



INTRODUCTION AND LITERATURE REVIEW OF CORROSION AND BIOFOULING IN MARINE ENVIRONMENT

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Abstract: This study aims to increase the power and the performance of marine structures by protecting them from corrosion and biofouling, which cause reduction of the vessels power.

There are many factors in marine environment such as salinity, pH, temperature, and velocity, which cause corrosion. There are three main reasons concerning the study of corrosion. These reasons are safety, economics, and conservation. In addition, there exists the aquatic organism bio-film, which covers the vessels hull. This phenomenon called fouling and it results in increasing hydrodynamic drags, lower the maneuverability of the vessels and increase the fuel consumption. All these factors lead to the deficiency of ships performance. There are many methods that can be used to prevent vessels from the results of fouling and corrosion, among these methods coating i.e. using a highly corrosion resistant material on the ship hull and cathodic method i.e. using zinc for electro mechanic interaction could be effective if implemented properly.

Keywords: Corrosion, biofouling, corrosion control methods, types of biofouling, biofouling mechanism.

I. INTRODUCTION

Ships sail on different water surfaces such as oceans, seas, lakes and rivers. Oceans, seas and lakes are considered as the most corrosive environment that ships could encounter. Therefore, it is important to find suitable maintenance measures and protection system to resist tough atmosphere and to increase the performance of sea vessels.

Ships maintenance has paramount role in ensuring ship's high performance operation and makes it free from corrosion. However, lack of maintenance principles may cause corrosion accumulation to the ship's hull and deficiency of vessels performance. The researcher, therefore, is intended to find a suitable way to increase ships performance by controlling the factors the affects ship's hull

to corrode using Impressed Current Cathodic Protection System 'ICCP' to instantly monitor these factors and react against; besides setting an effective maintenance measures.

Maintenance does not only keep any mechanical equipment or machinery going but also can help with prolonged life and a favorable outcome and increase it is performance. For a ship, maintenance is the one thing that keeps machinery in smooth running condition and it has a paramount feature of the national economy. Each year, large amounts of money are located for maintenance purpose. Poor or failed maintenance planning can result in serious incidents and high penalty costs arising from operation downtime (Dekker 1996).

It is observed that the ships are not enrolled effectively in service due to many circumstances. First, the regulations of ship maintenance are not followed effectively. Second, the corrosive environment in seas and oceans extremely damages the ship's hull.

In addition, the accumulation of biofouling organisms on surface of marine structures is a problem added to corrosion. Biofouling is a complex process, which involves the attachment and growth of a community of organisms on a surface in contact with an aqueous medium. For the shipping industry in particular, biofouling is a critical problem, leading to the reduction of the maximum speed and upraise of the fuel and maintenance costs. Consequently, as known, higher fuel consumption also translates into higher emission of greenhouse gases such as NO_x and SO_x. In addition, the International Maritime Organization (IMO) estimated an increase of at least 50% of CO₂ emissions until 2030, under extreme scenarios. The settlement and accumulation of marine organisms also leads to the increase of the drag created between the ships' hull surface and the seawater. Drag friction increases up to 40% could be reached (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).



II. LITERATURE REVIEW

A. Corrosion

The ship's hull protection to resist the rough surrounding environment requires knowledge about the different factors that affect vessels frame and how to protect it from the damage due to accumulation of corrosion and fouling. The researcher therefore should give an overview about the phenomena of corrosion, bio-fouling, factors that affect hull structure and various hull protection methods (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

There are three main reasons concerning the study of corrosion. These reasons are safety, economics, and conservation. Early failure of vessels hull due to corrosion can result in human injury or even loss of life. Failure of operating equipment can have the same disastrous results. Corrosion is defined as the degradation of a material's properties or mass over time due to environmental effects. It is the normal inclination of a material's compositional elements to return to their most thermodynamically stable state. For most metallic materials, this means the formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores. Luckily, the accumulation rate of these processes is low enough to enable the making of useful building materials. Only inert environments and vacuum can be considered free of corrosion for most metallic materials. Under usual circumstances, iron and steel corrode in the presence of both oxygen and water. If either of these materials is not present, corrosion usually will not take place. High corrosion rates may take place in water, in which the rate is increased by the acidity or velocity of the water, due to the movement of the metal, and the increase in the temperature or it may take place in aeration, due to the presence of microorganisms, or takes place due to other less common factors. On the other hand, films (or protective layers) generally stop corrosion consisting of corrosion products or adsorbed oxygen; high alkalinity of the water also reduces the rate of corrosion on steel surfaces. The amount of corrosion is controlled by either water or oxygen, which are necessary for the process to take place. For example, steel will not corrode in dry air and corrosion is insignificant when the relative humidity of the air is below 30% at normal or reduced temperatures (Wells, 1948). Protection from corrosion by dehumidification is based on this fact. All structural metals corrode to some degree in natural environments. These corrosion processes follow the basic laws of thermodynamics. Corrosion is an electrochemical process and as such, under controlled conditions, it can be measured, repeated, and predicted. Since it is governed by reactions on an atomic level, corrosion processes can act on isolated regions, uniform surface areas, or result in subsurface microscopic damage. These forms of corrosion are complicated with further subdivisions. Just consider adding basic environmental variables such as pH,

temperature, and stress, and the predictability of corrosion begins to be more difficult.

Seawater is a biologically active medium that contain a large number microscopic and macroscopic organisms. Many of these organisms are commonly observed in association with solid surface in seawater, where they form bio-fouling films, these bio films play a vital role in aggravating corrosion on vessels hull. Immersion of any solid surface in seawater initiates a continuous, dynamic process, beginning with absorption of nonliving, dissolved organic material and continuing through the formation of bacterial, and algae slime films and the settlement and growth of various macroscopic plants and animals. This process by which the surface of all structural materials immersed in seawater become colonized, adds to the variability of ocean environment in which corrosion occurs (Rodgers, 1968)

The amount of oxygen and other gases dissolved in seawater depends on the temperature and salinity of the seawater and the depth of water. In some seawater compositions, hydrogen sulfide is also present. Hydrogen sulfide is formed in seawater by the action of sulfate-reducing bacteria (SRB), usually under deposit where oxygen is depleted or when the seawater is stagnant or polluted and becomes anaerobic, even in large volumes. Silt deposit in estuarial waters are also contributory. Mineral and organic materials are also carried in suspension by the seawater, particularly near the mouth of the river (Craig & Anderson, 1995).

Since seawater is a complex environment, delicately balanced solutions of many salts containing living matter, suspended silt, dissolved gases and decaying organic materials, the individual effect of each of the factors affecting the corrosion behavior is not readily separated. Because of the interrelation between many of the variables in the seawater environment, an alteration of one variable may affect the relative magnitude of the other variables. In the following subsections, the roles of oxygen, biological activity, temperature, velocity, salinity, and Ph. are presented (Fink, 1993).

The dissolved oxygen content is a major factor affecting the corrosively seawater. The oxygen level in seawater is of different range up to 12 ppm. Photosynthesis of green plants, wave action etc., tends to increase the oxygen level, whereas the biological oxygen demand of decomposing of dead organisms will reduce it. For a given location, seasonal variation in oxygen level will influence corrosion behavior. For metals like copper and iron, complete elimination of oxygen will reduce the corrosion to negligible amounts. However, metals that depend on formation of a passive film for corrosion protection, i.e. stainless steel, often corrodes rapidly where the oxygen supply to the metal surface is restricted.

When a metal or other surface is first immersed in seawater, a biological slime tends to develop in a matter of hours.



During an active season, great varieties of organisms are found in an immersed surface. From a corrosion point of view, the sessile organisms are of most concern. They arrive at slime-covered surface in minute emergent form and become firmly attached. Once attached, they rapidly transform to the mature form and become immobile. Organisms, which build hard shells, are annelids, barnacles, encrusting, bryozoans, mollusks, and corals. Organisms without hard shell are marine algae, filamentous bryozoans, coelenterates, or hydroids, tunicates, calcareous, and siliceous sponges.

An increase in temperature is normally expected to speed up a chemical reaction according to thermodynamic considerations. This also would be the case for the corrosion reaction in seawater where it is possible to hold all other variables fixed. Since it is not normally possible to do this, the effect of temperature has to be established indirectly. Oxygen solubility decreases with increase in temperature, biological activity increases as the water temperature increases, and the chemical equilibrium involved in the precipitation (production) of calcium carbonate and magnesium hydroxide is altered (replaced) so that calcareous scale is more likely to deposit on the metal as the temperature is increased. For temperature variations of seasonal (cyclic) nature, iron, copper, and many of their alloys show a high rate of attack during the warm months.

Many metals are sensitive to velocity effects in seawater. For metals like iron or copper, corrosion becomes excessive beyond a critical velocity. Stainless steel and certain nickel-chrome-molybdenum alloys tend to be more resistant in high-velocity seawater. Special forms of corrosion are associated with seawater velocity, i.e. (erosion-corrosion caused by high-velocity silt-bearing seawater, impingement attack, where air bubbles are present, and cavitation, where collapsing vapor bubbles cause mechanical damage and often corrosion damage as well.

The major oceans of the world are completely connected and mixing is continuous. The average salt content of the sea is 3.5 wt. % with the composition comprised mainly of the following ions: sodium, magnesium, calcium, potassium, chloride, bromide, carbonate, and sulfate. In addition, seawater contains measurable quantities of iodide, fluoride, phosphate, gold, silver, arsenic, rubidium, copper, barium, manganese, lithium, lead, iron, strontium, and zinc ions. Ammonia is also present, with free oxygen, nitrogen, and other gases. Variations in salinity in open-ocean surface water typically range from 3.25 – 3.75 wt. %.

PH is a number range from 0 to 14 which shows how strongly acid or alkaline a substance is. The number below PH 6.5 is acid and above PH 7.5 is alkaline.

In a case of marine environment, the PH of seawater may vary slightly depending on the photosynthetic activity. Plant matters consumes carbon dioxide and affects the PH during the daylight hours. The carbon dioxide in seawater, close to the surface is influenced by the exchange with carbon

dioxide in the atmosphere. The slight daily shift in PH has little direct effect on the corrosion behavior; however, it can be a factor in calcareous-scale deposition, which affects the corrosivity. As pressure is increased, PH is reduced according to thermodynamic considerations. Thus, at great depths, there is some evidence of fewer tendencies for protective carbonate-type scale formation.

The luster, ability to conduct heat and electricity, malleability of some and ductility of others are only some of the main characteristics, which define metals. However, it is the varying ability of a metal to lose its electrons and form a positive ion that is essential in understanding the range of metals that are capable of corroding. It is this understanding, which is used widely in industry as the first measure for corrosion control (i.e. choosing a metal that will not corrode easily by giving up its electrons). The electrochemical field has developed a list, which details the range of most metals relative tendency to be oxidized, called an electromotive series. The list provide nearly all the information required to determine which metals are most subjective to corrosion. The series tells us which species behaves best as the anode undergoing oxidation and the cathode undergoing reduction. The list begins with metals most easily oxidized; end with the metals least capable of oxidation, or with the greatest capability of reduction. In other words, the list begins with metals, which are most easily corrode (i.e. behave as anode in the corrosion reaction), and ends with metal, which can best behave as cathode in the corrosion reaction. The tendency of each metal to be oxidized is given in terms of 'the standard electrode potential' or 'oxidization potential' and is expressed in volts, which is measured relative to the standard oxidation of hydrogen gas, which is assigned as an arbitrary potential of (0 volts). Table 2.1 below provides an electromotive series as a list of major industrial metals. As you can see from the list, metals such as magnesium, zinc and iron will oxidize easier and therefore corrode easier than platinum or gold. This list should provide the sufficient background needed to predict which metal during the experiment should corrode more easily. Furthermore, the electromotive series has a large influence on a particular type of corrosion, known as galvanic corrosion. Table 1 below shows electromotive potential series.

Table 1 Electromotive Potential Series

Element	Reaction	Electrode Potential
Gold	$Au^+ + e^- = Au$	1.692
Platinum	$Pt^{2+} + e^- = Pt$	1.18



Silver	$\text{Ag}^+ + \text{e}^- = \text{Ag}$	0.7996
Copper	$\text{Cu}^+ + \text{e}^- = \text{Cu}$	0.521
Copper	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	0.3419
Hydrogen (Acid)	$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0
Iron	$\text{Fe}^{3+} + 3\text{e}^- = \text{Fe}$	-0.037
Lead	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	-0.1262
Tin	$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	-0.1375
Iron	$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	-0.447
Chromium	$\text{Cr}^{2+} + 2\text{e}^- = \text{Cr}$	-0.913
Titanium	$\text{Ti}^{2+} + 2\text{e}^- = \text{Ti}$	-1.63
Aluminum	$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	-1.662
Magnesium	$\text{Mg}^+ + \text{e}^- = \text{Mg}$	-2.7
Sodium	$\text{Na}^+ + \text{e}^- = \text{Na}$	-2.71
Calcium	$\text{Ca}^{2+} + 2\text{e}^- = \text{Ca}$	-2.868
Potassium	$\text{K}^+ + \text{e}^- = \text{K}$	-2.931
Lithium	$\text{Li}^{3+} + \text{e}^- = \text{Li}$	-3.0401
Calcium	$\text{Ca}^+ + \text{e}^- = \text{Ca}$	-3.8

The electromotive series serve as a corrosion map for metals in particular concentrations of their own salts. It fails in

describing the behavior of such metals in various corrosive environment based on varying temperature, humidity, salinity, etc. Therefore, a more general table developed by electrochemists, called galvanic series is used in practical application, (Efrid & Lee, 1997).

Common structural metals are obtained from their ores or naturally occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.

Virtually all corrosion reactions are electrochemical in nature. At anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current". Since the corrosion current must also flow through the electrolyte by ionic conduction, the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

B. Types of Corrosion

There are several forms of corrosion that can occur. Each form of oxidization has specific arrangement of anodes and cathodes and the corrosion, which occurs, has specific location and pattern. Each form of corrosion can be effectively controlled during design if it is anticipated. By understanding the various forms of corrosion, the conditions under which they occur, and how they are quantified, then they can be addressed and controlled. The most common types of corrosion are: (Khayal, O.M.E.S., 1993).

B.1 Uniform Corrosion

Uniform corrosion results from the sites, is not necessarily fixed in location, and is distributed over a metal surface where the anode and cathode reactions happen. Uniform corrosion damage, something called wastage (wear), is usually manifested in the progressive thinning of a metal

part until it virtually dissolves away (melts). (Khayal, O.M.E.S., 1993).

B.2 Pitting (Hole) Corrosion

The initiation of a pit (hole/cavity) occurs when electrochemical or chemical breakdown exposes a small local site or a metal surface to damaging species such as chloride ions. The sites where pits (dents) initiate are not completely understood, but possibly could be found at scratches, surface composing heterogeneous inclusions, or place where environmental variations exist. The pit grows if the high current density and the area of breakdown initiation are exceedingly small. If the rate of repassivation is not sufficient to choke off (block) the pit growth, two new conditions develop. First, the metal iron produced by the breakdown process are precipitated as solid corrosion products (such as $\text{Fe}(\text{OH})_2$) which usually cover the mouth of the pit. This covering traps the solution in the pit and allows the building of positive hydrogen ions through a hydrolysis reaction. Then, chloride or another damaging negative iron diffuses into the pit to maintain charge neutrality. Consequently, the repassivation becomes considerably difficult because the solution in the pit is highly acidic, contains a large concentration of damaging ions and metallic iron, and contains a low oxygen concentration. Thereby, the rate of pit growth accelerates.

The pit is the anode of an electrochemical corrosion cell, and the cathode of the cell is the non-pitted surface. Since the surface area of the pit is a very small fraction of the cathodic surface area, all of the anode corrosion current flows to the extremely small surface area of the breakdown initiation site. Thus, the anodic current density becomes very high and pitting can be rapid. (Khayal, O.M.E.S.).

B.3 Crevice (Crack) Corrosion

Crevice corrosion results when a portion of a metal surface is shielded in such a way that the shielded portion has limited access to the surrounding environment. Such surrounding environments contain damaging corrosion species, usually chloride ions. A typical example of crevice corrosion is the crevice formed at the area between two metal surfaces in close contact with a gasket and another metal surface. The environment that eventually forms in the crevice are similar to that formed under the precipitated corrosion product that covers a pit. Similarly, an electrochemical corrosion cell is formed from the couple between the unshielded surface and the crevice interior exposed to an environment with a lower oxygen concentration compared with the surrounding medium. The combination of being the anode of corrosion cell and existing in an acidic, high chloride environment where repassivation is difficult to make the crevice interior to corrosive attack. Figure 1 shows the chemical mechanism of crevice corrosion.

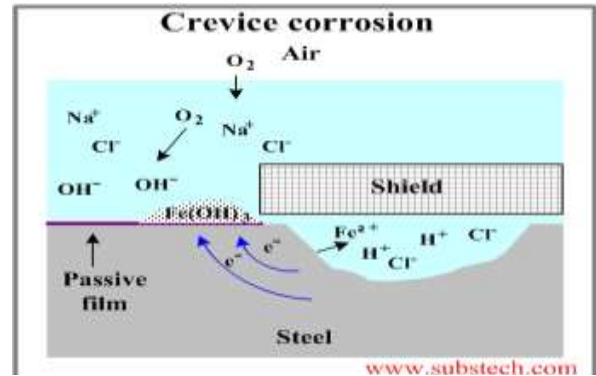


Figure 1 Crevice Corrosion

B.4 Galvanic and Thermo Galvanic Corrosion

Two metals having different potentials in a conducting electrolyte result in the more anodic metal usually being attacked by galvanic corrosion. Because of electrical contact between the two different metals, galvanic corrosion differs from the other forms of corrosion described previously in that anode and cathode sites of the corrosion cell reside (stay) separately on the two coupled different metals comprising the corrosive cell, while for the other forms of corrosion, the cathodes and anodes exist on the surface of the same metal.

The value for the difference in potential between two dissimilar metals is usually obtained from a listing of the standard equilibrium potentials for the various metals.

Another factor besides the coupling of two different metals that can lead to galvanic corrosion is a difference in temperature at separate sites on the same metal surface. Such a situation leads to thermo galvanic corrosion. This type of corrosion can be found in heat exchanger systems where temperature differences are common. (Khayal, O.M.E.S., 2018).

B.5 Selective Leaching (leak)

This kind of corrosion occurs when the components of an alloy are removed selectively by corrosion because of differences in potential between different constituents of an alloy i.e. a situation analogous to that of the galvanic corrosion of couple dissimilar metals. This results in an increase in the concentration of the remaining components and selective leaching occurs. This type of corrosion is also called parting. The most common example is selective leaching out of 'zinc' from 'brass' (dezincification).

B.6 Erosion Corrosion

Erosion corrosion is caused by the disruption of protective passive films by erosive (wearing) or abrasive (scratch) processes. Once the protective or passive film is removed in an aqueous electrolyte, the electrochemical processes for the types of corrosion described above take place.

B.7 Stress Corrosion Cracking, Hydrogen Damage and Corrosion Fatigue

Stress corrosion cracking (SCC) is a form of localized corrosion, which produces cracks in metals by the simultaneous action of a corroding and tensile stress. The electrochemical cell between the exterior and the interior environment of a crack is similar to that described above in section (2.6.3) for a crevice. Because of the necessity for the application of the stress, the breakdown of the passive layer on a metal service surface in SCC is generally attributed to mechanical causes but many suggest that electrochemistry is significant factor because it controls the rate of repair of the passive layer cracked by mechanical stress.

Corrosive fatigue has a somewhat similar mode of failure to SCC. It mainly differs from SCC in that it involves situation where the stress is applied cyclically rather than as a static sustained tensile stress. With both corrosion fatigue and SCC, the issues of film mechanical breakdown, repassivation, and adsorption of damaging species, hydrogen embrittlement and electrochemical dissolution are to greater or lesser extents involved in determining weakness. (Khayal, O.M.E.S., 1993).

B.8 Inter - granular Corrosion

Figure 2 below shows the different types of corrosion that is found in metallic structures. With the exception of metallic glasses, the metals used in practical devices are made up of small crystals (grains) whose surface join the surfaces of other grains to form grains boundaries. Such boundaries or the small regions neighboring to these boundaries can under certain conditions be considerably more reactive (by being more anodic) than the interior of the grains. The resulting corrosion is called inter - granular corrosion. It can result in a loss of strength of metal part or the production of debris (grains that have fallen out). (Khayal, O.M.E.S., 1993).

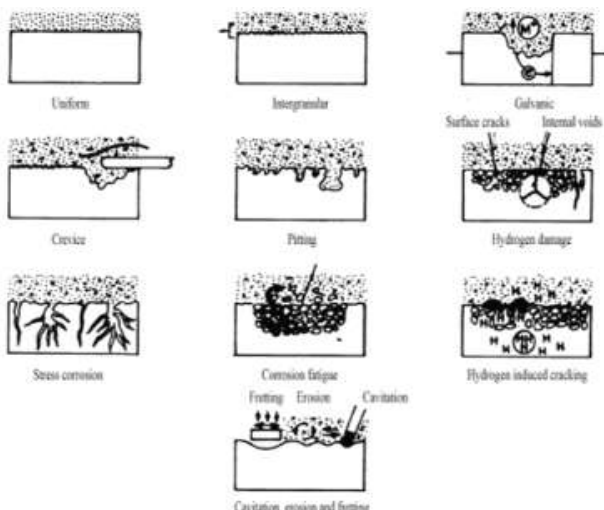


Figure 2 Types of Corrosion

C. Corrosion Control Methods

In marine technology, the application of organic coating is an old method used to stop corrosion but this method has a limited time then the hull starts to corrode again. However, by selecting a suitable coating the ship hull could be protected for the lifetime span of the ship. Barrier (coating), cathodic (electrochemical) and inhibitive (oxygen deprivation) are the main three methods of controlling the corrosion. (Khayal, O.M.E.S., 1993) and (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

C.1 Water-Resistant Coatings

The most commonly used method of preventing corrosion is to place a water resistant barrier between the sheet metal and the electrolyte (sea water). The type of anti-corrosive coating required is dependent on two main factors: the type of antifouling to be used and the location of application on the ship. Obviously, the antifouling and the anti-corrosive must be compatible, there must be good adhesion between them and also no reaction to impair the properties of either coating. Different areas of the ship require specific anti-corrosives; for example, around the steering gear, the hull and the splash zone where the environmental situations are very different.

Although it is not ideal, in practice only one anticorrosive coating is used and this is based either on a chlorinated rubber resin or a pitch base, the system being chosen to be compatible with the antifouling to be used.

Inevitably the coatings will not be continuous and pinhole free, and in service are likely to be damaged. There are also areas of the ship, such as steering gear, propulsion units and anchorage points which cannot be permanently coated, consequently other techniques to combat corrosion have been developed.

C.2 Cathodic Protections

Cathodic protection is an established corrosion control method for protection of underground and undersea metallic structures, such as ships' hull, oil and gas pipelines, cables, utility lines and structural foundations. Cathodic protection is generally useful in the protection of ships' hull platforms, dockyards, jetties, submarines, condenser tubes in heat exchangers, bridges and decks, civil and military aircraft and ground transportation systems. The designing of cathodic protection systems is rather complex. However, it is based on simple electrochemical principles. Corrosion current flows between anodes and cathodes due to the existence of a potential difference between the two elements. (Khayal, O.M.E.S., 2018).

As can be seen in Figure 3 below which shows cathodic protection, electrons released in an anodic reaction are consumed in the cathodic reaction. If we supply additional electrons to a metallic structure, more electrons would be available for a cathodic reaction, which would cause the rate

of cathodic reaction to increase and that of anodic reaction to decrease. This action would finally minimize or eliminate corrosion. This is the purpose of cathodic protection. The additional electrons are supplied by direct electric current. If enough direct current is applied, the potential difference between the anode and cathode is eliminated and corrosion would finally stop.

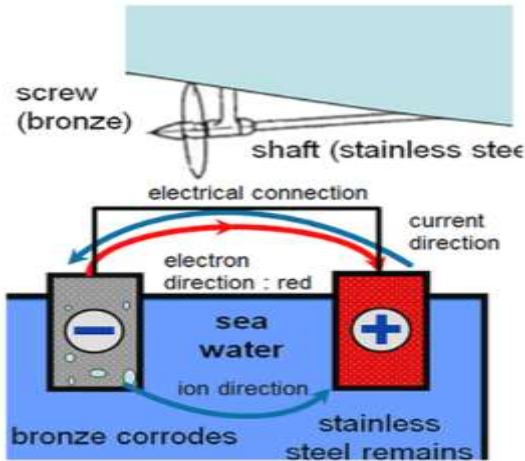


Figure 3 Cathodic Protection

Figure 4 and Figure 5 below demonstrate how cathodic protection works in terms of E-pH diagram. Cathodic protection brings down the potential of a metal that has a free corrosion potential at the active potential and pH to a lower potential that is defined as an “immune” area.

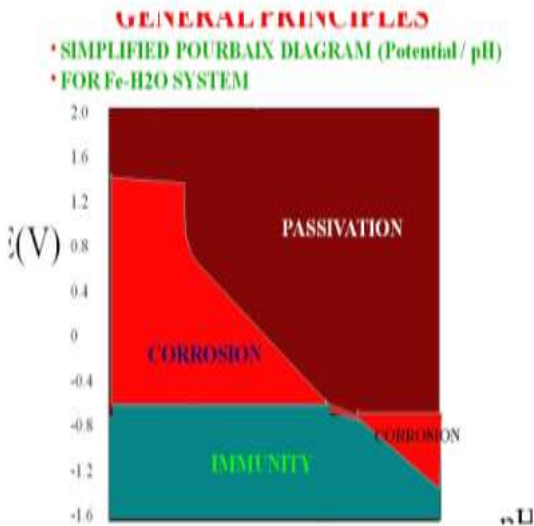


Figure 4 pH Diagram

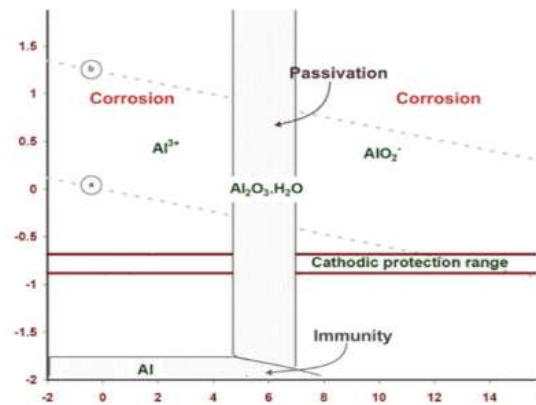


Figure 5 Potential / pH Diagram

C.2.1 The Principles of Cathodic Protection

The main principle of cathodic protection is reducing the potential of the metal surface to a protective potential E where $E < E_{corr}$. In elaborating cathodic protection in terms of polarization diagram, the figure below could be used. Figure 6 below attempts to explain cathodic protection by schematic polarization diagram showing corrosion point ‘C’ and protective point ‘P’ for iron (assuming that oxygen reduction occurs and no other oxidizing agents are present).

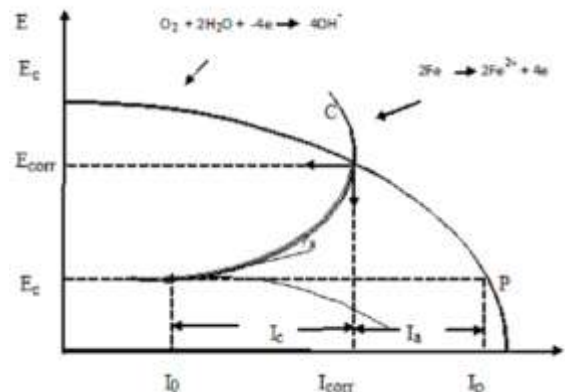


Figure 6 Cathodic Protection Polarization Diagram

From Figure 6 above, if the applied potential E , and the applied current I are more than E_a and I_a respectively, metal dissolution is possible along the curve $E_a - C$. External supply of electron must be provided to the system to reduce metal dissolution if the applied potential and current are between E_a and E_{corr} and I_a and I_{corr} respectively. Ideal cathodic protection is achieved if applied potential is the open circuit potential of the metal ($E \leq E_a$) and the applied current is purely cathodic ($I \leq I_p$). If applied potential is less than E_{at} the metal is also protected at a higher current, but hydrogen evolution is possible leading to coating defects or hydrogen embrittlement. The principle above is applied in the real world mainly by two methods. One method involves

current supplied to protected metal using a sacrificial metal that is galvanic ally more active than the protected metal, which is termed “sacrificial anode”. The other method involves supply from an external DC current source termed “impressed current” method (Perez. N., 2004).

C.2.2 Cathodic Protection by Sacrificial Anode

In cathodic protection, the structure to be protected must be given a cathodic current flow so that it operates as a cathode. The requirement for an external DC current to achieve this can be eliminated by using an anode constructed of a metal that is more active in the galvanic series than the metal to be protected called a sacrificial anode. A galvanic cell is established with the current direction as required.

One example of sacrificial anode material is magnesium or magnesium-based alloys. Magnesium is more active than steel, has a greater tendency to ionize. The open-circuit potential difference between magnesium and steel is about 1 volt. This means that one anode can protect only a limited length of pipeline or over a defined surface area. This low voltage can have an advantage over higher impressed voltages in that the danger of overprotection to some portions of the structure is less and because the total current per anode is limited; the danger of stray-current damage to adjoining metal structures is reduced. Magnesium rods have also been used in steel hot water tanks to increase their service life. The greatest degree of protection is in more conductive electrolyte such as hard waters, compared to soft waters which have lower conductivity. Figure 7 shows sacrificial anode cathodic protection (SACP).

Cathodic Protection
Steel protected by a Sacrificial anode

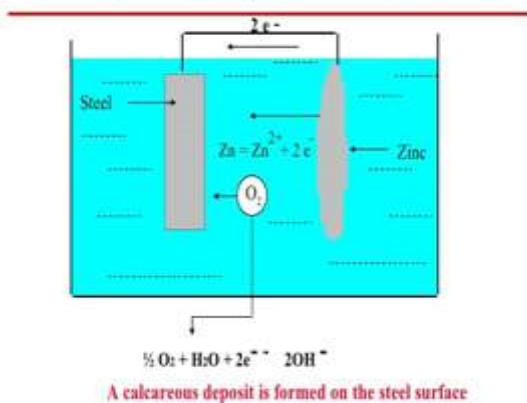


Figure 7 Sacrificial Anode Cathodic Protection (SACP)

Zinc and Aluminium have been used extensively in seawater applications. Sacrificial anodes for offshore structures in seawater are commonly made of special Aluminium alloys because these anodes are low in cost and provide the highest current output per anode weight. Zinc

anodes are used on coated and buried pipelines offshore, where the risk for passivation of Aluminium anodes is higher due to a lower current density requirement. Zinc and Aluminium sacrificial anodes used on ship hulls are usually combined with a paint system. The anodes are placed close to each other on the area around the propeller because the current could leak to the propeller, and the current demand is high due to turbulence around this area. Ballast tanks on tankers and bulk carriers also use Zinc and Aluminium anodes (Bardal, 2004). The energy content and efficiency of these metals are shown in Table 2 below. Table 2 shows the efficiencies of several common anode materials.

Each of the anodes have their own limitations. Zinc is more economical to use than magnesium, but because of the relatively small cell voltage it produces, it is primarily useful to protect ships in seawater or to prevent corrosion in systems that require only small currents. Although magnesium is more expensive and consumed faster than zinc or Aluminium, it provides the largest potential and current. Aluminium cannot be used in environments with pH more than 8, since alkaline conditions will make Aluminium self-corrodes rapidly.

Table 2 Efficiencies of Several Common Anode Materials

Energy Content	Anode material		
	Magnesium	Zinc	Aluminium
Theoretical Energy content, ampere-hour per kilogram of mass (Ah/kg)	2205	816	2965
Typical Anode % , Efficiency	50	90	60
Practical Energy content = Theoretical energy x Anode efficiency (Ah/kg)	1102	734	1779

C.2.3 Cathodic Protection by Impressed Current (ICCP)

This system uses external source of electricity. High voltage from the external source is converted to low voltage DC current by means of a transformer-rectifier. This direct current is impressed between buried anodes and the structure to be protected. Use of inert anode is preferred, as this will last for the longest possible time. Typical anodes used are graphite, titanium, silicon and niobium plated with platinum. The applied current is limited by electrolyte resistivity and by the anodic and cathodic polarization. Impressed current system makes it possible to apply the potential level that is necessary to obtain the current density required by means of the rectifier, whatever the value of the potential is. Electric current flows in the soil from the buried anode to the underground structure to be protected. Therefore, the anode is connected to the positive terminal of the rectifier and the protected structure to the negative terminal. All cables from the rectifier to the anode and to the structure are electrically insulated. If not insulated, wires from the rectifier to the anode can act as an anode and

deteriorate rapidly, while cables from the rectifier to the structure may pick up some of the electric current, which would then be lost for protection (Durham & Durham, 2005). Figure 8 shows impressed current cathodic protection.

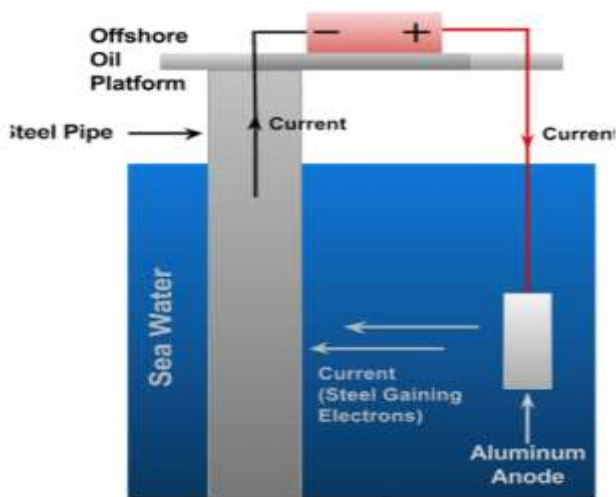


Figure 8- Impressed Current Cathodic Protection

C.2.4 Impressed Current Method Requirements

Metal to be protected and the environment it is exposed to determine the current density required for complete protection. The applied current density must always be larger than the current density equivalent to the measured corrosion rate under the same conditions. Therefore, as the corrosion rate increases, the impressed current density must be increased to provide protection. Three factors affect current requirements: 1. the nature of the electrolyte, 2. resistivity of the electrolyte, 3. the degree of aeration.

The current requirement increases with increasing acidity of the electrolyte. For example, surroundings with high resistance have a lower cathodic current needed to provide protection. The required current to provide cathodic protection can vary from 5 to 220 mA/m² of bare surface. Application of impressed current technique in the real world requires field testing to determine the necessary current density to provide cathodic protection in a specific area. The testing techniques are only some way to obtain approximations. After installation of the system, it is necessary to conduct a potential survey and make the necessary adjustments to provide the desired degree of protection (Zakoski, K and Darowicki, 2004).

C.2.5 Anode Materials & Surrounding for Impressed Current System

The determination of anode materials and the surrounding (atmosphere) material used in impressed current systems in different environments and applications play a major role, because these anodes are the mean through which the

protective current is delivered to the protected structure or metal. The type of anode is vital in influencing the reactions on the anode surface. For consumable metals such as scrap steel or cast iron, the main reaction is the anodic metal dissolution. Metal dissolution is negligible if the anode has passive surfaces and the main reactions are gas evolutions. For example, oxygen is evolved in the presence of water, and chlorine gas is evolved if the electrolyte contains chloride ions. The gas evolution reactions also happen on non-metallic conducting anodes surfaces such as graphite. On partially passive surfaces, both the metal dissolution and gas evolution reactions could happen. Corrosion product buildup is associated with the metal dissolution reaction.

A wide range of materials can be used for impressed current anodes. The balance between anode performance and costs play a big role in determining the right anode material to be used (Shrier .L.L & Hayfield, 1986).

The properties of atmosphere that hold the impressed current anodes are also important. To increase the effective anode size and lower the resistance of soil, carbonaceous material such as coke breeze and graphite are used. This type of atmosphere also reduces consumption of the anode material because the anodic reaction is transferred from the anode to the holder atmosphere. Three factors are considered to ensure low resistivity of the surroundings material: 1. Composition, 2. Particle size, and 3. Degree of compaction.

The particle size and degree of compaction also influence how anode-generated gases escape. Since it is quite problematic to properly establish the above surrounding properties properly in the ground, ready-made anodes and atmosphere inside metal containers that are factory-prepared according to the best of the above factors are used. These metal containers will be eventually consumed under operational conditions. A set of parallel cylindrical anode rods placed vertically deep underground are commonly used in the industry (termed vertical deep anode). These provide minimized anode bed resistance and induced stray currents, smaller right-of-way surface area, and improved current distribution. However, vertical deep anodes also incur higher capital expenditure per unit of current output, are difficult to repair in case of any anode damage, and may block gas generated at the anode from escaping (PETRONAS, 1987).

D. Bio Fouling

Bio fouling is associated to bio-corrosion of surfaces, reducing the lifetime of the structures under a marine environment, which is also promoted by the corrosive effect of seawater itself. Microbiological fouling should be strictly controlled since it can create Microbial Induced Corrosion (MIC). For example, Sulphur-reducing Bacteria (SRB) come from the marine sediment and gain energy using electrons from the steel structures, chemically reducing the sulphates from the sea water to sulphides, causing the pitting

corrosion of steel surfaces (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021). Additionally, bio-fouling also contributes to the emigration of certain marine species to other areas, as occurred in Ponta Delgada, Island, and Portugal, where alien species of fouling organisms such as barnacles were found. Amphibalanus Amphitrite was one of the species of barnacles detected and it is assumed that it is originated from the Indo-Pacific Ocean. Therefore, it is presumed that due to the fouling propensity of the reported species and given their origin, this reallocation was caused by the increasing boat traffic in the last years. Figure 9 below shows fouling and bio corrosion on the hull of a ship.



Figure 9 Fouling and Bio Corrosion on the Hull of a Ship

E. Types of Bio-Fouling

The bio-fouling organisms are classified into two different groups. The groups are 'Plant Bio-fouling' and 'Animal Bio-fouling'. The following section elaborates the species of biofouling (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

E.1 Plant Fouling

There are three types of plant fouling species as discussed in the following subsections: Figure 10 below shows plant fouling.



Figure 10 Plant Fouling

E.1.1 Bacteria and Bacterial Slimes

The bacteria, which cause bacterial slimes, are present in the sea water all the year round; they present a major fouling problem as settlement occurs within minutes of immersion. The slime is generated after the settlement of the bacteria by secretion of mucus, the species of bacteria being classified by this mucus. Once attached, these bacteria begin to reproduce by cell division, the daughters not normally being released into the sea water but being held in the parents 'mucilage thus very quickly the slime thickness and the fouled area increases. The slime thickness can vary from a few microns to several millimeters depending on the conditions, and this thickness directly affects the hull surface roughness and reduce the ship power due to the drag caused by these bacterial slimes. However, these bacterial slimes are important because they can influence the rate at which toxins are released from an antifouling coating by forming a diffusion barrier on the surface. But the slime can also trap spores and larvae of other fouling organisms thus promoting macro fouling and worsen the roughness of hull surfaces.

E.1.2 Diatoms

Diatoms are microscopic plants with a characteristic brown color, they are similar to bacteria in size and again secrete mucus through their external siliceous shell although this is less slippery than that produced by the bacteria to those listed above, and it also affects the hull surface and causes drag that reduce ship performance.

E.1.3 Seaweeds

Diatoms cause similar problems. These are algae and three main classes are found; namely, green, brown, and red seaweeds.

The commonest species of green seaweed is enteromorpha (sea grass) and this is found near the waterline forming a carpet up to 10 centimeters thick and extending to a depth of several meters on the hull. Its success as a fouling organism stems from its ability to tolerate a wide spectrum of toxins and also its worldwide distribution. This marine algae exists as long 'grass like' filaments which contain up to five million cells in an average from 7 – 8 centimeters long, each cell being capable of producing eight zoospores (reproductive spores). These spores leave the parent cell as free-swimming zoospores directed by four flagellae, they settle preferentially in surface irregularities. When the zoospore makes contact with the surface the flagellae act as brushes and clean the point of settlement, a cement is released and within seconds the organism is firmly bound to the surface. It is at this stage that it is most vulnerable to toxins as it is surrounded by only a thin membrane, but within four hours a protective wall is formed and the zoospores begin to develop into the mature algae, after a few days it is already a few millimeters long and a centimeter or more within two weeks.

The most common brown seaweed is *Ectocarpus* which reproduces in a similar fashion to enteromorpha and again has worldwide distribution. The plant is composed of two parts, the rhizoidal, a root-like part and an upright part supporting the spore bearing structure, this being branched and limp. Each plant is capable of producing 40 x 10 spores and each of these spores have two flagellae. They swim in the sea until a suitable settlement site is found (usually in surface defects) where they attach themselves and begin to develop a protective wall, this occurring at a slower rate than with enteromorpha; usually taking 24 hours, after which time growth of the new plant will have started. These seaweeds are found lower down on the hull than enteromorpha.

The commonest red seaweeds found are ceromium and polysiphonia, their reproduction and settlement behavior is similar to that described above but these seaweeds are highly branched and much larger than either of the other two species; they are found much lower down on the hull where the light intensity is very low. It has been shown that these fouling organisms, like the other seaweeds are most vulnerable to toxins during their settlement period; the resistance of the mature seaweeds to toxins is considerably higher than that of animal fouling organisms.

E.2 Animal Fouling

The second type of bio fouling is 'Animal Fouling' which is sorted into seven groups: Figure 11 below shows animal fouling.



Figure 11 Animal Fouling

E.2.1 Arthropods

This is a class of the animal kingdom that includes all organisms with chitinous external skeleton and joined appendages, many of these have a skeleton, which is hardened by calcareous deposits.

The barnacle (cirripedia), of which there are many different types, is the most common arthropod to be found on a ship's hull. It is a hermaphrodite, but sexual reproduction is

preferred, a sexual reproduction occurring only under adverse conditions. The eggs are produced in the parent shell, when the conditions are correct the nauplii (free swimming) larvae are liberated, and depending on the species they metamorphose up to eight times, the final transformation producing the cypris (settling) larvae. The cypris larvae either swim or crawl around until they find a suitable area in which to settle, this is often a site, which has previously been inhabited by a barnacle community. Mature barnacles secrete a protein, arthropodine, and it is this, which acts as a reference for renewed settlement.

The settling stage is the most vulnerable period for the young barnacles, the toxins in conventional anti-fouling coatings effectively kill the majority at this stage, and hence on recently painted ships there is no serious fouling problem due to barnacles. If they do survive and grow to their adult form not only do they cause increased surface resistance but also their shells tend to cut through the underlying coatings causing a corrosion problem.

A particularly difficult type of barnacle fouling is that produced by the goose barnacle: its settlement and growth occurring rapidly and vigorously even in the open sea.

There are many other arthropods found in the sea, these include isopods, amphipods, crabs, shrimps and insects, but these only foul static structures and therefore do not present a fouling problem on seagoing vessels.

E.2.2 Tubeworms (Annelids)

The coral effect on fouled underwater surfaces results from the activity of tubeworms. Reproduction can be either sexual which results in free swimming larvae and thus a new area of infestation, or asexual when the parent acts as host to the new larvae which eventually bore holes through the calcareous shell of the parent and grow as new entities although still attached to the parent. This process produces a random frosted effect on the surface. As the creature grows, the shell is extended; this continues until the death of the animal, by which time there may be a large hard calcareous growth, which remains attached to the surface, and this can only be removed by abrasive treatments such as grit blasting. The presence of tube worms can be used as a good indication of the state of exhaustion of the matrix toxins in antifouling paints as they are normally vulnerable to toxins.

E.2.3 Mussels (Pelecypods)

The mussel is one of the few shellfish, which foul vessels since generally shellfish are very susceptible to toxins not only during settling but also in the adult organism. This is due to their method of feeding and also the susceptibility of the settling larvae to toxins. Many mussels reproduce sexually although some species are reproduced asexually, the resulting fertilized eggs being either held within the parent which releases free swimming larvae or the eggs are liberated into the water and hatch to produce the free swimming larvae. These larvae initially settle by means of



a foot followed by the formation of a byssus (a web like system of roots) which firmly secures the adult. Again the shell remains attached to the surface after the death of the organism and is difficult to remove.

E.2.4 Bryozoa

These may be divided into three main groups depending on their pattern of growth. Encrusting Bryozoa grow over the substrate to produce a network of shell growth similar to tubeworms. Erect Bryozoa grow outwards from the substrate, and Stolunate Bryozoa have an intermediate pattern of growth. Reproduction is again sexual or asexual, the fertilized eggs being either retained by the parent or existing in the sea. Settlement occurs several hours after hatching, and then the adult develops. The most susceptible time for poisoning Bryozoa is during the settling period, after which time it is difficult to kill this species of fouling .

E.2.5 Sea Squirts

These produce free-swimming larvae, which become attached to a surface before metamorphosis can occur. The parent is a very lowly form of vertebrate existing as a sack through which water is filtered. They are not a common fouling organism on ships as, like mussels, they feed via filtration of water and so are very susceptible to toxins.

E.2.6 Hydroids

The free-swimming hydroid larvae, produced either sexually or asexually, cements itself to a hard surface and grows into the adult. The adult is very firmly attached to the surface and resembles seaweed; it is quite resistant to toxins unlike the young free-swimming hydroid ,which is easily poisoned.

E.2.7 are single cell animals, which range in size from 0.002 mm to several centimeters. Their small size and their inability to form large colonies render them unimportant as fouling organisms. They do however provide, like the micro fouling organisms in the plant kingdom, sites for settlement of other fouling organisms.

Generally, plants are more resistant to toxins than animals because their method of feeding involves the absorption of nutrients by osmosis, which prevents the ingestion of the toxin whereas animals take in food and toxins directly and are therefore more easily killed. The resistance of fouling organisms to commonly used toxins is shown in Table 3 below.

Table 3 Resistance of Fouling Organisms towards Toxins

No	Resistance	Organism
1	Very High	Bacteria and Diatoms

2	Very High	Ectocarpus, Enteromorpha, Hydroids, Barnacles and Polyzoans
3	Moderate	and Barnacles Tubeworms, Hydroid
4	Low	Weeds (Green & Red), Sea Squirts, Mussels and Oysters Sea Squirts and

F. Bio-Fouling Mechanism

There are some factors affecting the settlement of fouling organisms; the more important factors being the geographical location, the season, the movement of the water relative to the surface, the texture of the surface, the intensity of illumination and the presence of slime films.

The geographical and seasonal influence are of major importance as the reproduction of the fouling organism is governed by the water temperature consequently, in some areas of the world's oceans no fouling may occur during the winter. The longer the summer season the greater the fouling, as the reproduction of fouling organisms is far more prolific during the warmer season. Wherever there is a warm water current, excessive fouling can be expected, as is found in the Gulf Stream. One of the implications of the geographical and seasonal factors is that it may be necessary to have several different types of anti-fouling paint that are suitable for the different areas in which ships operate (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

The first step in fouling is settlement and this cannot occur when the ship is moving above 13 km, thus a stationary ship is an ideal site for fouling. The majority of fouling occurs when the ship is in harbor, as there is a higher water temperature, consequently a larger fouling population and the flow of water past the hull is usually very slow. Ships that spend a very short time in harbor are found to be relatively free from animal fouling although they have a large amount of plant fouling, this being due to the ease and rapidity of settlement of the latter.

The surface texture of the coating is important because imperfections in the surface provide sheltered environments where the fouling organisms can settle and be protected from the flow of water past the hull. The settlement of fouling on a moving ship is thought to be due to a combination of static flow patterns created on certain areas of the ship and also micro fouling organism's entrapping the settling larvae of macro fouling organisms in their mucilage, thus enabling the larvae to grow into the adult form.



The light intensity plays an important role in plant fouling, as this can only exist where there is sufficient light to allow photosynthesis to occur. Consequently, the seaweeds requiring most light (green) are found near the water line, whereas those requiring less light (brown and red) are found lower down on the hull. Animal fouling is independent of the light intensity although some animal fouling organisms settle preferentially near the water line.

G. Stages of Bio-Fouling

Bio fouling is characterized by four main stages throughout the time. The first stage initiates after the earliest minutes of immersion, where the physical adhesion of organic molecules of proteins, polysaccharides, glycoproteins and others, occur. In this stage, Van der Waal's forces and electrostatic interactions promote this adsorption phenomenon. The movement of water leads to the contact and colonization between the microorganism and the surface. This attachment leads to the second phase, after 24 hours of immersion, where the reversible adsorption of bacteria and unicellular algae occurs. Bacteria and other colonizing microorganisms secrete Extracellular Polymeric Substances (EPS) to enclose and hold the substrate, forming a microbial film. Consequently, the local surface chemistry is altered, being propitious to stimulate further growth and settlement of macro-organisms.

This microbial film feeds spores of microalgae, allowing their attachment, which will constitute a bio-film (1 week, third stage). The bio-film generated is a mass of microorganisms and the EPS secreted creates a gel matrix providing enzymatic interaction and high resistance to biocides. Also, the arrangement of the microorganisms in the biofilm protects them from the predators and from environmental variations, facilitating the obtainment of the nutrients necessary for the settlement of other microorganisms. This bio-film is capable of attracting more particles and organisms as larvae of marine macro-organisms, characterizing the fourth stage, after 2 or 3 weeks of immersion. The roughness of the surface created by the irregular microbial communities will also help the accommodation of the new attracted organisms. All of these conditions will contribute to the adhesion and attachment of macro algae and marine invertebrates.

H. Antifouling Coating Formulation and Methods

H.1 Coating System

The coating system on a ship is required to prevent corrosion and fouling, this being achieved by using an anticorrosive paint and an antifouling paint (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

H.1.1 Formulation of Anti Fouling Paints

There are two sets of criteria, which must be applied when formulating antifouling paints, one set applying to the toxin and the other to the paint film. With current conventional antifouling coatings, toxins are the most important ingredients, since they are the components, which prevent fouling. They function by controlled release of toxin from the paint matrix into the laminar sub layer thus in theory killing the fouling organism before settlement. The important characteristics of the toxins are:

They should have a low solubility in seawater, a wide spectrum of toxicity to marine fouling organisms; they should not create an ecological problem, and be compatible with the paint medium in which they are placed. Also, they should be of reasonably low price, and should not present an application problem.

Many toxins are patented each year most of which are of little use to the antifouling chemist as the above criteria are not satisfied. The main biocides which are used in commercially available anti-fouling today are: copper I oxide, copper I thiocyanate, zinc oxide, and triphenyl tin fluoride, often a combination of these being used to broaden the range of toxicity of the coating.

The role of the paint film is that it must be able to release the toxin at a rate, which allows the prevention of fouling, while retaining its structural integrity so that its ability to adhere to the hull and withstand mechanical stresses is not reduced.

The paint formulation is dependent on the toxin and the mode of release of the toxin. The compounds used in a successful paint formulation have generally been selected based on a trial and error approach as there is at present no satisfactory method by which the antifouling nature of the paint can be predicted.

The ultimate test for an antifouling is to paint a ship's hull but prior to these cheaper and less expensive tests are conducted. Test panels coated with the new antifouling are immersed in seawater, usually under a raft in an estuary, the flow of water past these panels simulating the ship's passage through water. This tests the ability of the coating system to prevent fouling and gives a guide to its active life and to the integrity of the film after prolonged exposure. If a new coating system appears to be promising, the next stage in testing is to attach coated bilge keel panels to a ship in-service, the last stage before full-scale ship trials are test patches (50-100m) painted on various ships. The expense involved in each of the test methods increases. Therefore, it is essential that only antifouling which are virtually certain to prove adequate are applied as test patches. The development of a new antifouling can take up to six or seven years due to the lengthy testing periods required.

The leaching of toxins from an antifouling coating can be determined very easily in the laboratory as can the lethal dose to the fouling organism, although it is impossible to apply this data to the real situation; generally a much higher



leaching rate is required in practice than would be predicted on the basis of laboratory estimates. This illustrates that the factors, which influence leaching rates, form a complex matrix of interacting physical and chemical parameters impossible to quantify.

I. Antifouling Methods

The advice to protect the ship hulls from marine bio fouling, to avoid material damages and excessive fuel consumption, has led to an intensive research for economical and environmentally friendly solutions. Therefore, "traditional" and "modern" antifouling methods are elaborated in the following subsections (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

I.1 Traditional Antifouling Methods

Marine bio fouling has been an annoyance for more than 2000 years. At that time due to the lack of advanced technology and in order to overcome this problem, natural products were used to resist corrosion and biofouling.

For example, Phoenicians and Carthaginians were said to have used pitch and possibly copper sheathing on ship hulls, whereas other ancient cultures used wax, tar and asphalt. The use of coatings made with arsenic and sulphur mixed with oil were also used to resist shipworms, in the past.

A brief description of the ancient (old) antifouling methods is presented below:

I.1.1 Lead Sheathing

As mentioned above, pitch, copper sheathing, wax, tar, asphalt or a mixture of arsenic and sulphur with oil, were applied to protect ship hulls. Alternatively, lead sheathing was also used for this purpose.

Lead sheathing consisted of covering the ship hulls with lead patches in order to protect them from biofouling and corrosion. Ancient cultures such as Phoenicians employed this prevention method in 700 B.C., while the Greeks were reported to use lead sheathing and tar and wax, in the third century B.C. Greeks and Romans also used copper nails to secure the sheathing.

In the period between 45 and 125 A.D., Plutarch mentioned the method of scraping the ship's sides to remove weeds, slime and filth, in order to facilitate the motion of the ship on the water.

Later, in 10 A.D, Vikings occasionally used seal tar. From the 13th to 15th century, the use of pitch was abundant, being sometimes mixed with oil, resin or tallow.

In the 16th century, lead sheathing was largely adopted, being employed by Spain, France and England, although wood sheathing was more usual.

However, the British Admiralty discarded the use of lead sheathing, in 1682, due to the corrosion caused on the iron components of the ships. Subsequently, lead sheathing was then alternated with wood sheathing. After applying the latter, it was painted with several mixtures such as tar,

grease, pitch and brimstone and then nailed with large headed copper or iron nails very adjacently, in order to form a metallic sheathing.

I.1.2 Copper Sheathing

The first reference regarding to the underwater use of copper was in 1618, during the reign of the Danish King Christian IV, who used a coppered keel.

However, the first reference regarding the use of copper as an antifouling agent was patented by William Beale, who used a mixture of cement, powdered iron and a copper compound (copper sulphates or copper arsenic ore).

The use of copper sheathing was firstly reported in 1758 on 'His Majesty's Ship' (HMS) Alarm frigate, whose success motivated other ships to use copper, mostly the British Navy, around 1780. The application of copper on wooden ships was so successful that England prohibited the exportation of this metal.

Only in the 19th century, Humphrey Davy showed that the fouling prevention was attained due to the dissolution of copper in the seawater.

Anyhow, the use of copper sheathing on iron ships (introduced late in the 18th century) was discontinued, due to the uncertainty of its antifouling action and corrosion effects on iron.

I.1.3 Other Sheathing Elements

Due to the introduction of iron ships and the abandonment of copper sheathings on this type of boats, more alternatives were tried, to obtain protection against bio fouling.

Sheathings of zinc, lead, nickel, arsenic, galvanized iron and alloys of antimony, zinc and tin and coppered wooden sheathings were the alternatives tested. Non-metallic alternatives such as soaking felt in tar or using cork, rubber and plain brown paper were often applied to separate the copper sheathing from the iron hull. Wooden sheathings were also tested on these ships, although without success, due to its high cost.

I.2 Modern Antifouling Methods: Protective Paints

Novel antifouling systems were developed to overcome the limitations of the ancient methods. These systems consisted of paints such as enamels, varnishes, primers, sealers and many others. A primer (anticorrosive) and a topcoat mainly compose the majority of antifouling coatings. The latter incorporates anti-foul ants to protect the hull from bio fouling.

I.2.1 Antifouling Paints

In the mid of 1800, different paints were created, by dispersing a toxicant in a polymeric base. These toxicants consisted of copper oxide, arsenic and mercury oxide, whereas the solvents used were turpentine oil, naphtha and benzene. Linseed oil, shellac varnish, tar and diverse types of resin were employed as binders.



Nevertheless, these paints required the application of a primer in order to protect the steel hull from the pigments used, since its direct utilization on the hull caused corrosion. In the meantime, more paints were launched, such as “hot plastic paints” consisting of copper sulphates in a metallic soap composition, shellac based paints (rust preventive) and “cold plastic paints” which used diverse synthetic resins or natural products either solely or in mixtures. The latter effectively decreased fouling and were easily applicable due to “airless” spraying, enabling dry docking periods of up to 18 months.

However, the antifouling industry changed after the Second World War, leading to the appearance of new synthetic petroleum based resins with improved mechanical characteristics. Also during this period, organo metallic paints were introduced and contained tin, arsenic, mercury and many others, which after several developments, led to tributyltin (TBT) based paints. The TBT based paints revealed remarkably efficient against bio fouling.

Additionally, more paints’ technologies were developed to overcome the environmental issues of organo metallic-based paints, and classified according to the chemical properties of the binder and by their water solubility: soluble matrix and insoluble matrix paints.

Soluble Matrix Antifouling Paints

Soluble matrix antifouling paints contain rosins and their derivatives as binders and toxic pigments (copper, iron, zinc oxides, arsenic and mercury). The toxic compounds can dissolve in seawater, forming a thin leached layer, which easily releases the toxic material as the seawater penetrates. The thickness of the leached layer decreases when the ship speed increases, which consequently leads to an exponential increase of the release rate. On the other hand, at static conditions, the settlement of organisms is accentuated and the insoluble salts can block the coating’s pores, which consequently decreases the release rate of the biocides. In addition, these paints are less mechanically resistant than the insoluble paints due to the brittleness of the resin and its instability to oxidation and as consequence, the life span of these paints is short (12 to 15 months). Nonetheless, they present the advantage of being easily applied on smooth bituminous-based primers.

Insoluble Matrix Antifouling Paints

Insoluble matrix antifouling paints have a polymeric matrix such as acrylic, vinyl or chlorinated rubber, which are insoluble in sea water. When the coating is immersed in sea water, the soluble toxic materials dissolve and consequently leave a multiporous layer known as leached layer, which enables the further penetration of the water and the release of more poisonous compounds. The advantage of this type of paint is the high mechanical resistance and stability to oxidation and photo degradation. Although the coatings are thick to increase the content of toxic material, at some stage,

the efficiency will decrease due to the gradual release of the toxic compounds. Consequently, the empty space left by the dissolved biocides will modify the roughness of the surface and capture pollutants from the sea water, which will restrain the water penetration and as a result decrease the release rate, leading to the reduction of the life span of this type of paint to 12 to 24 months.

Tributyltin Self-Polishing Copolymer Coatings

Since the insoluble and soluble matrix paints have some drawbacks, alternative coatings have been developed in order to improve these paints.

Milne and Hails patented the first tributyltin self-polishing copolymer (TBT-SPC) technology, in 1974, revolutionizing the entire shipping industry. Organic tin and its derivatives have been generally used as antifoulants due to their broad-spectrum characteristic. Tributyltin oxide (TBTO) and tributyltin fluoride (TBTF) were the organotin compounds used, also known as powerful fungicides, completely capable of inhibiting the growth of most fouling organisms at a very low concentration.

As known, every paint contains pigments to confer the desired color. Usually, metallic copper, copper thiocyanate and cuprous oxide are the dominant copper pigments used in antifouling paints. However, the copper ions as Cu^{2+} have a major role in antifouling, yet they can only target specific fouling organisms.

TBT-SPC paints were based on acrylic polymer (usually methyl methacrylate) with TBT groups tethered to the polymer backbone by an ester. When immersed in water, the soluble pigment particles such as zinc oxide (ZnO) or copper oxide (CuO) would begin to dissolve.

The water penetration was prevented by the hydrophobic nature of the polymer of TBT methacrylate and methyl methacrylate. Thus, the water could only fill in the pores created by the dissolution of the soluble pigment particles. Furthermore, the carboxyl-TBT bond is easily hydrolyzed in slightly alkaline environments as seawater (pH of 7.5 to 8.5), which slit the TBT portion from the copolymer and then released the biocides into the water. As the TBT portions were split, the partially reacted brittle polymer backbone became prone to be washed off by the moving sea water, exposing a fresh coating surface. The hydrolysis process provided a low hull roughness (about $100 \mu m$), which did not influence significantly the drag friction of the ship’s hull.

One of the advantages of this kind of coating was the control of the polishing rate by the manipulation of the polymer chemistry, being possible to balance the high effectiveness and a long life span in function of the ships’ operating conditions and sailing speed. Studies have proven that the release rate of TBT in the seawater is almost constant with the sailing speed, which confers a high antifouling performance even at static or low speed.



Additionally, TBT-SPC paints had high mechanical resistance, high stability to oxidation and short drying times. This type of paint was widely applied in the shipping industry due to its high efficiency and versatility.

Consequently, the extensive use of TBT introduced high levels of contamination in the environment and thus negatively affected the marine communities. TBT is extremely toxic to non-target organisms ranging from bacteria to fish and mammals, affecting their growth, development, reproduction and survival. For example, before the 1980's, populations of gastropods were ceased due to the presence of TBT compounds in the seawater. This disappearance is explained by the fact that TBT causes a hormonal imbalance, which leads to the development of male sex organs on female gastropods, which hinders the breeding of gastropods.

In 2001, IMO (International Maritime Organization) (IMO) banned the use of TBT in the manufacturing of paints from 1st January 2003 and the presence of these paints on ship hulls from 1st January 2008. However, this ban did not apply to copper, since it is an essential element needed for the growth of all plants and animals, besides being naturally present in the seawater. It is also lipophilic and thus less bio accumulative. Nevertheless, copper-based paints may end up facing the similar regulations as TBT. For instance, Sweden, Denmark and USA are planning to strengthen the legislations regarding the use of copper-based antifouling paints, since the excessive boat traffic can lead to the contamination of the marine environment.

I.2.2 Environmentally Friendly Antifouling Paints

Due to the ban of the most efficient and versatile TBT-SPC paints, the paint producers felt the urge to develop new and less environmentally harmful paints. Therefore, Tin-free SPC technology was developed and commercially introduced.

The tin-free coatings can be divided into three categories: tin-free controlled depletion paints (tin-free CDPs), tin-free self-polishing copolymers (tin-free SPCs) and hybrid paints (conjugation between the CDPs and SPCs).

Despite the fact that these paints are free of TBT, their mechanism consists of biocide release, whose action has not always been fully explained. Considering this, the development of fully biocide-free antifouling paints is still in course.

Tin-Free Controlled Depletion Paints (Tin-Free CDPs)

The tin-free CDPs are an improved version of the traditional soluble matrix paints, where organically synthesized resins reinforce the binder, although presenting the same antifouling mechanism as the conventional rosin matrix paints. The synthesized resins are more resistant than rosins and control the dissolution of the soluble binder.

These paints are also known as ablative/erodible paints, containing polymeric compounds capable of controlling the

relative rate of dissolution/erosion. They also contain a large proportion of a non-toxic binder, which is soluble in seawater. The biocide content is high and dissolves in the seawater, in conjunction with the soluble binder. The rate of erosion becomes constant after short time of immersion.

However, these paints transform into an empty matrix, due to the dissolution of the soluble compounds incorporated in the paint into the seawater, affecting their behavior. Consequently, a high amount of copper and co-biocide is needed, which rises the concern towards the environment. Also, as the compounds dissolve, the roughness of the coating increases, thus promoting biofouling formation. The leached layer formed may be removed prior to recoating.

Regarding to the lifespan of these paints, these confer a protection a bit longer than 3 years. They do not require a tie coat when repainted and are less expensive than TBT-based self-polishing paints.

Usually, leisure boats and small ships with short service time apply these paints.

Tin-Free Self-Polishing Copolymer Paints (Tin-Free SPCs)

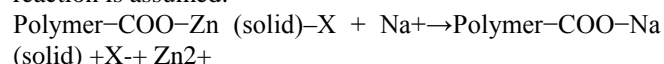
The tin-free SPCs contain an acrylic copolymer matrix combined with booster biocides, where different pendant groups are linked to the polymeric backbone and released after the contact with seawater. This process resembles the hydrolysis of TBT-SPC paints.

In this type of paint, the antifouling activity is induced as the chemical reaction through hydrolysis of copper, zinc or silyl acrylates occurs, forming an acidic polymer, which is soluble in sea water and can be washed from the surface.

The hydrolysis process is followed by the loss of the dissolved layer of polymer, smoothening the surface.

These paints present a life span 3 to 5 years, due to their high polishing rate. Anyhow, they are not as efficient as TBT-based-self-polishing paints.

For instance, when insoluble Zn acrylate is used, it hydrolyzes to soluble acidic polymer and the following reaction is assumed:



The Zn^{2+} is released into the seawater for antifouling properties and the soluble acidic polymers can be washed from the surface. Currently, metallic copper, copper thiocyanate and cuprous oxide are the dominant compounds used in antifouling paints.

In comparison with the TBT antifouling paints and as mentioned before, copper-containing coatings can only target specific fouling organisms. To improve the antifouling properties and thereby the selectivity to macro algae, barnacles and bryozoans, booster biocides such as Irgarol 1051, Diuron, copper pyrithione, zinc pyrithione, isothiazolone, Zineb, Ecomea and many others are added, as an alternative to TBT derivatives. Although the toxicity of the majority of the biocides aforementioned has not been



fully assessed, zinc pyrithione and Zineb seem to be the least toxic, whereas Irgarol and Diuron are reported to be more poisonous.

Hybrid Paints

The antifouling mechanism of hybrid paints is a conjunction of the mechanisms of both CDPs and TF-SPCs. The leached layer, cost and the performance of these paints is intermediate.

An example of these hybrid paints are the microfibers incorporated in paints, by Hempel.

Biocide-Free Coatings

Due to the toxicity of the biocides used in the antifouling paints, novel biocide-free technologies have been investigated to replace the biocide based coatings.

Non-stick “fouling-release” coatings, containing fluoro polymers and silicone, have been tested regarding to the release of macro fouling organisms, using robust hydrodynamic conditions. Apparently, fluoro-polymers and silicone appear to possess the desired properties to promote antifouling by release. Some low surface energy coatings have also been prepared with modified acrylic resin and nano-SiO₂. Moreover, accumulated fouling organisms are not easily released, being difficult to develop an environmentally friendly and simultaneously effective coating.

Additionally, these methods have some drawbacks such as high cost, poor mechanical properties and the difficulty of recoating.

Recently, researchers have been focusing in combining “fouling-release” coatings with hydrogel technology. For example, Hempel has been investing in this technology by modifying the surface of commercial PDMS (polydimethylsiloxane) coatings in order to generate a hydrogel in contact with water, with weak adhesion properties. This layer promotes its detachment from the former paint layer together with any attached bio fouling (e.g. slime or algae) on the coating. Experiments were also performed on ships, showing that this new coating is able to keep the surface clean even at low speeds.

In summary, despite the fact that hydrogel based “fouling-release” coatings are showing positive results on the bio-fouling prevention, their durability and effect on the environment are still unknown, which should motivate a deep research in this field in order to develop an effective, durable and non-toxic coating.

For this purpose, advanced characterization techniques should be performed to evaluate the mechanical characteristics and the environmental compatibility, to proceed to further improvements and finally introduce new potential benign products in the market.

J. Characteristics of Antifouling Paints

After developing the desired polymeric matrix of the coating, it is necessary to proceed to characterization tests in order to check if the coating is in accordance with the standards.

Generally, the requirements for an optimal antifouling coating consist of being anticorrosive, environmentally acceptable, economically viable, durable, smooth, compatible with the underlying system, resistant to abrasion, biodegradation and erosion (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

J.1 Anti-Corrosiveness

If the substrate (ship's hull) is steel, the paint should protect it from corrosion caused by the exposure to the marine environment.

To prevent this problem, at least one coating of primer or anticorrosive paint is applied before the layer of antifouling paint. The latter may contribute materially to the protection of the hull from corrosion, depending primarily on the thickness of the antifouling coating and its resistance to the ingress of sea water. Thus, thick paints impede corrosion and provide the necessary toxic storage for extended fouling prevention. The paint providers in the technical data sheet of the product generally specify the adequate thickness. For instance, Jotun's antifouling paints' thickness ranges from 75 to 150 μ m, whereas the primers' thickness ranges from 40 to 250 μ m.

Also, the chemical compounds added into the coating should be taken into account, since they might tend to quicken the corrosion effect. For instance, common toxic pigments such as metallic copper and salts of copper and mercury have the tendency to intensify corrosion if they are applied directly on the hull.

J.2 Durability

The durability of a coating is dependent on its resistance to mechanical damage, on the erosion caused by the water motion and on the components present in the paint formulation. If it contains any biocide, the coating disintegration must be also taken into account, since it degrades as the seawater penetrates and releases the toxic biocide. Therefore, a balance between toxicity and durability should be established.

The resistance to the erosive effect of the water motion is a notable problem in high speed vessels, such as motor torpedo boats and hydroplanes. Considering this, it is necessary to develop suitable paints, which can confer a hard and thus resistant surface to overcome this drawback.

The loss of durability is more accentuated near the waterline, due to the mechanical damage caused by the floating debris and the alternation between the wet and dry conditions and due to the exposure to the sun. These factors



intensify the coatings' cracking, being necessary to develop a paint, which can resist all of this harm.

J.3 Adhesion

The adhesion is an important property, since the paint should adhere adequately to the substrate where it is applied, regardless of the natural conditions existing during this procedure. This means that the paint should either adhere suitably when it is applied during winter (high moisture and low temperature) or summer (low moisture and high temperature).

Low adherence may lead to the disintegration of the coating and therefore exposes the hull to the marine environment, leaving it unprotected.

J.4 Abrasion

The assessment of the abrasion resistance of antifouling paints is a relevant factor, since it can indicate the paints' resistance to friction caused by moving particles transported by the wind or water. These particles can erode the paint, when the ship is in motion or in the port, compromising the durability of the coating.

J.5 Smoothness

The paint must be applied uniformly to confer a smooth surface, which, therefore, will create less frictional drag and bio-fouling attachment.

Additionally, it is also desirable that paints with a high viscosity (needed to form thick coatings) have sufficient elasticity to fill up the minor irregularities present on the ship's surface.

J.6 Drag Friction

As known, a ship must be designed to move efficiently through the water with a minimum of external force. However, when it is propelled through the water, it has drag associated with it, which must be overcome by thrust to move forward.

Drag is defined as the force that opposes forward motion through the fluid and is parallel to the direction of the free-stream velocity of the fluid flow. When moving on the water, the drag of a ship presents two major components: wave-making drag and skin frictional drag. The frictional drag typically accounts 60-90% of the total resistance and can be reduced by applying an appropriate surface coating, which softens the surface. The roughness of the surface and, thereby, the frictional resistance is influenced by different factors such as the age or condition of the ship hull, the surface preparation, the paint application, the paint system and marine fouling.

The skin frictional drag is increased when microbial communities, present in the sea, attach to the surface of the coating, leading to extreme fuel and maintenance costs of the ships and CO₂ emission. Several papers

have studied the effect of marine fouling on the hydrodynamic performance of a surface. For example, Bohlander (1991) performed full scale power trials on a frigate and concluded that microfilms of bio-fouling increased the drag friction by 8 to 18%.

For this purpose, it is of utmost importance to assess the coating regarding the drag friction effect, to avoid excessive fuel consumption and subsequent penalties.

Several experiments have been applied to measure the drag friction of the coatings, including a rough plate or a rotating disc or cylinders.

It is important to mention that the selection of the coating type does influence the drag friction effect. Several studies have been carried out to compare the drag resistance of silicone based "foul release" coatings with tin-free self-polishing coatings. The former has shown positive results in comparison with the latter, mainly due to its surface texture (less rough).

J.7 Wettability

The wet ability of a solid by a liquid can be determined by measuring the contact angle (or wetting angle), Θ . The contact angle is described as the angle between the surface of the liquid and the outline of the contact surface, when an interface between a liquid and a solid exists.

K. Environmental Risk Assessment

Since the main mechanism of action of the majority of antifouling paints consists of releasing biocide into the seawater, a severe environmental compatibility assessment should be carried out before the introduction of these paints in the market.

After the ban of TBT based paints, alternative biocides have been used in conjunction with copper, which can be less or equally harmful.

For instance, the leaching of copper from the antifouling paints on Swedish boats tends to be harmful to the Baltic Sea's key-species bladder wrack and *Fucus vesiculosus*, leading the Swedish Chemicals Agency to restrain the use of paints leaching excessive copper and prohibit copper based paints on leisure boats (length < 12 m).

Another example is regarding a study carried out in Hong Kong, which consisted of testing the toxicity of five commonly used booster biocides (Irgarol, Diuron, Zinc pyrithione, Copper pyrithione and Chlorothalonil) on the growth or survival of 12 marine species, concluding that Irgarol is even more toxic than TBT and copper pyrithione is as toxic as TBT.

Considering this, it is important to perform an accurate evaluation of the environmental risks that these paints can pose to the marine species, by carrying out biodegradability tests or mechanical tests that enable the collection of leachates for toxicity analysis.



L. The Hull Friction (Drag) and Roughness

The frictional resistance to a ship's movement through water (Drag). The total resistance to a ship's movement through water is normally defined as the force required to tow a ship at a given speed in calm waters. The total resistance is the sum of the frictional resistance and the residual resistance, the latter being a feature of the ship's design whereas the former is due to the tangential shear forces caused by the movement of water parallel to the ship's hull. It can be seen that only the surface coatings or surface treatment can influence the frictional resistance.

In 1874, Froude showed experimentally that the frictional resistance for towed planks could be expressed by the equation:

$$R_f = f \cdot s \cdot v^n$$

Where R_f = frictional resistance, f = frictional coefficient, s = the wetted surface area, v = the velocity, and n = a number nearly equal to 2.

From the results Froude obtained that it was obvious that the frictional resistance depends on the nature of the surface, the values of n being very nearly equal to two whereas the values of ' f ' varied greatly depending on the smoothness of the surface; these observations were not utilized until well into the twentieth century.

L.1 Flow around a Ship's Hull

The resistance caused by the flow of water around a ship's hull, the residual resistance, is governed by the hull geometry and operational speeds, this can be approximated to the flow around a plane plate for which the formulation below is applicable:

$$Re = \frac{Vl}{\nu}$$

Where v = the velocity of the flow past the hull, l = the distance from the bow of the ship and ν = the kinematic viscosity which is the ratio of the viscosity to density, the units being Stokes. "Re" is called the Reynolds Number, is a dimensionless parameter, which provides a useful indicator of the type of flow around the hull: when its value is below 5×10^5 laminar flow is observed, whereas at a value $\geq 10^7$ the flow is turbulent, 5×10^5 and 10^7 are critical values of "Re" between which the flow changes from laminar to turbulent.

It has been shown by Izubuchi from tests on the Japanese destroyer 'Yudachi' that at normal operating speeds the residual resistance forms a relatively small proportion of the total resistance. These results were in agreement with those obtained by the U.S. Navy using the U.S. Destroyer 'Hamilton' as the test craft. Work that is more recent has demonstrated that the relative contribution of each of these resistance components to the total resistance depends on both the size and the speed of the vessel.

The reduction of frictional resistance is of major importance for efficient operation, the residual resistance only becomes important at relatively high operating speeds and is affected

by the design and building of the vessel; most commercial vessels operate in the 10-20 KN range. A vast amount of research has been and continues to be conducted on design whereas; the frictional resistance can be very significantly lowered, with consequent economic benefit, by the application of a high performance antifouling.

The water around the hull of a ship moving at low speed can be divided into two parts; a laminar sub layer which is a continuous layer of water adjacent and parallel to the ship's hull and moving with the ship, the thickness of this layer being dependent on the speed of the ship; at greater distance from the hull flow becomes turbulent due to the shear forces created by the passage of water around the hull; the faster the ship moves the thinner the laminar sub layer. At a low Reynolds Number for a given ship operating under standard conditions a relatively thick laminar sub layer is present, with increasing speed (and therefore increasing Reynolds Number) the thickness of the laminar sub layer decreases and between certain Reynolds Numbers the laminar sub layer becomes discontinuous.

The smoother the hull, the lower the kinematic viscosity and so the greater the Reynolds Number. The increase in resistance created by turbulent flow (i.e. the energy required to produce turbulence) is thus related to the surface roughness and is directly proportional to the Reynolds Number.

A surface is considered to be rough if the peaks of roughness protrude through the thickness of the laminar sub layer, if the peaks are smaller and remain within the laminar sub layer the surface is considered to be hydro dynamically smooth.

The thickness of the laminar sub layer is dependent on the velocity of the hull and it has been determined that for a ship operating at V knots a hydro dynamically smooth hull occurs when the surface roughness is less than or equal to $\frac{230}{v} \mu$. This criterion is very rarely satisfied even for a freshly painted hull (Surag Mohammed Saeed Ali, and Osama Mohammed Elmaridi Suleiman Khayal, 2021).

L.2 Sources of Hull Roughness

Hull roughness is directly related to the frictional resistance and may be affected by numerous factors, these being described in the following sections.

L.2.1 Structure of the Paint

Because of the cost of dry-docking and repainting, ship owners have sought shorter dry-docking times.

This has led paint manufacturers to compromise between adhesive paints that spray smoothly, but sag easily when sprayed thickly, and thixotropic paints which tend to ripple on the surface but can be applied in thicker coats without sagging. Both of these paint systems cause hull roughness, the former being less than the later.



L.2.2 Inadequate Surface Preparation

The removal of fouling organisms and the repair of surface defects to provide a smooth finish to which the new antifouling is to be applied is of major importance in producing a smoothly painted hull. This, however, is not always realized because of the cost of preparation, consequently in many instances surface roughness is built in this way, the roughness increasing with each repainting.

L.2.3 Poor Application Standards

The application of any coating system is really a skilled job but due to working conditions and pay, the average worker is either unskilled or untrained and consequently the manufacturer ~ spraying instructions are often not followed closely. The environment also plays an important role; for example, variations in humidity and wind speed can result in poor application.

L.2.4 Failure of the Paint System

This occurs when the ship is in service and the main problems are: blistering, detachment and corrosion.

L.2.5 Mechanical Damage

This includes berthing and grounding damage as well as that incurred from cable chafing.

L.2.6 Fouling

This is the major cause of hull roughness; an ineffective or exhausted antifouling coating, thus the roughness caused by fouling increases with time, causes it.

M. Measurement of Hull Roughness

Surface roughness of a ship's hull is expressed as the maximum peak height to minimum valley depth over a distance of 50 mm, this is more commonly known as the mean apparent amplitude or MAA per 50 mm. This method of measurement gives reasonable correlation between hull roughness and ship's resistance.

Many instruments are available to measure surface roughness in the laboratory, Talysurf, Surf meter, Electron Microscope, etc. but it is only recently that the British Ship Research Association (BSRA) have developed an instrument which can measure the surface roughness of a ship's hull in dry dock. The instrument (B.S.R.A. Roughness Gauge) consists of three wheels supporting a carriage through which protrudes a stylus. When the apparatus is pushed across the hull, the stylus records the surface profile. The gauge's sample length is 50 mm and it measures the maximum peak to minimum trough distance.

This apparatus gives reasonable correlation with the standard laboratory instruments but it does not account for waves with a large wavelength as the sampling distance per measurement is too short and there is no fixed reference.

The results obtained by measuring a ship's roughness have to be corrected for defects which cause residual resistance, i.e. plate curvature, welds, etc. and then the surface roughness of the hull may be calculated, this being displayed usually as a histogram.

To measure the ship's roughness in practice the hull is divided up into sections and each section is measured using the B.S.R.A. gauge before painting, the same procedure is followed after painting, sufficient measurements being taken to ensure a random sampling. The data may then be correlated to the ship's performance before and after painting to provide evidence for the increased fuel consumption due to surface roughness.

Scott has shown that the cost of surface roughness for a typical ship results in a one per cent increase in power to maintain the ship at a constant speed for every 10 μ of roughness above 100 μ . The surface roughness of a new ship is generally about 130 μ , this figure increasing with service time for a ship painted with a conventional anti-fouling preparation as was shown by the Norwegian Ship Research Institute (Surag Mohammed Saeed Ali, and Osama Mohammed Elmardi Suleiman Khayal, 2021).

III. CONCLUSIONS

In the present study, a comprehensive introduction and literature review of corrosion and biofouling in marine environment have been presented. The study was considered from different viewpoints. These points include general introduction to corrosion and biofouling in ship structures; a comprehensive literature review that deliberates the present subject from the consideration of corrosion recognition and definition, types of corrosion, corrosion control methods, biofouling, types of biofouling, biofouling mechanism, stages of biofouling, antifouling coating formulation and methods, antifouling methods, characteristics of antifouling paints, environmental risk assessment, the hull friction (drag) and roughness, and the measurement of hull roughness.

The objective of the present study is to maintain the vessel hull from corrosion and biofouling to increase its power and performance, and to detect the factors that affects the corrosion and biofouling of ships' hull.

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