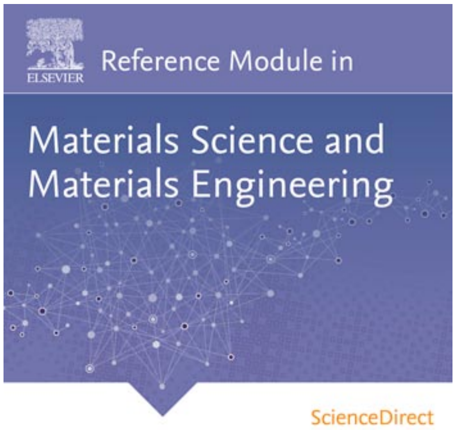

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Marine Corrosion☆

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Abbreviations

ALWC	Accelerated low water corrosion
BOD	Biological oxygen demand
CCT	Critical crevice temperature
CP	Cathodic protection
CP	Commercial purity (of titanium)
CPT	Critical pitting temperature
DO	Dissolved oxygen
H	Heat treatment term in aluminum alloys (aged condition)
HE	Hydrogen embrittlement
IGC	Intergranular corrosion
L	Low carbon
Max.	Maximum
MCA	Multiple crevice assembly
MSF	Multistage flash (distillation)
O	Heat treatment term in aluminum alloys (annealed condition)
P	Perforation
PH	Precipitation hardening
PREN	Pitting resistance equivalent number
PTFE	Poly tetra fluoro ethylene
RH	Heat treatment term in PH stainless steels
SCC	Stress corrosion cracking
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
SRB	Sulfate reducing bacteria
T	Temper heat treatment term in aluminum alloys
T	Temperature
TDS	Total dissolved solids
YS	Yield strength

☆*Change History*: December 2015. A.A. Abdullahi added Abstract and Keywords; expanded Introduction section with additional recent review of literature; equations were numbered; and list of references was updated.

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Symbols

C_0 Bulk concentration of oxygen (moles cm^{-3})

d Diameter

D Diffusion constant

Pr Prandtl number

U_0 Bulk flow rate (cm s^{-1})

α Alpha phase

β Beta phase

ν Kinematic viscosity

υ Velocity

1 Introduction

This chapter focuses on corrosion and behavior of important engineering materials in seawater. It is customary to define marine environments in terms of 'zones' in which materials might be exposed, *viz.*, atmospheric, splash and spray, tidal, immersion or submerged, and bottom-mud or sediment. Materials are subjected to seawater conditions in numerous applications, for example, ships, pleasure boats, submarines, offshore platforms, subsea pipelines and telecommunications cables, wharfs, seawater-cooled power and chemical plants, desalination plants, fishing gear, and so on. Seawater is a critical resource for food (primarily fish), table salt, and conversion to freshwater (desalination). It is also the primary source for extraction of magnesium and subsequent production of its alloys. Despite the multitude of seawater benefits, it is a highly corrosive environment which attack quite a number of engineering materials.

In the year 2010 World Corrosion Organization (WCO) estimated that the annual cost of corrosion worldwide was around $US2.2 trillion (3% of the world's GDP).[1,2] State-of-the-art review of the fundamentals and corrosion mechanisms of structures in marine environment is presented in the literature.[3,4] Developments in mathematical modelling strategies, in association with *in situ* thickness measurements, have significantly enhanced the qualitative understanding of the corrosion processes at various locations within marine structures.[3] Corrosion degradation leads to loss of material and sometimes ultimate failure of the marine structure.[5]

As in so many other environments, there is a multitude of factors, which can affect corrosion of materials in seawater. Many of these factors are interrelated, resulting in complicated behavior of materials in specific applications. Meanwhile, this chapter focuses on the important factors influencing corrosion mechanisms and corrosion behavior of common engineering materials in seawater. In addition, corrosion test methods in seawater environments are discussed briefly.

2 Environmental Characteristics of Seawater

Seawater covers ~70% of the earth's surface. It is a highly complex medium that contains almost every element in the periodic table and a multifarious plethora of living organisms. Hence, it is sometimes described as a 'living' medium and considered to be the most corrosive of the natural environments.

2.1 Seawater Constituents

Conventional wisdom attributes the corrosivity of seawater is because of its salt (primarily NaCl) content. However, as discussed later in this section, it is not the salt *per se*, but other constituents – especially the dissolved oxygen (DO) and pollutants such as sulfides that often play critical roles. The total salt content is typically expressed in terms of salinity and/or chlorinity. Salinity is the total solid matter (grams) in one kilogram of seawater (after all the organic matter has been oxidized, carbonate converted to oxide, and bromine and iodine replaced by chlorine). From an analytical viewpoint, it is easier to determine the chlorine content, which is expressed as chlorinity – the total amount of chlorine (grams), plus equivalent chlorine assumed to replace bromine and iodine, in 1 kg of seawater. Salinity is related to chlorinity by the following empirical expression:

$$\text{Salinity} = (1.80655 \times \text{Cholorinity}) + 0.03 \qquad [1]$$

Salinity and chlorinity are usually expressed as grams per kilogram or parts per thousand (g kg^{-1}, ppt or ‰). Multiplying by 1000 converts g kg^{-1} or ppt to parts per million (ppm). Salinity can also be considered as total dissolved solids (TDS), stated as mg l^{-1} (ppm). The properties of seawater can vary considerably by geographical location, seasons, and water depth. **Table 1** shows a comparison of the relative approximate salinities of a number of seas and oceans in the world. River outflows, evaporation, rainfall, melting ice, wind, and wave action – all can exert a strong influence on salinity. Littoral waters are often rendered brackish (i.e., less salty) due to significant river outflow and may contain considerable sediments and pollutants.

The 'average' salinity of open ocean waters (i.e., well away from land) is in the range ~32–36 ppt, and the corresponding average chlorinity in the ~18–20 ppt range. The salinity of the landlocked Dead Sea is an order of magnitude higher. **Table 2** shows the 'average' concentrations of ionic constituents in open seawater of 35‰ salinity. From a corrosion viewpoint, all the ocean waters can be considered as sufficiently corrosive toward carbon steel, typically the most commonly used constructional

Table 1 Salinity of various ocean waters expressed as approximate total dissolved solids (mg l^{-1} or ppm)

Seawater	*Approximate TDS (ppm)*
Arabian Gulf	47 000
Red Sea	43 000
Mediterranean Sea	41 000
Atlantic Ocean	36 000
Indian Ocean	35 000
Pacific Ocean	34 000
North Sea	33 000
Bering Sea	32 000
Black Sea	22 000
Caspian Sea	13 000
Baltic Sea	8 000
Dead Sea	322 000

Table 2 Major ionic constituents in seawater of 35‰ salinity (35 000 ppm TDS)[6]

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

material, such that corrosion control in some form or another is essential for extended structure and component life and functionality in most cases.

In terms of salt content, the 'average' seawater composition corresponds to ~3.5% NaCl solution. Thus, many researchers who do not have easy access to natural seawater often use this composition as a synthetic substitute. Others use artificial seawater solutions[7] that attempt to more closely mimic real seawater, at least in terms of dissolved salts. The chloride (Cl^-) ion is considered to be the most aggressive specie in seawater, particularly for localized corrosion. Sulfate (SO_4^{2-}) ions play an important role in the activity of sulfate-reducing bacteria (SRB) which proliferate under anaerobic conditions, and can cause serious corrosion problems for certain materials and applications as discussed later in this section.

Calcium (Ca^{2+}) and bicarbonate (HCO_3^-) ions in seawater contribute toward calcium carbonate ($CaCO_3$) scale formation, which is especially enhanced on heat transfer surfaces because of the inverse solubility of $CaCO_3$ with temperature. Such scales can impede transport of DO to the metal surface, and hence, reduce general corrosion of active metals and the effects of seawater velocity so long as the scale is not dislodged. However, the scale reduces heat transfer, and can significantly increase the probability of localized (under-deposit) corrosion attack, particularly on materials with passive films that are susceptible to such conditions (e.g., 300-series stainless steels, aluminum alloys, nickel–copper alloys, etc.) in aerated seawater. Of course, Ca^{2+} and HCO_3^- are also critical species in the formation of undersea corals and protective shells by numerous marine organisms such as clams, oysters, barnacles, crabs, lobsters, star fish, urchins, and so on.

Organic matter necessary for biological processes contains carbon, oxygen, hydrogen, nitrogen, and phosphorus. Carbon, oxygen, and hydrogen (e.g., as polysaccharides and lipids) are available in abundance, but usable nitrogen and phosphorus compounds (primarily nitrates and phosphates) are generally limiting nutrients. The main sources of these latter nutrients include river runoff into the sea, decaying organic matter, and upward water flow from deeper ocean areas. In littoral waters, these nutrients can reach very high concentrations where water runoff from land (e.g., in rivers) discharges large amounts of sewage and fertilizers from anthropogenic sources. Nutrient-rich waters encourage excessive plant growth, which depletes oxygen and kills animal life – a process known as eutrophication. An example of this is 'red tides,' which are associated with phytoplankton (algae) blooms.

Industrial waste from anthropogenic sources that is discharged into any body of water is technically a source of pollutants, which can consist of, for example, heavy metals and inorganic and organic compounds. The introduction of high levels of pollutants can alter the corrosivity of seawater toward certain materials, for example, copper-ion effects on aluminum alloys, sulfides and ammonia on copper alloys, sulfur compounds on steels, and so forth.

2.2 Effect of Dissolved Gases

DO represents the most important species that controls the corrosion behavior of many materials in seawater, even more so than chloride. DO concentration is reported either as ml l^{-1} or mg l^{-1} ($\text{ml l}^{-1} \times 1.429 = \text{mg l}^{-1}$). The primary factors that control DO content of seawater include temperature, salinity, biological activity, and mixing (flow). The inverse solubility of dissolved oxygen versus temperature and dissolved oxygen versus salinity is depicted in **Figures 1** and **2**, respectively. The DO concentration of the Dead Sea, which has a salinity of ~322 ppt, is apparently ~0.1 mg l^{-1}.

Oxygen dissolves in seawater either from the atmosphere and/or from plant photosynthesis, which is most prevalent over a depth ~100 m. Thus, surface waters at normal atmospheric pressures tend to be saturated or supersaturated in oxygen, including the thin liquid environment in the splash zone. However, quiescent flow conditions that favor algal growth and proliferation of decaying matter can reduce DO content markedly because of biological oxygen demand (BOD).

The principal reaction in seawater that controls corrosion is oxygen reduction. For any given DO concentration, the corrosion process is often strongly influenced by seawater velocity. This is discussed under corrosion mechanisms later in this chapter. The role of carbon dioxide is discussed in the following section. Other gases such as hydrogen sulfide and ammonia can be generated by bacteria from decaying matter and can influence corrosion of certain materials as discussed later.

2.3 Seawater pH

Clean surface seawater is typically slightly alkaline. This is related to the carbon dioxide (CO_2) equilibrium with the atmosphere. Seawater contains bicarbonate (HCO_3^-) ions, carbonate (CO_3^{2-}) ions, undissociated carbonic acid (H_2CO_3), and dissolved CO_2.

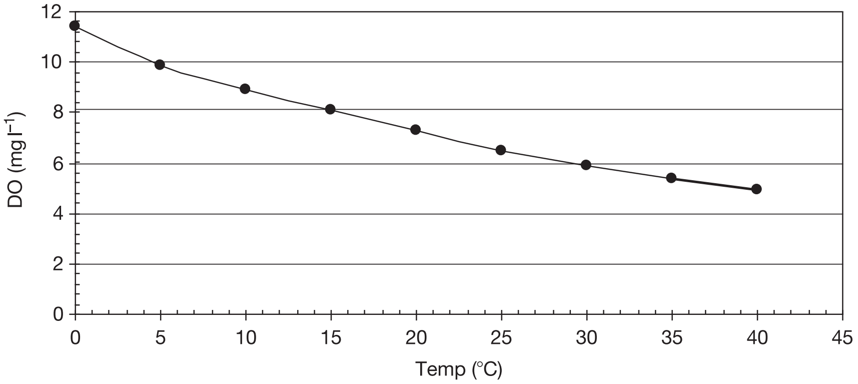

Figure 1 Dissolved oxygen (DO) versus temperature in natural seawater of 35‰ salinity at 1 atm pressure.

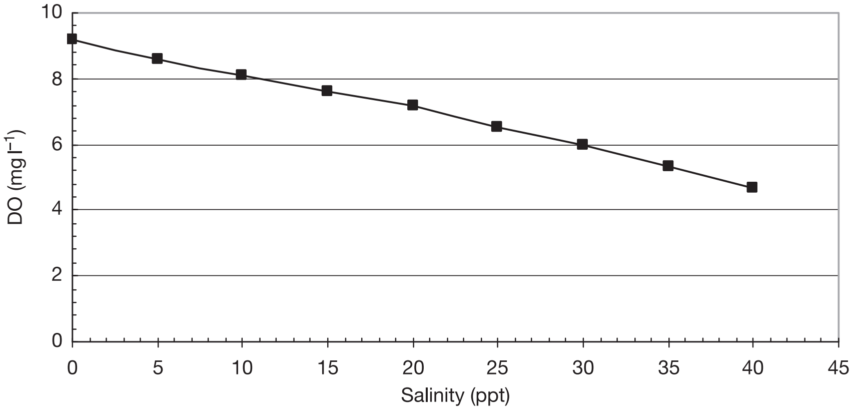

Figure 2 DO versus salinity in synthetic seawater at 20 °C and 1 atm pressure.

The pH is influenced by temperature, CO_2 partial pressure (which affects carbonate in solution), photosynthesis, and to a lesser extent by boric acid. These factors interact to maintain the pH in a surprisingly alkaline range (8.1–8.3), and hence, seawater is said to be highly buffered. Hydrogen sulfide, for example, from sulfate-reducing bacterial (SRB) activity, can lower the pH considerably and affect the performance of certain materials.

2.4 Calcareous Deposits

Calcium, bicarbonate, and magnesium in seawater are important constituents that can result in the formation of calcareous deposits on metal surfaces. Calcareous deposits form on cathodic surfaces and can slow down the corrosion process by inhibiting diffusion of DO and, consequently, its reduction at the metal surface. Calcareous deposit formation is particularly important when large, bare structures (e.g., steel offshore platforms) are cathodically protected in seawater. Without calacareous deposits, current demand for cathodic protection would remain at a high level, consequently, sacrificial anode life would be considerably reduced and the structure may not polarize to adequate protection levels. Calcareous deposit morphology and thickness are affected by current density at the cathode, seawater composition, temperature, and velocity.

2.5 Effect of Seawater Temperature

Temperature of seawater is influenced by many geographical factors, but decreases with depth. It also varies seasonally at the surface, ranging from $\sim 35\ ^{\circ}C$ at the equator to $\sim -2\ ^{\circ}C$ at the poles. Increasing temperature lowers solubility of dissolved gases and scale-forming calcium compounds such as calcium carbonate, but generally increases biofouling. All these factors can have a complex effect on corrosion behavior as discussed later in this chapter.

2.6 Effect of Depth

Figures 3 and **4** illustrate how various parameters can vary with depth[7] and geographic location.[8] Generally, DO, temperature, and pH decrease steeply with depth over the first several hundred meters while salinity increases. Hydrostatic pressure increases with depth while light penetration decreases. It has been postulated that the increase in DO at several 1000 m in the Atlantic Ocean is due to the flow of cold seawater through the 'funnel' in the north; but in the Pacific Ocean, this effect is prevented because of a minor flow through the Bering Strait.[9] It is important to recognize that the data shown in **Figures 3** and **4**, for example, are very site specific. Thus, quite wide variations in parameters can occur from one location to another, which can only be determined from actual measurements. Consequently, these variations can influence corrosion behavior of certain materials.

2.7 Fouling, Macro- and Microorganisms

Fouling constitutes the attachment of macro- and microorganisms, most prevalent on stationary surfaces. Biofilms apparently start forming on all metallic and nonmetallic surfaces within hours of exposure to seawater.[10] Biofilms which are associated with organic matter and molecules (exopolymers) in seawater are colonized by various bacterial microorganisms. As the films become established, heavier slime formation is followed by attachment of macro species,[11] for example, barnacles, oysters, clams, sea squirts, and vegetable species such as seaweed, bryozoa, hydroids, and codium. The macrofouling species predominate in the tidal zone and can slow down diffusion of dissolved gases, and hence overall corrosion of certain materials. However, shielding of the surface can lead to local anaerobic conditions, anaerobic bacterial activity, and subsequently, localized attack. Some materials (e.g., copper-rich alloys) are more resistant but not entirely immune to macro fouling compared with other materials that foul copiously (e.g., carbon steel, stainless steel, titanium, and even nonmetallics).

2.8 Effect of Velocity

Velocity can influence corrosion behavior in seawater in multiple ways. If the velocity is too low (quiescent conditions), solids may settle out, subsequently leading to under-deposit attack (e.g., on susceptible grades of stainless steel such as Type 410, 430, 304, 316, etc.). At intermediate velocities, such deposits may be suspended in the flow (once deposits have formed, much higher flow rates may be necessary for their removal than preventing settlement in the first place). As velocity continues to increase, biofilm and calcareous deposit formation diminishes. However, increased wall shear stress, turbulence, and impingement create conditions conducive for the removal of protective films on solid surfaces – thus, increasing the risk of erosion–corrosion of susceptible materials (e.g., carbon steel, copper-base alloys, aluminum-base alloys). At extreme velocities, even otherwise highly corrosion-resistant materials become increasingly susceptible to cavitation damage. Generally, for active materials, increasing the velocity increases corrosion rate as more DO is transported to the metal surface. For passive materials, the enhanced diffusion of DO due to higher velocities is usually beneficial as long as the attack (e.g., crevice corrosion) has not been

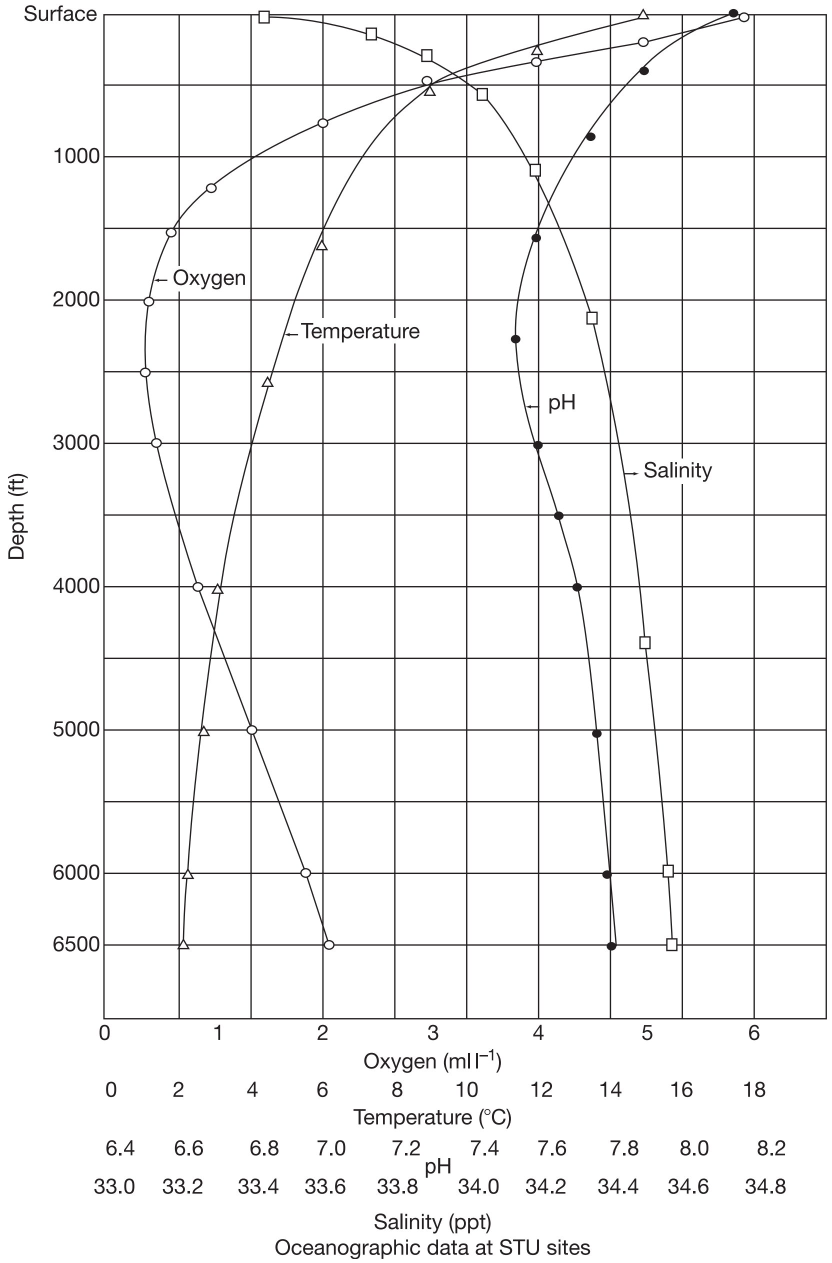

Figure 3 Variations in DO, temperature, pH, and salinity at a specific Pacific Ocean corrosion test site. Reproduced from Dexter, S.C., Culberson, C., 1980. Meter. Perform. 19 (9), 23.

already initiated. Macroorganisms, calcareous deposits, and coatings generally reduce velocity effects, partly by slowing diffusion of oxygen to the metal surface. However, at higher velocities these protective mechanisms may be negated as discussed earlier.

2.9 Seawater Resistivity

Seawater typically has low electrolytic resistivity (resistivity is reciprocal of conductivity) due to its significant dissolved salt content. Low resistivity generally corresponds to greater local cell action, larger anode–cathode interaction distances, and consequently, higher corrosion rates (particularly for active materials such as carbon steel), higher galvanic corrosion rates, and higher current output from cathodic protection anodes. **Table 3** shows that resistivity decreases with increasing salinity and temperature; the resistivity values shown in **Table 3** were converted from the conductivity data.[12] Thus, higher resistivities can be expected for seawater affected by fresh water outflows, for example, in coastal areas and for colder waters.

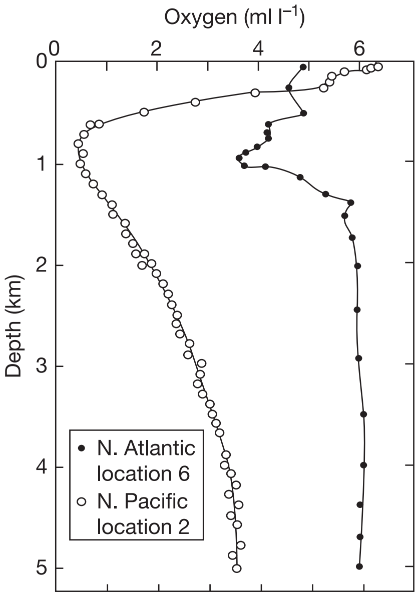

Figure 4 DO-depth profiles at two specific open ocean test sites. Reproduced from Compton, K.G., 1970. Corrosion 26, 448.

Table 3 Resistivity (Ω cm) as function of salinity and temperature

Salinity (‰)	*Temperature (°C)*					
	0	*5*	*15*	*20*	*25*	*30*
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

Source: Whitfield, M., Jagner, D. (Eds), 1981. Marine Electrochemistry, A Practical Introduction. Wiley, p. 513.

3 Corrosion and Protection Mechanisms

From a corrosion standpoint, chloride ions are considered to be the most aggressive constituent in seawater. The precise role of chloride in the corrosion process is still not fully understood. For instance, chloride contributes to increased electrolytic conductivity by ion transport. Higher conductivity means that current between anodic and cathodic areas can flow over larger distances, for example, in galvanic couples; the magnitude of local cell currents can also be higher. Thus, the overall effect is typically higher general and/or localized corrosion rates. Corrosion attack at anodic areas is supported by reduction reaction(s) at cathodic sites – typically oxygen reduction in aerated seawater.

Corrosion products can provide some degree of protection if they impede oxygen diffusion to cathodic sites. Reduction in general corrosion rate of steel in seawater due to formation of corrosion products and macrofouling is illustrated in Figure 5.

Oxygen reduction is obviously a critical reaction for metallic corrosion in seawater. Deoxygenation of seawater is a recognized method of corrosion control for carbon steel, for example, in multistage flash distillation plants and water injection in offshore oil/gas production during secondary recovery. Thus, chloride ions are rendered relatively harmless in the complete absence of oxygen. Typical polarization curves for steel in aerated and deoxygenated seawater are shown in Figure 6. It is apparent that although the corrosion potential is nearly 400 mV more 'active' in the absence of oxygen, the corrosion rate is significantly lower when compared with aerated seawater.

Differences in oxygen levels between local areas produce potential differences that give rise to concentration cells – commonly referred to as differential oxygenation or differential aeration cells. The low oxygen or anoxic (oxygen-free) area becomes anodic because of its more active (electronegative) potential; conversely, the area of higher oxygen becomes cathodic because of its less

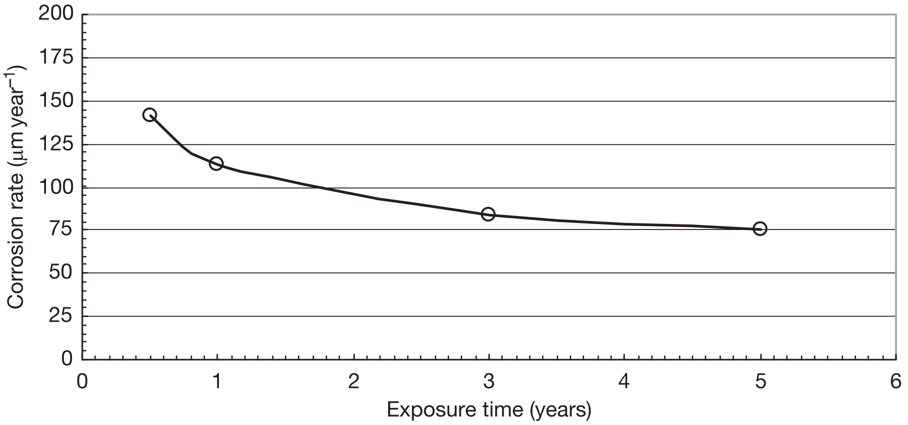

Figure 5 Decrease in general corrosion rate of carbon steel in quiescent seawater associated with development of corrosion products and macrofouling.

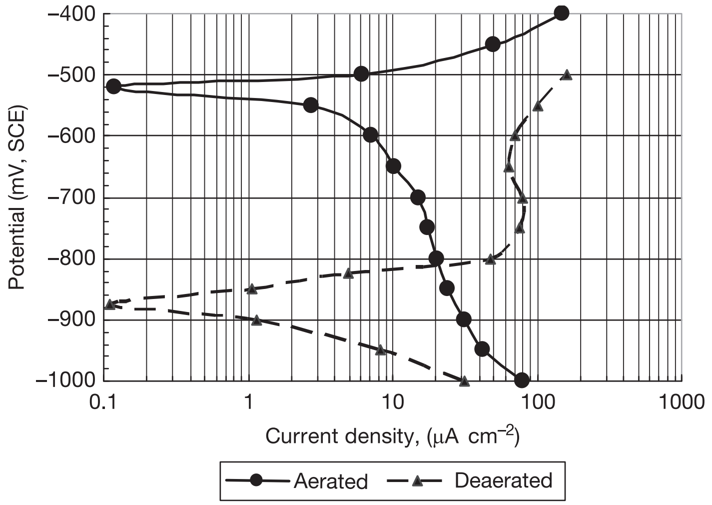

Figure 6 Polarization curves for carbon steel in aerated versus deaerated seawater.

active (more electropositive) potential. This is usually demonstrated in the laboratory by setting up a partitioned cell in which one-half is aerated and the other half is deaerated with a steel electrode immersed in each half. The measured open-circuit potentials and couple current flow direction indicates the afore-mentioned anode/cathode relationship. However, as noted by Tomashov,[13] actual corrosion rate of the steel electrode in the aerated half of the cell is greater in chloride solutions, despite being the cathode in the differential-aeration macrocell, than in the deaerated half. This apparent contradiction is due to enhanced microcell action in solutions containing chloride that prevents anodic passivation of the steel. Lower corrosion rates of steel piles in the mud zone (low oxygen environment) relative to the submerged zone above it (aerated environment) were cited as a practical manifestation of this apparently anomalous behavior. In other words, in seawater, chloride ions and associated high conductivity generates microcell activity that overrides the differential-aeration macrocell. In environments where steel can 'passivate,' for example, chloride-free waters or soils, the classical differential-aeration mechanism is operative.

In anaerobic seawater environments, the oxygen reduction reaction is negated. However, high corrosion rates observed under anoxic conditions have been attributed to microbiological activity, in particular, sulfate-reducing bacteria (SRB, e.g., *Desulfovibrio desulfuricans*). These bacteria reduce sulfate to sulfide under favorable conditions.[14–16]

While SRB can influence corrosion in anaerobic environments, propagation of corrosion attack is generally most prevalent under conditions of alternate exposure to anaerobic and aerobic environments. In principle, an impervious sulfide film covering the entire metal surface may be protective. However, in practice, such films are rarely impervious and/or continuous. Thus, corrosion at small exposed areas of the substrate is accelerated as the sulfide film serves as a large cathodic surface. The adverse effect of sulfide on corrosion of copper heat exchanger alloys is well known and discussed later in this chapter. Bacteria other than SRB can also influence corrosion behavior in seawater.

As discussed earlier, calcareous deposits form on cathodic surfaces. Although enhanced under cathodic protection conditions, such deposits can also form at cathodic areas associated with corroding surfaces. Hydroxyl ion generation by the oxygen reduction reaction at the cathodes increases the pH at the metal surface. The increase in pH alters the equilibrium, which can result in precipitation of calcium carbonate scale.

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

Under cathodic overprotection conditions, formation of magnesium hydroxide is favored.

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \qquad [3]$$

Adherent calcareous deposits slow the diffusion of oxygen to the metal surface. For immersed surfaces, this implies polarization of the oxygen reduction reaction, and hence a decrease in cathodic protection current demand or a decrease in general corrosion rate when there is no cathodic protection.

Calcareous deposits play a critical role in cathodic protection of bare metal structures in seawater. Early pioneering work by Cox generated several patents, which described the 'best' current density ranges to produce the most protective calcareous deposits[17,18] that were referred to as 'electrocoating.' Over the years, many research efforts have been pursued for a better understanding and optimization of calcareous deposits.[19–29] It has been shown that the deposits are affected by many variables that include current density, potential, seawater velocity, temperature, and chemistry.

For example, **Figure 7** shows current densities associated with calcareous deposits formed in synthetic seawater at several potentiostatically controlled protection potentials in 50 h. Variation of deposit morphology with protection potential is illustrated in the SEM photomicrographs in **Figure 8**. At − 1100 mV (SCE), the deposits consisted predominately of $CaCO_3$ (aragonite) and a

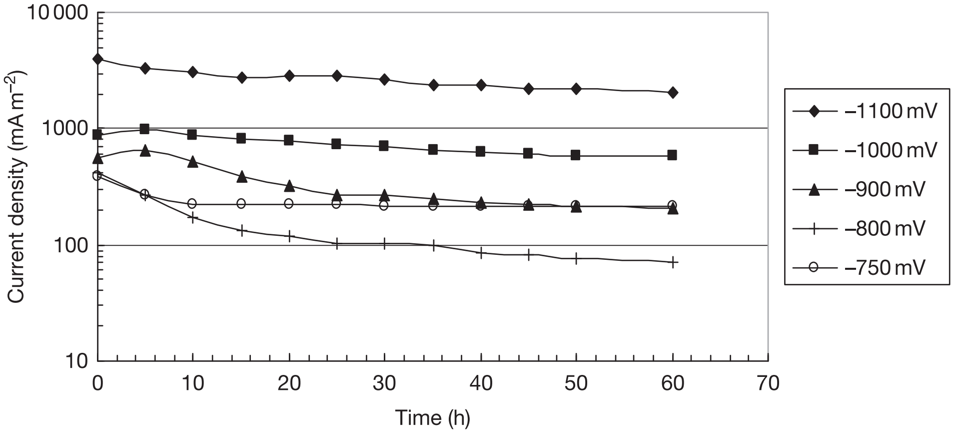

Figure 7 Current density versus time for clean steel at various protection potentials versus SCE.

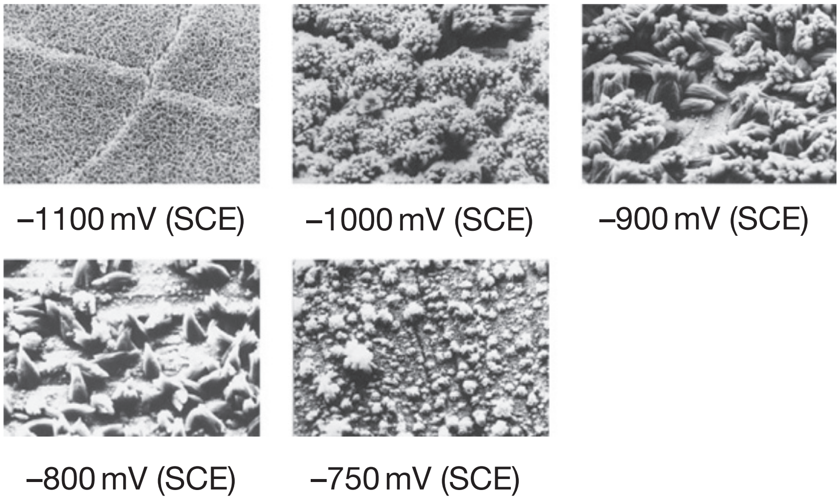

Figure 8 Morphology of calcareous deposits formed at various potentials in synthetic seawater in 50 h.

trace of $Mg(OH)_2$ (brucite). Although the deposits were thick, they were poorly adherent and not very protective since the current density did not decrease significantly. More adherent and protective deposits, composed primarily of $CaCO_3$ (aragonite), were formed at -800, -900, and -1000 mV (SCE). At -750 mV (SCE), complete cathodic protection was not attained, and the deposits comprised a mixture of $CaCO_3$ and iron corrosion products (Fe_2O_3 and Fe_3O_4). Data are not included in **Figures 7** and **8** for deposits formed at -1200 mV (SCE); however, the current density was $>10^4$ mA m^{-2}, the deposits were thick, gelatinous, mainly $Mg(OH)_2$, and nonprotective. In practice, many impressed current cathodic protection systems operate at constant current. As calcareous deposits form under constant current conditions, the current density increases at local areas, the potential of the protected metals shifts in the negative direction, and the morphology of the calcareous deposits changes. From a research viewpoint, it is easier to study the formation of, and protection afforded by, calcareous deposits under potentiostatic conditions rather than constant current conditions. Moreover, cathodic protection from well-designed sacrificial-anode systems, which are more common in seawater applications, approximates potentiostatic conditions, that is, anode output decreases as calcareous deposits are formed. However, Humble[19] has shown that the Ca/Mg ratio in calcareous deposits decreases with increasing current density as illustrated in **Figure 9**. Surprisingly, it has been found that Mg^{2+} ions in seawater inhibit $CaCO_3$ crystal nucleation and precipitation.[30] However, the greater concentration of Mg^{2+} in open seawater compared to Ca^{2+} assures that $CaCO_3$ will precipitate as aragonite.[31] In other natural waters, precipitation of $CaCO_3$ as calcite is favored because the concentration of Ca^{2+} is usually much greater than that of Mg^{2+}.

Table 4 provides some quantitative and qualitative data on calcareous deposit properties relative to cathodic protection current densities. The solubility of $CaCO_3$ decreases with increasing temperature, while that of $Mg(OH)_2$ increases. Thus, precipitation of $CaCO_3$ is favored in warm seawater, and that of $Mg(OH)_2$ in colder seawater. This has been postulated as one possible explanation of higher current density requirements for cathode protection of steel structures in colder seawater. It is apparent that calcareous deposit formation involves complex phenomena; thus, ideally, characterization and optimization of calcareous deposits for specific applications are best performed locally, *in situ*.

It is generally accepted that protection for materials such as aluminum alloys, titanium alloys, stainless steels, and nickel alloys is conferred by surface passive oxide films. In other words, these materials possess active–passive characteristics. In seawater, active corrosion is suppressed if the material exhibits passive behavior. The air-formed oxide films are thin (typically <10 nm). The composition of the base metal, heat treatment, surface cleaning, surface finish, and the exposure environment are among the

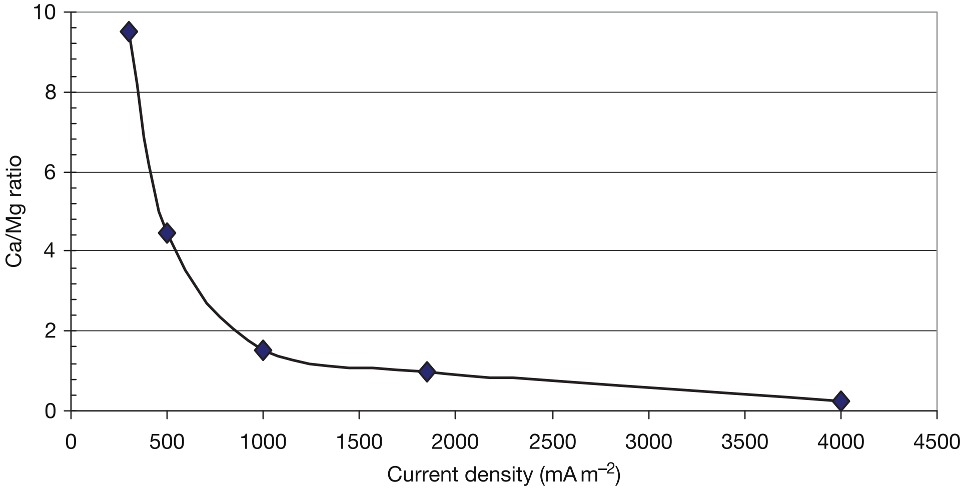

Figure 9 Ca/Mg ratio in calcareous deposits formed in seawater at various cathodic protection current densities over 3 months. Reproduced from Humble, H.A., 1948. Corrosion 4 (7), 358–370.

Table 4 Calcareous deposits properties relative to cathodic protection current densities

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, E. P., Doremus, G. L., 1950. Corrosion 6 (7), 216–224.

primary factors that determine the stability of the passive film. There is some evidence that adsorbed species from the exposure environment, for example, oxygen, contribute to the properties of the passive film.[32]

The most deleterious species toward passive films in seawater is chloride. Film breakdown and rehealing is a dynamic process. However, under certain conditions rehealing may not occur after corrosion has initiated at local areas. This can lead to propagation of attack and high rates of localized corrosion. A classical case of this is crevice corrosion of susceptible stainless steels, for example, under gaskets, under O-rings, at threaded joints, under silt and macrofouling deposits, and so on. Previously, this type of attack was ascribed to oxygen concentration cells, that is, absence of oxygen in the crevice and plentiful supply outside the crevice. However, the modern view is a little more complex. Crevice corrosion has been modeled mathematically and experimentally in a number of ways.[33–37] Deeper and tighter crevices are more susceptible to both the initiation and propagation of crevice corrosion. Metal-to-nonmetal crevices are generally tighter than metal-to-metal crevices because of the easier deformation of the nonmetal. However, metal-to-metal crevices, although less tight, may be equally susceptible to attack because both metal surfaces can contribute metal ions for hydrolysis. In dissimilar alloys, crevice attack on the more susceptible metal occurs first. As the crevice electrolyte becomes more aggressive by the autocatalytic process, crevice corrosion can initiate subsequently on the more resistant alloy.[38]

Electrochemical measurements have been used to demonstrate potential ennoblement and increased cathodic kinetics on passive surfaces covered by biofilms in seawater.[39,40] It has also been shown that biofilms are more prevalent in warm seawater, and hence decrease crevice corrosion initiation time compared to cold seawater. Above a threshold temperature of $\sim 50\ ^\circ\mathrm{C}$, crevice corrosion susceptibility in natural seawater apparently decreases.[36] It has been hypothesized that this behavior is due to reduced microbial activity in biofilms above such temperatures. This is analogous to reduction in crevice corrosion propensity in seawater treated with biocide, for example, 2 ppm residual chlorine, which inhibits biofilms and microbial activity. Crevice corrosion observed at elevated temperatures where biofilms are absent and microbial activity diminished must be explained by other mechanisms. For example, crevice corrosion of titanium is considered to occur at temperatures $>70\ ^\circ\mathrm{C}$.

Empirical data and experience indicate that some alloys are clearly much more resistant to crevice corrosion than others under the same crevice geometry and seawater conditions. It has been postulated that this is due to more stable passive films formed as a result of certain minimum combinations of alloying additions, primarily Cr, Mo, and N. Interestingly, it has been shown that hydrolysis of Cr^{3+} and Mo^{3+} produces the lowest pH values for the crevice electrolyte.[41] This appears to be the case when insufficient Cr and Mo (and possibly other synergistic elements) are present on the alloy surface to produce a passive film that prevents hydrolysis, acidification, and anodic dissolution. It has been suggested that addition of N to stainless steels can produce ammonium ($\mathrm{NH_4}^+$) ions that raise the pH and effectively neutralize any acidification due to hydrolysis in the crevice.[42]

It is often stated that increasing oxygenation of seawater (e.g., by increasing flow rate) alleviates crevice corrosion. This is based on the widely held view that higher flow rates minimize biofilm attachment and allow easy access of oxygen which is necessary to maintain passivity. That would be the case if oxygen was able to reach all areas of the metal (including the crevice) quickly. In fact, increasing oxygen supply worsens the situation because the oxygen-reduction cathodic reaction is enhanced by depolarization on surfaces outside the crevice, while oxygen diffusion into the crevice and neutralization of the acidic conditions within the crevice, both necessary for repassivation, remain severely restricted by the crevice geometry. In other words, the trapped acidic electrolyte in the crevice and lack of oxygen ingress keeps the crevice very active, while the area outside the crevice serves as an efficient cathode. Moreover, the rate of attack within the crevice can be very severe since the ratio of the cathode (area outside the crevice) to anode (area inside the crevice) is often quite large in many components in seawater immersion applications. This is illustrated by the example in **Figure 10**.[43]

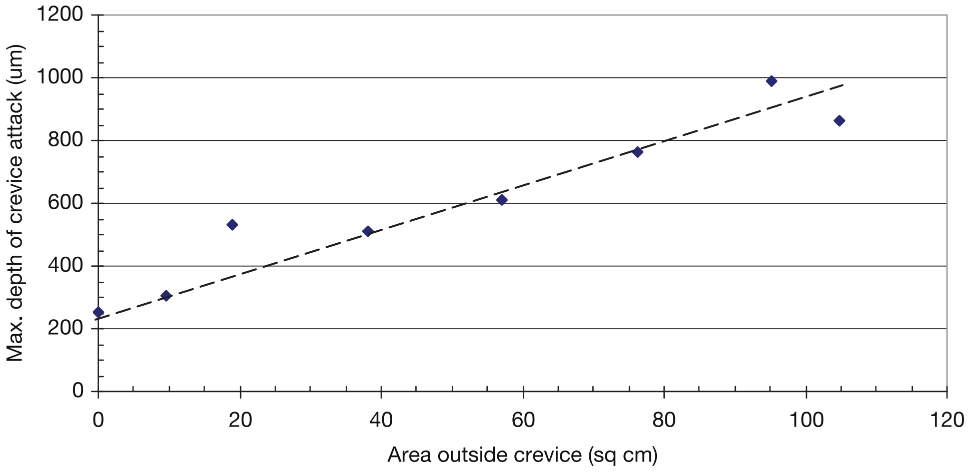

Figure 10 Maximum depth of crevice attack on 17-Cr stainless steel in seawater versus exposed cathodic (passive) surface area outside crevice. Adapted from Ellis, O.B., LaQue, F.L., 1951. Corrosion 7 (11), 362.

Another poorly appreciated fact is the behavior of active–passive metals in deaerated solutions. As stated previously, materials such as stainless steels depend on the formation and maintenance of a passive film on the alloy surface exposed to seawater. A widely held but mistaken view is that deaerated seawater is detrimental because oxygen is unavailable to sustain passivity. However, the fact of the matter is that removal of oxygen from seawater is not normally deleterious toward such alloys because oxygen reduction is the primary cathodic reaction that controls the propagation of pits and/or crevice attack. This has been demonstrated experimentally. Since the seawater pH is near-neutral, the alternative hydrogen-discharge cathodic reaction is negligible. Thus, even if oxygen is unavailable to maintain passivity, corrosion of active–passive alloys in seawater will be imperceptible unless some other cathodic reaction is viable. Even with anaerobic bacteria active under anoxic conditions, corrosion damage occurs predominately when subsequent exposure to aerated conditions occurs.

3.1 Galvanic Corrosion

Figure 11 is a depiction of the typical galvanic series of metals and alloys in seawater that is widely available to engineers. Unfortunately, the severe limitations of adequately predicting galvanic corrosion from such a series alone are commonly underestimated. The series basically represents a ranking of metals and alloys according to their free corrosion potentials in a given environment (in this case, flowing natural seawater at ambient temperature). For a given metal or alloy, the ranking can be influenced by a number of variables, for example, temperature, flow rate, fouling, chlorination, crevices, oxygen content, and so forth. The series provides only qualitative information on likely galvanic corrosion if two dissimilar materials in the series are electrically coupled in the environment. Corrosion of the anodic material (i.e., one with a relatively more electronegative corrosion potential) is likely to be accelerated, and corrosion of the cathodic (i.e., one with a relatively more electropositive corrosion

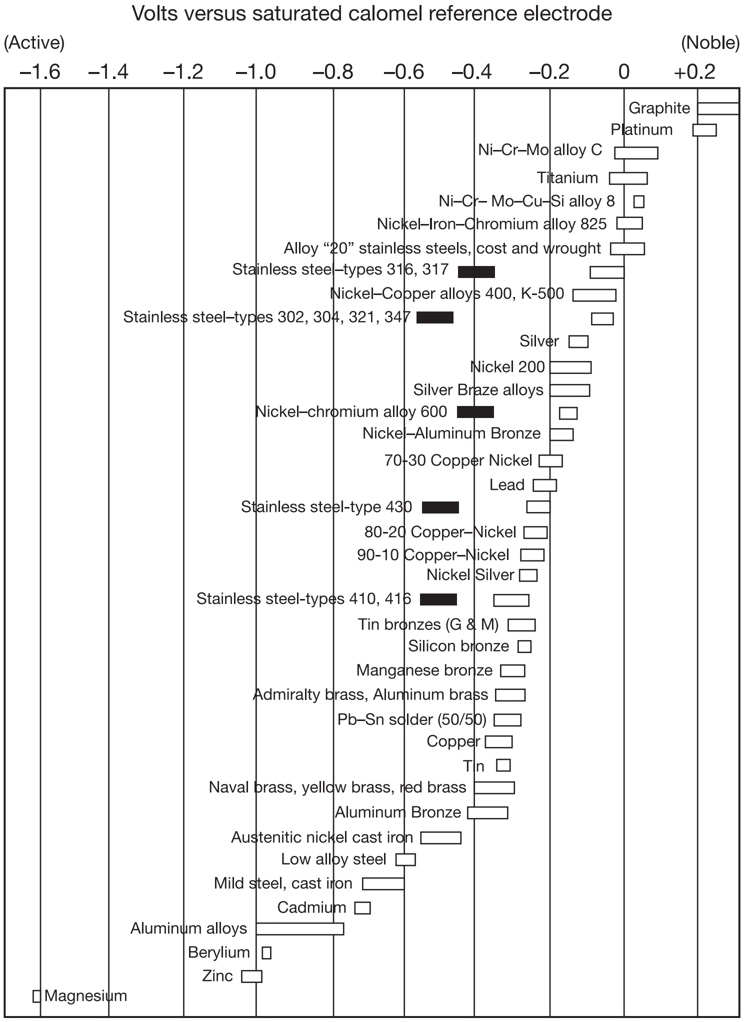

Figure 11 Typical galvanic series of metals and alloys in flowing natural seawater. Solid bars represent active corrosion potentials for otherwise passive alloys.

potential) material is slowed or stopped. However, the degree of galvanic interaction cannot be determined quantitatively from the series alone. If Ohm's law applied, then the amount of galvanic attack would be a function of the potential difference between the two dissimilar materials and the total circuit resistance. However, polarization behavior of the materials and their relative area ratios has been found to be much more significant than the potential difference. The example **Figure 12** shows that the potential difference between titanium and steel in seawater is nearly double that of copper versus steel. However, for the same anode/cathode area ratio, the galvanic current density for the titanium/steel couple (and hence expected corrosion rate of steel) is nearly nine times lower compared to the copper/steel couple. This behavior is due to the polarization of the cathode, for example, oxygen reduction on titanium is less efficient than on copper. Polarization is influenced by surface films. For example, biofilms on metal surfaces generally enhance reduction reactions and hence galvanic corrosion in certain couples.[44] Although chlorination is used for biofouling control (e.g., to maintain heat transfer), low levels have also been found to reduce galvanic corrosion, for example, of copper alloys coupled to more noble alloys, because reduction reactions are polarized appreciably.[45,46] If calcareous deposits form on cathodic surfaces, they hinder oxygen diffusion, and hence can reduce galvanic corrosion effects.

It is generally accepted that galvanic attack on the anodic member in a dissimilar metal couple intensifies as the cathode/anode area ratio increases. However, geometry and spatial disposition of the anode and cathode can also play an important role. For example, in a retubed seawater heat exchanger, titanium tubes represent a large surface area with respect to the original copper–nickel tube sheet. This generally results in high galvanic corrosion rate of the latter. In a plate-type heat exchanger, the surface area of the titanium plates is very large compared to say the adjoining copper–nickel piping. However, galvanic corrosion of the latter is not usually significant because the tortuous pathways between the titanium plates represent a high electrolytic resistance.

The galvanic series only relates to consideration of two materials at a time in a galvanic couple. In many practical applications, multiple metals may be involved. For example, if aluminum, steel, copper, and titanium components are all coupled in a system, the galvanic series only indicates that titanium would be cathodic and aluminum would be anodic with respect to each other. The galvanic series would not indicate whether steel and copper would behave anodically or cathodically in the overall system. This could only be determined after measuring the mixed potential (when all the subject metals are electrically coupled).

Another widely misunderstood aspect of galvanic corrosion is the interaction of graphite with other metals. Because of its typically most noble position in the galvanic series, it is often misstated that graphite forms adverse galvanic couples with all metals. Graphite (and graphite-containing materials) can certainly accelerate corrosion of metals such as copper, steel, and aluminum, especially for large cathode/anode area ratios. However, graphite is galvanically compatible with titanium, most Ni–Cr–Mo alloys, and many stainless steels. For example, attack observed on stainless steels in contact with graphite gaskets is often incorrectly attributed to galvanic corrosion. However, practical experience indicates that such attack (and of similar magnitude) is in fact due to crevice corrosion which occurs even when the graphite is replaced by a nonconductive gasket material.[47]

4 Carbon Steels

Carbon steels are widely used in seawater applications because of their ready availability, extensive range of mechanical properties, ease of fabrication, and usually lowest initial cost. However, carbon steels are very susceptible to corrosion in marine environments,

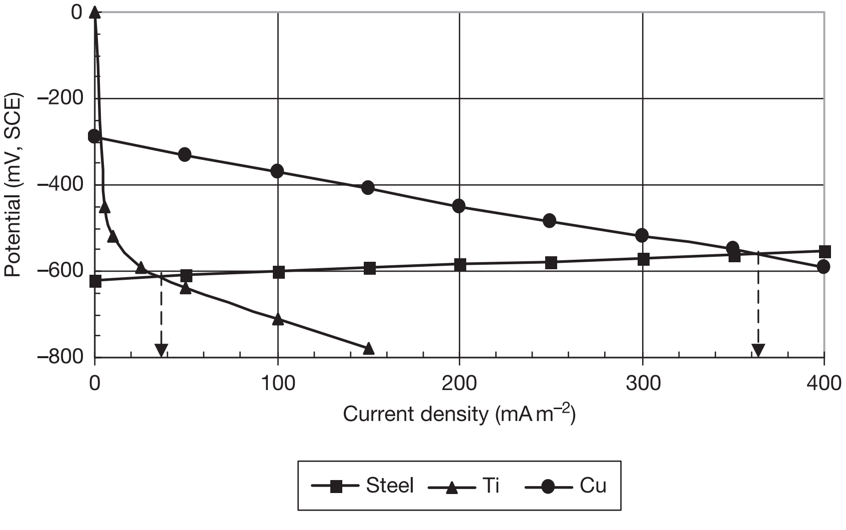

Figure 12 Polarization curves for carbon steel (anode) versus copper (cathode) and titanium (cathode), illustrating galvanic current density depends on polarization behavior rather than galvanic couple potential difference. Adapted from LaQue, F.L., 1975. Marine Corrosion: Causes and Prevention. Wiley, p. 195.

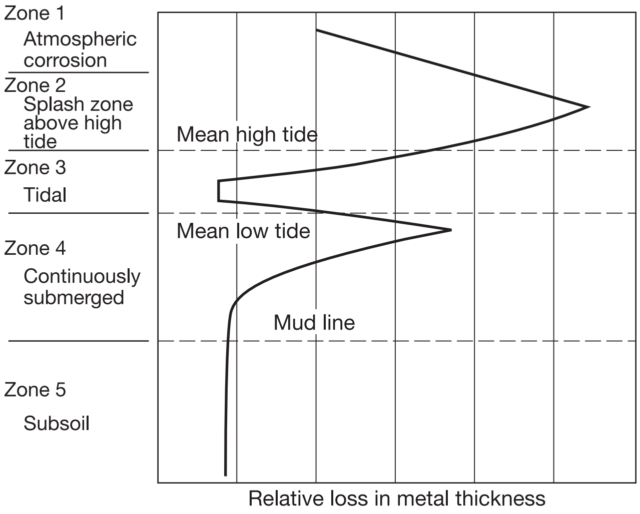

Figure 13 Corrosion profile of steel piling exposed to various zones in a natural marine environment for 5 years. Reproduced from Humble, H.A. 1948. Corrosion 5 (9), 23–28.

Table 5 Seasonal variations in corrosion rate of steel in natural seawater at $\sim 0.2\ \mathrm{m\ s^{-1}}$

Period	*Ave temp (°C)*	*Ave dissolved oxygen (ppm)*	*pH*	*Ave corrosion rate (μm year^{-1})*
Jan–Mar	10.5	9.2	8.0	100
Apr–Jun	22.4	6.9	8.0	130
Jul–Sep	27.2	6.0	8.0	140
Oct–Dec	14.1	8.2	8.1	110

and hence require some form of corrosion control. As stated earlier, corrosion rate is affected by a complex interaction of factors that include DO, temperature, depth, flow rate, and microbiological activity.

Figure 13 illustrates the typical corrosion profile of steel piling subjected to various marine zones. The highest corrosion rate in the splash and spray zone is attributed to constant wetting that produces a thin film of seawater through which oxygen diffuses readily. The high corrosion rate, constant wetting conditions, and the mechanical effects of splashing preclude development of protective corrosion products. Even if coatings are applied prior to installation, they are virtually impossible to maintain in this zone. However, successful long-term protection has been achieved with metallic sheathing[48,49] (e.g., using alloys such as NiCu alloy 400 and 90/10 CuNi). Nonmetallic wraps have also been used for protection in the splash zone.[50,51]

In the tidal zone, the structure is exposed to alternate immersion. The lower general corrosion rates in this zone are ascribed to oxygen shielding by macrofouling. However, localized attack can be aggressive if SRB activity under anaerobic macrofouling conditions is high. A particularly severe form of attack known as 'accelerated low water corrosion (ALWC)' afflicts steel sheet piling in some ports and harbors at areas just above the lowest astronomical tide.[52–54] The phenomenon is not fully understood presently. However, empirical evidence suggests a strong influence of microbiological organisms, especially SRB possibly synergized by acid producing bacteria; corrosion penetration can exceed 1 mm year^{-1} on a given steel surface. Apparently, structures affected by ALWC are usually exposed to tidal and brackish waters.

As discussed earlier, reduction of DO is the primary cathodic reaction controlling corrosion of steel in aerated marine environments. Although oxygen solubility decreases with increasing temperature, corrosion of steel immersed in seawater generally increases with temperature and with flow rate. The data in **Table 5** illustrate the increase in corrosion rate of steel in warmer seawater during the summer months despite the lower oxygen content. **Figure 14** depicts increase in corrosion rate with flow velocity in ambient temperature seawater in the absence of significant corrosion products.[55] Adherent corrosion products can diminish the effect of flow. However, above a critical wall shear stress, corrosion products are prevented from forming and existing ones removed by erosion.

The corrosion rate of steel, based on mass loss, in quiescent seawater is typically on the order of ~ 0.13 mm year^{-1} after several years of exposure. A 5-year worldwide seawater corrosivity test program indicated that local conditions can exert a strong influence on corrosion rate and types of attack.[56] In some cases, pitting rates were much higher than general corrosion rates, as illustrated by the data in **Figure 15**. Complete localized penetration of the 6-mm plate thickness occurred on some, but not all test panels at

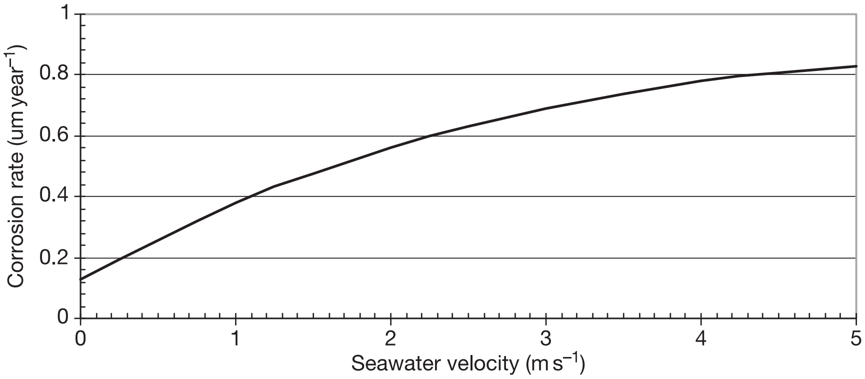

Figure 14 Corrosion rate of clean carbon steel in ambient temperature flowing natural seawater on 38 days. Reproduced from Oubner, R., Beech, I., 1999. Corrosion/1999. Houston, TX: NACE International. Paper No. 99318.

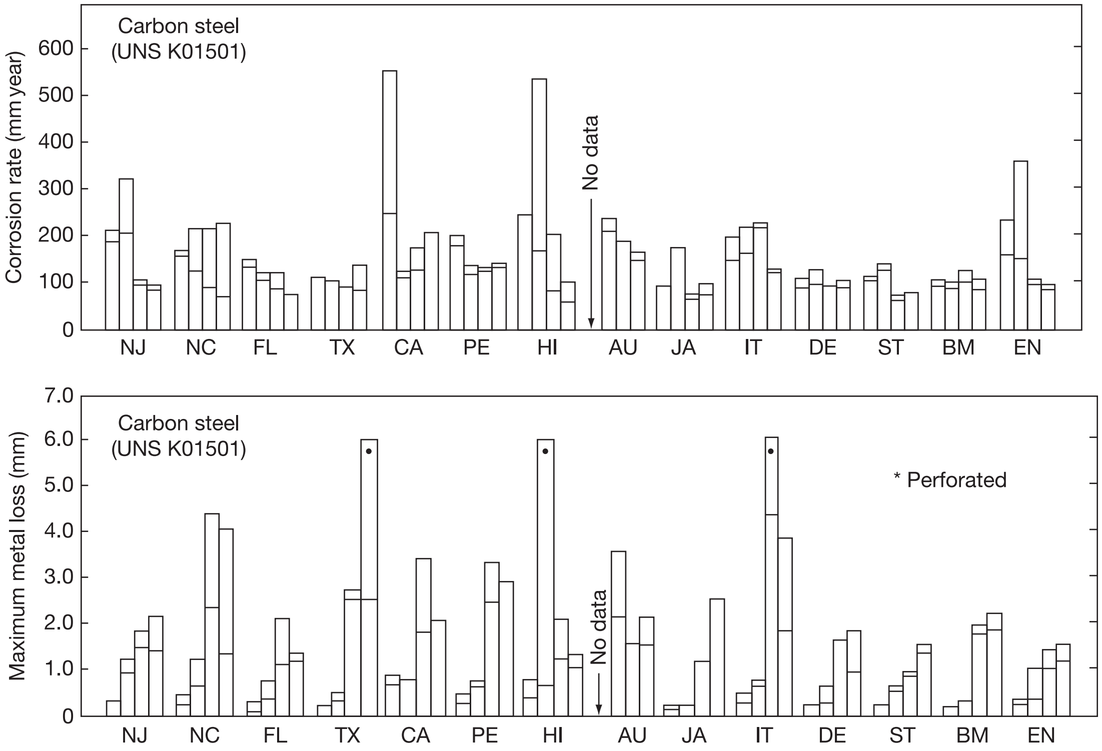

Figure 15 Mass loss corrosion rate and maximum depth of pitting attack on carbon steel in seawater at 14 worldwide test locations. For each location, the bars represent (from the left) 0.5, 1, 3, and 5-year exposures. NJ, New Jersey; NC, North Carolina; FL, Florida; TX, Texas; CA, California; HI, Hawaii; AU, Australia; JA, Japan; IT, Italy; DE, Denmark; ST and BM, Sweden; EN, England. Reproduced from Phull, B.S., Pikul, S.J., Kain, R.M., 1997. ASTM STP 1300. West Conshohocken, PA: American Society for Testing and Materials, pp. 34–73.

specific exposure locations. This type of accelerated localized attack resulting in large, round pits has been attributed previously to sea urchins[57] – which apparently 'scrub' corrosion products, and thus expose fresh metal surface to enhanced corrosion rate. Extensive data analysis and modeling on corrosion of steel in seawater have been performed by Melchers[58]; the primary conclusions were that velocity affects corrosion in the early stages until marine fouling and corrosion products develop – thereafter, influence of fouling thickness is significantly reduced. DO and temperature rather than depth *per se* affect corrosion; for a given exposure period, test specimens first exposed during autumn and winter exhibited less corrosion than those first exposed in spring and summer.

It is commonly believed that macrofouling reduces oxygen transport and, consequently, overall corrosion rate of steel in seawater. However, data from tests indicate similar corrosion behavior for carbon steel in filtered and unfiltered seawater – suggesting that microfouling may be more important than macrofouling in controlling corrosion behavior. This appears

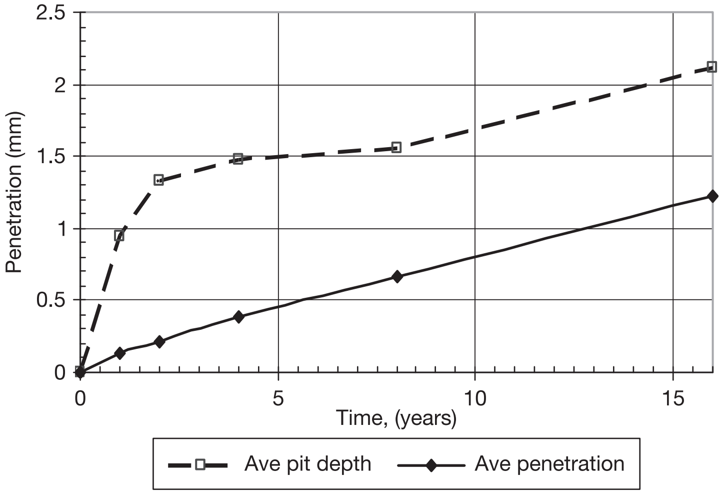

Figure 16 Corrosion of carbon steel in natural seawater. Average penetration calculated from mass loss of six replicate test panels – slope corresponds to ~0.07 mm year^{-1} corrosion rate; average pit depth is the mean of 60 measured pits, five deepest pits on each surface of six test panels. Reproduced from Southwell, C.R., Alexander, A.L., 1970. Mater. Prot. 9 (1), 14–23.

contradictory to the view that biofilms enhance the oxygen reduction reaction, for example, in microbiologically influenced corrosion of stainless steels.

In shallow immersion, pitting depths on carbon steel can be an order of magnitude higher than general corrosion rates calculated from mass loss as illustrated in **Figure 16**.[59] Determination of pitting rates can be an onerous task. A common but mistaken practice involves measuring the maximum or average pit depth and calculating a pitting rate. There are a number of flaws with this approach. First, pitting is not linear with time, especially for long-term exposures in seawater. Second, the data are usually based on measuring different pits on different test samples, that is, specific pits are not monitored as a function of time owing to the obvious experimental shortcomings of this approach. Pitting is a statistical process; the number, size, and locations of pits on a given metal surface can vary over a wide range. Thus, computing pitting rates from limited data, and assuming linear growth rate with time is fraught with problems.

Figure 17 shows the general corrosion rate of carbon steels exposed for 1 year and DO content as a function of seawater depth.[60] It is apparent that the corrosion profile closely follows that of the oxygen concentration. The following relationship derived from linear regression analysis[61] indicates a greater dependence on oxygen content compared to temperature:

$$\text{Corrosion rate } (\mu\text{m year}^{-1}) = 21.3 + 25.4\left[\text{O}_2\left(\text{ml l}^{-1}\right)\right] + 0.356\left[\text{T}\left({}^{\circ}\text{C}\right)\right] \qquad [4]$$

Other data have indicated more complex corrosion behavior. For example, in unpolluted seawater, corrosion rate was dependent on oxygen content, whereas in polluted seawater, temperature had a greater influence.[62] Polluted seawater typically has the following characteristics (compared to unpolluted seawater): lower oxygen content, lower pH, higher sulfide and sulfate-reducing bacteria concentrations, and higher ammonia content. Corrosion data suggest that at similar temperatures, the effect of lower oxygen content in polluted seawater is offset by the presence of pollutants,[62] especially sulfides.

Under immersion conditions, low alloy steels behave fairly similar to carbon steels. Small amounts of alloying additions do not evidently alter the corrosion rate of steel significantly in seawater. However, as the alloy content is increased further (e.g., >5 wt%, especially Cr addition), a reduction in general corrosion rate is often replaced by deep, localized pits. It has been reported that low-alloy steels can cause galvanic corrosion of plain carbon steels despite a small difference in their corrosion potentials.[63]

Higher strength carbon steels are susceptible to hydrogen embrittlement (HE) in seawater, especially when polarized to excessively negative potentials. Factors that affect the susceptibility of steels in seawater to HE include yield strength (which is influenced by composition and heat treatment), electrochemical potential, and pollutants (especially sulfide). In general, susceptibility increases with increasing yield strength. High-strength steels are generally considered to be those with YS > 700 MPa. Steels with YS < 700 MPa are generally considered resistant to hydrogen embrittlement. Since alloying additions affect yield strength, it is difficult to delineate their influence on HE behavior. However, limited data[64] on steels of varying compositions but similar yield strengths indicate negligible effects of S or P (each <0.03%), Si or Cr (each <2.1%), Mo (<1.2%), and Co (<3%). Detrimental effects were indicated for C (0.3–0.4%), Mn (0–3%), and slightly deleterious for Ni (>6%). Tempering or aging heat-treatments at higher temperatures lower yield strengths and hence typically increase HE resistance. Ultra high-strength steels (e.g., with YS ≥ ~1400 MPa) can suffer HE even in distilled water. Elevated temperatures increase crack growth rates, probably as anodic dissolution rate increases, following Arrhenius behavior.[65]

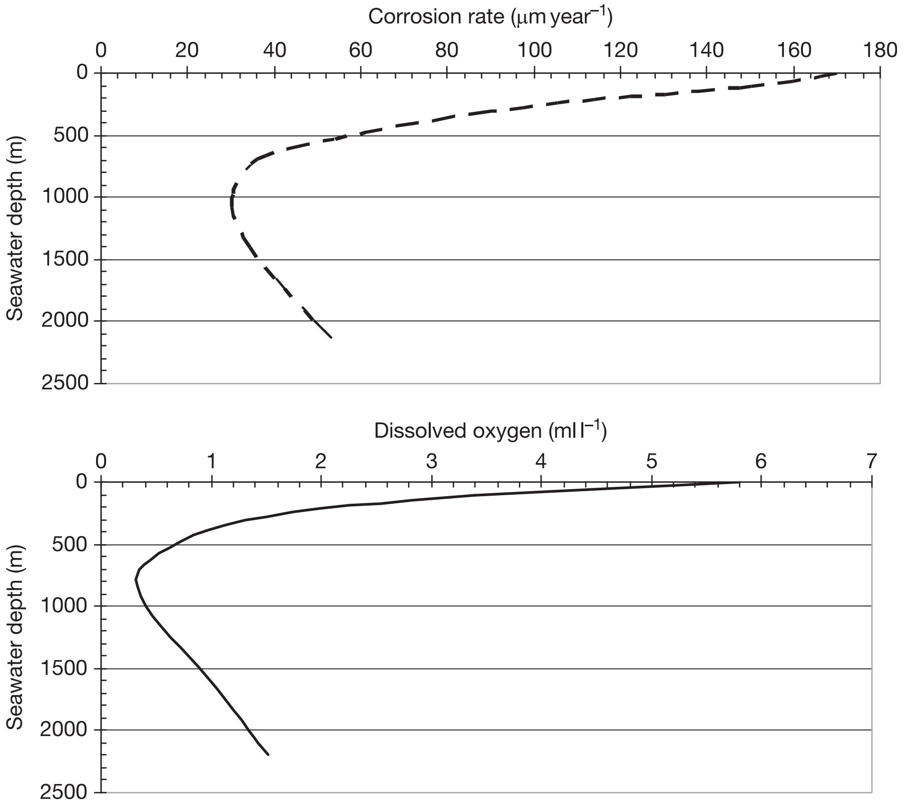

Figure 17 Corrosion rate of carbon steel exposed for 1 year and DO concentration versus seawater depth (DO ml l^{-1} × 1.429 = mg l^{-1}); note similarity in profiles versus depth. Reproduced from Reinhart, F.M., 1976. Corrosion of Metals and Alloys in the Deep Ocean. Port Hueneme, CA: Civil Engineering Laboratory, p. 14. Technical Report No. R-834.

Polarization of high-strength steel to more noble potentials than the free corrosion potential can markedly increase HE propensity as indicated by significantly shorter time to failure. Cathodic polarization to a narrow potential range (e.g., -0.8 to -0.9 V SCE) is generally beneficial since anodic dissolution processes are stifled. However, cathodic polarization to more active potentials (especially more negative than -1 V, SCE) again lowers cracking resistance. Pollutants, in particular sulfur-containing species, have been found to increase susceptibility to HE.

Carbon steel has been used extensively in the past for construction of flash chambers in thermal desalination plants. In principle, the corrosion rate should be negligible if DO is completely stripped from the seawater used in the process. However, in practice, it is very difficult to deoxygenate the seawater fully. Typically, oxygen concentration is reduced from ppm to ppb levels. However, increasing temperature has a far greater effect on corrosion than low oxygen levels. For example, data from a thermal desalination pilot-plant test revealed that even at a 100 ppb DO level and seawater flow-rate of ~1.7 m s^{-1}, the corrosion rate of carbon steel doubled from 0.3 mm year^{-1} at 81 °C to 0.6 mm year^{-1} at 120 °C.[66] Oldfield and Todd[67] developed the following expression for calculating corrosion rate:

$$\text{Corrosion rate (mm year}^{-1}) = \left(0.0117 \times C_0 \times U_0^{0.9}\right)/Pr^{0.75} \qquad [5]$$

where C_o is bulk concentration of oxygen in moles cm^{-3}, U_o is bulk flow rate in cm s^{-1}, and Pr is the Prandtl number (defined as ratio of kinematic viscosity, v, to diffusion coefficient, D). The predicted corrosion trends were in good agreement with previously published field and test data; lower actual corrosion rates in the field were attributed to presence of corrosion products and scaling.

Millscale on steel surfaces is cathodic to the substrate. While the general corrosion rate of steel, based on mass loss data, may not appear significantly different, the presence of millscale can produce deep pitting by galvanic action due to the adverse cathode (millscale) to anode (exposed steel) area ratio.

5 Cast Irons

The initial corrosion behavior and corrosion rates of unalloyed gray and ductile cast irons in seawater are similar to those of carbon steels. However, in gray cast irons, as corrosion progresses, dissolution of the ferrite phase exposes increasing the amounts

Table 6 Effect of increasing Ni content in cast irons on erosion–corrosion behavior in seawater at 8 m s^{-1} at 28 °C for 60 days

Alloy	*% Ni content*	*Ave corrosion rate (mm year^{-1})*
Cast iron	–	6.9
2% Ni cast iron	2	6.1
Type 1 Ni-Resist	13.5–17.5	0.74
Type 2 Ni-Resist	18–22	0.79
Type 3 Ni-Resist	28–32	0.53

Source: Shreir, L.L. (Ed.), 1979. Corrosion. Newnes Butterworths, vol. 1, pp. 3–106.

of the flake graphite network. This dealloying phenomenon is known as graphitic corrosion. It is commonly but incorrectly referred to as graphitization – which is really a metallurgical term used to describe decomposition of iron carbide (Fe_3C) to iron (Fe) and graphite (C) at elevated temperatures. At low velocities, the iron corrosion products are often 'trapped' by the flake graphite network. In such cases, visual inspection can greatly underestimate material degradation because reduction in section thickness is not apparent. Ultrasonic inspection and/or destructive examination are usually necessary to monitor graphitic corrosion before catastrophic failure occurs.

Graphitic corrosion may advance to a stage where it can induce galvanic corrosion of other materials coupled to the cast iron. For example, initially steels are galvanically compatible with gray cast iron, while copper alloys are cathodic. However, graphitic corrosion of the cast iron can eventually generate or reverse the galvanic couple where the exposed graphite behaves cathodically to steels and copper alloys and accelerate their dissolution by galvanic action.[68] Graphitic corrosion and its consequences are not a major problem with ductile irons because the graphite is present as discrete nodules instead of a flake graphite network.

Addition of ~20% Ni to cast iron increases toughness and shock resistance. However, the austenitic microstructure is still susceptible to graphitic corrosion, if the graphite is present in the flake form. Depending on alloy composition, small Mg additions (e.g., ~0.1%) during production convert the flake graphite to nodular form. This significantly increases the tensile strength, impact resistance, and graphitic corrosion resistance. Corrosion rates of austenitic cast irons (commonly referred to by a trade name, NiResist®) in seawater are often an order or magnitude lower than gray or ductile irons. The benefit of increasing Ni content in the cast iron is particularly notable for erosion–corrosion resistance in seawater at high velocities as illustrated by the data in **Table 6**. Sporadic stress corrosion cracking (SCC) problems observed in austenitic cast iron seawater pumps have been attributed to improper stress-relief heat treatment.[69]

6 Stainless Steels

The addition of >11% Cr to Fe generates a Cr- and Fe-containing passive oxide film on the metal surface. There is a very marked reduction in general corrosion rate in seawater compared to carbon steel or low alloy steels. However, the stainless steels are highly susceptible to localized corrosion unless much more Cr and/or other alloying additions such as Mo, N, and Ni are also present. Thus, determination of general corrosion rates of stainless steels in seawater from weight loss results can be misleading because most of the metal dissolution is typically associated with pitting and crevice corrosion.

There are several hundred commercial grades of stainless steels, with widely ranging compositions and properties. Obviously, a large number of grades are unsuitable for seawater applications. Typically, stainless steels are divided into several broad classifications, *viz.* martensitic, ferritic, austenitic, superaustenitic, duplex, superduplex, and precipitation hardening (PH). Even within each classification, there can be a wide range of compositions.

Martensitic stainless steels are susceptible to pitting, crevice corrosion, SCC, and hydrogen embrittlement (especially under cathodic protection) in seawater.

High-Cr ferritic grades, such as Type 29–4 C (29Cr–4Mo), are considered to have much greater resistance to localized corrosion compared to more leaner grades such as Type 430 (17Cr). Ferritic grades are resistant to chloride stress corrosion cracking (Cl^- SCC), but susceptible to hydrogen embrittlement, especially when subjected to cathodic protection, unintentional or otherwise.

Despite their popularity, particularly for marine atmospheres, many austenitic grades (such as many of the 300-series) are unsuitable for seawater service; unfortunately, they are often selected because of their attractive mechanical and welding properties, that is, without a complete understanding of their limitations, especially corrosion resistance. They are susceptible to Cl^- SCC; susceptibility trend decreases with increasing Cr or Cr + Ni content. They are resistant to hydrogen embrittlement except in the severely cold-worked condition. Type 304 is highly susceptible to pitting corrosion in seawater; Type 316 is more resistant due to the Mo addition but certainly not immune. The biggest limitation of these grades is their high propensity to crevice corrosion, for example, under gaskets, O-rings, washers, sleeves, macrofouling deposits, silt, and so on which are discussed later. Superaustenitic grades have higher alloy content (~20% Cr, 25% Ni, and ~6% Mo, or more) for increased resistance to crevice corrosion; their higher Ni content also enhances resistance to SCC.

In seawater, the localized corrosion resistance of duplex stainless steels is similar or slightly better than many austenitic grades. They are slightly magnetic and susceptible to hydrogen embrittlement, for example, under cathodic over-protection conditions, or in the presence of hydrogen sulfide. Superduplex stainless steels have higher Cr and nitrogen contents (e.g., alloy 2705; 27Cr–5Ni–3Mo–0.2N), which improve corrosion resistance notably, but does not make them immune under all conditions. They are much more resistant to chloride SCC than austenitic stainless steels.

PH stainless steels are susceptible to pitting, crevice corrosion, SCC, and hydrogen embrittlement (especially under cathodic protection) in seawater.

The highly-oxygenated thin liquid film environment, and absence of biofouling in the splash zone represent conditions under which stainless steels generally perform well at ambient temperatures and if critical crevices are not present. Leaner compositions may develop superficial rust staining. Stainless steel sheathing fabricated from 300-series austenitic stainless steel (e.g., Types 304 and 316) has been successfully used for long-term splash-zone protection at ambient temperatures.

The leaner grades of stainless steel are susceptible to localized attack under biofouling attachments that usually proliferate in the intertidal zone. **Figure 18** shows classical crevice corrosion of Type 304 stainless steel under barnacles.

The data in **Table 7** show localized corrosion penetration for several stainless steels after 16 years exposure in the intertidal and full immersion zones in Panama.[70] There was complete perforation of the 6-mm thick plate material by localized corrosion for all the grades tested under full immersion conditions. In the intertidal zone, the martensitic Type 410 material was also completely perforated, while the deepest pits on the other three grades ranged from ~1 to ~3 mm. Type 304 stainless steel pits in seawater like Type 302 and Type 321 (Type 321 is an analog of Type 304L, but stabilized with Ti for averting sensitization in lieu of lowering the carbon content). Attack typically initiates under biofouling attachments and at cut edges where inclusions in the material are exposed prominently. The acidic environment generated in the pits by metal-ion hydrolysis often leads to subsurface attack in the form of tunneling. On stationary structures, such attack often progresses vertically downward due to gravity. The addition of 2–3% molybdenum in Type 316 stainless steel imparts some resistance, but not immunity to pitting in seawater compared to Type 304. Sufficiently high flow rates that prevent macrofouling attachments would be expected to mitigate

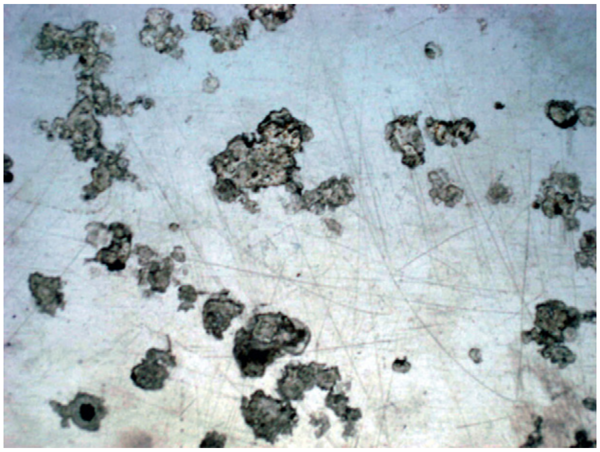

Figure 18 Crevice corrosion of Type 304 stainless steel under barnacles in natural seawater.

Table 7 Depth of localized corrosion attack on various stainless steels in natural seawater intertidal and immersion zones after 16 years' exposure

Alloy	*Exposure zone*	*Ave of 20 deepest pits 1 year*	*Ave of 20 deepest pits 8 years*	*Ave of 20 deepest pits 16 years*	*Deepest pit over 16 years*
410 SS	Tidal	1.17	1.70	2.72	P*
	Immersion	1.55	4.08	5.38	P
302 SS	Tidal	0.15	1.47	1.27	2.79
	Immersion	1.78	3.56	3.84	P
321 SS	Tidal	0.18	1.42	1.40	2.36
	Immersion	1.63	4.90	6.02	P
316 SS	Tidal	0.13	0.41	0.33	0.91
	Immersion	1.14	3.96	2.41	P

Source: Southwell, C.R., Bultman, J.D., Alexander, A.L., 1976. Mater. Prot. 15 (7), 9–26.

P – Perforation (of 6-mm plate).

Figure 19 Crevice corrosion of Type 316L stainless steel pump shaft sleeve in natural seawater.

pit initiation. However, even in the absence of macrofouling, attack can initiate if the inclusion (e.g., MnS) concentration is high. For example, rampant pitting is encountered in Type 303 'free machining' stainless steels because they contain sulfur or selenium alloying additions, which produce copious electrochemically active inclusions in the microstructure.

Localized corrosion experienced with Type 304 stainless steel often leads to selection and specification of Type 316 stainless steel in many seawater applications. This is unfortunate despite a wealth of available information in the published literature. Virtually all 300-series stainless steels are susceptible to crevice corrosion in seawater. It is not widely appreciated that Type 316 stainless steel is just as susceptible to this form of localized corrosion as Type 304 in typical seawater applications containing crevices, for example, at flange faces, under gaskets, under O-rings, under washers, at threaded connections, under lap joints, and so on. Crevice corrosion can also occur under disbonded paint films, under biofouling, under silt, and so forth. There is another mistaken, but again, unfortunately, widely held view that low carbon 'L' grades of 300-series stainless steels are somehow more resistant to pitting and crevice corrosion in seawater. This is simply not the case. The 'L' grades are beneficial for mitigating intergranular attack, which would otherwise occur at sensitized areas of the microstructure, for example, heat-affected zones associated with welds. **Figure 19** shows typical crevice corrosion of a Type 316L stainless steel pump shaft bearing sleeve in seawater service. Thus, if crevices are present, and some form of corrosion-control, for example, cathodic protection, is not applied, Type 316 stainless steel will crevice corrode in most aerated seawater applications. This fact is used in crevice corrosion testing in seawater where Type 316 specimens are routinely used as susceptible controls. In other words, the test is invalid if the Type 316 stainless steel controls do not crevice corrode.

Crevice corrosion of stainless steels in seawater has been investigated extensively over the past 30 years. The importance of DO transport to the stainless steel surface to maintain passivity is widely accepted. For example, the following minimum velocity relationship was derived from one laboratory study[71] on smooth-wall, Type 316 stainless steel tubes to prevent fouling in seawater:

$$v = 2.74 + 0.56 \log d \qquad [6]$$

where v is the velocity (m s^{-1}) and d is the tube inside diameter (m).

Another rule-of-thumb $\sim$2 m s^{-1} minimum seawater velocity is commonly recommended to prevent settlement of silt and macrofouling under which localized attack can initiate and propagate. This type of approach is fraught with problems in practice because it is virtually impossible to maintain flow without interruptions. Experience indicates that macrofouling which attaches during extended stoppages is not usually removed when flow is resumed. Furthermore, it is very difficult to eliminate 'man-made' crevices completely in most components and seawater applications. The seawater electrolyte in the crevice is stationary even if high flow conditions exist outside the crevice. Thus, if a material is susceptible to crevice corrosion, maintaining sufficient flow to prevent fouling (outside the crevice) will not prevent attack within the crevice, as also discussed earlier.

The data in **Table 8** show that the maximum depth of crevice attack in seawater for three stainless steel alloys at 28 °C seawater temperature is greater than at 12 °C, but decreases markedly at 50 °C.[72] As discussed earlier, this behavior is often attributed to enhanced biofilm activity in warm seawater compared to cold or hot seawater.

As stated earlier, Cr and Mo are the primary alloying elements that influence localized corrosion resistance of stainless steels in seawater. Service experience[73] and tests[74] have shown that significant crevice corrosion resistance in ambient temperature seawater is attained with austenitic stainless steels of the nominal composition 20Cr–25–Ni–6Mo. However, even these 6Mo alloys have been shown to be prone to crevice attack if the seawater temperature exceeds their critical crevice corrosion temperatures (CCT),

Table 8 Maximum depth of crevice attack in natural seawater in 30-day test at three temperatures

Alloy	*Maximum depth of crevice attack (mm)*		
	12 °C	*28 °C*	*50 °C*
304 SS	0.56	0.81	0.12
316 SS	0.34	0.57	0.05
Alloy 20	0.18	0.20	0

Source: Asphahani, A., Manning, P.E., Silence, W.L., Hodge, G.F., 1980. In Corrosion/80. Houston, TX: NACE International. Paper No. 29.

Table 9 Typical PRE numbers versus CCT and CPT values for various stainless steels

Alloy	*UNS No.*	*PRE*	*CCT (°C)*
316L	S31603	26	<5
317L	S31783	28	0
2205	S31803	34	17.5–25
904L	N08904	36	15–25
2507	S32750	43	35–43
254SMO	S31254	46	30–60
AL–6XN	N08367	47	43
654SMO	S32654	63	60 +

Source: Davies, M., Scott, P.J.B., 2003. Guide to Use of Materials in Waters. Houston, TX: NACE International, p. 90.

typically in the 30–45 °C range depending on the exact composition. Crevice attack on these alloys has also been demonstrated in tests conducted on painted panels even with relatively small areas left uncoated.[75]

Duplex stainless steels are also potentially susceptible to crevice corrosion depending on alloy composition, crevice geometry, and service or test conditions. The higher Cr-containing alloy 2507 is generally more resistant to crevice corrosion than the lower Cr alloy 2205. Successful use of higher Cr duplex stainless steel has been reported in offshore and desalination seawater pumps, valves, and piping systems[76] normally at temperatures below their CCT (~ 40 °C) and chlorine levels of 0.5 ppm or less.

Critical crevice corrosion temperatures of stainless steels are usually determined using the ASTM G 48 standard test.[77] Test conditions are accelerated by using an aggressive test solution consisting of 6% $FeCl_3 + 1\%$ HCl. Test specimens are fitted with PTFE multiple crevice assembly (MCA) washers torqued to 0.28 N m and exposed to the test solution at various thermostatically controlled temperatures. The CCT of the test alloy is the temperature at which crevice attack ≥ 0.025 mm is detected after 72 h immersion. Critical pitting temperatures (CPT) also commonly reported in the literature refer to pitting corrosion observed in the absence of artificial crevices; any edge attack on the test specimens is discounted. For any given alloy, the CPT is always greater than the CCT. However, the latter is generally considered more meaningful for practical applications because it takes into account the unavoidable crevices that are either man-made (e.g., gaskets, O-rings, sleeves) or naturally occurring (e.g., barnacles, thermal scale, silt).

In addition to CCT, stainless steels are also frequently ranked for likely crevice corrosion behavior in seawater based on their pitting resistance number (PREN). The following is a typical empirical expression for PREN based on alloy (wt%) composition:

$$\mathrm{PREN} = \%\mathrm{Cr} + 3.3\%\mathrm{Mo} + A\%\mathrm{N} \qquad [7]$$

where the value of A is typically chosen to be 30 for austenitic stainless steels, and 16 for duplex stainless steels. **Table 9** shows the PREN and CCT values for a number of stainless steels.[78] It is apparent that as the PREN increases, the CCT increases. The following expression was proposed[79] for austenitic stainless steels:

$$\mathrm{CCT} = (2.7 \times \mathrm{PREN}) - 0.81 \qquad [8]$$

At first sight, this appears to be a very convenient method for ranking alloy performance in terms of expected localized corrosion resistance. However, for reliable materials selection, neither the PREN nor the CCT (as determined by the ASTM G 48 test method) provides a consistently accurate prediction of actual crevice corrosion resistance in seawater service. In other words, even alloys with high PREN and CCT values have been shown to crevice corrode, for example, in tests with severe crevice geometries.[75]

In crevice corrosion testing in seawater, crevice geometries can be created in a number of ways. For example, for flat sheet or plate stock, nonmetal or metal crevice-forming washers are commonly used as bolted assemblies; rubber O-rings and vinyl sleeves are used for tubular and round bar, and so on. Some of these devices and methods are described in ASTM standard G 78.[80] For irregular-shaped components or surfaces, for example, protruding weld beads, that do not readily permit the use of conventional crevice-formers, the use of paint coatings as crevice-formers has been proposed.[81] This methodology is based on the observation of crevice attack under coatings (e.g., marking inks, paint overspray, disbonded coatings, etc., on stainless steel surfaces) in actual practical applications.

Surface finish can also affect crevice corrosion resistance of stainless steels. The generally greater resistance of rough-ground surfaces to crevice attack, compared to smooth polished ones, is explained in terms of crevice tightness with respect to the crevice former. A certain degree of surface grinding and/or pickling is considered essential to remove the surface layer that is considered to have suffered some Cr depletion during manufacturing and/or fabrication (e.g., hot rolling, annealing, welding, etc.). The surface treatment is also intended to remove any extraneous particles (e.g., embedded iron) from tools, which can impair corrosion resistance; removal of embedded iron by immersion in acid solution (e.g., HNO_3) is often erroneously referred to as 'passivation.' Chromium carbide ($Cr_{23}C_7$) precipitation occurs at grain boundaries, typically in the 500–800 °C temperature range during welding and heat treatment of austenitic stainless steels. Corrosion resistance of areas adjacent to the carbide particles is lowered because of Cr depletion. However, despite this, no significant incidences of intergranular corrosion in ambient temperature seawater have been reported. On the other hand, precipitation of sigma phase (FeCr intermetallic), which can form in the temperature range 565–925 °C in Mo-containing austenitic steels, is considered more deleterious for seawater corrosion resistance.[82] Although their compositions are not exactly the same, cast stainless steels often exhibit lower resistance to localized corrosion than the corresponding wrought material. In the case of austenitic stainless steels, this is generally due to the residual ferrite phase in castings (necessary to counteract shrinkage during solidification). Welds represent 'miniature' castings, and hence their corrosion resistance can be lower than the parent material of similar nominal composition. Laboratory tests have shown that pickling of welds increased the critical pitting temperature of a 25-Cr duplex stainless steel by ~20 °C[83]; presumably, the reason for this is elimination of heat tint and surface Cr depletion. A 'soft' start up has been recommended in situations where pickling is not possible in piping systems; apparently the procedure consists of initial exposure to cold seawater for at least 2 days, followed by exposure to cold chlorinated seawater for at least 5 days, before turning on the heat exchangers.[76] This method may not be very practical in geographical areas where cold seawater is not readily available.

As stated earlier, the type of crevice geometry and its dimensions can play a critical role in the determining crevice corrosion resistance of stainless steels. Generally, crevice corrosion severity increases with decreasing crevice gap (tightness) and increasing crevice depth. This has been demonstrated by mathematical modeling[84] and by experimental evaluations.[85,86] The critical values of pH and chloride concentration of crevice solutions to initiate crevice attack have also been determined[84]; results for four different stainless steels are depicted in **Table 10**. In crevice corrosion testing, ideally, the actual crevice geometry (gap and depth) and crevice-formers (gaskets, washers, O-rings, etc.) intended for the service environment should be used. Lack of proper simulation could result in incorrect indication of corrosion behavior in service, for example, insufficiently tight and deep crevices could lead to a false prediction of corrosion resistance and vice versa.

Polluted seawater containing sulfides have not adversely affected the performance of stainless steels in seawater,[87,88] both at moderate (2.4 $m\ s^{-1}$) as well as high velocities[89] (up to 50 $m\ s^{-1}$). This observed corrosion resistance is based on the results of testing and experience in seawater, which either already contained sulfide or to which sulfide was deliberately added. Lean stainless steel grades can however, be subjected to microbially influenced corrosion (e.g., especially at welds) where the sulfide is generated biogenically as a byproduct, especially under quiescent conditions.

In the absence of solid particulate matter (e.g., entrained sand), stainless steels can generally tolerate seawater velocities in the order of 40 $m\ s^{-1}$ without any erosion–corrosion problems.[89] However, in service application such as pumps and valves, proper hydraulic design and operation are essential to preclude cavitation problems. Stainless steels are not immune to cavitation, but typically exhibit greater resistance than 'softer' materials such as carbon steels, copper-base alloys, and aluminum-based alloys.

In the passive condition, stainless steels are galvanically compatible with each other in seawater despite their somewhat different positions in the galvanic series. In the passive condition, stainless steels are not usually adversely affected by galvanic

Table 10 Critical crevice corrosion solution values

Alloy	*[Cl^-] (M)*	*pH*
430 SS	1.0	2.90
304 SS	2.5	2.10
316 SS	4.0	1.65
904L	4.0	1.25

Source: Oldfield, J.W., Sutton, W.H., 1980. Br. Corros. J. 15 (1), 31–34.

corrosion when coupled to more noble materials, for example, titanium, gold, graphite, etc. As stated earlier, when localized corrosion of stainless steel is observed at areas in intimate contact with such noble materials, there is a common tendency to attribute attack on the stainless steel to galvanic corrosion. Tests conducted with inert gasket materials, such as PTFE and graphite-impregnated gaskets have shown that attack on 300-series stainless steel flanges is just as severe as, or more so, with the PTFE gaskets compared to graphite-containing ones.[47] The attack on the stainless steel can be explained as crevice corrosion with both types of gasket. Conversely, it can be argued that if it was galvanic corrosion, graphite should produce attack on even those stainless steels that exhibit resistance to crevice attack with PTFE gaskets. It has been shown that high alloy stainless steels are adversely affected when coupled to graphite in chlorinated but not natural seawater.[90] But this is also the case when stainless steels with nonabsorbent inert gasket materials are subjected to chlorine levels >2 ppm.[91] It has been reported that crevice corrosion associated with synthetic fiber gasket materials which absorb water is less severe because of dilution of the crevice electrolyte.[92] This phenomenon has been used to advantage in the design of an electrochemical corrosion cell where crevice corrosion of a flat-stock test specimen is eliminated by flooding the specimen sealing gasket with distilled water.[93]

Crevice corrosion has been investigated electrochemically in a number of ways.[81] For example, in a remote crevice assembly, crevice formers are used to sandwich a small specimen (anode) which is then coupled to a separate, larger cathode specimen made of the same alloy as the anode. In an alternative compartmentalized cell design, the anode and cathode are exposed to two different solutions (anode – acidic, deaerated, high Cl^- solution; cathode – neutral, aerated solution), respectively. In both these designs, the crevice corrosion current associated with the couple is usually measured using a zero-resistance ammeter (ZRA). Although the anode and cathode members are made from single pieces of the test alloy to eliminate unwanted crevices and immersed connections, unfortunately localized attack is sometimes observed on one or both electrodes at the waterline. Such attack is usually associated with salting out due to evaporation of the test solutions.

Comparisons have been made between pitting corrosion of stainless steels and crevice attack. This stems from the similarity observed between chemistry (low pH, high Cl^-) of the electrolyte trapped in a pit and in a crevice. Pits can be regarded as microcrevices (e.g., initiating at sulfide, inclusions) associated with the microstructure, extraneous embedded particles (e.g., iron), under heat tints, 'peaks' folded over by mechanical processes such as coarse machining, grinding, and so on. **Table 11** shows that pitting corrosion of Type 316 stainless steel is reduced by more than an order of magnitude in 'deaerated' seawater at 105 °C, but not eliminated because 25 ppb O_2 is probably sufficient to initiate and sustain some attack. The degree of localized corrosion attack on susceptible stainless steels shows a decreasing trend with exposure depth in the ocean as the dissolved O_2 content decreases in the deeper water; however, this trend is general but not necessarily always one-to-one, indicating that other factors are probably implicated in the corrosion process.

In ambient temperature seawater, nonsensitized austenitic and ferritic stainless steels are considered resistant to stress corrosion cracking (SCC). SCC of Type 316 stainless steel was reported in the vapor zone above boiling seawater, but not on fully immersed specimens.[82] Since oxygen is usually essential for SCC, the likely explanation is that boiling eliminated dissolved O_2 from the seawater. Other data indicated that SCC of Type 316 stainless steel in hot seawater (126 °C) containing 600 ppb O_2 was mitigated when the O_2 level was reduced to 30 ppb.[94]

Martensitic and precipitation-hardening (PH) stainless steels are more prone to SCC. In deep-ocean water tests,[95] SCC of 15–7PH in the RH950 and RH1150 condition, and 17–7PH in the RH1050 condition, was reported. No correlation between SCC susceptibility and tensile strength was observed. These failures occurred at low O_2 levels, leading to the inference that hydrogen embrittlement may be the operative mechanism, for example, due to acidity generation associated with localized corrosion. Extrapolation of results of accelerated SCC tests in boiling NaCl and $MgCl_2$ solutions (e.g., per ASTM standard G 38) to seawater applications should be done very cautiously. Although temperatures >50 °C are often cited as necessary for SCC of stainless steels, experience indicates that failures can occur even at ambient temperatures where localized corrosion (e.g., crevice attack) generates low-pH conditions; of course, the material has to be in a susceptible condition, for example, sensitized, containing martensite, or containing high tensile stresses, and so on. Dynamic tests such as slow strain rate and crack growth rate are now strongly favored over static tests which may otherwise falsely indicate resistance, because the former expose the base metal by almost constantly deforming and cracking the passive film above certain strain rates. Another major attribute of the dynamic SCC tests is the much shorter testing time compared to the static tests.

The greater SCC resistance of cast stainless steels over wrought material is usually ascribed to residual ferrite phase in the former. Polluted or putrid seawater containing sulfides may increase the susceptibility to hydrogen embrittlement of martensitic and PH and stainless steels; this propensity is increased when the material is deliberately or inadvertently under cathodic protection. Duplex stainless steels may also be susceptible under the latter condition. If SCC propensity decreases above a certain

Table 11 Maximum pit depths on stainless steel in natural and deaerated seawater[94]

Alloy	*Seawater conditions*	*Exposure (days)*	*Max. pit depth (mm)*
316 SS	Aerated, natural, ambient temperature	486	2.4
316 SS	Deaerated, 105 °C, 25 ppb DO	547	0.12
304 SS	Deaerated, 105 °C, 25 ppb DO	547	0.60

threshold temperature, especially in sulfide environments, it is reasonable to infer that the cracking mechanism is hydrogen embrittlement since outward diffusion of atomic hydrogen is temperature dependent. On the other hand, cathodic polarization increases the susceptibility to hydrogen embrittlement.

SCC failure of Type 316 stainless steel in venting systems of MSF desalination plants has been attributed to bromine.[96] Chlorination of seawater for biofouling control converts the bromide ions present in the seawater to bromine, which dissolves to produce hypobromous and bromic acids. If ammonia is present, bromoamines are also produced. Acidification of the seawater downstream for scale control releases hydrogen bromide into the vapor, which can then attack the susceptible stainless steels such as Type 316 in the venting system:

$$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^- \qquad [9]$$

$$Br_2 + H_2O \rightarrow HBr + HOBr \qquad [10]$$

Cavitation susceptibility and ranking are often performed in laboratory tests in which the test specimen is vibrated ultrasonically in seawater by a magnetostrictive transducer. Cavitation resistance is based on mass loss per unit time and visual examination. Results for a number of alloys are discussed in the literature.[97–99] Such laboratory tests have shown decreased cavitation damage due to cathodic protection.[98]

7 Copper Alloys

Copper alloys rely on the formation of protective corrosion product films for corrosion control in marine environments. These films are sometimes described as 'passive.' In the authors' opinion, the term 'passive film' should be reserved for situations (materials and conditions) where the film is very thin (typically < 100 nm), optically transparent, extremely adherent, ennobles the potential of the metal appreciably, and not formed as a 'voluminous' deposit by the incorporation of species from the environment. For example, films on stainless steel, titanium, and aluminum would be considered as passive. The protective corrosion product films on copper alloys are much thicker and also quite complex; in clean seawater, copper hydroxychloride is often a major component.

In the splash and intertidal zones, 90/10 copper–nickel sheathing has been successfully used for corrosion control on offshore platforms. Unlike paint coatings, such sheathing requires little maintenance – which is extremely difficult in the splash zone as discussed earlier. Because of high resistance to macrofouling, copper–nickel has also been used for the construction of small boat hulls and as adhesive-backed foils on ferries and fireboats.[100] Macrofouling resistance is apparently reduced when the copper–nickel is galvanically coupled to a more anodic material such as steel, or if it is subjected to cathodic protection, *albeit* inadvertently. However, the macrofouling attachments are relatively easily removed compared to bare or coated steel.

Copper alloys are very desirable for seawater applications because of high resistance to biofouling. They have been widely used for heat exchanger tubing because of high heat transfer properties. However, they are relatively soft and hence subject to erosion–corrosion in seawater above certain velocities. The high turbulence in seawater pumps restricts the choice of copper alloys largely to nickel–aluminum–bronze. As a general rule of thumb critical velocities for small diameter heat exchanger tubing determined from laboratory testing and field experience are shown in **Table 12**.[101] These values are still widely used in design and operation of copper-alloy heat exchangers. It has been postulated that each copper-based alloy has a critical shear stress associated with it.[102] When this shear stress exceeds the adhesion strength of the protective corrosion product film, attack of the base metal ensues. Critical shear stresses, depicted in **Table 13**,[102] determined using fluid mechanics and evaluated by laboratory testing now support the view that as the piping diameter increases, higher critical velocities than those shown in **Table 12** can be used without increasing the risk of erosion–corrosion for the alloy in question.

Table 12 Rule of thumb maximum velocities for copper alloy heat exchanger tubing in seawater

Alloy	*Suggested max. design velocity* ($m\ s^{-1}$)[a]
Copper	0.9
S-bronze	0.9
Admiralty brass	1.5
Aluminum brass	2.4
90/10 CuNi	3.0
70/30 CuNi	3.7

[a] Velocities may be increased by 0.3–0.6 $m\ s^{-1}$ in deaerated brines encountered in heat recovery exchangers in desalination plants.

Source: LaQue, F.L., 1975. Marine Corrosion: Causes and Prevention. Wiley, p. 267.

Table 13 Critical velocities and shear stresses for copper alloys in seawater

Alloy	*UNS No.*	*Test temp (°C)*	*Critical velocity (m s^{-1})*	*Critical shear stress (N m^{-2})*
DHP Copper	C12200	17	1.3	9.6
As-inhibited Al brass	C68700	12	2.2	19.2
90/10 CuNi	C70600	27	4.5	43.1
70/30 CuNi	C71500	12	4.1	47.9
Cr-modified 90/10 CuNi	C72200	27	12.0	296.9

Source: Efird, K.D., 1977. Corrosion 33 (1), 3–8.

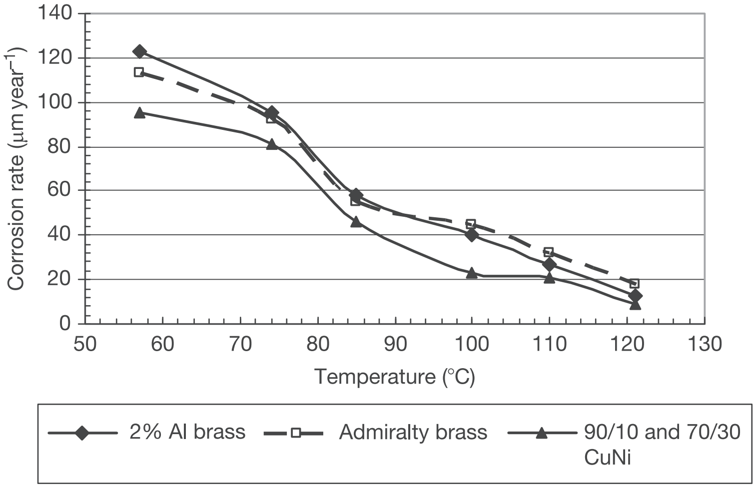

Figure 20 Corrosion rate versus temperature for three copper-base alloys in seawater; DO 40–600 ppb, pH 6.2–7.8, 156 days. Reproduced from Mattson, M.E., Fuller, R.M., 1965. A study of materials of construction in distillation plants. Joint Report by Office of Saline Water and the International Nickel Company. Research report No. 163.

One of the most important corrodents toward copper alloys in seawater service is sulfide. Sulfide can be entrained in the seawater (e.g., from bottom sediment or polluted harbors) or generated *in situ* by sulfate-reducing bacteria, as discussed previously. The latter mechanism is very common when initially clean seawater putrifies after a few days of stagnation, for example, in heat exchangers, pumps, and piping systems during outages or shutdowns. The role of sulfides has been extensively investigated.[103–109] The evidence suggests that protective corrosion product films allowed to form on copper alloys in clean seawater for several months can resist short subsequent exposure to sulfides. Conversely, exposure to sulfide conditions from the outset interferes with the formation of desirable protective films. In such cases, sulfides have a deleterious effect on pitting corrosion and erosion–corrosion resistance. Thus, commissioning of copper alloy equipment such as heat exchangers using clean seawater for several months initially appears to be critical. However, this task should not be underestimated as access to large quantities of clean seawater at coastal areas is difficult at best. Experience indicates that once incorporated in the corrosion product film, sulfides are very difficult to remove completely and problems continue.

A classical laboratory study[103] of the effects of sulfide on 90/10 and 70/30 CuNi in seawater disclosed the following: corrosion rate increased as the sulfide content was increased from 7 to 250 ppb; attack was localized at lower sulfide concentrations, and more general at higher ones; once attack initiated, there was minimal seawater velocity effect over the 0.5–5.3 m s^{-1} range; attack continued even in clean seawater after initial exposure to 1000 ppb sulfide for 1–5 days, or 10 ppb sulfide for 30 days. Addition of 0.2 ppm ferrous ions which is sometimes used to mitigate erosion–corrosion was found to reduce but not eliminate sulfide-related corrosion of the CuNi alloys.[104]

Protective corrosion product films reduce the corrosion rate markedly in clean seawater with time.[110] In the ambient temperature range, the corrosion rate increases with increasing temperature. However, at high temperatures, such as in MSF desalination plants, the corrosion rate decreases with increasing temperature[111] in the 54–121 °C temperature range as illustrated in **Figure 20**. This may be due to the lower oxygen levels and precipitation of scales due to inverse solubility. However, at elevated temperature, corrosion rate increases with increasing dissolved O_2 even in the ppb range as depicted in **Figure 21**.[112] Decrease in corrosion rate has also been reported for deep waters where oxygen levels were lower.[113]

It should be emphasized that copper alloys with >70% copper are resistant to biofouling compared, for example, to carbon steel, stainless steels, aluminum, titanium, but not completely immune. Macrofouling resistance of copper alloys is usually

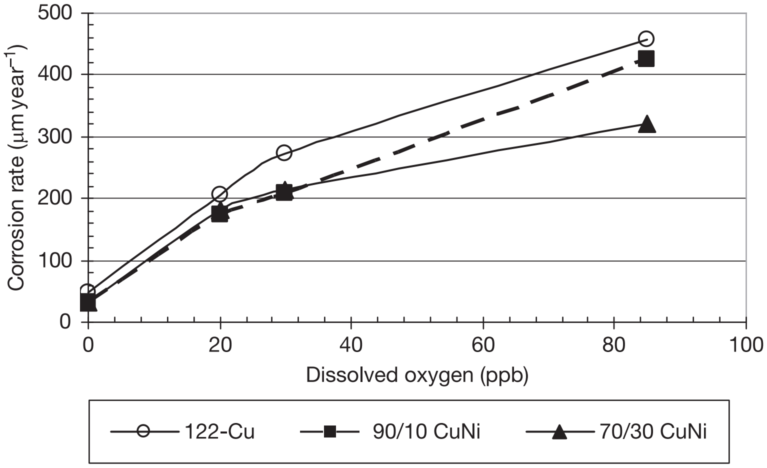

Figure 21 Corrosion rate versus DO in seawater for three copper-base alloys at 107 °C in a once-through desalination system; seawater flow rate ~2 m s^{-1}, pH 7.2–7.5, CO_2 <10 ppm, 15–30 days. Reproduced from Schreiber, C., Osborn, O., Coley, F.H., 1968. Mater. Perform. 7 (10), 20–25; Houston, TX: NACE International.

explained in terms of either continuous, but slow release of copper ions, or presence of copper-rich corrosion products on the metal surface – both of which are purportedly 'toxic' toward macroorganisms.[114,115] The situation is confounded by the fact that while increasing alloy content lowers the copper ion release (and hence likelihood of fouling), it also affects the nature of corrosion products. It is not known why, for instance, barnacles attach at some but not most areas of such copper alloys. It has been suggested that attack on the metal under macrofouling occurs after the organisms die.[114] Fouling is more likely in quiescent than flowing seawater. A minimum velocity of 1–2 m s^{-1} was proposed to mitigate macrofouling.[116] Higher velocities to prevent macrofouling may increase the risk of erosion–corrosion.

Pitting corrosion of copper alloys can occur under deposits due to differential aeration, and is often exacerbated by sulfides. Another factor that can increase pitting susceptibility is the presence of residual carbon films on the copper surface.[117] The carbon is believed to derive from oxidation of lubricating oil residues left behind from manufacturing (e.g., tube drawing) and subsequent annealing heat treatment. It has been hypothesized that the carbon film acts as a cathode and promotes localized corrosion of the base metal at exposed areas in the film. Ideally, the carbon film should be removed after manufacturing. Detection of the carbon film is not always easy. Since the carbon film is insoluble, one method involves placing a drop of nitric acid on the test surface and visually observing any flakes of thin gray/black matter float up to the top. The films are often even more difficult to detect after corrosion failures have occurred. Potential measurement has been proposed as a detection method in such cases.[118]

A number of copper-based alloys tested concurrently in an ancillary seawater condenser operated for over 8 months revealed that Admiralty brass (70/30 Cu/Zn) suffered from impingement corrosion at the inlet and outlet ends as well as adjacent to deposits.[119] Iron and manganese additions to copper–nickel alloys have been shown to enhance erosion–corrosion resistance.[120] However, some other tests indicated iron additions to be deleterious,[121] especially >1%.[122] This was probably related to the distribution of iron in the microstructure. Uniform distribution improves corrosion resistance, while segregation increases susceptibility to localized attack. A simple magnetic permeability test is used to detect iron segregation.[123] Small Cr additions to copper–nickel alloys improves erosion–corrosion resistance; however, localized corrosion resistance in quiescent conditions may be impaired by Cr segregation. Any restrictions on flow caused by macrofouling (e.g., shells) or pebbles lodged in the tube can cause severe local turbulence, and hence erosion–corrosion or impingement attack at associated (usually immediately downstream) areas. Experience shows that less protective scales are formed as the seawater pH is lowered, for example, by pollutants or dissolved CO_2. This is not unexpected since corrosion products and mineral scales are more difficult to form at lower pH values. Absence of protective scales at lower pH will increase erosion–corrosion tendency.

The role of gas bubbles in promoting erosion–corrosion has been discussed.[122,124] In rotating spindle and disc tests, air bubbles in the seawater were stated to be beneficial toward CuNi alloys.[122,125] However, results of impingement attack in flowing loop tests indicated that both air and nitrogen bubbles were harmful.[122] Since collapsing bubbles are thought to be the cause of cavitation damage, copper alloys, being considerably softer are more likely to be affected by this form of damage compared to, say, stainless steels, nickel-based alloys, and titanium.

Investigations on the effect of entrained sand particles on erosion–corrosion resistance of aluminum brass indicated the following: erosion–corrosion increased with increasing sand content (>300 ppm) and particle size[126]; cathodic protection with or without ferrous iron injection was beneficial when the sand particles were 50 μm in size, but not when they were 250 μm[127]; less attack in polluted seawater containing sand was attributed to protective sulfide films.

Galvanic corrosion of copper alloys is problematic in seawater when they are coupled to cathodic materials such as stainless steels, nickel-based alloys, titanium, and graphite, especially for small anode/cathode area ratios. In chlorinated seawater, a reduction in galvanic corrosion of copper alloys coupled to stainless steels has been observed[46,128] and ascribed to reduced biofilm activity, which affects cathodic polarization kinetics, and hence galvanic corrosion rate.

Copper alloys are cathodic to many materials, and can thus cause unacceptable galvanic corrosion of anodic materials such as carbon steel, cast iron, aluminum, and zinc – particularly for large cathode/anode area ratios. Gray cast irons are initially anodic to copper; however, graphitic corrosion of gray cast iron can eventually expose enough graphite at the exposed surface so as to reverse the galvanic couple and accelerate corrosion of the copper alloy. In principle, the free corrosion potentials of copper-based alloys in seawater are fairly close to one another, and thus one might expect them to be galvanically quite compatible. In principle, this is the case. However, regardless of potentials, an adverse cathode/anode area ratio between two copper alloys can produce unacceptable galvanic attack on the more anodic material. Increasing flow rate and temperature typically accelerates galvanic corrosion of copper alloys. Presence of sulfides (especially 50 ppb) in seawater was found to promote galvanic attack on Naval M-bronze and nickel aluminum bronze fittings coupled to 90/10 or 70/30 CuNi piping.[128] The effect of sulfides appears to be greater at lower seawater temperatures.[129]

Electrically isolated copper components in a system can undergo self-corrosion in seawater environments. The release of even imperceptible amounts of copper ions can pose an indirect problem for anodic materials that come in contact with them. For instance, copper ions can plate out on aluminum, steel, and zinc, leading to deposition or cementation corrosion. In other words, copper ions plate out on the anodic material (as a cathodic reaction) and cause corrosion of the base metal. However, once the ions have plated out, galvanic corrosion (usually as pitting) of the base metal ensues even if the original source of the copper ions is removed. Copper-colored areas surrounding pits in the anodic material are usually a telltale sign of this phenomenon. For example, it has been observed in aluminum fuel tanks on pleasure boats, particularly those operating in seawater environments. Copper corrosion products enter the tank from water condensate in copper piping and/or copper alloy valves in the fuel system.

Copper-based alloys are quite resistant to SCC in clean seawater. SCC of brasses is generally associated with ammonia, amines, or nitrates that are either entrained as pollutants or can form *in situ* under decaying biofouling attachments. Copper–nickel alloys are considered resistant to such environments. Stress relief of cast nickel aluminum bronze alloys is recommended to minimize the risk of SCC failure in critical seawater service applications.

Dealloying is quite common in many copper-base alloys. It is often observed in marine artifacts submerged for long periods in seawater. Reddish coloration due to copper deposition is a telltale sign of dealloying. Alpha brasses (e.g., 85/15 Cu/Zn) can be inhibited against dealloying with Sn or As additions. Unfortunately, such additions are usually not considered to be as effective in beta brasses (e.g., 60/40 Cu/Zn). Unlike in brasses, dealloying in copper–nickels is usually superficial. In nickel aluminum bronzes, dealloying involves the selective dissolution of aluminum from the alloy. Proper heat treatment to minimize the beta phase alleviates this problem.

Copper-base alloys can suffer from another form of localized attack known as metal-ion concentration cell corrosion. Attack usually occurs at the mouth of a crevice, in contrast to localized corrosion that occurs inside the crevice, for example, in susceptible stainless steels and nickel-based alloys.

8 Nickel-Based Alloys

The primary nickel-based materials used in seawater include nickel–copper alloys (e.g., the 70/30 NiCu alloy 400, or its high strength version, alloy K-500) and Ni–Cr–Mo–Fe alloys (e.g., alloy 625, C-276, alloy 59, alloy 686, etc.). As with stainless steels, these nickel-based alloys are also believed to depend on the formation of passive films for corrosion resistance.

Because of its established record of good performance in the splash zone, alloy 400 has been successfully used as sheathing for protection of carbon steel in the splash zone.[48] Unlike the copper–nickel alloys described in the previous section, the NiCu and other nickel-based alloys are not resistant to macrofouling in the tidal and immersion zones. In fact, nickel-base alloys tend to behave more like stainless steels. General corrosion rates in clean seawater are low to negligible, and when attack occurs, it is usually as pitting and/or crevice corrosion; corrosion initiation is more likely in quiescent or low flow seawater.

For unalloyed nickel and nickel–copper alloys (e.g., alloys 400 and K-500), pitting in low flow seawater is common. Unlike with susceptible stainless steels, the pits tend to be open, hemispherical, and do not grow significantly in depth, for instance, after ~1 year in seawater.[130] Alloying nickel with copper appreciably improves the pitting resistance. Seawater temperature has been shown to dramatically affect pitting corrosion behavior of alloy 400; maximum pit depth increased in the 18 to 30 °C range, but then decreased markedly at 50 °C.[131] A similar trend was discussed earlier for crevice corrosion of stainless steels and attributed to 'degraded' biofilms at 50 °C. The pitting potential of alloy 400 determined electrochemically decreased with temperature.

Corrosion rate of alloy 400 has been shown to increase as the sulfide concentration in seawater increased from 0 to 5 ppm.[128] Ni–Cr alloys were not affected by sulfides in ambient temperature seawater.

Alloying additions of ~20% Cr and ~8% Mo to nickel-based alloys (e.g., in alloy 625) impart significant resistance to pitting and crevice corrosion in seawater. As with stainless steels, addition of ~20% Cr alone does not ameliorate localized attack.

Table 14 Localized corrosion resistance of some Ni-based alloys after ~18 months' exposure in quiescent ambient-temperature seawater

Alloy	*Max depth of crevice attack (μm)*
Unalloyed Ni	2.06
400	432
K-500	51
600	457
825	229
625	0
C 276	0

Source: Lennox Jr., T. J., 1982. In Corrosion/82. Houston, TX: NACE International. Paper No. 64.

Table 15 Corrosion resistance of Ni-based alloys at ambient-temperature high velocity seawater

Alloy	*Seawater velocity ($m\ s^{-1}$)*	*Corrosion rate ($\mu m\ year^{-1}$)*
C	39	50
825	43	75
718	41	50
X-750	41	50
600	41	75
400	43	100
K-500	41	100

Source: Boyd, W.K., Fink, F.W., 1978. Corrosion of Metals in Marine Environments, Battelle Columbus Labs, OH, p. 103. Report No. MCIC-78–37.
Moller, G.E., 1977. Soc. Pet. Eng. J. 17 (2), 101–110.

Table 14 provides a comparison of relative corrosion resistance of several nickel-based alloys immersed in quiescent seawater for ~18 months.[132] Apparently, from a corrosion resistance viewpoint, cobalt in Ni-based alloys behaves like nickel. Alloy C-276 was found to be highly-resistant to localized and general corrosion in seawater up to 288 °C[72]; it also exhibited crevice corrosion resistance at 107 °C in deaerated seawater (DO 28 ppb).

Crevice corrosion of alloy 400 is not generally as severe as, say, for 300-series stainless steels. This can be explained by the fact that hydrolysis of Ni and Cu ions from alloy 400 does not produce a highly acidic and aggressive crevice solution compared to Cr and Mo ions from susceptible stainless steels.

The erosion–corrosion behavior of nickel-based alloys is quite similar to that of stainless steels, that is, notably superior to that of copper–nickel alloys. Thus, nickel alloys can tolerate high velocities, turbulence, and impingement which makes them candidates for seawater pumps, valves, piping systems, and so on. Test data summarized in **Table 15** [133,134] show that, like stainless steels, most nickel-based alloys exhibit acceptably low erosion–corrosion rates up to ~40 m s^{-1}. With the exception of the NiCu alloys, their cavitation resistance is also expected to be similar to that of stainless steels.

Nickel–copper alloys are often selected for seawater service because their higher Ni content provides enhanced resistance to chloride stress corrosion cracking (Cl^- SCC) compared to stainless steels. Deep ocean tests of 2 years duration confirmed the SCC resistance of Alloy 825 and Alloy C.[135] Alloys G-3, 625, and C-276 were resistant to SCC in U-bend tests of several hundred hours duration in synthetic seawater.[82]

Because of their austenitic microstructure, nickel-based alloys are generally resistant to hydrogen embrittlement in the annealed condition. However, risk of hydrogen embrittlement (HE) increases as the strength level increases due to cold work or heat treatment. At similar strength levels, increasing aging temperature is apparently favorable in lowering HE risk. HE of 70/30 NiCu alloy K-500 bolts has been reported for an offshore platform application under cathodic protection conditions.[136] Susceptibility to HE was traced to high hardness and subsequent cathodic protection. Annealing after rolling the threads to alleviate high hardness before precipitation hardening was recommended to mitigate the problem.

Accelerated attack would be predicted for active materials coupled to Ni-based alloys because of the noble positions of the latter in the galvanic series. However, the successful use of alloy 400 sheathing on carbon steel in the splash and tidal zones, even in the absence of cathodic protection, suggests galvanic compatibility which has been attributed to easy cathodic polarization of the nickel alloy.[137] It should be emphasized that this would not be the case if the steel/nickel-alloy area ratio was small. Pitting and crevice corrosion of NiCu alloy trim in pumps and valves is mitigated by cast iron bodies. Although nickel-based alloys are anodic to titanium, they are galvanically compatible because the increased corrosion rates are still very small from a practical viewpoint.[138]

9 Titanium Alloys

Titanium alloys are among the most corrosion resistant materials in seawater service. The general corrosion rate in seawater is extremely low, for example, 0.8 nm year^{-1},[139] not surprisingly, it is often reported as 'nil.' Titanium alloys are immune to pitting and crevice corrosion in all marine environments at ambient temperatures. Thus, no localized corrosion is encountered in the atmospheric, splash, tidal, immersion, or mud zones. Titanium is not resistant to biofouling. Therefore, macrofouling attachments similar to those on carbon steel, stainless steel, and aluminum alloys are also commonly observed on titanium alloys. However, unlike the other alloys, there is no localized corrosion of titanium under the biofouling or any silt deposits. No corrosion allowance is necessary for titanium because of its very high corrosion resistance in ambient-temperature seawater. Thus, titanium is widely used for heat exchanger applications, especially retubing in shell-and-tube heat exchangers. Grade-1 titanium is the premier material of choice for plate-and-frame heat exchangers because of high corrosion resistance and easy fabrication properties. However, because of extensive demand, there is currently a worldwide shortage of grade-1 titanium. Other materials such as Ni–Cr–Mo alloys and superaustenitic stainless steels are being evaluated as alternatives.

Crevice corrosion of titanium in seawater has been reported in tight crevices at temperatures $>70\ ^\circ\text{C}$.[140,141] The crevice electrolyte was also found to be acidic, suggesting that a similar oxygen-depletion and metal-ion hydrolysis mechanism (as discussed earlier for stainless steels) may be operative. However, the actual mechanism is probably more complex since crevice corrosion resistance is increased by small additions of Pd, Mo, or Ni to the titanium. Iron, carbon steel or low-alloy steel particles embedded accidentally into a titanium surface can lead to localized attack at temperatures $>80\ ^\circ\text{C}$. This has been proposed as a special case of crevice corrosion,[141] that is, occlusion by titanium metal smears or laps may create micro crevices that allow the generation of acidic conditions, preventing repassivation and localized attack, and possibly hydrogen adsorption. Thus, the mechanism is probably more complex than the presence of just micro crevices, since the attack has not apparently been observed if austenitic stainless steel, nickel, or copper particles are embedded in the titanium surface. Evidently, the Pd-containing grades exhibit significant resistance to attack associated with smeared iron particles.

Titanium is quite noble in the galvanic series for seawater. It can sometimes exhibit potentials anodic to graphite, platinum, zirconium, Ni–Cr–Mo–Fe alloy C, and NiCu alloy 400, and even some 300-series stainless steels in the passive condition. However, titanium is galvanically compatible with these materials. Any attack on the titanium is more likely to be crevice corrosion in tight crevices at temperatures $>70\ ^\circ\text{C}$, as discussed earlier. In fact, despite being slightly more noble than titanium, attack is much more likely on the 300-series stainless steels, alloy 400, and even alloy C, at crevices regardless of galvanic coupling to titanium. Corrosion of the more active materials such as copper-base alloys, carbon steels, cast irons, aluminum alloys, zinc, and magnesium will be accelerated if galvanically coupled to titanium. The degree of attack acceleration will depend on the relative anode/cathode area ratio, system geometry, and cathodic reduction reaction kinetics on the titanium, which are influenced by seawater temperature, velocity, fouling, and so on. **Figure 12** shows that in seawater, titanium is more easily polarized than copper due to its higher overvoltage for oxygen reduction. Consequently, galvanic attack on carbon steel coupled to titanium is less severe compared to corrosion of steel coupled to copper, in each case for the same anode/cathode area ratio. The potential difference between titanium and steel is nearly double that between steel and copper – affirming that potential difference is not reliable for predicting galvanic attack on the anodic material. The free corrosion potential of titanium in aerated and deaerated seawater is fairly steady in the ~ 20–$135\ ^\circ\text{C}$ temperature range. However, as temperature increases further, the potential shifts in the electronegative direction by ~ 500 mV at $\sim 200\ ^\circ\text{C}$. Potentials of other alloys also exhibit electronegative shifts.[142]

Unfortunately, titanium is susceptible to hydriding when its potential shifts more electronegative than -0.7 V (SCE) at elevated temperature.[143] This can happen when titanium is cathodically polarized by coupling to anodic materials such as steel, aluminum, or zinc, or by impressed current cathodic protection. In ambient temperature seawater applications, a potential shift to no more than -1 V (SCE) has been suggested.[143] Hydrogen is generated by a two-step process: (1) discharge of H^+ to atomic H by electron consumption and (2) H recombination to generate molecular H_2 gas bubbles. If excessive hydrogen is generated, there is an increasing uptake of atomic hydrogen, which diffuses into the titanium, reacts with the α phase, and precipitates as brittle, acicular, titanium hydride (TiH_2) needles at grain boundaries. Hydriding is exacerbated at temperatures $>80\ ^\circ\text{C}$. About 500–600 ppm, hydrogen can cause excessive hydriding which embrittles the titanium, causing potentially significant reduction in ductility and fracture toughness. Anodizing reduces hydrogen uptake. The beta titanium alloys do not hydride easily because of considerably higher solubility of hydrogen (several 1000 ppm) in the beta phase.

It was prematurely concluded from early tests that unwelded titanium was highly resistant to stress corrosion cracking (SCC) in seawater[144] even when stressed to 75% of the yield strength. However, those tests used smooth test specimens. Subsequent tests disclosed that while alloy composition and heat treatment influenced SCC resistance, presence of notches simulating stress risers was essential. Environmental variables did not greatly affect the SCC behavior, this is not surprising because of the very high resistance of titanium to corrosion in seawater. Generally, all the α alloys (e.g., Ti–8Al–1Mo–1 V and Ti–7Al–3Nb–2Sn), and near α alloys that contain small amounts of β phase stabilizers such as Al, Zr, Sn, and O (e.g., Ti–6Al–5Zr–0.5Mo–0.2Si and Ti–8Al–1V–1Mo) are susceptible to SCC in seawater. SCC resistance is markedly reduced when Al $>5\%$ and oxygen $>0.4\%$ in α alloys. For the $\alpha+\beta$ alloys, such as grade 5, oxygen concentration $<0.1\%$ is necessary to preclude SCC; commercial alloys contain typically 0.15% oxygen. In $\alpha+\beta$ alloys, cracking occurs primarily in the α phase. Contradictory behavior has been indicated for the effect of β stabilizers on SCC resistance in seawater. In some cases, V and Nb additions were detrimental, in others, $>2\%$V was advantageous when Al in the 7–8% range was present in the alloy. In $\alpha+\beta$ alloys, Si and Mn were apparently deleterious.[145]

The SCC resistance of titanium alloys in seawater is greatly affected by heat treatment. Generally, small grain size is attained by aging just below the β transus (above the β transus, α or $\alpha+\beta$ phases transform to β) which enhances SCC resistance. For the susceptible alloys, the SCC behavior is also highly influenced by stress concentration; for example, there is a significant decrease in fracture stress in seawater at a notch radius of 125 μm compared to 250 μm. In slow strain rate tests in simulated seawater, SCC behavior of a number of titanium alloys was found to be highly influenced by the strain rate[146]; typically, they were most susceptible at strain rates of $\sim 7\times10^{-5}\ \mathrm{s}^{-1}$. Other laboratory tests revealed that crack velocity decreased linearly with cathodic polarization of titanium alloys over the -400 to -900 mV (SCE) potential range[147]; the opposite behavior would be expected if there is sufficient uptake of hydrogen, for example, due to extended precharging time and/or polarization to more negative potentials in test. Crack velocity was found to increase with temperature, exhibiting Arrhenius behavior.[148] In tests performed in surface seawater and at depths of ~ 800 and ~ 2000 m, only butt-welded, nonstress relieved, Ti–13V–11Cr–3Al alloy stressed to 75% of yield strength exhibited SCC.[149]

The passive oxide film, its ability to reheal, and high inherent hardness of titanium confer high resistance to erosion–corrosion and cavitation in seawater. Velocities as high as $\sim 37\ \mathrm{m\ s}^{-1}$ can be tolerated in clean seawater. Minimum velocities of the order of $>2\ \mathrm{m\ s}^{-1}$ are necessary to prevent attachment of macrofouling in seawater heat exchanger tubing and piping. Provided they are galvanically compatible, titanium inserts can be used in the inlet ends of heat exchanger tubing experiencing erosion–corrosion at those locations. Ordinary silt in seawater does not lower erosion–corrosion appreciably. Higher-strength titanium alloys, such as grade 5 (Ti–6Al–4 V), can be substituted for enhanced resistance if large, angular, abrasive particles produce erosion of the commercial purity (CP) grades.

The anodic breakdown potential of titanium in ambient temperature seawater is ~ 10 V. This allows titanium to be used as a substrate for platinum in impressed current anodes. If higher breakdown voltages are necessary in specific applications, niobium is substituted for titanium.

10 Aluminum Alloys

The low density of aluminum alloys ($\sim 2700\ \mathrm{kg\ m}^{-3}$) makes them attractive for marine engineering applications such as seacraft. However, the corrosion resistance is quite variable depending on alloy composition and heat treatment. **Table 16** summarizes a commonly used designation system for aluminum alloys. For some applications, ‘Alclad’ products are specified. Alclad refers to a composite wrought (e.g., sheet) material which has an aluminum-alloy core with a metallurgically bonded thin ‘skin’ of either pure aluminum or another aluminum alloy on its surface for corrosion protection, for example, high-purity (more corrosion resistant) aluminum over alloy 2024, or alloy 7072 applied over alloy 6061 as sacrificial coating.

Aluminum relies on the formation of a passive aluminum oxide (Al_2O_3) film for corrosion resistance. However, the film properties are affected by alloy composition, metallurgical condition, and environmental factors, and widely ranging corrosion behavior is exhibited in seawater. In seawater immersion, the major corrosion concerns with aluminum alloys are galvanic

Table 16 Aluminum wrought alloy designations

Series	*UNS No.*	*Major alloying element(s)*	*Heat treatable*
1xxx	A91xxx	None	No
2xxx	A92xxx	Cu	Yes
3xxx	A93xxx	Mn	No
4xxx	A94xxx	Si	No
5xxx	A95xxx	Mg	No
6xxx	A96xxx	Mg, Si	Yes
7xxx	A97xxx	Zn, Mg	Yes
8xxx	A98xxx	Ti, Li	No
Temper (heat treatment) designations			
O		Annealed	
H (e.g., H1, H2, etc.)		Strain-hardened only	
T (e.g., T4, T6, etc.)		Solution heat treated; aged	

Table 17 Corrosion rates of 5xxx aluminum alloys in seawater

Alloy	*Exposure duration (months)*	*Exposure depth (m)*	*Corrosion rate (μm year^{-1})*
5052-O	35	1700	78
5052-H22	35	1700	10
5052-H34	13	770	5
5454-H32	6.5	760	18
5454	13	770	15
5456-H321	13	770	28
5456-H32	13	770	15
5456-H343	6.5	770	10
5085	13	770	13
5085-H113	13	770	15
5086	13	770	20
5086-H32	13	770	10
5086-H34	13	770	15
5086-H112	6	2	28

Source: Reinhart, F.M., 1976. Corrosion of Metals and Alloys in the Deep Ocean. Port Hueneme, CA: Civil Engineering Laboratory, pp. 204–209. Technical Report No. R-834.

corrosion when electrically coupled to cathodic materials, crevice corrosion and pitting under macrofouling and silt deposits, exfoliation, stress corrosion cracking, and metal-ion (especially Cu) deposition corrosion. The high strength 2xxx series and the 7xxx series aluminum alloys are widely used in aerospace applications. However, the alloying additions of Cu (in 2xxx) and Zn (in 7xxx) also make them more susceptible to corrosion in seawater.

Unalloyed aluminum has very low general corrosion rate in the splash zone because DO diffuses easily through the thin seawater layer to sustain passivity associated with the Al_2O_3 film. However, pure aluminum is considered too 'soft' for many splash-zone applications. The stronger 5xxx and 6xxx alloys are more suitable. In the tidal zone, aluminum alloys are subject to biofouling and localized attack (pitting and/or crevice corrosion) underneath macrofouling attachments. Long-term exposure tests[133] showed that the average penetration for alloys 1100 and 6061 in the tidal zone after 16 years exposure was very low, $<15\ \mu m$; however, the maximum pit depths were ~ 1–1.5 mm. Under immersion conditions, the average penetration increased but was still very low from a practical viewpoint, $<30\ \mu m$; however, maximum pit depths were in the range ~ 1–2 mm.

The effect of alloying additions is complex. For example, depending on specific alloy, $<0.2\%$ Cu and ~ 0.5–1.2% Mn were beneficial, but 0.4–0.8% Fe was detrimental toward corrosion resistance of aluminum in synthetic seawater.[150] Heat treatment affects the distribution and size of the intermetallic particles that influence mechanical properties by precipitation hardening. The desired mechanical properties of 5xxx alloys cannot be attained by conventional heat treatment alone; instead, they are strain hardened by mechanical working and, depending on alloy, may be subjected to some annealing treatment. The selected data in **Table 17** show that the general corrosion rate of alloy 5052 in the H22 temper was an order of magnitude lower than in the annealed 'O' condition; the H32 temper reduced the corrosion rates of alloys 5086 and 5456 by half, but the H113 temper did not significantly affect the corrosion rate of alloy 5085.[151]

The increase in corrosion rate of aluminum alloys with seawater depth is often attributed to lower oxygen content of seawater, which presumably prevents rehealing of the aluminum oxide film. Lower seawater pH (and hence less likelihood of calcareous deposit formation) in deep water has been proposed as an alternative explanation.[152] However, this rationalization appears to be contradicted by data[153] from artificial seawater tests indicating that corrosion rate of Al–3Mg alloy decreased with decreasing pH in the 6–9 range. The mechanism is probably much more complex since alloy composition appears to affect corrosion behavior even at the same seawater depth. For example, maximum depth of pitting was $<50\ \mu m$ for alloys 5086-H34 and 5083-H113 exposed for 1 year at a depth of ~ 250 m, whereas the maximum pit depths for alloys 2219-T81 and 6061-T6 at the same depth were almost 2 mm.

Tests on alloys 3004, Alclad 3004, Aclad 3003, and 5052 exhibited less mass loss, but more pitting in cold seawater ($\sim 10\ ^\circ C$); in warm seawater ($\sim 27\ ^\circ C$), overall mass loss was greater but corrosion was uniform with no discernible pitting.[154] It was shown electrochemically that the pitting potential was not significantly altered by temperature,[152] however, ennoblement of the free corrosion potential indicated greater propensity to pitting in colder seawater. Data for Al–3Mg alloy indicate that corrosion rate increased steadily with temperature in the ~ 20 to $\sim 70\ ^\circ C$ range, it then decreased somewhat with a minimum at $\sim 90\ ^\circ C$, and finally increased rapidly above boiling to $\sim 125\ ^\circ C$.[153] Increased corrosion at the lower temperatures was attributed to DO. A significant decrease in pitting corrosion of alloy 5052 was reported for hot, flowing seawater environment associated with desalination when the temperature increased from 82 to 108 °C.[155]

Alloy composition and heat treatment appear to affect pitting corrosion behavior as illustrated by the data in **Table 18** which show maximum depths of attack on selected aluminum alloy plate specimens after 10 years exposure in seawater. Electrochemical studies have indicated that alloying additions of Zn lower the pitting potential of aluminum; Cu additions raise it, while Mg

Table 18 Maximum depths of attack on some aluminum alloy plate specimens after 10 years immersion in natural seawater at ambient temperature

Alloy	*Maximum pit depth (mm)*
1100-H14	1.02
3003-H14	0.53
6061-T4	0.36
6061-T6	2.41
7072	1.42 (perforated)
7075-T6	1.68

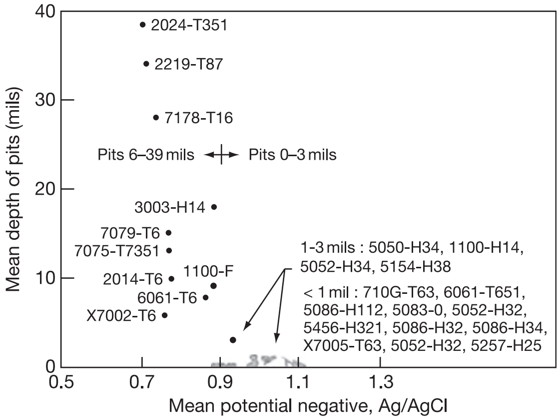

Figure 22 Depth of pitting on Al alloys versus free corrosion potential in seawater. Reproduced from Schumaher, M. (Ed.), 1979. Seawater Corrosion Handbook. Park Ridge, NJ: Noyes Data Corporation, p. 61.

additions exhibit a minor effect. However, heat treatment to attain maximum hardness lowered the pitting potential of Al–Cu alloys; this is probably related to grain boundary depletion of Cu associated with precipitation of $CuAl_2$ intermetallics particles at grain boundaries. **Figure 22** shows an interesting relationship between pitting propensity and free corrosion potential for a number of aluminum alloys.[156] There is no general agreement on the growth rate of pits with time. Some data suggest that pit depth decreases with time; other data imply opposite behavior. Despite wide variations in pitting corrosion behavior, aluminum alloys are highly susceptible to crevice corrosion, and therefore require protection, especially when tight crevices are present. It is not known with certainty whether the crevice corrosion mechanism in aluminum alloys is similar to that in stainless steels because it has not been studied as extensively.

Aluminum alloys have been reported to be generally resistant to seawater up to velocities of $\sim 6\ \mathrm{m\ s^{-1}}$.[157,158] However, critical velocities vary with alloy composition, heat treatment, and exposure time[159,160]; and attack morphology can change from pitting to increased general metal loss as velocity increases. Aluminum alloys being relatively soft are more susceptible to cavitation damage under turbulent flow conditions than, for example, stainless steels, nickel-based alloys, and titanium alloys. This means that aluminum alloys can be used, for example, in the construction of seacraft hulls operating at moderately high velocities, but not for seawater pump applications.

Aluminum alloys have high thermal conductivities, which should make them very attractive for heat transfer surfaces, for example, in seawater heat exchanger applications. However, several factors limit their widespread utility. For example, aluminum alloys are highly susceptible to galvanic corrosion when coupled to components made of cathodic materials such as copper-based alloys, stainless steels, nickel-based alloys, and titanium alloys. Even if they are electrically isolated, only tens of ppb levels of copper ions (e.g., generated by self-corrosion of copper-based alloys upstream) are sufficient to cause severe corrosion by the cementation mechanism[161] (also known as deposition corrosion). Aluminum alloys are prone to biofouling such that sufficient velocities would be required to prevent crevice corrosion under macrofouling attachments.

An extensive study was performed in simulated seawater on galvanic corrosion rates determined from current density measurements for a number of aluminum alloys coupled to dissimilar materials as well as between the aluminum alloys themselves.[162] The data showed that all of the aluminum alloys tested were incompatible with Cu, Ag, and Ni. In addition, alloys 1100, 6061, and 7075 were not compatible with all the stainless steels, nickel alloy 718, low alloy steel 4130, and Ti–6Al–4 V. However, surprisingly, alloy 2024 and 2219 were compatible with these materials (low alloy 4130 excepted). The aluminum alloys were compatible with each other except alloy 1100 with alloy 7075. In another test, alloy 5086-H32 incurred accelerated attack when coupled to carbon steel, 90/10 CuNi, Type 304 stainless steel, and 60/40 brass.[163] The degree of galvanic attack is influenced by the anode/cathode area ratio. Laboratory tests[164] have confirmed that increasing seawater velocity will increase galvanic attack on aluminum alloys in seawater because the most common cathodic reaction is oxygen reduction, which is under diffusion control.

Pure Al is generally considered resistant to stress corrosion cracking (SCC) in seawater. Aluminum 5xxx alloys are prone to intergranular SCC failure when the Mg addition is $>5\%$ which results in supersaturation and allows precipitation of a continuous Mg_2Al_3 intermetallic phase at the grain boundaries; this phase is anodic to the matrix. Restricting the Mg addition to $<4\%$ results in discontinuous Mg_2Al_3 phase and SCC resistance. This was confirmed by immersion tests in seawater.[165] In Mg additions $>5\%$, addition of small amounts of Bi, Cr, Zr, B, and Be have been found to enhance SCC resistance. Alloy 6061 in the fully aged T6 temper is resistant to SCC in seawater.[165]

Several of the highest strength 7xxx aluminum alloys were found to be susceptible to SCC in natural seawater,[166] especially in the T6 temper to attain maximum strength.

Lithium additions lower the density of the aluminum alloy but increase strength and elastic modulus. However, fracture toughness and SCC resistance are lowered.

Alloy 6061 is susceptible to SCC in the T4 temper if slow quench follows high heat treat temperature. However, the T6 temper (fully aged) imparts high SCC resistance.

Exfoliation is a form of corrosion that occurs along grain boundaries in rolled aluminum alloy sheet and plate products. Corrosion often initiates at exposed grain boundaries (end-grain attack) or at pit sites that have exposed the elongated grain microstructure to the environment.The voluminous corrosion products of aluminum, $Al(OH)_3$, introduce internal stresses that are sufficiently to cause exfoliation, that is, lifting off of material in layers that comprise corrosion products and unaffected metal. Exfoliation resistance is derived from the absence of second phase precipitates, especially at grain boundaries, and where the free corrosion potentials of the precipitates and matrix are closely matched. The 5xxx aluminum alloys are resistant to exfoliation in seawater at Mg additions $<3\%$. 6xxx series are resistant to intergranular corrosion (IGC) except when excess Si is present. Al alloys 5456-H116 and-H117 have been used for boat hull plates to resist IGC in H321 temper.

As-quenched T3 or T-4 tempers, or naturally aged 2xxx alloys are prone to SCC and exfoliation, but only slightly to IGC, whereas 7xxx alloys are more susceptible to IGC. Overaging to T6 and T8 tempers improves SCC and exfoliation resistance but not IGC. As for 2xxx alloys, rapid quenching and overaging increases resistance significantly, for example, 7075-T63 and T-73, 7178-T76.

Cathodic protection can mitigate SCC of aluminum alloys when they are polarized to a potential in the -1.2 to -1.4 V (SCE) range. However, overprotection, for example, with Mg anodes, and especially quiescent conditions raise the surface pH significantly as OH^- ions accumulate at the aluminum alloy surface. The high-pH conditions can result in 'cathodic corrosion' of the aluminum alloy by the formation of an aluminate complex:

$$Al + 2OH^- \rightarrow AlO_2^- + H_2 \qquad [11]$$

Seawater flowing at moderate velocities can prevent build-up of OH^-, and hence reduce risk of cathodic corrosion. Even in quiescent conditions, the cathodic corrosion issue for aluminum alloys can be almost entirely eliminated by the use of zinc anodes for cathodic protection.

Aluminum is an active metal in the galvanic series. Therefore, in principle, it could be considered for cathodic protection of carbon steel and other engineering alloys. However, the application is not straightforward. As stated earlier, a passive Al_2O_3 film usually forms on aluminum and its structural alloys. This is contrary to the requirements of a sacrificial anode material which must corrode efficiently to provide protective current for cathodic protection. Thus aluminum is alloyed with small amounts of Zn or Sn and trace levels of In or Sn (although Hg was used previously) to activate the aluminum surface. Aluminum alloys find widespread usage as sacrificial anodes in seawater, for example, on offshore platforms and pipelines because of their significant weight advantage and high current capacity ($A\,h\,kg^{-1}$) compared to zinc. The development and performance of aluminum anodes have been reviewed extensively in the literature.

11 Magnesium

Magnesium and its alloys are not normally utilized in seawater because they are highly reactive. Reduction of DO is not normally the primary cathodic reaction, but rather the reduction of water to evolve hydrogen.

This reaction occurs particularly easily on cathodic impurities in Mg such as Fe, Cu, Cd, Zn, Ni, and so on. Being anodic and very reactive, corrosion of Mg is greatly accelerated by galvanic coupling to most other engineering materials, for example, carbon steel, stainless steels, nickel-based alloys, copper-based alloys, titanium alloys, and so on. In fact, Mg sacrificial anodes are widely used for cathodic protection of steel used in soil environments. Use of Mg for cathodic protection in seawater environments is rare because of the risk of overprotection of steel, which can cause hydrogen embrittlement in high strength steels, cathodic blistering and disbondment of coatings, and cathodic corrosion of amphoteric materials such as aluminum alloys, and high rate of self corrosion of the magnesium.

Mg alloys have been used in a very limited capacity for deep-sea diving suits – the main attraction being very light weight due to the low density of Mg. However, the Mg has to be properly coated to prevent direct contact with seawater which would otherwise result in severe corrosion. This could be especially catastrophic at any holidays in the coating if the Mg was inadvertently coupled to a cathodic material.

The very high corrosion rate of Mg can be used to advantage in special applications, for example, 'time release' links on oceanographic instruments deployed in deep ocean environments.

12 Zinc

Although zinc is also an active metal in the galvanic series, it is much less reactive than magnesium. While the self corrosion of zinc is surprisingly low, its other major limitations are similar, that is, susceptibility to galvanic attack when coupled to steel, stainless steels, copper alloys, and so on. Historically, zinc is the most common sacrificial material used for cathodic protection in seawater.

13 Nonmetallic Materials

Nonmetallic materials do not generally corrode in the same manner as metals and alloys in seawater, that is, by thinning. Instead, they may suffer marine borer attack which is usually not very deep, except in wood. In addition, nonmetallics may undergo swelling and some reduction in mechanical strength – which is usually less for synthetic materials than those derived from nature (e.g., to make ropes). Deterioration is generally greater in warm seawater and close to the seabed. Other hazards are fish bites, for example, on cables. Results of long-term exposures of polymeric materials have been reviewed.[167,168] Nonmetallic materials are often reinforced to increase strength, for example, glass fibers in epoxy resins, carbon fibers in epoxies and aluminum, steel in concrete, and so on. Reinforcements can affect the performance of the composite material in seawater, for instance, carbon fibers can accelerate galvanic corrosion of aluminum and corrosion of steel reinforcement can lead to spalling of concrete. Rubber linings and reinforced polymer (e.g., flake glass polyester) coatings applied to metal substrates can provide corrosion protection. However, elastomers exhibit reduction in elongation with prolonged exposures; silicone–rubber and ester-based polyurethanes deteriorate more extensively. Thus, meticulous attention to selection, application, inspection, and maintenance is essential for successful usage. While they may provide adequate corrosion protection, the major limitations of polymeric materials include elevated service temperatures, high pressure containment, and fatigue life.

For seawater service, concrete with sulfate resistance (Type V cement) must be specified. The steel reinforcement requires corrosion protection for long-term performance, for example, by cathodic protection. Ceramics are generally considered resistant to seawater.

14 Corrosion Protection Methods

In principle, most of the methods used for corrosion control in other aqueous environments are applicable to seawater. However, the major factors contributing to the corrosivity of seawater that must be taken into consideration include high chloride and sulfate content, presence of microorganisms, biofouling, and putrefaction.

Carbon steel corrodes in aerated seawater at rates that require either a corrosion allowance or other means of corrosion control if a long service life is required. Corrosion allowance requires careful monitoring to avoid unexpected failures. It is probably most useful for applications where some areas of localized perforation caused by seawater can be tolerated without loss or mixing of fluids, or reduction in structural (load-bearing) properties, for example, nontubular structural support members.

Coatings are the most common method of corrosion control. Apart from suitability for seawater service, the single most important requirement for a successful coating is proper surface preparation and application conditions – which are often best achieved under shop conditions. Once a coating system is applied, even under initially optimal conditions, repairing or replacing it in service can be extremely challenging. For applications such as the underwater areas of ship hulls, it is fairly easy to perform coating inspections, repairs, and replacements during periodic dry docking. In the case of fixed structures, such as offshore platforms and pipelines, similar access to the underwater areas is almost impossible. Building cofferdams around the structure and evacuating them to carry out repairs and replacements can only be done more economically in very shallow waters. Although some coatings that can be applied underwater (e.g., by divers) are available, they are fraught with problems, for example, surfaces cannot usually be adequately cleaned and prepared, and coating application and inspection are very difficult. Hence, such coatings are typically only considered for emergency situations. Antifouling coatings are utilized on ships for controlling macrofouling. Presently, most antifouling coatings contain either copper or cuprous oxide as the antifouling agent. Other coatings based on low surface energy are also available to minimize adhesion of macrofouling, but they are more expensive. Both types of coatings are consumed with time and lose their effectiveness, and thus need replacement periodically.

As mentioned previously, it is possible to protect simple structural steel shapes by sheathing. For example, splash-zone areas on offshore platforms have been successfully protected by alloy 400 (nickel–copper) or 90/10 CuNi sheathing. Hot risers are not usually protected by sheathing because of periodic visual inspection requirements that would require removal of the sheathing. Metallurgically cladding steel with a more corrosion resistant alloy can also be used but is again applicable to only relatively simple geometries such as piping.

The most widely used method for corrosion control of steel structures immersed in seawater is cathodic protection using sacrificial zinc or aluminum anodes. Cathodic protection is only effective below the waterline, regardless of tide level. Cathodic protection and coatings complement each other if they can be used together for corrosion control. The coating reduces the area of metal requiring protection; conversely, cathodic protection can extend the coating life. However, it is essential to select a coating that is compatible with cathodic protection to obviate cathodic disbondment (blistering) of the coating. The anode material must meet tight alloy composition and performance requirements before it is specified. Sacrificial anodes generally require no maintenance, except replacement when consumed. However, it must be recognized that replacement of anodes on stationary structures is difficult and very costly; thus, in such cases, the original anodes are typically designed to last the life of the structure (e.g., 30 years). Impressed current cathodic protection systems serve the same function but, contrary to popular belief, require more attention, for example, in monitoring proper operation of rectifiers and reference electrodes, especially for systems with automatic control, stray current effects, diver safety concerns, and so on. Impressed current anodes based on platinized niobium are now preferred in seawater over platinized titanium because of the much higher breakdown voltage of niobium (~70 V) compared to titanium (~9 V). Cathodic protection of structures and components in seawater is extensively covered in the published literature.

Calcareous deposits (discussed previously), formed in seawater on cathodically protected metal surfaces are essential for polarization of the structure, and to achieve significant reduction in current demand by the structure. Although used extensively for carbon steels, cathodic protection can also be used to mitigate corrosion of nonferrous materials in seawater, for example, for pitting and crevice corrosion of stainless steels. In fact, carbon steel can be used as sacrificial anode material. Cathodic protection can also be effective for controlling galvanic corrosion between dissimilar materials, for example, between waterbox, tube sheet, and tubes; and erosion–corrosion of copper alloys, for example, inlet-end impingement in heat exchangers.

Cathodic protection for corrosion control in the interior of pipes has been investigated but is not commonly used for a variety of reasons. The biggest problem is limited 'throwing power' of the protective current. Thus, depending on pipe size, an anode may be required, say, every few meters for protecting bare steel. Continuous anodes along the length of the pipe for internal cathodic protection have also been investigated but present many limitations including economics.

Modification of the seawater by deoxygenation is an effective method of corrosion control. As discussed previously, it is used in a number of applications, for example, MSF desalination and seawater injection during secondary recovery. For steels, while corrosion rate decreases with oxygen content, it increases markedly at elevated temperatures even when only a few hundred parts per billion oxygen is present. Thus, effective control and monitoring of oxygen is essential for this method of corrosion control, especially at high temperatures. Deaeration has not been found to be harmful for passive materials such as stainless steels that often rely on oxygen for film healing.

Conflicting requirements often preclude use of a single material in most engineering applications. Since dissimilar materials are often unavoidable, the issue of galvanic corrosion must be addressed. In principle, electrical isolation between anode and cathode members can be effected by using nonconductive (insulating) hardware to mitigate galvanic corrosion. However, in many applications, this is difficult to achieve because alternative electrical grounding paths exist, for example, hangers or pedestal supports in piping systems. In many systems, however, even if electrical isolation is possible, it is not permitted for personnel safety reasons, for example, electrical safety codes may preclude galvanic isolation in systems where ground fault currents would otherwise pose potential electrical shock hazards. In design, a small cathode/anode area ratio is usually selected to minimize galvanic corrosion. Coating either the cathode or both the cathode and anode can be a practical means of controlling galvanic corrosion. The anode alone should not be coated since inevitable holidays and flaws in the coating can severely accelerate corrosion attack at those locations because of the resulting very adverse anode/cathode area ratio. However, it should be recognized that coatings for galvanic corrosion control have limitations where they are difficult to apply and maintain, and where they can incur damage rather easily, for example, in pumps.

Mitigation of galvanic corrosion in piping systems at dissimilar-metal flanged-joints, without electrical isolation, has been addressed in a number of ways. Since the galvanic corrosion damage of the anodic material is restricted over a relatively short distance that is either known from experience or can be determined by mathematical modeling, one approach is to insert a heavier-wall waster spool between the original anode and cathode. The length of the spool piece is a function of the pipe diameter and polarization characteristics of the cathode.[169] Consumption of the waster spool piece can be monitored, for example, by ultrasonic thickness gauging from the outside, so that it can be replaced in a timely manner. A novel technique known as the 'bi-electrode' method[170,171] has been proposed to control galvanic corrosion. Two ring or sleeve electrodes with inert metal surfaces are inserted in the piping system on either side of the joint. The sleeves which are electrically isolated from the piping system are polarized with respect to each other by an external DC power supply, such that the electrical field created by current flow annuls the galvanic current. Since the galvanic current can vary with operating conditions such as flow, temperature, oxygen content, and so on, the externally applied counter current between the bielectrodes has to adjust automatically – a problem that has been found to be challenging to date.

For many components, coatings and/or cathodic protection are not practical methods of corrosion control, for example, pumps, valves, entire heat exchanger tubing in shell-and-tube heat exchangers, plates in plate-and-frame heat exchangers, internal piping, and so on. In such cases, corrosion resistant materials must be selected. The selection is based on practical experience and test data. For example, as discussed earlier, Type 304 and 316 stainless steels are unsuitable materials for seawater service because of extreme susceptibility to crevice corrosion in aerated seawater; in other words, they should not be used for immersion service in seawater without protection (e.g., cathodic protection) if crevices are present. The use of a resistor-controlled cathodic protection system has been proposed for controlling internal corrosion in chlorinated stainless steel piping systems.[172,173]

Unfortunately, selection of more highly alloyed grades such as Type 317 stainless steel or alloy 825 that contain greater amounts of Cr and Mo does not bestow sufficient resistance to crevice corrosion. Crevice corrosion initiation time is usually longer in cold seawater. Conversely, it is known that localized corrosion susceptibility increases with increasing temperature. Critical pitting and critical crevice corrosion temperature data are used to provide guidelines for the upper limits of alloys. For example, it is generally recommended that superaustenitic 20Cr–25Ni–6Mo stainless steels should not be subjected to seawater temperatures $> \sim 35$ °C for prolonged periods. Pitting resistance equivalent numbers (PREN) based on alloy composition (primarily Cr, Mo, and N) have been advocated as indicators of localized corrosion resistance of stainless steels and nickel-based alloys in seawater and other chloride environments. However, crevice corrosion resistance does not depend just on alloy content; it is also affected by crevice geometry, tightness, depth, crevice-forming materials, their deformability, and surface finish of both the crevice formers and the alloy in question.[174] Thus, although many materials, such as Ni–Cr–Mo–Fe alloy C-276, have very high resistance to crevice corrosion in seawater, they are by no means completely immune under all crevice conditions. This is also the case with titanium, which is very resistant to localized attack in seawater at ambient temperatures, but is susceptible to crevice corrosion at > 70 °C. Titanium alloys containing noble metals additions, such as palladium in grade 7, are more resistant to crevice corrosion.

Copper–nickel alloys have been successfully used for heat exchanger piping, waterbox and sheathing applications in clean seawater. In the freely corroding condition, they are resistant to macrofouling but not entirely immune. Their major limitations are high susceptibility to accelerated corrosion by sulfides, for example, in polluted seawater and bottom silt; or generated *in situ* as a result of putrefaction of stagnant seawater by sulfate reducing bacteria. Avoiding contact with polluted seawater is difficult in certain situations, for example, when shipboard piping and heat exchangers are commissioned in harbors. Guidelines based on practical experience suggest that the risk of sulfide production and consequent initiation of corrosion of copper–nickel alloys increases when they are exposed to stagnant seawater in closed systems for more than ~ 2 days. Thus, it is imperative that such conditions be avoided by draining the system, flushing with fresh water, and drying, if possible. Alternatively, the water can be treated with suitable biocides that are compatible with the alloy. Nickel aluminum bronze pumps have been used successfully in unpolluted seawater. This is not a good choice of material for auxiliary pumps because of the risk of seawater putrefaction during protracted standby periods and hence sulfide attack. However, heat treatment is necessary to preclude dealloying, especially in the heat-affected zones associated with welds, and the consequent increased risk of fatigue cracking. Such areas are often beyond the reach of cathodic protection from bare steel piping that might be beneficial in other situations where the current ‘throwing power’ is more effective.

Other factors that need to be considered in the selection of copper-base alloys include sensitivity to erosion–corrosion at high flow rates and galvanic corrosion when coupled to stainless steels, titanium, and Ni–Cr–Mo alloys. For instance, copper–nickel heat exchanger tubes that have suffered from sulfide and/or erosion–corrosion attack are often retubed with titanium. This results in unacceptable galvanic corrosion of the copper–nickel tube sheet. This situation is usually alleviated by the application of cathodic protection which must be controlled and monitored carefully to preclude hydriding of the titanium tubes that can be caused by overprotection. Tube support plate spacing also has to be addressed to preclude vibration of the low-modulus, thin-walled titanium tubes, and subsequent mechanical fatigue failure.

Chlorination is widely used for controlling biofilms and macrofouling; the latter interferes with seawater flow. Both biofouling and macrofouling can initiate corrosion of engineering materials such as many stainless steels, nickel–copper alloys, and even some copper-based alloys. At low levels, ~ 0.5 ppm residual, chlorine does not accelerate corrosion of these materials or carbon steel significantly. However, as the chlorine concentration increases to ~ 1–2 ppm, risk of general corrosion on the active metals and localized corrosion on certain passive metals increases. Reduction of galvanic corrosion of certain materials, for example, copper-alloys coupled to stainless steels and nickel alloys, has been observed especially in laboratory tests and explained on the basis of biofilm suppression and attendant reduction reaction kinetics on the cathode. As the chlorine content increases to ~ 5 ppm or more, corrosion propensity of many stainless steels and nickel–copper alloys increases noticeably. Titanium is unaffected by even very high levels of chlorine in seawater – in fact, titanium electrodes are commonly used in the electrolytic cells to generate chlorine from seawater.

15 Test Methods

Test methods for assessing materials performance in seawater are extensively described in the literature and standards. In principle, most of these test methods are not applicable exclusively to seawater. However, it is important to recognize the important differences between natural seawater that contains micro and macroorganisms that can influence corrosion behavior of materials, and synthetic seawater that does not contain representative species which mimic biological effects. The equipment used for testing in seawater must also be corrosion resistant to prevent test interruptions or confounding of results by extraneous corrosion products introduced into the system.

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