

Minimization of corrosion in aquatic environment – a review

Abstract

Corrosion is the gradual deterioration of a material through an electro-chemical reaction with its environment. Electrochemical conditions can be created at the film's base by bacterial film and salt water of marine environment acts as electrolyte according to the marine science. While corroding, dissolved oxygen and other species as well as the metal surfaces pH can be impact electrochemical process on the metal, which in turn affects. To overcome this problem, there are several methods of preventing a material from corroding. Among them, cathodic protection (CP) and coatings are very popular and effective methods for marine corrosion protection that can provide very good protection over a long period of time. Developing anticorrosive additives that are more effective than the conventional inorganic pigments currently used in paint, may have adverse impacts on environment and human health. In this study, we have focused on cathodic protection (CP) and coatings and the combination of them for providing good protection over a long period.

Keywords: marine corrosion, aquatic environment, coating, and cathodic protection (CP)

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Introduction

In the current era, the corrosion has become one of the most dynamic research areas. Corrosion is the continuous destructive phenomenon of a material or its properties through the effects of unwanted chemical or electrochemical reactions with its environment which may cause deterioration of the surface and structural properties of the iron component.^{1,2} Corrosion depends on the pH, temperature and concentrations of many inorganic and organic species at the metal-water interface.³ Marine corrosion can exist in several forms such as pitting, galvanic, stray current and cavitation corrosion. The high salt concentration in most marine environments combined with high electrical conductivity makes marine bodies a highly conducive environment for corrosion to occur on metal surfaces. The marine structures such as ships and aquatic platforms are under continuous attack from their surrounding environment.⁴ Sometimes these structures are allowed to corrode. The seawater mostly contains two ions that are chloride and sodium. These two ions make up over 90% of all dissolved ions in seawater. The chloride ions continuously react with marine structure in contact of water and damage the structure. Firstly, chloride ions destroy the passive layer (cathode) and accelerate the transfer of the material with producing soluble ferrous chloride (FeCl₂). Hydrolysis of chloride reduces the pH of the surrounding environment, which further promotes dissolution of the non-passive layer (anode). When oxide film (iron oxides) reacts with chloride ions, it decomposes and FeCl₂ is formed. FeCl₂ is a complex which dissolve in the surrounding solution and releasing chloride ions for causing more soluble corrosion. Thus, chloride ions remain as ion which don't participate in a specific reaction to become chlorine molecule. The impacts of microorganisms on corrosion of marine structure have also been identified since the beginning of this century where the organisms can form the microscopic films on structure within a few hours.³

The corrosive materials need to be prevented with high strength.⁵ So, Considerable effort has been made to develop corrosion prevention strategies. Initially, paints, pigments, and organic coatings have been applied to prevent metal corrosion.⁵ Consequently, cathodic protection, conjugated polymers, epoxy resin, phenolics, acrylic polymers, and many thermoplastics as well as thermoset resins have been used to inhibit corrosion. Lately, nanofillers such as fullerene,

nano-diamond, graphene, graphene oxide, carbon nanotube, carbon black, nano clay, and inorganic nanoparticle have been introduced.⁵ The cathodic protection (CP) method is the most widely used system of shielding a material from corrosion in a marine environment. This is an electrical anticorrosion method which is used to protect many surface structures especially underground storage tanks, lock gates and dams, water treatment facilities, well casings, rubbish racks, bridge decks, steel pilings, ship-wetted hulls which is buried in soil or immersed in water.² The most primitive use of this method has been found in ships. In 1824, Sir Humphry Davy has practiced the process on marine ships who described a method to inhibit corrosion of the copper-clad wooden hulls of British marine containers in a series of papers.^{6,7} Today, Davy's procedure is still being used to minimize corrosion damage by connecting zinc anodes on ships through the world.

Coating is another outstanding effective method for preventing the corrosion of marine structure. Different coating approaches have been studied in the past, including ceramic coatings,⁸ polymer coatings,⁹ electrodeposition of nano-crystalline materials,¹⁰ and self-assembled nano-coatings.¹¹ A combination of coatings using nano-paints, which contain nanomaterials in polymer paints, and multiphase nanomaterial-based coatings that can withstand high temperature.¹² Nanomaterials have high surface area and high adhesion to substrates which provide effective corrosion resistance and can be used for protective coatings on various surfaces.¹³ Polymeric coatings and paints are widely used in industries for corrosion protection.¹⁴ Organic coatings are also an efficient way to protect metallic materials from corrosion¹ those are generally adopted in most part of the world owing to their simplicity in application, flexibility, toughness, adhesion, chemical resistance and their durability. Each individual method has its own benefits and drawbacks whereas the combination of CP and coatings is the most effective and popular method of corrosion prevention. This combination can provide very good protection over a long period of time.²

What is corrosion?

Corrosion is the regular destructive phenomenon (electrochemical or chemical) of a material or its properties through a chemical reaction with its environment which may cause physical failure. **Roberge** states

that, “corrosion is the destructive attack of a material by reaction with its environment” [18]. When steel and iron go through the corrosion process, a very well-known corrosive product is produced which is called rust. Figure 1 gives a basic schematic of a corrosion cell. Marine corrosion is an electrochemical reaction that happens when electrons flow between metals that are connected through water. One of the metals is practically eaten away by this electrical process. If the water has a lot of salt, brackish, or mineral content, the process will go much faster. Humidity, wind, temperature, airborne pollutants, location, and biological species are all elements that impact corrosion rates in maritime environments. Coatings such as cathodic protection and alloy selection are standard approaches for preventing corrosion on various components. An Anode, a Cathode, Electrolyte, and a Metallic Path are all necessary for corrosion to occur. It is impossible to avoid corrosion, but the right precautions may be taken to slow it down. A corrosion cell may easily grow in salt water due to its high conductivity and near-total ionization.

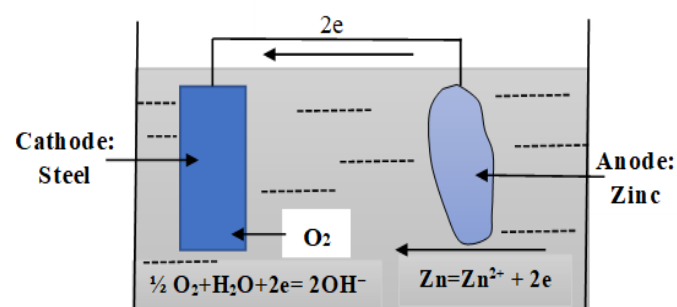


Figure 1 A corrosion cell.

Background history of marine corrosion

There are numerous corrosion-related damages that are seen nowadays. As a result, millions of dollars have been spent over the past few years in the United States on inspection and restoration programs, mostly for marine structures [Stewart and Rosowsky, 1998]. As a consequence, numerous studies are carried out to pinpoint the forms of degradation and offer guidance on how to reduce the likelihood of this kind of corrosion in newly constructed marine structures. The resistance of materials to corrosion when in contact with seawater is a crucial topic in the subject of marine corrosion. Following the International Congress on Marine Corrosion held in Cannes in 1964, the Working Party “Marine Corrosion” was created to address this issue. The Working Party has been engaged over time in a number of areas. Studies on marine corrosion testing, seawater crevice corrosion, and non-ferrous metal corrosion have all been done, according to the working party documentation. Throughout its existence, the Working Party has held and sponsored numerous workshops, seminars, and conferences. Early in 1990, the Working Party conducted a round-robin test at multiple test sites to investigate crevice corrosion on stainless steel in seawater. Ten years later, the working group launched a project with funding from the European Commission that developed procedures for assessing crevice corrosion that should be able to forecast service performance in seawater.

Cathodic protection, or CP, is a tool that employs electricity to protect steel structures including subsurface storage tanks, lock gates, dams, water treatment plants, well casings, trash racks, bridge decks, steel pilings, and of course, ship-wetted hulls. The early applications of cathodic protection systems were on ships. Sir Humphry Davy was the first to equip navy ships with cathodic protection systems in 1824. Today, zinc anodes are still used aboard ships all over the

world to limit corrosion damage to steel vessels. The cathodic protection system had yet another substantial breakthrough in the United States in 1945. In order to prevent corrosion damage and extend the life of the subterranean pipelines, CP systems were put in place.⁶ Additionally, cast iron pipes with larger walls and low pressure were widely employed in the UK. But until the early 1950s, CP systems were rarely used to protect the pipelines. Then, in 1952, a CP system was set up to safeguard a 1000-mile network of gasoline lines. This was discovered to be successful in preventing corrosion. The adoption of CP systems has exploded as a result of this success. As a result, besides coatings, the cathodic protection system is the most often utilized strategy for preventing corrosion of the material in a marine environment. Many ships and offshore constructions are now protected from corrosion using a CP system. Cathodic protection can be used alone or in combination with other safety measures. The most efficient corrosion prevention from a practical and financial standpoint is the particular mix of CP and coatings. In spite of this, several corrosion inhibitors have been developed recently.

Problem statement

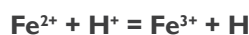
It is known that the marine structures and aquatic platforms are always under attack from their surrounding environment.⁴ Sometimes these structures are allowed to be corrode. The seawater mostly contains two ions that are chloride and sodium. These two ions make up over 90% of all dissolved ions in seawater. Moreover, sulfate ions are also having into the sea water. The hazardous chloride ions continuously react with marine structure in contact of water and cause damaging of the marine structure and aquatic platform. Firstly, chloride ions destroy the passive layer (cathode) and accelerate the transfer of the material with producing soluble metal chloride (MCl_2). Let, the metal is iron (Fe). Hydrolysis of chloride reduces the pH of the surrounding environment, which further promotes dissolution of the non-passive layer (anode). When oxide film (iron oxides) reacts with chloride ions, it decomposed and $FeCl_2$ is formed.



$FeCl_2$ is a complex which dissolve in the surrounding solution and releasing chloride ions for causing more soluble corrosion. Thus, chloride ions remain as ion which don't participate in a specific reaction to become chlorine molecule. The impacts of microorganisms on corrosion of marine structure have also been identified since the beginning of this century where the organisms can form the microscopic films on structure within a few hours.³

The theory of corrosion

Many years ago, Baylis, 1926¹⁵ have stated that before the treatment of corrosion prevention, it is actually necessary to describe the theories in which corrosion reaction takes place. There is a slight affinity for iron to interact with solution. As suggested by Whitney¹⁶ in 1903, if the reaction is electrochemical, the ferrous ions will take up a positive charge from the hydrogen ions of the solution to liberate atomic hydrogen (H).



Classification- There are 3 theories of corrosion

- I. Wet or Electrochemical or Galvanic theory of corrosion.
- II. Dry or chemical theory of corrosion.
- III. Acid theory of corrosion.

Wet or electrochemical theory of corrosion

A conductive liquid can cause this form of corrosion to develop. Any chemical reaction has two components: an anode and a cathode. The hydrogen atom must be removed from the iron reaction to form a ferrous hydroxide precipitate. The chemical in the surroundings serves as an electrolyte, with the metal surface acting as an anode and the remainder as a cathode. A galvanic cell is therefore formed on the surface of metals as a result of this process. Anode oxidation occurs whereas cathode reduction occurs in corrosion. Two examples of this phenomenon are shown below:

This phenomenon is described below in two cases:

Case I: Evolution of H₂

- I. At anode: $\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$ (oxidation)
- II. At cathode: Due to the acidic environment, the hydrogen ions (H⁺) are formed.
- III. $2\text{H}^+ + 2\text{e}^- = \text{H}_2\uparrow$ (reduction)
- IV. The overall reaction: $\text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2\uparrow$

Case II: Absorption of O₂: This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The layer of iron oxide covers the surface of the iron.

- I. At anode: $\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$ (oxidation)
- II. At cathode: $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^-$ (reduction)
- III. The overall reaction: $\text{Fe} + \text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{OH}^- = \text{Fe}(\text{OH})_2$

Dry or Chemical theory of corrosion

Metal surface corrosion is caused by the direct reactivity of various ambient gases (such as oxygen, halogens, SO_x, NO_x) with the metal. When compared to other metals, oxygen is the primary cause of corrosion. Dry corrosion can be classified into three broad categories:

Oxidation corrosion (Reaction with oxygen): In the absence of moisture, the alkali and alkaline earth metals create matching oxides by directly reacting with oxygen at ambient temperature. When a metal undergoes the process of oxidation, a very thin layer of metal oxide is produced on the surface of the metal. This film serves to shield the metal against further corrosion.

Corrosion by other gases such as Cl₂, SO₂, H₂S, and NO_x: Corrosion brought on by other gases, such as Cl₂, SO₂, H₂S, and NO_x: These gases react with the metal in an environment devoid of moisture to produce corrosion products that, depending on the circumstances, may or may not be protective. The formation of a protective layer known as AgCl is produced when dry Cl₂ interacts with silver.

Liquid metal corrosion: Corrosion caused by liquid metal in several different sectors, molten metal is transported via metallic pipes, which leads to corrosion either as a result of dissolution or as a result of internal penetration. For instance, the liquid metal mercury can dissolve most metals through the formation of amalgams, which then causes the metals to corrode.

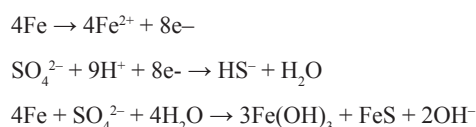
Acid theory of corrosion

According to the acid theory, iron corrosion is caused by the presence of acids in the environment. It is hypothesized that atmospheric CO₂, water vapor, and oxygen corrode iron. Iron (Fe), iron oxide (FeO), and iron sulfate (Fe³⁺) are all formed during the corrosion of iron (Fe). Most hydrogen in alkaline solutions will interact with oxygen

to produce water, while in acidic solutions, the reaction may mostly release hydrogen gas. Natural water is likely to have more hydrogen oxidation than gas liberation between these process extremes. When a new iron surface is uncovered, it is likely to be in excess. Corrosion beneath iron rust may, in some situations, result in hydrogen gas being liberated, even though the water outside of the rust has an abundance of oxygen-containing negative ions. In these cases, the predominant reaction is likely the liberation of hydrogen gas.

Effects of bacterial film on corrosion

Microbial corrosion is a form of corrosion that occurs when biological organisms attack and deteriorate metal (such as bacteria). It is a microbiologically induced corrosion caused by Sulfate-Reducing Bacteria (SRB). The first phase in the biocorrosion process is the creation of a biofilm. After then, a chemical reaction happens, degrading the material. Corrosion produced or encouraged by microorganisms is known as bacterial corrosion, bio-corrosion, or microbiologically influenced corrosion (MIC).¹⁷ It is the presence and aggressive metabolites of the bacteria that cause pitting corrosion to commence, resulting to localized corrosion underneath the biofilm. Mechanism **Reactions** of microbial Corrosion:¹⁸



Responsible bacteria for microbial corrosion:

- I. Sulfate-reducing bacteria (SRB), including *Desulfuromonas sp.*, *Desulfobacter sp.*, *Desulfococcus sp.*, etc. The SRB is strictly anaerobic.
- II. Sulfur-oxidizing bacteria, primarily of the genus *Thiobacillus*. These organisms notably form sulfuric acid during oxidation and are capable of both oxidizing sulfur and ferrous iron.
- III. Iron²⁺ bacteria, of which there are two types: ‘stalked’ (notably *Gallionella sp.*) and ‘filamentous’ (*Leptothrix sp.*, *Clonothrix sp.*, *Sphaerotilus sp.*, etc.). These bacteria primarily oxidize or reduce iron species during respiration.¹⁹

Causes of microbial corrosion

- I. There must be an organic supply of carbon for heterotrophic bacteria to grow. They can assimilate a broad variety of organic compounds and release carbon dioxide, metabolites, and organic acids into the surrounding environment. Corrosion is caused by a change in the environment, not by bacteria themselves.
- II. These organisms, known as autotrophic bacteria, thrive in the presence of inorganic substances such as carbon dioxide or sunlight.²⁰

Minimization of microbial corrosion

- I. Treatment by use of physical and mechanical means (pigging, ultrasound).
- II. Electrification (cathodic protection)
- III. Biotechnical (microorganism against another).
- IV. Biocides can be used as a chemical therapy (oxidizing, non-oxidizing, chelate former, electrophiles, and membrane-active).
- V. Chemicals can impact microbial adhesion or control microbial growth.

To control both aerobic and anaerobic microbes, they need to have a wide range of activity. Coal tar, asphaltic bitumen, zinc-aluminum, lead, and plastic are just a few of the materials that are prone to MIC. Biofilm generation and microbial adherence can all be suppressed to lessen the corrosion-causing effects of micro- and microorganisms as well as the rate of pitting, stress, and general corrosion.²¹

Formation of the Fe (II)–Fe (III)

Fe (II)–Fe (III) formation has been mentioned by Refait et al.²² In marine corrosion, the Fe^{2+} and Fe^{3+} ions form and bond with hydroxy sulfate as green rust, which can be seen on the surface of the steel. These steel sheet piles were immersed 1m above the mud line for 25 years, and rust layers formed on them were analyzed using Raman spectroscopy, SEM, and X-ray mappings of elements (Fe, S, O). It has a core of magnetite, a middle layer of iron (III) oxyhydroxides, and an outer layer of green rust green rusts (GR) hydroxy sulfate green rust (SO_2^{-4}). The electrochemical reaction between marine metals and their environment causes the sea's corrosion. Hydroxyl ions form a byproduct of this anode-to-cathode reaction, which occurs when metals act as an anode while oxygen and water act as cathode. For example, when steel is exposed to water, it corrodes. Fe^{2+} ions and electrons are produced due to the metal's anodic behavior. Ferrous hydroxide is formed due to the cations transporting through the electrolyte (seawater) to the cathode Figure 2.

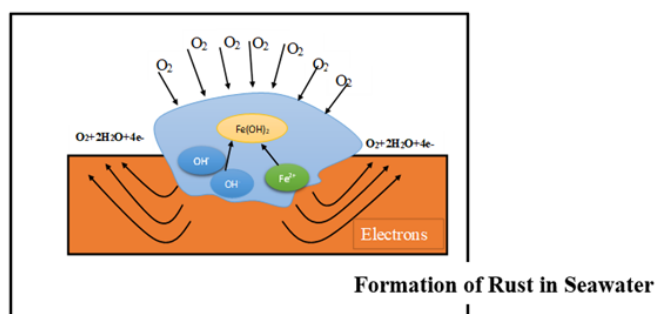


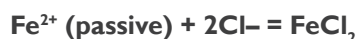
Figure 2 Formation of Fe^{2+} from metal [Refait et al. 2003].

Corrosion process in marine structure

We know that the Earth's surface is covered by more than 70% water, with seawater accounting for nearly 90% of that total. Therefore, seawater must contain chloride, sulfate, and sulfuric acid. Investigating a variety of objects^{11,12,22} revealed the following corrosion process. When ships and structures in the marine/sea domain come into contact with seawater containing water and oxygen (O_2), there is corrosion in marine science. Storage tanks, lock gates, dams, water treatment facilities, well casings, trash racks, bridge decks, steel pilings, and ship-wetted hulls are some of the sea structures found in the ocean. Metals and alloys that come into contact with sea water have a specific electrical potential at a specific pH level, determined by the acidity or alkalinity of the seawater in question.²³ **Factors which aggregate marine corrosion:** Seawater (Cl^- , Na^+), living organisms (microbiological, weed clustering's), limpet, sand deposition, oxygen content, velocity, temperature, and biological organisms are all factors that contribute to marine corrosion.

Chloride and sodium ions make up most of the ions in seawater. Over 90% of the dissolved ions in seawater are made up of these two ions. 3.4% of seawater is salty (alkaline, pH 8). It is an excellent electrolyte that can cause galvanic and crevice corrosion. Cathode refers to the non-passive layer, while cathode refers to the passive layer.

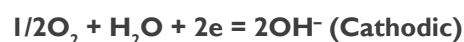
In the presence of water, chloride ions corrode marine structures, resulting in structural damage. To begin with, chloride ions degrade the passive layer (cathode) and speed up the transfer of material by forming soluble ferrous chloride. (source) (FeCl_2). Hydrolysis of chloride reduces the pH of the surrounding environment, which further promotes dissolution of the non-passive layer (anode). When oxide film (iron oxides) reacts with chloride ions, it decomposed and FeCl_2 is formed. FeCl_2 is a soluble complex which dissolve in the surrounding solution and releasing chloride ions for causing more corrosion.



When dissolved, these materials release Cl^- ions, which can be used in the event of future corrosion. In this way, chloride ions remain as ions rather than a chlorine molecule because they do not participate in any specific reaction to break down the passivity. Dissolved iron allows electrons to escape.



To get to the cathode (passive layer), electrons from O_2 and H_2O are absorbed by O_2 and H_2O to form OH^- , which occurs on the cathodic side.



Since the beginning of this century, it has been known that microorganisms can form microscopic films on marine structures in just a few hours.³

Methods of marine corrosion prevention

Preventing marine structure corrosion can be accomplished in several ways, some of which are discussed here.

- I. Cathodic shielding
- II. Paint and coatings
- III. Polyaniline as a corrosion prevention agent in the marine environment

Cathodic protection system

Cathodic Protecting steel structures from corrosion by using cathodic protection (CP) is an electrical method. As a result, it has been applied to many structures, including underground tanks, water treatment facilities, well cabling, trash receptacle racks, bridge decks, and steel pilings. Cathodic protection systems were first used on ships. Using cathodic protection systems, Sir Humphry Davy made naval ships safer in 1824. An anti-corrosion method for copper-clad wooden naval vessels has been described by Sir Davy in several papers.⁶ He attached a small amount of iron or zinc, which served as a sacrificial metal, to copper submerged in seawater. Zinc anodes, developed by Davy, are still used today to reduce corrosion damage to steel ships all over the world. In chapter three, we discussed the overall process. The cathodic protection system is the most widely used marine corrosion protection method with coatings. A CP system protects ships and offshore platforms from corrosion today. Using cathodic protection as a stand-alone system or in conjunction with other safeguards is entirely up to you. When it comes to protecting metal surfaces from corrosion, there is no better option than combining CP and coatings. Moreover, High silicon cast iron that can be used as an anode to prevent ship corrosion.²⁴ The presence of nano silica in ultra-high-performance concrete effectively is delayed the initiation of corrosion of the steel bars. The LPR and Tafel results is confirmed that the nano silica embedded bars increased the polarization resistance and reduced

the corrosion rate. It is also shown that the presence of nano titanium and nano CaCO_3 sodium nitrate has achieved significant improvement in durability, strength, Green concrete acts as a carbonation and corrosion inhibitor.²⁵

Paint and coatings

Any liquid, liquefiable, or mastic product that contains pigments and is transformed into an opaque film after application to a substrate in a thin layer constitutes paint, according to Tezdogan and Demirel.² The substrate is protected and/or enhanced by the film. A binder, color pigment, extender (filler), solvent, and additives round out most of the paint's ingredients (auxiliary substances). In the following section, we will discuss paints based on their ability to prevent corrosion.

Different types of coating agent used in marine ships is given below:²⁶

Silane-based coatings that can be used in marine ship for decreasing the corrosion rate. The examples of the silane-based coatings are fluoroalkyl silane (FAS)/ CeO_2 , Perfluorooctyl tri-ethoxy silane (PFOTES)- SiO_2 , PDMS/ ZnO NRs (0.5 wt%), PDMS/b- MnO_2 NRs(0.5wt%), PDMS/ $\text{GO-Al}_2\text{O}_3$ NRs (1.0 wt%), FDTs PDMS- ZnO , polydimethylsiloxane (PDMS), furan and meso-porous SiO_2 (SBA-15), PDMS-PEG 20%, HPA-Si-GO.

Epoxy-based coatings that can be used in marine ship for reducing corrosion rate. The examples of the epoxy-based coatings are Silicone, Inert pigments, Cardanol, Phenalkamine, Br/pani, ZnO -APTES, Go/PPy/ Zn , Silicone-Acrylate/ Cu (self-polishing).

Polyurethane based coatings that can be used in marine ship for minimizing the corrosion rate. The examples of the polyurethane-based coatings are polyurethane/multiwalled carbon nanotubes, polythiourethane (PTU)/ ZnO , polyurethane modified with hard//soft segment (PPG-TDI-BDO), polyurethane/polydimethylsiloxane.

There are three ways in which paint protects against corrosion;

providing a barrier effect: the barrier effect generates a barrier between the material and the environment. There are no rust-inhibiting pigments in the paints, so they only serve as a protective layer. This category includes most paints, primers, intermediate coats, and top coats. Preparation with aluminum and glass flakes enhances the barrier effect in most cases.

providing an inhibitor effect: Inhibiting pigments such as zinc phosphate are used in paints that provide an inhibitory effect. Primers are the only place you will find these pigments. Unfortunately, despite their name, these paints are not suitable for use in the ocean.

providing a galvanic effect: Pure zinc pigment is the only component in galvanic-effect paints, which are used solely as primers. When zinc comes into contact with steel, it acts as an anode; this is the underlying principle of the galvanic effect. Because zinc pigments act as a cathode, the steel remains protected even if a paint coating fails.

The surface of a material is protected from corrosion by an impervious coating, which acts as an inert barrier. Figure 3 depicts a simple impervious coating system in simple terms. A ship's protective coating must meet the following criteria in order to be applied successfully:

- Preparation of surface
- Pre-treatment of the surface
- Barrier or anticorrosive coatings
- Applying an antifouling coating

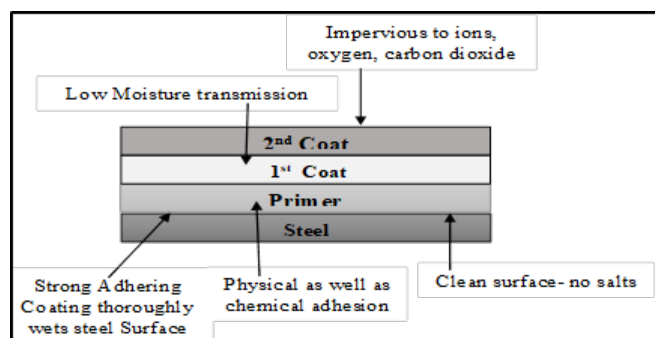


Figure 3 An impervious coating system.

Before applying a coating, the surface should be prepped to ISO 8501-1 standard grade Sa 21/2 to ensure good adhesion. High-pressure water jetting can also be used because it provides a more paint-friendly substrate.

Polyaniline as marine corrosion prevention agent

As Wang et al.²⁷ reported, the two main causes of marine corrosion damage and failure in marine environments are microbiological corrosion and bio-fouling. Because of SRB and IOB, as well as their biofilms, MIC is the result. Antifouling properties of conductive polyaniline have been discovered. An epoxy or polyurethane coating of conducting polyaniline can last 6-9 months.²⁸ Other antifouling agents, such as cuprous oxides, benefit from the conducting polyaniline's synergetic antifouling effect. Polyaniline's conductivity was found to be crucial to its antifouling properties. A new method for processing corrosion prevention coating containing emeraldine base was developed by using aliphatic polyamine as both the emeraldine base solvent and the epoxy resin curing agent. The emeraldine base and epoxy resin were blended at the molecular level. This was a solvent-free method that worked extremely well. Here is an illustration of marine corrosion protection and coatings.

Methods of cathodic protection

There have two leading ways of achieving cathodic protection. These are the Sacrificial Anodes Cathodic Protection (SACP) system and the Impressed Current Cathodic Protection (ICCP) system.

The sacrificial anodes cathodic protection (SACP) system

If no anodes were attached to a ship's hull, the steel would begin to interact with electrolytes and oxygen dissolved in seawater and would undergo corrosion to return back to a naturally-occurring ore, such as iron oxide. In this way, sacrificial anodes can protect a structure from corrosion. There will be a galvanic cell formed between the two metals because of their differing electrochemical potentials. The sacrificial anode and the steel hull serve as the anode and cathode, respectively, in this cell. In this case, an electron transfer from the anode to the cathode can take place as a result of a redox reaction. Due to electron donation from the anode's cathode, the anode undergoes oxidation, resulting in the formation of positively charged metal ions (cations) on its surface. Anode corrosion is caused by the interaction of these cations with dissolved oxygen in saltwater, which results in the development of metal oxides (corrosion). Only the anode attached to the sacrificial anode corrodes because of the advantageous electrochemical potential difference between it and the ship's hull. This prevents corrosion on the hull itself - instead, only the attached anode undergoes corrosion, and thus it is given the term "sacrificial

anode”.⁶ These anodes are generally made of aluminum, zinc or magnesium alloys, which are anodic with respect to steel materials. A schematic illustration of a typical SACP system is given in Figure 4. It is recommended that 15% - 20% of the sacrificial anodes should be installed to the stern and rudder area of the ship.² A typical installation of sacrificial anodes around the stern of a ship is shown in Figure 4.

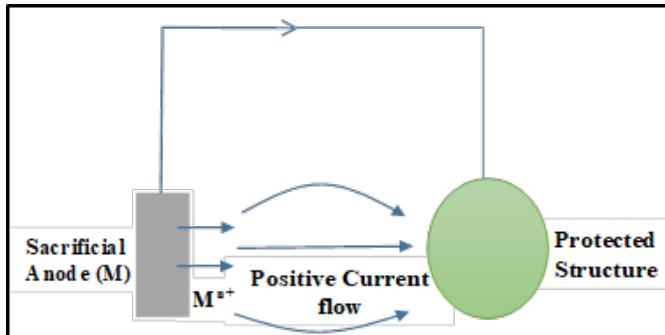


Figure 4 The sketch of a typical SACP.²

The impressed current cathodic protection (ICCP) system

Figure 5 is a sketch of the ICCP system, which comprises reference electrodes, a rectifier, a controlling unit, and anodes. The figure also shows a control unit. An external DC power source is used by this system to create electrons. The requisite positive current is supplied by the rectifier and is delivered by the anodes to the structure that is to be protected. The reference electrodes monitor the protection level during this process, and the controlling unit adjusts the amount of current that is generated as a direct result of this monitoring. At some point in time, the structure of the metal will become negatively charged.² It is generally acknowledged that the steel is cathodically shielded when it has a potential that is -800 mV or higher negative. This value serves as the threshold for this standard. The ICCP system's corrosion-resistant qualities may be advantageously utilized by any vessels, offshore platforms, pipelines, ports, and steel piles. Nevertheless, despite the many benefits that ICCP offers, there are still some drawbacks, which are as follows:

- I. It is essential to have skilled laborers.
- II. There must be a steady supply of the requisite electrical current.
- III. The electric current must be made to go in the right direction at all times.
- IV. If permanent anodes are utilized, the installation of current shields will be necessary.

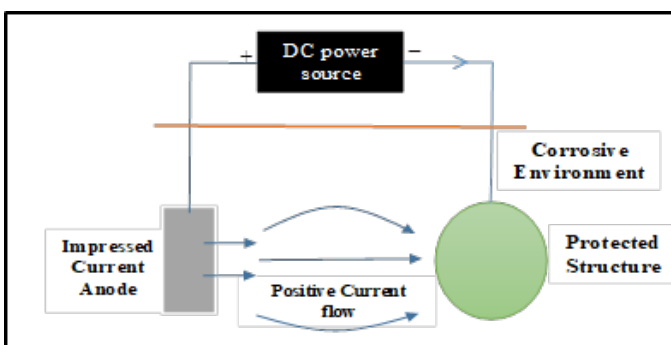


Figure 5 The sketch of ICCP.²

As an added benefit, installing a power supply in an SACP system is unnecessary. This technique also requires very little maintenance

and can be used immediately. However, despite the lower initial costs, long-term operating costs are higher than with an ICCP system. ICCP systems are inappropriate for many older ships because their remaining service lives are so short that adding one is not worth it. Installing an ICCP system on these ships would be prohibitively expensive, so it is preferable to use a SACP system. The low cost of SACP makes it ideal for short-term operations.

Combined use of both CP and coatings for ships

Over time, a painted covering is prone to decomposition. It is common for the system's characteristics to fall below the requirement after a specific amount of time in service. This leads to a significant remodeling expense in the long run. Cathodic protection, on the other hand, has the potential to enhance system security. It is possible to add anodes to a ship twice in its lifetime. One alternative is to insert the anodes during the vessel's fabrication. The anodes can be installed after a certain amount of time. Corrosion prevention works best when anodes are installed early in the shipbuilding process, according to previous experience. "If a flaw occurs, the calcareous deposit will precipitate immediately."² Once corrosion has progressed to the point where the anodes are needed, a coating of calcareous deposit and pre-existing rust forms on the steel's surface. Compared to the above scenario, the protective characteristic of this layer will be less, but it will still safeguard the underlying material. Additionally, it should be noted that a perfect coating applied to a hull consumes hardly any anodes. When the coating deteriorates, the anodes will only serve as a safety net and begin working immediately. Figure 6 depicts the effect of cathodic protection on the coating as support. A CP system can be installed following a coating failure, although this is a short-term and costly option. The combination of CP and coating from the building stage is the most efficient and cost-effective corrosion protection method, as shown in the figure. To achieve appropriate cathodic protection, the paint system's compatibility with the cathodic protection must also be considered in the CP design. Tests like ASTM G8 are used to evaluate the compatibility of the coatings.

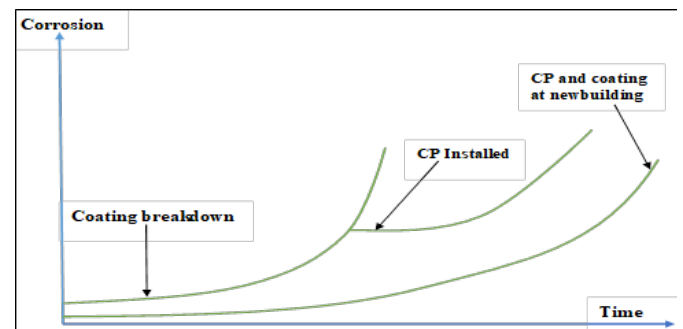


Figure 6 Corrosion vs. time curves in different corrosion protection methods.²

Challenges, future outlook, and inference

Metals are distinguished by their superior intrinsic qualities, which include strong electrical conductivity, strength, flexibility, and brittleness. As a result, metal is frequently used in structural, engineering, electrical, and electronic applications.²⁹ Metals, however, can react with their surroundings and get rusted. It is common for the corrosion extent and underlying mechanism to be determined by the corroding environment. Corrosion weakens mechanical properties and may pose health and environmental risks. As a result, there has been a recent uptick in interest in and focus on corrosion research.³⁰ Cathodic prevention (CP) and coatings such as polymers have been utilized as corrosion inhibitors, although their effectiveness is limited.³¹ Polymeric nanocomposite coatings and corrosion protection films

have piqued researchers' interest. Future research in this area should focus on several aspects of these materials. Nanofiller distribution in the matrix has a significant impact on the coating's corrosion resistance. The uniform distribution of nanoparticles in a polymer matrix is difficult to achieve. It is possible to improve the dispersion by employing a proper dispersion method. Polymerization and quick sonication techniques used *in situ* may be effective in this area as well.

Furthermore, particle size, shape, aspect ratio, content, and surface characteristics all play an important influence in the dispersion of nanofillers. Better corrosion protection can also be achieved by increasing the thickness of better-dispersed coatings. In addition to temperature and ambient conditions, coatings' corrosion performance is directly affected by these elements. Nanocomposite coatings may be better able to tolerate temperature changes and the aging effect than neat polymers. When compared to pure polymers, the scratch and impact resistance of polymer coatings with nanofiller is much higher. Consequently, the mechanical/wear strength and corrosion performance of nanocomposite coatings are delicately balanced. The connection between matrix and nanofiller may be improved by including functionalized nanoparticles into polymers.³² It is also critical to understand the anti-corrosion mechanism and adhesion capabilities supplied by a certain nanocomposite. In order to better understand the adsorption energies of corrosion inhibitors, thermodynamics and molecular dynamic simulations should be used. For nanocomposites to be non-wettable, rough, and resistant to corrosion, contact angle, salt spray test, and scale inhibition must be conducted. Improved anti-corrosion properties and mechanisms will be required for future aircraft applications, which necessitate novel approaches. Researchers must keep looking for ways to improve the mechanical and transport capabilities of nanomaterials. Carbon nanotube-based coatings may help future fuel cells maintain strong conductivity while increasing the hydrophobicity of their bipolar plates. In a fuel cell, nanocomposite coatings could take the role of chromium and other potentially harmful substances. For the future generation of fuel cell bipolar plates, polymer/CNT and polymer/graphene offer good corrosion-resistant and strength capabilities. To replace biomedical materials, sophisticated nanocomposite materials such as artificial bone and tissue implants are needed. Research on green nanoparticles' effect on the environment has recently opened new doors in corrosion research for green polymeric materials. Environmentally friendly nanomaterials should look at better structural and corrosion resistance qualities.

Conclusion

The corrosive materials need to be prevented with high strength. An overview of cathodic protection and coating techniques for minimizing the corrosion of aquatic environment has been provided in this review. Cathodic protection can be done the two primary cathodic protection methods ICCP and SACP which have been discussed in separate sections. Additionally, a number of articles have been studied the application of coatings to prevent corrosion. Coatings, including ceramic coatings, polymer coatings, electrodeposition of nano-crystalline materials, and self-assembled nano-coatings, are a very effective technique for protecting ships. Each individual method has its own benefits and drawbacks whereas the combination of CP and coatings is the most effective and popular method of corrosion prevention. This combination can provide very good protection over a long period of time. There have huge research gaps on the marine corrosion minimization for long time. The future scholar are researching on it. For all types of marine structures, these efforts are expected to result in long-term prevention of fouling and corrosion, while cutting down on necessary repairs.

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Conflicts of interest

The author declares there is no conflict of interest.

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