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Naval Corrosion--Causes and Prevention

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Abstract

Year upon year the cost of naval corrosion has increased until it is estimated today at 4 % of the Gross National Product. An enlightened approach to materials selection, protection and corrosion control is needed to reduce this burden of wasted materials, wasted energy and wasted money. This paper have been compiled to help marine designers, engineers, and equipment users, understand the causes of naval corrosion and the way in which protective systems and more resistant materials can be used to reduce or entirely eliminate sea water corrosion problems.

Keywords: Anticorrosion coatings; Cathodic protection; Coatings; Corrosion; Corrosion protection; Hulls..

Introduction

Many different types of destructive attack can occur to structures, ships and other equipment used in sea water service. The term 'naval corrosion' describes the majority of the most troublesome problems encountered in contact with sea water, but atmospheric corrosion of metals exposed on or near coastlines, and hot salt corrosion in engines operating at sea or taking in salt-laden air are equally problematical and like aqueous corrosion require a systematic approach to eliminate or manage them.

Long-term preservation is a difficult objective for anything that resides in an exposed environment, and this is particularly true for ships in the naval environment. Wooden ships are often considered the most problematic due to insects, funguses, bacteria, and marine animals. Yet iron ships, while not subject to such organic attack, are hardly less temporary. When man produces iron to build a ship he is taking a relatively stable substance - iron ore - and purifying it until it becomes an unstable substance, so unstable in fact that it wants to decompose in the presence of oxygen. A nearly universal element, oxygen is hard to get away from on this planet and, as if that is not bad enough, these creations is then tossed into one of the most corrosive environments there is - sea water.

For naval applications, mild steel remains the number one metal for constructional purposes by virtue of its relatively low cost, mechanical strength and ease of fabrication. Its main drawback is that is

corrodes easily in seawater and unless adequately protected, rapidly loses strength which may result in structural failure

Corrosion Mechanism

In general terms corrosion can be defined as the spontaneous reaction between a material and its environment which results in the degradation of that material. To be more specific, metallic corrosion is the oxidation of the metal at the metal/environment interface. This reaction subsequently results in a deterioration in the mechanical properties of the metal.

The majority of metals in nature are found in their mineral state, i.e. in their stable oxidised condition as oxides, chlorides, carbonates, sulphates, sulphides, etc. The extraction of a metal from the appropriate mineral involves a reduction process in which a great deal of energy is absorbed. As a consequence of this large energy input the metal is in a high energy condition and will endeavour to return to its former stable, oxidised, low energy state as quickly as environmental conditions will allow. It is the energy difference between the pure metal and its oxidised forms which is the driving force for corrosion.

Mild steel is an impure, heterogeneous material. This is a major factor contributing to its poor resistance to corrosion. The presence of what are referred to as anodic and cathodic sites on the steel surface and their reaction with oxygen and

water results in the transformation of a metal atom to a metal ion by the loss of electrons.

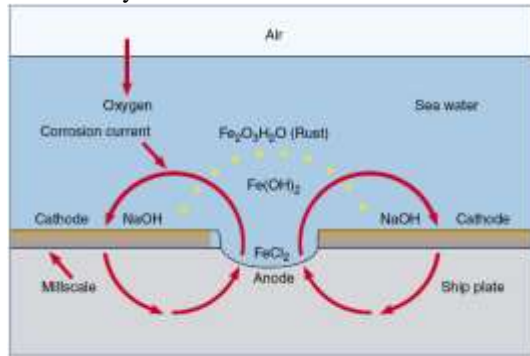


Figure 1. Corrosion mechanism (AkzoNobel)

Causes Of Naval Corrosion

Naval environmental conditions that accelerate corrosion and degradation include moisture, salt water, oxygen, ultraviolet light, and high temperatures. These ambient conditions may not only significantly accelerate corrosion, but they may also degrade protective coating systems.

Moisture: Moisture in naval air often condenses on naval structures where it accelerates corrosion and deteriorates coatings. Thus, a coating system is required that will be impermeable not only to atmospheric moisture but also to water in which these structures may be immersed.

Salt: Salt is electrically conductive and thus promotes corrosion which is an electrochemical reaction. Because of the concern for salt contamination of cleaned surfaces prior to application of marine coatings, conductivity or other analyses for salt contamination are conducted to see if further cleaning is necessary before coating. Winds and waves can carry seawater onto steel decks, and winds can blow seawater spray onto all elevations of marine structures.

Oxygen: Surface marine waters are relatively heavily oxygen overloaded compared to seawater at a greater depth, and oxygen greatly accelerates corrosion. Thus, corrosion of immersed steel naval structures is usually greatest in tidal areas.

Ultraviolet light: The sun's ultraviolet light can deteriorate some types of protective coatings used in corrosion control. Epoxy coatings are particularly susceptible to this type of deterioration. Fortunately, much of the coatings on maritime structures are not exposed to sunlight most of the time.

High temperatures: The rate of corrosion of steel almost doubles for every 10° C rise in temperature.

Types Of Naval Corrosion

Localised Corrosion

In naval environment stainless steel will never corrode uniformly. Corrosion is localized, i.e. crevice corrosion. Localized corrosion often is being promoted by a biofilm. Crevice corrosion is a major problem in naval environment because of the low resistivity of the water (seawater resistivity is about 0.35 Ohm•m). Even 6% Mo SS at 30°C can suffer crevice corrosion in seawater.



Figure 2: Crevice corrosion in seawater cooler (Wraglen p.179)

Stress corrosion cracking

At temperatures above 60°C stainless steel 304 and 316 are sensitive to chloride cracking. Oxygen must be present, which means that produced water from oil or gas production does not cause stress corrosion cracking, even at high temperature. Duplex stainless steel and 6% Mo are much less sensitive to this phenomena, however under extreme conditions, i.e. high temperature and high stresses and cold deformation it may occur. Sometimes stress corrosion cracking occurs from the outside; especially longitudinal welded pipes at higher temperature are sensitive to this type of 'corrosion under insulation'.

Galvanic Corrosion

Like crevice corrosion, the low resistivity of seawater also promotes strongly galvanic corrosion. Galvanic corrosion is seen as a major concern for materials performance in naval environment. A well known example is bronze bearings in ships, where sacrificial zinc anodes need to protect the steel hull for galvanic corrosion. Also stainless steel can suffer galvanic corrosion, or it causes galvanic corrosion to other, less noble, alloys.

Oxidation

All metals are subject to oxidation. Oxidation is the natural process of the metal returning to its base elements by combining with oxygen from the atmosphere or the local

environment, for example, oxygen from the surrounding seawater. Some metals use the oxidation process to protect themselves, while the process destroys other metals. Rusting is the common name for the metallic flaking of steel and iron, however it is still oxidation.



Figure 3. A large rust patch was started by water getting under the protective paint work at the edge of the hole and has resulted in substantial damage.

The effects of oxidation on metals such as mild steel are immediately apparent and are very destructive to the metal component. Metals such as stainless steel, titanium and anodised aluminium are protected from further destruction by the oxidation process as they form a thin oxygen-impervious layer over the surface. As long as a supply of oxygen is available from the atmosphere or the surrounding environment, for example seawater, the thin oxidation layer is self-healing if subjected to scratching or abrasion.

Cavitation

Cavitation occurs when the local water pressure falls to near zero. This causes cavities or bubbles in the water. If the bubbles collapse on the surface of a metal component, such as a propeller blade, the implosion is so violent that the surface is mechanically attacked and some of the metal is plucked from the surface, resulting in a pit on the surface.

Some metals have a greater resistance to attack from cavitation than others. The more noble metals are much more resistant to cavitation attack than metals such as mild steel. As a general guide, cavitation resistance is increased with the hardness of the metal.



Figure 4. The pitted area closed to the blade tip is caused by cavitation

Corrosion by Seawater

Corrosion by sea water, *naval corrosion*, is an electrochemical process, and all metals and alloys when in contact with sea water have a specific electrical potential (or corrosion potential) at a specific level of sea water acidity or alkalinity - the pH.

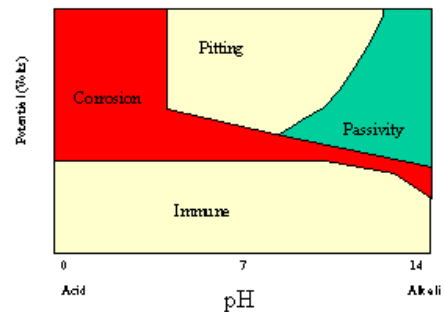


Figure 5. Region of corrosion

This typical diagram shows the regions where the metal will freely corrode; the region of passivation where stable oxide or other films form and the corrosion process is stifled; the region of pitting corrosion where the corrosion potential of the metal exceeds that of its oxide; and the region of immunity where the metal is normally fully safe to use. More resistant alloys mean less corrosion, metals like gold platinum and tantalum can resist virtually all corrosion, but for marine service the final choice will always be a compromise with cost.

Pitting corrosion

The main characteristic of this type of corrosive attack is that it is extremely localized and steel penetration can be deep in relation to the area under attack. This is one of the most dangerous forms of corrosion and can be most intense on millscaled or coated steel.



Figure 6. Pitting Corrosion

Pitting frequently occurs in metals that use an oxide layer to protect themselves. Metals such as stainless steel tend to pit in seawater if the mechanism that maintains the film breaks down for any reason. The hindering of the self-repairing film is usually the result of changes in the environment over the surface of the metal. Some examples include: differences in temperature, variations in the oxygen supply over the surface, or an uneven flow of water over the surface of the metal component.

Bacterial corrosion

Also referred to as micro-biological corrosion or anaerobic (without oxygen) corrosion, this type of corrosion may occur if local operating conditions support bacterial activity.



Figure 7. Bacterial Corrosion

Effects Of Naval Corrosion

The Underwater Hull

The portion of an iron ship most vulnerable to corrosion is the underwater hull, and this is where corrosion can have the most terrible effect. Along with coatings, an effective weapon for preserving the underwater hull.

Topsides

The impressed current system will not, however, protect a ship's topsides, which must continue to rely on anti-corrosive coatings. The area of greatest concern is the wind-and-water line, where

the combination of wind and splashing sea water invariably causes severe corrosion and wastage (this is often the thinnest area of a hull and where leaks usually begin).

Bilges

Bilges are a common corrosion problem because they remain damp. If sloshing bilge water is present, the lower interior of the hull can suffer corrosion rates as severe as those of the wind-and-water line.

Factors which aggravate Naval corrosion

Sea water, if not destructive enough on its own, has several powerful allies assisting the breakdown of metals and non metals alike. Living allies in sea water also enhance its destructive power. Microbiological organisms, clusterings of weed, limpets as well as deposits of sand, silt or slime not only exclude oxygen but often create locally corrosive conditions under these deposits which aggravate attack. Coatings and composite structures can experience rapid degradation. Sulphate reducing bacteria, left undisturbed in marine silt or mud deposits, will produce concentrations of hydrogen sulphide which are particularly aggressive to steel and copper based alloys.

Controlling the Naval corrosion

Protection by painting

Painting the ship isolates the steel from the corrosive media. The paint must also be resistant to the naval environment and the application strictly controlled to ensure full and effective coverage of the steel. Regular inspection and repair of the coating may be necessary to achieve reliable and lasting protection.

Cathodic protection

Sacrificial anodes enable the potential of the system to be changed and will provide temporary protection to steel exposed by wear or damage of the protective coating. Systematic location of the anodes is critical to their overall effectiveness. They must likewise be regularly serviced and replaced when spent.

Inhibition

Inside the ship inhibitors which modify the corrosion process may effectively prevent attack in bilges and other areas where sea water will collect and stagnate. Reliable systems to monitor and maintain the correct concentration of the inhibitor are an essential aspect of this prevention strategy.

Galvanic corrosion

In practice ships are rarely made just from a single metal or alloy. Modern engineering systems use a wide range composites and of metals and alloys, some more, some less resistant to marine corrosion than steel. The more resistant alloys may aggravate the attack on adjacent unprotected less resistant alloys. This galvanic effect is not always confined to separate metals, some alloys improperly processed in manufacture or fabrication carry the seeds of their own destruction in their microstructures which contain phases so widely separated in corrosion potential that without further overall protection by coating, anodes or inhibitors, selective attack of the less resistant phase is inevitable.

Using corrosion resistant alloys

Depending on design factors including the severity of the application and the levels of strength, damage tolerance, reliability, safety and life required, components and systems can be manufactured from composites, or from stainless steels of increasing resistance, or from copper based alloys such as cupro-nickel or nickel aluminium bronze, nickel alloys or titanium, using these materials exclusively or in conjunction with each other or less resistant alloys. Protection for the least resistant alloys by anodes, or impressed potential, requires careful control of the system potential to avoid the possibility of hydrogen uptake by the more highly corrosion resistant alloys such as super duplex steel and titanium.

Monitoring the Rate of Corrosion

To determine the degree of success of preservation efforts, the rate of corrosion and attendant wastage of a vessel should be monitored closely. Visual inspections should be carried out on a routine basis, with particular attention to some of the problem areas noted above. Measuring shell plate thickness is probably the single most important method for establishing the overall condition and rate of deterioration of an iron hull. The tool of choice for this is the ultrasonic caliper, which measures the thickness of metal by sending an ultrasonic signal through the material. These tools have become cheaper and more sophisticated in recent years and would be a useful addition to the maintenance tool kit of any large vessel. The process of ultrasonic testing (UT) is straightforward, but difficulties are sometimes encountered when attempting to measure some types of malleable iron plate due to imbedded layers of silicone slag. These layers tend to bounce the signal back, thereby giving only a partial reading.

An experienced operator can learn to accurately decipher these signals and some newer UT gauges can be calibrated to overcome this problem entirely.

Conclusion

Key factors in prevention of marine corrosion are design, selection of materials, construction, use and maintenance. Failings in any one of these may lead to a total failure to prevent attack, which once started may cost far more to correct or eliminate than any notional savings on materials achieved at the outset. In a recent survey corrosion was found to be responsible for 30% of failures on ships and other marine equipment.

There are five main methods for controlling the tendency of metals to corrode in sea water:

- By isolation of the corroding metal from the sea water by painting, or other coating
- Changing the potential of the metal to a point where corrosion ceases - by impressed voltage or coupling to a sacrificial anode.
- By making the metal passive, using corrosion inhibitors.
- Changing the pH of the local environment by chemical dosing.
- Use of non metallic materials including composites may offer a solution for some applications.
- And finally by making a change to a more corrosion resistant material.

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