

Evaluation of the effects of highly saline and warm seawaters on corrosivity of marine assets

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Abstract In marine environment, the corrosion rate of metallic structures vary remarkably with the change in climatic conditions and seawater composition across geographical locations. The corrosion in brackish and polluted seawaters is even more complicated due to the presence of different chemical species and untreated effluents. The complex correlation between the above average temperature and salinity with the high nutrient content in polluted seawater tends to accelerate the rate of biological activities and microbiological induced corrosion (MIC). This research paper has investigated the short-term corrosion of cupronickel (Cu-Ni) 90/10 alloy, and mild steel in the highly saline and warm seawaters. Field experiments for general corrosion under fully immersed condition were conducted at two site locations, represented as site 1 for pollutant-rich seawaters and site 2 for natural seawaters in the North Indian Ocean. The experiments were conducted for a period of up to two months and coupons for each metal alloy were recovered from both sites after an exposure period of 15, 30, 45, and 60 days, respectively. In both environmental conditions, significantly high mass loss and corrosion rates were recorded for each metal alloys. Despite the same temperature of seawater and immersion depth at both sites, average corrosion losses at site 1 were found to be 5 and 3 times higher than that of site 2 for Cu-Ni alloy 90/10, and mild steel coupons, respectively.

Keywords: cupronickel (Cu-Ni), mild steel (MS), dissolved inorganic nitrogen (DIN), sulphide reducing bacteria (SRBs)

1. Introduction

Corrosion is one of the most prominent degradation mechanisms in marine structures, adversely affecting their structural integrity by inducing strength loss, thickness reduction, buckling, corrosion fatigue, brittle fracture, and cracking. Static and shock loads, metal erosion, and turbulent seawater flows are the other challenging factors that can be exacerbated in rough weather conditions [1–3]. Corrosion is an electrochemical process that occurs when a metal reacts with its immediate environment. In aqueous conditions, it occurs due to the availability of water along with an electron acceptor element, like oxygen. The research literature reveals the majority of offshore structural failures are attributed to the direct and indirect involvement of various corrosion mechanisms [4,5]. The severity of climatic conditions leads to rapid degradation of metallic structures exposed to the marine environment. Subsequently, the desired mechanical properties decline over the years spent in situ and increase the probability of system functional failures. The variations in ambient climate, loading conditions, applied protective measures, and the selected maintenance strategies influence the structural reliability of assets operating in the marine environment [6].

The presence of various hazardous compounds in seawater, especially in pollutant-rich seawaters can lead to higher localised and general corrosion rates. Various research studies presented that the rate of the corrosion mechanism is highly influenced by the physical, environmental factors, the chemical constituents in seawater, and any microbiological activity [6–13]. Table 1 illustrates the categories of significant environmental factors.

Table 1 Influential environmental factors for marine corrosion

| Type | Factors |
|------------|--|
| Biological | Bacteria (including SRBs), biomass, pollutants, marine growth |
| Chemical | Dissolved oxygen, salinity, CO ₂ , dissolved inorganic nitrogen |
| Physical | Temperature, pH level, water velocity, surface wetting |

The cupro-nickel (Cu–Ni) 90/10 alloy is widely used in marine applications due to its superior resistance towards biofouling, uniform and localized corrosion, and erosion resistance in chlorinated seawater [14]. By virtue of its composition (especially the nickel content), Cu–Ni 90/10 alloy provides higher corrosion resistance in natural (low pollutant level) seawaters because a protective oxide film develops on the metal surface soon after immersion in seawater [15]. In marine, this alloy is used in piping, cladding, heat exchangers tubes [16–19]. Pervizi *et al.* [20] presented the long term corrosion data on Cu-Ni 90/10 tubes of naval condensers operated in natural seawaters and estimated their average service life over 20 years. However, some premature failures can occur either due to the manufacturing shortcoming during heat treatment and surface treatment or consistent operation under harsh exposure environments, and higher fluid flows [21].

Syrett [21,22] conducted an experimental study contrasting unpolluted and sulphide-rich seawater and established that the coexistence of sulphide compounds and high oxygenation in seawater results in a far higher rate of corrosion than that estimated for either deaerated sulphide or fully oxygenated seawaters. As such, these two species have a synergistic effect on the corrosion rate. An experiment based study was led by Drach *et al.* [23] on Cu-Ni 90/10 samples, placed under tension and unloaded conditions. It was observed that the corrosion rate of under tension samples was 39% higher than those in unloaded condition. This research reported that the corrosion rate decreased 2.4 times between 3 months to 12 months of the exposure period.

Generally, in natural seawaters, the protective layer formed on the surface of copper alloys consist of copper oxides ($\text{Cu}_2\text{O}/\text{CuO}$) or copper chlorides ($\text{CuCl}/\text{CuCl}_2$) whereas in presence of polluted seawaters, other complex compounds may also exist [23–26]. Cuprous oxide is thermodynamically unstable, therefore over time, it oxidises into the cupric ion. When the immersion period is increased, the cupric oxide film thickens and the diffusion of ions towards bare metal surface becomes difficult, hence corrosion rate is reduced [27]. A study on the uniform and pitting corrosion of Cu-Ni 90/10 was conducted by Phull *et al.* [11] around 14 global sites and demonstrated that corrosion data from these different sites resulted in a high degree of scatter. In most of cases, higher corrosion loss was found near-coast locations because of the presence of pollutants and high nutrient content. Overall, for most of the exposure sites, the experimental results for corrosion indicated a decrease in corrosion rate as a function of exposure time. Phull *et al.* concluded that the effect of the rise in temperature (30 C) is insignificant during the corrosion of Cu-Ni 90/10 alloy, however, it highlighted the considerable influence of sulphide content in seawater on the acceleration of corrosion rate.

The corrosion rate of steel alloys is much high than seen in the Cu-Ni 90/10 alloy. In case of mild steel, the oxide layer developed during initial corrosion is weak to protect the metal surface from further corrosion. Zayed *et al.* [28] reported that if the DO concentration is held constant in a closed system, the corrosion rate in low-carbon steel nearly doubles for every 30 C rise in temperature. Melchers presented a non-linear bimodal corrosion model for several types of marine alloys, including low carbon steel/mild steel, cupro-nickel, and aluminium alloys in sea/fresh/brackish water [29–33]. Figure 1 illustrates the Melchers bi-modal model for corrosion. This model categorises aqueous corrosion in four phases in which the early two stages are governed by kinetic, concentration activation, and diffusion controlled oxidation/polarisation, whereas, the latter two are principally controlled by the biological activities, nutrients content in water.

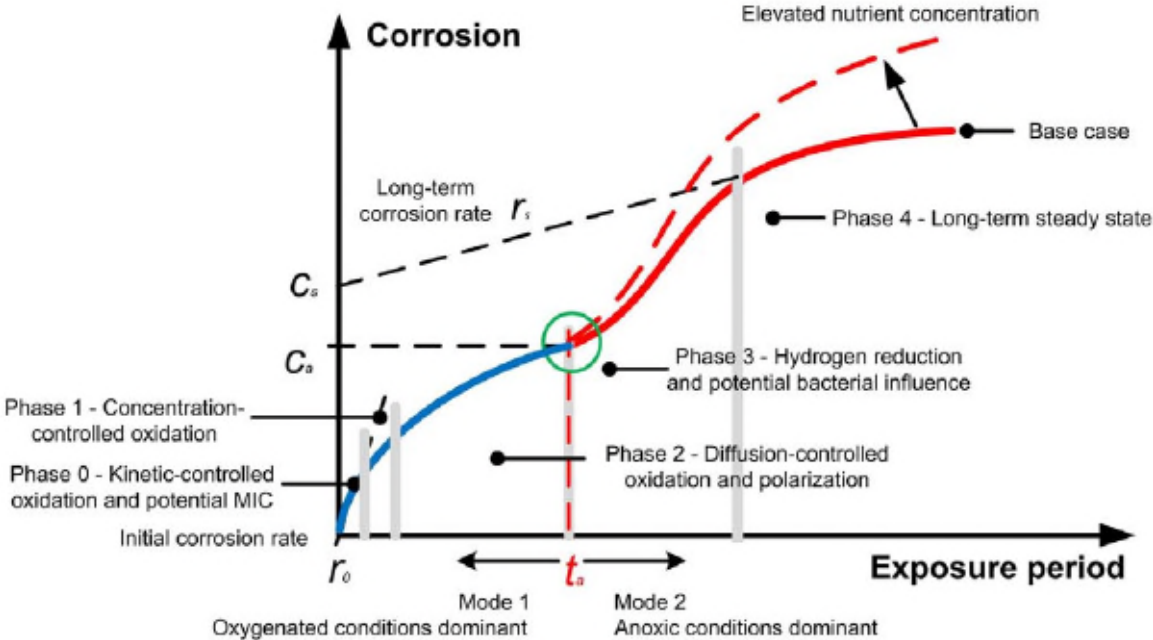


Figure 1 Melcher bimodal corrosion model [34]

After extensive research studies and data analyses, Melchers observed that, in the earliest corrosion phases (phase 0,1), the corrosion rate tends to double for every 10 C rise in temperature. In the second phase (phase 2), oxygen solubility decreases with the rise seawater temperature, which subsequently reduces the ability for oxygen molecules to diffuse through

the corrosion product accumulated on the metal surface. In this condition, around 30 C rise in temperature doubles the corrosion rate [29,30].

Available literature reveals that contrary to the carbon steel alloy, the higher corrosion rates in Cu-Ni 90/10 have been reported only between the temperature range of 18-28 C, however, no significant variation in corrosion loss behaviour has been noticed at the temperatures below and above this range [17,28]. Hodgkiess and Vassiliou [35] analysed the corrosion behaviour of Cu-Ni 90/10 under various conditions, such as flow velocities (up to 86 m/s), ambient temperature, 3.5% NaCl solutions, and with/ without cathodic protection; to differentiate purely mechanical erosion process from electrochemical corrosion. The application of cathodic protection resulted in a substantial reduction in overall weight losses, nevertheless some material loss was still observed on higher flow velocities, hence depicting the impact of mechanical erosion towards the total mass loss.

A linear relationship between DO and rate of early corrosion phases (0,1,2) has been reported. The DO concentration in seawater is a function of temperature, whereas, it is also influenced by the water turbulence, exposure period, pH, and the extent of biological activities [18]. The photosynthesis process can cause a substantial surge in DO concentration, on the other hand, the presence of pollutant compounds, nutrients and bacterial activities deplete the oxygen concentration and facilitate anoxic conditions; which is a conducive environment for the growth of MIC. A research study at Ref. [28] stated that the oxygen concentration declines with temperature from about 8.0 ml/l for surface waters in the Arctic to around 4.5 ml/l in the tropical regions. In active metals, corrosion rate in aerated seawaters is a direct linear function of DO content; provided the temperature is constant. Contrarily, in the absence of DO, the corrosion rate found negligible at room temperature.

The literature reveals that the pH level in natural seawater usually lies between 8.1 and 8.5. A small shift in pH level has minimal effect on the rate of corrosion. In coastal regions, basins and estuaries, the DO concentration drops due to biological oxygen demand (BOD), and presence of sulphide-rich pollutants. Under these conditions, the pH of the water may also drop to around 6.5-7 which can significantly accelerate short-term and long-term corrosion rates [29]. Water velocity is another crucial factor for elevated corrosion rates in low carbon steel alloys, especially during the early phase of corrosion. Some researchers have found that the general corrosion of marine steel structures increases non linearly with velocity; however, after the accumulation of corrosion deposits and biofoulings, this effect can be shrunk, substantially [36]. Water velocity tends to increase marine growth, probably because of the increased supply of nutrients and oxygen level [29]. The loosely bonded corrosion product erodes by the shear force of high water velocity and new metal surface become exposed to the seawater which intensifies corrosion rates [37].

The concentration of dissolved inorganic nitrogen (DIN) in seawater is a crucial factor in nutrients which has high significance to determine the rate of microbiological activities in seawater. Generally, DIN exists in polluted seawater in the form of nitrates, nitrites, ammonia, and various anthropological amalgams. The severity of Accelerated low water corrosion (ALWC) is correlated with the DIN concentration in seawater [38]. Melchers [39] investigated the corrosion loss for marine steel structures in polluted seawaters and revealed that the mass loss increases tremendously with the combined effect of high DIN concentration and water temperature. During a study on long-term corrosion of carbon steel pipe, an analysis on pit morphology and pit depth was conducted by Wang and Melchers [34]. It demonstrated the DIN (Nitrate) addition enormously increased the localized corrosion, which is attributed as a synergistic effect between MIC and under-deposit corrosion.

The seawater reservoirs in the polar regions have comparatively low temperatures, salinity but high DO concentration. On the other hand, some of the tropical/sub-tropical regions such as the North Indian Ocean and the Red Sea exemplifies extremely high seawater temperature and salinity level. The salinity of global seawater bodies varies between 30,000 to 45,000 ppm [40,41], and the temperature variation lies between -4 C on poles to 35 C in the hot countryside [28]. In the Arabian Sea, the surface temperature of seawater ranges between 28 C to 41 C in the summer season [42]. In a recently conducted research study, Jilani [43] presented significant parameters of seawater quality and quantitative details on various pollutant contents near the coasts of Arabian sea.

This research paper investigates the corrosion behaviour of cupro-nickel 90/10 (Cu-Ni 90/10) alloy, and mild steel in the warm and highly saline seawaters of North of Indian. It encompasses the field experiments for a period of up to 2 months, to investigate the short-term corrosion of these widely used metal alloys in the specified climatic conditions as a function of the exposure period. The fully submerged specimens for both alloys in natural seawater and pollutant seawaters were recovered after 15, 30, 45, and 60 days of the exposure period and evaluated for average mass loss. From the experimental results, a comparative analysis of the mass loss and corrosion rate between both types of metal alloys was carried out. The effect of physical environmental/chemical factors and pollutant species, particularly DIN compounds on the rate of MIC in the early immersion periods has been discussed at length.

2. Material and Methods

Various standard methods have been used to evaluate the corrosion factor of metallic coupons; however, the mass loss method is considered the simplest and most reliable one for estimating the general corrosion rate [44,45]. In hot corrosion, a novel method, 'dimensional metrology' has also been introduced by some researchers so as to avoid the uncertainties associated with the conventional average mass loss method [46–49]. Nevertheless, in here the corrosion loss, rate of corrosion for both metal alloys have been evaluated using the standard mass loss method. The standard corrosion rate formula is given as:

$$C_R \text{ (mm/yr)} = 87.6 \times (\Delta m / DAT) \quad (1)$$

Where C_R = corrosion rate

Δm = mass loss in milligrams

D = metal density in grams/cm^3

A = area in cm^2

T = exposure time in hours

The coupons with the dimensions of 30 mm x 30 mm x 2 mm were selected for exposure testing of Cu-Ni 90/10 alloy and 30 mm x 60 mm x 2 mm were selected for mild steel. Coupons were placed in a vertical position in two locations, represented as site 1 and 2. Site 1 shows the location of the pollutant-rich coastal seawater, and site 2 represents clean natural seawaters of the North Indian ocean, also known as Arabian Sea. To provide electrical isolation between the coupons, Nylon rods were used to suspend the coupons. The composition of both selected metal alloys is illustrated in table 2.

Table 2 Composition percentage for experimental material

| | | | | | | |
|-------------------|------|-----|-------|-------|-----------|-----------|
| Cu-Ni 90/10 alloy | Ni | Fe | Mn | Pb | C | Cu |
| | 10.5 | 1-2 | 0.5 | 0.03 | 0.05 | Remainder |
| Mild steel | C | Mn | P | S | Fe | |
| | 0.17 | 0.3 | <0.04 | <0.05 | Remainder | |

The surfaces of the coupons were cleaned and prepared according to the ASTM standard G52 [50]. A weight measurement of all coupons was carried out using analytical weigh scale with tolerance limit in micrograms. The metallic coupons were immersed in very close proximity to ensure the homogenous environment on each coupon during its entire period. The seawater samples from the two selected locations were tested frequently during the experimental period, to estimate the variability of contributing parameters for corrosion, as shown in Table 3.

Table 3 Seawater specifications of selected locations [43]

| Parameters | Pollutant rich Seawater (site 1) | Natural (site 2) seawater |
|------------------------|----------------------------------|---------------------------|
| PH | 6.94-7.0 | 7.5-8.2 |
| DO (mg/l) | 1 ± 0.39 | >3.5 |
| Conductivity (mS/m) | 63± 4.8 | 50-55 |
| Temperature (C) | 28-32 | 28-32 |
| Chloride (mg/L) | 23,000± 2000 | 19,300 |
| Sulphate (ppm) | 2922±100 | 1900 |
| DIN (mg/L) | 1.1-1.7 | >0.1 |
| Turbidity (NTU) | 6.0±0.7 | - |
| Ortho Phosphate (mg/L) | 0.5±0.1 | - |
| Total solids (mg/L) | 76,600 ± 2197 | 35,000 |

Because of the amalgamation of pollutants from various sources (e.g. industrial, agricultural and untreated domestic wastages) directly into the seawater, the quality of water at site 1 is merely different from the natural seawaters in the adjacent location i.e. site 2. It is assumed that the physical environmental factors and immersed level of coupons are similar for both site locations. The depth of immersed coupons from the sea surface is also assumed to be the same. The post-immersion mechanical/chemical cleaning for each coupon was carried out according to the ASTM standards G1-03 [51].

3. Results

At each recovery with the same exposure time period, no prominent localised corrosion marks were visible on the metallic specimens recovered from both test environments. The most probable reason for the lack of localised corrosion despite the availability of more favourable anoxic conditions at site 1 was the very short exposure period. The results for average corrosion loss, and corrosion rate both metal alloys in either site is illustrated in Table 4 and 5 below.

Table 4 Weight loss table for coupons of cupro-nickel 90/10 alloy in both locations

| | Submerged duration | Percent mass loss | Corrosion loss (μm) | Corrosion rate ($\mu\text{m}/\text{yr}$) |
|---------------|---------------------------|--------------------------|--|--|
| Site 1 | | | | |
| 1 | 15 days | 0.77 | 16.4 | 400 |
| 2 | 30 days | 1.16 | 24.7 | 301 |
| 3 | 45 days | 2.12 | 42.5 | 345 |
| 4 | 60 days | 2.43 | 50.13 | 305 |
| Site 2 | | | | |
| 1 | 15 days | 0.17 | 3.7 | 90 |
| 2 | 30 days | 0.22 | 4.93 | 60 |
| 3 | 45 days | 0.30 | 6.16 | 50 |
| 4 | 60 days | 0.40 | 8.21 | 50 |

Table 5 Weight loss table for mild steel coupons in both locations

| | Submerged duration | Percent mass loss | Corrosion loss (μm) | Corrosion rate (mm/yr) |
|---------------|---------------------------|--------------------------|--|-------------------------------|
| Site 1 | | | | |
| 1 | 15 days | 2.89 | 78.3 | 1.9 |
| 2 | 30 days | 3.17 | 89.28 | 1.09 |
| 3 | 45 days | 3.58 | 106.0 | 0.86 |
| 4 | 60 days | 4.71 | 129.46 | 0.78 |
| Site 2 | | | | |
| 1 | 15 days | 1.19 | 31.98 | 0.78 |
| 2 | 30 days | 1.07 | 29.06 | 0.38 |
| 3 | 45 days | 1.28 | 35.17 | 0.29 |
| 4 | 60 days | 1.45 | 41.02 | 0.25 |

The graphical representation of corrosion loss and corrosion rate observed during the field experiments is shown in figure 2 (a,b), and 3 (a,b) below. The line in black colour represents the average corrosion loss and corrosion rate for site 1, whereas, green colour represents corrosion trend of site 2.

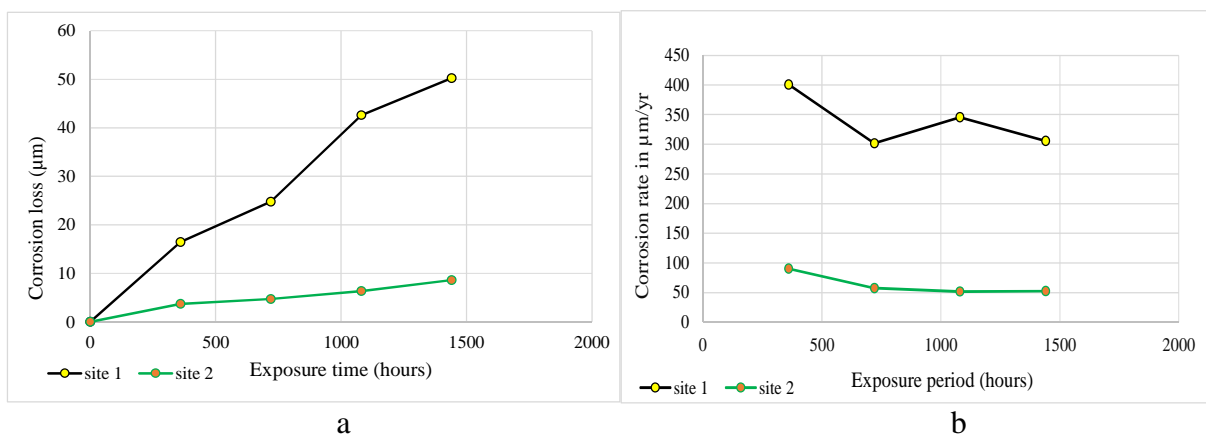


Figure 2 (a,b) Corrosion loss and corrosion rate for Cu-Ni 90/10 alloy

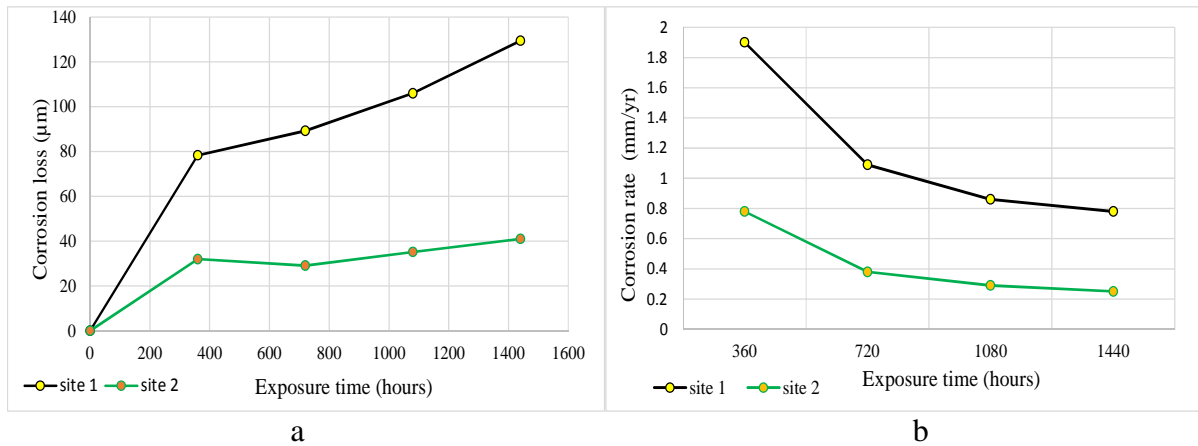


Figure 3 (a,b) Corrosion loss and corrosion rate for mild steel

4. Discussion

From the experimental results in table 4 and 5, it is evident that the average corrosion loss and corrosion rate is comparatively higher for both metals in natural seawaters of site 2, hence it can be affirmed that the warmness and higher salinity of sub-tropical seawaters of North Indian Ocean are influential factors towards the corrosion phenomena. The decreasing trend of corrosion rate with the exposure period is also evident for both metal alloys on either site location, because of the gradual rise in the thickness of corrosion deposit layer and stoop in the diffusion process between oxygen molecules and metal surface. The declining corrosion trend with the exposure period is more common in metal alloys subjected to the marine environment and it is also aligned with the theoretical credence of the corrosion phenomena. On the contrary, a few research studies have stated that the corrosion rate can increase over the period, mainly in the presence of substantial nutrient concentration such as DINs, an abundance of biological agents in seawater, and high loading/ stress concentrations [52–54].

The corrosion loss trend for both metal alloys at site 1 is found to be enormously higher than that of site 2. Although the influential environmental factors (temperature, salinity, depth exposure, surface wetting) for corrosion were almost similar for both sites, however, the chemical constituents are merely different because of high nutrients and pollutant content in the seawater of site 1. The higher amount of pollutants, especially the high nutrient concentration in the form of DINs (nitrates) in the water of site 1 can be attributed as the primary reason for the accelerated corrosion. The rate of corrosion is equally higher for both alloys for site 1. In the case of Cu-Ni 90/10, after 2 months the corrosion loss in polluted coastal water was nearly five times higher than that in the natural seawater. It implies that the impact of pollutant factors can be more detrimental than the physical factors and DO concentration. On the other hand, the corrosion loss is around three times higher for mild steel in the polluted waters. The high turbidity factor and total dissolved solids (TDS) at site 1 can be another reason for the accelerated corrosion losses. Particularly, Cu-Ni 90/10 alloy has a greater sensitivity towards silicon content and its particulate size in the seawater, as larger sand particles tend to break protective oxide film and enhance erosion-corrosion [7]. From the experimental results in table 4 and 5, it is evident that the average corrosion loss and corrosion rate is comparatively higher for both metals in natural seawaters of site 2, hence it can be affirmed that the warmness, and higher salinity of sub-tropical seawaters of North Indian Ocean are influential factors towards the corrosion phenomena. The decreasing trend of corrosion rate with the exposure period is also evident for both metal alloys on either site location, because of the gradual rise in the thickness of corrosion deposit layer and stoop in the diffusion process between oxygen

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The rate of biological activities significantly increases with the rise in seawater temperatures (up to 50 C). Therefore, it can be reasoned that the warm seawaters in this region can be helpful to enhance the MIC. In the literature, several research studies have also reported that the corrosion of carbon steel in seawater is mostly governed by the rate of diffusion of oxygen molecules through the oxide layers of rust and biological content deposited on exposed surfaces. The higher corrosion rates in near-surface water have been attributed to continuous exposure of metal surfaces to nutrient-rich polluted waters, which in turn catalyse the metabolism of biological agents during long-term corrosion, SRBs in particular [32,34,38,55,56]. Melchers [55] presented a modified bi-modal corrosion prediction model for polluted waters that attributed the elevated mass loss during long-term corrosion as a function of DINs concentration and seawater temperature. Figure 4 (a,b) represents this relationship.

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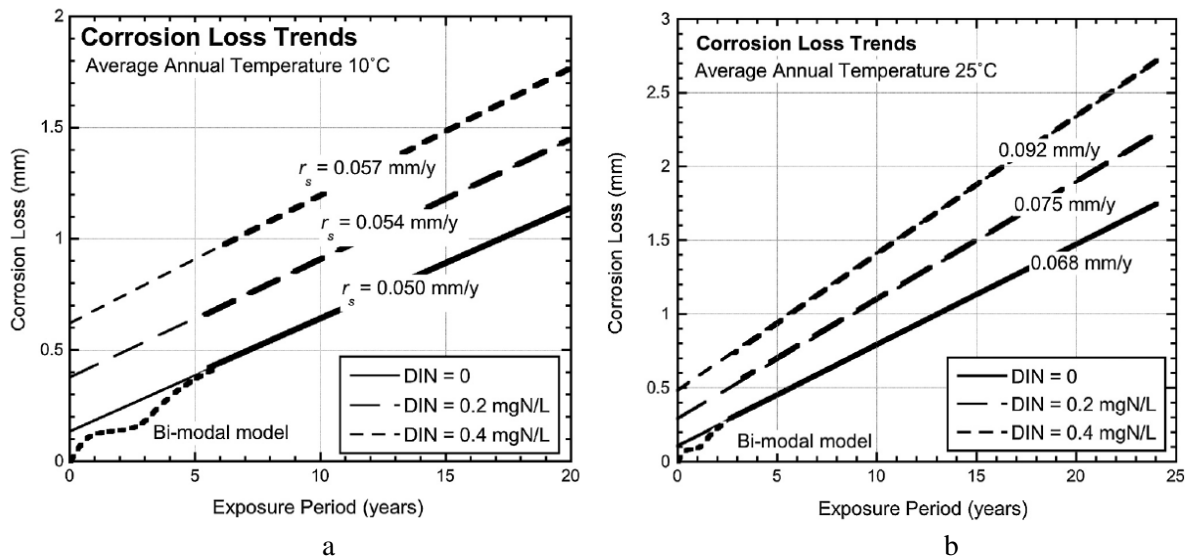


Figure 4 (a,b) Estimated corrosion loss trends as a function of average DIN concentration and seawater temperature [55]

Figure 4 highlights the influence of DIN on the long-term corrosion (phase 3 and 4 in Melcher bimodal) at 25 C and 10 C, respectively. However, it does not elucidate the effect of nutrients on short-term corrosion (phases 0,1, and 2). Neither it provides any explanation to account for the impact of nutrients concentration on short-term corrosion parameters c_a and r_o in Melchers bi-modal model.

This research paper highlights that, to the best knowledge of the authors, no research work has been found that explain the relationship between high DIN concentration in seawater and corrosion mechanism of metal alloys during early phases of corrosion. The field experiments results presented in this paper demonstrated that the higher DIN concentration in polluted seawater not only affect the long term corrosion process, but it can also influence the corrosion rates for short-term exposures (up to 2 months). More, it is suggested that further field and laboratory-based research is incumbent in future to understand the complexity of phenomena as well as to correlate the nutrient concentration with the accelerated early phase of corrosion. Presently, very limited literature is available which can provide a deep understanding to unearthed this complex phenomenon and indicate ways to develop a quantitative methodology for corrosion loss prediction. With this research study, it is also considered appropriate to investigate the combined effect of DINs at various temperatures and salinity levels of seawaters on various phases of corrosion. Based on these observations, an updated corrosion prediction model can be formulated or existing models can be updated.

5. Conclusion and recommendations for future work

The experimental results for the short-term corrosion of Cu-Ni 90/10 alloy and mild steel in the two site location of the North Indian Ocean revealed that:

- a. The higher seawater temperature and salinity level provide favorable environment for high corrosion losses.
- b. The experiments were performed to investigate general corrosion for two types of metal alloys (Cu-Ni 90/10 and mild steel) under shallow immersed condition. Two site locations were selected for experiments where metal samples were simultaneously placed for corrosion loss investigation. Site 1 represented the pollutant rich coastal seawater whereas site 2 signified the natural seawaters.
- c. The seawater temperature in both site location were assume to be same at both locations. The chemical factors were however found to be different because of the pollutants and high nutrient content in the seawaters of site 1.
- d. Comparatively higher average corrosion loss and corrosion rate was observed for both metal alloys in the natural seawater conditions of site 2. This high corrosion loss can be attributed to high temperature and salinity level in the seawaters of North Indian Ocean.
- e. On the other hand, enormously high average corrosion loss and corrosion rate were observed for Cu-Ni 90/10 alloy and mild steel coupons immersed at site 1. The higher pollutants content, especially high DIN concentration has been attributed for accelerated short-term corrosion which tends to catalyse the metabolism process and the rate of MIC.
- f. Although the significance of physical environmental factors towards accelerated corrosion still stays valid in this study, however, pollution-induced nutrients at site 1 vehemently surpassed the overall contribution towards the acceleration of the corrosion process.
- g. Based on the field survey of marine installation and expert opinion from regional corrosion/maintenance experts, a substantial reduction in the estimated service life of assets, high operation costs and enormous challenges for maintenance and asset management have been noticed in this region, particularly in platforms operating in the polluted waters near the coast.
- h. This paper provides future avenues for short term corrosion modelling in nutrient-rich polluted seawaters, where corrosion losses can range between 3-5 times than the nominal corrosion losses in the natural seawaters. Further, this study also proposes an adjustment in the short-term corrosion phases of previously developed models, which were initially developed based on the corrosion data acquired for clean natural seawater conditions.

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