptible to corrosion. As mentioned in chapter 5.7 paint layer is usually thinner in sharp edges and sharp edges may provide a sharp break in the coating. There should take extra care when painting these areas. Work plan for this claim was rust removal by sand, treatment with rust converter and painting with two layer of epoxy paint.



*Figure 36. Corrosion in the crevice and sharp edge.*

### **7.2.2 Main pool divider - paint failure**

In this claim top coat paint has been failed as seen in Figure 38 and there are some bubbles in the paint as seen in Figure 37. These may occur due to improper top coat application or improper paint. As mentioned in chapter 5.7 blistering may occur due to hydro soluble salts at the interface of metal surface and paint. All contaminants on the surface should be cleaned before painting to avoid blistering. These areas were grinded and then painted with three layers of paint, between painting of each layer, drying was needed.



*Figure 37. Bubbles in the paint coating.*



*Figure 38. Paint failure in divider.*

### **7.2.3 Lifeboats, tenderboats and rescue boats - corrosion at winches**

In this claim the primer was forgotten to apply on the metal surface. As seen in Figure 39, the paint is peeling off. The paint can be easily removed by hand without usage of power tools. The importance of primer is explained in the chapter 5.2. Primer provides adhesion on the metal surface and it act as a barrier. Without primer the adhesion of the



topcoat is not as good as when applying also primer on the surface. Also, the moisture can easier penetrate through the paints on the metal surface.

Work plan for this claim was to de-rusting the affected area by careful cleaning, sanding and brushing. After this it is painted with primer and then painted with TUI “Mein Schiff” color while paying attention to the color coating thickness and sealed if necessary.



**Figure 39.** *Paint failure.*

### **7.3 Material selection**

Material selection is important for corrosion prevention especially in marine environments since it is very corrosive atmosphere. The most used materials on the ship are stainless steel, steel, galvanized steel and aluminum. In cruise ships many corrosion related claims are aesthetic problems. Material may still be mechanically functional, but for the cruise passenger it looks poor. In this chapter I present some claims which are result of wrong material selection.

### 7.3.1 Lifeboat + tenderboats - lifeline with rusting ropeclamps

In this claim the rope clamps have been rusted since wrong material selection as seen in Figure 40. The rope clamps did not withstand marine environment. The rope clamps have been prepared probably from stainless steel with grade that do not withstand marine environment. In this case subcontractor delivered new rope clamps with higher quality.



*Figure 40. Corrosion in the rope clamps.*

### 7.3.2 Pool area - stage curtain - corrosion at bushing

In this claim the materials are stainless steel AISI 440C/AISI 304 and shaft is AISI 316. This assembly, presented in Figure 41, locates in the open deck and that is why the materials should withstand marine atmosphere.

In chapter 4.2 has been told that stainless steel AISI 304 is prone to pitting in marine environments. In Figure 15, Figure 16 and Figure 17 the effect of PREN number and molybdenum content is presented. Stainless steel AISI 304 does not contain molybdenum and its PREN number is approximately 20. From these figures can be seen that the corrosion rate and pit depth are much higher than for example the ones of AISI 316. Usually the AISI 304 should not use in marine environments due to its ability to pitting and corrode in the presence of chloride ions.

Subcontractor informed that these are only materials available to these parts. AISI 304 should be painted to get adequate corrosion resistance. Work plan for this claim was cleaning the corrosion by grinding and then painting bearing housings achieve adequate corrosion resistance for off shore conditions. Used primer was a two-component, polyamide-cured high-build epoxy primer containing zinc phosphate. Used top-paint was a two component, semigloss polyurethane paint, hardener aliphatic isocyanate.



*Figure 41. Corrosion at bushing.*

### **7.3.3 All lifeboats - corrosion at window frame gaskets**

The inner components are corroding due to wrong material selection, as seen in Figure 42. Even there was sealing, it was not completely tight so that underlying metal corroded. If the sealing is not completely tight, the material below it should resistance corrosion.

Old frame gaskets were removed, the area was cleaned of rust and new gaskets with adequate material and better sealing were installed.



*Figure 42. Corrosion at window frame gasket.*

#### **7.3.4 Lifeboats and tenderboats - rusted caps**

In this claim all lifeboats and tenderboats were found with rusted oil caps. Material apparently does not withstand marine environment as seen in Figure 43. Materials used in lifeboats and tenderboats should have good corrosion resistance since they are located in open decks. In this case subcontractor found an alternative design from rustproof material and new oil caps were delivered on the ship.





**Figure 43.** *Rusted oil cap.*

### **7.3.5 Lifeboats - securing pin corroded**

In this claim the securing pin has been corroded due to wrong material selection as seen in Figure 44. The pin can be either corroded by marine exposure or galvanically. New pins were stainless steel quality. There were many claims of corroded pins, screws and other joining parts. It is important to choose stainless steel pins for open decks and when joining stainless steel parts together.



**Figure 44.** *Corroded pin.*

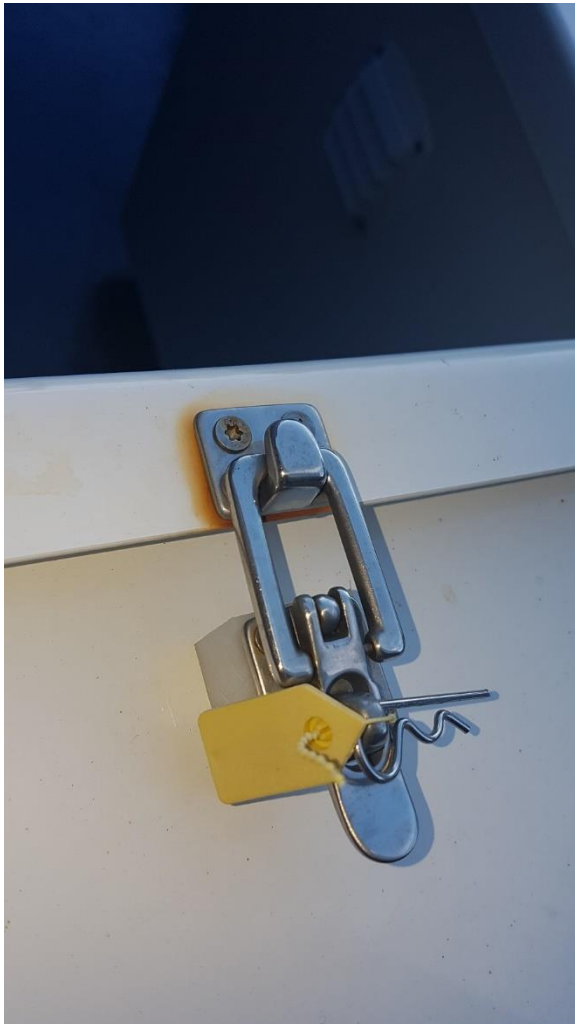


## 7.4 Maintenance

As mentioned in chapter 5.8 even stainless steel surfaces need to maintain. Contaminants on the surface should be flushed away regularly. In this chapter I present some maintenance problems from Meyer Turku ships.

### 7.4.1 Boat deck - descending units - corrosion at storage

This claim is a typical maintenance issue. Impurities usually accumulate on surfaces that are anomalous from even surface as in Figure 45. In this case corrosion should be removed and the area should be cleaned and if the paint surface has been damaged it should be repainted. This kind of claim can be prevented by good maintenance and cleaning or by good design.



**Figure 45.** Corrosion on the boat deck.

### 7.4.2 LSA davits - corrosion at pins

Even the stainless steel should maintain to prevent rusting. In this claim there is some light rust on the surface as seen in Figure 46. Actions on this claim were that the affected areas were properly de-rusted by careful cleaning, sanding and / or brushing. Ground areas were primed after appropriate preliminary work, then painted (with appropriate consideration of the TUI "Mein Schiff" color and attention to the color coating thickness). Also, some anti-corrosion wax was used to protect the surface.



*Figure 46. Corrosion at pins.*

### 7.4.3 Lifeboat and tenderboats - lifeline with rusting ropeclamps

In this claim there is corrosion on the surface of wires as seen in Figure 47. Wires are made of galvanized steel. Galvanized steel needs to maintain even it has better corrosion resistance than steel without any protection. Galvanized steel has to maintain by cleaning and greasing. Wires need to brush carefully away from rust and grease. Rust have probably came from other impurities on the galvanized surface.



*Figure 47. Rust on the wire.*

## **7.5 Design**

The amount of corrosion claims may be reduced by right design. For example, narrow gaps and sharp corners should be avoided. In this chapter I present some claims from Meyer Turku ships that are related to design problems.

### **7.5.1 Main pool forward showers - rusted lower edge**

Water ingress between wall and floor. This cause recurrent corrosion problem, even the corroded area is removed and cleaned, and new grouting is installed as seen in Figure 48. Any gaps in the structure should be avoided for the corrosion prevention.



*Figure 48. Rusted lower edge.*

### **7.5.2 LSA steel base of HPUs – corrosion**

In this claim there are corrosion due to paint failures. In Figure 49 there is corrosion due to sharp edge. As mentioned in chapter 5.7, paint failures often occur on sharp edges, since the paint may be thinner than in surrounding area. Sharp edges should be grinded to get smoother edge and extra circumspection should be used while painting. In Figure 50 there is corrosion due to inner corner. As mentioned in chapter 5.7, corrosive particles easily accumulate in the corners and may cause corrosion. Sharp inner corners should be avoided, if possible. Damaged areas were grinded, washed, painted with primer two times and painted with paint two times.





*Figure 49. Corrosion in the sharp edge.*



*Figure 50. Corrosion in the corner.*

### **7.5.3 Washing baskets - corrosion at bushings**

In this claim bushings have been corroded due to marine exposure as seen in Figure 51. Bushings are only available with stainless steel AISI 304. As mentioned in chapter 4.2, stainless steel AISI304 should not use in marine environments since it may have pitting and it may corrode in the presence of chloride ions. There should be used some protection if used stainless steel AISI 304 on the exterior decks. Action for this claim were to install protective cover cups on the bushings. These cups can be seen in Figure 52.



**Figure 51.** *Corrosion at bushing.*



**Figure 52.** *Bushing covered by protective cover cups.*

## 8. DISCUSSION

In this discussion part I go through the results of this thesis. I also consider some possible corrective actions related to these corrosion problems.

### 8.1 Coating

Coating failures were the most general cause of claim related to corrosion, 43% of the corrosion related claims were about coating failures. The most general types of paint failures were caused by negligence. Surfaces should clean carefully from sea salts, rust scale, mill scale, corrosion products and other possible impurities.

Other reasons for paint failures are the lack of some paint layer, such as the lack of primer, wrong thickness of the paint, paint that not withstand marine use, defect in the paint due to mechanical damage and too sharp edges. Primers and top paints should be compatible to each other. They may have a negative effect to each other if they are not compatible to each other. In the painting should pay attention to the circumspection so that the thickness of the paint is suitable for object and it is uniform.

Subcontractors supply most of their products already coated. It makes supervision difficult. Quality control should be required to ensure that painting can withstand marine environment.

### 8.2 Material selection

The greatest part of claims related to material selection, were about selection of materials that do not withstand marine environment. Almost only material used without any extra protecting on exterior decks is AISI 316 stainless steel. As mentioned in chapter 4.3 it is the most used stainless steel in marine environment.

22 % of claims were related to the material selection. Many claims were about wrong materials used in joining, such as pins, clips and screws. As mentioned in chapter 4.8, to join stainless steel parts should only use stainless steel joining materials. Steel and galvanized steel screws may corrode due to marine exposure and galvanic effect. Workers should be emphasized that it is important to use specific screws, especially in areas that are exposed to marine atmosphere. Mistake in using screws from wrong material will cost multiple times more than the cost of correct material screw.

Subcontractors are responsible for many material selections. All materials may not be suitable for marine use. Subcontractors may produce their products to other companies as well and they may not have same environment as cruise vessels and subcontractors may

not have knowledge about marine corrosion. Subcontractors should inform the materials of their products, so that shipyard can ensure their suitability for marine use. In the shipyard there is not always knowledge about corrosion resistance of materials in marine environment and how materials behave together. Materials should be tested for the suitability to marine atmosphere and test document used as a condition for subcontractors purchase order.

### **8.3 Flying rust**

There are many impurities in ship building environment, these include sea salts, rust scale, mill scale and corrosion products. These particles may come from the grinding, cutting or welding of steel nearby. While building the ship there are many overlapping construction stages. This leads to metal dust which will deposit to surfaces which lead to the corrosion of metal dust in crevices, inside and below coatings and coverings and on stainless steel surfaces. Metallic dust is hard to remove, especially from crevices and corners.

21 % of claims were related to the flying rust. Many claims relating to the flying metal dust are related to the cracks and corrosion in the grouting. When applying grouting on the surface should the surface be cleaned carefully from the rust scale, mill scale, corrosion products and other impurities. Grouting should also be applied carefully so cracks are not formed since impurities accumulate to the cracks.

The amount of flying rust is not easily decreased in ship building, but the amount of flying rust on the surfaces may be decreased. Surfaces can be protected by different covers and surfaces can be designed so that they do not collect flying rust so easily. Horizontal surfaces and crevices should be avoided. Surfaces should be cleaned regularly from flying rust particles.

### **8.4 Maintenance**

As mentioned in 5.8, even stainless steel surfaces need maintenance. 10 % of claims were related to the maintenance. Salts and other impurities need to be washed away from surfaces regularly. If the washing is not done properly and regularly, marine salts may cause pitting and other corrosion on the surfaces. There should be attention also to the design, uniform surfaces accumulate fewer impurities causing the corrosion, and they are easier to maintain. Ship yard should offer maintenance instructions to the crew and crew should record their maintenance action so that ship yard can observe it.

### **8.5 Design**

Corrosion may be prevented with right design. 4 % of corrosion claims were related to not suitable designing. By avoiding crevices, sharp corners and sharp edges probability



to corrosion decreases. By designing joining of materials properly probability of corrosion decreases. Also, the protection covers should design so that they do not allow moisture or harmful particles to enter.

## 9. CONCLUSIONS

The aim of this thesis was to study corrosion in marine environment, especially in ships and to determine the main reasons of corrosion in pool and life boat decks in the ships of Meyer Turku. The study of marine environment was done as literature survey and the experimental part was done by going through corrosion related claims from the ships of Meyer Turku.

Many factors have an effect on the corrosion of marine environment. Marine environment is highly corrosive due to high humidity and the presence of corrosive agents such as sodium chlorine. Corrosion rate vary a lot by different area and weather.

Pitting, crevice corrosion and galvanic corrosion are the most problematic corrosion types in marine environment. Many used materials in ship building are susceptible to these corrosion types.

Materials behave differently in marine atmosphere than in rural atmosphere or in seawater. This should take into account when selecting materials to marine atmosphere. Materials which do not have corrosion in rural atmospheres may have corrosion in marine atmosphere. Many factors such as corrosion resistance, cost, mechanical properties and availability has an effect to material selection.

There are many corrosion prevention methods that are used in ships. The most used corrosion prevention method is painting. Other methods are metallic coatings, inhibitors, passivators and electrical protection. However these corrosion prevention methods may fail in marine use. The probability for corrosion may also reduce by good material selection, by good designing and by maintenance.

Three main reasons for corrosion in ships of Meyer Turku were coating failures, materials selection and flying rust. The materials and coating materials should be adequate for marine use. The preparation of coating is important to decrease probability of coating failure. The amount of flying rust is hard to decrease but there is some ways to decrease probability to corrosion, such as cleaning, design and protective coating while building.

Since ship yard is purchasing majority of the outfitting material from various subcontractors, a simple quality gate before purchases are signed would decrease the number of warranty claims. Passing this gate subcontractors should provide indisputable documentation showing that the material can withstand marine environment.

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## APPENDIX A: GALVANIC SERIES IN SEAWATER

<b>Corroded end (anodic, or least noble)</b>
Magnesium
Magnesium alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys, 5052, 3004, 3003, 1100, 6053, in this order
Cadmium
Aluminum alloys, 2117, 2017, 2024, in this order
Low-carbon steel
Wrought iron
Cast iron
Ni-Resist (high-nickel cast iron)
Type 410 stainless steel (active)
50-50 lead-tin solder
Type 304 stainless steel (active)
Type 316 stainless steel (active)
Lead
Tin
Copper alloy C28000 (Muntz metal, 60% Cu)
Copper alloy C67500 (manganese bronze A)
Copper alloys C46400, C46500, C46600, C46700 (naval brass)
Nickel 200 (active)
Inconel alloy 600 (active)
Hastelloy alloy B
Chlorimet 2
Copper alloy C27000 (yellow brass, 65% Cu)
Copper alloys C44300, C44400, C44500 (admiralty brass)
Copper alloys C60800, C61400 (aluminum bronze)
Copper alloy C23000 (red brass, 85% Cu)
Copper C11000 (ETP copper)
Copper alloys C65100, C65500 (silicon bronze)
Copper alloy C71500 (copper nickel, 30% Ni)
Copper alloy C92300, cast (leaded tin bronze G)
Copper alloy C92200, cast (leaded tin bronze M)
Nickel 200 (passive)
Inconel alloy 600 (passive)
Monel alloy 400
Type 410 stainless steel (passive)

Type 304 stainless steel (passive)
Type 316 stainless steel (passive)
Incoloy alloy 825
Inconel alloy 625
Hastelloy alloy C
Chlorimet 3
Silver
Titanium
Graphite
Gold
Platinum
<b>Protected end (cathodic, or most noble)</b>