1

The Nature of Marine Environments

Bopinder Phull

Corrosion-Control and Materials-Selection Consultant, Wilmington, NC, USA

1.1 Introduction

More than two-thirds of the earth's surface is covered by seawater. It is a critical source of food and table salt and for conversion to fresh water (desalination), where the latter is naturally in short supply. Magnesium ions are extracted from seawater for subsequent production of Mg metal and its alloys. Seawater is a complex mixture of chemical, physical, and biological species whose characteristics can be influenced by many factors such as geography, temperature, depth, and ocean currents. For centuries, it has been recognized that seawater is the most corrosive natural environment toward engineering materials, particularly many metals and alloys. Some constituents and circumstances can accelerate attack, while others may retard it. Corrosivity can vary to some degree, for example, with geographic location; however, no seawater is considered to be noncorrosive anywhere in the world in its natural state. A good understanding of the influence of environmental factors on seawater corrosivity, coupled with experience and test data can help optimize selection and/or utilization of materials in practical marine applications.

Materials are exposed to marine environments in numerous applications such as ships, offshore platforms, subsea pipelines and telecommunications cables, oceanographic instruments, dock bulkheads; heat exchangers, piping, pumps, and valves in seawater-cooled power, chemical, and desalination plants; ferries, yachts, pleasure boats, fishing gear, and oceanfront buildings. Marine environments are typically classified in terms of "zones" to which materials are exposed in given situations, for example, atmospheric, splash-and-spray, tidal, immersion or submerged, and bottom-mud or sediment.

There are many complex environmental factors that influence seawater corrosivity. Many of these factors are interrelated and often synergistic. This can lead to unexpected behavior of materials performance in specific situations.

Several factors contribute to marine atmospheric corrosion, with the local environment the single most important factor. Moisture, temperature, wind, airborne contaminants like Cl^-, and SO_4^{2-}, pollutants such as SO_2, alloy content, location, and biological organisms affect initiation and propagation of atmospheric corrosion. The most aggressive condition is a warm tropical coastal location with prevailing winds that carry both chlorides and sulfates from the ocean to shore. A

LaQue's Handbook of Marine Corrosion, Second Edition. Edited by David A. Shifler.

critical humidity and time-of wetness, and ionic/pollutant content and concentration play a significant part in the degree of corrosion that occurs for a given material. A more detailed discussion of the factors associated with marine atmospheric corrosion is included in Chapter 4.

1.2 Seawater Chemistry

1.2.1 Chemical Composition of Seawater

Seawater contains a number of soluble salts. The total salt content is often expressed as salinity, which is defined as the total solid matter in grams contained in 1 kg of seawater when all carbonate has been converted to oxide, bromine, and iodine replaced by chlorine, and all organic matter completely oxidized. It is customary to express salinity is parts per thousand (ppt) with the symbol ‰. Seawater salinity is not uniform throughout the world as shown in Figure 1.1. The North and South Atlantic have zones of relatively high salinity compared with the Pacific Ocean, which is diluted by rainfall during the monsoon season. It is higher in the tropics, particularly in the enclosed basins where concentration by evaporation is favored. Conversely, Arctic and Antarctic regions have lower salinity values.

Conversely, salinity can be substantially lower in areas where seawater is diluted by freshwater runoff from inflowing rivers or near melting glaciers. Littoral waters can also discharge considerable amounts of sediments and pollutants downstream. Table 1.1 shows the approximate salinities of various seawaters around the world. In the vast majority of open seawaters (i.e. well away from land), the salinity is in the 32–36‰ range. It varies from a low of about 8‰ in the Baltic Sea up to about 47‰ in the Arabian Gulf. In the landlocked Dead Sea, it is an order of magnitude higher than normal seawater. Thus, although seawater salinity can vary widely from one location to another, all natural seawaters are corrosive toward many common construction materials such that some form of corrosion-control is often necessary to maintain structure/component integrity and functionality for long-term applications.

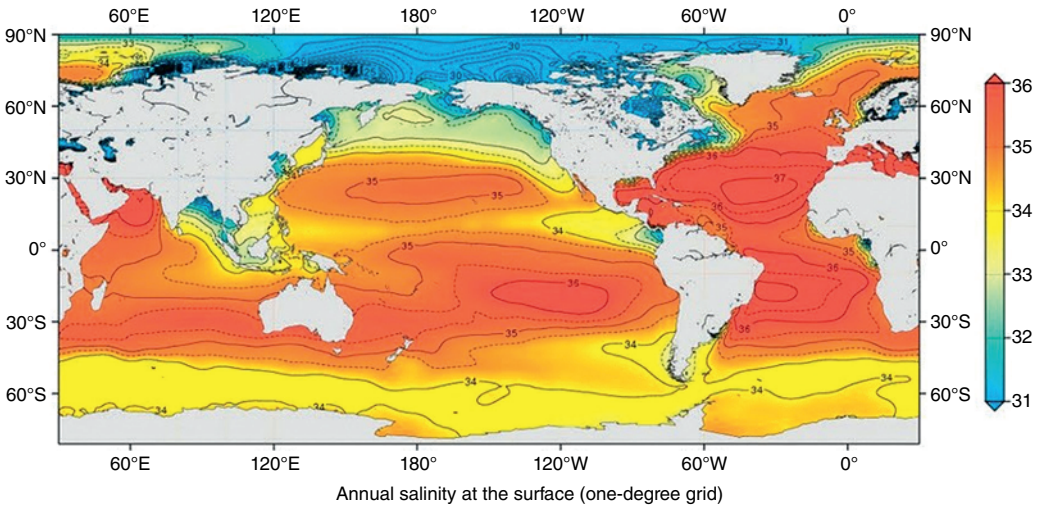


Figure 1.1 Average annual mean sea surface salinity for the world's oceans, 1955–2012. The North and South Atlantic Ocean have higher salinity values than the Pacific Ocean. Colder regions tend to have lower salinity than tropical zones. *Source:* National Oceanic and Atmospheric Administration (NOAA), National Centers for Environmental Information, "Ocean Climate Laboratory Team, World Ocean Atlas 2013 Version 2, WOA13F V2 Interactive image Access".

Table 1.1 Approximate average salinities of major ocean waters.

Seawater	Salinity (ppt or ‰)
Dead Sea	322
Arabian Gulf	47
Red Sea	43
Mediterranean Sea	41
Atlantic Ocean	36
Indian Ocean	35
Pacific Ocean	34
North Sea	33
Bering Sea	32
Black Sea	22
Caspian Sea	13
Baltic Sea	8

An alternative method of measuring and reporting the salt content of seawater is in terms of chlorinity which is defined approximately as the total amount of chlorine (grams), plus equivalent chlorine assumed to replace bromine and iodine, in 1 kg of seawater. Chlorinity is related to salinity as follows:

$$\text{Salinity} = \left(1.80655 \times \text{Chlorinity}\right) + 0.03$$

Like salinity, chlorinity is also expressed in parts per thousand (ppt; symbol ‰). Thus, salinity of 32–36‰ for the majority of seawater corresponds to chlorinity of ~18–20‰. In many cases, salinity can be estimated with sufficient precision by determining the specific gravity or density of seawater and adjusting for temperature. For example, at a salinity of 35‰, the density of surface seawater varies from 1028 kg/m^3 at 5 °C to 1022 kg/m^3 at 30 °C. In deep oceans, under high pressure and low-temperature conditions, the density of seawater can increase to 1050 kg/m^3.

1.2.1.1 Role of Ions

Table 1.2 (Lyman and Abel 1958) shows the "average" concentrations of ionic constituents in open seawater at a salinity of 35‰. It is apparent that the major ionic constituents are chloride (Cl^-) and sodium (Na^+) ions derived from the soluble salt, NaCl. Figure 1.2 shows the effect of dissolved NaCl concentration on relative corrosion rate of iron in air-saturated water at room temperature (Uhlig and Revie 1985). Carbon steels are also expected to follow this behavior. The corrosion rate increases at first, reaching a maximum at a NaCl concentration of ~3 wt% (which, by a remarkable coincidence, corresponds to salinity of about 30‰ for natural seawater). The corrosion rate then decreases steadily with further increase in NaCl concentration; at saturation (26% NaCl), surprisingly, it is even lower than that for distilled water. An explanation of this behavior is detailed elsewhere (Uhlig and Revie 1985). Briefly, it is attributed to changes in the rust-film diffusion-barrier properties at up to 3% NaCl concentrations; and at higher concentrations, the dominant influence of inverse O_2 solubility. Many researchers who don't have ready access to natural seawater typically resort to testing in 3.5% NaCl solutions as a substitute. Others utilize more elaborate artificial compositions, such as one exemplified in ASTM standard D1141 (ASTM International 2021).

Table 1.2 Major ionic constituents in seawater of 35‰ salinity.

Ion	Concentration (ppm)
Chloride, Cl^-	19 353
Sodium, Na^+	10 760
Sulfate, SO_4^{2-}	2712
Magnesium, Mg^{2+}	1294
Calcium, Ca^{2+}	413
Potassium, K^+	387
Bicarbonate, HCO_3^-	142
Bromide, Br^-	67
Strontium, Sr^{2+}	8
Borate, $B_4O_7^{2-}$	4
Fluoride, F^-	1

Source: Based on Lyman and Abel (1958).

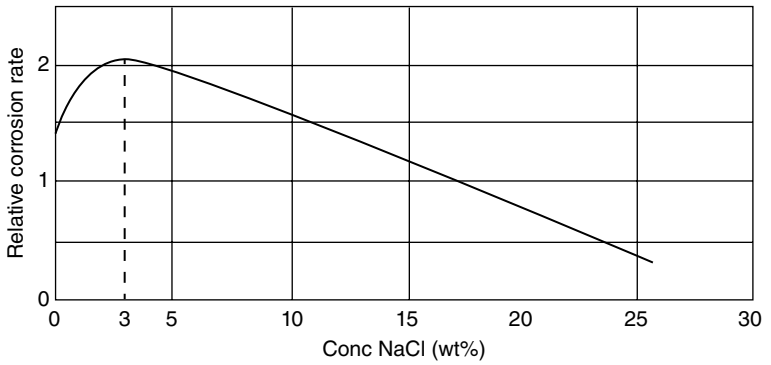


Figure 1.2 Effect of NaCl concentration on corrosion rate of iron in aerated water at room temperature; composite data from several investigations. *Source:* Figure 14, p. 108. Uhlig and Revie (1985). Reproduced with permission of John Wiley & Sons.

However, these synthetic seawaters do not contain micro- and macroorganisms found in natural seawater that can profoundly influence corrosion behavior of many materials. Dupont et al. (1998) observed ennoblement of stainless steels exposed in "biochemical artificial seawater," seawater amended with glucose and glucose oxidase. The enzyme catalyzes the oxidation of glucose to gluconic acid and H_2O_2 (Dupont et al. 1998).

Chloride (Cl^-) ions are considered to be the most aggressive species in seawater and many other environments in which they are encountered, even at relatively low concentrations. The small size of Cl^- ions and high molar polarization strongly favor adsorption closer to metal surfaces (inner Helmholtz layer) and hence active participation in corrosion reactions. Chloride ions can interfere with the formation and maintenance of protective films, or breakdown existing films, which often manifests as localized corrosion attack. In seawater, Na^+ ions have only a very weak polarizing effect on Cl^- ions and, hence, exert no significant influence on corrosion processes.

At similar concentration, sulfate (SO_4^{2-}) ions are more aggressive than Cl^- ions despite the higher molar polarization and higher adsorbability of the latter. However, when Cl^- ions are present, SO_4^{2-} ions at relatively high concentrations can provide a degree of corrosion inhibition

(Pistorious and Burnstein 1992). In seawater, SO_4^{2-} concentration (~2700 ppm) is insufficient to inhibit the strong corrosive effect of the Cl^- ion concentration (~19 000 ppm). On the other hand, in the presence of an organic carbon food source, sulfate-reducing bacteria (SRB) in seawater can reduce SO_4^{2-} ions to sulfides (S^{2-}) under anaerobic conditions. In principle, S^{2-} films can be protective if they cover the entire metal surface and if cathodic depolarizers such as O_2 are absent. However, in practice, the galvanic nature of such films can greatly accelerate localized corrosion, especially in carbon steels and copper alloys, when alternate exposure to anaerobic and aerobic conditions occurs.

Other ions such as bromide (Br^-) and fluoride (F^-) are present at very low concentrations in natural seawater and, therefore, not generally considered to be corrosive. Natural seawater contains trace amounts of copper and other heavy metals; however, since they are usually present as electrochemically inactive compounds, they do not usually exert a strong influence on corrosion behavior. In contrast, even a relatively small concentration of copper (Cu^{2+}) ions generated by corrosion of copper alloys or leached from copper-containing antifouling paints can cause aggressive corrosion of aluminum and its alloys (ASM Handbook, 1987). The mechanism is called deposition or cementation corrosion (Dexter 1981), where Cu^{2+} ions plate out on aluminum by electrochemical reduction as metallic copper (Cu), which subsequently promotes corrosion by galvanic (dissimilar metal) action. Similarly, ferrous (Fe^{2+}) ions, generated by corrosion of upstream steel components, can deposit on downstream aluminum components in desalination plants and accelerate corrosion of the aluminum (Cook and McGeary 1964).

Under certain conditions, calcium (Ca^{2+}) ions, bicarbonate (HCO_3^-) ions, and magnesium (Mg^{2+}) ions in seawater can react at cathodic sites to produce protective calcareous deposits, discussed later in this chapter.

1.2.1.2 Dissolved Gases

The primary dissolved gas in natural seawater is oxygen (O_2). Dissolved oxygen (DO) is of major importance in controlling the corrosion behavior of metallic materials in seawater, even more so than chloride (Cl^-) ions. It plays a predominant role in cathodic reactions and accelerating corrosion of metals in the active state. Conversely, O_2 contributes to the development and preservation of passivity, via complex oxide films, e.g. on stainless steels, nickel–chromium alloys, titanium alloys, and aluminum alloys. The O_2 concentration in seawater in equilibrium with a normal atmosphere varies with temperature and salinity. For example, at 25 °C and a salinity of 35‰, the equilibrium DO concentration is 6.5 mg/l. At the same salinity, the equilibrium DO concentration at 5 °C is 9.7 mg/l. The equilibrium DO concentration also decreases as the salinity increases and vice versa. The DO concentration of the Dead Sea, for example, which has a salinity of around 322‰ is about 0.1 mg/l. In contrast, for freshwater at room temperature (~25 °C), the equilibrium DO concentration is typically around 10 mg/l.

DO concentration is reported either as mg/l (ppm) or ml/l (ppt). The conversion factor from one unit to the other is shown below.

$$\text{mg/l} = \text{ml/l} \times 1.429$$

In addition to salinity and temperature, the DO concentration of seawater can be strongly influenced by marine plants and organisms and mixing with other waters. Photosynthesis increases the O_2 content and decomposition of organic matter lowers it. These processes account for variations in O_2 concentration, for example, with depth as described later in this chapter. At normal atmospheric pressure, surface waters tend to be saturated or supersaturated in O_2; this includes the thin seawater liquid environment in the splash zone. Formation of organic biofilms commences almost instantaneously on immersed surfaces in seawater. Microorganisms and microorganisms

incorporate, grow, and form complex colonies, slime films, and biofouling encrustations on these surfaces with time. Aerobic bacteria in these colonies use O_2 as an electron acceptor; in the O_2-depleted areas, obligate and facultative anaerobic bacteria can proliferate. Many of these bacterial species (especially anaerobic SRB) can lead to microbiologically influenced corrosion (MIC) of various materials.

The role of O_2 in seawater corrosion is a complex one. For carbon steels, it accelerates corrosion by serving as a cathodic depolarizer, i.e. O_2 reduction reaction at cathodic areas.

$$O_2 + 2H_2O + 4e^- \qquad 4OH^-$$

Figure 1.3 illustrates the direct relationship between corrosion rates of carbon and low alloy steels and dissolved O_2 concentration which varies with ocean depth (Reinhart 1976). However, at elevated temperatures in thermal desalination processes, for example, the corrosion rate of carbon steel, copper, and aluminum brass can be very high unless the O_2 concentration is reduced to very low levels, typically 10 ppb or less, as shown in Figure 1.4. Copper–nickel and aluminum alloys are much less affected.

Differences in O_2 concentration can occur, for example on metal surfaces exposed to seawater and occluded areas such as under silt deposits, biofouling growths, in man-made crevices such as under gaskets, O-rings, at threaded joints. This gives rise to O_2-concentraion cells, frequently referred to as differential oxygenation cells in which the O_2-rich area acts as a cathode and the O_2-deficient area behaves as an anode that incurs accelerated localized attack.

Seawater normally contains carbon dioxide (CO_2) in equilibrium with the atmosphere from which it comes. The total CO_2 content as carbonic acid, bi-carbonates, and carbonates ranges from about 60 to about 100 ppm. A balance with respect to carbonic acid is achieved by the growth or solution of the carbonate shells of marine organisms and by the absorption of CO_2 in photosynthesis.

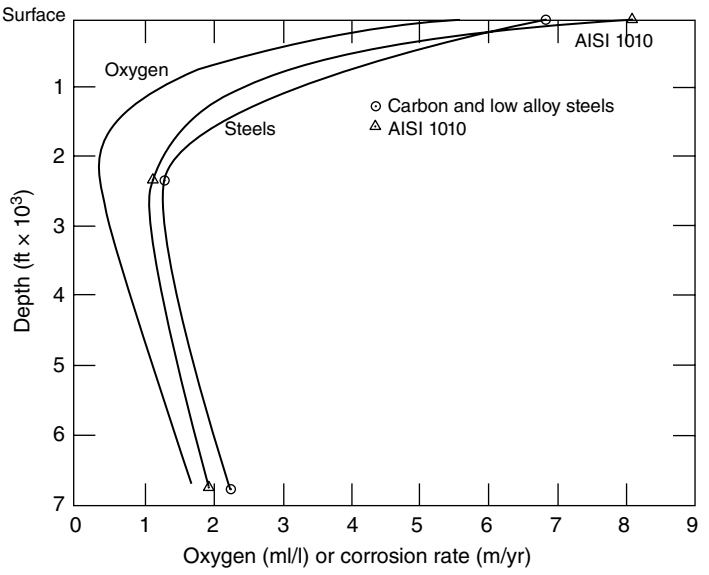


Figure 1.3 Illustration of direct relationship between dissolved O_2 concentration in seawater and corrosion rate of carbon and low alloy steels. *Source:* Reinhart (1976).

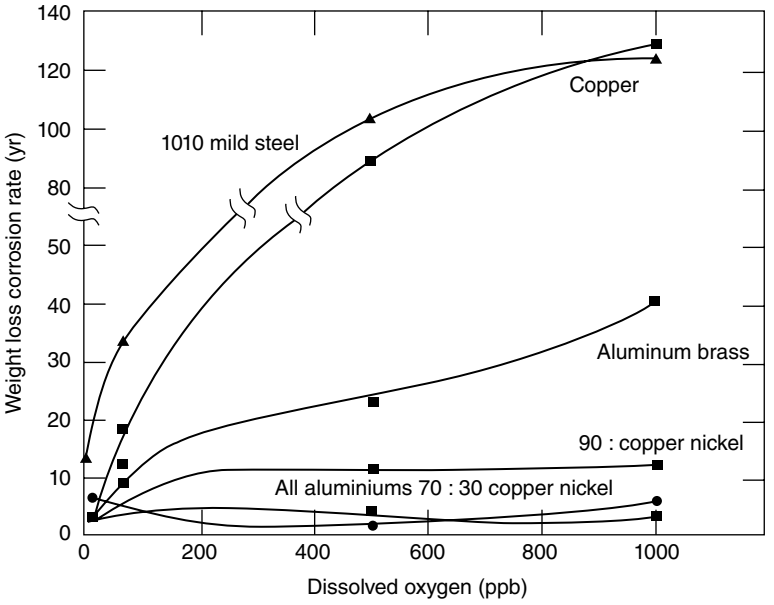


Figure 1.4 Effect of low level dissolved O_2 concentration range on corrosion rate of steel and copper alloys in hot seawater; temperature 121 °C; pH 7.0; velocity 1.5 m/s, flow – once through; salinity 26–33; exposure duration 25–30 days. *Source:* Figure 4-35, p. 136. LaQue (1975). Reproduced with permission of John Wiley & Sons.

Pollution can lead to small amounts of ammonia (NH_3), typically about 50 ppb. This can become an important factor in corrosion in spaces in steam condensers, where noncondensable NH_3, CO_2, and O_2 may accumulate to produce condensates capable of producing aggressive attack and stress corrosion cracking (SCC) of brasses. Copper–nickel alloys are therefore preferred where NH_3 pollution is a factor.

Hydrogen sulfide (H_2S) and other sulfides can be present in seawater as a by-product of SRB activity and a frequent result of organic pollution discharge. High sulfide concentrations are prevalent in undersea hydrothermal vents. In severely polluted estuarine or harbor waters, the H_2S concentration may reach levels of 50 ppm or even higher. Bottom sediments carrying large amounts of decomposing organic matter may also have very high sulfide contents. Sulfides accelerate attack and especially pitting in copper alloys used for heat exchanger tubes and piping. For example, ship propeller wash in shallow estuarine waters can churn up sulfide-containing bottom sediment that is entrained in cooling water used by power plants, leading to acceleration of corrosion attack on copper alloys.

Table 1.3 demonstrates that even small concentrations of H_2S can accelerate corrosion of copper alloys to a serious extent. Sulfide films can be protective so long as they are continuous, adherent, dense, and intact. This may explain why the phosphor copper in Table 1.3 did not exhibit corrosion acceleration in the presence of H_2S compared to clean seawater. Local breakdown of sulfide films can promote severe pitting when O_2 is present. The ruptured areas in the sulfide film are anodic and undergo accelerated localized attack because the surrounding sulfide film acts as a cathode for O_2 reduction. In the absence of O_2, pitting attack is usually significantly less severe. The harmful effects of sulfide films persist even after the source has been removed. Therefore, it is very important to precondition new or cleaned copper alloy heat exchanger tubes by initial exposure to unpolluted seawater, typically for about three months (Francis 2010; Gudas and Danek 1976; Gudas et al. 1978; Eiselstein et al. 1983; Jasner et al. 1998).

Table 1.3 Effect of H_2S in seawater on corrosion of condenser tube alloys.

	Corrosion rate (μm/y)	
Alloy	**Clean seawater**	**Seawater + 4 ppm H_2S**
Phosphor copper	356	381
Admiralty brass	330	889
70/30 copper-nickel	127	660

Velocity 2.3 m/s; temperature 27 °C; test duration 64 days.
Source: Boyd and Fink (1978).

H_2S in vapors released from polluted seawater in thermal desalination plants can exacerbate vapor-side corrosion of susceptible copper alloys. H_2S can increase hydrogen embrittlement susceptibility of high-strength steels and martensitic, ferritic, precipitation-hardening, and duplex stainless steels under deliberate or inadvertent cathodic protection conditions.

1.2.1.3 Scale-Forming Compounds

Ca^{2+}, HCO_3^-, and Mg^{2+} ions in seawater can react with hydroxyl (OH^-) ions to form in situ scales on metal surfaces that are cathodically protected, on nobler metals in galvanic couples, and sites that act as cathodes in normal corrosion reactions. The most common constituent of such scales is calcium carbonate; hence, such scales are also known as calcareous deposits.

$$Ca^{2+} + HCO_3^- + OH^- \qquad CaCO_3 + H_2O$$

Magnesium hydroxide is more prevalent in cathodic overprotection situations.

$$Mg^{2+} + 2OH^- \qquad Mg(OH)_2$$

Smaller amounts of strontium compounds may also be present in calcareous scales. Scales rich in $Mg(OH)_2$ are gelatinous, thicker, and considerably less protective compared to $CaCO_3$ (Humble 1948). Calcareous scales can form profusely at elevated temperatures, e.g. on heat-transfer surfaces, because of the inverse solubility of $CaCO_3$ with increasing temperature.

Calcareous deposits serve as diffusion barriers for O_2 which is a cathodic depolarizer that enhances corrosion on metals such as carbon steels. Large, bare steel structures (e.g. offshore platforms) are typically cathodically protected. Formation of calcareous deposits is of paramount importance in such cases to reduce long-term current demand for continued cathodic protection, provide more uniform current distribution and protection, and increase anode life. Calcareous deposit morphology, thickness and protective properties are affected by many factors (Cox 1940; Guillen and Feliu 1966; Shigeno et al. 1975; Wolfson and Hartt 1981; Phull 1981; Hartt et al. 1983; Ambrose et al. 1983; Culberson 1983; Fisher and Finnegan 1989a,b; de Oliveira and de Souza Pimenta 1993) such as current density at the cathode, seawater composition, temperature, velocity, and possibly biofilms. Typical current density versus time behavior for carbon steel is illustrated in Figure 1.5. A comparison of protective, primarily $CaCO_3$ (aragonite) deposits, and poorly protective, predominantly $Mg(OH)_2$ (brucite) deposits, is shown in Figure 1.6. The former develop at the more optimum protection potentials (e.g. –800 to –1000 mV SCE); and the latter at overprotection potentials (e.g. –1200 mV SCE). For incomplete protection conditions (e.g. –750 mV SCE), the deposits consist of a mixture of $CaCO_3$ and iron corrosion products (Fe_2O_3 and Fe_3O_4). Cathodic

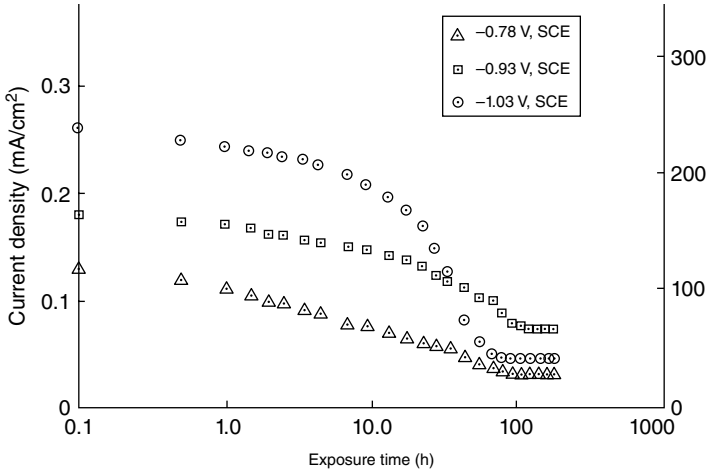


Figure 1.5 Illustration of current density decrease as a result of calcareous deposit formation on steel in seawater at three different cathodic protection potentials; seawater velocity 8 cm/s. *Source:* Wolfson and Hartt (1981).

Figure 1.6 Illustration of morphology of calcareous deposits formed in seawater. (a) Protective deposits formed at −1000 mV SCE; (b) nonprotective deposits formed at −750 mV SCE (underprotection); and (c) nonprotective deposits formed at −1100 mV SCE (overprotection). *Source:* Phull (1981).

protection systems are usually designed on the basis of current density necessary to achieve the desired protection potential. Table 1.4 exemplifies the change in calcareous deposit properties at various current densities (Doremus and Doremus 1950).

Reportedly, Mg^{2+} ions in seawater interfere with the nucleation and precipitation of $CaCO_3$ crystals (Pytkowich 1965). Precipitation of $CaCO_3$ as aragonite in natural seawater environments is favored because of the high concentration of Mg^{2+} ions relative to Ca^{2+} ions (Philipponeau et al. 1981); evidently, in other environments, a Ca^{2+}/Mg^{2+} ratio greater than about 4, promotes precipitation of $CaCO_3$ as calcite crystals.

1.2.1.4 Suspended Matter

Sand, insoluble salts, and other abrasive particles suspended in seawater can aggravate deterioration of materials by water in motion. This includes the simple scouring effects of mechanical abrasion (erosion) and the frequently greater effect of the removal or prevention of formation of what would otherwise be protective corrosion products or scales (i.e. by erosion–corrosion). Suspended solids can abrade coatings and calcareous deposits. Silt deposits can also serve to exclude O_2 from surfaces on which they rest and thereby create oxygen concentration corrosion cells leading to underdeposit localized attack. Where seawater carrying suspended matter is used in heat

Table 1.4 Relationship between cathodic protection current density and properties of calcareous deposits formed in seawater.

Initial current density (mA/m^2)	Duration (days)	Calcareous film formed	Current density for continued protection (mA/m^2)
2000	1	Soft with high Mg content	20–30
1000	2–3	Fairly hard	20–30
500	5–6	Hard, mainly calcareous	20–30
200	20–30	Medium thickness, hard	30–40
100	60–90	Medium thickness, hard	40
60	180	Light, hard	40–50

Source: Doremus and Doremus (1950). Original chart from information in article.

exchangers with alloy tubes sensitive to underdeposit attack, such deposits must be frequently or continuously removed by appropriate cleaning practices. Large shells and pebbles can lodge in condenser tubes and create turbulence capable of causing impingement attack (erosion–corrosion) downstream of such partial obstructions to seawater flow.

1.2.1.5 pH

The hydrogen ion concentration of normal, unpolluted seawater is usually in the slightly alkaline range of 8.1–8.3. This represents the balance between CO_2 from the atmosphere and the basic ions in the water. Seawater alkalinity can increase to more than pH 9 if the concentration of the CO_2 is reduced, for example, by plant photosynthesis processes and temperature changes. Normal seawater is highly buffered. The alkaline pH also explains why the O_2 reduction reaction is more important than H_2 evolution in seawater corrosion processes. However, decomposition of marine organisms resulting in loss of O_2 and generation of H_2S can lower the pH well below 8. Increasing the temperature of normal seawater can raise the pH if dissolved CO_2 is driven off or consumed by excessive photosynthetic activity of plants at the higher temperatures.

In thermal desalination processes, the seawater is treated to prevent carbonate scale deposition that would otherwise interfere with heat transfer. One water-treatment technique to prevent scale deposition involves addition of acid to lower the pH to 4, followed by neutralization with caustic soda to bring the pH back to 7.3. Scale-forming carbonates are thus broken down to release CO_2. The condensed vapors from the acid treatment have a pH of about 4, and, in the presence of O_2 can be very corrosive to iron and many nonferrous alloys.

Seawater adjusted to a lower pH by such scale-control treatment becomes more corrosive, partly because of its lower pH and partly by elimination of what otherwise would be protective scales. This can be offset to a major extent by reducing O_2 to very low concentrations, typically well under 50 ppb, especially at elevated temperatures.

1.2.1.6 Chlorination

Continuous or intermittent dosing with chlorine (Cl_2) or hypochlorite (OCl^-) is a commonly used method for biofouling control, for example to maintain heat transfer on condenser tubes. Chlorine can be easily generated electrolytically from seawater. At low concentrations, e.g. <1 ppm residual

for continuous dosing, chlorine is not considered to increase seawater corrosivity appreciably. In fact, at low levels, chlorine has been found to reduce galvanic corrosion, e.g. of copper coupled to noble stainless steels (Wallen and Henrikson 1989). This has been attributed to suppression of biofilm activity by the chlorine. However, chlorine is a powerful oxidant, and at higher concentrations, it ennobles the corrosion potential of stainless steels and increases risk of pitting and crevice attack. Higher temperatures increase the corrosivity of chlorine.

1.3 Physical

1.3.1 Temperature

Seawater temperature can vary over a wide range. At the surface, it ranges from about 35 °C at the equator to about −2 °C at the poles. Seawater temperature is also subject to seasonal variations caused by climate and ocean currents. Thus, it can vary widely even at the same location, and, in general, it decreases with ocean depth. Higher temperatures lower the solubility of dissolved O_2 but increase diffusion rate. The net effect can be higher corrosion rates even though O_2 solubility is lower. In the absence of supplementary effects of biofouling, the general trend of increasing corrosion rate of steel as seawater ambient temperature increases is illustrated in Figure 1.7. However, if heavy biofouling growth is allowed to occur, the effects of the higher temperatures of tropical waters are offset by the barrier to O_2 diffusion.

Biofilms are produced on metal surfaces by microorganisms (bacteria) in seawater. Initially, there is an increase in bacterial activity, and hence increased corrosion propensity, as seawater temperature increases. However, once the temperature exceeds a critical value (e.g. ~50 °C) bacteria become less viable and biofilm-associated corrosion activity of the seawater is diminished.

The effect of higher elevated temperature on corrosion rates of carbon steels and copper alloys in a hot seawater test loop simulating thermal desalination is shown in Figures 1.8 and 1.9, respectively. It is apparent that despite the very low O_2 concentration in the hot seawater environment, the corrosion rates for carbon steels nearly doubled as the temperature increased from about 82 °C to about 118 °C. The effect on copper alloys was much smaller in the same temperature range.

For materials such as stainless steels, the ability of the Cl^- ion to penetrate and destroy otherwise passive films increases with temperature, which consequently increases the danger of failure by pitting or crevice corrosion. It has become common practice to determine the critical pitting

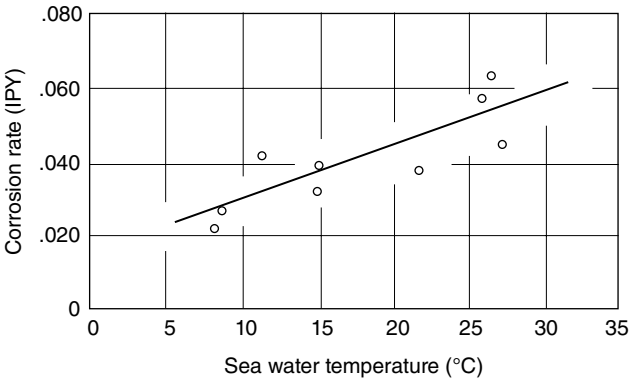


Figure 1.7 Effect of increasing seawater temperature in ambient range on corrosion rate of steel. *Source:* Figure 4-30, p. 134. LaQue (1975). Reproduced with permission of John Wiley & Sons.

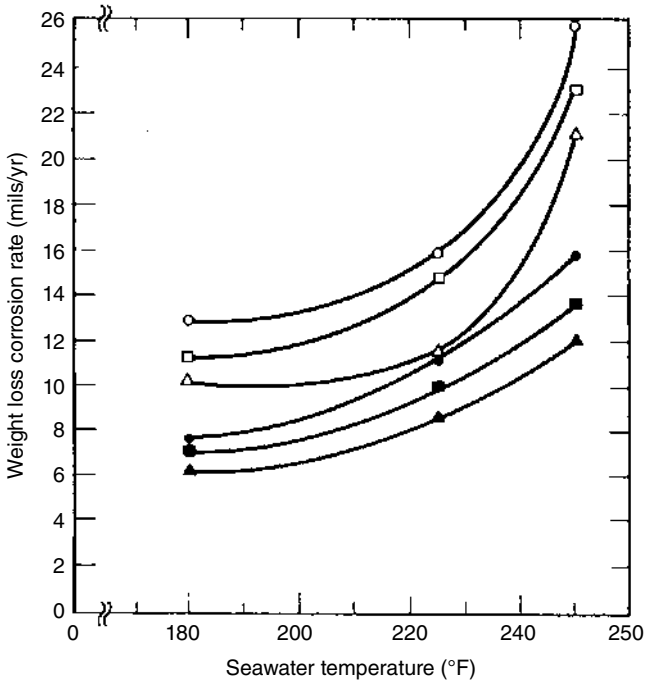


Figure 1.8 Effect of temperature and velocity on corrosion rate of 1010 carbon steel and ASTM A242 low alloy steel. pH 7.3; dissolved O_2 <5 ppb; CO_2 <3 ppm; duration 10–14 days. Open points 1010 mild steel, solid points ASTM A242 low alloy steel; solid and open triangle points 0.9 m/s, solid and open square points 1.2 m/s, solid and open circle points 2 m/s. *Source:* Figure 4-31, p. 134. LaQue (1975). Reproduced with permission of John Wiley & Sons.

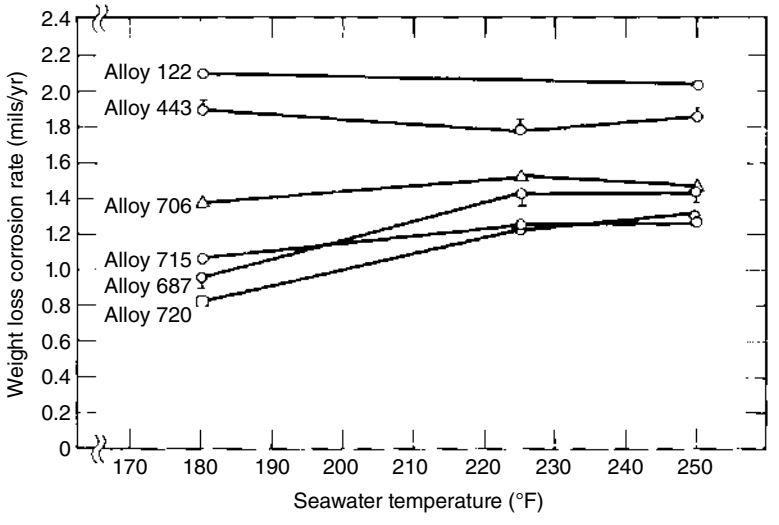


Figure 1.9 Composite plot of corrosion rate of six copper alloys versus seawater temperature in hot seawater loop. Dissolved O_2 <5 ppb; CO_2 <3 ppm; velocity 1.5 m/s; pH 7.3. *Source:* Figure 4-33, p. 135. LaQue (1975). Reproduced with permission of John Wiley & Sons.

temperature (CPT) and the critical crevice corrosion temperature (CCT) of such alloys in standardized laboratory tests such as ASTM G48 (ASTM International 2020). Alloys having CPT and CCT values above the seawater temperature are then considered as candidates for the intended application.

Titanium is susceptible to crevice corrosion in seawater environments at temperatures greater than about 70 °C (Covington 1979). The acidic crevice electrolyte suggests an oxygen-depletion and metal-ion hydrolysis mechanism similar to that for stainless steels.

In the absence of pitting or crevice attack, nonsensitized austenitic and ferritic stainless steels are considered resistant to SCC in ambient temperature seawater. SCC susceptibility increases greatly above about 60 °C where there is an opportunity for chloride concentration by evaporation. Oxygen is usually essential for SCC. At ambient temperatures, SCC can initiate at active pit and crevice sites where the local electrolyte is usually highly acidic – suggesting that the operative mechanism may be hydrogen embrittlement instead of chloride SCC.

Bromine has been implicated in SCC failure of Type 316 stainless steel in the venting systems of multi-stage flash distillation (MSF) desalination plants (Lee et al. 1983). Reportedly, bromide (Br^-) in seawater is oxidized to bromine (Br_2) during chlorination of seawater for biofouling control. Dissolution of Br_2 in seawater produces bromic (HBr) and hypobromous (HOBr) acids, and bromoamines, if ammonia is present. Hydrogen bromide, which is released into the vapor during acid treatment of the seawater for scale-control downstream, can attack susceptible stainless steels.

Cavitation damage, a special case of extreme erosion or erosion–corrosion, is discussed later in this chapter. Cavitation damage can increase with temperature up to a certain point, above which it may be reduced by increased vapor pressure within the cavities.

The corrosion potentials of metals and alloys can be affected by temperature. For example, the temperature of zinc becomes more noble with increase in seawater temperature. This shift is about 30 mV between 10 and 30 °C. Over the same temperature range, the potential of steel becomes less noble by about 60 mV. In some fresh waters containing critical concentration of nitrate and bicarbonate ions, zinc can become nobler than steel above about 71 °C. However, this potential reversal between zinc and steel has not been observed in seawater, probably due to its high Cl^- content.

With regard to cathodic protection in seawater, temperature can have a compound effect. Increasing seawater temperature reduces O_2 solubility, but increases the O_2 reduction rate; in principle, the latter increases the cathodic protection current density. The higher initial current density and inverse solubility of $CaCO_3$ in warm seawater both increase the propensity for calcareous deposit formation which consequently lowers the current density for continued protection. In contrast, the higher solubility of $CaCO_3$ in cold seawater impedes calcareous deposit formation making cathodic protection more difficult. It has also been speculated that deposition of $Mg(OH)_2$, which is considerably less protective, is more favorable in cold seawater because, unlike $CaCO_3$, its solubility has a direct rather than inverse relationship with temperature.

The inverse solubility of $CaCO_3$ with increasing temperature also commonly leads to scale formation on heat transfer surfaces. As discussed earlier, such scales hinder O_2 diffusion, and consequently, are beneficial in reducing general corrosion of active metals where the scales are adherent. However, these scales reduce heat transfer and increase the propensity for localized (underdeposit) corrosion attack on passive materials such as susceptible grades of stainless steels.

1.3.2 Electrolytic Resistivity of Seawater

The abundance of mainly chloride and sodium ions makes natural seawater highly conductive electrolytically. The high electrolytic conductivity corresponds to lower resistivity. Resistivity (ρ) is commonly reported in ohm-centimeters (Ω-cm) and conductivity (k) in micro-Siemens (μS – same

Table 1.5 Seawater resistivity (ohm cm) as function of salinity and temperature (from Covington 1979).

Salinity $^0/_{00}$	°C	5°C	15°C	20°C	25°C	30°C
10	107.1	92.5	80.9	71.6	64	57.7
20	57.3	49.6	43.5	38.5	34.5	31.1
30	39.6	34.4	30.2	26.8	24	21.6
31	38.5	33.4	29.3	26	23.3	21
32	37.4	32.4	28.5	25.3	22.6	20.4
33	36.3	31.5	27.7	24.6	22	19.9
34	35.3	30.7	27	23.9	21.4	19.4
35	34.4	29.9	26.3	23.3	20.9	18.9

Author converted the reported conductivity values (mmho/cm) to resistivity values (ohm-cm).
Source: Appendix XII in Marine Electrochemistry by Whitfield and Jagner (1981), has table which shows specific conductivity.

as μmho/cm). The resistivity of seawater decreases with increasing salinity and increasing temperature as illustrated by the data in Table 1.5 (Covington 1979). Corrosion currents between anodic and cathodic areas in local cell action are higher due to the low resistivity of seawater; and discrete anodes and cathodes can interact over greater distances. The consequence of these effects is generally higher corrosion rates at actively corroding areas. A benefit of low resistivity is higher current output from cathodic protection anodes and better current distribution (i.e. greater throwing power) on cathodic areas being protected.

1.3.3 Velocity Effects

Structures and components in seawater can encounter a wide range of water flow conditions, for example, from near zero on surfaces encrusted by heavy marine biofouling growths to well over 40 m/s on hydrofoils, pump impellers, and ship propellers. Velocity can either increase or retard corrosion depending on the material. Increase in velocity can have multiple effects, for example, reducing the thickness of the diffusion boundary layer on the metal surface, removing or preventing biofilm formation, enhancing mass transport of species such as dissolved O_2, increasing surface shear stress, increasing local turbulence, removal of protective films or coatings by erosion–corrosion or impingement attack, and so on. Figure 1.10 shows that in the absence of biofouling growths, corrosion of steel at ambient temperature accelerates as seawater velocity increases. A more dramatic effect of velocity on corrosion of zinc is shown in Figure 1.11.

Calcareous deposits formed as result of cathodic protection can hinder diffusion of O_2 to the metal surface and reduce the depolarizing effects of flow. However, high velocity, turbulent conditions, or sand/silt scour can remove such deposits or obstruct their formation.

Copper and its alloys are subject to erosion–corrosion and impingement attack with increasing velocity and turbulence effects. Figure 1.12, based on statistical data, provides a guide to critical velocities that should not be exceeded for condenser tube copper alloys. It has been demonstrated (Efird 1977) for 90 : 10 and 70 : 30 copper–nickel alloy piping that higher velocities than those shown in Figure 1.12 can be tolerated as the pipe diameter increases. This is based on the fact that the velocity required to reach the critical shear stress necessary for removal of protective corrosion product films increases with pipe diameter.

Conversely, there are situations where some minimum velocity is necessary to minimize settlement of entrained solids, development of thick biofilms, attachment and growth of

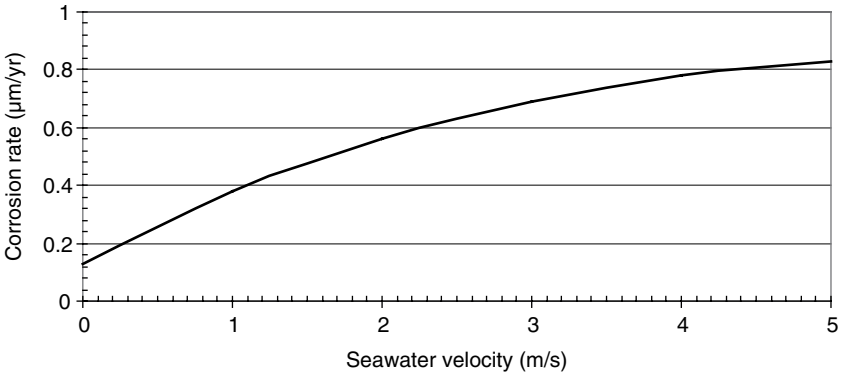
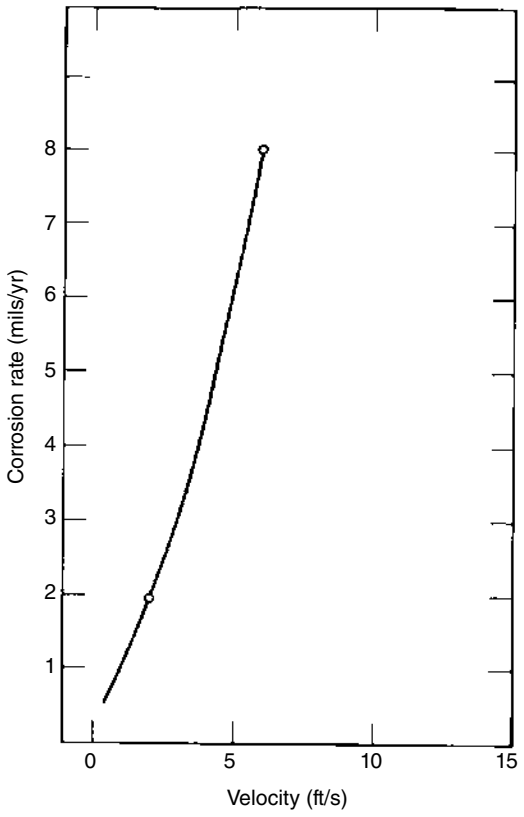


Figure 1.10 Corrosion rate of carbon steel in ambient temperature flowing natural seawater for 38 days in the absence of macrofouling. *Source:* Based on Figure 4-43 (page 143) in LaQue's (1975).

Figure 1.11 Effect of seawater velocity on corrosion rate of zinc at ambient temperature. *Source:* Based on Figure 4-45, p. 144. LaQue (1975).



macroorganisms, and so forth. For instance, a minimum velocity of about 2 m/s is commonly suggested for stainless steel tubes which would otherwise be susceptible to underdeposit crevice corrosion. In general, stainless steels, Ni–Cr–Mo alloys, and titanium and its alloys can withstand very high seawater velocities, e.g. in the order of 40 m/s. This is true only if no abrasive solids are present or no pitting or crevice corrosion has initiated. Contrary to popular thinking, increasing velocity is not a reliable way to prevent initiation and propagation of localized corrosion of stainless steels.

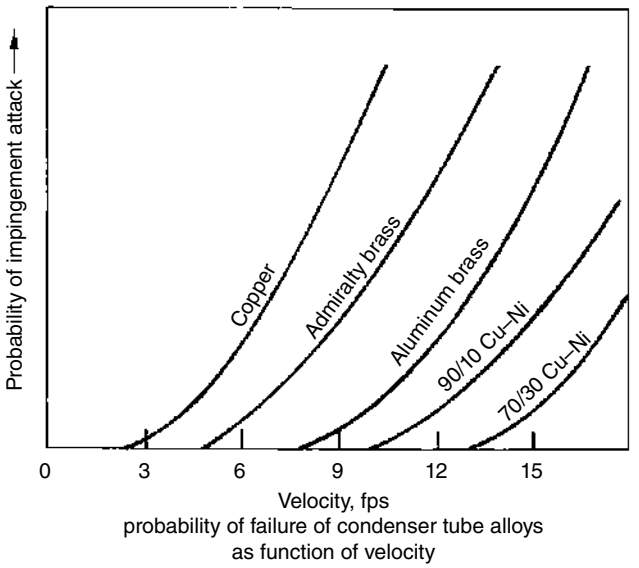


Figure 1.12 Probability of failure of copper-base condenser tube alloys as a function of velocity. *Source:* Figure 4-42, p. 142, LaQue (1975). Reproduced with permission of John Wiley & Sons.

Cavitation damage is an extreme effect of velocity and flow on materials under certain circumstances. Very low-pressure regions resulting from distortion of flow patterns can produce cavities in applications such as propellers and pump impellers, or as a result of high-frequency vibrations, e.g. in piping systems, or narrow cooling-water flow channels such as in internal-combustion engines. The collapse of these cavities, which can occur extremely frequently over a small area, exerts tremendous stresses akin to hammering action on the surfaces on which collapse takes place. The magnitude of these stresses can exceed the yield strength of the material.

Cavitation is distinguished from ordinary erosion or erosion–corrosion by the extent to which a mechanical hammering effect contributes to the total damage. The hammering action results in distortion of the grain microstructure and work-hardening of the metal surface. In many cases of severe cavitation, the mechanical effect is predominant. As might be expected, under the same cavitation conditions, the greater corrosivity of seawater compared to freshwater can lead to more cavitation damage in seawater for certain materials such as carbon steels and copper alloys. As stated earlier in this chapter, cavitation damage can increase with temperature; however, above a certain temperature, it may be retarded by increased vapor pressure within the cavities – offsetting the opposite effect of vapor bubble collapse. In pumps, the danger of cavitation increases if they are designed to operate with high suction heads. In general, components that must move through seawater or have seawater move over them at high velocity should be designed to avoid sharp changes in contour or bends which can lead to extreme turbulence, resulting in cavitation.

Since cavitation results from the combination of mechanical and corrosion effects, the corresponding properties of metals can influence their respective cavitation propensities. A similar combination of properties contributes to corrosion-fatigue behavior. Consequently, it can be expected that metals demonstrating high resistance to corrosion fatigue will also have relatively good resistance to cavitation damage. The spongy or honeycomb appearance of metals affected by cavitation may be ascribed to a sequence of corrosion fatigue cracks which later intersect so as to dislodge particles of metal. Metals that work-harden easily also seem to resist cavitation damage better. The most resistant metals combine a high level of resistance to mechanical damage, usually reflected by a high hardness, with resistance to corrosion by the liquid in which cavitation is occurring, for example, Co–Cr–W alloys, Ni–Cr–Mo and Ni–Cr–Mo–Fe alloys, titanium and its alloys, super-austenitic, and super-duplex stainless steels. Rubber and elastomeric coatings that exhibit good adhesion and have sufficient resilience to reflect mechanical

forces without transmitting them to the underlying metal can also provide protection against cavitation. Reducing cavitation damage by the application of cathodic protection is usually impractical where high velocities and excessive turbulence are present because of the extremely high currents that would be required for protection. Moreover, it may be argued that cathodic protection would be beneficial only against electrochemical corrosion but not the mechanical effects of cavitation.

Air bubbles mechanically entangled in seawater by the action of pumps, scoops, propellers, etc., are believed to play a role in aggravating impingement attack on condenser tubes and seawater piping. On the other hand, deliberate introduction of air bubbles is considered to reduce cavitation damage because the air bubbles cushion the mechanical forces associated with the collapse of vacuum cavities (vapor bubbles).

1.3.4 Effects of Depth

As stated earlier, there are seasonal variations in seawater properties at any given location. However, there are variations also with the depth of water, as illustrated in Figure 1.13 for a test site

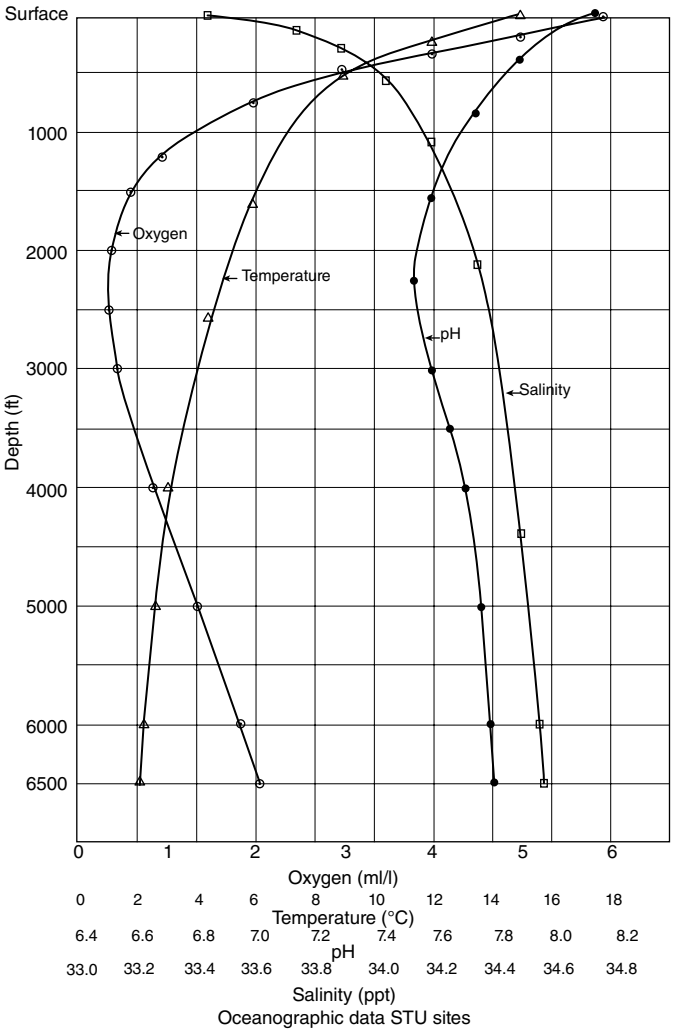


Figure 1.13 Illustration of variations in dissolved O_2, temperature, pH, and salinity at a specific Pacific Ocean corrosion test site. *Source:* Reinhart (1976).

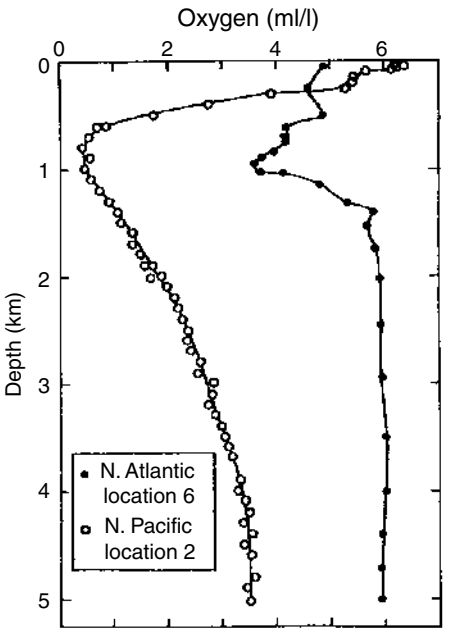


Figure 1.14 Dissolved O_2-depth profiles at two specific open ocean test sites. *Source:* Based on Dexter and Culberson (1980).

in the Pacific Ocean (Reinhart 1976). It should not be assumed that these profiles are similar within the same depth range at other sites. In fact, this point is reinforced by Figure 1.14, in which O_2 profiles with depth are compared at two sites, one in the Pacific Ocean and the other in the Atlantic Ocean (Dexter and Culberson 1980). The higher O_2 concentration at greater depths in the Atlantic Ocean is attributed to the flow of cold seawater through the "funnel" in the north, whereas in the case of the Pacific Ocean, minor flow through the Bering Strait prevents this effect (Compton 1970).

The direct correlation between corrosion rate of carbon steels and O_2 concentration with depth at a Pacific Ocean test site was discussed earlier (see Figure 1.3). The almost opposite effect of depth and O_2 on corrosion of aluminum alloys at the same test site is indicated in Figure 1.14 (Reinhart 1976). Initially, increase in corrosion rate of aluminum alloys with seawater depth was attributed to lower O_2 concentration preventing re-healing of the protective aluminum-oxide film. Subsequently, it was hypothesized that this behavior was due to the lower seawater pH and, consequently, less likelihood of calcareous deposit formation in deep water (Dexter 1980). It cannot be emphasized enough that the data shown in Figures 1.3 and 1.15, for example, are very site-specific. Thus, the effects of depth observed at one location cannot be used to predict behavior at the same depth at other locations.

Forms of corrosion observed on susceptible materials in surface seawater are also encountered in deep ocean environments, for example, general attack, pitting, crevice corrosion, dealloying, SCC, and so on, although the rates may be different. Conversely, materials such as titanium, and Ni–Cr–Mo (e.g. alloy C) found to be immune to all forms of attack in deep water are also resistant in surface seawater. The hydrostatic pressures of deep ocean environments do not appear to play a significant role in electrochemical corrosion of metals.

1.3.5 Splash and Tidal Zones

The typical corrosion profile of carbon steel, for example for unprotected piling is shown in Figure 1.16. It is apparent that the highest corrosion rate is in the splash and spray zone. This is a

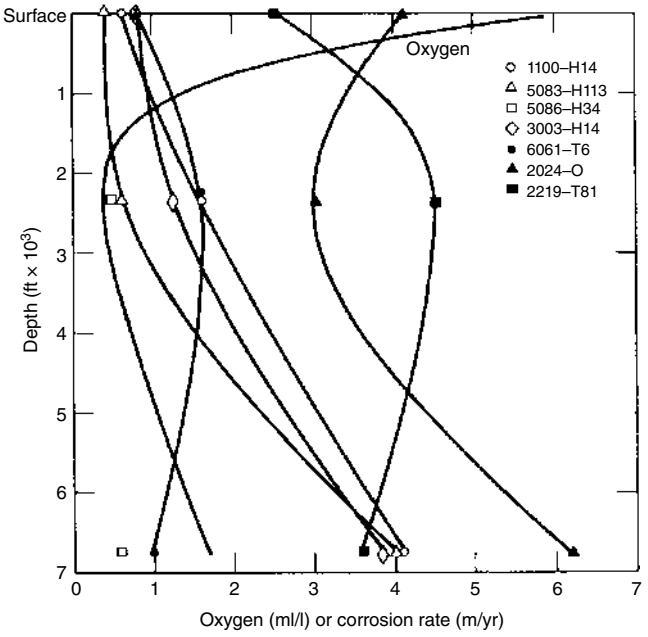


Figure 1.15 Corrosion rates of aluminum alloys exhibiting no simple relation to dissolved O_2 at various depths after one-year exposure. *Source:* Reinhart (1976).

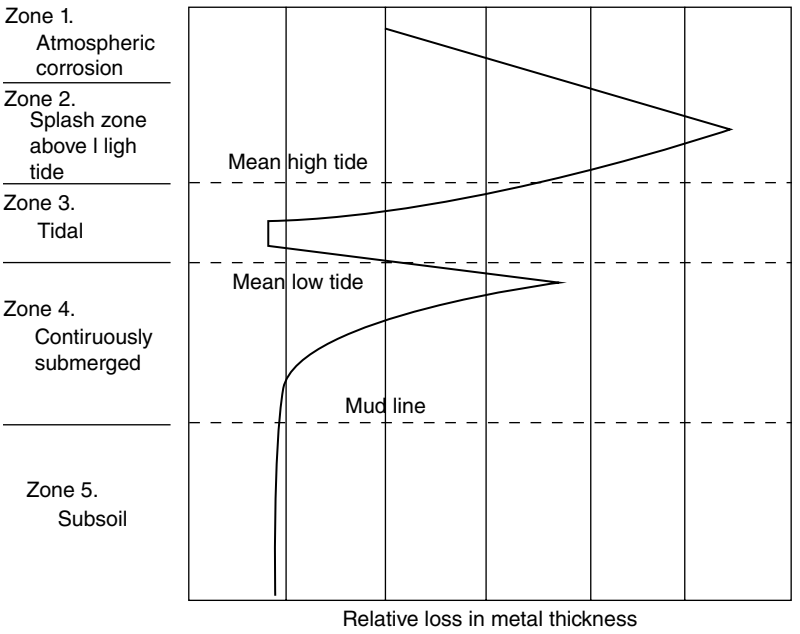


Figure 1.16 Corrosion profile of steel piling exposed to various zones in a natural marine environment for five years. *Source:* Figure 4-17, p. 116. LaQue (1975). Reproduced with permission of John Wiley & Sons.

very aggressive environment toward carbon steel because the metal surface is in continuous contact with high-aerated seawater. The minimum corrosion within the tidal zone is due to a differential aeration cell. The area in the high tide (with more readily aerated seawater) acts as a cathode

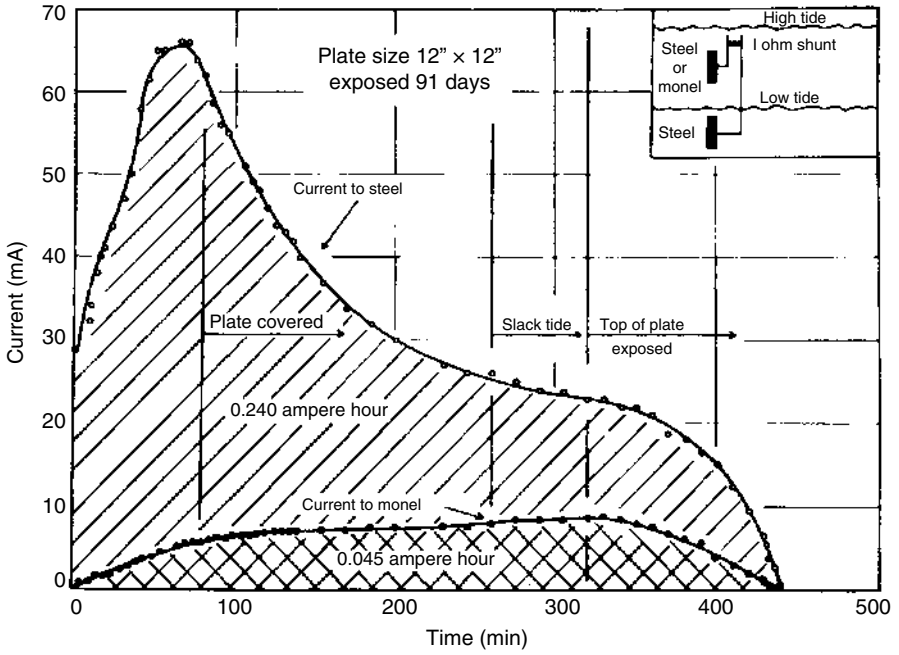


Figure 1.17 Current flow to steel and nickel-copper alloy (Monel-400) in tidal zone when coupled to submerged steel. *Source:* Figure 4-16, p. 115. LaQue (1975). Reproduced with permission of John Wiley & Sons.

to the area just below low tide which is anodic. This corrosion cell is demonstrated, in Figure 1.17, by the current flow between two steel plates, one immersed below the low tide level and the other placed at the half tide level. Also shown in Figure 1.16 are the results of a similar test setup in which the steel plate in the tidal zone was replaced with the Ni–Cu alloy (Monel-400). In spite of the greater potential difference between the steel and Ni–Cu alloy, the current flow was considerably less because the Ni–Cu alloy polarized much more readily than steel acting as a cathode in O_2-saturated seawater.

In the splash and spray zone, stainless steels generally perform much better than carbon steels because the highly oxygenated seawater aids the passivation of the former. However, in the tidal zone, susceptible stainless steels (just like carbon steels) can suffer from localized corrosion under macrofouling growths.

Accelerated low water corrosion (ALWC) of steel sheet piling in a number of European ports and harbors at areas just above the lowest astronomical tide, especially in brackish waters, has been reported (Linder 1999; Oubner and Beech 1999; Breakell et al. 2005). Although the precise mechanism of corrosion attack is still unclear; however, a strong influence of microbiological organisms, especially SRB and possibly synergized by acid producing bacteria, is suspected. Localized penetration rates exceeding 1 mm/yr can perforate sheet piling in a very short period.

1.3.6 Bottom Sediments

The anaerobic conditions encountered under marine organisms and SRB are also encountered in sea bottom sediments. If a metal is completely covered by sediment, the corrosion rate is generally low because of the absence of O_2. Corrosion behavior of metals partially buried in the sediment is more complex. For passive metals (e.g. susceptible stainless steels), corrosion is accelerated on the buried areas because of film breakdown and consequently differential aeration cells. The potential

difference between the active (buried) and passive (submerged) areas can be hundreds of millivolts. In other words, the overall corrosion mechanism can be ascribed to crevice corrosion. The almost opposite behavior is observed for active metals (e.g. carbon steels), in which corrosion of buried areas is usually less severe than that in the adjacent seawater–submerged areas. This is commonly observed on steel piling exposed to bottom sediment and seawater for many years. It is attributed to greater local cell action in the seawater (due to its chloride content, low electrolytic resistivity, and O_2 content) compared to the differential-aeration-cell effect (Tomashov 1966).

1.4 Biological Effects

1.4.1 Microorganisms, Biofilms, and Biofouling

Seawater contains a great variety of microscopic organisms (microorganisms) that include many species of bacteria, algae, and fungi. The attachment and growth of microorganisms on solid surfaces immersed in seawater results in the formation of biological films (biofilms) that can influence corrosion of materials. Seawater also contains an abundance of hard-shelled macroorganisms such as mussels, oysters, barnacles, clams, sea squirts; and softer, "vegetable" species such as seaweed, hydroids, bryozoan, and codium. These macroorganisms usually form heavy encrustations on materials that do not have antifouling properties or coatings, or those that are not subjected to biofouling-control treatments such as chlorination. This type of biofouling, which is most prevalent in the seawater tidal zone, may also affect corrosion behavior of the underlying material.

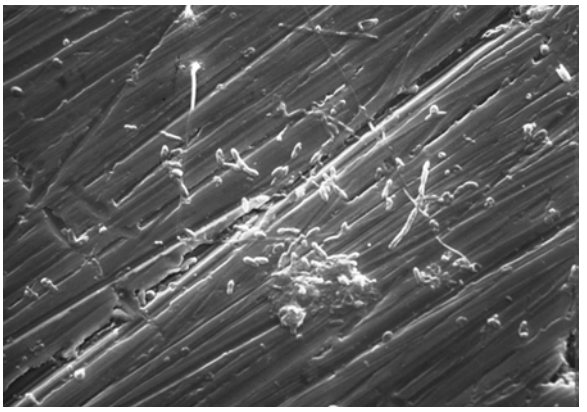
Biofilms are complex, and their formation is described in more detail in the literature (Savage and Fletcher 1985; Little et al. 1991; Evans 2000; Korbin 1993; Dexter 2003).

Basically, biofilm formation begins on all metallic and nonmetallic surfaces within minutes of immersion in seawater. Planktonic microorganisms (bacteria) from the bulk seawater excrete extracellular polymeric (exopolymer) substances, anchor to the substrate, begin a sessile existence and replicate. The biofilm thickens with time and conditions at the base of the film change as colonization by different species produces a consortium of microorganisms. The development of a biofilm containing bacterial cells and eventually colonies is illustrated in Figure 1.18. A mature biofilm may develop in a matter of days or weeks, and it may be visible as a slime layer. However, the film is dynamic; for example, many cells die, weak areas in the film may be sloughed off (exposing the substrate), exposed areas may be recolonized by new organisms, diffusion of dissolved gases and chemical species between the bulk seawater, and the substrate may be altered, nutrients may be trapped and concentrated, and so on. Thus, conditions under the biofilm are often significantly different from those in the bulk seawater.

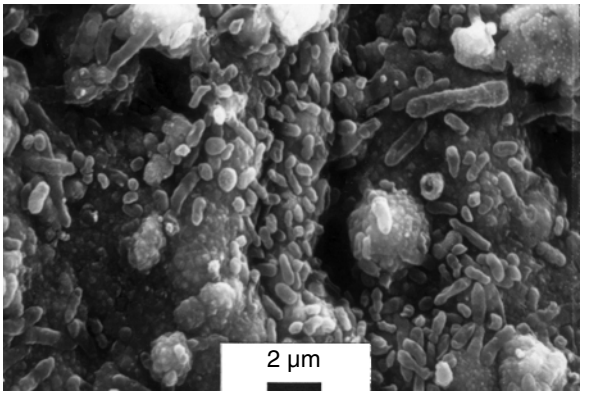
MIC is not a new form of attack on materials. It merely connotes biological influence on the occurrence and/or rate of corrosion, for example due to generation of sulfides under anoxic conditions, production of organic and inorganic metabolic by-products, creation of O_2 or chemical concentration cells, and so on. However, the mere presence of bacteria alone cannot be used to assert that any corrosion attack observed is MIC. Many other factors need to be taken into consideration.

It has been shown (Mollica and Trevis 1976; Johnsen et al. 1983; Johnsen and Bardal 1986; Holthe et al. 1988; Gallagher and Malpas 1989) conclusively that biofilms on stainless steels in natural seawater ennoble the corrosion potentials by several hundred millivolts in a matter of weeks, and increase the cathodic O_2-reduction reaction rate. This behavior has also been reported for Ni–Cr–Mo alloys and titanium (Holthe et al. 1987; Mollica 1988 and 1989). Biofilm activity is enhanced with increasing seawater temperature. However, above a critical temperature, typically

(a)



(b)



(c)

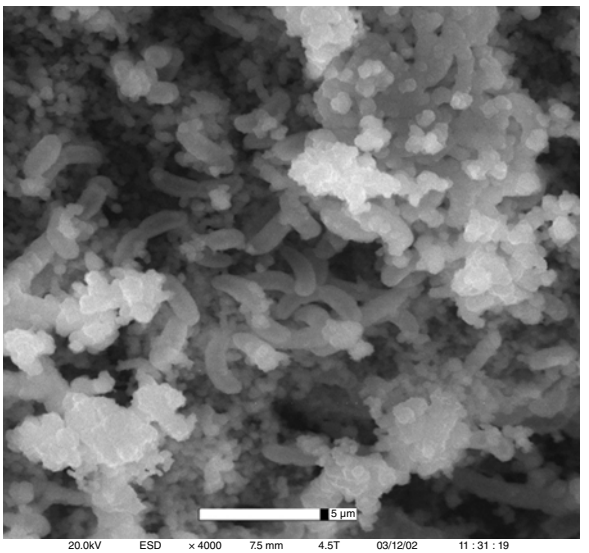


Figure 1.18 Examples of bacteria and biofilms that can influence corrosion. (a) Individual bacterial cells (microorganisms); (b) Bacteria in semicontinuous slime film; (c) Bacterial cells in a colony. *Source:* U.S. Navy; (a) Mansfeld et al. (1990); (b and c) Lee et al. (2004).

about 25–50 °C, depending on geographical region and bacterial species, the biofilm loses its catalytic effect (The role of biofilms on corrosion of stainless steels may be more complex than first thought; presently, there is no unified agreement on the precise corrosion mechanism (Dexter and Gao 1988)).

Biofilms increase the risk of pitting and crevice corrosion of susceptible materials. They also accelerate galvanic corrosion of anodic metals which are coupled to more noble materials on which biofilms form (Dexter and LaFontaine 1998).

Heavy macrofouling growths can develop on top of biofilms. Macrofouling is undesirable because it can impede flow in piping systems and heat exchanger tubes, increase drag on ship and boat hulls, increase wave loading on offshore structures, and so forth. Macrofouling can decrease the general corrosion rate of carbon steel because O_2 reaching the metal surface is restricted. However, anaerobic conditions develop under the macrofouling and favor SRB activity. Consequently, if coverage by macrofouling is not complete and uniform, the propensity for localized corrosion is increased. This was apparent from a worldwide seawater corrosivity test program (Phull et al. 1997). The typical seawater properties at the 14 test sites are summarized in Table 1.6. The data in Figure 1.19 for carbon steel show variations in mass-loss corrosion rates and maximum pit depths. The 6-mm-thick plate specimens at some locations were completely perforated by localized corrosion. The differences in corrosion behavior are attributed mainly to variations in macrofouling. It has been suggested by others that velocity influences corrosion of steel until macrofouling and corrosion products develop – after which dissolved O_2 and temperature have a more dominant effect on corrosion (Melchers 1997). Macrofouling is more likely in quiescent seawater than at high velocities.

Table 1.6 Average seawater properties reported for 14 worldwide seawater test sites.

Location	Dissolved O_2 (ppm)	Salinity (ppt)	Temperature (°C)	pH
Ocean City, NJ	5.2–11.7	31–34	1–29	7.5–8.2
Wrightsville Beach, NC	5.0–9.6	31.8–37.6	7–30	7.9–8.2
Key West, FL	4–8	33–39	16–31	8.0–8.2
Freeport, TX	1.5–6.0	11.7–19.4[a]	15–27	7.5–8.6
Port Hueneme, CA	3.6–5.3	33	14–21	7.9–8.1
Talara, Peru	5–6	19.8[a]	18–22	8.2
KeAhole, Kona, Hawaii	6–14	34.6–35	24–28	8–8.3
Innisfail, Australia	5.1–6.5	31.7–37.2	23–30	8–8.5
Sakata Harbor, Japan	7.1–13	16.8–18.3[a]	2–28	8.4
Genoa, Italy	6.5–6.0	35	11–25	8.1
Sjaelland, Denmark	NA[b]	18–28	0–18	7.5–8.0
Studsvik, Sweden	6–10	7.8–8.1	2–20	7.4–7.6
Bohus-Malmon, Sweden	6–10	21–28	2–20	8.0–8.2
Isle of Wight, UK	88–118[c]	34–34.6	5–22	7.8–8.4

[a] Reported as chlorinity (g/l).
[b] Not available.
[c] Reported as % saturation.
Source: Phull et al. (1997). Table 2 in STP 1300.

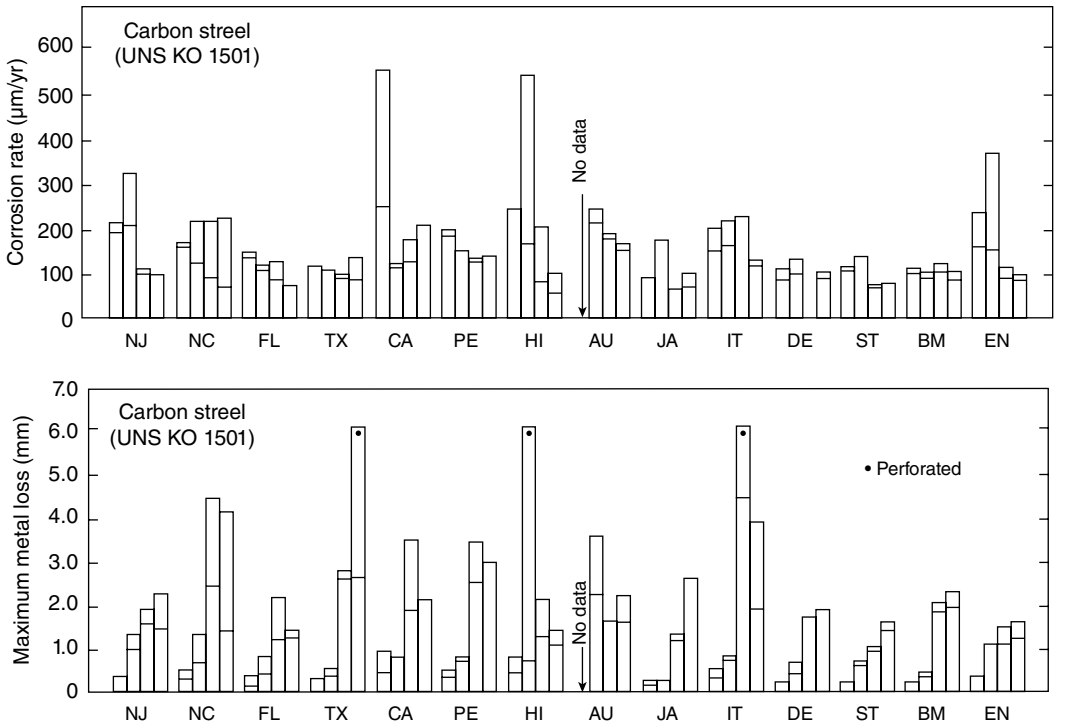


Figure 1.19 Mass loss corrosion rate and maximum depth of pitting attack on carbon steel in seawater at 14 worldwide test locations. For each location, the bars represent (from the left) 0.5, 1, 3, and 5-year exposures. NJ-New Jersey, NC-North Carolina, FL-Florida, TX-Texas, CA-California, HI-Hawaii, AU-Australia, JA-Japan, IT-Italy, DE-Denmark, ST and BM-Sweden, EN-England. *Source:* Phull et al. (1997). Table 2 STP 1300.

Copper alloys with more than about 70% copper exhibit very significant resistance (but not necessarily complete immunity) to macrofouling compared to carbon steel, stainless steels, aluminum, titanium, and nonmetallic materials. This resistance is ascribed to either slow release of copper ions or the presence of copper-rich corrosion products that are toxic toward the macroorganisms (Efird and Anderson 1975). The significant antifouling properties of copper alloys have been used to advantage for controlling macrofouling, e.g. as sheathing on offshore platform legs in the tidal zone, copper-rich antifouling coatings for ship hull, linings for cooling water intakes and outfalls.

1.5 Testing

Corrosion testing is important in evaluating materials in seawater and related marine environments. Tests can ascertain the performance of different materials, measure the degradation processes, and evaluate alternative materials and designs that optimize service life for given marine environments. Marine environments may include high temperature oxidizing or reducing conditions found in marine gas turbines or waste incinerators; testing may also be done in the marine environmental zones discussed earlier. Testing should be properly planned and should be relevant and correlate with actual field use (Griffin 2006). More details on testing in the Marine environment are discussed in Chapter 15.

References

Ambrose, J.R., Yaniv, A.E. and Lee, U.R. 1983. Corrosion/83, Paper No. 60. Houston, TX: NACE International.

ASTM G48-10. 2020. *Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*. West Conshohocken, PA: ASTM International.

ASTM D1141-98. 2021. *Standard Practice for the Preparation of Substitute Ocean Water*. West Conshohocken, PA: ASTM International.

Boyd, W.K. and Fink, F.W. (1978). Corrosion of Metals in Marine Environments, MCIC Report 7*8-37, Metals and Ceramics Information Center, Battelle Columbus Laboratories*.

Breakell, J.E., Foster, K., and Siegwart, M. (2005). *Management of Accelerated Low Water Corrosion in Steel Maritime Structures (C634)*. London: CIRIA, Columbus, OH.

Compton, K.G. (1970). The unique environment of sea water and its effect on corrosion of metals. *Corrosion* 26: 448.

Cook, E.H. and McGeary, F.L. (1964). Electrochemical deposition of iron from aqueous solutions onto an aluminum alloy. *Corrosion* 20 (4): 111t.

Covington, L.C. (1979). The influence of surface condition and environment on the hydriding of titanium. *Corrosion* 35 (8): 378–382.

Cox, G.C. (1947). Inventor. US Patent 2,417,009, March 11.

Culberson, C.H. (1983). Corrosion/83, Paper No. 61. Houston, TX: NACE International.

Dexter, S.C. (1980). Effect of variations in seawater upon the corrosion of aluminum. *Corrosion* 36 (8): 423–432.

Dexter, S.C. (1981). Localized corrosion of aluminum alloys in OTEC heat exchangers. *Journal of Ocean Engineering and Science* 8 (1): 109.

Dexter, S.C. (2003). Microbiologically Influenced Corrosion. In: *ASM Handbook*, vol. 13A, 398–416. Materials Park, OH: ASM International.

Dexter, S.C. and Culberson, C. (1980). Global variability of natural sea water materials performance. *Materials Performance* 19 (9): 23.

Dexter, S.C. and Gao, G.Y. (1988). Effect of seawater biofilms on corrosion potential and oxygen reduction of stainless steel. *Corrosion* 44 (10): 717–723.

Dexter, S.C. and LaFontaine, J.P. (1998). Effect of natural marine biofilms on galvanic corrosion. *Corrosion* 54 (11): 851–861.

Doremus, E.P. and Doremus, G.L. (1950). Cathodic protection of fourteen offshore drilling platforms. *Corrosion* 6 (7): 216–224.

Dupont, I., Feron, D., and Novel, G. (1998). Effect of glucose oxidae activity on corrosion potential of stainless steels in seawater. *International Biodeterioration and Biodegradation* 41: 13–18.

Efird, K.D. (1977). Effect of fluid dynamics on the corrosion of copper-base alloys in sea water. *Corrosion* 33 (1): 3–8.

Efird, K.D. and Anderson, D.B. (1975). Sea water corrosion of 90/10 and 70/30 Cu–Ni: 14-year exposures. *Materials Performance* 14 (11): 37–40.

Eiselstein, L.E., Syrett, B.C., Wing, S.S., and Caliguiri, R.D. (1983). Accelerated corrosion of CuNi alloys in sulfide polluted seawater: mechanism 2. *Corrosion Science* 23: 223–239.

Evans, L.V. (ed.) (2000). *Biofilms: Recent Advances in Their Study and Control*. Harwood Academic Publishers.

Fisher, K.P. and Finnegan, J.E. (1989a). Corrosion/89, Paper No. 581. Houston, TX: NACE International.

Fisher, K.P. and Finnegan, J.E. (1989b). Corrosion/89, Paper No. 582. Houston, TX: NACE International.

Francis, R. (2010). *The Corrosion of Copper Alloys: A Practical Guide for Engineers*, 27. Houston, TX: NACE International Press.

Gallagher, P. and Malpas, R.E. 1989. Corrosion/89, Paper No. 113. Houston, TX: NACE International.

G.C. Cox (1940). Anticorrosive and antifouling method of application. US Patent 2,200,469, USA.

Griffin, R.B. (2006). Corrosion in marine atmospheres. In: *ASM Handbook*, vol. 13C Corrosion: Environments and Industries, 42. Materials Park, OH: ASM International.

Gudas, J.P., Danek, G.S. and Niederberger, R.B. (1976). Corrosion/76, Paper No. 76. Houston, TX: NACE International.

Gudas, J.P., Hack, H.P. and Taylor, D.W., (1978). Corrosion/78, Paper No. 93. Houston, TX: NACE International.

Guillen, M.A. and Feliu, S. (1966). *Revisita de Metalurgia* 2 (6): 519–532.

Hartt, W.H., Culberson, C.H. and Smith, S.W. (1983). Corrosion/83, Paper No. 59. Houston, TX: NACE International.

Hollingsworth, E.H., Hunsicker, H.Y. (2006). Corrosion of Aluminum and Aluminum Alloys. *ASM Handbook*, Edition IX, vol. 13: Corrosion, ASM International, Materials Park, OH, p. 589.

Holthe, R., Gartland, P.O. and Bardal, E. (1987). EuroCorr/87; 1987 April; held in Karlsrhue, Germany. Published by DECHEMA, Frankfurt. pp. 617–623.

Holthe R, Gartland PO and Bardal E. (1988). Comite International Permanent pour la Recherche sur la Preservation de Materiaux en Milieu Marine. *Proceedings of the 7th International Congress on Marine Corrosion and Fouling*, Valencia, Spain (November 1988).

Humble, H.A. (1948). Cathodic protection of steel in sea water with magnesium anodes. *Corrosion* 4 (7): 358–370.

Jasner, M., Hecht, M. and Beckmann, W. (1998). *Heat Exchangers and Piping Systems from Copper Alloys – Commissioning, Operating and Shutdown*, KME publication No. 1098 005 0104, Osnabruck, Germany.

Johnsen, R., Bardal, E. and Drugli, J.M. (1983). *Proceedings of the 9th Scandinavian Corrosion Congress*, Copenhagen, Denmark, Vol. 1, (12–14 September 1983). pp. 371–382.

Johnsen, R. and Bardal, E. (1986). Corrosion/86, Paper No. 227. Houston, TX: NACE International.

Johnsen, R. and Bardal, E.1986. Cathodic properties of stainless steels in seawater and some practical consequences of these properties. *Proceedings of the U.K. Corrosion/86 Conference*, Birmingham, UK (17–19 November 1986). Northampton, UK: Institute of Corrosion. pp. 287–299.

Korbin, G. (ed.) (1993). *Microbiologically Influenced Corrosion*. Houston, TX: NACE International.

LaQue, F.L. (1975). Causes and Prevention. *Marine Corrosion*. Wiley-Interscience.

Lee, W.S.W., Oldfield, J.W., and Todd, B. (1983). Corrosion problems caused by bromine formation in additive dosed MSF desalination plants. *Desalination* 44 (5): 209–221.

Lee, J.S., Ray, R.I., Lemieux, E.J., Falster, A., and Little, B. (2004). An evaluation of carbon steel corrosion under stagnant seawater conditions. *Biofouling* 20: 237–247.

Linder, B. (1999). Cathodic protection of sheet steel piling in seawater, containing sulfate-reducing bacteria, particularly with respect to accelerated low water corrosion (ALWC), *Swedish Corrosion Institute Report No. 55467*.

Little, B., Wagner, P., and Mansfeld, F. (1991). Microbiologically influenced corrosion of metals and alloys. *International Metallurgical Reviews* 36 (6): 253–272.

Lyman, J. and Abel, R.B. (1958). Chemical aspects of physical oceanography. *Journal of Chemical Education* 35 (3): 113–115.

Mansfeld, F., Tsai, R., Shih, H., Little, B., Ray, R. and Wagner, P. (1990). Results of exposure of stainless steels and titanium to natural seawater. CORROSION/90. Houston, TX: NACE International.

Melchers, R.E. (1997). *ASTM STP 1300, American Society for Testing and Materials*. West Conshohocken, PA: ASTM International. pp 20–33.

Mollica, A. (1988). Cathodic behavior of nickel and titanium in natural seawater. *International Biodeterioration* 24: 221–230.

Mollica, A. (1989). Cathodic protection of stainless steels in natural seawater as a function of microorganism settlement and temperature. *Corrosion* 45 (1): 48–56.

Mollica, A. and Trevis, A. (1976). *Proceedings of the 4th International Congress on Marine Corrosion and Fouling*, Antibes, France (14–16 June 1976). pp. 351–382.

National Oceanic and Atmospheric Administration (NOAA) and National Centers for Environmental Information. (2013). Ocean Climate Laboratory Team, World Ocean Atlas 2013 Version 2, WOA13F V2 Interactive image Access.

de Oliveira, R. and de Souza Pimenta, G. (1993). An initial investigation of calcareous deposits upon cathodically polarized steel in brazilian deep water. *12th International Corrosion Congress*, Houston, TX: NACE International. pp. 2278–2284.

Oubner, R. and Beech, L. (1999). Corrosion/99, Paper No. 99318. Houston, TX: NACE International.

Philipponeau, G., Dagbert, C., Galland, J. and Lemoine, L. (1981). Contribution to the study of magnesium and calcium deposits occurring during steel protection in seawater. *8th International Congress on Metallic Corrosion*, Mainz, Germany (6–11 September 1981). Frankfurt, Germany: DECHEMA. Vol. 2. pp. 196–199; pp. 1327–1332.

Phull, B.S. (1981). A study of calcareous deposits in relation to cathodic protection. PhD Thesis. University of Manchester, Manchester (UK).

Phull, B.S., Pikul, S.J. and Kain, R.M. (1997). *ASTM STP 1300, American Society for Testing and Materials*. West Conshohocken, PA: ASTM International. pp. 34–73.

Pistorious, P.C. and Burnstein, G.T. (1992). Growth of pits on stainless steel in chloride solution containing dilute sulfate. *Corrosion Science* 33 (12): 1885–1897.

Pytkowich, R.M. (1965). Rates of inorganic calcium carbonate nucleation. *Journal of Geology* 73 (1): 196.

Reinhart, F.M. (1976). Corrosion of Metals and Alloys in the Deep Ocean (Civil Engineering Laboratory, Port Hueneme, CA). *Technical Report No. R-834; Govt Accession No. DN 244098*.

Savage, D.C. and Fletcher, M. (eds.) (1985). *Bacterial Adhesion*, 650–654. Plenum Press.

Shigeno, H., Umino, T., and Fukazawa, H. (1975). *Proceedings 5th International Congress on Metallic Corrosion*, 619–623. Houston, TX: NACE International.

Tomashov, N.D. (1966). *Theory of Corrosion and Protection of Metals*, 470. New York: Macmillan Company.

Uhlig, H.E. and Revie, R.W. (1985). *Corrosion and Corrosion Control*, 3e. New York: Wiley.

Wallen, B. and Henrikson, S. (1989). Effect of chlorination on stainless steel in seawater. *Werkstoffe und Korrosion* 40 (Oct): 602–615.

Whitfield, M. and Jagner, D. (eds.) (1981). *Marine Electrochemistry, A Practical Introduction*. New York: Wiley. Not in text.

Wolfson, S.L. and Hartt, W.H. (1981). An initial investigation of calcareous deposits upon cathodic steel surfaces in sea water. *Corrosion* 37: 70–76.