Non-linear Corrosion Model for Immersed Steel Plates Accounting for Environmental Factors

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ABSTRACT
The effects of different marine environmental factors on the corrosion behavior of steel plates totally immersed in salt water are studied. A new corrosion wastage model is proposed, based on a non-linear time-dependent function. This model accounts for the effects of various environmental factors, including salinity, temperature, dissolved oxygen, pH and flow velocity. A numerical example is illustrated for ships trading in different routes in the Pacific Ocean.

KEY WORDS: corrosion, deterioration, steel, wastage

INTRODUCTION
Corrosion is one of the most critical degrading mechanisms that pose direct threat to the structural integrity of ships and offshore structures. In the last two decades, various theoretical approaches have been suggested to determine the strength and reliability of corroded structures (e.g. White, and Ayyub, 1992, Shi, 1993)

A ship’s hull may collapse when bent globally as a free-free beam. The most critical failure mode for a ship is often the hull girder collapse in sagging condition, when the deck panels are subjected to compressive loads. Corrosion wastage aggravates the situation as the bending stress increases and the buckling and ultimate strength of deck decreases.

Often, general corrosion has been assumed to vary linearly with time. The uncertainties in predicting residual strength of corroded structures are mainly dependent on the variability in remaining plate thickness (Guedes Soares 1988, 1997).
This linear model of corrosion growth was adopted in early studies of structural reliability considering corrosion wastage, such as Hart et al. (1986), Guedes Soares and Ivanov (1989), Wirsching et al (1997) adopting a time dependent reliability formulation, and Guedes Soares and Garbatov (1996) introducing a time variant reliability formulation.

It has been realized that the quality of an analysis on collapse and reliability depends to a large degree on the corrosion model. As a result, there has been a need to develop more refined corrosion wastage model.

Southwell et al., (1979) proposed linear and bilinear models for corrosion wastage that were considered appropriate for design purposes. Melchers, (1998) suggested a steady state trilinear and another power function for corrosion wastage. Yamamoto and Ikegami, (1998) proposed a three-stage corrosion model based on analyzing data collected from plate thickness measurements.

Guedes Soares and Garbatov, (1999) proposed a non-linear model that describes the growth of corrosion wastage in three phases: durability of coating, transition to visibly obvious corrosion with an exponential growth, and the progress and leveling of such corrosion. Several authors have proposed some variants of this model or have compared it with other modifications, as described hereafter.

Sun and Bai, (2001) used the same mathematical formulation to describe the corrosion rate instead of the corrosion wastage. Qin and Cui, (2002) assumed that the corrosion rate is defined by equating the volume of pitting corrosion to uniform corrosion. The corrosion model of Paik et al., (2003) also categorizes the corrosion behavior into three phases. The model of Ivanov et al., (2003) assumes that the transition phase of non-linear thickness reduction increases with time by a linear relation.

A different probabilistic model is currently being developed by Melchers, (2003c), which divides the corrosion process into four stages: initial corrosion, oxygen diffusion controlled by corrosion products and micro-organic growth, aerobic activity with limited food supply, and anaerobic activity.

Wang et al., (2003) have collected a very large databank of measurements of thicknesses of ships in service. They have used it to derive regression relations of corrosion wastage as a function of time that provide a consistent fitting to the collected thickness measurement data. Garbatov et al., (2005) have fit the model of Guedes Soares and Garbatov, (1999) to the data from Wang et al., (2003) and found that this nonlinear model represents the data very well. They also derive the duration of the coating system, or in a broader sense, the time to initiation of the corrosion process.

The models of corrosion wastage, referred up to now, assumed time as a unique parameter, and defined various corrosion phases. However, none of them accounts for the influences of contributing environmental factors.

To improve the corrosion models, it is necessary to not only account for time but also include contributing variables. Some of environmental factors have been identified as important for the corrosion wastage of steel structures by Melchers, (2003b)

It has been recognized that corrosion is a very complex phenomenon and influenced by many factors. Identifying key issues that can lead to corrosion can not be achieved through only statistical investigations of corroded aging ships. There is a need to develop models based on the corrosion mechanisms and to combine them with the corrosion wastage databases to achieve a better understanding and also more proper prediction of corrosion in marine structures.

The main objective of this work is to define the impact of environmental factors on the corrosion behavior of steel plates totally immersed in water and to propose a new model to account for those factors. The focus is placed on external shell plating below the lowest waterline, i.e., the bottom shell and side shell below the lowest waterline, which are always in contact with water. Prediction of corrosion wastage is based on the theory of immersion corrosion including the various contributing environmental factors.

The need to emphasize that the model applies only to the part of the hull that is immersed is because the hull above the waterline corrodes as a result of marine atmosphere, but not being in direct or continuous contact with the water. The environmental factors will act in a different way.

A new corrosion wastage model is presented by generalizing the non-linear time dependent corrosion model of Guedes Soares and Garbatov (1999) to account for the effects of salinity, temperature, dissolved oxygen, pH and flow velocity of water. A numerical example is also presented that models corrosion in different ships navigating on different routes through the Pacific Ocean.

DEVELOPMENT OF IMMERSION CORROSION MODEL FOR BOTTOM AND SIDE SHELL

Corrosion wastage involves the interaction between a metal or alloy and its environment and is affected by the properties of both the material or alloy and the
environment (Kutz, 2005). Corrosion can take different forms, for example: general corrosion, pitting corrosion, stress corrosion cracking, corrosion fatigue, fretting corrosion, filiform corrosion, weld corrosion, bimetallic corrosion and bacterial corrosion. In general corrosion, which is the most common form of corrosion, the wastage is spread over the surface of the metal. Through the different forms of corrosion, the uniform general corrosion is the type that is considered here.

The immersion corrosion model deals with the corrosion mechanisms in steel that is continuously in contact with water. This model can be used to describe the behavior of bottom shell and side shell under the lowest waterline of vessels.

The development of a corrosion model is not based solely on theory, because corrosion is a function of many variables and uncertainties. Steel hulls operate in a complex environment. Water properties such as salinity, temperature, oxygen content, pH level and chemical composition can vary according to location and seasons. Time in ballast or cargo, tank washing and inerting, corrosion protection effectiveness and component location and orientation have a great effect on the corrosion phenomena.

Also the inside face of the plates will be exposed to aggressive environments existing in cargo tanks. Significant corrosion of elements in ballast tanks adjacent to heated cargo tanks or tanks with consumables is also possible. However this work does not discuss corrosion on the surface that is inside tanks and only treats the surface that is totally immersed in water.

The environmental factors that affect on corrosion behavior of steel plates permanently in contact with water are salinity, pH value, temperature and flow velocity of water.

The process of corrosion initiation coated surfaces is modeled through three steps. The first step involves penetration of water particles through the coating, since it is considered as a semi-permeable membrane. The second step includes the formation of a two-dimensional invisible oxide monolayer. The third step considers the formation of discrete nuclei of three-dimensional oxide on the surface which expands laterally at an ever-increasing rate. The coating effective life is considered to be the summation of the period necessary for the water particles to penetrate the coating until reaching the metal surface, plus the period necessary for forming the two-dimensional oxide monolayer.

**Influence of Salt Content**

The variations in the chemistry of seawater tend to take place slowly (over time periods of 3 to 6 months) and over horizontal and vertical distances that are large in comparison to the dimensions of most marine structures. Such gradual changes may produce an equally gradual change in the corrosion rate of structural materials with season and location, but they are unlikely to produce sharp changes in either the corrosion mechanism or rate.

The major chemical constituents of seawater are the same worldwide. The salt content of the waters of the open sea, away from shore influences, is remarkably constant.

The salt content is usually expressed as $S\%o$, a convention which approximates to the weight in grams of dry salts contained in 1000 g of sea water. The salt content of the waters of the open sea is on average 35 parts per thousand, and is rarely outside the range of 33 to 38 parts per thousand. The concentration of salts in seawater can also be expressed in terms of the chloride content. The salinity can be related with Chlorinity by the empirical relationship $Salinity = 0.03 + 1.805*Chlorinity$, established by the International Council for the Exploration of the Sea (ICES).

According to the classical experimental work by Mercer and Lombard, (1995), the effect of small changes in salinity appears to be marginal for steels in quiescent conditions. Melchers, (2003c) also states that salinity reduction does not necessarily mean a reduced corrosion. Buzovkina et al., (1990) found that a decrease in salinity from 35 percent to 20 percent leads to an increase in corrosion rate by about 30 percent for carbon steel. This can be attributed to the salinity variations in natural seawater being accompanied by other changes, such as oxygen solubility and carbonate solubility. A ship can be subjected to salinity variations when trading trough ocean areas with important differences of temperature or when approaching ports specially in river entrances.

The relation between the corrosion rate correction factors for salinity and salinity ratio, based on the results presented by Uhlig and Revie, (1985) (see Figure 1), can be modeled by a truncated log-normal function as follow:

$$f(S_r) = \frac{\gamma}{\varepsilon \sqrt{2\pi(S_r+\delta)}} \exp \left[ -\frac{\ln(S_r+\delta) - \beta)^2}{2\varepsilon^2} \right] \quad S \geq 0 \quad (1)$$

where $f(S_r)$ is the corrosion rate correction factor for salinity (corrosion rate at actual salinity / corrosion rate at nominal conditions), $S_r$ is the salinity ratio (actual salinity / nominal salinity), $\gamma$ is a constant introduced as a magnification factor to adjust the values of the corrosion rate correction factor ($\gamma \geq 0$), $\delta$ is a constant introduced to adjust the truncated portion ($\delta \geq 0$) and $\beta$, $\varepsilon$ are constants corresponding to mean value and standard deviation of the distribution. It must be
stressed that this function has been chosen just to represent the form of the curve and not as a probability density function.

When the value of the salinity ratio is \( S_r = 1 \), the actual salinity equals the nominal value and the actual corrosion rate is equal to the nominal one. To control Equation (1), some constraints are introduced at the nominal state when \( S_r = 1 \) and \( f(S_r) = 1 \) and as a result of that, Eqn. (1) is limited by:

\[
\gamma = \varepsilon \sqrt{2\pi (1 + \delta)} \exp \left[ \frac{\ln(1 + \delta) - \beta^2}{2\varepsilon^2} \right]
\]  

(2)

By differentiating the corrosion rate correction factor with respect to salinity ratio and equating the result to zero, the salinity ratio \( S_{\text{max}} \) corresponding to maximum corrosion rate correction factor can be obtained as follow:

\[
\frac{d}{dS_r} f(S_r) = 0 \quad \Rightarrow \quad S_{\text{max}} = e^{\beta - \varepsilon^2} - \delta
\]  

(3)

Since the maximum corrosion rate corresponds to salinity, \( S_{\text{max}} \) of 3%, then the maximum correction factor is also corresponding to this value:

\[
\frac{S_{\text{max}}}{S_{\text{nom}}} = \frac{3}{S_{\text{nom}}} = S_{\text{max}}
\]  

(4)

Taking into account Equations (3) and (4), Equation (1) will be constrained by:

\[
\delta = e^{\beta - \varepsilon^2} - \frac{3}{S_{\text{nom}}}
\]  

(5)

where \( S_{\text{nom}} \) is the nominal salinity value. The effects of different parameters are shown in Figures 2 and 3.

**Figure 1** Relative corrosion as a function of NaCl

**Figure 2** Corrosion rate correction factor as a function of salinity and \( \varepsilon \), Eqn (1)

**Figure 3** Corrosion rate correction factor as a function of salinity and \( \beta \), Eqn (1)

### Influence of Temperature

The temperature of the surface waters of the oceans tends to vary directly with the latitude, and its range is from about -2°C at the poles to 35°C on the equator. In the tropics the annual variations are smaller than those in the temperate zones where their values are around 10°C (Chandler, 1985). In open systems (as in seawater), where dissolved oxygen is able to escape, the rate of corrosion increases with temperature to about 80°C and then falls to a very low value at the boiling point (Uhlig and Revie, 1985). The falling off of corrosion above 80
C is related to decreased solubility of oxygen in water (Uhlig and Revie, 1985).

In a closed system, oxygen cannot escape and the corrosion rate continues to increase with temperature. If the dissolved oxygen concentration remains constant, the corrosion rate of low-carbon steel in seawater will approximately double for every 30°C increase in temperature (Korb and Olson, 1987). In one series of tests carried out in seawater at different temperatures, the corrosion rate of carbon steel at a temperature of 25°C was nearly double than that at 10°C (Chandler, 1985).

Melchers, (2001) divided the seawater into moderate and low temperature seawater. In moderate temperature seawater, the first phase of corrosion is controlled by electrochemical kinetics, and the corrosion rate doubles for every 10°C increase in temperature. In the diffusion-controlled phase, increased water temperature reduces the solubility of oxygen in seawater. In turn, this will reduce the ability for oxygen to diffuse through the corrosion product layer. Under these conditions, a rise in temperature of about a 30°C is required to double the corrosion rate (Ijsseling, 1989). Below about 5°C, corrosion rate appears to become temperature independent. Mercer and Lumbard, (1995) using real and artificial seawater, found that corrosion increases with temperature above 10°C, gradually and then sharply reduces as the temperature approaches boiling point. In low temperature seawater, corrosion might tend to increase with temperatures lower than about 5°C – 10°C (Melchers, 2003b), according to short-term laboratory observations by Mercer and Lumbard, (1995).

Fontana, (1987) has indicated that temperature rises caused exponential rise in corrosion rate. An almost negligible temperature effect is followed by a very rapid rise in corrosion rate at higher temperatures. LaQue, (1975) illustrated that higher temperature resulted in increased corrosion of steel in seawater in the absence of the supplementary effects of marine organisms.

Open ocean temperature variations make corrosion rates in tropical surface waters about twice those in the Polar Regions or in deep water. Corrosion rates are usually higher in warm surface waters than in cold deep waters (Korb and Olson, 1987).

Based on the experimental evidence, a correlation factor is proposed to adjust for the effect of temperature. It is assumed that corrosion rate is a linear function of temperature for seawater temperatures below 80°C, as shown in Figure 4:

\[ f(T_c) = c T_c + d \]  \hspace{1cm} (6)

where \( f(T_c) \) is the corrosion rate correction factor for temperature (corrosion rate at actual temperature / corrosion rate at nominal conditions), \( T_c \) is the temperature ratio (actual temperature / nominal temperature), \( c \) is the constant representing the slope of the \( f(T_c) - T_c \) relationship and \( d \) is the constant represents the \( f(T_c) \) value at zero \( T_c \).

![Figure 4 Corrosion rate correction factor as a function of temperature](image)

When the value of the temperature ratio \( T_c = 1 \), the actual temperature equals the nominal value and the corrosion rate is equal to the nominal one. The following boundary conditions may control Equation (6) at nominal conditions when \( T_c = 1 \) and \( f(T_c) = f(T_c) \). Then Equation (6) can be written as:

\[ f(T_c) = (1-d) T_c + d \]  \hspace{1cm} (7)

The effect of parameter \( d \), is indicated in Figure 4.

**Influence of Dissolved Oxygen**

The concentration of dissolved oxygen is by no means solely a function of temperature; it is also affected by the degree of movement of the water, the length of time it has been in contact with atmosphere and by biological activity. Through photosynthesis, the plants growing in the surface layers of the sea can cause a considerable increase in oxygen concentration, while the activities of some bacteria can reduce it to zero (Chandler, 1985).

The surface waters of the ocean are in equilibrium with the oxygen in the atmosphere at a specific temperature. Two sets of conditions, however, can lead to the waters becoming substantially supersaturated with oxygen. The first of these conditions is oxygen production due to photosynthesis by microscopic marine plants. During high growth periods, intense photosynthesis can produce concentrations as high as 200% saturation for periods of up to a few weeks. Such oxygen super
saturation is most often found in near-shore regions as a transient phenomenon. The second condition that may cause oxygen super saturation is the entrainment of air bubbles due to wave action. This factor usually will not cause super saturations greater than about 10%.

In contrast, deep waters are often under saturated because of the consumption of oxygen during the biological oxidation of organic matter. The oxygen profiles for the open Atlantic and Pacific stations both go through a minimum at intermediate depths and increase again at great depths. In the Atlantic Ocean, the surface oxygen concentrations are usually lower. In addition, the oxygen concentrations in the deep Atlantic are higher than those in the deep Pacific, and they can be even higher than those in the Atlantic surface waters (Korb and Olson, 1987).

Oxygen varies with temperature from about 8.0 ml/l for surface waters in the Arctic to around 4.5 ml/l in the tropics. In the Atlantic Ocean a minimum value of about 1-2 ml/l is found at depth of 200-1000 m. However, at a depth of 1500 m the oxygen concentration increases to 5-6 ml/l, near that of the surface layers and it remains fairly constant below this depth (Chandler, 1985). The depth of the oxygen minimum ranges from 400 m in the equatorial eastern Pacific to over 2400 m in the central south Pacific. The concentration of oxygen at the depth of the minimum ranges from 0.01 to 0.40 mg.atm/L (Korb and Olson, 1987).

The solubility of oxygen in seawater varies inversely with both temperature and salinity, but the effect of salinity is greater. If the absolute temperature $T$ $(^\circK)$ and salinity $S$ $(\%)$ are known, the solubility of oxygen can be calculated from the relation:

$$
\text{ln}(O_2) = A_1 + A_2 \left( \frac{100}{T} \right) + A_3 \ln \left( \frac{T}{100} \right) + A_4 \left( \frac{T}{100} \right) + S \left[ B_1 + B_2 \left( \frac{T}{100} \right) + B_3 \left( \frac{T}{100} \right)^2 \right]
$$

(8)

where the oxygen concentration is given in milliliters per liter (mL/L), and the salinity $S$ is in parts per thousand $(\%)$. The constants $A_i$ through $B_3$ can be found in Kester, (1975).

The corrosion rate of active metals (for example, iron and steel) in aerated electrolytes such as seawater at constant temperature is a direct linear function of the dissolved oxygen concentration. In the absence of dissolved oxygen, the corrosion rate at room temperature is negligible (Uhlig and Revie, 1985). When oxygen and temperature vary together, as they do in the marine environment, the oxygen effect tends to dominate. The corrosion rate decreases with dissolved oxygen down to the oxygen minimum, then increases again with oxygen at greater depths, despite a continuing decrease in temperature (Korb and Olson, 1987).

Melchers, (2003a) has shown that there is a linear relationship between dissolved oxygen and rate of corrosion. Fontana, (1992) has proposed a schematic diagram showing the effect of oxygen and oxidizers on the corrosion rate.

Based on the mentioned results, the relation between the corrosion rate correction factor for dissolved oxygen and the dissolved oxygen concentration ratio is proposed as a linear relationship as shown in Figure 4:

$$
f(O_2) = a(O_2) + b
$$

(9)

where $f(O_2)$ is the corrosion rate correction factor for dissolved oxygen concentration (corrosion rate at actual oxygen concentration / corrosion rate at nominal conditions), $O_2$ is the dissolved oxygen concentration ratio (actual oxygen concentration / nominal oxygen concentration), $a$ is a constant representing the slope of the $f(O_2) - O_2$ relationship and $b$ is a constant representing the corrosion rate correction factor $f(O_2)$ at zero $O_2$.

When the dissolved oxygen concentration ratio is $O_2 = 1$ the actual dissolved oxygen concentration is equal to the nominal value and the actual corrosion rate is equal to the nominal one. For nominal conditions of $O_2 = 1$ and $f(O_2) = 1$, Equation (9) can be written as:

$$
f(O_2) = (1 - b) O_2 + b
$$

(10)

**Influence of pH**

The pH is defined as the negative of the base ten logarithm of the hydrogen ion activity, (Robinson and Stokes, 1959):

$$
\text{pH} = -\log_{10}a^+_{H} = -\log_{10}\gamma_{H}^{+}m_{H}^{+}
$$

(11)

where $a^+_{H}$ is the hydrogen ion activity, $\gamma_{H}^{+}$ is the hydrogen ion activity coefficient and $m_{H}^{+}$ = the molality (mol/1000 cm$^3$ of water).

Seawater is normally alkaline and the pH of the surface layers of the ocean, where the water is in equilibrium with the carbon dioxide of the atmosphere, lies between 8.1 and 8.3. The presence of large quantities of hydrogen sulphide tends to lower the pH value, i.e., the water becomes more acidic. A considerable photosynthesis activity of plants, which reduces the CO$_2$ content of the water, will raise the pH values (decreased H$^+$ contents) and the water will be more alkaline. The pH of seawater changes with temperature. Usually a rise in temperature leads to a reduction in the pH. In the open ocean the pH is usually below 8.0.
Melchers, (2003a) indicated that pH values change with water depth. The intermediate layers may sometimes become more acid due to the decomposition of organisms, which sink as they die off in the upper layers (Chandler, 1985). At greater depths, pressure increases and pH reduces due to thermodynamic considerations. A comparison of the corresponding pH and oxygen profiles reveals that the oxygen and pH minima are reached at the same depth for a given location (Korb and Olson, (1987).

In most cases, seawater is near neutral (4<pH<10), and pH no longer plays a direct role in corrosion in carbon steel. In this condition the oxide or the hydroxide layers tend to remain on the surface. In addition, the corrosion kinetics become independent of pH (Uhlig and Revie, (1985).

It follows, therefore, that so long as oxygen diffusion through the oxide layer is controlling, which is the case within pH 4-10, any small variations in the composition of steel and its heat treatment (whether it is cold worked or annealed) has no impact on corrosion properties provided the diffusion barrier layer remains essentially unchanged. Oxygen concentration, temperature, and velocity of the water determine the reaction rate. Because in almost all natural waters the pH ranges from 4 to 10, all the observed corrosion rates in shipbuilding steel in a given environment are essentially the same (LaQue, 1975).

Melchers, (2003a) has shown that the small daily shift of pH from about 8.0 – 8.2 is thought to have little direct effect on corrosion. However, the effect of a drop in pH on corrosion rate can be quite dramatic, even for short-term corrosion.

The corrosion rate dependence on hydrogen concentration may be in the form of (Korb, 1987):

\[ r = k C_H^{n+} \]  

where \( r \) is the corrosion rate, \( k \) is the rate constant, \( C_H^{n+} \) is the hydrogen ion concentration and \( n \) is an exponent. The value of \( n \) can be dependent on the hydrogen ion concentration. The corrosion rate increases with hydrogen ion concentration (decreasing pH), according to Equation (12).

The model proposed here considers that there is no effect of pH in the region of \( pH=4-10 \). For the cases where the \( pH \) is outside that region the corrector factor is modeled following Equation (12), as shown in Figure 5 where the \( pH \) ratio is defined as actual \( pH \) value / nominal \( pH \) value.

\[ r(pH)=k10^{(n \cdot pH)} \]  

Equation (13) relates the corrosion rate, \( r(pH) \), with the \( pH \). It is proposed that the relationship between the corrosion rate correction factor for \( pH \) and \( pH \) ratio follows the same function of Equation (13), as indicated in Figure 6:

\[ f(pH)=k10^{(n \cdot pH)} \]  

where \( f(pH) \) is corrosion rate correction factor for \( pH \) (corrosion rate at actual \( pH \) / corrosion rate at nominal conditions) and \( k \) and \( n \) are constants.
When the value of pH ratio = 1, the actual pH equals the nominal value and the actual corrosion rate is equal to the nominal one. For nominal conditions $pH_r = 1$ and $f(pH_r) = 1$, Equation (14) can be written as:

$$f(pH_r) = 10^{n(1-pH)}$$ (15)

The effect of parameter $n$ is indicated in Figure 6.

**Influence of Water Velocity**

Flowing water can result in an increase in the amount of dissolved oxygen that reaches the metal surface. Flowing water can remove protective films over the metal surface. Higher velocity of water particles will lead to an increase in corrosion rate of carbon steel. The corrosion rate may double when water moves at 1 m/s (Chandler, 1985). Uhlig and Revie, (1985) has stated that in seawater, the corrosion rate is proportional to the velocity until some critical velocity is reached, beyond which there is little further increase in corrosion.

Short term observations by Melchers, (2001, 2003a) indicate that immersion corrosion of steel increases with velocity. However, for longer exposures, the corrosion product layers will provide some protection and the velocity is unlikely to have a continued direct influence on corrosion (LaQue, 1975). Fontana, (1992) has represented the schematic relationship between water velocity and the corrosion rate for different materials.

$$f(v_r) = \lambda \left[1 - e^{-\theta(v + \theta)}\right]$$ (16)

where $f(v_r)$ is the corrosion rate correction factor for velocity, $v_r$ is the flow velocity ratio, $\lambda$ is a magnification factor to adjust the value of the corrosion rate correction factor ($\lambda \geq 0$), $\theta$ is a constant introduced to adjust the truncated portion from the distribution ($\theta \geq 0$) and $\eta$ is a factor to adjust the curvature and the slope of the curve ($\eta \geq 0$).

When the flow velocity ratio is $v_r = 1$, the actual flow velocity equals the nominal value and the actual corrosion rate equals the nominal one. For nominal conditions when $v_r = 1$ and $f(v_r) = 1$, Equation (16) may be re-written as follows:

$$f(v_r) = \lambda \left[1 - \exp\left(\frac{v + \theta}{1 + \theta} \left(1 - \frac{1}{\lambda}\right)\right)\right]$$ (17)

The effect of parameters ($\lambda$, $\theta$) are indicated in Figure 7 and 8.
NONLINEAR CORROSION WASTAGE MODEL FOR GENERAL CORROSION

Nonlinear corrosion model

The non-linear corrosion wastage model proposed by Guedes Soares and Garbatov, (1999) describes the growth of corrosion wastage by a non-linear function of time in three phases. In the first phase, it is assumed that there is no corrosion because a corrosion protection system is effective. Failure of the protection system will occur at a random point in time and the corrosion wastage will start a non-linear process of growth with time, which levels off asymptotically at a long-term value of corrosion wastage.

Figure 9 illustrates this time dependent model of corrosion degradation, separated into four phases, where in the first one there is no corrosion \((t = 0 - \Omega)\). The second phase \((t = \Omega - B)\) corresponds to the initiation of failure of the corrosion protection system, which leads to corrosion with the rapid decrease in the plate thickness. The third phase, \((t = B - C)\), corresponds to slowly growing corrosion and the last one, \((t > C)\), corresponds to a stop in the corrosion process when the corrosion rate becomes zero.

This model has been recently validated against measured data reported by Wang et al., (2003), consisting of measured corrosion wastage of ship deck plates of ballast and cargo tanks (Garbatov et al., 2005).
\[ d_{n,i}(t) = d_\infty \left(1 - e^{-(t - \tau_\infty) / \tau_\infty}\right) \quad t > \tau_\infty \]
\[ d_{n,i}(t) = 0, \quad t \leq \tau_\infty \]

Coating breakdown

Corrosion will eventually initiate on the surface of a coated metal because water or vapour particles will pass through coating. Coating is a semi-permeable membrane and when exposed long enough, water or moisture will penetrate it. Every coating has its own water absorption rate, which depends on the difference in the concentrations inside and outside the coating, leading to osmosis. Water absorption can be rapid and with a high rate in the early stages due to higher differences in concentrations inside and outside of the coating. As time passes, this difference in concentrations reduces due to the water absorbed, and as a result, the absorption rate is reduced with time. Eventually, the coating reaches saturation conditions, and the water or vapor particles inside coating become stabilized with the conditions outside of the coating (Aragon and Short, 2000). The time required for reaching the saturation condition corresponds to the time required for the water or vapor particles to reach the substrate or the metal surface, where another stage begins. The time required to reach a certain saturation ratio \( SR \) may be represented as an exponential function of the saturation ratio:

\[ SR = 1 - e^{-t / \tau_\infty} \]

where \( SR \) is saturation ratio, \( SR = 1 \), for fully saturated coating, \( \tau_\infty \) is constant controlling the slope at \( t = 0 \), \( 1/\tau_\infty \) represent the slope at \( t = 0 \).

As soon as the water or vapor particles reach the substrate, oxygen gas is chemisorbed on the metal surface until a complete two-dimensional invisible oxide monolayer forms. If there is a strong adhesion between the coating particles and the substrate, the formation of this monolayer starts as points in the void spaces between the coating particles and the substrate. The time required for the formation of the monolayer depends on the type and the composition of the coating. If the coating or primer contains any inhibitive pigments, it will ionize sufficiently to react with the metal surface when subjected to moisture or humidity and maintain the metal in a passive or inactive state. This state will elongate the time required for the formulation of the two-dimensional monolayer. This shows that the time required for the formulation of this monolayer will vary with inhibitive pigments or additives. When the coating is applied over a surface that is unclean or contains chlorides, sulphates, or other ions, this monolayer will be formed through the region between the coating layer and the substrate where there is no adhesion. The formation of the monolayer in this case will be more aggressive and occur in a shorter time.

After the monolayer being formed, discrete nuclei of three-dimensional oxide appear on the surface and begin expanding laterally at an ever-increasing rate. These nuclei may be of a large number that may act as a uniform corrosion. The nuclei may originate at structural defects, such as grain boundaries, impurity particles, and dislocations. These oxide islands grow outwards rapidly by surface diffusion of adsorbed oxygen, destroying the adhesion between the adjacent coating particles and the substrate. Then, a complete film three or four monolayers thick covers the metal, which leads to coating breakdown an increased in corrosion rate. The oxidation rate then drops abruptly. This stage is considered to be the stage where corrosion growth starts through the metal thickness, which may be represented by the corrosion growth rate model proposed by Guedes Soares and Garbatov, (1999).

The coating effective life is considered to be the summation of the period necessary for the water particles to penetrate the coating until reaching the metal surface (saturation condition) plus the period necessary for forming the two-dimensional oxide monolayer as can be seen in Figure 11.

Inclusion of the environmental factors

The model, proposed here, is based on the one of Guedes Soares and Garbatov, (1999), considering that Equation (19) represents the corrosion wastage as a function of time at nominal conditions \( d_{ci,n}(t) \). To evaluate the corrosion wastage at different conditions of salinity, temperature, dissolved oxygen, pH and velocity, the last relation is corrected for these conditions, as:

![Figure 11 Corrosion initiation mechanics](image-url)
\[ d_{c,i}(t) = f_{c,i}(S_i) f_{t,i}(T_i) f_{o,i}(O_i) f_{p,i}(pH_i) f_{d,i}(v_i) d_{n,i}(t) = \prod_{j=1}^{i} f_{i,j} d_{n,j}(t) \]  

(21)

where \( d_{c,i}(t) \) represents the corrected corrosion wastage, and \( f_i \) are the environmental correction factors described by the models proposed in the earlier sectors.

**Long-term effect of the environmental factors**

A ship may encounter a wide range of environmental conditions. Its entire life may be regarded as a large number of short intervals, during which the environmental conditions remain constant. This means that the number of intervals of relatively constant environmental conditions will depend on the extension of the route and on the variability of the conditions along each route. Relatively the values of corrected corrosion rate computed for each interval throughout the lifetime of a ship will be characterized by a weighting factor that results from the product of all environmental corrosion factors indicated in Eqn (21).

The corrosion rate as a function of time calculated for any stationary period in a route is considered a short-time contribution to the corrosion damage and the long-term prediction of corrosion wastage for the entire life of ship is calculated as:

\[ d_L(t) = \sum_{i=1}^{n} p_i d_{c,i}(t) = \sum_{i=1}^{n} p_i \prod_{j=1}^{i} f_{i,j} d_{n,j}(t) \]  

(22)

where \( p_i \) is the weighting factor representing the relative duration of the \( i \)th stationary period along the lifetime of ship and \( d_{c,i}(t) \) is the short-term corrosion wastage of the \( i \)th period.

**NUMERICAL EXAMPLE**

This example, based on the model presented here, aims to demonstrate the effect of the different characteristics of the marine environment on the corrosion of the immersed steel surfaces throughout the ship’s life. To illustrate this model, six routes in the Pacific Ocean were assumed as shown in Figure 12, and impacts of marine environments were studied. The weighting factors \( p_i \) for the stationary periods in the routes chosen for the example presented here are 0.14, 0.20, 0.24, 0.12, 0.12 and 0.17 respectively. The weighing factors are calculated based on the relative duration of each of them with respect to the total duration of all routes.

The different seawater characteristics (salinity, temperature, dissolved oxygen and pH) of the Pacific Ocean were used from charts prepared by Dexter and Culberson, (1980). Different points were assumed through each route as indicated in Figure 13 to 19 and the different seawater characteristics at each point were estimated, from which the mean value for each of the seawater characteristics through each route was estimated.

The coating is assumed to perform in the same way through the different routes. The relationships controlling the coating performance and the corresponding factors during the different stages of coating effectiveness deterioration are assumed as shown in Figure 20 to 23.
Figure 14 Pacific Ocean surface dissolved oxygen (January - March)

Figure 15 Pacific Ocean surface dissolved oxygen (July - September)

Figure 16 Pacific Ocean surface salinity (February)

Figure 17 Pacific Ocean surface salinity (August)
Figure 18 Pacific Ocean surface temperature (February)

Figure 19 Pacific Ocean surface temperature (July)

Figure 20 Saturation ratio as a function of time and $\tau_o$

Figure 21 Inhibitive pigmentation ratio as a function of $t_m$ and $t_{mo}$
The nominal corrosion wastage is shown in Figure 24 as a function of time. The relationships between the corrosion rate correction factors for the different environmental factors and their corresponding ratios are assumed to be estimated at the same nominal conditions. The factors controlling these relationships are also considered, as may be seen in Figure 25.

The actual value/nominal value for the different environmental variables is estimated for each route and the corresponding correction factors are obtained from Figure 25, as shown in Tables 1 to 6.

The nominal relationship of corrosion wastage versus time is corrected for the actual marine environment variables corresponding to each route, as indicated in Figure 26.

Several assumptions have been made with respect to the factors controlling the coating performance through the different stages. Water penetration period, in the \([\text{SR}-t]\) relationship is considered as \(\tau_w = 0.4\). The time necessary to reach to the saturation condition (\(\text{SR}=1\)) is considered as \(t = 2\) years (see Figure 20). Formation of the two-dimensional monolayer period, in the \([\text{IPR}-t_m]\) relationship is taken as \(t_{mo} = 0.5\), \(a = 12\) and \(b = 2\) (see Figure 21 to Figure 23). The time necessary for the formation of the two-dimensional monolayer oxide film considering \(\text{IPR} = 0.36\) is \(t_m = 2\) years.

The total coating effectiveness period equals the time necessary to reach the saturation condition plus the time necessary for the formation of the two dimensional monolayer, which results to 4 years.

The nominal relationship of corrosion wastage versus time is estimated as Salinity = 34 ‰, Temperature = 15 °C, Dissolved oxygen = 0.5 mg. atm \(\text{O}_2/L\), pH = 8.0 and Velocity = 10 knots (see Figure 26).

Under these nominal conditions, the factors controlling the nominal relationship of corrosion wastage versus time are assumed to be \(\tau_t = 5\) years, \(\tau_c = 4\) years and \(d_e = 3\) mm.

The relationships between the corrosion rate correction factors for the different environmental variables and the corresponding ratios are estimated at the same nominal conditions stated above. It has been assumed that the factors controlling these relationships are for the \([f(S_r) - S_r]\) relationship \(\beta = 1.5\) and \(\varepsilon = 0.2\); for the \([f(T_r) - T_r]\) relationship, \(d = 0.1\); for the \([f(O_r) - O_r]\) relationship, \(b = 0.1\); for the \([f(pH_r) - pH_r]\) relationship, \(n = 0.2\) and for the \([f(v_r) - v_r]\) relationship \(\theta = 0.1\) and \(\lambda = 1.1\). It is also assumed that the actual velocity is constant for all routes and equal to 10 knots.
Figure 24 Nominal corrosion wastage as a function of time

Figure 25 Correction factors for the different environmental variables

Table 1 Ratios and correction factors for the different environmental variables of route "1"

<table>
<thead>
<tr>
<th>Variable</th>
<th>Actual (mean) value</th>
<th>Nominal value</th>
<th>Variable ratio</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (‰)</td>
<td>33.12</td>
<td>34</td>
<td>0.974</td>
<td>1.004</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>11.4</td>
<td>15</td>
<td>0.760</td>
<td>0.928</td>
</tr>
<tr>
<td>Dissolved oxygen (mg. Atm O₂/L)</td>
<td>0.567</td>
<td>0.5</td>
<td>1.134</td>
<td>1.134</td>
</tr>
<tr>
<td>pH</td>
<td>8.164</td>
<td>8</td>
<td>1.021</td>
<td>0.99</td>
</tr>
<tr>
<td>Velocity (knots)</td>
<td>10</td>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2 Ratios and correction factors for the different environmental variables of route "2"

<table>
<thead>
<tr>
<th>Variable</th>
<th>Actual (mean) value</th>
<th>Nominal value</th>
<th>Variable ratio</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (‰)</td>
<td>34.9</td>
<td>34</td>
<td>1.026</td>
<td>0.996</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>19.217</td>
<td>15</td>
<td>1.281</td>
<td>1.084</td>
</tr>
<tr>
<td>Dissolved oxygen (mg. Atm O₂/L)</td>
<td>0.49</td>
<td>0.5</td>
<td>0.980</td>
<td>0.98</td>
</tr>
<tr>
<td>pH</td>
<td>8.159</td>
<td>8</td>
<td>1.020</td>
<td>0.991</td>
</tr>
<tr>
<td>Velocity (knots)</td>
<td>10</td>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
### Table 3 Ratios and correction factors for the different environmental variables of route "3"

<table>
<thead>
<tr>
<th>Variable</th>
<th>Actual (mean) value</th>
<th>Nominal value</th>
<th>Variable ratio</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (‰)</td>
<td>34.499</td>
<td>34</td>
<td>1.015</td>
<td>0.998</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>19.431</td>
<td>15</td>
<td>1.295</td>
<td>1.089</td>
</tr>
<tr>
<td>Dissolved oxygen (mg. Atm O₂/L)</td>
<td>0.494</td>
<td>0.5</td>
<td>0.988</td>
<td>0.988</td>
</tr>
<tr>
<td>pH</td>
<td>8.152</td>
<td>8</td>
<td>1.019</td>
<td>0.991</td>
</tr>
<tr>
<td>Velocity (knots)</td>
<td>10</td>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Table 4 Ratios and correction factors for the different environmental variables of route "4"

<table>
<thead>
<tr>
<th>Variable</th>
<th>Actual (mean) value</th>
<th>Nominal value</th>
<th>Variable ratio</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (‰)</td>
<td>34.265</td>
<td>34</td>
<td>1.008</td>
<td>0.999</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.725</td>
<td>15</td>
<td>1.448</td>
<td>1.134</td>
</tr>
<tr>
<td>Dissolved oxygen (mg. Atm O₂/L)</td>
<td>0.474</td>
<td>0.5</td>
<td>0.948</td>
<td>0.948</td>
</tr>
<tr>
<td>pH</td>
<td>8.143</td>
<td>8</td>
<td>1.018</td>
<td>0.992</td>
</tr>
<tr>
<td>Velocity (knots)</td>
<td>10</td>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Table 5 Ratios and correction factors for the different environmental variables of route "5"

<table>
<thead>
<tr>
<th>Variable</th>
<th>Actual (mean) value</th>
<th>Nominal value</th>
<th>Variable ratio</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (‰)</td>
<td>34.5</td>
<td>34</td>
<td>1.015</td>
<td>0.998</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.182</td>
<td>15</td>
<td>1.412</td>
<td>1.124</td>
</tr>
<tr>
<td>Dissolved oxygen (mg. Atm O₂/L)</td>
<td>0.468</td>
<td>0.5</td>
<td>0.936</td>
<td>0.936</td>
</tr>
<tr>
<td>pH</td>
<td>8.182</td>
<td>8</td>
<td>1.023</td>
<td>0.989</td>
</tr>
<tr>
<td>Velocity (knots)</td>
<td>10</td>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Table 6 Ratios and correction factors for the different environmental variables of route "6"

<table>
<thead>
<tr>
<th>Variable</th>
<th>Actual (mean) value</th>
<th>Nominal value</th>
<th>Variable ratio</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (‰)</td>
<td>34.742</td>
<td>34</td>
<td>1.022</td>
<td>0.996</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>24.346</td>
<td>15</td>
<td>1.623</td>
<td>1.187</td>
</tr>
<tr>
<td>Dissolved oxygen (mg. Atm O₂/L)</td>
<td>0.438</td>
<td>0.5</td>
<td>0.876</td>
<td>0.876</td>
</tr>
<tr>
<td>pH</td>
<td>8.184</td>
<td>8</td>
<td>1.023</td>
<td>0.989</td>
</tr>
<tr>
<td>Velocity (knots)</td>
<td>10</td>
<td>10</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 26 Corrected corrosion wastage as a function of time for various routes through the Pacific Ocean.

Finally, Figure 27 shows the application of the new time dependent model for the corrosion wastage of a ship hull taking into account the impact of various environmental factors on the degrading effect of corrosion for various route studied as a short-term predictions. Based on the results for the short-term prediction of corrosion wastage the long-term prediction corrosion wastage over the ship’s lifetime is calculated as can be seen in Figure 27.

As can be seen from Figure 27 the shape of the long-term corrosion wastage is the same shape as the one for nominal corrosion wastage but the characteristic parameters are different. For the case studied the nominal corrosion wastage is defined by $\tau_i = 5$ years, $\tau_c = 4$ years and $d_\infty = 3$ mm and the long-term corrosion wastage by $\tau_i = 5$ years, $\tau_c = 4$ years and $d_\infty = 3.62$ mm respectively.

CONCLUSIONS

The effects of major marine environmental factors on corrosion wastage of the immersed external hull surfaces have been studied. A model is developed for the long-term corrosion wastage for the submerged shell plating. This model is based on immersion corrosion mechanisms, and calibrated with measured corrosion wastage database for tankers.

This long-term corrosion model express the corrosion wastage as a nonlinear function of time; it accounts for different trading routes, the associated environmental conditions, and the percentage of time spent in each of these environments.

This model has the advantage over most others that, instead of providing only the average corrosion wastage, it also provides information about how the corrosion wastage changes with respect to the environmental factors associated with the navigation routes which can also be reflected in the entire life of ship.

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REFERENCES


Non-linear Corrosion Model for Immersed Steel Plates Accounting for Environmental Factors


