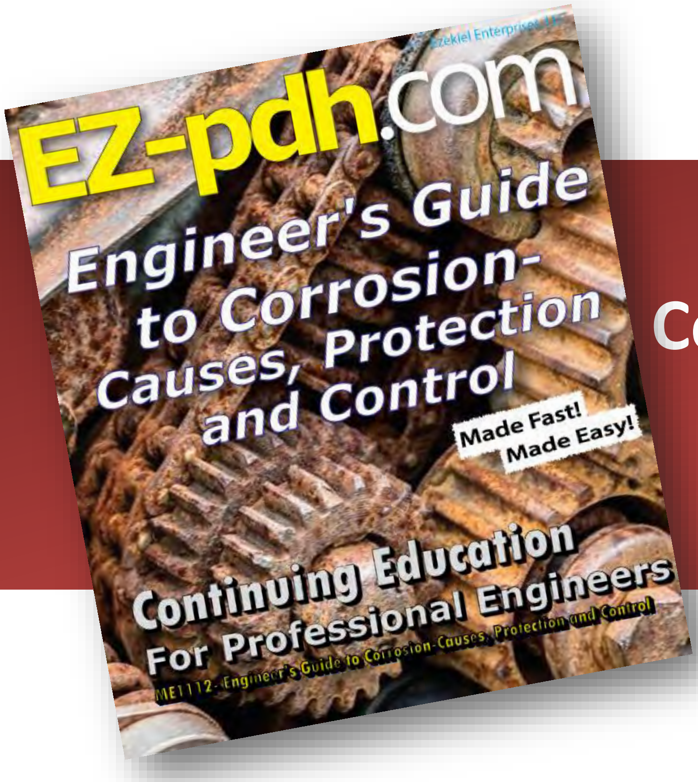

Engineer's Guide to Corrosion-Causes, Protection and Control

Eight (8) Continuing Education Hours
Course #ME1112

Approved Continuing Education for Licensed Professional Engineers

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Course Description:

The Engineer's Guide to Corrosion-Causes, Protection and Control course satisfies eight (8) hours of professional development.

The course is designed as a distance learning course that overviews corrosion in metals from its causes and effects into protection and control.

Objectives:

The primary objective of this course is to enable the student to understand corrosion on a variety of metals and methods to mitigate and control corrosion over the life of a material.

Grading:

Students must achieve a minimum score of 70% on the online quiz to pass this course. The quiz may be taken as many times as necessary to successful pass and complete the course.

A copy of the quiz questions are attached to last pages of this document.

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Engineer's Guide to Corrosion-Causes, Protection and Control

1.0 Environments and Their Affects on Corrosion Processes

The environment plays a major role in the selection of materials for corrosion resistance. Environmental factors that may influence corrosion include the environment's composition, pH level, humidity, wind or water currents, and temperature. These factors exist in the following types of environments, atmospheric, fresh water, saltwater, and soil, which will be discussed in this section. Additional micro-environments, such as specific acid susceptibilities of metals and microorganisms will be covered.

1.1 Atmospheric Environments

Atmospheric corrosion can vary widely depending on contaminants present, humidity and rainfall, wind and temperature. Extensive atmospheric testing programs have been conducted to compute corrosion rates of metals and to characterize metals' susceptibilities to various forms of corrosion. A typical atmospheric testing rack is shown in Figure 1. Such studies have lead to the broad categorization of environments into rural, urban, industrial, marine, and combinations of them. A general characterization of the four main types is listed in Table 1.

Deviations of corrosion rates within the four categories have lead to a further subcategorization based upon weather and climate. These additional factors influencing corrosion are temperature, humidity and rainfall. The relative corrosion rates for these environments are found in Table 1.

Figure 1 Atmospheric Corrosion Test Rack[2]

Table 1 Types of Atmospheric Environments[6]

Atmosphere Type	Description
Rural	▪ generally the least corrosive ▪ does not contain any significant amounts of pollutants ▪ principal corrodants are oxygen and moisture content
Urban	▪ similar to rural but with sulfur oxides (SO_X) and nitrous oxides (NO_x) from vehicle and domestic fuel emissions.
Industrial	▪ pollutants of sulfur dioxide, chlorides, phosphates, and nitrates exist from heavy industrial processing facilities ▪ special cases include contaminants of hydrogen sulfide, hydrogen chloride, and chlorine which are highly corrosive to most metals.
Marine	▪ generally high corrosivity ▪ characterized by chloride particles ▪ deicing salts used in cold weather regions produce an environment similar to marine

Table 2 General Corrosion Rates for Different Atmospheric Environments[3]

Rate of Corrosion	Type of Environment		
High	Tropical	Industrial	Marine
Moderate	Temperate	Suburban	
Low	Arctic	Rural	Inland

1.1.1 Atmospheric Contaminants

The primary sources of atmospheric contaminants come from chlorides in marine locations, and industrial and automobile pollutants. These contaminants deposit onto metal surfaces where they react primarily with oxygen, water, and free electrons producing metal compounds which have varying degrees of solubility; producing varying increased corrosion rates over non-corrosive environments.

The presence of chloride salts in the atmosphere significantly increased the corrosion rates of most metals. In the case of ferrous metals, chloride anions combine with ferrous cations to produce iron chloride. Iron chloride is more soluble than the ferrous hydroxide produced in a benign environment, leading to an increased corrosion rate. Other metals such as copper and zinc produce metal chlorides which are less soluble than ferrous chlorides. These metals therefore experience increased corrosion rates, but not to the extent of ferrous metals. It is notable that deicing salts used on roadways in winter months produce corrosivity in those environments similar to marine atmospheric environments.

Sulfur dioxide (SO_2) and nitrous oxides (NO_x) are found in industrial and urban environments from the burning of fossil fuels. Sulfur dioxide deposited on metal surfaces will react with oxygen and free electrons from the metal surface, producing sulfate ions, as expressed in

Equation 1. The sulfate ions lead to the formation of metal sulfates, which in turn react with water to complete the corrosion process, Equation 2.

$$SO_2 + O_2 + 2e^- \longrightarrow SO_4^{2-} \qquad \text{Equation 1}$$

$$FeSO_4 + 2H_2O \longrightarrow FeOOH + SO_4^{2-} + 3H^+ + e^- \qquad \text{Equation 2}$$

As seen in Equation 2, sulfate ions are again produced in the case of ferrous metals, producing a self-contained corrosion process once sulfur dioxide is present. This process may not occur as readily with other metals nor are most of the metal sulfates produced as soluble as iron sulfate. The presence of nitrous oxides may also increase corrosion rates of metals in a like manner, although they do not deposit on metals as readily as sulfur dioxide.

There are a few additional atmospheric contaminants that are less abundant or may be found in special industrial environments. Hydrogen sulfide is extremely corrosive to most metals. This compound is readily found in oil-refining and petroleum industries. Hydrogen chloride and chlorine gas have been found to produce higher corrosion rates than chloride salt environments. Ammonia, sulfur trioxide, and smoke particles will also increase atmospheric corrosion of most metals. The typical concentrations of these major contaminants are found in Table 3.

Table 3 Typical Concentrations of Several Atmospheric Contaminants[3]

Contaminant	**Region**	**Season**	**Typical Concentration (μg/m^3)**
Sulfur Dioxide (SO_2)	Industrial	Winter	350
		Summer	100
	Rural	Winter	100
		Summer	40
Sulfur Trioxide (SO_3)	-	-	Approximately 1% of the SO_2 content
Hydrogen Sulfide (H_2S)	Industrial	Spring	1.5-90
	Urban	Spring	0.5-1.7
	Rural	Spring	0.15-0.45
Ammonia (NH_3)	Industrial	-	4.8
	Rural	-	2.1
Chloride (Cl^-, Air Sampled)	Industrial inland	Winter	8.2
		Summer	2.7
	Rural Coastal	Annual (Avg.)	5.4
Chloride (Cl^-, Rainfall Sampled)	Industrial Inland	Winter	7.9
		Summer	2.7
	Rural Coastal	Winter	57 mg/l
		Summer	18 mg/l
Smoke Particles	Industrial	Winter	250
		Summer	100
	Rural	Winter	60
		Summer	15

1.1.2 Humidity and Rainfall

Humidity is also a major factor in determining the corrosion rate of metals, as moisture provides the electrolyte, which is required for corrosion reactions to take place. In general, the corrosion rate increases as humidity increases. The critical level of relative humidity in order for serious corrosion to occur in the absence of other electrolytes is usually taken to be 60%.[3] This critical level of relative humidity may vary depending on the impurities present in the atmosphere. Rainfall can increase or decrease corrosion processes. In areas where stagnant water may accumulate, a localized corrosion cell will most likely be the result. However, rain may also wash corrosive deposits off from metal surfaces, decreasing corrosivity.

1.1.3 Wind

The wind plays a role in the direction and distance atmospheric contaminants are dispersed. The corrosivity of atmospheric environments and therefore general corrosion rates of metals, are related to their distance and proximity to coastal waters and industrial plants.

1.1.4 Temperature

Temperature can have a significant effect on the corrosion of metals, with increased rates of corrosion as temperature is increased. Temperature may also affect the form of attack that the corrosion takes on; for example, changing the temperature may change the corrosion mechanism from uniform to pitting. It can also evaporate condensed moisture on metallic surfaces leaving behind corrosive contaminants. High temperatures can produce a form of corrosion where gas becomes the electrolyte as opposed to a liquid medium.

11.5 Atmospheric Corrosivity Algorithms

There has been some corrosion algorithms developed to compute corrosivity values for given environmental conditions. A couple methods are described here which include the Pacer Lime Program sponsored by the USAF, and ISO Standard 9223. These methods however, use average values to compute their corrosivity indices and only provide a general characterization of atmospheric corrosivity for various environments.

An atmospheric corrosivity severity classification system was developed by Summit and Fink under the Pacer Lime Program to provide management information for the maintenance of aircraft [4] Measurements of environmental conditions were made at numerous USAF bases to compute a corrosivity algorithm. Environmental conditions considered as part of the algorithm are distance to coastal waters, SO_2 content, total suspended particles, humidity, and rainfall. A severity index was created and used to schedule the frequency of various preventive maintenance tasks on aircraft. The algorithm developed to schedule the frequency of washing aircraft, is shown in Figure 2.

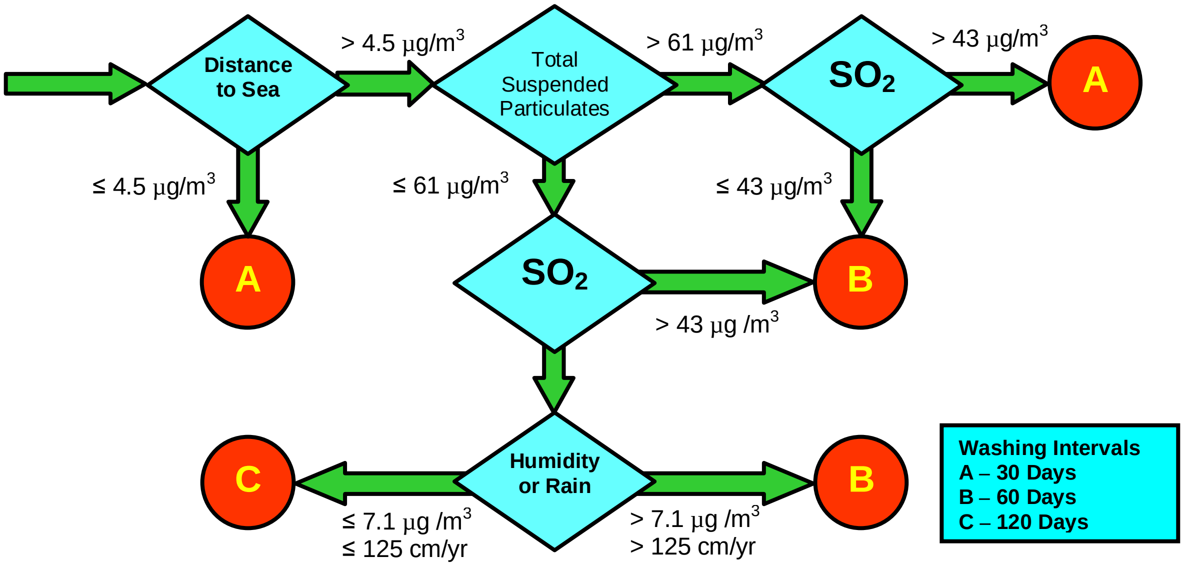


Figure 2 Corrosion Severity Algorithm for Planning an Aircraft Washing Schedule[6]

The ISO 9223 Standard uses the time of wetness and the deposition rates of sulfur dioxide and chlorides to compute an atmospheric corrosivity index.[6] The time of wetness is in units of hours per year, and consists of the time when the relative humidity is >80% and the temperature is >0ºC. The three conditions are divided into five ranges of values used to produce five corrosion categories represented in Table 4.

Table 4 ISO 9223 Corrosion Categories/Rates after One Year Exposure[6]

Corrosion Category	**Steel (g/m^2-yr)**	**Copper (g/m^2-yr)**	**Aluminum (g/m^2-yr)**	**Zinc (g/m^2-yr)**
C_1	≤ 10	≤ 0.9	negligible	≤ 0.7
C_2	11 – 200	0.9 – 5	≤ 0.6	0.7 – 5
C_3	210 – 400	5 – 12	0.6 – 2	5 – 15
C_4	401 – 650	12 – 25	2 – 5	15 – 30
C_5	651 - 1500	25 - 50	5 - 10	30 - 60

1.1.6 Managing Atmospheric Corrosion

General methods to minimize the effects of atmospheric corrosion include the following:

- Proper selection of material for the type of environment and corrosive contaminants present.
- Proper component/system design to limit contaminants and water build-up.
- Use organic and/or metallic coatings and sealants wherever feasible.
- Vapor phase corrosion inhibitors may be used in microenvironments, such as the inside of boilers.

1.2 Water Environments

Factors contributing to the corrosivity of water environments include the composition, pH level, temperature, water velocity, and biological organisms. Water environments are divided into natural or fresh water, and seawater type environments. Fresh waters are used extensively in cooling systems, boiler feed waters, processing of materials and products, washing and drinking waters.

1.2.1 Water Compositions

The composition of water can be quite different, dependent upon the materials and contaminants picked up from the atmosphere during rainfall, the surrounding soil, and man-made pollutants dumped or spilled into waterways. The compounds most responsible for general water corrosivity are dissolved gases and salts. There may additionally be dissolved compounds present in specific areas from pollutants.

The primary dissolved gases affecting corrosion in waters are oxygen and sulfurous gases. Oxygen is by far the biggest concern, as it directly relates to higher corrosion rates for many metals. The concentration of oxygen is greatest at water surfaces and in the presence of algae. Sulfur dioxide and hydrogen sulfide significantly increase corrosivity and are found in waters as a result of pollutants and/or microorganisms. Sulfate reducing bacteria converts sulfates to sulfides. Nitrogen, like in atmospheric environments, is less abundant, but will increase corrosion rates of metals where present.

The ions from dissolved salts mostly responsible for increased water corrosivity are chlorides and sulfates. These ions react with metal cations to produce corrosion reactions. A run down of the most common constituents and ions present in seawater are listed in Table 5. Cations present may reduce corrosion by reacting with available anions. The measure of calcium and magnesium solid precipitates determines the hardness of water. Table 6 represents the general characteristics of some natural waters. A measure of the water's electrical resistivity gives a general indication of corrosivity.

Table 5 Typical Contents and Ions Found in Seawater[5]

Constituent	**Content (g/kg of seawater)**	**Cations**	**Percent**	**Anions**	**Percent**
Chloride	19.353	Na^+	1.056	Cl^-	1.898
Sodium	10.76	Mg^{++}	0.127	SO_4^-	0.265
Sulfate	2.712	Ca^{++}	0.040	HCO_3^-	0.014
Magnesium	1.294	K^+	0.038	Br^-	0.0065
Calcium	0.413	Sr^{++}	0.001	F^-	0.0001
Potassium	0.387				
Bicarbonate	0.142	Total	0.262	Total	2.184
Bromide	0.067				
Strontium	0.008				
Boron	0.004				
Fluoride	0.001				

Table 6 Typical Natural Water Analyses[6]

Characteristic	**A**	**B**	**C**	**D**	**E**	**F**	**G**
pH level	6.3	6.8	7.4	7.5	7.1	8.3	7.1
Chloride (ppm)	5	11	24	21	4	94	149
Sulfate (ppm)	6	20	39	50	17	109	463
Total hardness (ppm)	10	53	120	230	340	70	559
Total dissolved solids (ppm)	33	88	185	332	400	620	1670

A = very soft lake water
B = moderately soft surface water
C = slightly hard river water
D = moderately hard river water
E = hard borehole water
F = slightly hard borehole water with bicarbonate ions
G = very hard groundwater

1.2.2 pH Level

The pH level of both natural and seawaters is usually within 4.5 to 8.5. Copper is one metal in which the corrosion rate increases in acidic water. Copper from the corrosion process will then deposit on other materials present producing a greenish stain. The deposition of copper onto aluminum or galvanized metals sets up pitting corrosion.

1.2.3 Temperature

Higher temperatures normally produce increased corrosion rates in water, like other environments. Increased temperatures do decrease oxygen solubility in water. However, warm temperatures will also increase biological growth which can increase oxygen content. And like in any environment, higher temperatures generally speed up corrosion reactions. The temperature, as well as oxygen content and salinity as a function of ocean depth are depicted in Figure 3.

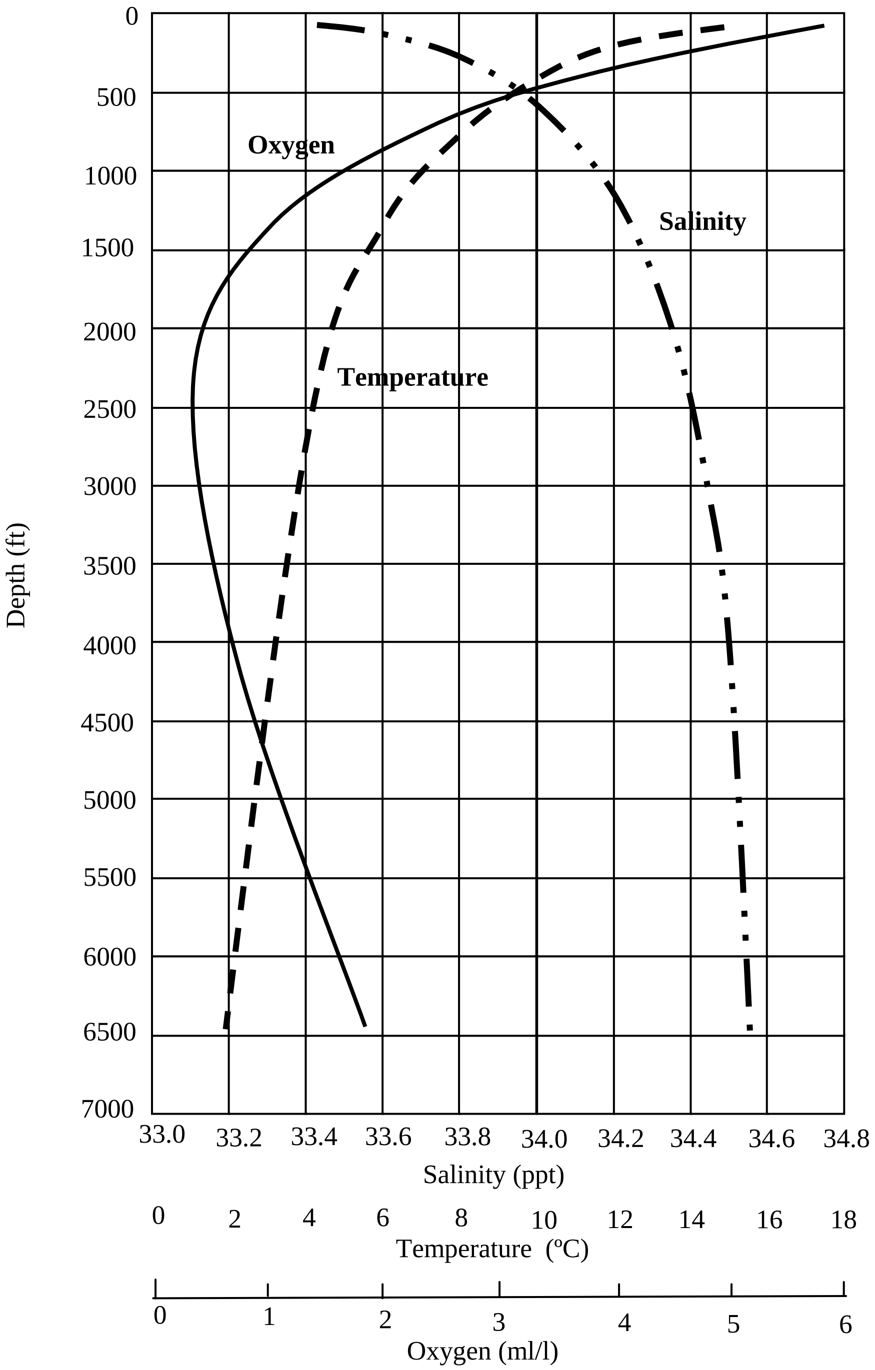


Figure 3 Some Corrosivity Factors as a Function of Depth in the Pacific Ocean (West of Port Hueneme, California)[5]

1.2.4 Water Velocity and Agitation

The water velocity and agitation may increase or decrease corrosion rates, dependent upon the particular metal. The relative degree of attack on some marine metals is shown in Figure 4. Most metals have a critical velocity, beyond which significant corrosion occurs.

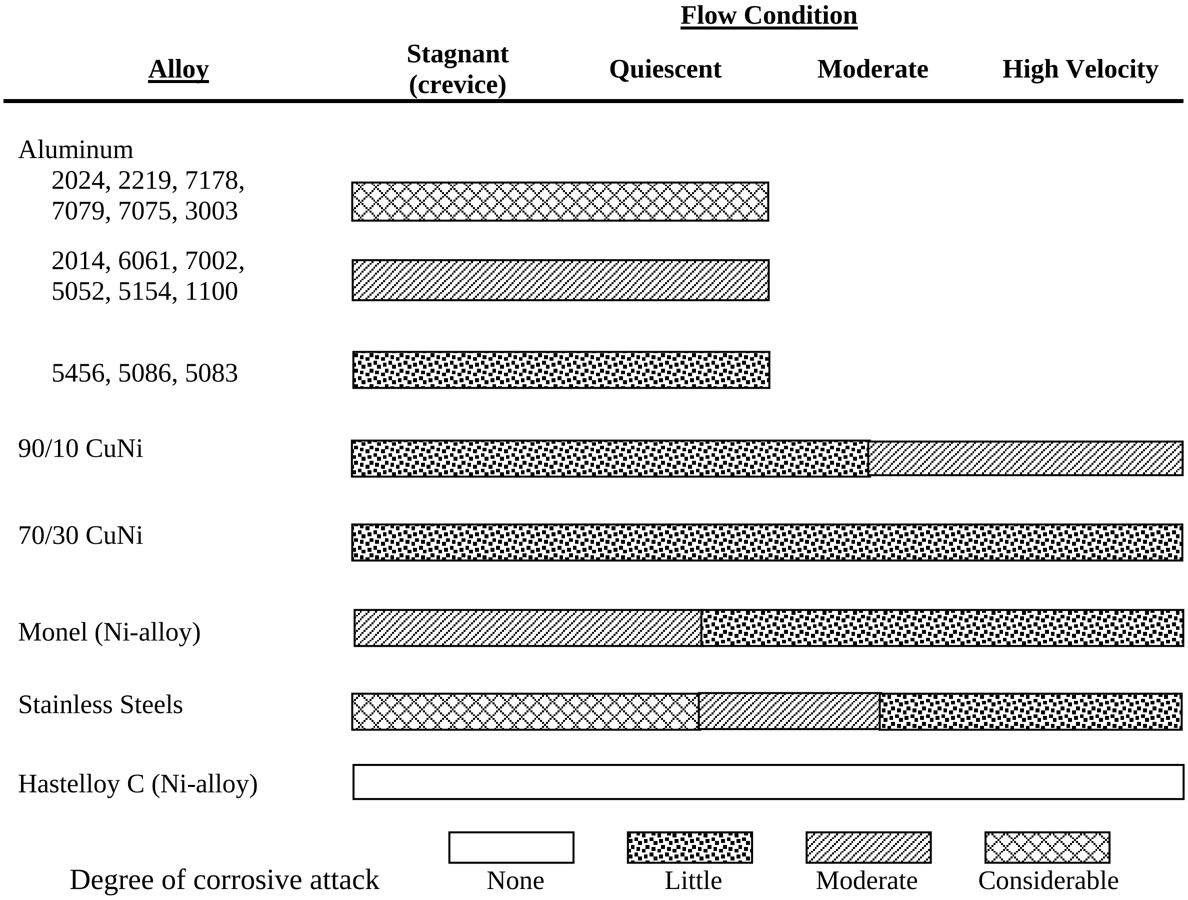
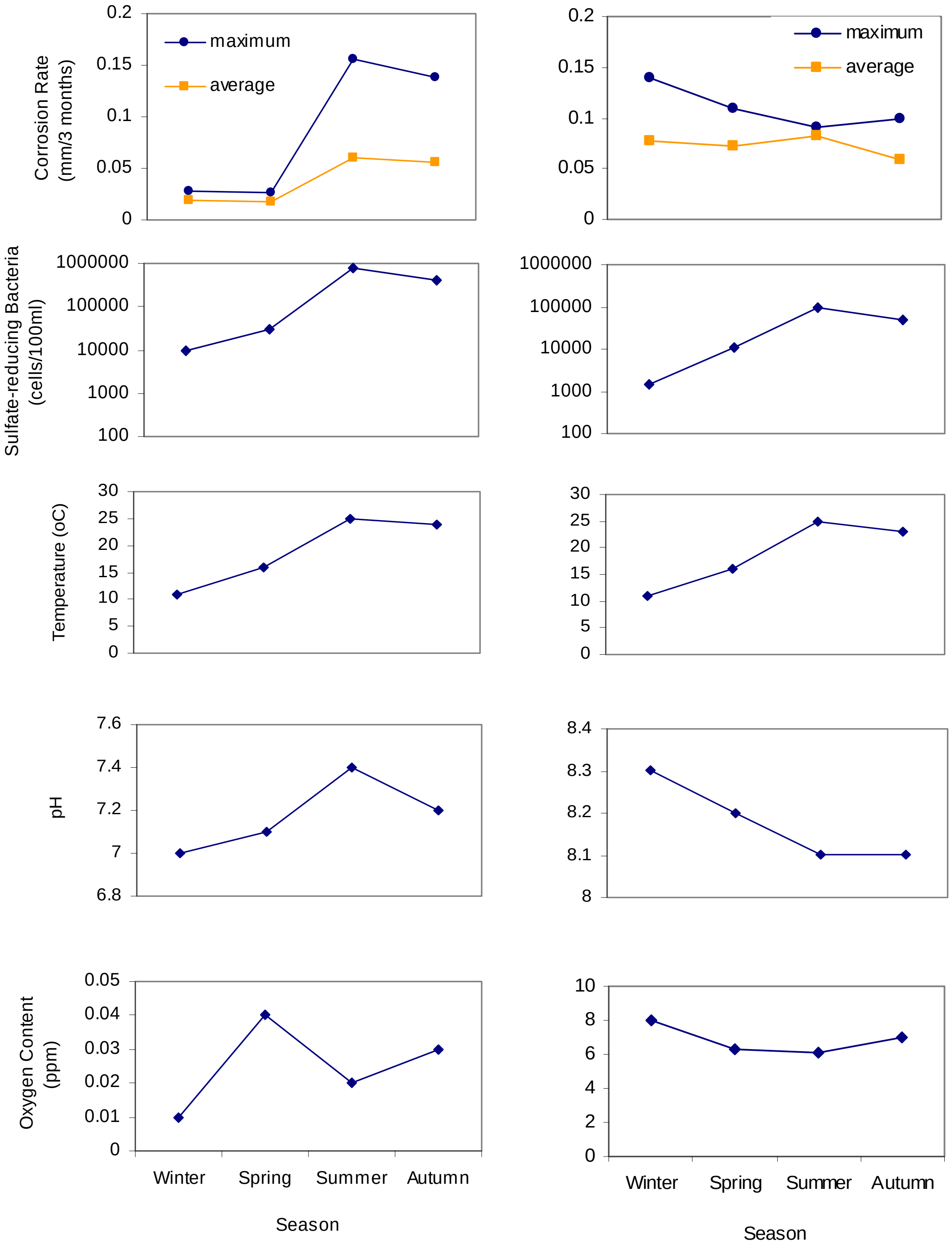


Figure 4 Localized Attack (Crevice and Pitting) of Some Metals in Flowing Seawater[5]

1.2.5 Biological Organisms

All biological organisms, either animals or plants, alter the composition of surrounding water, which may result in increased or decreased corrosion rates. Some organisms merely provide a protective layer, limiting oxygen from reaching the metal’s surface. Others increase the oxygen or sulfide content, increasing the corrosive attack on metals. Microorganisms will be discussed further in Section 2.9.6. Figure 5 shows some corrosivity factors and their effect on the uniform corrosion rate of carbon steel in the Pacific Ocean.



(a) polluted seawater (Okudokai Harbor) (b) non-polluted seawater (Kaman Strait)

Figure 5 Factors Affecting the Corrosion of Carbon Steel in the Pacific Ocean[7]

1.2.6 Managing Underwater Corrosion

Methods to limit uniform underwater corrosion include:

- Proper selection and design of materials.
- Specialized underwater paints should be used where feasible (to include formulations for the deterrence of microorganisms.
- Cathodic protection should be used when practical.
- Preventive maintenance to remove microorganisms and other marine animals from surfaces.

1.3 Soil Environments

The corrosivity of soils is affected by water, the degree of aeration, pH level, temperature, salt content, and biological activity. The soil's particle size plays a role in that smaller particle sizes will hold water, and have less oxygen content; while the opposite exists for large particle sizes. Loose soil will also have greater oxygen content. The oxygen content is highest near or at the soil's surface and decreases with increasing depth. Soils normally have pH levels in the range 5 to 8. At these levels, the corrosion rate is not significantly affected. However, acidic soils will increase the rate of attack on most metals, and will affect other factors such as microbiological activity. Salt content affects soils in the same manner as atmospheric and water environments, with the major corrosive species once again being chloride and sulfate ions. Sulfate reducing bacteria is the most detrimental microorganism to metal corrosion. Like the water environment, a measure of the soil's electrical resistivity is a general indication of its corrosiveness. Lower resistivity equates to higher corrosivity. Table 7 lists soil resistivity ratings based upon resistivity. Mappings of soil resistivities are used to determine where to lay underground piping. It is beneficial to route pipelines through soil with like resistivities and ideally, high resistivities. Care must be taken when laying pipelines in the vicinity of other structures, such as railways, to minimize their exposure to stray currents.

Table 7 Soil Corrosivity Ratings[6]

Soil resistivity (Ω -cm)	Corrosivity rating
> 20,000	essentially non-corrosive
10,000 – 20,000	mildly corrosive
5,000 – 10,000	moderately corrosive
3,000 – 5,000	corrosive
1,000 – 3,000	highly corrosive
< 1,000	extremely corrosive

1.3.1 Managing Corrosion in Soil

Methods to limit corrosion in soils include:

- Proper selection and design of materials.
- Metals should be coated where possible. Bituminous coal tar and asphalt dip coatings are effective for under ground piping. Imbedding pipes in concrete has also been used to limit corrosion.
- Cathodic protection should be used where possible.
- Pipes in the vicinity of electric railroad tracks or other similar equipment must be electrically insulated. One method is to coat the piping with hot asphalt followed by a concrete encasement. Organic dielectric coatings have also been developed for this purpose.

2.0 Forms of Corrosion

There are eight major forms of corrosion accounting for the vast majority of corrosion problems observed, along with several lesser seen forms occurring in specific environments. Uniform or general corrosion proceeds independent of the material’s microstructure and component design. It is highly dependent upon the environmental conditions and the material’s composition, generally occurring at a slow rate. All the remaining forms of corrosion are localized, dependent upon the environments, the components and systems designs, and/or the microstructure of the materials. These forms typically produce higher corrosion rates than uniform corrosion, and in some cases can be quite rapid. Each of the various forms of corrosion should be evaluated for a material and environment when designing new systems. The following sections cover all the forms of corrosion observed with some materials’ susceptibilities and general protection schemes for the various forms.

2.1 Uniform Corrosion

Uniform corrosion is a generalized corrosive attack that occurs over a large area on the surface of a material. It is only dependent upon the material’s composition and the environment. The result is a thinning of the material until failure occurs. Uniform corrosion rates are fairly predictable, following an exponential relationship as follows.

$$p = At^{-B} \qquad \text{Equation 3}$$

where,

p –corrosion rate
t – exposure time
A, B – constants, dependent upon material and environment

The decrease in corrosion rate with time is a direct result of an oxide scale layer forming on the metal’s surface, which then deters further corrosion from occurring. There are extreme cases however, where the corrosivity of the environment is severe and prevents an oxide layer from forming. In this case, the corrosion rate will be constant with time. Figure 6 depicts this relationship for uniform corrosion. Equation 3 may be used to predict the long-term corrosion damage from short-term tests. There are some problems with this prediction however. Environments usually change over time so that corrosion rates will deviate from those predicted by the equation. Also, the development of additional forms of corrosion will likely accelerate attack in localized areas.

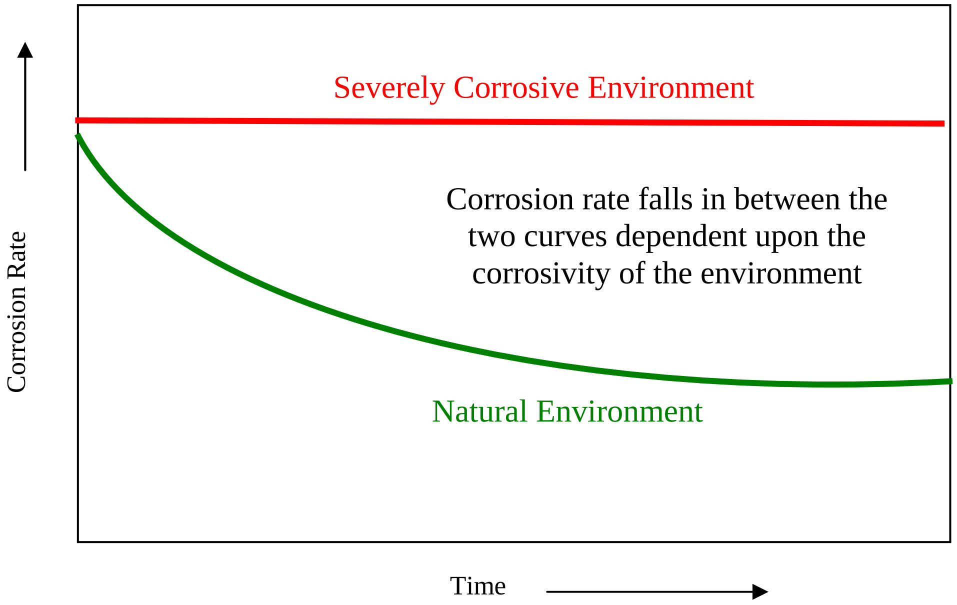


Figure 6 Uniform Corrosion Rates

Uniform corrosion is measured in weight loss or thickness loss and is converted from one to the other using the equation.

$$t = \frac{534w}{\rho AT} \qquad \text{Equation 4}$$

where

t – thickness loss in mils/yr

w – weight loss in mg.

ρ – density in g/cm^3

A – area of exposure in $inches^2$

T – exposure time in hrs.

2.1.1 Metal Susceptibilities to Uniform Corrosion

Magnesium and low alloy ferrous alloys are by far the most susceptible metals to uniform corrosion as shown in Figure 7. Additional metal classes, not addressed in the figure, normally have negligible uniform atmospheric corrosion rates. For the susceptible metals, increased alloying with specific elements can increase uniform corrosion resistance. Alloying for general corrosion resistance of the different metal classes is covered in Section 4.0, Corrosion Characteristics and Properties of Metals. Alloying should also consider the environmental composition and degree of corrosivity. The relative uniform corrosion susceptibilities of a steel piling exposed to marine environments are shown in Figure 8.

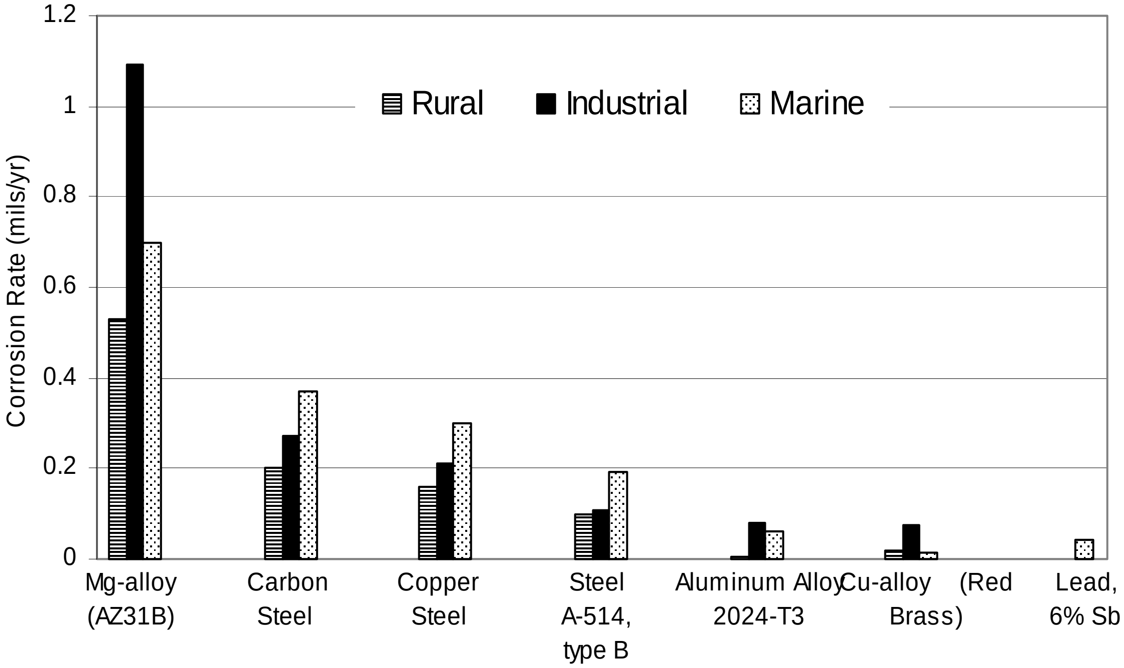
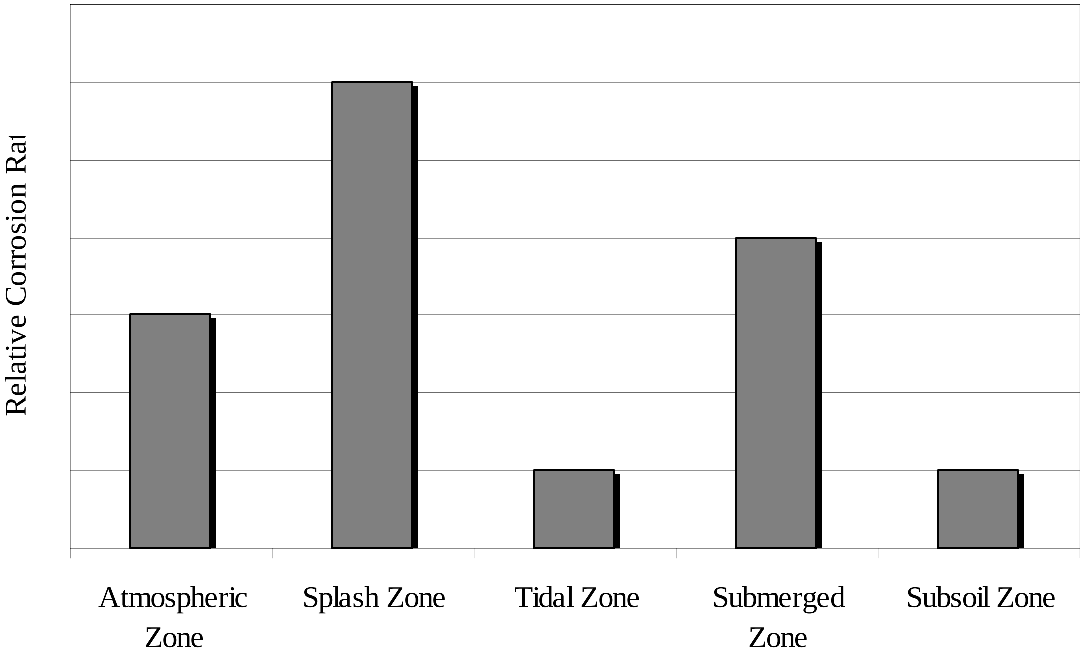


Figure 7 Atmospheric Corrosion Rates of Various Metals[8]



Splash Zone – above high tide
Tidal Zone – below high tide and above low tide

Figure 8 Relative Uniform Corrosion Rates of a Steel Piling in Marine Environments[58]

2.1.2 Managing Uniform Corrosion

The selection of materials for uniform corrosion resistance should simply take into consideration the susceptibility of the metal to the type of environment that will be encountered. Organic or metallic coatings should be used wherever feasible. When coatings are not used, surface treatments that artificially produce the metal oxide layer prior to exposure will result in a more uniform oxide layer and the thickness may be controlled. There are also surface treatments where additional elements are incorporated for corrosion resistance, such as chromium. Also, vapor phase inhibitors may be used in such applications as boilers to combat corrosive elements and adjust the pH level of the environment.

2.2 Galvanic Corrosion

Galvanic corrosion occurs when two metals having different electrical potentials (dissimilar metals) are electrically connected, either through physically touching each other or through an electrically conducting medium, such as an electrolyte. Systems meeting these requirements essentially form an electrochemical cell which will conduct electricity. The induced electrical current can then attract electrons away from one of the metals, which thus acts as the anode in the electrochemical cell. This usually results in acceleration of the rate of corrosion of the anode. The opposing metal, the cathode, will consequently receive a boost in its resistance to corrosion, since it can supply any imminent corrosion reactions with electrons from an external source. Galvanic corrosion is usually observed to be greatest near the surface where the two metals are in contact. Figure 9 shows galvanic corrosion on a metal component near a dissimilar metal fastener.

Figure 9 Galvanic Corrosion between a Stainless Steel Screw and Aluminum[2]

In general, corrosion is the result of an electrochemical reaction that occurs between an anode and a cathode. In the case of uniform corrosion, the metal being corroded acts as both the anode and the cathode in the reaction, where localized areas on the surface of the metal have slightly different electrical potentials. However, galvanic corrosion occurs between two dissimilar metals. The metal with a lower potential relative to the other metal acts as the anode, while the metal with a higher potential acts as the cathode. The corrosion reaction/corrosion current (flow of electrical current) is driven by an electrical potential gradient. Some typical electrical potentials for some common metallic elements are shown in Table 8. (Note – these potentials were taken in standard conditions, but actual potentials vary in metals and alloys, especially under various environmental conditions.)

Table 8 Electromotive Series of Metals[9]

Metal	**Ion Formed**	**Reactivity**	**Potential**
Sodium	Na^{+}	↑ Less Noble – Anodic	-2.714
Magnesium	Mg^{++}		-2.363
Beryllium	Be^{++}		-1.847
Aluminum	Al^{+++}		-1.663
Titanium	Ti^{++}		-1.628
Manganese	Mn^{++}		-1.180
Zinc	Zn^{++}		-0.763
Chromium	Cr^{++}		-0.744
Iron (Ferrous)	Fe^{++}		-0.440
Cadmium	Cd^{++}		-0.403
Cobalt	Co^{++}		-0.277
Nickel	Ni^{++}		-0.250
Tin	Sn^{++}		-0.136
Lead	Pb^{++}		-0.126
Iron (Ferric)	Fe^{+++}		~ -0.4
Hydrogen	H^{+}	Neutral	0.000
Antimony	Sb^{+++}	More Noble – Cathodic ↓	+0.152
Copper (Cupric)	Cu^{++}		+0.342
Copper (Cuprous)	Cu^{+}		+0.521
Mercury	Hg^{++}		+0.788
Silver	Ag^{+}		+0.799
Palladium	Pd^{++}		+0.987
Platinum	Pt^{++++}		~ +1.2
Gold (Auric)	Au^{+++}		+1.498
Gold (Aurous)	Au^{++}		+1.691

2.2.1 Factors Influencing Galvanic Corrosion

There are a number of driving forces that influence the occurrence of galvanic corrosion and the rate at which it occurs. Among these influencing factors are the difference in the electrical potentials of the coupled metals, the relative area, and the system geometry. Other driving forces that factor into promoting or preventing galvanic corrosion include the polarization (the shift in electrode potential during electrolysis) of the metals, the electrical resistance and electrical current of the system, the type, pH, and concentration of the electrolyte, and the degree of aeration or motion of the electrolyte.[96]

2.2.1.1 Potential Difference

The main driving force for galvanic corrosion is the electrical potential difference between the two dissimilar metals; thus, typically the bigger the difference, the more rapid the rate of galvanic corrosion. Galvanic corrosion occurs mainly at the contact area of the two metals and dissipates with distance from the junction. A fundamental expression that shows the electrical potential of a galvanic system is given in Equation 5.

$$E_c - E_a = I(R_e + R_m) \qquad \text{Equation 5}$$

where

E_c – electrical potential of the cathode

E_a – electrical potential of the anode

I – electrical current

R_m – resistance of the electrodes (external circuit)

R_e – resistance of the electrolyte solution path in the galvanic circuit (internal circuit)

There are numerous resources from which the standard electrode potentials of specific metals and alloys can be obtained. The rate of galvanic corrosion in specific environments, however, should not be determined based on the standard electrode potentials of metals. These standard potentials are determined as the potential of a metal in equilibrium with a specific concentration of the electrolyte.[96] Furthermore, a galvanic system is dynamic and the reactions are dependent on a number of other factors, including electrolyte concentration, temperature, and pH, as well as oxygen content and fluid motion.

It is not always necessary, however, to have two distinct metals in order to create a galvanic couple. There are instances where galvanic corrosion occurs within the same metal. This can happen when the metal has both an active and passive state, for example, one part is covered with an oxide film and hence passivated, while another part of the metal is exposed to the atmosphere. This condition would create a potential difference causing the unpassivated area of the metal to galvanically corrode.

2.2.1.2 Relative Area

The size of the metal components in the galvanic system also influences the rate and degree of corrosion. For example, a system with a relatively large cathode (less reactive metal) and a relatively small anode (more reactive metal) will corrode via galvanic corrosion to a greater extent than will a system with electrodes of equal size. Furthermore, a system with a relatively large anode compared to a small cathode will not typically exhibit galvanic corrosion on the anode to a significant extent. In general, corrosion of the anode is proportional to the relative area of the cathode. That is, the induced electrical current increases proportionally with an increase in cathodic area relative to the area of the anode. The opposite is generally true as well: current decreases proportionally with a decrease in relative cathodic area.

2.2.1.3 Geometry

Component geometry is another factor affecting the flow of current, which consequently influences the rate of galvanic corrosion. Current does not easily travel around corners, for instance.

2.2.1.4 Electrolyte and Environment

The rate of galvanic corrosion is partially dependent on the concentration, oxygen content and motion of the electrolyte, as well as the temperature of the environment. For instance, higher temperatures typically cause an increase in the rate of galvanic corrosion, while higher concentrations of the electrolyte will result in a decrease in the corrosion rate.96 The pH of the electrolyte solution may also affect the occurrence of galvanic corrosion in a dissimilar metal system. For example, a metal that is the cathode in a neutral or basic electrolyte may become the anode if the electrolyte becomes acidic.96 A higher oxygen content in the electrolyte also typically results in an increase in the rate of galvanic corrosion. Electrolyte motion can also increase the rate of corrosion, since it may remove some of the oxidized metal from the anode surface, allowing for further oxidation of the metal.

2.2.2 Material Selection

In most cases, galvanic corrosion can be easily avoided if proper attention is given to the selection of materials during design of a system. It is often beneficial for performance and operational reasons for a system to utilize more than one type of metal, but this may introduce a potential galvanic corrosion problem. Therefore, sufficient consideration should be given to material selection with regard to the electrical potential differences of the metals.

2.2.2.1 Galvanic Series

The potential difference of two metals is qualitatively determined by their relative placement on the Galvanic Series, shown in Table 9. Some metals are listed more than once. This is either because they exhibit different galvanic properties when given different heat treatments, or because they can be in two different states. The metal is in an active state when the metal surface has direct interaction with the environment, and the metal is in a passive state when a noble film has formed on the surface.

This table can be helpful in estimating the likelihood of corrosion of a specified bimetallic system by gauging the distance between the two metals on the galvanic series. To state it simply, avoid using metals that are far apart on the galvanic series. The chart is not useful, however, in predicting the degree or rate of corrosion, since there are several other factors that influence the magnitude of corrosion in a given bimetallic system.

The metal that is higher on the Galvanic Series chart is less reactive and thus acts as the cathode, while the metal appearing lower in the series is more reactive and acts as the anode in the electrochemical cell. For example, if copper was to be electrically coupled with tin and immersed in seawater, then copper would be the anode and would corrode more readily than tin, which would act as the cathode. In environments other than seawater, the metal with the least resistance to corrosion in the surroundings acts as the anode and is then more readily corroded than the other, more noble metal.

2.2.2.2 Other Material Selection Charts

There have been a number of charts and tables created in order to aid in the material selection process and eliminate the potential for galvanic corrosion. Table 10 lists specific metal and alloy compatibilities with other specific metals and alloys in seawater with respect to galvanic corrosion. This table shows whether a certain combination of metals or alloys is compatible, unfavorable or uncertain. Note that the stainless steels listed in the table are all in the same state (active or passive). Table 11, on the other hand, lists metal and alloy compatibilities with respect to galvanic corrosion in environments other than seawater, such as marine and industrial atmospheres.

Table 9 Galvanic Series in Seawater[2, 10, 96]

Noble (least active)

Platinum
Graphite
Gold
Titanium
Silver
AM350 (passive)
Titanium 75A
Titanium 13V-11Cr-3 Al (solution treated and aged)
Titanium 8Mn
Titanium 6Al-4V (annealed)
Titanium 6Al-4V (solution treated and aged)
Titanium 13V-11Cr-3Al (annealed)
Titanium 5Al-2.5Sn
Chlorimet 3
Hastelloy C
Stainless Steel, Type 286 (passive)
AM355 (passive)
Carpenter 20 (passive)
Stainless Steel, Type 202 (passive)
AM355 (active)
Stainless Steel, Type 316 (passive)
Stainless Steel, Type 286 (active)
Stainless Steel, Type 201 (passive)
Stainless Steel, Type 321 (passive)
Stainless Steel, Type 301 (passive)
Stainless Steel, Type 304 (passive)
Stainless Steel, Type 410 (passive)
7Ni-33Cu alloy
75Ni-16Cr-7Fe alloy (passive)
Nickel (passive)
Silver solder
M-Bronze
G-Bronze
70-30 cupro-nickel

Silicon bronze
Stainless Steel, 17-7 PH (passive)
Stainless Steel, Type 309 (passive)
Stainless Steel, Type 321 (active)
Carpenter 20 (active)
Stainless Steel, Type 201 (active)
Monel 400
Stainless Steel, Type 202 (active)
Copper
Red brass
Molybdenum
Stainless Steel, Type 347L (active)
Aluminum bronze
Admiralty brass
Yellow brass
Chlorimet 2
Hastelloy B
76Ni-16Cr-7Fe alloy (active)
Nickel (active)
Naval brass
Manganese bronze
Muntz metal
Tungsten
Stainless Steel 17-7 PH (active)
Stainless Steel, Type 430 (passive)
Stainless Steel, Type 301 (active)
Stainless Steel, Type 310 (active)
AM350 (active)
Tantalum
Tin
Lead
Stainless Steel, Type 316 (active)
Stainless Steel, Type 304 (active)
Stainless Steel, Type 410 (active)

Cast iron
Mild steel
Aluminum Alloy 5052-H16
Aluminum Alloy 2024-T4
Aluminum Alloy 2014-0
Indium
Aluminum Alloy 6061-0
Aluminum Alloy 1160-H14
Aluminum Alloy 7075-T6
Aluminum Alloy A360 (die cast)
Aluminum Alloy 6061-T6
Aluminum Alloy 3003-H25
Aluminum Alloy 1100-0
Aluminum Alloy 5052-H32
Aluminum Alloy 5456-0, H353
Aluminum Alloy 5052-H12
Aluminum Alloy 5052-0
Aluminum Alloy 218 (die cast)
Uranium
Cadmium
Aluminum Alloy 7079-T6
Aluminum Alloy 1160-H14
Aluminum Alloy 2014-T3
Alclad
Aluminum 6053
Galvanized steel
Beryllium (hot pressed)
Zinc
Magnesium alloys
Magnesium

Anodic (most active)

Table 10 GalvanicCorrosion Compatibilities of Metals and Alloys in Seawater[11]

S - Small Metal A to Metal B Area Ratio
E - Equal Area Ratio
L - Large Metal A to Metal B Area Ratio

● Unfavorable - Galvanic Acceleration Expected
x Uncertain - Variable Direction and/or Magnitude of Galvanic Effect
o Compatible - No Galvanic Acceleration Expected

Metal B → Metal A ↓		Magnesium Alloys	Zinc	Aluminum Alloys	Cadmium	Mild Steel, Wrought Iron	Cast Iron	Low Alloy High Strength Steel	Brasses, Mn Bronze	Copper, Si Bronze	Lead-Tin Solder	Tin Bronze (G & M)	90/10 Copper-Nickel	70/30 Copper-Nickel	Nickel-Aluminum Bronze	Silver Braze Alloys	Types 302, 304, 321 & 347 Stainless Steel	Alloys 400, K-500	Types 316 & 317 Stainless Steel	Alloy 20, Alloy 825	Titanium, Alloys C, C-276, 625	Graphite, Graphitized Cast Iron
Magnesium Alloys	S	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	■	●	●	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Zinc	S	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	■	x	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	■	o	o	o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Aluminum Alloys	S	●	o	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	x	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	■	x	x	x	x	●	●	●	●	●	●	●	●	x	●	x	x	x	●
Cadmium	S	x	o	x	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	x	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	■	o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Mild Steel, Wrought Iron	S	●	o	x	o	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	■	o	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	●	■	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	●
Cast Iron	S	●	o	x	o	o	■	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	o	■	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	●	●	■	●	x	x	x	x	x	x	x	x	x	x	x	x	o	x
Low Alloy High Strength Steel	S	●	o	x	o	o	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	x	x	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	●	●	x	■	o	o	o	o	o	o	o	o	o	o	o	o	o	●
Brasses, Mn Bronze	S	●	●	●	●	o	x	o	■	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	■	x	x	x	x	x	x	x	●	●	x	x	x	●
	L	●	●	●	●	●	●	●	■	x	x	x	x	x	x	x	●	o	x	o	o	●
Copper, Si Bronze	S	●	●	●	●	o	x	o	x	■	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	■	x	x	x	x	x	●	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	■	x	x	x	x	x	x	●	o	●	●	o	●
Lead-Tin Solder	S	●	●	●	●	o	x	o	x	x	■	●	x	x	x	●	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	x	■	x	o	o	o	x	●	●	●	x	x	●
	L	●	●	●	●	●	●	●	●	●	■	x	x	x	x	x	●	o	o	o	o	●
Tin Bronze (G & M)	S	●	●	●	●	o	x	o	x	x	x	■	x	x	x	●	●	●	x	x	x	●
	E	●	●	●	●	●	●	●	x	x	x	■	o	x	x	●	●	o	x	o	o	●
	L	●	●	●	●	●	●	●	●	●	●	■	x	o	o	x	●	o	x	o	o	●
90/10 Copper-Nickel	S	●	●	●	●	o	x	o	x	x	x	x	■	●	x	x	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	x	o	o	■	o	o	x	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	x	x	■	o	o	x	●	o	o	o	o	●
70/30 Copper-Nickel	S	●	●	●	●	o	x	o	x	x	x	o	o	■	o	x	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	x	o	x	o	■	o	x	●	x	x	o	o	●
	L	●	●	●	●	●	●	●	●	●	x	x	●	■	o	x	●	o	o	o	o	●
Nickel-Aluminum Bronze	S	●	●	●	●	o	x	o	x	x	x	o	o	o	■	x	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	x	o	x	o	o	■	x	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	x	x	x	o	■	x	●	o	o	o	o	●
Silver Braze Alloys	S	●	●	●	●	o	x	o	x	x	x	x	x	x	x	■	●	x	x	x	x	●
	E	●	●	●	●	●	●	●	x	●	x	●	x	x	x	■	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	●	●	x	x	x	■	●	x	x	x	x	●
Types 302, 304, 321 & 347 Stainless Steel	S	●	●	x	●	o	x	o	●	●	●	●	●	●	●	●	■	●	●	●	●	●
	E	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	●	●	●	●	●
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	x	●	●	●	●
Alloys 400, K-500	S	●	●	●	●	o	o	o	o	o	o	o	o	o	o	x	x	■	x	x	x	●
	E	●	●	●	●	●	●	●	●	x	●	o	x	x	x	x	●	■	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	●	x	●	■	x	x	x	●
Types 316 & 317 Stainless Steel	S	●	●	x	●	o	x	o	●	●	●	●	●	●	●	●	●	●	■	x	x	●
	E	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	x	x	●
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	x	x	●
Alloy 20, Alloy 825	S	●	●	x	●	o	o	o	●	●	o	o	o	o	o	x	●	x	x	■	x	●
	E	●	●	●	●	●	●	●	x	x	x	o	x	o	x	x	●	x	x	■	x	●
	L	●	●	●	●	●	●	●	●	●	●	x	●	●	●	x	●	x	x	■	x	●
Titanium, Alloys C, C-276, 625	S	●	●	x	●	o	o	o	o	o	o	o	o	o	o	x	●	x	x	x	■	x
	E	●	●	●	●	x	x	x	x	x	x	o	x	o	x	x	●	x	x	x	■	x
	L	●	●	●	●	●	●	●	●	●	●	x	●	●	●	x	●	x	x	x	■	x
Graphite, Graphitized Cast Iron	S	●	●	●	●	●	x	●	●	●	●	●	●	●	●	●	●	●	●	●	x	■
	E	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	x	■
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	x	■

Table 11 Galvanic Corrosion Compatibilities of Metals and Alloys in Marine and Industrial Environments[96]

M - Marine Atmosphere
I - Industrial Atmosphere

● Unfavorable - Galvanic Acceleration Expected or Uncertain
o Compatible - No Galvanic Acceleration Expected

		Zinc, Zinc Coating	Cadmium, Beryllium	Aluminum, Mg-Coated Aluminum, Zn-Coated Aluminum	Cu-Coated Aluminum	Steels-Carbon, Low Alloy	Lead	Tin, Tin-Lead, Indium	St. Steels - Martensitic, Ferritic	Chromium, Molybdenum, Tungsten	St. Steels-Aust., PH, Super Strength, Heat Resis	Brass-Lead Bronze	Brass-Low Copper, Bronze-Low Copper	Brass-High Copper, Bronze-High Copper	Copper-High Nickel, Monel	Nickel, Cobalt	Titanium	Silver	Palladium, Rhodium, Gold, Platinum	Graphite
Magnesium	M	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Zinc, Zinc Coating	M	■	o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I	■	o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Cadmium, Beryllium	M		■	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I		■	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Aluminum, Mg-Coated Aluminum, Zn-Coated Aluminum	M			■	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I			■	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Cu-Coated Aluminum	M				■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I				■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Steels-Carbon, Low Alloy	M					■	●	●	●	●	●	●	●	●	●	o	●	●	●	●
	I					■	o	●	●	●	●	●	●	●	●	o	●	●	●	●
Lead	M						■	o	o	o	o	o	●	●	●	●	●	o	●	●
	I						■	o	o	o	o	o	●	o	o	o	o	o	o	o
Tin, Tin-Lead, Indium	M							■	●	●	●	o	o	o	o	o	o	o	●	●
	I							■	●	o	o	o	o	o	o	o	o	o	●	●
St. Steels - Martensitic, Ferritic	M								■	●	●	●	●	●	●	●	●	●	●	●
	I								■	o	●	●	o	●	●	●	●	●	●	●
Chromium, Molybdenum, Tungsten	M									■	o	o	●	●	o	o	o	o	o	o
	I									■	o	o	o	●	o	o	o	o	o	o
St. Steels-Aust., PH, Super Strength, Heat Resistant	M										■	●	●	●	o	o	o	o	o	o
	I										■	●	●	●	o	o	o	o	o	o
Brass-Lead Bronze	M											■	o	o	●	o	●	o	o	o
	I											■	o	o	o	o	o	o	o	o
Brass-Low Copper, Bronze-Low Copper	M												■	o	o	o	●	o	●	●
	I												■	o	o	o	o	o	o	o
Brass-High Copper, Bronze-High Copper	M													■	●	o	●	o	●	●
	I													■	o	o	o	o	o	o
Copper-High Nickel, Monel	M														■	o	o	o	o	o
	I														■	o	o	o	o	o
Nickel, Cobalt	M															■	o	o	o	o
	I															■	o	o	o	o
Titanium	M																■	o	o	o
	I																■	o	o	o
Silver	M																	■	o	o
	I																	■	o	o
Palladium, Rhodium, Gold, Platinum	M																		■	o
	I																		■	o

Note – Joined metals presented in this table are of equal area.
PH – Precipitation Hardening is a specific type of heat treatment/aging

2.2.3 Managing Galvanic Corrosion

If proper design, material selection, implementation, and maintenance steps are followed, it is relatively simple to avoid the occurrence of galvanic corrosion in a new system. MIL-STD-889 (active) is a DOD standard on dissimilar metals. The purpose of this standard is to define and classify dissimilar metals and establish requirements for protecting coupled dissimilar metals in all military equipment parts, components and assemblies.[96] To further aid in properly avoiding this form of corrosion, Table 12 provides a brief list of guidelines to minimize galvanic corrosion. Some of these are explained in more detail in the sections to follow.

Table 12 Guidelines for Minimizing Galvanic Corrosion[11]

- Use one material to fabricate electrically isolated systems or components where practical.
- If mixed metal systems are used, select combinations of metals as close together as possible in the galvanic series, or select metals that are galvanically compatible.
- Avoid the unfavorable area effect of a small anode and large cathode. Small parts or critical components such as fasteners should be the more noble metal.
- Insulate dissimilar metals wherever practical [for example, by using a gasket]. It is important to insulate completely if possible.
- Apply coatings with caution. Keep the coatings in good repair, particularly the one on the anodic member.
- Add inhibitors, if possible, to decrease the aggressiveness of the environment.
- Avoid threaded joints for materials far apart in the series.
- Design for the use of readily replaceable anodic parts or make them thicker for longer life.
- Install a third metal that is anodic to both metals in the galvanic contact.

2.2.3.1 Area Effects

Taking into account the relative areas of galvanically coupled metallic systems can minimize galvanic corrosion. The size of the cathodic metal in the bimetallic system should not be significantly larger than the size of the anodic metal, since this would cause a greater degree of corrosion of the anodic member. Instead, the anodic metal should have an equal or larger area. For example, the more noble metal should be used for rivets, bolts and other fasteners, thus making the area of the anode much greater than that of the cathodic component.

2.2.3.2 Cathodic Protection

Galvanic corrosion can be intentionally induced in order to protect a more important metallic component. This method of protection involves using a highly active metal, one that is lower on the galvanic series, to be sacrificially corroded. This sacrificial anode protects the more important, cathodic metal from corrosion. Magnesium and zinc are commonly used as sacrificial anodes. Sacrificial anodes are often replaced in-service as they are consumed through galvanic corrosion, as intended.

2.2.3.3 Insulate Dissimilar Metals

Electrically resistive, non-metallic materials can be used to insulate two dissimilar metals. This in effect, breaks the electrical connection or at least increases the electrical resistivity resulting in a reduction, if not elimination, of the potential for galvanic corrosion.

2.2.3.4 Coatings

Metallic coatings are commonly used to protect bimetallic systems against galvanic corrosion. These coatings can provide protection by acting as barriers to corrosion or by readily accepting corrosion, thereby saving the important metal component from being corroded. For example, zinc is often used as a coating for steel, and since it is not very corrosion resistant, it will corrode preferentially to protect the steel. Thus, the zinc coating acts as a sacrificial anode.

Noble metal coatings are typically used as barrier coatings, since they are relatively unreactive. These coatings can isolate the important metal from the surrounding environment; however, pores, defects, or damaged areas in these barrier coatings are areas still susceptible to being galvanically corroded. Furthermore, the areas under these discontinuities (also known as holidays) in the coating system are likely to be targeted for severe localized corrosion. In addition, if the anodic metal in the galvanically coupled system is coated with a barrier coating without coating the cathodic member as well, it can have severe negative effects due to the reduced anodic area. Moreover, if the anode is coated, while the cathode is not, the former cathode may become anodic to the former anode.

2.2.3.5 Crevices

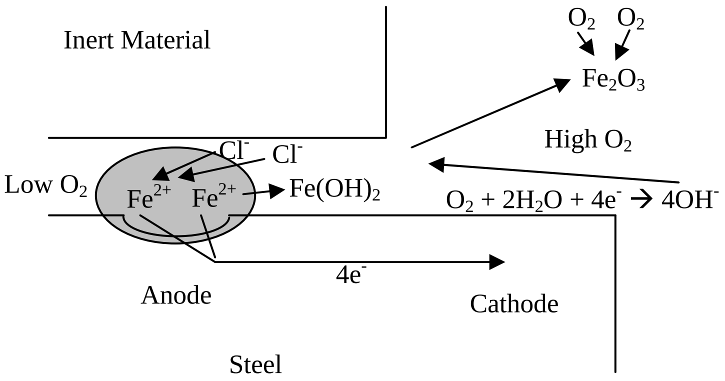
Threaded joints with dissimilar metals that are far apart on the galvanic series should be avoided. It is recommended that crevices be sealed either by welding or brazing to protect against galvanic corrosion.

2.3 Crevice Corrosion

Crevice corrosion occurs as a result of water or other liquid entrapment in localized areas dependent upon component/system design. These designs include primarily sharp angles, fasteners, joints, washers and gaskets. Crevice corrosion can also occur under debris build up on surfaces, sometimes referred to as “poultice corrosion.” Poultice corrosion can be quite severe, due to an increasing acidity in the crevice area.

2.3.1 Crevice Corrosion Mechanism

The combination of low oxygen content in the crevice area compared to the surroundings, sets up an anodic imbalance creating a highly corrosive microenvironment, as depicted in Figure 10. Crevice corrosion is of particular concern in aircraft lap joints. In severe cases, the build up of corrosion products in the lap joint can cause separation of the two metals, known as pillowing.



Local acidification of electrolyte by the reactions:

$$Fe^{2+} + 2Cl^{-} \rightarrow FeCl_2 \text{ (unstable)}$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

Figure 10 Crevice Corrosion Process in Steel[6]

2.3.2 Crevice Geometry

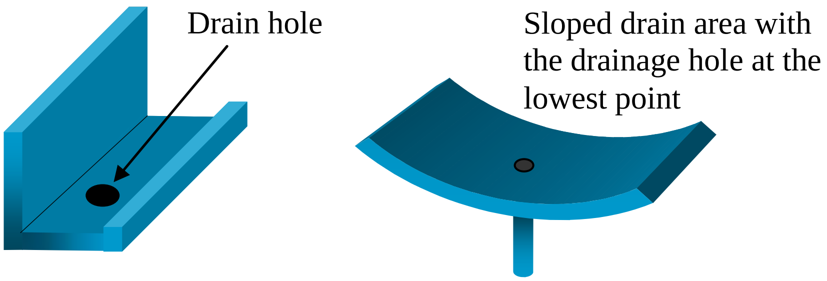
The crevice gap, depth, and the surface ratios of materials can all affect the degree of crevice corrosion. Tighter gaps have been known to increase the rate of crevice corrosion of stainless steels in chloride environments. This has been attributed to the reduced volume of electrolyte that becomes acidified resulting in a higher rate of attack. The larger crevice depth and greater surface area of metals will generally increase the rate of crevice corrosion.

2.3.3 Metals Susceptible to Crevice Corrosion

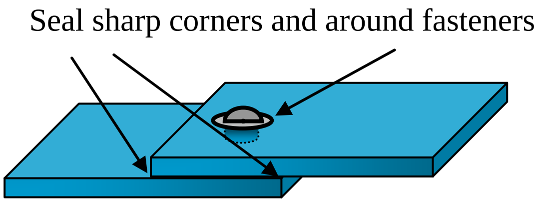
In general, materials that are passive have a greater susceptibility to crevice corrosion. These include aluminum alloys and particularly stainless steels. Titanium alloys normally have good resistance to crevice corrosion. However, they may become susceptible in elevated temperature, acidic environments containing chlorides. In seawater environments, copper alloys can experience crevice corrosion that occurs on the outside of the crevice.

2.3.4 Managing Crevice Corrosion

New components and systems should be designed to minimize areas where crevice corrosion may occur. Welded joints are preferable to fastened joints. Where crevices are unavoidable, metals with a greater resistance to crevice corrosion in the intended environment should be selected. Avoid the use of hydrophilic materials in fastening systems and gaskets. Crevice areas should be sealed to prevent the ingress of water. Also, a regular cleaning schedule should be implemented to remove any debris build up. Figure 11 illustrates several methods that may be implemented to decrease crevice corrosion.



(a) Avoid buildup of corrosive debris



(b) Prevent the ingress of liquids

Figure 11 Methods to Mitigate Crevice Corrosion

2.4 Pitting Corrosion

Pitting corrosion, also simply known as pitting, is an extremely localized form of corrosion that occurs when a corrosive medium attacks a metal at specific points causing small holes or pits to form. This usually happens when a protective coating or oxide film is perforated, due to mechanical damage or chemical degradation. Pitting can be one of the most dangerous forms of corrosion because it is difficult to anticipate and prevent, relatively difficult to detect, occurs very rapidly, and penetrates a metal without causing it to lose a significant amount of weight. Failure of a metal due to the effects of pitting corrosion can thus occur very suddenly. Pitting can have side effects too, for example, cracks may initiate at the edge of a pit due to an increase in the local stress. In addition, pits can coalesce underneath the surface, which can weaken the material considerably. Figure 12 shows the result of pitting of an aluminum railing that was located near an ocean.

Figure 12 Pitting Corrosion of an Aluminum Railing near the Atlantic Ocean[2]

2.4.1 Pitting Mechanism

Pitting often begins at a specific area of a passivated metal where there is a break in the passivation layer, which then acts as the anodic area, while the rest of the metal acts as the cathodic area. With a potential difference between the anode and cathode, extremely localized corrosion initiates, and since the surrounding area is passivated, the corrosion remains localized and causes pits to form in the metal. Moreover, since the anodic area is significantly smaller than the cathodic area, corrosion continues at a rapid pace.

A further danger of pitting is that corrosion in pits becomes self-sustaining by an autocatalytic process. Such a process involves the progression of pit growth by the dissolution of the metal near the bottom of the pit. It is thought that the environment is very acidic near the bottom of the pit, thus propagating the dissolution of the metal. The dissolution reaction, where electrons associated with a metal-metal bond are dispelled and a metal ion breaks away from the bulk material, works in conjunction with a cathodic reaction near the surface adjacent to the pit. The cathodic reaction supplies excess electrons to facilitate a reduction reaction by forming hydroxide ions from water molecules and diatomic oxygen. To maintain neutrality, anions (negative ions) from the electrolyte migrate into the pit where there is an excess of positive charge, and associate with the metal ions. Subsequently, this species is dissociated in water to form a metal hydroxide and an acid, which results in a reduction in the pH near the bottom of the pit. This means that there is an excess of positively charged hydrogen ions and anions, which stimulate and propagate further dissolution of the metal near the bottom of the pit. These reactions are shown in Equation 6, Equation 7, and Equation 8.

$$M \rightarrow M^{n+} + ne^{-} \qquad \text{Equation 6}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad \text{Equation 7}$$

$$M^{+}I^{-} + H_2O \rightarrow MOH + H^{+}I^{-} \qquad \text{Equation 8}$$

where

M – metal

M^+ – metal ion

e^- – electron

I^- – anion (i.e. Cl^-)

Pitting corrosion is also very difficult to measure and predict, as there are usually numerous pits of varying depths and diameters, which do not form consistently under specified conditions. The holes that form from corrosive attack, however, tend to be greater in depth than in diameter. These pits typically form on the top-surface of a metal and proceed to deepen in the same direction as gravity. Thus, they do not usually form on surface planes that are parallel to the direction of gravity, but rather on those that are perpendicular to gravity. Moreover, pits do not tend to proceed away from the direction of gravity. Basically, they do not form on the bottom surface of a metal and proceed away from the direction of gravity. Initiation of the holes is a gradual and fairly long process, but once they are formed, the rate of growth of the pit increases significantly. Pitting usually occurs in static or low velocity fluid systems, since pitting corrosion will tend to decrease as fluid velocity increases. Pitting is often difficult to measure since the metal usually experiences minimal weight loss during the corrosion process. Also, pits can be filled in with corrosion products.

2.4.2 Metals Susceptible to Pitting Corrosion

Stainless steels tend to be the most susceptible to pitting corrosion among metals and alloys. For example, stainless steels tend to form deep pits in seawater, and environments containing higher concentrations of chlorine or bromine solutions. Polishing the surface of stainless steels can increase the resistance to pitting corrosion compared to etching or grinding the surface. Alloying can have a significant impact on the pitting resistance of stainless steels. The effects of some of the alloying elements of stainless steels on the corresponding resistance to pitting are provided in Table 13.

Table 13 Effects of Alloying Elements on Pitting Resistance of Stainless Steel Alloys[12]

Element	Effect on Pitting Resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and Niobium	Decreases resistance in $FeCl_3$; other mediums no effect
Sulfur and Selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

Conventional steel has a greater resistance to pitting corrosion than stainless steels, but is still susceptible, especially when unprotected. Aluminum in an environment containing chlorides and aluminum brass in contaminated or polluted water are usually susceptible to pitting. Titanium is strongly resistant to pitting corrosion. The relative pitting resistance of some metals is shown in Figure 13.

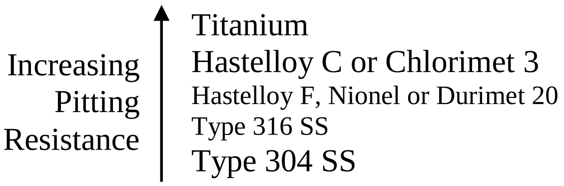


Figure 13 Relative Pitting Resistance of Some Metals

2.4.3 Managing Pitting Corrosion

Proper material selection is very effective in preventing the occurrence of pitting corrosion. Field testing, though, is often necessary to determine whether the chosen material is suitable for the proposed environment. Another option for protecting against pitting is to mitigate aggressive environments and environmental components (e.g. chloride ions, low pH, etc.). Inhibitors may sometimes stop pitting corrosion completely. Further efforts during design of the system can aid in preventing pitting corrosion, for example, by eliminating stagnant solutions or by the inclusion of cathodic protection.

2.5 Intergranular Corrosion

Intergranular corrosion attacks the interior of metals along grain boundaries. It is associated with impurities which tend to deposit at grain boundaries and/or a difference in phase precipitated at grain boundaries. Heating of some metals can cause a “sensitization” or an increase in the level of inhomogeniety at grain boundaries. Therefore, some heat treatments and weldments can result in a propensity for intergranular corrosion. Susceptible materials may also become sensitized if used in operation at a high enough temperature environment to cause such changes in internal crystallographic structure.

2.5.1 Metals Susceptible to Intergranular Corrosion

Intergranular corrosion can occur in many alloys. The most predominant susceptibilities have been observed in stainless steels and some aluminum and nickel-based alloys. Stainless steels, especially ferritic stainless steels, have been found to become sensitized, particularly after welding. Welding causes the precipitation chromium carbide phases at grain boundaries in the heat affected zone (HAZ). This in turn results in intergranular corrosion within the HAZ of the stainless steels. Aluminum alloys also suffer intergranular attack as a result of precipitates at grain boundaries that are more active. Alloys that fall into this type of corrosion include 5083, 7030, 2024, and 7075. Exfoliation corrosion is considered a type of intergranular corrosion in materials that have been mechanically worked to produce elongated grains in one direction. This form of corrosion has been experienced in certain aluminum alloys. High nickel alloys can be susceptible by precipitation of intermetallic phases at grain boundaries. The intergranular corrosion process is however more complicated in nickel-alloys than in stainless steels or aluminum alloys.

2.5.2 Managing Intergranular Corrosion

Methods to limit intergranular corrosion include:

- Keep impurity levels to a minimum
- Proper selection of heat treatments to reduce precipitation at grain boundaries.
- Specifically for stainless steels, reduce the carbon content, and add stabilizing elements (Ti, Nb, Ta) which preferentially form more stable carbides than chromium carbide.

2.6 Selective Leaching (Dealloying Corrosion)

Dealloying, also called selective leaching, is a rare form of corrosion where one element is targeted and consequently extracted from a metal alloy, leaving behind an altered structure. The most common form of selective leaching is dezincification, where zinc is extracted from brass alloys or other alloys containing significant zinc content. Left behind are structures that have experienced little or no dimensional change, but whose parent material is weakened, porous and brittle. Dealloying is a dangerous form of corrosion because it reduces a strong, ductile metal to one that is weak, brittle and subsequently susceptible to failure. Since there is little change in the metal’s dimensions dealloying may go undetected, and failure can occur suddenly. Moreover, the porous structure is open to the penetration of liquids and gases deep into the metal, which can result in further degradation. Selective leaching often occurs in acidic environments.

2.6.1 Dezincification

There are essentially two forms of dezincification: uniform and localized. Uniform dezincification occurs when zinc is leached from a broad area of the brass surface, whereas, the localized form, also known as plug-type dezincification, penetrates deeply into the brass. In the localized form, the metal in the surrounding area is not significantly corroded by dezincification.

The widely accepted mechanism of dezincification involves the dissolution of brass where the zinc remains suspended in the corrosive solution while the copper is plated back on to the brass. Although dezincification can occur in the absence of oxygen, its presence accelerates the corrosion rate. Copper-zinc alloys with greater than 15% zinc are susceptible to dezincification. Figure 14 shows a photograph of corrosion by dezincification.

Figure 14 Dezincification of Brass Containing a High Zinc Content[13]

2.6.2 Susceptible Metals

Although brass with a relatively high zinc content is the most common alloy to experience the selective leaching form of corrosion, other metals and alloys, as shown in Table 14, are susceptible to this form of corrosion.

2.6.3 Managing Selective Leaching

Reducing the aggressive nature of the atmosphere by removing oxygen and avoiding stagnant solutions/debris buildup can prevent dezincification. Cathodic protection can also be used for prevention. However, the best alternative, economically, may be to use a more resistant material such as red brass, which only contains 15% Zn. Adding tin to brass also provides an improvement in the resistance to dezincification. Additionally, inhibiting elements, such as arsenic, antimony and phosphorous can be added in small amounts to the metal to provide further improvement. Avoiding the use of a copper metal containing a significant amount of zinc altogether may be necessary in systems exposed to severe dezincification environments.

Table 14 Combinations of Alloys and Environments Subject to Dealloying and Elements Preferentially Removed

Alloy	Environment	Element Removed
Brasses	Many waters, especially under stagnant conditions	Zinc (dezincification)
Gray Iron	Soils, many waters	Iron (graphitic corrosion)
Aluminum Bronzes	Hydrofluoric acid, acids containing chloride ions	Aluminum (dealuminification)
Silicon Bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin Bronzes	Hot brine or steam	Tin (destannification)
Copper Nickels	High heat flux and low water velocity (in refinery condenser tubes)	Nickel (denickelification)
Copper-Gold (single crystals)	Ferric chloride	Copper
Monels	Hydrofluoric and other acids	Copper in some acids, and nickel in others
Gold Alloys with Cu or Ag	Sulfide solutions, human saliva	Copper, silver
High-Nickel Alloys	Molten salts	Chromium, iron, molybdenum and tungsten
Medium- and High-Carbon Steels	Oxidizing atmospheres, hydrogen at high temperatures	Carbon (decarburization)
Iron-Chromium Alloys	High-temperature oxidizing atmospheres	Chromium, which forms a protective film
Nickel-Molybdenum Alloys	Oxygen at high temperature	Molybdenum

2.7 Erosion Corrosion

Erosion corrosion is a form of attack resulting from the interaction of an electrolytic solution in motion relative to a metal surface. It has typically been thought of as involving small solid particles dispersed within a liquid stream. The fluid motion causes wear and abrasion, increasing rates of corrosion over uniform (non-motion) corrosion under the same conditions. Erosion corrosion is evident in pipelines, cooling systems, valves, boiler systems, propellers, impellers, as well as numerous other components. Specialized types of erosion corrosion occur as a result of impingement and cavitation. Impingement refers to a directional change of the solution whereby a greater force is exhibited on a surface such as the outside curve of an elbow joint. Cavitation is the phenomenon of collapsing vapor bubbles which can cause surface damage if they repeatedly hit one particular location on a metal.

2.7.1 Factors Affecting Erosion Corrosion

All the factors that influence the resistance of material to erosion corrosion and their exact relationship are difficult to define. One property that factors in is hardness. In general harder materials resist erosion corrosion better, but there are some exceptions. Surface smoothness, fluid velocity, fluid density, angle of impact, and the general corrosion resistance of the material to the environment are other properties that factor in. Equation 9 predicts the erosion rate of metals using some of these factors. However, this prediction is only for erosion and does not include the added effects of corrosion. Erosion in a corrosive environment would be expected to occur at a higher rate.

$$\frac{\text{Erosion loss}}{\text{Quantity of impacting erodent}} = CF(\varphi)\frac{\rho v^{2}}{HV} \qquad \text{Equation 9}$$

where,

C is a system constant

φ is the angle of impact

ρ is the density of the erodent

ν is the erodent velocity

HV is the hardness of the metal

2.7.2 Managing Erosion Corrosion

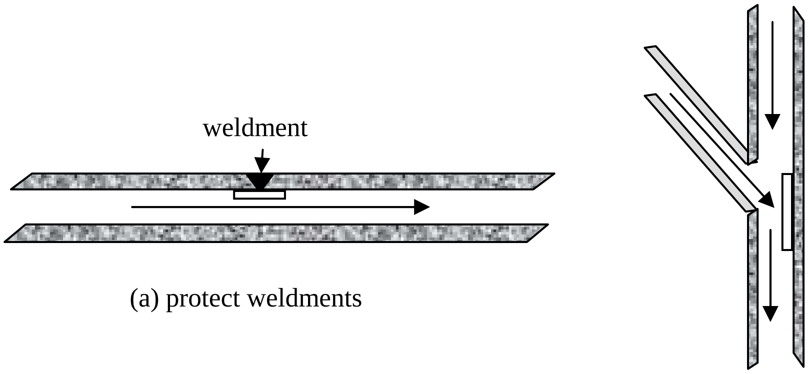
There are some design techniques that can be used to limit erosion corrosion as listed below with a couple methods depicted in Figure 15.

Avoid turbulent flow.

Add deflector plates where flow impinges on a wall.

Add plates to protect welded areas from the fluid stream.

Put piping of concentrate additions vertically into the center of a vessel.



(a) protect weldments

(a) protect impingement areas

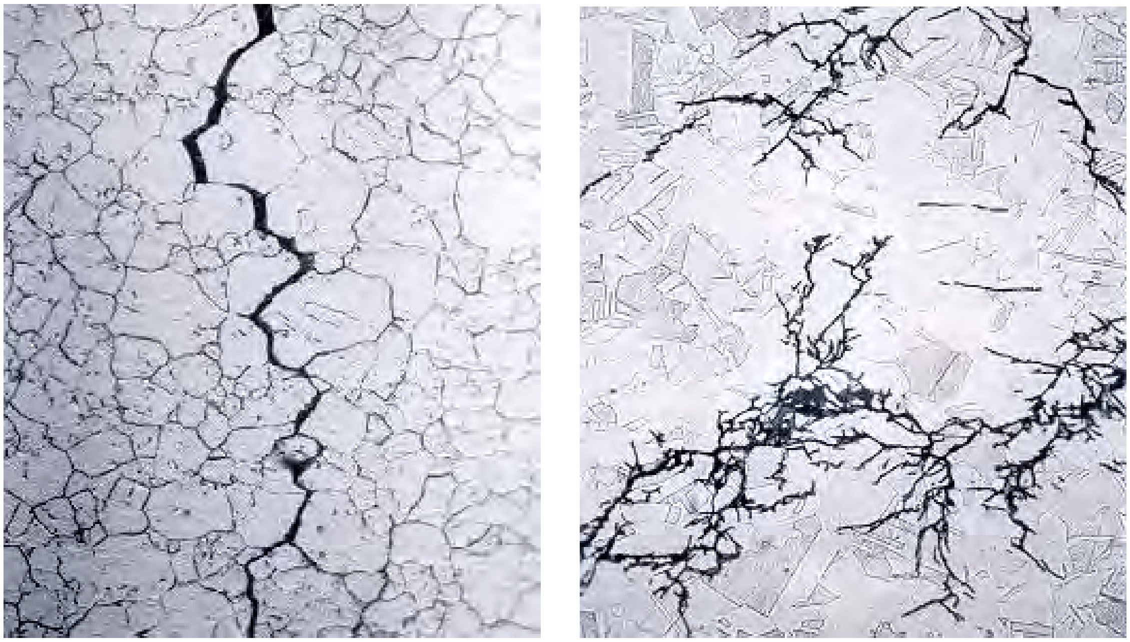
Figure 15 Techniques to Combat Erosion Corrosion

2.8 Stress-Corrosion Cracking

Stress corrosion is an environmentally induced cracking phenomenon that sometimes occurs when a metal is subjected to a tensile stress and a corrosive environment simultaneously. This is not to be confused with similar phenomena such as hydrogen embrittlement, in which the metal is embrittled by hydrogen, often resulting in the formation of cracks. Moreover, SCC is not defined as the cause of cracking that occurs when the surface of the metal is corroded resulting in the creation of a nucleating point for a crack. Rather, it is a synergistic effort of a corrosive agent and a modest, static stress. Another form of corrosion similar to SCC, although with a subtle difference, is corrosion fatigue, and is discussed in Section 2.9.1. The key difference is that SCC occurs with a static stress, while corrosion fatigue requires a dynamic or cyclic stress.

Stress corrosion cracking (SCC) is a process that takes place within the material, where the cracks propagate through the internal structure, usually leaving the surface unharmed. Furthermore, there are two main forms of SCC, intergranular and transgranular. For the intergranular form, the cracking progresses mostly along grain boundaries, whereas, in transgranular SCC, the cracking does not strictly adhere to the grain boundaries, instead it can penetrate grains. Most cracks tend to propagate in a direction that is perpendicular to the direction of applied stress. Aside from an applied mechanical stress, a residual, thermal, or welding stress along with the appropriate corrosive agent may also be sufficient to promote SCC. Pitting corrosion, especially in notch-sensitive metals, has been found to be one cause for the initiation of SCC.

SCC is a dangerous form of corrosion because it can be difficult to detect, and it can occur at stress levels which fall within the range that the metal is designed to handle. Furthermore, the mechanism of SCC is not well understood. There are a number of proposed mechanisms that attempt to explain the phenomenon of SCC, but none have done so with complete success. Figure 16 shows pictures of the two types of stress corrosion cracking.



(a) (b)

Figure 16 Pictures of Stress Corrosion Cracking, (a) Intergranular, (b) Transgranular[14]

2.8.1 Environmental Influence on SCC

Stress corrosion cracking is dependent on the environment based on a number of factors including temperature, solution, metallic structure and composition, and stress.[12] However, not all environments are equally potent to all metals; that is, specific metals are susceptible to specific chemical species, and some alloys are susceptible to SCC in one environment while others are more resistant.

Increasing the temperature of a system often works to accelerate the rate of SCC. The presence of chlorides or oxygen in the environment can also significantly influence the occurrence and rate of SCC. SCC is a concern in alloys that produce a surface film in certain environments, since the film may protect the alloy from other forms of corrosion, but not SCC. Some specific environments that can cause SCC of certain metals are listed in Table 15.

Table 15 Environments that May Cause Stress Corrosion of Metals[12]

Material	Environment
Aluminum alloys	NaCl-H_2O_2 solutions
	NaCl solutions
	Seawater
	Air, water vapor
Copper Alloys	Ammonia vapors and solutions
	Amines
	Water, water vapor
Gold Alloys	$FeCl_3$ solutions
	Acetic acid-salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	NaCl-K_2CrO_4 solutions
	Rural and coastal atmospheres
	Seawater
	Distilled water
Monel	Fused caustic soda
	Hydrofluoric acid
	Hydrofluorosilicic acid
Nickel	Fused caustic soda
Ordinary steels	NaOH solutions
	NaOH-Na_2SiO_2 solutions
	Calcium, ammonium, and sodium nitrate solutions
	Mixed acids (H_2SO_4-HNO_3)
	HCN solutions
	Acidic H_2S solutions
	Seawater
	Molten Na-Pb alloys
Stainless steels	Acid chloride solutions such as $MgCl_2$ and $BaCl_2$
	NaCl-H_2O_2 solutions
	Seawater
	H_2S
	NaOH-H_2S solutions
	Condensing steam from chloride waters
Titanium alloys	Red fuming nitric acid, seawater, N_2O_4, methanol-HCl

2.8.2 Managing Stress Corrosion Cracking

There are several methods that may be used to minimize the risk of SCC. Some of these methods include:

Choose a material that is resistant to SCC.

Employ proper design features for the anticipated forms of corrosion. Corrosion pits may produce crack initiation sites.

Minimize stresses including thermal stresses.

Environment modifications (pH, oxygen content).

Use surface treatments (shot peening, laser treatments) which increase the surface resistance to SCC.

Any barrier coatings will deter SCC as long as it remains intact.

Reduce exposure of end grains (i.e. end grains can act as initiation sites for cracking because of preferential corrosion and/or a local stress concentration).

2.9 Other Forms of Corrosion

Not all types of corrosion can be easily classified as one of the eight major forms of corrosion described in the preceding sections. Therefore, some of the less common or more unique forms of corrosion are described in the following sections. These forms of corrosion may, in some instances, be considered as a subgroup of one of the eight major forms.

2.9.1 Corrosion Fatigue

Corrosion fatigue is a decrease in fatigue strength due to the effects of corrosion. Corrosion fatigue cracking differs from SCC and hydrogen induced cracking in that the applied stresses are cyclic rather than static. Fatigue cracking is often characterized by “beach marks” or striation patterns which are perpendicular to the crack propagation direction, as shown in Figure 17. Both the stress required for crack initiation and propagation can be lower in corrosive environments. Factors influencing corrosion fatigue include material strength, fracture toughness, and environmental conditions. There are two primary material properties used to assess fatigue, the number of cycles to failure for an applied stress level or the crack growth per cycle for a stress intensity factor.

Figure 17 Characteristic Fatigue Striation Pattern[15]

2.9.1.1 Factors Affecting Corrosion Fatigue

The selection of materials for increased fracture toughness involves a trade-off with strength. Increased strength normally reduces fracture toughness and vice versa. One method to enhance fracture toughness while maintaining strength is reducing the metal's average grain size. Additionally, highly polished surfaces resist crack initiation better as do lower temperatures. There are a couple of surface treatments that may be used to induce residual compressive stresses, thereby increasing fatigue strength. They include shot peening, laser shock peening, and recently, low plasticity burnishing. The metals' particular susceptibility to environmental conditions, as always, is a factor.

2.9.1.2 Stress-Life (S-N) Data

One type of reported fatigue data is stress-life or S-N curves, which plot the stress amplitude versus the number of cycles to failure. This follows the empirical relationship

$$\frac{\Delta\sigma}{2} = \sigma'_f \left(2N_f\right)^b \qquad \text{Equation 10}$$

where,

$\Delta\sigma$ = change in stress

σ_f' = fatigue strength coefficient

N_f = number of cycles to failure

b = fatigue strength exponent

In a fully reversed, constant stress amplitude fatigue test, $\frac{\Delta\sigma}{2} = \sigma_a$, the stress amplitude.

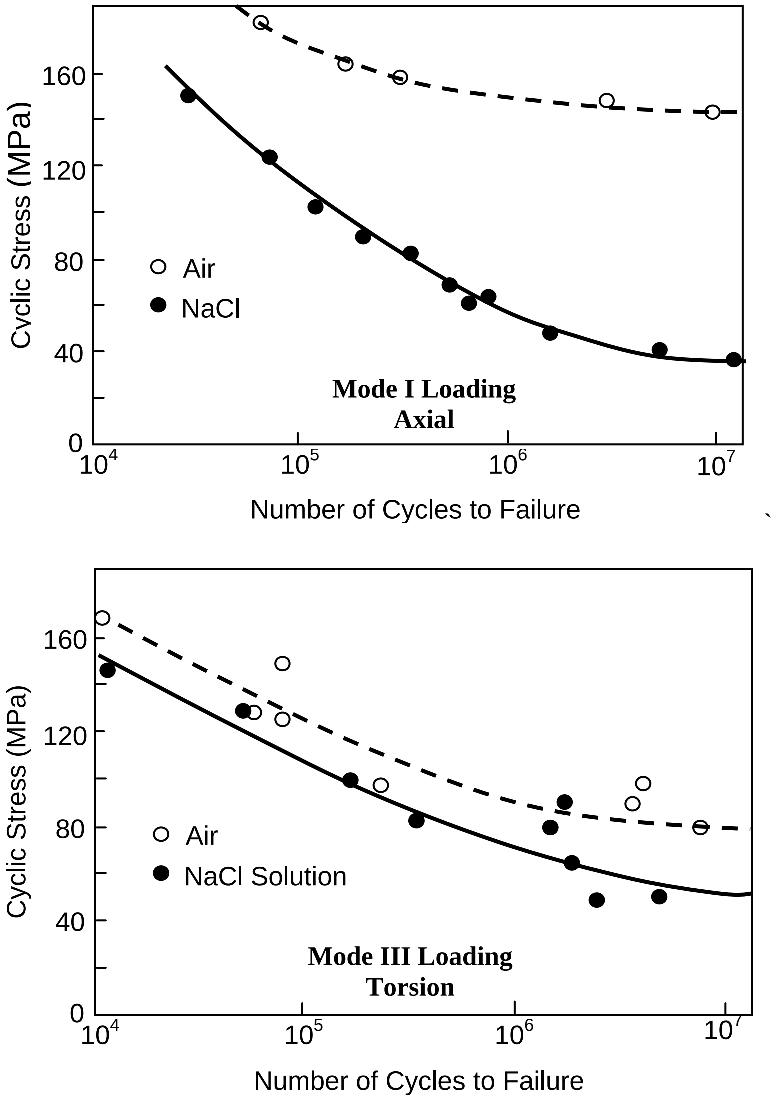


Figure 18 S-N Data for 7075-T6 in Air and NaCl Solution[16]

2.9.1.3 Fatigue Crack Growth Data

Information on fatigue can also be found in the form of crack growth plots. The relation in this case is

$$\frac{da}{dN} = C(\Delta K)^m$$

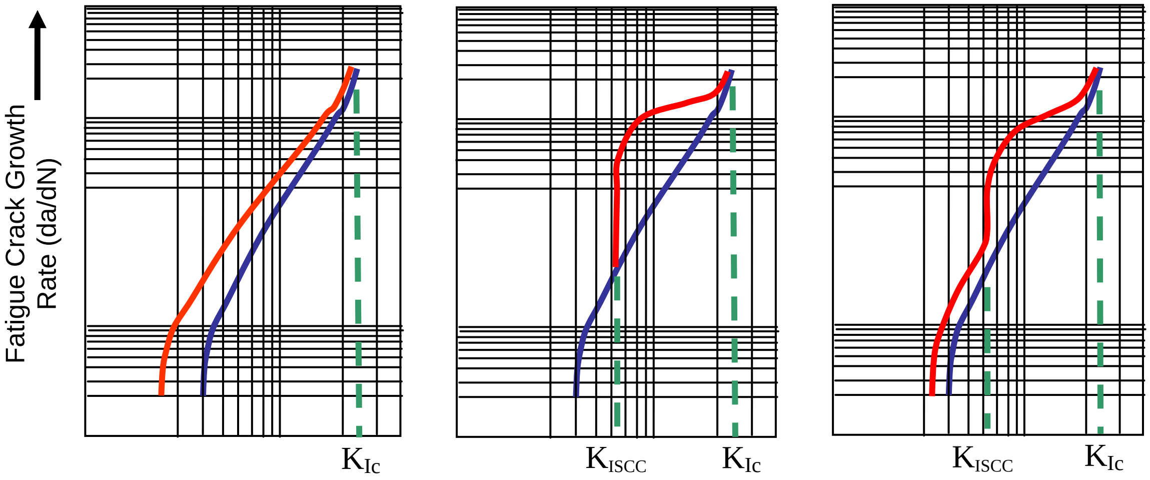
$$K = \sigma\sqrt{\pi a}$$

Equation 11

where,

a = one half crack length
N = number of cycles
K = stress intensity factor
σ = stress amplitude
C,m = empirical constants

There are three types of fatigue crack growth behavior as depicted in Figure 19. Type A exists for materials affected by the corrosive environment for crack initiation and crack growth. Type B behavior exists for materials where no environmental effect exists below the stress intensity threshold fro SCC. Type C is a combination of types A and B. Aluminum alloys in seawater follow type A behavior as can be seen in Figure 20.



Type A Type B Type C

Figure 19 Types of Fatigue Crack Growth Rates

2.9.1.4 Managing Corrosion Fatigue

Methods to deter corrosion fatigue include the following:

- Employ designs which minimize stresses to the components
- Choose heat treatments that reduce residual stresses
- Use surface treatments that enhance corrosion fatigue resistance such as shot peening or laser treatments
- Use barrier coatings or corrosion preventive compounds to block corrosive species from the metal.

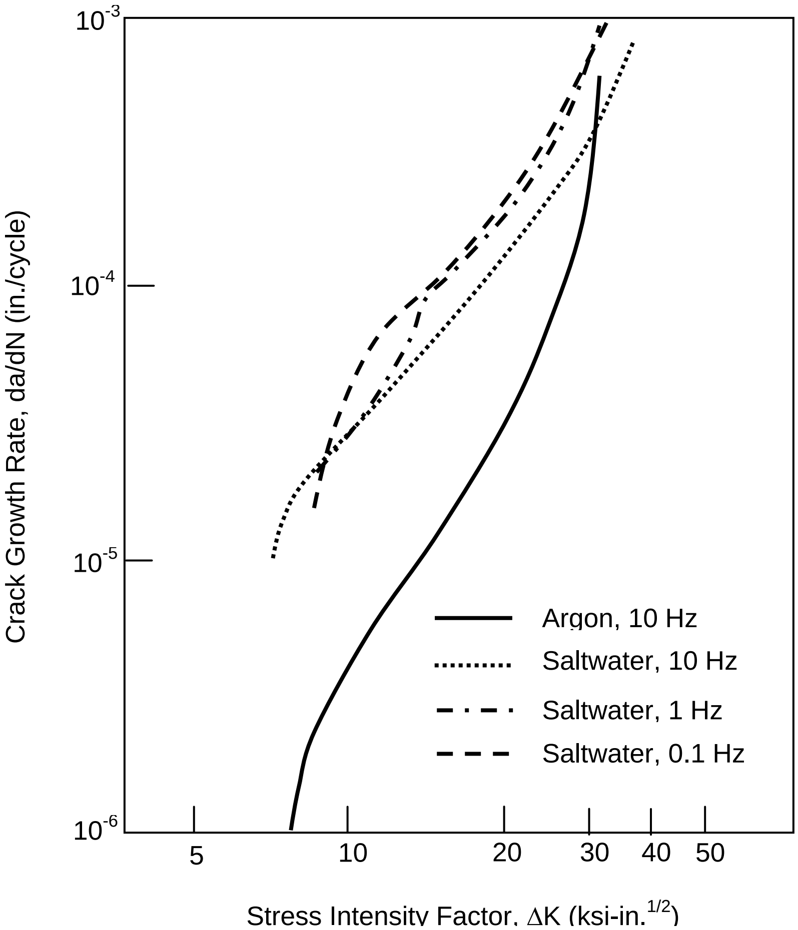


Figure 20 Crack Growth rates for 7075-T6[17]

2.9.2 Fretting Corrosion

Fretting corrosion occurs where two metals are in contact and there is a relatively small motion between the materials. It can be thought of as the combination of wear and a corrosive environment. This process usually presents itself in material interfaces not designed to be in motion with respect to each other. Typical applications that have produced fretting corrosion are motor shafts and electrical contacts. In the case of motor shafts, machinery vibration causes fretting and usually results in decreased fatigue life, known as fretting fatigue. Proper alignment of the rotating shafts is critical to reducing fretting fatigue failures. A second form of fretting corrosion appears in electrical contacts where thermal expansion and contraction cycles result in degradation of the contacting materials. Electrical contacts are most often coated with a noble metal, which are resistant to fretting corrosion. Cyclic motion, however, can cause wear and failure of the coating leaving the base metal vulnerable to fretting corrosion and other forms of attack. Once the base metal is exposed, the formation of highly resistive oxides occurs resulting in intermittent or open electrical circuits. Fretting corrosion is often undetected due to the nature of its existence in hidden material interfaces. The best way to mitigate fretting corrosion is to be knowledgeable of the typical material combinations and applications where it occurs and the methods used to combat it.

Factors contributing to fretting corrosion include contact conditions, environmental conditions, and materials properties.[18] These factors all interact to produce fretting corrosion or fretting fatigue, as represented in Figure 21.

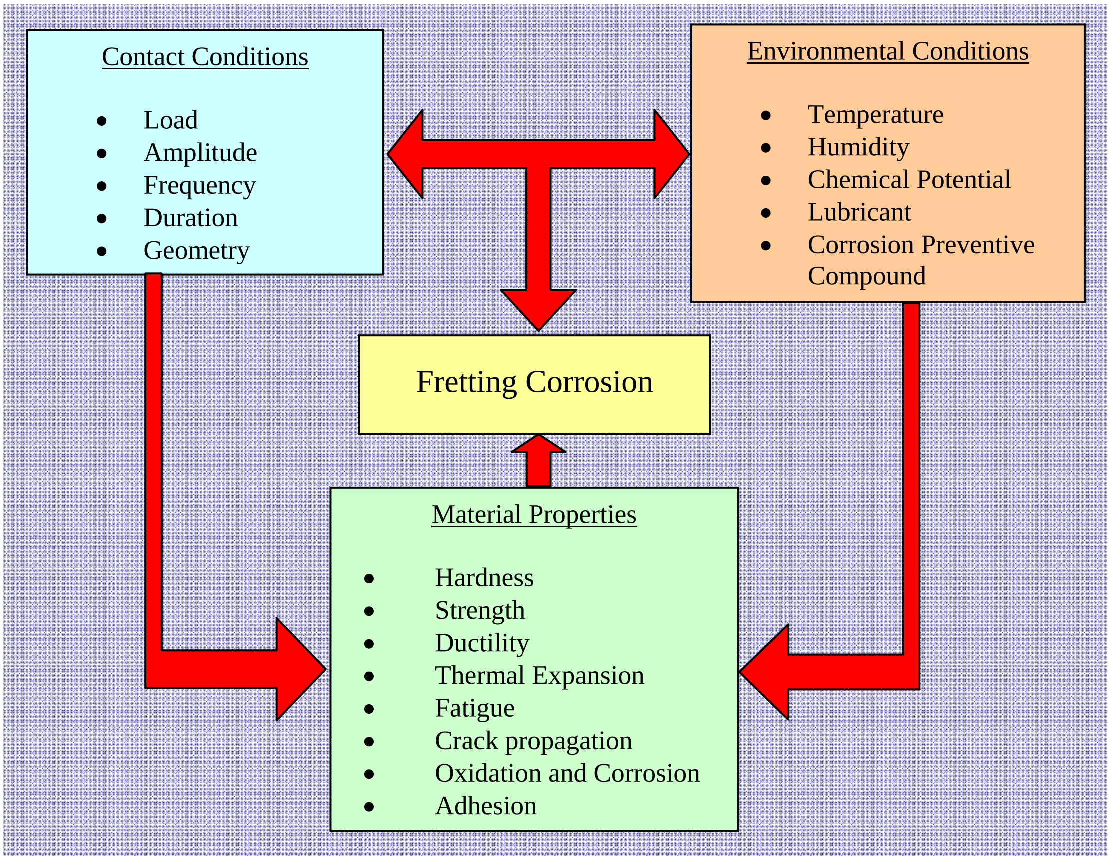


Figure 21 Contributing Factors to Fretting Corrosion[18]

2.9.2.1 Metals’ Susceptibilities to Fretting Corrosion

The susceptibilities of some material combinations to fretting are listed in Table 16.

2.9.2.2 Managing Fretting Corrosion

Methods used to reduce fretting corrosion include the following:

- Soft metal against hard metal contacts
- Roughen surface to reduce slippage
- Increase load to reduce relative motion
- Low viscosity fluids in combination with phosphate treated surfaces
- Increase surface hardness of contacting metals
- Use one metal with a low coefficient of friction
- Use corrosion preventive compounds on electrical contacts

Table 16 Resistance to Fretting Corrosion of Various Material Couples under Dry Conditions[19]

High Resistance	Medium Resistance	Low Resistance
Lead against Steel	Cadmium against Steel	Steel against Steel
Silver Plate against Steel	Zinc against Steel	Nickel against Steel
Silver Plate against Aluminum Plate	Copper Alloys against Steel	Aluminum against Steel
Steel with a conversion coating against Steel	Zinc against Aluminum	Antimony Plate against Steel
	Copper Plate against Aluminum	Tin against Steel
	Nickel Plate against Aluminum	Aluminum against Aluminum
	Iron Plate against Aluminum	Zinc-Plated Steel on Aluminum
	Silver Plate against Aluminum	Iron-Plated Steel against Aluminum

2.9.3 Hydrogen Damage

There are a number of different forms of hydrogen damage to metallic materials, resulting from the combined factors of hydrogen and residual or tensile stresses. Hydrogen damage can result in cracking, embrittlement, loss of ductility, blistering and flaking, and also microperforation.

2.9.3.1 Hydrogen Induced Cracking

Hydrogen induced cracking (HIC) refers to the cracking of a ductile alloy when under constant stress and where hydrogen gas is present. Hydrogen is absorbed into areas of high triaxial stress producing the observed damage.

2.9.3.2 Hydrogen Embrittlement

Hydrogen embrittlement is the brittle fracture of a ductile alloy during plastic deformation in a hydrogen gas containing environment.

2.9.3.3 Loss of Tensile Ductility

The loss of tensile ductility occurs with metals exposed to hydrogen which results in a significant reduction in elongation and reduction in area. It is most often observed in low strength alloys and has been witnessed in steels, stainless steels, aluminum alloys, nickel alloys, and titanium alloys.

2.9.3.4 High Temperature Hydrogen Attack

High pressure hydrogen will attack carbon and low-alloy steels at high temperatures. The hydrogen will diffuse into the metal and react with carbon resulting in the formation of methane. This in turn results in decarburization of the alloy and possibly cracks formation.

2.9.3.5 Blistering

Blistering occurs primarily in low strength metals. It is a result of atomic hydrogen diffusion into defect areas of the alloy. The monotonic atoms combine into gas molecules in voids within the metal. Then, the high pressure of H_2 entrapped within the metal causes the material to blister or rupture. This form of attack has been observed in low strength steels exposed to H_2S or when cleaned in pickling baths.

2.9.3.6 Shatter Cracks, Flaking, and Fish Eyes

These forms of hydrogen damage are similar to blistering and are seen primarily during processing. Hydrogen is more soluble at the melting temperatures of metals allowing it to enter defect areas. The decreased solubility of hydrogen when cooled then produces the damage features.

2.9.3.7 Microperforation

Microperforation has been seen in steels in a high pressure hydrogen and room temperature environment. The hydrogen produces fissures in steel alloys such that gases and liquids can permeate the material.

2.9.3.8 Degradation in Flow Properties

An increase in creep rates occurs in iron alloys and steels under ambient conditions in hydrogen environments, and in several alloys at elevated temperatures.

2.9.3.9 Hydride Formation

The precipitation of metal hydride phases in magnesium, tantalum, niobium, vanadium, uranium, zirconium, titanium, and their alloys, in the presence of hydrogen produces a degradation of mechanical properties and cracking.

2.9.3.10 Metals' Susceptible to Hydrogen Damage

Table 17 lists susceptible metals to the various types of hydrogen attack..

Table 17 Metals' Susceptibilities to Hydrogen Damage[20]

Hydrogen Induced Cracking	**Hydrogen Embrittlement**	**Loss in Tensile Ductility**	**High Temperature Hydrogen Attack**	**Blistering**
Steels Nickel-alloys metastable stainless steel titanium-alloys	Carbon and low-alloy steels	Steels nickel-alloys Be-Cu bronze Aluminum-alloys	Carbon and low-alloy steels	Steels Copper Aluminum

Shatter Cracks, Flakes, Fisheyes	**Micro-Perforation**	**Degradation in Flow Properties**	**Metal Hydride Formation**
Steels (forgings and castings)	Steels (compressors)	Iron Steels Nickel-alloys	V Nb Ta Ti Zr U

2.9.3.11 Managing Hydrogen Damage

Methods to deter hydrogen damage are to:

- Limit hydrogen introduced into the metal during processing.
- Limit hydrogen in the operating environment.
- Structural designs to reduce stresses (below threshold for subcritical crack growth in a given environment)
- Use barrier coatings
- Use low hydrogen welding rods

2.9.4 High Temperature Corrosion

High temperature corrosion is an attack on a metal at elevated temperatures in a gaseous environment rather than in a liquid. The most prominent high temperature corrosion reaction is oxidation, although sulfidation and carburization may also occur. Most metals exposed to a high temperature oxidative environment will produce an oxide scale layer which protects the metal from further corrosion. It uniformly covers the entire surface. Ionic transport through the scale is the rate controlling process. The corrosion rate will normally decrease after the scale is produced following a parabolic relationship with time. In severe corrosive environments where a protective scale cannot form, the corrosion rate will follow a more linear path.

Sulfidation occurs when the concentration of sulfur gas is high enough such a sulfide layer forms. Sulfides are less stable and grow much faster than oxides. As a result, sulfides react more readily with metals and penetrate deeper into the metal. They are replaced with the more stable oxides as reactions continue to occur. It is preferred in such environments to have a protective oxide scale first produced, which then protects the metal against subsequent sulfidation.

Hot corrosion is a term describing the high temperature attack of gas turbine engine components in the path of hot gases. It is a sulfidation process involving the formation of condensed salts containing sodium sulfate and/or potassium sulfate. Increasing the chromium content in the metal alloys improves the corrosion resistance but also results in decreased strength.

Carburization is a rare form of high temperature corrosion where carbon atoms are absorbed into a metals' surface. It only occurs in environments with a very low oxygen partial pressure. Austenitic stainless steels are susceptible under such conditions due to the high solubility of carbon in austenite. Alloying studies to reduce carburization have shown that silicon, niobium, tungsten, titanium, and the rare earth metals increase resistance. Elements which increase damage include lead, molybdenum, boron, cobalt, and zirconium.

2.9.4.1 Metals' Susceptible to High Temperature Corrosion

Although high temperature corrosion testing, especially on superalloy materials for gas turbine applications, has been conducted, no qualitative relationship has been determined. Materials are selected for corrosion resistance dependent upon their comparative rates of attack from tests and from field experience.

2.9.4.2 Managing High Temperature Corrosion

Methods to reduce high temperature corrosion include:

- Proper metal selection.
- Change in operating conditions.
- Structural designs to limit corrosion.
- High temperature barrier coatings (ceramics)

2.9.5 Exfoliation

Exfoliation corrosion is considered a form of intergranular corrosion that attacks metals which have been mechanically deformed, primarily by extrusion or rolling, producing elongated grains directionally aligned. Most often, the attack is initiated at exposed endgrains, as has been the case with aircraft skins around fasteners see Figure 22. This form of corrosion is most evident in some of the aluminum alloys and is shown in Figure 23. Metals susceptible to exfoliation corrosion are aggressively attacked in environments corrosive to that particular metal. As an example, AA 2024-T4 is known to perform well in urban type environments, but is severely attacked in marine environments.

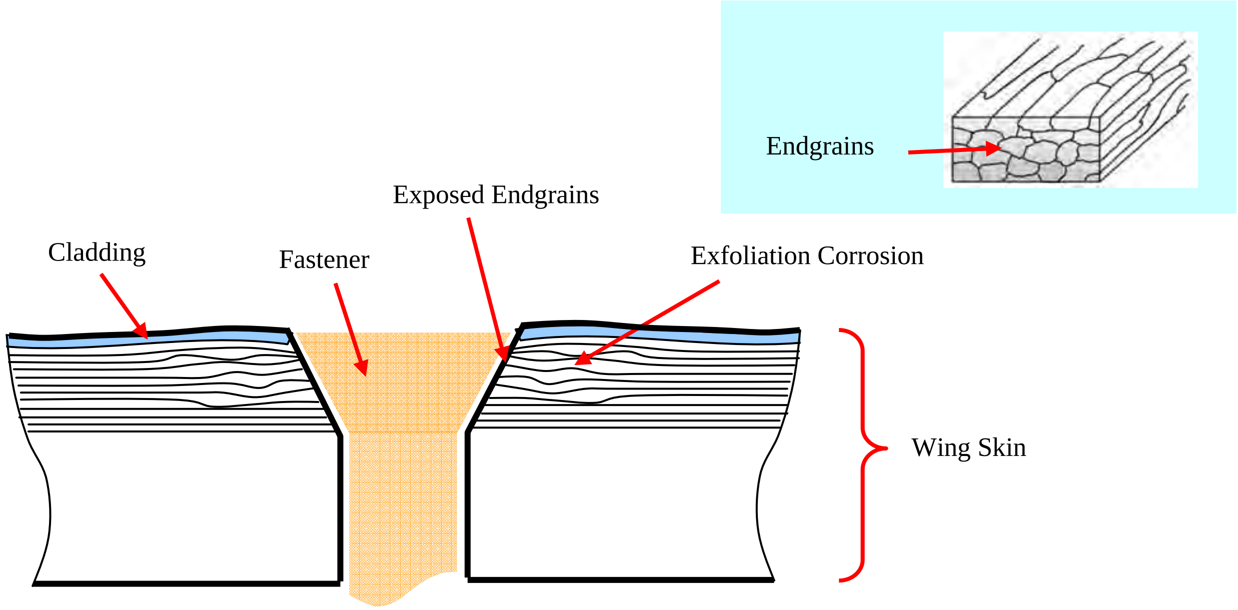


Figure 22 Exfoliation Corrosion Initiated at Endgrains

Figure 23 Exfoliation of an Aluminum Alloy in a Marine Environment[2]

2.9.5.1 Managing Exfoliation Corrosion

As with intergranular corrosion, the proper selection of alloy and heat treatment to avoid precipitation at grain boundaries is the primary method to combat exfoliation. Reducing the area of endgrain surfaces will limit the initiation of attack, as well as the use of barrier coatings.

2.9.6 Microbiological Corrosion

MIC is actually not a form of corrosion, but rather is a process that can influence and even initiate corrosion. It can accelerate most forms of corrosion; including uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, intergranular corrosion, dealloying, and stress corrosion cracking. In fact, if unfamiliar with MIC, some corrosion problems may be misdiagnosed as conventional chloride induced corrosion. One prominent indicator of MIC is a higher rate of attack than one would normally expect. MIC can affect numerous systems, and can be found virtually anyplace where aqueous environments exist. It is not exclusive to water-based systems, occurring in fuel and lubrication systems as well. Table 18 lists applications where MIC has been found to be prominent while Figure 24 shows one such location.

Table 18 Systems with Persistent MIC Problems[21]

Application/System	Problem Components/Areas	Microorganisms
Pipelines/storage tanks (water, wastewater, gas, oil)	Stagnant areas in the interior Exterior of buried pipelines and tanks, especially in wet clay environments.	Aerobic and anaerobic acid producers Sulfur reducing bacteria Iron/manganese oxidizing bacteria Sulfur oxidizing bacteria
Cooling systems	Cooling towers Heat exchangers Storage tanks	Aerobic and anaerobic bacteria Metal oxidizing bacteria Slime forming bacteria Algae Fungi
Docks, piers, and other aquatic structures	Splash zone Just below low tide	Sulfate reducing bacteria
Vehicle fuel tanks	Stagnant areas	Fungi
Power generation plants	Heat exchangers Condensers	Aerobic and anaerobic bacteria Sulfate reducing bacteria Metal oxidizing bacteria
Fire sprinkler systems	Stagnant areas	Anaerobic bacteria Sulfate reducing bacteria

Figure 24 Interior of a Ballast Tank on a Navy Ship[22]

2.9.6.1 Types of Microorganisms

The types of microorganisms with species attributable to MIC include algae, fungi, and bacteria.[23] Algae produce oxygen in the presence of light (photosynthesis) and consume oxygen in darkness. They can be found in most any aquatic environment ranging from freshwater to concentrated salt water. The availability of oxygen has been found to be a major factor in corrosion of metals in saltwater environments. Algae flourish in temperatures of 32 - 104ºF and pH levels of 5.5 – 9.0. Fungi consist of mycelium structures which are an outgrowth of a single cell or spore. Mycelia are immobile, but can grow to reach macroscopic dimensions. Fungi are most often found in soils, although some species are capable of living in water environments. They metabolize organic matter, producing organic acids.

Bacteria are generally classified by their affinity to oxygen. Aerobic species require oxygen to metabolize while anaerobic species require a lack of oxygen to do the same. Facultative bacteria can grow in either environment, although they prefer aerobic conditions. Microaerophilic bacteria require low concentrations of oxygen. Oddly enough, aerobic and anaerobic organisms have often been found to co-exist in the same location. This is because aerobic species deplete the immediate surroundings of oxygen creating an ideal environment for anaerobes. Bacteria are further classified by shape into spherical (bacillus), rod (coccus), comma (vibrio), and filamentous (myces) species. Figure 25 is an example of rod-shaped bacteria observed using transmission electron microscopy.

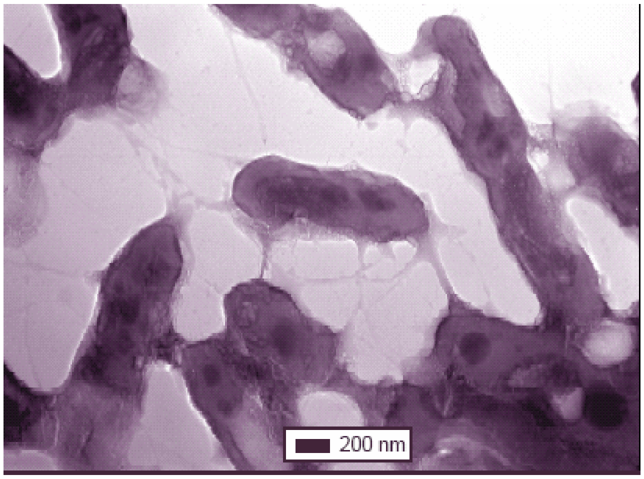


Figure 25 Rod-Shaped Pseudomonas Bacteria[24]

Microorganisms in the planktonic state refer to those organisms floating freely in the aqueous environment or in air. They can resist harsh environments including acids, alcohols, and disinfectants, drying, freezing, and boiling.[25] Some spores have the ability to last hundreds of years and then germinate once favorable conditions exist. Microorganisms in the sessile state are those that have attached themselves to a surface and have developed a protective membrane, collectively called a biofilm. Microorganisms have the ability to reproduce quickly; some doubling in as little as 18 minutes. When left untreated, they can rapidly colonize in stagnant aqueous environments, potentially introducing a highly active corrosion cell.

2.9.6.2 Microorganisms that Accelerate Corrosion

Once a microorganism forms a biofilm on a material’s surface, a microenvironment is created that is dramatically different from the bulk surroundings. Changes in pH, dissolved oxygen, and organic and inorganic compounds in the microenvironment can lead to electrochemical reactions which increase corrosion rates. Microorganisms may also produce hydrogen which can promote hydrogen damage in metals. Most microorganisms form an extracellular membrane which protects the organism from toxic chemicals and allows nutrients to filter through.[25] Biofilms are resistant to many chemicals by virtue of their protective membrane and ability to breakdown numerous compounds. They are significantly more resistant to biocides (chemicals used to kill microorganisms) than planktonic organisms. Some bacteria even metabolize corrosion inhibitors, such as aliphatic amines and nitrites, decreasing the inhibitor’s ability to control corrosion. Microorganisms’ metabolic reactions attributable to metallic corrosion involve sulfide production, acid production, ammonia production, metal deposition, and metal oxidation and reduction. Several groups of microorganisms have been attributed to MIC, and are listed below.[26] Following these recognized forms; Table 19 lists some specific microorganisms within these categories, along with their characteristics.

Sulfate Reducing Bacteria (SRB)

Sulfate reducing bacteria are anaerobic microorganisms that have been found to be involved with numerous MIC problems affecting a variety of systems and alloys. They can survive in an aerobic environment for a period of time until finding a compatible environment. SRB chemically reduce sulfates to sulfides, producing compounds such as hydrogen sulfide (H_2S), or iron sulfide (Fe_2S) in the case of ferrous metals. The most common strains exist in the temperature range of 25 - 35ºC, although there are some that can function well at temperatures of 60ºC. They can be detected through the presence of black precipitates in the liquid media or deposited on surfaces, as well as a characteristic hydrogen sulfide smell.

Sulfur/Sulfide Oxidizing Bacteria (SOB)

Sulfide oxidizing bacteria are an aerobic species which oxidize sulfide or elemental sulfur into sulfates. Some species oxidize sulfur into sulfuric acid leading to a highly acidic microenvironment. The high acidity has been associated with the degradation of coating materials in a number of applications. They are primarily found in mineral deposits and are common in wastewater systems. SRB is often found in conjunction with SOB.

Iron/Manganese Oxidizing Bacteria

Iron and manganese oxidizing bacteria have been found in conjunction with MIC, and are typically located over corrosion pits on steels. Some species are known to accumulate iron or manganese compounds resulting from the oxidation process. The higher concentration of manganese in biofilms has been attributed to corrosion of ferrous alloys including pitting of stainless steels in treated water systems. Iron tubercles have also been observed to form as a result of the oxidation process (Figure 26).

Table 19 Common Microorganisms Found in Conjunction with MIC[27]

	Genus or Species	pH	Temperature (ºF)	Oxygen Requirement	Metals Affected	Metabolic Process
Bacteria	Desulfovibrio	4-8	50-105	Anaerobic	Iron and steel, stainless steels, aluminum, zinc, copper alloys	Use hydrogen in reducing SO_4^{2-} to S^{2-} and H_2S; promote formation of sulfide films
	Desulfotomaculum	6-8	50-105 (some at 115-165)	Anaerobic	Iron and steel, stainless steels	Reduce SO_4^{2-} to S^{2-} and H_2S
	Desulfomonas	-	50-105	Anaerobic	Iron and steel	Reduce SO_4^{2-} to S^{2-} and H_2S.
	Acidthiobacillus thiooxidans	0.5-8	50-105	Aerobic	Iron and steel, copper alloys, concrete	Oxidizes sulfur and sulfides to form H_2SO_4; damages protective coatings
	Acidithiobacillus ferrooxidans	1-7	50-105	Aerobic	Iron and steel	Oxidizes ferrous (Fe^{2+}) to ferric (Fe^{3+})
	Gallionella	7-10	70-105	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous to ferric ions and manganous (Mn^{2+}) to manganic (Mn^{3+}) ions; promotes tubercule formation
	Siderocapsa	-	-	Microaerophilic	Iron and carbon steel	Oxidizes iron
	Leptothrix	6.5-9	50-95	Aerobic	Iron and steel	Oxidizes ferrous to ferric ions and manganous to manganic ions
	Sphaerotilus	7-10	70-105	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous to ferric ions and manganous to manganic ions; promotes tubercule formation
	Sphaerotilus natans	-	-	-	Aluminum alloys	-
	Pseudomonas	4-9	70-105	Aerobic	Iron and steel, stainless steels	Some strains reduce Fe^{3+} to Fe^{2+}
	Pseudomonas aeruginosa	4-8	70-105	Aerobic	Aluminum alloys	-
Fungi	Cladosporium resinae	3-7	50-115 (best at 85-95)	-	Aluminum alloys	Produces organic acids when metabolizing certain fuel constituents

Figure 26 Tubercles as a Result of MIC (courtesy of Metallurgical Technologies, Inc.) [28]

Slime Forming Bacteria

Slime forming bacteria are aerobic organisms which develop polysaccharide “slime” on the exterior of cells. The slime controls permeation of nutrients to the cells and may breakdown various substances, including biocides. Slime formers have been responsible for the decreased performance of heat exchangers as well as clogging of fuel lines and filters. They can prevent oxygen from reaching the underlying metal surface, creating an environment suitable for anaerobic organisms.

Organic Acid Producing Bacteria

Some anaerobic organisms also produce organic acids. These bacteria are more apt to be found in closed systems including gas transmission lines and sometimes closed water systems.

Acid Producing Fungi

Some fungi produce organic acids which attack iron and aluminum alloys. Like slime formers, they can create environments suitable for anaerobic species. These organisms have been attributed to the widespread corrosion problems observed in aluminum fuel tanks in aircraft.

2.9.6.3 Metals Affected by MIC

Since MIC is a mechanism that accelerates corrosion, it should be expected to occur more often in metal alloys with susceptibilities to the various forms of corrosion, and in environments conducive to biological activity. Metals used in the applications listed in Table 1, and thus exposed to microbial activity and the potential of MIC, include mild steels, stainless steels, copper alloys, nickel alloys and titanium alloys. In general, mild steels can exhibit everything from uniform corrosion to environmentally assisted cracking, while the remaining alloys usually only show localized forms. Mild steels, stainless steels, aluminum, copper, and nickel alloys all have shown effects of MIC, while titanium alloys have been found to be virtually resistant to MIC under ambient conditions.

Mild Steels

MIC problems have been widely documented in piping systems, storage tanks, cooling towers, and aquatic structures. Mild steels are widely used in these applications due to their low cost, but are one of the most readily corroded metals. Mild steels are normally coated for corrosion protection, while cathodic protection may also be used for select applications. Galvanization (zinc coating) is commonly used to protect steel in atmospheric environments. Bituminous coal tar and asphalt dip coatings are often used on the exterior of buried pipelines and tanks, while polymeric coatings are used for atmospheric and water environments. However, biofilms tend to form at flaws in the coating surfaces. Furthermore, acid producing microorganisms have been found to dissolve zinc and some polymeric coatings.[29] Numerous cases have also been documented where microorganisms caused debonding of coatings from the underlying metal. Underneath the delaminated coating in turn, creates an ideal environment for further microbial growth.

Poor quality water systems and components with areas that accumulate stagnant water/debris are prone to MIC. In some extreme cases, untreated water left stagnant within mild steel piping has caused uniform corrosion throughout the low lying areas. This has been seen to occur in underground pipes that have been left unused for periods of time.[29] Many power plant piping failures have been found to be the result of introducing untreated water into a system. SRB has been the primary culprit in such cases. A change to a more corrosion resistant material is not always the answer when it comes to solving MIC problems. For example, an upgrade from carbon steel to stainless steel in a nuclear power plant caused a change in MIC problems that in some instances were even more severe. SRB has also been found in conjunction with underdeposit corrosion occurring in cooling towers. Wet soils containing clay have played a major role in the occurrence of underground MIC problems. Under such conditions, the exterior of underground piping and storage tanks have experienced coating delamination and corrosion as a result of biofilm growth.

Stainless Steels

Stainless steels have suffered MIC problems in the same type of scenarios as mild steels - primarily in locations where water accumulates. There are two notable problems that have surfaced with stainless steel MIC. One is an accelerated corrosion rate, primarily through pitting or crevice corrosion that occurs in low lying areas, joints, and corner locations. Stainless steel tanks and piping systems are sometimes hydrotested subsequent to manufacture and prior to field use. Several cases of severe MIC have been documented whereby hydrotesting using well water was performed, and the product was then stored for a period of time before being placed into service.[29] The tanks and piping were not adequately dried, nor was a biocide used to deter biofilm growth. In one particular case, a 304 stainless steel pipeline for freshwater service, failed 15 months after being hydrotested.[30] A second MIC problem discovered with stainless steels occurs adjacent to weldments. Microorganisms readily attack areas around welds due to the inhomogeneous nature of the region. In one case, perforation occurred in a 0.2 inch diameter 316L stainless steel pipe adjacent to a welded seam after four months in service under intermittent flow conditions.[31] Stainless steels containing 6% molybdenum or greater, have been found to be virtually resistant to MIC.[29]

Aluminum Alloys

The major applications where MIC has attacked aluminum alloys have been in fuel storage tanks and aircraft fuel tanks.[29] MIC problems exist in the low-lying areas of tanks and at water–fuel interfaces. Contaminants in fuels, such as surfactants and water soluble salts, have largely contributed to the formation of biofilms in these systems. Fungi and bacteria have been found to be the main culprits. Cladosporium resinae, a fungus, has widely been attributed to corrosion of aircraft fuel tanks. Its presence decreases the pH to around 3-4, which can attack the protective coatings and underlying metal. Pseudomonas aeruginosa and Candida species are also likely to be found in conjunction with MIC of aluminum fuel tanks.

Additionally, heavy fungal growth on interior surfaces of helicopters has occurred subsequent to depot maintenance and prior to returned field use.[32] Fungal growth had been reported in passenger areas of the H-53 helicopter and was therefore slated for cleaning during refurbishment. Fungi could be found on virtually all interior surfaces of the helicopter. The surfaces were cleaned with 100% isopropanol, treated with a biocide, followed by application of a corrosion preventive compound. The procedure removed most of the microorganisms present and was effective at killing spores. However, some biofilms remained, which rapidly reproduced before the aircraft was even returned to service.

Copper Alloys

Copper alloys find use in seawater piping systems and heat exchangers, which are susceptible to MIC. Microbial products that can be harmful to copper alloys include CO_2, H_2S, NH_3, organic and inorganic acids, and sulfides.[29] MIC observed in copper alloys includes pitting corrosion, dealloying and stress-corrosion cracking. Higher alloying content in copper usually results in a lower corrosion resistance. Although MIC has been found in both, more problems have been documented with 70/30 than with 90/10 Cu/Ni alloys. MIC has also been documented in Admiralty brass (Cu-30Zn-1Sn), aluminum brass (Cu-20Zn-2Al), and aluminum bronze (Cu-7Al-2.5Fe). Ammonia and sulfides have gained considerable attention as compounds that are corrosive to copper alloys. Admiralty brass tubes have been found to suffer stress-corrosion cracking in the presence of ammonia. Seawater that is high in sulfide content, has caused pitting and stress-corrosion cracking in copper alloys. SRB has also been known to attack copper alloys causing dealloying of nickel or zinc in some cases.

Nickel Alloys

Nickel alloys are used in high velocity water environments including evaporators, heat exchangers, pumps, valves, and turbines blades, as they generally have a higher resistance to erosive wear than copper alloys.[29] However, some nickel alloys are susceptible to pitting and crevice attack under stagnant water conditions, so that downtime and unused periods can lead to potential MIC problems. Monel 400 (66.5Ni-31.5Cu-1.25Fe) has been found to be susceptible to underdeposit MIC. Pitting corrosion, intergranular corrosion, and dealloying of nickel have all been observed with this alloy in the presence of SRB. Ni-Cr alloys have been found to be virtually resistant to MIC.

2.9.6.4 Monitoring/Detection Methods

Early detection of potential MIC is crucial to the prevention of equipment failure and extensive maintenance. The most common detection methods involve sampling bulk liquids from within the system and monitoring physical, chemical, and biological characteristics. The goal is to identify favorable conditions for biofilm formation and growth, so that the internal environment may be adjusted as appropriate. Visual inspections of accessible areas should also be performed on a routine basis. Additional methods that may be utilized include coupon monitoring, electrochemical sensor and biosensor techniques.

Monitoring equipment is available for measuring a number of properties of the bulk system. A common practice has been to monitor temperature, pH, conductivity, and total dissolved solids directly from the operating system, while taking samples for portable or laboratory testing methods to evaluate dissolved gases, bacteria counts, and for bacteria identification.[21] Bacteria counting, via cultured growth, may be helpful, but strict conditions must be followed to produce meaningful results. The most important factor in bacterial counts is observing changes in trends rather than in actual numbers. Consistency is crucial where deviations in sample location, temperature, growing media, growth time, and even changes in technicians can affect results. A strict schedule must also be maintained. Changes in bacteria counts are used to adjust biocide usage and may also be indicative of biofilm growth in the case of differences in counts across a system. Bacteria cultures can also be used to identify specific species present (Figure 27). Direct bacteria counts can be performed using a microscope to inspect bacteria which have been placed onto a slide and may also be stained for viewing, as shown in Figure 28. Visual inspections should be performed on exposed surfaces where algae and fungal growth can occur, and on surfaces exposed during maintenance procedures. The presence of SRB can be detected by observing black particles in the liquid media and/or deposited on surfaces, a result of iron sulfide and/or copper sulfide formation, or a distinct hydrogen sulfide odor.[33] Fluorescent dyes can be used to enhance visual detection, as biofilms absorb some of the dye whereby an ultraviolet light is then used to expose the microorganisms.

Figure 27 Bacteria Culture[34]

Figure 28 Inspection of Bacteria on a Stained Microscope Slide[35]

Coupons have been found quite useful in detecting MIC, especially when used in conjunction with additional monitoring techniques. Coupons are small metal samples placed within the system and periodically extracted to measure corrosion rates through weight loss and possibly to collect microorganisms from biofilms on the coupon for identification. Proper placement of the coupons within the system plays a key role in MIC monitoring and detection. Coupons should be placed in locations where MIC is likely to occur. Electrochemical sensing techniques, such as electrical impedance spectroscopy and electrochemical noise, are other means of detecting MIC. Electrochemical sensors detect characteristics of corrosion reactions, such as changes in electrical conductivity. As with coupons, strategic placement of the sensors in the systems is crucial to detecting MIC.

One type of sensor designed specifically for biofilm detection uses a probe that attracts microbial growth.[36] Utilizing experience of the electrochemical conditions under which biofilms occur, probes have been developed that replicate these preferred conditions. The sensor then alerts operators when biofilm activity is present. Sensors should ideally be placed in areas where biofilm growth is more likely. Another method that may be used specifically to detect microorganisms in water systems is the use of fluorogenic bioreporters.[37] These are compounds (dyes) that change their fluorescence upon interaction with microorganisms. Activity is determined by the ratio of fluorescence of the reacted dye, extracted from the system or measured in-service, to the unreacted dye. The ratio increases with biological activity and can be used to effectively regulate the use of biocides. This method however, does not distinguish between planktonic and sessile organisms. Thus, problems could be growing in the system without being detected.

2.9.6.5 Mitigation Methods

Clearly, the best way to prevent MIC is to prevent the growth of biofilms altogether. Once a biofilm has formed, it is more resistant to biocides, and can rapidly grow if not completely removed. The emphasis is placed on cleanliness and incorporating established corrosion prevention and control techniques for the various metal alloys and forms of corrosion. Monitoring and detection of microorganisms will effectively guide preventive maintenance procedures.

Cleanliness of systems involves monitoring the quality of water, fuel, or lubricants present in the system. This includes water content in fuel and lubrication systems. Water should be monitored and removed when the content becomes too high. All fluids should be monitored for solid particles and filtered to prevent particle contamination. Contaminants increase the likelihood of biofilms through their use as nutrients. Bacterial counts and biosensing help to adjust the level of biocides introduced to the system. Biocides are widely used and are effective at killing planktonic microorganisms. The cost of biocides is significant however, and along with their toxicity, effective management of biocide use can reduce costs and damaging effects on the environment. Cleanliness also includes scheduled cleaning of exterior components where any debris accumulation has occurred. Non-abrasive cleaning methods are preferred as to not damage coatings. Inspection/cleaning should also be performed on normally inaccessible components that are exposed during maintenance/repair procedures. Designing systems that minimize MIC prone areas and providing accessibility for maintenance as appropriate helps to promote system cleanliness. This involves eliminating stagnant and low-flow areas, minimizing crevices and welds, incorporating filtration, drains, and access ports for treatments, monitoring/sampling, and cleaning.

Established corrosion prevention and control methods that are employed to protect metals from the various forms of corrosion will also help mitigate MIC. This includes designing systems to minimize stagnant water conditions, proper base material and coating selection, possible cathodic protection, sealing crevices and around fasteners, using gaskets to minimize galvanic corrosion, proper heat treatments, and post weld treatments. For underground structures, providing ample drainage by backfilling with gravel or sand will help prevent MIC. In some cases, a change to an alternate material such as PVC piping has greatly reduced underground pipeline corrosion problems. Coatings can be formulated with biocides, though such coatings are not generally used on the interior of systems. Smooth surface finishes with minimized defects are preferred. Research into alternative coatings that may deter MIC has shown polydimethylsiloxane coated 4340 steel to have favorable results.[38] In laboratory tests, the silicone compounds significantly reduced MIC of the steel in a 0.6M NaCl solution over a two year period.

2.9.7 Liquid and Solid Metal Embrittlement

Liquid metal embrittlement (LME) is a brittle fracture of a normally ductile metal when in contact with a liquid metal and stressed in tension. There is no change in the yield behavior of the metal; however, fracture can occur well below the metal’s yield strength. The stress required for crack propagation is lower than that for crack initiation. As a result, the crack initiation and propagation are seen instantaneously with a complete fracture of the metal. Fracture surfaces are usually completely covered with the liquid metal. The movement of the liquid metal into the crack is attributed to the rapid crack propagation through the material. In some cases, solid metals at temperatures in the vicinity of their melting points have also been shown to cause embrittlement. This phenomenon has been termed solid metal induced embrittlement (SMIE). Table 20 lists LME interactions of various metals.

Table 20 Liquid Metal Embrittlement Observed in Various Metals[20]

Liquid	**Bi**	**Na**	**Pb**	**Sn**	**Ga**	**Hg**	**In**	**Li**
Solid	Al Al alloy Cu Cu alloy Ge	Al Alloy Cu Mg alloy	Al Al alloy Cu Cu alloy Fe alloy Ge Ni Ni alloy Zn	Al alloy Cd Cu alloy Fe alloy Ge Ni alloy Zn	Ag Al Al alloy Cd Cu alloy Fe alloy Ge Sn Zn	Ag Al Al alloy Bi Cu Cu alloy Fe alloy Ni Sn Zn	AL Al alloy Cu alloy Fe alloy Ge Zn	Ag Ag alloy Cu Cu alloy Fe alloy Ni Ni alloy Pd Pd alloy

Liquid	**Cd**	**Cs**	**Cu**	**Sb**	**Te**	**Ti**	**Zn**
Solid	Al Ge	Cd	Fe Fe alloy	Fe alloy Ge	Fe alloy	Ge	Al alloy Fe alloy Mg alloy

Metals are pure species unless noted otherwise.

Liquid metal embrittlement has been seen in processing environments and a handful of operational applications. Plating some metals, such as cadmium plated titanium or steel can produce embrittlement. Zircalloy tubes in nuclear reactors have been known to be embrittled by liquid and solid cadmium. Lithium causes LME in lithium metal cooled reactors.

2.9.8 Molten Salt Corrosion

Molten salt corrosion is the degradation of metal containers by molten or fused salts. There are two general mechanisms attributed to this form of corrosion. The most common is the oxidation of the metal much like in aqueous environments. The second is the dissolution of the metal. To a lesser extent, all forms of aqueous corrosion have been observed in fused salts.

2.9.8.1 Effects of the More Common Molten Salts on Metals

These effects are summarized in Table 21.

2.9.8.2 Managing Molten Salt Corrosion

Methods to reduce molten salt corrosion include:

- Use materials that form a passive nonsoluble films
- Minimize the entry of oxidizing species
- Lower the temperatures

Table 21 Effects of the More Common Molten Salts on Metals[39]

Molten Salts	Effects
Fluorides	▪ prevent/deter the formation of the protective film on metals ▪ causes selective leaching of chromium leaving behind voids in some stainless steels and Inconel 600.
Chlorides	▪ readily attacks steels, most preferably carbides ▪ aluminum coatings for steel are ineffective ▪ nickel coatings on steel are beneficial ▪ nickel alloys decrease in resistance with an increase in oxygen partial pressure ▪ prevents the formation of a protective film on nickel alloys ▪ causes selective leaching of chromium from Fe-Ni-Cr alloys
Nitrates	▪ plain and low-alloy carbon steels good to 500°C. ▪ chromium addition is beneficial ▪ hydroxide addition further increases resistance of chromium containing steels ▪ never use aluminum alloys to contain nitrates (explosive hazard)
Sulfates	▪ high temperature alloys with chromium perform well ▪ insufficient chromium content results in severe corrosion ▪ metals that do not form protective films will be readily attacked
Carbonates	▪ austenitic stainless steels perform well up to 500°C ▪ nickel alloys containing chromium useful to 600°C ▪ 50% chromium alloys needed for use up to 700°C ▪ aluminum coatings on steels good up to 700°C ▪ alumina coatings required for higher temperatures ▪ nickel coatings are inadequate due to the formation of nickel oxides causing intergranular corrosion
Hydroxides	▪ peroxide content controls corrosivity ▪ causes selective leaching of chromium in stainless steels ▪ nickel alloys are more resistant than stainless steels and unalloyed steels ▪ aluminum alloys are more resistant ▪ most glass and silica materials are readily attacked

2.9.9 Filiform Corrosion

Filiform corrosion is an attack of a metal substrate material underneath a polymeric film. The corrosion initiation is generally due to a defect in the coating. Corrosive elements to the metal substrate deposit in the defect area causing corrosion of the metal as well as bulging and cracking of the coating. The corrosion tends to spread one-dimensionally in a random manner creating patterns resembling a worm path or tentacles emanating form a point, see Figure 29. There is an associated “head” where the corrosion is preceding and the “tail” where the corrosion originated. Filiform corrosion has been observed on steel cans, aluminum foils and painted aluminum alloys, as well as other lacquered metals. It normally occurs in high humidity (> 65% RH) although it may result in lower humidity environments of severe corrosivity. The width of the corrosion paths are in the range of 0.05 – 3 mm depending on the coating material and the corrosivity of the environment.

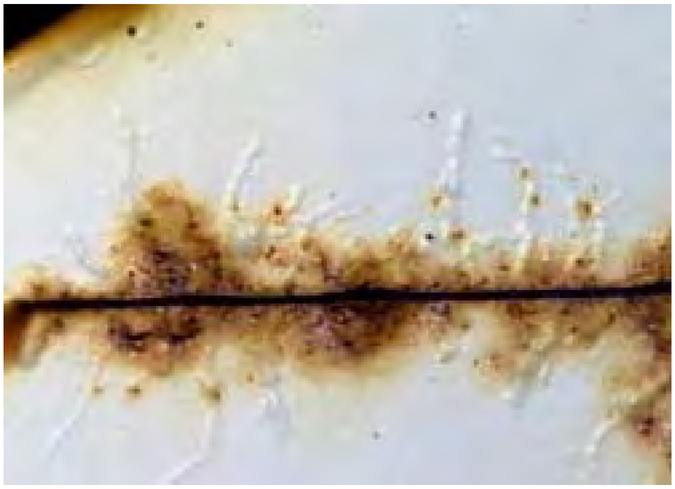


Figure 29 Filiform Corrosion[2]

2.9.9.1 Managing Filiform Corrosion

Methods that reduce filiform corrosion include the following:

- Use less active metal substrates
- Reduce humidity
- Use zinc primers on steel
- Use multiple coat/paint systems

Other corrosion protection methods can be used, and are discussed in terms of combating corrosion in general in Section 3.0.

2.9.10 Stray-Current Corrosion

Stray-current corrosion is an attack of a metal due to the formation of an electric current through that metal which is unintended. This corrosion form is independent of environmental conditions. A direct current is more damaging than alternating currents. In alternating currents, damage will decrease as frequency increases. A major source of stray-currents is underground power lines. Damage to active-passive metals such as aluminum alloys and stainless steels is greater than that for active metals.

2.9.10.1 Managing Stray-Current Corrosion

The best way to combat stray-current corrosion is to prevent the current using insulation techniques. Coatings will not protect the metal and may even accelerate the attack if a flaw in the coating exists. If the current cannot be prevented, methods to deter corrosion include the following:

- Grounding the Stray Current
- Sacrificial Anodes
- Insulation

2.9.11 Grooving Corrosion in Carbon Steel

Grooving corrosion in carbon steels is a specialized form of corrosion that exists for electric resistance welded piping subsequently exposed to aggressive waters.[40] This welding process produces a redistribution of sulfides along the weld line. The result is a preferred attack in the weld area producing grooves in the material. Post weld heat treatments appear to influence grooving corrosion with temperatures of around 750ºC producing a higher susceptibility and higher temperatures, on the order of 1000ºC, decreasing susceptibility.

3.0 Corrosion Characteristics and Properties of Metals

As discussed in the previous sections, the extent and form of corrosion occurring on a metal is predominantly dictated by the environmental conditions, and thus, the interaction of the metal with the surrounding environment. Some metals are inherently resistant to the effects of corrosion, while others are inherently susceptible. This section discusses the nature of the more common types of metals and alloys in terms of their corrosion characteristics and properties. This is not a comprehensive evaluation of metals and alloys, however; these are general observations, and are not intended to provide complete guidance in materials selection. Instead, an investigation of literature should precede the selection of a material.

The corrosion characteristics and properties of metals come from field experience and extensive testing in natural, simulated, and accelerated environments. The results of testing are used to rate materials and determine what alloying and heat treatments are beneficial to corrosion resistance. Field experiences, as well as test results, are used to document susceptibilities of materials under specific conditions. The following section uses information from both testing and field experience to facilitate the selection of metals for varying applications. The section is organized by the relative usage of the metal classes with the most widely used ferrous metals covered first.

3.1 Steels

Steels can be largely grouped into three categories with respect to corrosion resistance.[9] Carbon steels contain up to approximately 2% total alloying content with the primary additions of carbon, manganese, phosphorus and sulfur. The second group is the low alloy steels (or sometimes referred to as mild alloy steels) containing roughly 2 – 11% total alloying content. Corrosion resistance can be enhanced over carbon steels with additions of copper, nickel, chromium, silicon, and phosphorus. High corrosion resistant steels (stainless steels) can only be obtained with ≥ 11% Cr along with varying amounts of other elements.

3.1.1 Alloying for Corrosion Resistance

The primary alloying elements to increase corrosion resistance of steels are copper, chromium, silicon, phosphorus, and nickel. Broad categories of steel materials based upon alloying content include the low alloy steels, weathering steels, and stainless steels.

3.1.1.1 Carbon and Low Alloy Steels

For carbon steels, copper additions of 0.01 to 0.05% have the greatest effect for increasing general corrosion resistance, as seen in Figure 30. The relationship of the other elements on corrosion resistance is displayed in Figure 31. Small additions of chromium significantly increase tensile strength as well as increasing corrosion resistance leading to the high strength low alloy (HSLA) steels. Weathering steels is a term describing low-alloy steels with small additions of chromium, nickel, and copper. They can provide good service without any coatings in a non-marine atmospheric environment. Many inland bridge structures make use of weathering steels. Larger additions of chromium are required for a dramatic increase in corrosion resistance as previously mentioned.

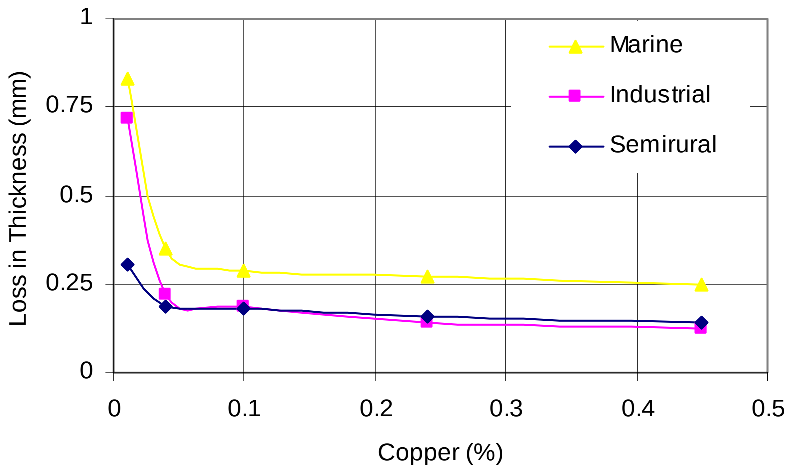


Figure 30 Effects of Copper Addition on the Uniform Atmospheric Corrosion of Steel[65]

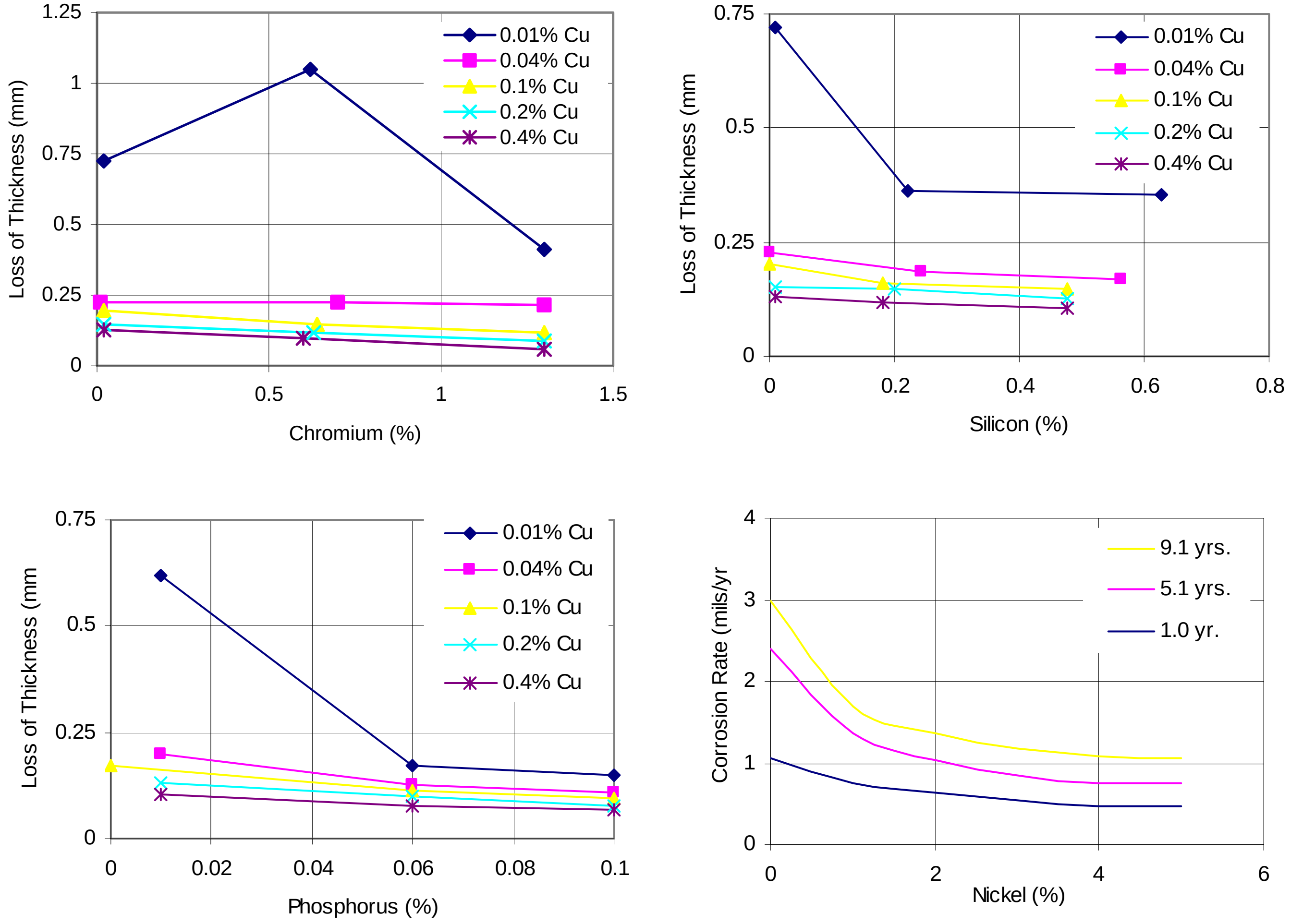


Figure 31 Effects of Alloying Elements on the Uniform Industrial Atmospheric Corrosion of Steels[65]

3.1.1.2 Stainless Steels

Stainless steels contain 11 percent or more of chromium. The higher chromium content results in the formation of a chromium oxide protective film, greatly increasing the oxidation resistance of the steel. Stainless steels are most often exposed to a passivating solution to improve formation of the protective film.[66] Corrosion resistance will generally increase with an increase in chromium content and decrease with an increase in carbon content. Stainless steels are excellent for oxidizing environments but are susceptible in halogen acids or halogen salt solutions. They are also susceptible to pitting in seawater.

3.1.1.3 Austenitic Stainless Steels

Austenitic stainless steels are the most commonly used class of stainless steels. They may be used in mild to severe corrosive environments, dependent upon alloying and are nonmagnetic compared with other steels.[66] They may be utilized in environments with temperatures reaching 600ºC and for low temperatures in the cryogenic range. Almost all austenitic stainless steels are modifications from the 18Cr – 8Ni (304) alloy. Difficulty in processing stainless steels limits increasing concentrations of chromium. The addition of nitrogen has been found to be an austenite phase stabilizer which allows higher additions of molybdenum, up to about 6%, increasing the material’s corrosion resistance in chloride environments. Other additions which improve corrosion resistance to specified environments include high chromium alloys for high temperature service and high nickel alloys for inorganic acids. Table 22 represents a summary of the austenitic stainless steel alloys and their modifications in regards to corrosion resistance.

Table 22 Austenitic Stainless Steel Alloys[8]

Austenitic Stainless Steel Alloy	**Aspects of Corrosion Resistance**
301, 302, 303, 303Se, 304, 304L, 304N	No significant change in general corrosion resistance between these grades. 304, including 304L and 304N, slightly better than the others. 303 the least resistant with a greater susceptibility to pitting.
302B	Modified 302 with 2.5% Si resulting in increased oxidation resistance at elevated temperatures.
321, 347, 348	Generally the same corrosion resistance as the above alloys, with the added benefit of near immunity to heat sensitization. They have been stabilized with the addition of titanium and/or niobium.
305, 384	Higher nickel contents result in higher corrosion resistance.
308, 309, 309S, 310, 310S	All are higher in chromium and nickel content resulting in increased corrosion resistance and oxidation at elevated temperatures.
314	Similar to 310 but with silicon addition for better resistance especially to sulfuric acid.
316, 316L, 316F, 316N, 317, 317L	Same general corrosion resistance as 310 but with an increase in localized corrosion resistance, especially pitting.

3.1.1.4 Ferritic Stainless Steels

Ferritic stainless steels generally do not match the corrosion resistance of the austenitic grades. They exhibit relatively high yield strength and a low ductility and are magnetic. The ferrites have a low solubility for some elements such as carbon and nitrogen. The ferritic stainless steels will transition from ductile to brittle over a small temperature range, occurring above ambient temperature for increasing carbon and nitrogen content and more so with increased chromium content. Ferritic alloys have been developed using an argon-oxygen decarburization (AOD) process, significantly reducing carbon and nitrogen levels. Also, reactive elements such as titanium and niobium may be added to precipitate some of the carbon and nitrogen. Ferritic stainless steel alloys containing carbon and nitrogen are susceptible to intergranular corrosion by heat sensitization through heat treating, welding, or other thermal exposure. Newer alloys, such as 444, have lower carbon and nitrogen content, using AOD, allowing higher chromium and molybdenum content resulting in an alloy more amenable to welding and somewhat tougher, although still limited by a lack of toughness. Ferritic stainless steels do offer use in thermal transfer applications as a result of their high resistance to SCC in chloride environments. The 409 alloy was specifically developed for use in automotive exhaust components. Table 23 lists the ferritic alloys with their corrosion characteristics.

Table 23 Ferritic Stainless Steel Alloys[8]

Ferritic Stainless Steel Alloy	Aspects of Corrosion Resistance
405	12.5% Cr, ≤ 0.08% C, 0.10 to 0.30 Al Low corrosion resistance, ideal for welding, used principally as a lining for pressure vessels
409	10.5 to 11.75% Cr, stabilized with Ti. Lowest corrosion resistance of all stainless steels
429	Contains 14.0 to 16.0% Cr and some carbon Developed for a higher degree of weldability than 430
430, 430F, 430FSe, 434, 436	17% Cr , high atmospheric corrosion resistance and resistance to many chemicals. 430F has reduced corrosion resistance with increased machinability 434 has 1.0% Mo for pitting resistance 436 has 1.0% Mo plus up to 0.7% Nb and Ta for carbide stabilization. Better for elevated temperature service.
442, 446	18.0 to 23.0% Cr for 442 and 23.0 to 27.0% Cr for 446 No appreciable increase in corrosion resistance, used in heat processing equipment as they have a high resistance to scaling through high temperatures.

3.1.1.5 Martensitic Stainless Steels

Martensitic stainless steels have a much lower corrosion resistance than austenitic grades, and usually slightly lower than the ferritic grades. The martensitic stainless steels contain lower Cr and higher C concentrations compared with the other stainless steels. This structure results in a strong but brittle class of materials. They may be tempered to improve toughness, but to limited degree. Additions of nitrogen, nickel, and molybdenum at lower levels of carbon have been found to produce alloys with better toughness and corrosion resistance properties. The corrosion characteristics of the martensitic grades are summarized in Table 24.

Table 24 Martensitic Stainless Steel Alloys[8]

Martensitic Stainless Steel Alloy	Aspects of Corrosion Resistance
403,410	Contain about 12.5% Cr with no other alloying elements
416, 416Se	Contain about 12.5% Cr with additives to improve machinability that results in somewhat less corrosion resistance.
414, 431	Both have nickel additions of about 2%. 414 is a 12-2 alloy and 431 is a 16-2 alloy. They have a higher corrosion resistance than the other martensitic stainless steels with 431 considered the highest corrosion resistance.
420, 420F	Contain higher Cr content but with no appreciable gain in corrosion resistance over 410. 420F has sulfur addition for machinability resulting in a slight sacrifice in corrosion resistance.
422	A 12.5% Cr alloy with additions to improve high temperature service.
440A, 440B, 440C	Higher Cr content and high carbon content. Lowest corrosion resistance of the martensitic due to the carbon.

3.1.1.6 Precipitation Hardening Stainless Steels

Precipitation-hardening (PH) stainless steels are Cr-Ni alloys that are hardened at moderately high temperatures, by adding elements such as copper and/or aluminum which form intermetallic precipitates. PH stainless steels may have austenitic, semi-austenitic, or martensitic structures. They must not be further exposed to elevated temperatures, once hardened, as the precipitates will be altered, degrading the material’s strength. This includes welding and environmental exposures. The corrosion aspects of the PH stainless steels are presented in Table 25.

Table 25 Precipitation-Hardened Stainless Steel Alloys[8]

Precipitation-Hardened Stainless Steel Alloy	Aspects of Corrosion Resistance
630	Copper addition is used as the hardening agent. Has a martensitic structure with corrosion characteristics similar to 304 austenitic stainless steels.
631	Has a duplex structure in the heat treated condition. Exhibits a high strength with good corrosion resistance.
632	Similar to 630 but with molybdenum addition which improves strength and resistance to pitting.
633	Has a duplex structure and a higher alloying content than the other PH stainless steels resulting in increased resistance.
634	Has a semi-austenitic structure with molybdenum addition for pitting resistance.

3.1.1.7 Duplex Stainless Steels

Duplex stainless steels are two phase materials containing roughly equal amounts of ferrite and austenite phases developed specifically as a high corrosion resistant material. They contain high levels of chromium (20 – 30%), Ni (5 – 10%), and low carbon content (< 0.03%). They may additionally contain molybdenum, nitrogen, tungsten, and copper as modifiers to increase corrosion resistance in specific environments. Duplex stainless steels offer strength about double that of austenitic stainless steels, with increased resistance to chloride induced SCC and pitting. They are typically used in temperatures ranging from -60 to 300°C. There are four primary alloys of duplex stainless steels used which are:

2304: Fe – 23Cr – 4N – 0.1N
2205: Fe – 22Cr – 5.5Ni – 3Mo – 0.15N
2505: Fe – 25Cr – 5Ni – 2.5Mo – 0.17N - Cu
2507: Fe – 25Cr – 7Ni – 3.5Mo – 0.25N – W – Cu

Duplex stainless steels have been used extensively in oil and gas production equipment having excellent resistance to the corrosive byproducts. They have also replaced other stainless steels that had corrosion problems in chemically corrosive environments and in heat transfer equipment due to their better resistance to SCC.

3.1.1.8 Iron-based Superalloys

Iron-based superalloys are also an extension of the stainless steels. They contain 20 – 30% chromium plus other alloying elements. They offer good corrosion resistance in a service temperature higher than the duplex stainless steels, but lower than nickel-based superalloys (up to about 815°C). The cost of the iron-based superalloys is lower than nickel-based superalloys making them marketable in this service temperature range. Iron-based superalloys are used in structural components for furnaces, in steam and gas turbines, and in chemical processing equipment.

3.1.2 Resistance to Forms of Corrosion

The resistance of steels to corrosion varies greatly with alloying content playing a major role. Carbon and low alloy steels have the second highest uniform corrosion rates of any metals, while high alloyed stainless steels are generally only susceptible to localized corrosion. The following sections highlight the susceptibilities of steels to forms of corrosion.

3.1.2.1 Uniform Corrosion

Carbon and low alloy steels are susceptible to uniform atmospheric corrosion while stainless steels are considered resistant. Figure 32 summarizes data collected on various carbon and low alloy steels tested for uniform corrosion in a natural atmospheric environment. The graphs clearly show the decline in corrosion rate over time, with the exception of the severe marine environment.

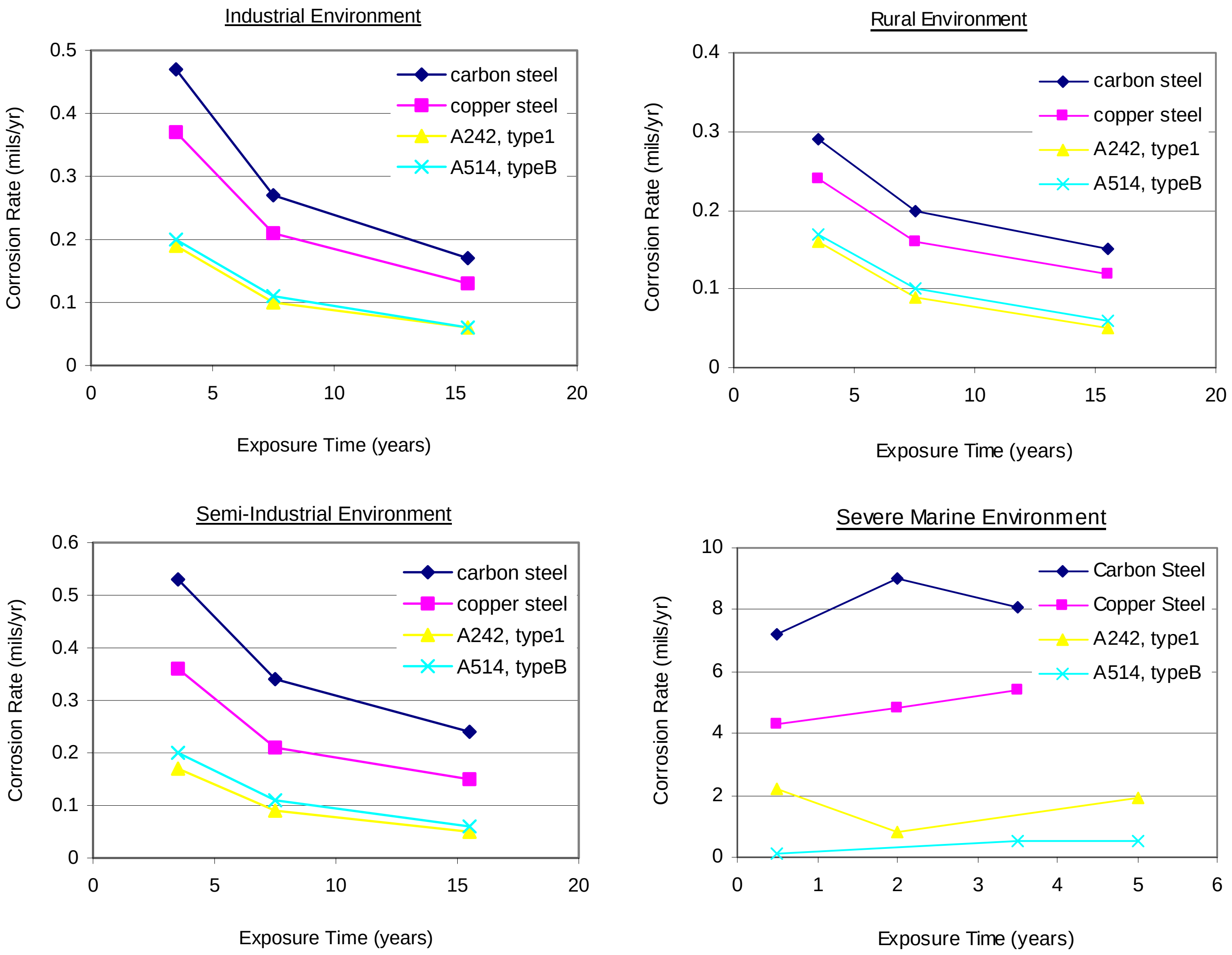


Figure 32 Uniform Corrosion of Steels in Various Atmospheric Environments

3.1.2.2 Pitting and Crevice Corrosion

Stainless steels are susceptible to pitting and crevice corrosion in marine environments, especially when fully immersed in saltwater. Stainless steels have been used on ships and can provide excellent service in marine atmospheric environments, as long as deposits are routinely washed off from surfaces. Accumulation of salt deposits will cause pitting and crevice corrosion to occur. All stainless steel alloys will exhibit pitting in low velocity seawater (less than five feet per second). Higher velocities prevent deposits and marine growth to occur so that pitting will not occur on exposed surfaces. Crevice corrosion has been found to occur, even at high velocities. The addition of molybdenum is beneficial for pitting and crevice corrosion resistance.

3.1.2.3 Stress Corrosion Cracking

Stress corrosion cracking of steels is largely a combination of their strength and environmental susceptibility. High strength steels are susceptible to SCC in corrosive environments. Failures of stainless steels in marine atmospheres have often been a result of SCC. Table 26, Table 27, and Table 28 categorize the SCC susceptibilities of steels in marine atmospheric environments.

Table 26 Steels with a High Resistance to Stress Corrosion Cracking in Atmospheric Marine Environments[67]

Materials	**Type**	**Heat Treatment**	**Remarks**
300 Series Stainless Steels Types 303, 304, 316, 321, 347	Austenitic	Annealing	Stressed material can crack in chloride solutions. Annealed materials are not of high strength. Cold worked materials can develop high strength, but must be stress relieved.
17-4 PH	Martensitic	H1000 and above	-
17-7 PH	Semi-austenitic	CH900	Strength is developed by cold work (60%) and aging (900ºF)
PH13-8Mo	Martensitic	H1000 and above	-
15-5 PH	Martensitic	H1000 and above	-
PH15-7Mo	Semi-austenitic	CH900	Strength is developed by cold work (60%) and aging (900ºF)
PH14-8Mo	Semi-austenitic	CH900	Strength is developed by cold work (60%) and aging (900ºF)
AM-350	Semi-austenitic	SCT1000 and above	-
AM-355	Semi-austenitic	SCT1000 and above	-
Custom-455	Semi-austenitic	H1000 and above	-
A-286	Austenitic	Solution treated and aged	
A-286	Austenitic	Cold worked and aged	Strength is developed by cold work (60%) and aging (1200ºF)

Table 26, continued - Steels with a High Resistance to Stress Corrosion Cracking in Atmospheric Marine Environments

Materials	**Type**	**Heat Treatment**	**Remarks**
Inconel 718	Face centered cubic	Solution treated and aged	-
Inconel X-750	Face centered cubic	Solution treated and aged	-
Rene 41	Face centered cubic	Solution treated and aged	-
MP 35N	Face centered cubic	Solution treated and aged	Solution Annealed and cold worked (60%) and aged
Waspaloy	Face centered cubic	Solution treated and aged	-
Low-alloy steels 4130, 4140, 4340, 8740	Martensitic	Solution treated and aged	High resistance to SCC of tempered to attain strength of 160 ksi or lower.-
Maraging steel	Martensitic	Solution treated and aged	High resistance if heat treated to 200 ksi or lower.

Table 27 Steels with a High Resistance to Stress Corrosion Cracking in Atmospheric Marine Environments if Used with Caution

Materials	Type	Heat Treatment	Remarks
Low-alloy steels 4130, 4140, 4340, 8740, D6AC, HY-TUF	Martensitic	Quenched and tempered	Good resistance to SCC if tempered to about 160 to 180 ksi.
Maraging steel	Martensitic	Solution treated and aged	All three grades; 200, 250, 300
400 series Stainless steels 410, 416, 422, 431	Martensitic	Quenched and tempered	Not susceptible if tempered at 1100°F or higher
15-5 PH	Martensitic	H950 to H1000	-
PH13-8Mo	Martensitic	H950 to H1000	-
17-4 PH	Martensitic	H950 to H1000	-
AM-355	Semi-austenitic	SCT950 to H1000	-

Table 28 Steels with a Low Resistance to Stress Corrosion Cracking in Atmospheric Marine Environments

Materials	Type	Heat Treatment	Remarks
Low-alloy steels 4130, 4140, 4340, 8740, D6AC, HY-TUF	Martensitic	Quenched and tempered	Very susceptible to SCC if tempered to attain strengths of 180 ksi and higher.
H-11	Martensitic	Quenched and tempered	-
17-7 PH	Semi-austenitic	All heat treatments except CH900	-
PH15-7Mo	Semi-austenitic	All heat treatments except CH900	-
AM-355	Semi-austenitic	Heat treatments below SCT900	-
400 series stainless steels 410, 416, 422, 431	Martensitic	Quenched and tempered	Very susceptible in the secondary hardening range, 500 to 1000ºF.

3.1.2.4 Intergranular Corrosion

Intergranular corrosion has been observed in some stainless steels primarily as a result of the precipitation of chromium carbides at grain boundaries. In austenitic stainless steels, chromium carbides are completed dissolved above temperatures of 1900ºF.[40] When slowly cooled from these temperatures, the formation of chromium carbides at grain boundaries can result. They may also be formed by reheating austenitic stainless steels into the temperature range of 800 – 1200ºF. The formation of chromium carbide precipitates at grain boundaries in ferritic stainless steels occurs for temperatures above 1700ºF. The sensitized area in welded austenitic stainless steels occurs in the heat affected zone while in ferritic stainless steels, the sensitized area is likely to be in the fusion zone and the weld itself. Methods to reduce sensitivity of stainless steels to intergranular corrosion include limiting carbon content and the addition of titanium and/or niobium which preferentially form carbides.

3.1.2.5 Hydrogen Damage in Steels

There are several different mechanisms of hydrogen attack as discussed in Section 2.9.3. Steels are susceptible to all except metal hydride formation. High strength steels are the most susceptible, although even ductile steels have been known to suffer from hydrogen damage.

3.1.3 Corrosion Resistance in Chemical Environments

Acidic environments are involved in most of the severe corrosion problems encountered with steels, as with most metals, although alkaline environments can also be responsible for increased corrosion. The corrosion rate of steels in acids depends upon the composition and concentration of acid, as well as temperature.[68] The corrosion rate of steels in hydrochloric acids will continuously increase with increasing acid concentration. In sulfuric acids, however, the corrosion rate increases until a level of concentration where passivity is reached, see Figure 33. If the passive film is damaged by mechanical or chemical means, the corrosion rate will significantly increase in concentrated solutions.

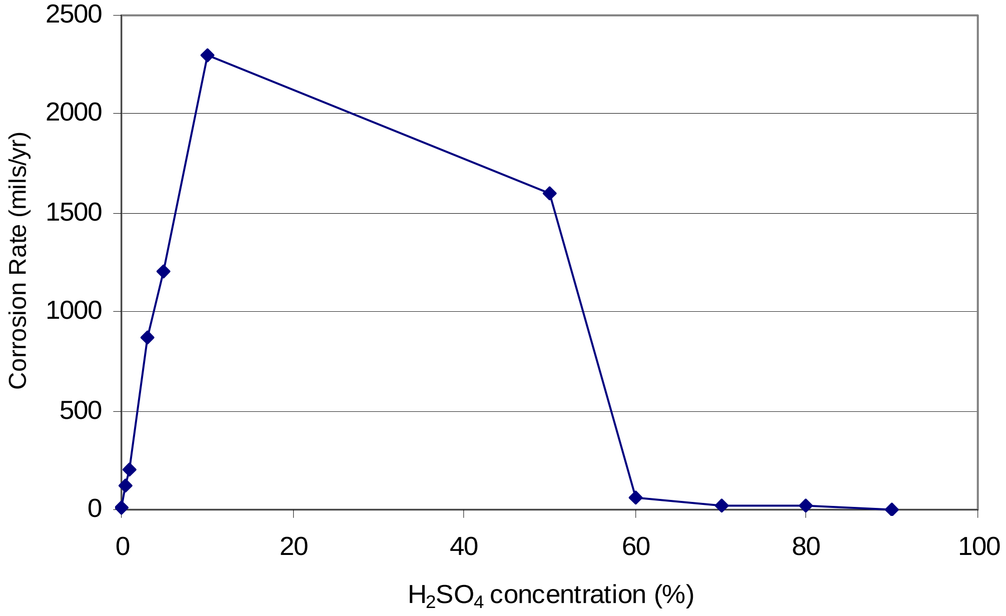


Figure 33 Uniform Corrosion of Carbon Steel by Sulfuric Acid at Room Temperature

Nitric acid readily attacks carbon and low alloy steels. Austenitic stainless steels, as well as aluminum alloys, form strong adherent oxide films. This makes them the most applicable metals for use with nitric acid.

Sodium and potassium hydroxides have similar effects on steels. The uniform corrosion rates are generally ≤ 2 mils/yr, for all concentration levels. The problem with exposure of low alloy steels to these materials is the susceptibility to SCC, sometimes referred to as caustic embrittlement. The relation of temperature and sodium hydroxide concentration to observed cracking is shown in Figure 34.

3.1.4 Corrosion Protection of Steels

Corrosion protection of carbon and low-alloy steels is almost always required. There a numerous coatings, coating processes, and methods used to limit corrosion of these steels, which include the following:

- Conversion coatings
- Inhibitors
- Metal claddings
- Continuous electrodeposition
- Organic coatings (paints)
- Porcelain enameling
- Vapor-deposited coatings
- Surface modification
- Corrosion preventive compounds
- Hot-dip coating processes
- Electroplating
- Zinc-rich coatings
- Thermal spraying processes
- Pack cementation coatings

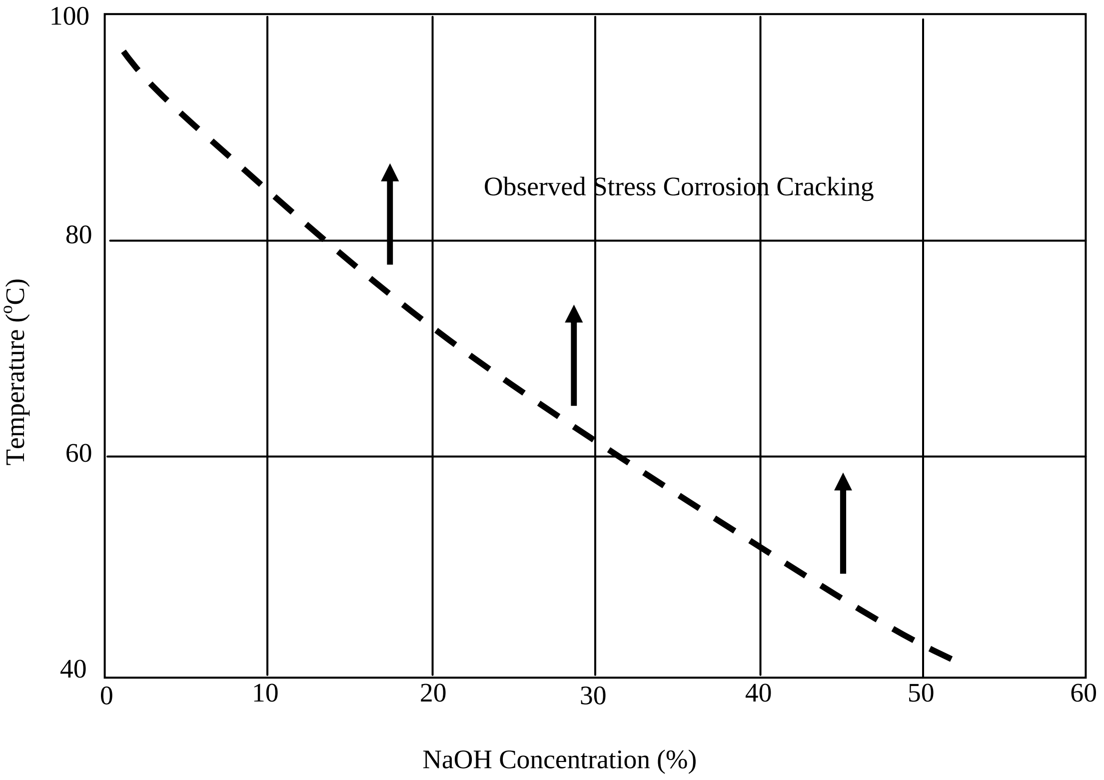


Figure 34 Susceptibility of low alloy steels to SCC in NaOH

3.2 Aluminum and Its Alloys

In general, aluminum and its alloys are more resistant to corrosion than mild steel. They are known to have a very good resistance to corrosion in a variety of environments and chemical compounds, even though aluminum is a relatively reactive metal. Aluminum and its alloys also have a good resistance to various forms of corrosive attack. For the most part, the lower temperature corrosion resistance of aluminum is virtually equivalent to that of stainless steel, and it provides reasonable protection at elevated temperatures. Pure aluminum, however, tends to have a greater corrosion resistance than its alloys, and impurities in the aluminum only act to increase the metal’s susceptibility to corrosion. This is true especially for surface impurities; clean surfaces are much more effective at resisting corrosion than are surfaces with deposits.

Aluminum’s excellent resistance to corrosion can usually be attributed to the rapid formation of an oxide film on the metal’s surface, which acts as a barrier to corrosive environments. For instance, the film inhibits corrosion very effectively in lower temperature, atmospheric and aqueous corrosive environments. An important aspect of the film is that it forms quickly in many environments, but can also be produced artificially by sending an electric current through the metal. This is called anodizing. The tough, virtually transparent, non-flaking, aluminum oxide film is capable quickly of repairing itself when it is scratched or abraded. Therefore, in order to defeat the protective film, continuous mechanical abrasion or chemical degradation in an oxygen deficient atmosphere is required. A further benefit is that the surface oxide film can be modified or thickened to enhance its corrosion protection.

3.2.1 Alloys and Alloying Elements

Although alloying other elements with aluminum can improve certain properties, it tends to have a negative effect on its corrosion resistance. Some elements, such as magnesium, however, can be alloyed in amounts of about <1% without significantly decreasing the corrosion resistance compared to pure aluminum. Common alloying elements include copper, magnesium, silicon, and zinc. Iron is not usually intentionally used as an alloying element, rather it is commonly a contaminant, and it is typically attributed as being the primary cause of pitting in aluminum alloys. Some of the general classes of aluminum alloys and their corrosion characteristics are described in the following sections. Although there are a number of specific aluminum alloys, only a few are discussed.

3.2.1.1 Aluminum (1000 Series)

The 1000 series of aluminum alloys has approximately 99% aluminum with the remaining percent consisting of other elements, which are considered impurities. Similar to pure aluminum, this series of metals has excellent corrosion resistance to many environments, but with increasing impurity content the corrosion resistance decreases.

3.2.1.2 Copper (2000 Series)

The 2000 series of aluminum alloys contains copper as the principal alloying element. These are higher strength alloys and are consequently used mainly for structural applications, but they have a much lower corrosion resistance compared to other aluminum alloys. Therefore, alloys with little or no copper are used for applications where corrosion resistance is important. This series of alloys, in general, is prone to stress corrosion cracking and exfoliation, and typically copper alloying results in the occurrence of uniform, pitting, and intergranular forms of corrosion to a greater extent. For instance, copper additions greater than 0.15% decreases the resistance to pitting corrosion. Alloys containing copper are also more susceptible to corrosion in seawater and marine environments.

If alloys in this series are slightly overaged, their resistance to SCC is improved to the point where the alloys are no longer susceptible to this form of corrosion. Solution heat treatment and artificial aging of 2000-series aluminum alloys, however results in $CuAl_2$ precipitates at grain boundaries, which causes the alloy to be susceptible to intergranular corrosion.[69]

Aluminum alloy 2020 in general is not suitable to be used for structural applications, but in the T651 condition it does exhibit an excellent resistance to SCC.[43, 69] Aluminum alloys 2024-T851 and 2219-T851 are also highly resistant to SCC.

3.2.1.3 Manganese (3000 Series)

Manganese is the primary alloying element in the 3000 series of aluminum alloys. These alloys exhibit a very good resistance to corrosion, in general, and are particularly very resistant to SCC.

3.2.1.4 Silicon (4000 Series)

Silicon is the main alloying element in the 4000 series of aluminum alloys, but it has little effect on the corrosion resistance of aluminum. In particular, this series of alloys is characteristically very resistant to SCC.

3.2.1.5 Magnesium and Silicon (5000 and 6000 Series)

Magnesium is the main alloying element in the 5000 series of aluminum alloys, and it provides extra protection against aqueous corrosion. Magnesium can also serve to increase the resistance to corrosion in salt water and under alkaline conditions compared to unalloyed aluminum. It may, however, also help to advance SCC and intergranular corrosion, if it is present in the grain boundaries as an anodic magnesium aluminum phase. If the magnesium content exceeds the specified limit, it tends to precipitate another phase with aluminum, and consequently causes an increase in susceptibility to intergranular corrosion. Aluminum-magnesium alloys also have a tendency to be susceptible to exfoliation.

Aluminum alloys 5083, 5086, and 5456 in the H30-series of conditions should not be used for structural applications since, they are very susceptible to SCC. Aluminum alloy 5454-H34, on the other hand, has an excellent resistance to SCC. Furthermore, the H116 and H117 tempers for the 5000-series of aluminum alloys offer a good resistance to exfoliation.

The 6000 series of aluminum alloys contain magnesium and silicon as the primary alloying elements. These alloys are stronger while maintaining the same excellent resistance to aqueous corrosion as the 5000-series alloys. However, silicon in amounts greater than 0.1% reduces the resistance to pitting corrosion, and decreases the corrosion resistance in marine environments. Furthermore, excess silicon decreases the resistance to intergranular corrosion. Alloys containing magnesium or magnesium and silicon tend to have the best resistance to corrosion in seawater and marine environments of any of the other aluminum alloys.

In general, similar to the 5000-series, the 6000 series alloys are susceptible to SCC. In particular these alloys with >3% magnesium can be very susceptible to SCC. Cold-worked aluminum-magnesium and aluminum-magnesium-silicon alloys containing <3% Mg, however, are very resistant to SCC.[43]

3.2.1.6 Zinc (7000 Series)

Zinc is the primary alloying element in the 7000 series of aluminum alloys, and in general, as an alloying element it only has a small influence on the corrosion resistance of aluminum. These alloys, however, are characteristically much more susceptible to aqueous corrosion. A high zinc content may result in decreased resistance to intergranular corrosion, SCC, and exfoliation corrosion. In addition, zinc may decrease the resistance of aluminum to acidic environments, but may increase the resistance to alkaline environments.

Within the 7000 series of aluminum alloys, some alloys are especially susceptible to SCC and are therefore not suitable for structural applications. Overaging in the 7000 series of aluminum, however, tends to reduce their susceptibility to SCC. Aluminum alloys 7079 and 7178 are not suitable for structural applications.[43] The high strength aluminum alloy 7075 in the T6 condition is very susceptible to SCC and exfoliation, but in the T73 condition it has a greater resistance to SCC.[69] 7075 in the T7351 condition has an excellent resistance to SCC.[69] In general for the

7000-series aluminum alloys, the T76 tempers have a greater resistance to exfoliation than the T73 tempers.

3.2.1.7 Chromium

Chromium can be a beneficial alloying element because it typically provides improved corrosion resistance. For instance, Cr improves the corrosion resistance of Al-Mg and Al-Mg-Zn alloys when added in small amounts (0.1-0.3%). Furthermore, Cr increases SCC resistance in high-strength alloys, however, it does tend to increase the pitting potential in water for high purity aluminum.

3.2.1.8 Lithium

Lithium is a chemically active metal and may increase aluminum’s susceptibility to corrosion. For instance, it seems that lithium additions of <3% result in a slightly more anodic aluminum.[70] This indicates that additions of lithium, however, may only increase the susceptibility of aluminum to corrosion marginally. Moreover, studies have shown that the susceptibility of the aluminum lithium alloy to corrosion is largely dependent on the δ phase, which is the AlLi phase. Increasing the amount of δ phase present, for example, increases the alloy’s susceptibility to corrosion.[71]

Two of the more common aluminum lithium alloys are 2090 and 8090. 2090 is similar to 7075 aluminum in terms of resistance to SCC, and has a higher resistance to exfoliation corrosion than 7075.[70] 8090 aluminum with an altered surface structure (heat treatment T82551) has been shown to have a greater general resistance to corrosion than 2090 aluminum. Both 2090 and 8090 aluminum have been shown to be susceptible to pitting and intergranular corrosion.[71] Alloy 2097 is another aluminum lithium alloy and has shown improved pitting corrosion resistance compared to an aluminum copper alloy (2124) and comparable general corrosion resistance.[72]

3.2.1.9 Comparison of the Corrosion Resistance of Aluminum Alloys

A comparison of the relative corrosion resistance of the various groups of aluminum alloys is provided in Table 29.

3.2.2 Resistance to Forms of Corrosive Attack

Although aluminum and its alloys have a good resistance to various forms of corrosive attack, they are still susceptible to some mechanisms including galvanic, pitting, SCC, intergranular, crevice corrosion, corrosion fatigue, and occasionally filiform corrosion. Susceptibility to other forms of corrosion is often dependent on alloy composition and heat treatment.

Table 29 Comparison of the General Corrosion Resistance for the Series of Aluminum Alloys

AA Series	Principal Alloying Element(s)	Relative Corrosion Resistance
1000 Series	None	Very High
2000 Series	Copper	Low
3000 Series	Manganese	High
4000 Series	Silicon	High
5000 Series	Magnesium	Very High
6000 Series	Magnesium, Silicon	High
7000 Series	Zinc	Intermediate

3.2.2.1 Galvanic

Aluminum, especially when joined with steel, is very susceptible to galvanic corrosion. In seawater, its place on the galvanic series is very low, and thus it is very anodic. It will, therefore, corrode preferentially when joined with a dissimilar metal that is higher up on the series. Graphite is very high on the galvanic series, and thus any contact with aluminum will adversely affect it in terms of corrosion. The significance of this is that graphite pencils used to make marks on aluminum may initiate corrosion by galvanic action.

3.2.2.2 Pitting

Pitting is one of the most common forms of corrosion found in aluminum and its alloys. Chloride containing environments pose one of the biggest threats to aluminum in terms of corrosion, since pitting corrosion tends to occur in salt water and marine environments. Seawater flowing at a high velocity relative to the aluminum is especially corrosive in the form of pitting since it will inhibit the protective oxide layer from automatically healing itself.

3.2.2.3 SCC

Additions of copper, magnesium and zinc in sufficient amounts can lead to SCC of aluminum alloys. SCC is dependent on the environment that the aluminum alloy is exposed to. For instance, chloride, bromide and iodide environments are particularly dangerous to aluminum since SCC tends to occur in such environments. Aluminum alloys tend to resist SCC in hydrogen, argon and air with no moisture content. Marine environments, which are commonly encountered in applications of aluminum alloys, typically promote SCC of aluminum alloys. Increasing the pH in chloride environments, however, works to inhibit SCC in aluminum and its alloys.

Furthermore, SCC can also be dependent on the heat treatment and grain orientation.[69] For example, 7075-T6 (or 2024-T4) is most susceptible to SCC when the tensile stress is applied in the short transverse direction, is less susceptible to SCC when it is applied in the long transverse direction, and is least susceptible to SCC when it is applied in the longitudinal direction.[69] (This is only the case for thick specimens; thin aluminum sheets and castings are typically not affected by this.) Shot peening can be used to improve resistance of aluminum alloy structural forgings, machined plates and extrusions to SCC and corrosion fatigue. Some environments that are known induce or retard SCC in aluminum alloys are given in Table 30. Table 31 provides a relative comparison of various aluminum alloys and their resistance to SCC.

Table 30 Some Environments Known to Cause or Not to Cause Stress Corrosion Cracking in Aluminum Alloys[3]

	Environments Known to Cause		Environmental Additions Known to Induce or Accelerate SCC
	No SCC	**SCC**	
Gases	Ar (dry), He (dry), O_2 (dry), H_2 (dry), N_2 (dry), dry air	H_2O	H_2O
Liquid Metals	Li, Se, Bi, Te, Cd, Pb	Hg, Ga, Na, Te, Sn, Zn	-
Molten Salts	$AlCl_3$-LiCl, LiCl-KCl	-	-
Inorganic Liquids	H_2SO_4	H_2O	H_2O, Br^-, Cl^-, I^-
Organic Liquids	-	CCl_4, alcohols, hydrocarbons, ketones, esters	H_2O, Cl^-, Br^-, I^-

Table 31 Rating for Resistance to Stress Corrosion Cracking Aluminum Alloys in the Short Transverse Grain Direction (STGD)[43]

Alloy and Temper	Rolled Plate	Rod and Bar	Extruded Shapes	Forgings
2014-T6	Low	Low	Low	Low
2024-T3, T4	Low	Low	Low	Low
2024-T6		High		Low
2024-T8	High	Very High	High	Intermediate
2124-T851	High			
2219-T351X, T37	Very High		Very High	Very High
2219-T6	Very High	Very High	Very High	Very High
6061-T6	Very High	Very High	Very High	Very High
7005-T53, T63			Low	Low
7039-T64	Low		Low	
7049-T74	Very High		High	High
7049-T76			Intermediate	
7149-T74			High	High
7050-T74	High		High	High
7050-T76	Intermediate	High	Intermediate	
7075-T6	Low	Low	Low	Low
7075-T736				High
7075-T74	Very High	Very High	Very High	Very High
7075-T76	Intermediate		Intermediate	
7175-T736			High	
7475-T6	Low			
7475-T73	Very High			
7475-T76	Intermediate			

3.2.2.4 Intergranular Corrosion

Inhomogeneities in the alloy structure are commonly the cause of intergranular corrosion in aluminum alloys. Furthermore, alloys with a high copper content tend to be susceptible to intergranular corrosion.

3.2.2.5 Crevice Corrosion and Exfoliation

Aluminum is also susceptible to crevice corrosion, and since it is often used in components where joining and fastening is required, crevices must be eliminated to avoid this particular form of corrosion. Exfoliation in aluminum is commonly a consequence of crevice or galvanic corrosion. Aluminum alloys that have elongated grain structures are susceptible to exfoliation.

3.2.3 Corrosion Resistance in Various Environments

Periodic cleansing (e.g. rain) of aluminum and aluminum alloys can extend their life significantly in terms of corrosion resistance. This is especially true if the metals are exposed to environments with high salt content or other air contaminants, such as in marine and industrial locations, respectively. Furthermore, aluminum should not be stored in humid environments unless coated with a corrosion inhibitor.

3.2.3.1 Water

Aluminum is strongly resistant to corrosion in normal atmospheric environments, fresh water environments, distilled water environments and other aqueous environments. Both water containing a significant amount of carbon dioxide and polluted water, however, can be more corrosive to aluminum.

3.2.3.2 Acid and Alkaline environments

Aluminum is resistant to neutral and acidic environments, in general, because of its ability to form an oxide film. However, aluminum is more prone to corrosion in alkaline environments. More specifically, aluminum has a general resistance to corrosion in environments with a pH in the range of 3 to 8.5. Under basic (alkaline) conditions the metal is attacked much more readily than the film. Thus, if the basic medium finds a hole in the oxide film, corrosion will occur usually in the form of pitting. Conversely, under acidic conditions the oxide film is attacked more readily than aluminum, thus, if corrosion occurs it will most likely be in the form of uniform corrosion. Corrosion inhibitors can expand the pH operating range of aluminum metals and alloys in alkaline environments up to approximately 11.5.

3.2.3.3 Soil

The corrosion resistance of aluminum and aluminum alloys in soil is dependent on the nature and conditions of the underground environment. In dry, sandy soil, aluminum and its alloys are sufficiently resistant to corrosion, but in wet, acidic or alkaline soils the metals are more susceptible to corrosion.

3.3 Copper and Its Alloys

Copper is a noble metal that has an inherent resistance to corrosion in a variety of environments. Despite its excellent corrosion resistance to a broad range of environments, copper corrodes rapidly in certain environments, unlike some other noble metals. Even so, it’s good corrosion resistance generally applies to atmospheric environments, industrial environments, freshwater environments, and seawater environments, as well as a number of acidic and alkaline conditions. Pure copper is especially resistant to the aforementioned environments.

Copper is a low-cost alternative to stainless steels and nickel-base alloys when selecting a material for a corrosion resistant application. Copper alloys provide good strength at lower temperatures with a good resistance to corrosion in a broad range of environments. Among other applications, copper is useful for architectural applications (e.g. roofing), freshwater handling systems and plumbing, seawater handling systems, chemical process equipment and heat exchangers, and electrical systems.

3.3.1 Alloys and Alloying Elements

There are three main types of copper alloys: copper-tin (bronze), copper-zinc (brass), and copper-nickel (cupro-nickels). Each of these main alloys may be alloyed with additional elements, which in some cases provides increased corrosion resistance and improved material properties. The following sections briefly describe the corrosion characteristics of some common copper alloys.

3.3.1.1 Pure Copper and High-Copper alloys

Pure copper is accepted as having greater than 99% copper, while high-copper alloys have greater than 96% copper. Both pure copper and high-copper alloys have excellent resistance to corrosion, especially in seawater. They are also highly resistant to microbiological-influenced corrosion, as copper is toxic to microorganisms. They are, however, susceptible to erosion-corrosion.

3.3.1.2 Bronze

Alloying tin (Sn) with copper improves the resistance to corrosion in fresh water and seawater environments. Hence, bronze has an excellent corrosion resistance in fresh water and in contaminated water, as well as a very good resistance to corrosion in marine environments. Furthermore, alloys that contain approximately 8 to 10% tin have a good resistance to attack by impingement, which is a form of erosion corrosion. Bronze has moderate resistance to pitting corrosion. Moreover, the addition of tin to copper pushes copper more toward the cathodic end of the galvanic series, further protecting it from galvanic corrosion.

Aluminum is added in 5-12% to Cu-Ni-Fe-Si-Sn systems to make aluminum bronze alloys, which show improvements in general corrosion resistance and exhibit excellent resistance to impingement attack (erosion corrosion) and high temperature corrosion. With an aluminum content of less than 8%, aluminum bronze alloys have an excellent resistance to pitting. Aluminum bronze alloys can be used in nonoxidizing mineral acids, organic acids, neutral saline solutions, alkalis, seawater, brackish water and fresh water without being significantly susceptible to corrosion.[73] They are not generally suitable, however, for use in nitric acid, metallic salts, humidified chlorinated hydrocarbons and ammonia.[73]

Phosphorous is added to copper-tin alloys to provide enhanced resistance to nonoxidizing acids (except HCl) and flowing seawater. These phosphor bronze alloys also have superior resistance to SCC compared to brass. The addition of silicon can make bronze susceptible to pitting, as well as embrittlement in the presence of high-pressure steam environments.[73]

3.3.1.3 Brass

Brass is a copper alloy with a significant zinc content. The content of zinc can be as great as about 40%, but corrosion by selective leaching (dezincification) can be significant when the content is more than 15%. The effect of zinc content on the susceptibility of brass to pitting and dezincification is shown in Figure 35. Copper alloys that have more than 85% copper are resistant to dezincification, but may also be more susceptible to corrosive attack by impingement. Low concentrations of zinc in brass leads to a very good resistance to pitting. The addition of zinc to copper moves it further down the galvanic series toward the anodic end, and therefore, it is more susceptible to galvanic corrosion. High zinc content can also lead to a greater susceptibility to SCC. Brasses with 20-40% Zn, for example, are highly susceptible to SCC, while brass alloys with less than 15% Zn are highly resistant to SCC. For marine environments, brasses with a copper content between 65 and 85% are the most resistant to corrosion. Copper-zinc alloys have a good resistance to corrosion in fresh water environments. The one type of brass that is considered to have the best corrosion resistance in fresh water is red brass (85% Cu, 15% Zn).

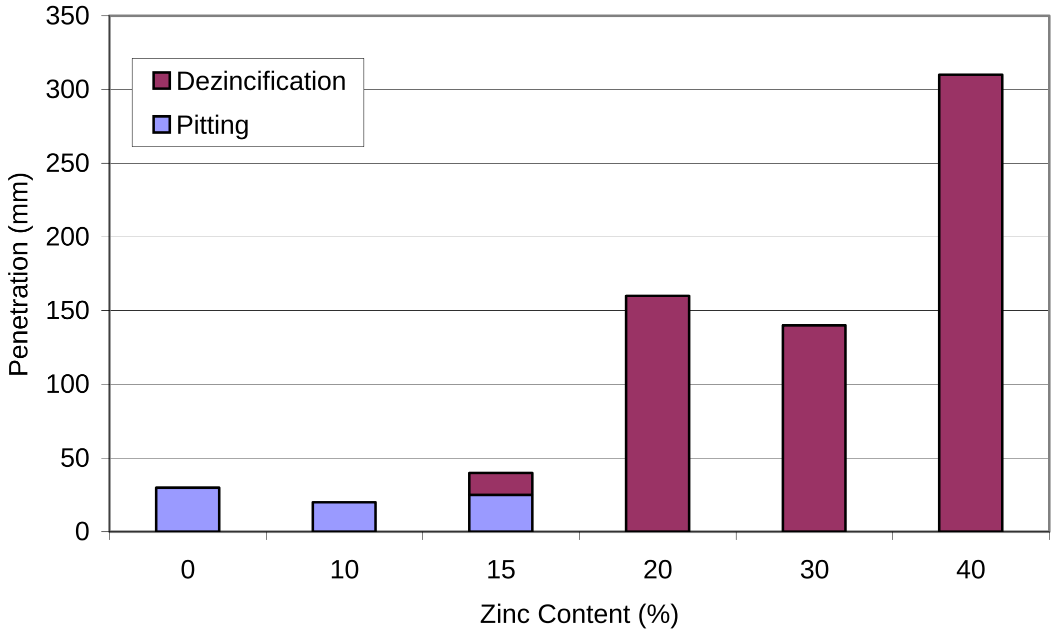


Figure 35 The Effect of Zinc Content on the Corrosion of Brass in an Ammonium Chloride Environment[73]

Alloying brass compounds with additional elements can enhance the corrosion resistance. The addition 1% Sn, for example, improves the resistance to dezincification in 70 Cu-30 Zn alloys; this alloy is called admiralty brass. (The addition of 0.75% Sn to 60 Cu-40Zn produces the alloy called Naval brass.) Alloying nickel with brass produces nickel-silver alloys, which have a good resistance to fresh water corrosion, are resistant to dezincification, and significantly improves corrosion resistance in salt water. The addition of Pb, Te, Be, Cr, or Mn to brass has no significant affect on its corrosion resistance.[73]

Al addition (2%) added to 76 Cu-22 Zn produces aluminum brass, which has improved corrosion resistance. These alloys exhibit improved resistance to impingement attack in seawater flowing at high velocities, but are still susceptible to dezincification.[73] The addition of arsenic, phosphorous or antimony can be used to increase the resistance of aluminum brass, admiralty brass or naval brass to dezincification.[73] Arsenic added to aluminum brass in an amount of approximately 0.10%, for example, improves dezincification resistance.

3.3.1.4 Copper-Nickel

Copper-nickel has a resistance to fresh water, contaminated water, and marine environments that is similar to that of bronze. It is also more noble than pure copper on the galvanic series, and therefore, less susceptible to galvanic corrosion. Copper-nickel alloys with a composition of 70% Cu and 30% Ni have the best resistance to corrosion in aqueous and acidic environments, in addition to having a very good resistance to SCC and impingement attacks. Copper-nickel alloys have a moderate resistance to pitting. Cu with 10% Ni also has a very good resistance to impingement attack and SCC. Copper-nickel alloys have a moderate resistance to pitting, although some specific alloys have an excellent resistance to pitting in seawater (e.g. alloys C70600 and C71500).[73] Copper-nickel alloys with additions of Fe are usually very resistant to SCC. Cu-18Ni-17Zn and Cu-18Ni-27Zn exhibit good corrosion resistance in freshwater and seawater, and a good resistance to dezincification.[73] Some copper-nickel alloys, however, are susceptible to crevice corrosion in seawater.

3.3.1.5 Other Alloying Elements

Copper-silicon alloys have a greater resistance to SCC than brass, in general. Copper-beryllium alloys are the only copper alloys that have shown a susceptibility to pitting in atmospheric environments. Additions of phosphorous in amounts greater than 0.04% can lead to serious SCC. Additions of aluminum result in a more anodic metal compared to pure copper, in terms of galvanic corrosion.

3.3.2 Resistance to Forms of Corrosive Attack

Despite its excellent corrosion resistance in general, copper and its alloys are susceptible to several forms of corrosion. Copper is susceptible, to some extent, to uniform corrosion, galvanic corrosion, dealloying (selective leaching), pitting, SCC, erosion corrosion, fretting, intergranular corrosion, and corrosion fatigue. These forms of corrosion with respect to copper and its alloys are described in the following sections. (They are also described in more general terms in Section 1.0.)

3.3.2.1 Uniform Corrosion

Copper and its alloys have a strong resistance to uniform corrosion under normal conditions, but over long periods of exposure they will exhibit to some extent this form of non-localized corrosion. Immersion in or uniform exposure to aerated or oxidizing acids or sulfur containing compounds, etc., will accelerate the process of uniform corrosion on copper and its alloys.

3.3.2.2 Galvanic Corrosion

Copper has a relatively noble (cathodic) position on the Galvanic Series compared to many structural metals and alloys, thus it will most likely not corrode preferentially when electrically coupled with one of them. When coupled with more noble metals, however, such as nickel, titanium, and some stainless steels, copper will corrode preferentially by galvanic action.

3.3.2.3 Dealloying (Dezincification)

When considering a copper alloy it is very important to realize its potential for dezincification, if it has a significant zinc content (>15% in Cu-Zn alloys). Dezincification is a process which leaches out the zinc leaving behind a less ductile, porous copper structure that is more susceptible to fracture. This often occurs in ambient waters or salt solutions. Dealloying also occurs in some copper-aluminum alloys, where the aluminum is selectively leached from the alloy. This has a greater occurrence in alloys with more than 8% aluminum.

3.3.2.4 Pitting

Most often, pitting does not occur to a significant extent in copper, that is, not enough to cause any considerable damage. If very thin copper or copper alloys are used, however, perforation is possible by pitting. Moreover, if copper is used in low flow velocity or stagnant seawater, it does have a slightly higher propensity for pitting.

6.3.2.5 Crevice Corrosion

Copper and its alloys are generally resistant to crevice corrosion, although a few specific alloys may have a tendency to experience a form of crevice corrosion. Typically, copper alloys containing aluminum or chromium have a higher susceptibility to crevice corrosion.

3.3.2.6 Erosion Corrosion

Copper and its alloys are susceptible to erosion corrosion, which is also characterized as impingement attack. This is especially the case for copper when immersed in polluted water, contaminated water, seawater, or water containing sulfur compounds. Erosion corrosion from cavitation also has a tendency to occur on copper alloys.

3.3.2.7 SCC

Copper and its alloys are susceptible to stress corrosion cracking, especially in the presence of ammonia and ammonium compounds. Stress corrosion cracking of copper alloys is presumed to be integrally related to dealloying.[73] Table 32 presents some copper alloys and their corresponding resistance to SCC.

Table 32 Resistance of Some Copper Alloys towards Stress-Corrosion Cracking[9]

Relative Rating	Alloy System
1. Low Resistance	• Brasses with more than 20% Zn • Brasses with more than 20% Zn plus small amounts of Sn, Pb, or Al (e.g., leaded high brass; naval brass; admiralty brass; aluminum brass)
2. Intermediate Resistance	• Brasses with less than 20% Zn (e.g., red brass; commercial bronze; gilding metal) • Aluminum bronze • Nickel (12%)-Silver
3. High Resistance	• Silicon Bronze • Phosphor-copper • Phosphor-bronze • Nickel (18%)-Silver
4. Superior Resistance	• Cupro-Nickel Alloys • Tough-pitch Copper • High-purity Copper

3.3.3 Corrosion Resistance in Various Environments

3.3.3.1 Atmospheric Environments

With the exception of instances where ammonia (NH_3), sulfur compounds (H_2SO_4) or certain other chemical agents are present, copper and its alloys generally exhibit an excellent resistance to corrosion in atmospheric environments, including clean (rural), polluted (industrial), marine and tropical. Copper and its alloys are therefore suitable for long-term use in atmospheric environments. Table 33 provides the corrosion rates of certain copper alloys in various atmospheric environments.

Table 33 Uniform Corrosion Rates of Some Copper Alloys in Several Atmospheric Environments[73]

Copper Alloy	Corrosion Rate (μm/year)					
	Industrial	Industrial Marine	Tropical Rural Marine	Humid Marine	Rural	Dry Rural
ETP Pure Copper	1.40	1.38	0.56	1.27	0.43	0.13
DLP Pure Copper	1.32	1.22	0.51	1.42	0.36	0.08
Red Brass	1.88	1.88	0.56	0.33	0.46	0.10
Cartridge Brass	3.05	2.41	0.20	0.15	0.46	0.10
Phosphor Bronze	2.24	2.54	0.71	2.31	0.33	0.13
Aluminum Bronze	1.63	1.60	0.10	0.15	0.25	0.51
Silicon Bronze	1.65	1.73	-	1.38	0.51	0.15
Tin Brass	2.13	2.51	-	0.33	0.53	0.10
Copper Nickel	2.64	2.13	0.28	0.36	0.48	0.10

ETP – Electrolytic Tough Pitch DLP – Deoxidized Low Phosphorous

3.3.3.2 Water Environments

In fresh water environments, copper tends to form a protective coating on the surface, and is typically very resistant to corrosion in such environments. The corrosion rate is slightly higher in soft water or water having a significant amount of dissolved CO_2. Marine environments typically pose little threat to copper and most copper alloys, although at high flow velocities in seawater copper is very susceptible to erosion corrosion. Copper and its alloys are also very resistant to biofouling.

Copper is generally resistant to corrosion in steam environments. If there is a significant concentration of CO_2, oxygen or ammonia in the steam, however, the copper is more susceptible to corrosion.

3.3.3.3 Acids/Alkalines

Copper does not usually corrode in the presence of acids unless there are oxidizing agents (e.g. oxygen, HNO_3) available. For instance, copper and sulfuric acid do not react unless oxygen is present. Hence, it is susceptible to oxidizing acids, in addition to oxidizing heavy metal salts, sulfur, and ammonia. Exposure to environments containing ammonia can result in rapid and severe attack in the form of uniform corrosion or SCC. However copper is resistant to neutral solutions and solutions with a pH slightly on the alkaline side. The most threatening environments are ammonia, cyanide solutions, oxidizing salts and acids, or salts and acids in oxidizing conditions. Table 34 provides the uniform corrosion rate of copper in three different acids.

Table 34 Corrosion Rate of Copper in Several Acids[73]

Acid	**Corrosion Rate (mils/year)**
32% HNO_3	9450
Concentrated HCl	30
17% H_2SO_4	4

3.3.3.4 Soil

Copper is generally very resistant to corrosion in soil, and copper-tin (bronze) alloys are especially resistant to corrosion in soil. The presence of organic compounds, ammonium compounds, sulfates, or cinder, however, adversely affects the corrosion resistance of copper. Figure 36 shows the rate of uniform corrosion for copper in four different types of soils over a long period of time.

3.4 Nickel and Its Alloys

Nickel and nickel alloys are commonly used for applications subject to severe corrosion problems, since they exhibit excellent corrosion resistant properties in addition to having other desirable material properties. They are more expensive, however, than copper alloys and stainless steels. Nickel is a relatively noble metal, and does not readily corrode without the presence of an oxidizing agent. Under certain conditions nickel will form a passive film that protects the metal from corrosion.

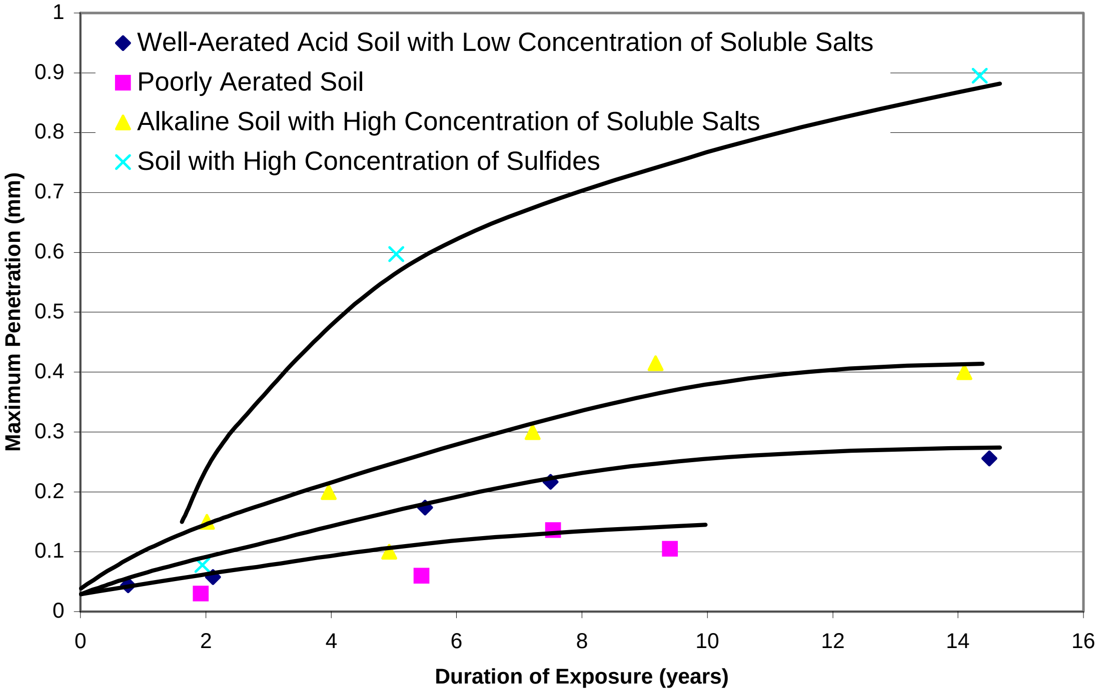


Figure 36 Rate of Corrosion of Copper in Different Types of Soils[73]

There is a wide range of environments that nickel and its alloys are resistant to. They typically show good resistance to corrosion in atmospheric environments, fresh water, distilled water, seawater and nonoxidizing acid environments. Nickel also has a very good resistance to corrosion in alkaline environments and solutions, halogens, reducing salts, and other oxidizing halides.[74] They have good resistance to corrosion at lower and higher temperatures, and in neutral solutions or solutions with a pH slightly less than 7. Nickel has a strong resistance to high stresses that may cause SCC. Nickel is susceptible to strong oxidizers (e.g. nitric acid, ammonia) and sulfuric environments at high temperature, however, which can cause general corrosion and possibly intergranular corrosion.

3.4.1 Alloys and Alloying Elements

Many of the superalloys are nickel-based or have a high nickel content, and have a good resistance to corrosion. Several of the key alloying elements and their impact on the corrosion resistance of nickel are reviewed in the following sections. In addition, some nickel-based alloys are considered as well.

3.4.1.1 Chromium

The addition of chromium enhances the resistance of nickel to high temperature corrosion. Chromium additions improve the resistance to oxidation at high temperatures and the resistance to oxidizing acids such as nitric and chromic acids. Furthermore, chromium improves the resistance of nickel to carburization and sulfidation at higher temperatures, but negatively impacts the resistance to corrosion in high temperature environments containing nitrogen or fluorine. Chromium forms a passive film on the nickel alloy in these types of environments. It also provides resistance to corrosion in liquid environments at lower temperatures, and to SCC, pitting and crevice corrosion. The maximum corrosion resistance is achieved with a chromium content of approximately 20%, and corrosion resistant superalloys usually contain 15-30% Cr.

3.4.1.2 Nickel-Chromium-Iron Alloys

Inconel 600 is a Ni-Cr-Fe alloy that is very resistant to corrosion in organic acids, caustic soda, and alkalis, but is only moderately resistant to corrosion in mineral acids. It is also resistant to atmospheric corrosion, high temperature corrosion, SCC, oxidation, carburization and nitridation.[74] Hastelloy G-30 has excellent resistance to corrosion in nitric acid, and also resistant to sulfuric acid, phosphoric acid, fluorides, and oxidizing acids in general. Inconel 690 exhibits excellent resistance to oxidizing agents, sulfuric acid, and nitric acid. It is also very resistant to high temperature corrosion.

3.4.1.3 Nickel-Chromium-Molybdenum Alloys

Inconel 617 is a nickel-chromium-molybdenum alloy that exhibits excellent resistance to oxidation. Inconel 625 is resistant to pitting, crevice corrosion and oxidation at high temperatures, as well as to highly corrosive environments.[74] It also shows resistance to corrosion in halides, as well as to carburization, which can cause corrosive degradation of the material. Hastelloys C-276 and C-4 offer resistance to localized corrosion as well as SCC. Inconel 625 and Hastelloy C-276 can be resistant to hydrochloric acid even in the presence of oxidizing agents. Hastelloy C-22 provides superior resistance to oxidation, as well as excellent resistance to SCC and localized corrosion. Hastelloy C-2000 offers very good resistance to uniform corrosion in a wide range of environments, as well as very good resistance to SCC and localized corrosion.

3.4.1.4 Nickel-Chromium-Iron-Molybdenum Alloys

Incoloy 825 is a nickel-chromium-iron-molybdenum alloy that exhibits excellent resistance to sulfuric acid and phosphoric acid, moderate resistance to hydrochloric acid, and less resistance to corrosion in alkalis and halogens. Incoloy 825 is resistant to SCC, pitting and intergranular corrosion.[74] Hastelloy G and Hastelloy G-3 are suitable for service in sulfuric acid and phosphoric acid. Hastelloy G-30 is resistant to corrosion in phosphoric acid, sulfuric acid, nitric acid, fluorides, and oxidizing acids.[74] Hastelloy D-205 exhibits excellent corrosion resistance in sulfuric acid at high temperatures and to oxidizing agents. Most of the alloys in this group are very resistant to atmospheric corrosion.

3.4.1.5 Copper

Nickel-copper alloys have excellent resistance to corrosion in seawater, some acids, alkalis, and halides. Additions of copper typically improve nickel’s resistance to nonaerated, nonoxidizing acids. For example, additions of 30-40% Cu typically result in nickel having a good resistance to sulfuric acid and an excellent resistance to hydrofluoric acid. Copper is the main alloying element in Monel superalloys, which contain approximately 70% Ni and 30% Cu and have a good resistance to hydrofluoric acid. Copper can be added to Ni-Cr-Mo-Fe alloys to improve their resistance to hydrochloric, sulfuric and phosphoric acids.[74]

3.4.1.6 Nickel-Copper Alloys

Nickel-copper alloys possess corrosion resistance similar to that of pure nickel, that is, they are resistant to corrosion in a broad range of environments. They are also similar to nickel in that they are susceptible to corrosion in oxidizing environments. Nickel-copper alloys have a good resistance to corrosion in sulfuric acid, seawater, and halogens.

Monel 400 is a nickel copper alloy with additional alloying elements, and is very resistant to seawater, sulfuric acid, alkalis, and halogen acids, including hydrofluoric acid as long as oxygen is not present in significant quantities. The resistance of Monel 400 to corrosion in low concentrations of nonoxidizing hydrochloric acid is very good even at higher temperatures (up to 200°C). It is much more susceptible to corrosion in hydrochloric acid containing oxidizing agents. Monel 400 is also very resistant to atmospheric corrosion and to corrosion in flowing seawater. Monel 400 exhibits very good resistance to erosion corrosion in seawater, but is susceptible to pitting and crevice corrosion in stagnant or low-flow velocity seawater. Monel K-500 has corrosion characteristics similar to Monel 400.

3.4.1.7 Aluminum

Aluminum additions help to provide resistance to oxidation, sulfidation (which can cause corrosive degradation) and carburization at high temperatures, but may also make nickel more susceptible to high temperature corrosion in nitriding environments. With greater than 4% Al content, an oxidation inhibiting aluminum oxide film is capable of forming on the surface of the nickel alloy; however, it only occurs at high temperatures (>870°C). Once the film is formed it will protect against lower temperature oxidation too, but if it is abraded or removed, the alloy will no longer have the same oxidation resistance. Aluminum may result in a degradation of the hot corrosion resistance in superalloys, but it is also dependent on Cr content and the temperature of the environment.

3.4.1.8 Titanium

Additions of titanium to nickel are not typically used in nickel alloys intended for use in lower temperature applications. Titanium may provide some improvement in nickel’s resistance to hot corrosion, but it may also degrade the resistance to SCC, if carbon, oxygen or nitrogen is present. Titanium additions are used in superalloys with aluminum to improve the strength, and a high titanium to aluminum content ratio results in improved hot corrosion resistance.

3.4.1.9 Molybdenum

Additions of molybdenum improve the resistance of nickel to crevice corrosion, pitting corrosion in seawater, and to corrosion in nonoxidizing acids. Up to 28% Mo is used for nonoxidizing environments of hydrochloric, phosphoric, hydrofluoric and sulfuric acids. However, molybdenum also degrades nickel’s resistance to hot corrosion and to nitric acid, and decreases the resistance of nickel to oxidation at high temperatures. Furthermore, nickel-molybdenum alloys are susceptible to corrosion in oxidizing acid environments.

3.4.1.10 Nickel-Molybdenum Alloys

Nickel-molybdenum alloys exhibit excellent corrosion resistance in hydrochloric, sulfuric, and phosphoric acid environments. They are however, more susceptible to corrosion in oxidizing environments, and are especially susceptible to corrosion in nitric acid environments.

Hastelloy B and Hastelloy B-2 exhibit good resistance to corrosion in hydrofluoric acid environments at low temperatures. Welded components made from Hastelloy B may be susceptible to intergranular corrosion. Hastelloy B-2 is a nickel-molybdenum alloy that has excellent resistance to aluminum-chloride environments, while Hastelloy B-3 exhibits good resistance to SCC. Both of these alloys exhibit superior resistance to corrosion in hydrochloric acid compared to all of the nickel-based alloys, but they are more susceptible to this environment if oxidizing agents are present.

3.4.1.11 Tungsten

Tungsten additions improve the resistance of nickel to localized corrosion and corrosion in the presence of nonoxidizing acids. Tungsten can quickly increase the density of a nickel alloy, however, because of its relatively high atomic weight. When used with 13-16% Mo in amounts of 3-4%, tungsten provides extra local corrosion resistance. However, alloying tungsten with nickel superalloys can result in a poorer resistance to hot corrosion. Tungsten may negatively affect the resistance of nickel to oxidation at high temperatures.

3.4.1.12 Silicon

Nickel alloys containing silicon often have it in small amounts as a contaminant from a processing step during fabrication. Silicon additions however, are sometimes intentionally used (typically 9-11%) to provide hot corrosion resistance in concentrated sulfuric acid environments. Moreover, silicon additions improve the resistance of nickel to high temperature corrosion; specifically oxidation, nitridation, sulfidation and carburization.[74]

3.4.1.13 Iron

Additions of iron can be used to reduce the cost of nickel, since nickel is more expensive than iron, but it does not offer much in terms of corrosion resistance. Iron additions, though, can improve nickel’s resistance to sulfuric acid, and may also improve the resistance to carburization at high temperatures.

3.4.1.14 Cobalt

Cobalt is not typically used in significant amounts since it has corrosion resistance characteristics very similar to nickel and is more expensive. It does however, provide improvement to high temperature carburization and sulfidation resistance in nickel alloys.[74]

3.4.1.15 Other Alloying Elements

Yttrium, lanthanum, and other elements may also improve the corrosion resistance of nickel and its alloys. Yttrium generally improves the resistance to high temperature oxidation, sulfidation and carburization. Tantalum and niobium can improve the corrosion resistance at higher temperatures and the resistance of nickel alloys to intergranular corrosion. Niobium may increase the resistance of nickel to carburization at high temperatures, but may also decrease the resistance of nickel to nitridation at high temperatures. Carbon can improve the resistance of nickel to nitridation and carburization at high temperatures, but decreases the resistance to high temperature oxidation. Manganese typically reduces the resistance of nickel to high temperature oxidation and nitridation.

3.4.2 Resistance to Forms of Corrosive Attack

In general, nickel and its alloys have an excellent resistance to corrosion. In certain conditions, of course, they may be susceptible to some forms of attack. A few of the forms of corrosion are described below in terms of the resistance or susceptibility of nickel and its alloys.

3.4.2.1 Uniform Corrosion

Nickel and its alloys are very resistant to general corrosion in a wide range of environments. Since it is a relatively noble metal, alloys with a high nickel content typically exhibit a good resistance to uniform corrosion.

3.4.2.2 Galvanic Corrosion

Since nickel is a relatively noble metal and also a fairly cathodic in the Galvanic Series compared to most other metals, it is not very susceptible to galvanic corrosion. It may however, exhibit a degree of corrosion due to galvanic action, if it is coupled with a more noble metal.

3.4.2.3 Pitting and Crevice Corrosion

Nickel is somewhat susceptible to pitting and crevice corrosion in seawater and other environments. Typically, surface impurities are the cause of pitting, since they can act as a nucleating point for corrosion. Crevice corrosion can occur, particularly in areas where there is stagnant seawater.

3.4.2.4 Intergranular Corrosion

Nickel has a good resistance to intergranular corrosion, although in certain nickel alloys with inappropriate heat treatments it may be susceptible to this particular form of corrosion. In general, a higher nickel content corresponds to a better resistance to intergranular corrosion. In environments containing sulfur, nickel alloys have an increased susceptibility to intergranular corrosion.

3.4.2.5 Stress Corrosion Cracking

Alloys that contain mostly nickel with a small amount of iron tend to be susceptible to SCC. Nickel alloys seem to have a greater resistance to SCC compared to stainless steels.

3.4.2.6 High Temperature Corrosion

Nickel and its alloys may be susceptible to oxidation, carburization, nitridation, sulfidation and halogenation at high temperatures.[74] Certain alloying elements however, can provide augmented resistance to high temperature corrosion in environments where these contaminants are present.

3.4.3 Corrosion Resistance in Various Environments

3.4.3.1 Atmospheric Environments

Nickel and nickel alloys demonstrate very good resistance to corrosion in atmospheric environments, although after extended periods of exposure many alloys will develop a thin, adherent film, especially in industrial environments. Even so, nickel and its alloys are generally suitable for use in atmospheric environments, due to their strong corrosion resistance. Table 35 gives corrosion data on some nickel-based alloys after exposure to the atmosphere.

Table 35 Atmospheric Corrosion of Nickel-Base Alloys[74]

Alloy	**Average Weight Loss/Surface Area (mg/dm^2)**	**Average Corrosion Rate (mils/year)**
Nickel 200	468.6	<0.1
Incoloy 800	27.9	<0.1
Inconel 600	19.7	<0.1
Monel 400	644.7	<0.1
Incoloy 825	8.7	<0.1

3.4.3.2 Water Environments

Fresh water environments do not pose much of a threat to nickel and nickel alloys, since they generally exhibit a good corrosion resistance in these environments. Therefore, they are suitable for applications that require the exposure to or handling of fresh water environments.

The resistance of nickel and nickel-based alloys to corrosion in seawater is dependent on factors such as the velocity of flow of seawater. Some alloys may exhibit good corrosion resistance to flowing seawater, for example, but are susceptible to corrosion in stagnant or low-flow seawater. Table 36 shows the corrosion resistance of several nickel-based alloys exposed to stagnant seawater.

Table 36 Corrosion Resistance of Several Nickel-Based Alloys Exposed to Stagnant Seawater.

Alloy	**Maximum Pit Depth (mils)**
Inconel 625	-
Incoloy 825	0.98
Monel K-500	34
Monel 400	42
AISI type 316 Stainless Steel	62

3.4.3.3 Acids/Alkalis

Nickel and nickel-based alloys are generally resistant to corrosion in nonaerated and nonoxidizing acids. Since sulfuric acid is not considered to be an oxidizing acid up to a concentration of about 50-60 wt.%, for example, most nickel alloys are generally resistant to corrosion in this environment.[74] The corrosion rate of these alloys, though, typically increases with increasing sulfuric acid concentration. Nickel and its alloys are generally resistant to corrosion in acrylic acid and fatty acids.[74]

The presence of oxidizing agents in acids or the aeration of acids can significantly increase the corrosion rate of the nickel alloy. For instance, nickel alloys are typically resistant to HCl in low concentrations, but the presence of Cu^{2+} or Fe^{3+}, for example, may increase the corrosion rate of these alloys considerably. Some alloys, however, offer a better resistance in acids with oxidizing agents present, than others. Alloys containing chromium are more resistant to these types of acids, such as nitric and chromic acids, while molybdenum additions tend to degrade the resistance of nickel to these acid environments. The uniform corrosion rates of some nickel-based alloys in several acid environments are given in Table 37.

Table 37 Corrosion Rate of Several Nickel-Based Alloys in Various Acid Environments[74]

Nickel-Based Alloy	**Corrosion Rate (mils/yr)**		
	5% HF Acid	**99% Acetic Acid**	**40% Formic Acid**
Inconel 600	9.0	-	10.0
Hastelloy C-276	10.0	0.3	2.9
Hastelloy C-22	13.5	-	-
Hastelloy B-2	15.0	1.2	0.35
Hastelloy C-4	15.0	0.02	3.0
Inconel 625	16.0	0.4	7.3
Nickel 200	18.0	4.5	10.4
Hastelloy G	-	1.2	5.1
Hastelloy G-2	-	0.2	-
Hastelloy G-3	20.0	0.6	2.0
Hastelloy G-30	30.0	-	-
Monel 400	-	0.6	2.1
Incoloy 825	-	-	7.9

Nickel is strongly resistant to corrosion in alkalis, but environmental contaminants can cause an increase in the corrosion rate. Nickel is not, however, resistant to ammonium hydroxide solutions.[74] The corrosion resistance of nickel alloys in alkalis tends to decrease with decreasing nickel content.

3.5 Titanium and Its Alloys

Titanium is an inherently reactive metal, but it performs very well against a wide range corrosive environments. It may be the best available metal for corrosion resistance, but it is also very expensive, thus it is not used for many applications. This inherent corrosion resistance can be primarily attributed to a continuous, self-healing, protective oxide film, which forms in the presence of oxygen or water vapor. The protective film helps resist corrosion in oxidizing environments. In environments that do not contain an oxygen source, however, titanium is susceptible to corrosion.

3.5.1 Alloys and Alloying Elements

In general, additions of large amounts of an alloying element reduce the corrosion resistance of pure titanium. Small amounts of palladium, platinum, and rhodium, however, increase the resistance to corrosion, including corrosion in moderate concentrations of hydrochloric and sulfuric acids. Additions of approximately 30% molybdenum improve the resistance to hydrochloric acid.

Other typical alloying elements used in titanium alloys include aluminum, chromium, iron, manganese, molybdenum, tin, vanadium, and zirconium. Aluminum additions above 6% causes a significant degradation in the SCC resistance, while titanium aluminide intermetallics may have increased resistance to oxidation and oxygen embrittlement. Additions of approximately 2% nickel improves crevice corrosion resistance in hot brine environments, but reduces the resistance to hydrogen embrittlement and also degrades the formability of titanium. Table 38 shows the resistance or various titanium alloys to SCC in a hot-salt environment.

Table 38 Relative Resistance of Titanium Alloys to Hot-Salt Stress Corrosion[3]

Least Resistance	**Moderate Resistance**	**Most Resistance**
Ti-5Al-2.5Sn (M.A.)	Ti-8Mo-8V-2Fe-3Al	Ti-4Al-3Mo-1V
Ti-12Zr-7Al	Ti-5Al-5Sn-5Sr-1Mo-1V	Ti-10Sn-5Zr-2Al-1Mo-0.2Si
Ti-8Al-1Mo-1V (M.A.)	Ti-6Al-2Sn-4Zr-2Mo	Ti-11.5Mo-6Zr-4.5Sn
Ti-5Al-5Sn-5Zr	Ti-5Al-2.75Cr-1.25Fe	Ti-8Mn
Ti-6Al-6V-2Sn	Ti-13V-11Cr-3Al	
Ti-5Al-1Fe-1Cr-1Mo	Ti-8Al-1Mo-1V (T.A.)	
	Ti-2Fe-2Cr-2Mo	
	Ti-4Al-4Mo	
	Ti-6Al-4V	

M.A. – Mill Annealed
T.A. – Triple Annealed

3.5.2 Resistance to Forms of Corrosive Attack

Titanium and its alloys typically exhibit an excellent resistance to corrosion. Titanium is generally resistant to oxidation, galvanic corrosion, SCC, corrosion fatigue, and erosion corrosion. A few of the forms of corrosion and their correlation to titanium are briefly discussed in the following sections.

3.5.2.1 Stress Corrosion Cracking

Titanium is susceptible to SCC in the presence of hot-salts or gaseous chloride ions and residual stresses. Severe SCC usually only occurs in the presence of hydrobromic acid or red fuming nitric acid at elevated temperatures; otherwise SCC is not much of a threat to titanium, which is also generally resistant to SCC in seawater, fresh waters and body fluids. Titanium has exhibited susceptibility to SCC in liquid and gaseous oxygen at cryogenic temperatures.

3.5.2.2 Pitting

The occurrence of pitting on titanium is rare, although it can result from iron adsorbed on the surface of titanium. Titanium resists pitting better than stainless steels and copper-nickels.

3.5.2.3 Other Forms

Titanium is susceptible to crevice corrosion, to liquid metal embrittlement in the presence of Cd and Ag, and is also susceptible to embrittlement as a result of the dissolution of hydrogen, oxygen, and nitrogen. Furthermore, titanium and its alloys have a high susceptibility to fretting at interfaces with titanium or other metals, which can significantly reduce its fatigue life.[43] Titanium does, however, have a strong resistance to erosion corrosion and impingement attack, as well as a good resistance to corrosion fatigue.

3.5.3 Corrosion Resistance in Various Environments

Titanium has an excellent resistance to atmospheric corrosion in unpolluted, marine, and industrial environments. It is also highly resistant to corrosion in water, seawater, and chloride solutions. In a wide variety of other chemical environments its corrosion resistance is similar to or better than most other metals. Furthermore, outstanding corrosion resistance at lower temperatures is characteristic of titanium.

Corrosion in inorganic salts and acids and ammonia solutions is easily resisted by titanium. The corrosion resistance of titanium in seawater and body fluids is superior to all other structural metals, and is therefore often used in orthopedic implants. Titanium is also resistant to hypochlorites, chlorine solutions, molten sulfur, wet chlorine gas, H_2S gas up to 260°C, and carbon dioxide up to 260°C. It is susceptible to dry chlorine gas and ionizable fluoride compounds (e.g. sodium fluoride, hydrogen fluoride). Furthermore, molten sodium hydroxide and hot, strong alkali solutions are a couple of the few substances which can attack titanium severely.

Titanium is resistant to most oxidizing acids and organic acids, but is susceptible to reducing acids, strong sulfuric and hydrochloric acids, phosphoric acids, oxalic acids, and fuming nitric acids. The corrosive effects of fuming nitric acid and chlorine gas, however, can be mitigated by adding small amounts of water. Moreover, oxidizing inhibitors and heavy metal ions are effective in mitigating the corrosive attack of acids.

3.6 Magnesium and Its Alloys

Magnesium has the lowest density of the metals but it also has the highest susceptibility to corrosion effectively eliminating it from use in most applications. An oxide layer will form on magnesium; however the thin film layers that form are usually soluble in water and readily breakdown in the presence of ions such as chloride and bromide. Increasing temperatures will also accelerate degradation of the protective film leading to widespread corrosion of magnesium. Galvanic corrosion of magnesium is always a consideration since it is anodic to most metals. Coatings should always be used to protect magnesium alloys in structural applications. Use of Mg alloys in moving components has led to rapid breakdown of the coating system leading to corrosion of the unprotected Mg alloy material. Therefore, magnesium alloys are almost entirely used in non-moving structural applications with proper protective methods.

3.6.1 Alloying for Corrosion Resistance

Alloying magnesium does not lead to any improvements in its corrosion resistance and in some cases can lead to a severe degradation in corrosion resistance. The effects of various alloying elements on the uniform corrosion rates of magnesium are shown in Figure 37.

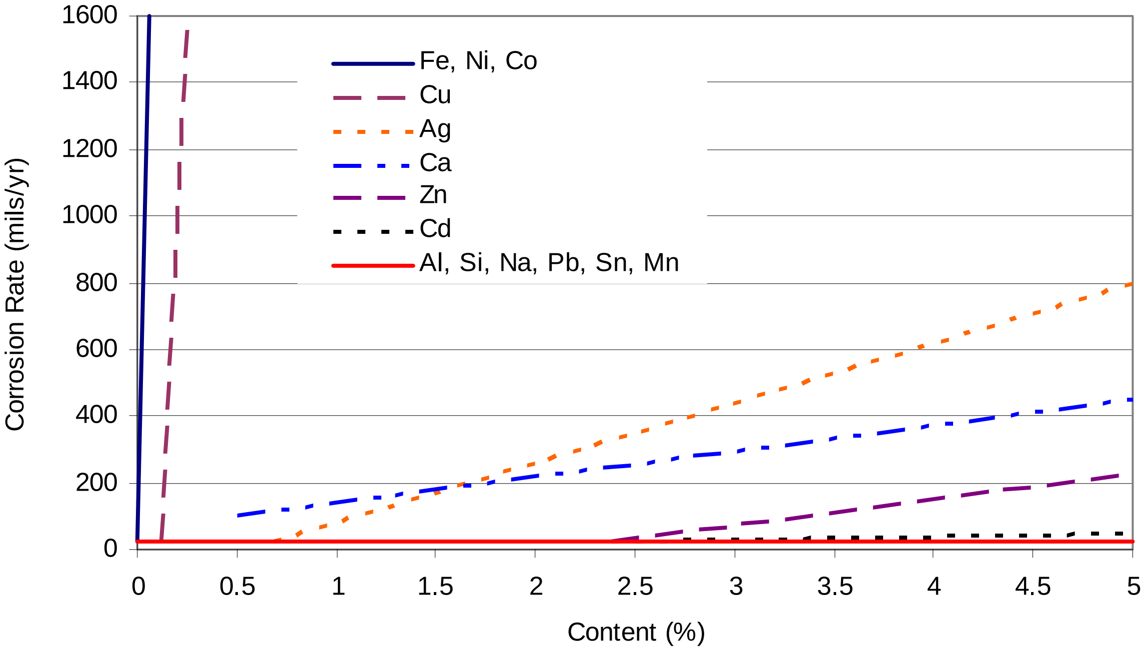


Figure 37 Effect of Alloying on the Uniform Corrosion Rate of Magnesium[75]

Iron, with a concentration of ≥ 0.017%, and also Ni, Co, and Cu significantly increase the corrosion rate of Mg. Aluminum improves the strength and hardness of Mg without seriously degrading its corrosion resistance. A content of 6% Al provides the best combination of strength and ductility. Although it may lead to an increase in corrosion rate, zinc is second to aluminum in its strengthening effect on Mg. It is used in combination with small amounts of other elements such as zirconium and the rare earths to produce a precipitation hardenable alloy. Zn also counters the corrosion effects of Fe and Ni contaminants found in Mg alloys. Manganese has been found to slightly increase resistance to salt water environments by interacting with iron and other heavy metal elements in the alloy. Mn has a low solubility in Mg and thus is used in small amounts, about 1.5% maximum and 0.3% with Al. Some common magnesium alloys with their respective applications are listed in Table 39.

Table 39 Common Magnesium Alloys[76]

Alloy	Alloying Elements	Applications	Remarks
AZ31	3.0 wt% Al 1.0 wt% Zn 0.2 wt% Mn	General purpose wrought alloy	Good extrudability
AZ91	9.0 wt% Al 0.7 wt% Mn	General purpose cast alloy	Good warm temperature mechanical properties
AZ81	8.0 wt% Al 0.7 wt% Mn	Automotive cast alloy	Air-cooled engines (high creep strength)
AM50	5.0 wt% Al 0.3 wt% Mn	High pressure die cast alloy	Automotive structural alloy
ZE41	4.2 wt% Zn 1.0 wt% RE* 0.7 wt% Zr	Special cast alloy for helicopter gearbox	Good creep strength at elevated temperatures
AS41	4.2 wt% Al 1.0 wt% Si 0.3 wt% Mn	Used for automotive crankcases	Better creep resistance than AZ91 at warm temperatures
QE22	2.5 wt% Ag 2.2 wt% RE* 0.7 wt% Zr	Sand and permanent mold casting alloy	Used in aircraft and missile housings
EZ33	3.0 wt% RE* 3.0 wt% Zn	Aluminum-free sand and permanent mold casting alloy	Excellent castability and pressure tightness; easily weldable
WE43	4.3 wt% Y 2.4 wt% RE*	Cast alloy for helicopter gearbox	Better creep resistance than AS41 at warm temperatures.

* rare earth element

3.6.2 Resistance to Forms of Corrosion

Magnesium and magnesium alloys can be highly susceptible to a number of corrosion forms including general corrosion. Issues unique to Mg alloys will be covered in this section. Corrosion prevention and protection methods are almost always necessary when using magnesium materials.

3.6.2.1 Uniform Corrosion

Magnesium alloys have the highest uniform corrosion rates of any metal as shown previously in

Figure 22 in Section 1.1-Uniform Corrosion. An oxide protective layer will form on magnesium once exposed, however this film is easily degraded by a number of environmental conditions and chemical compounds. Corrosion protection methods are almost always used with magnesium alloys. Magnesium alloys are not normally used in moving components where the coatings are easily damaged.

3.6.2.2 Galvanic Corrosion

All metals are cathodic to (more noble than) magnesium. Aluminum alloys are closest to magnesium in the galvanic series, although some aluminum alloys may still pose galvanic corrosion problems when in contact with magnesium alloys. Copper, nickel, and iron cause severe galvanic corrosion to magnesium, and thus aluminum alloys absent of these elements (5000 and 6000 Al series) are preferred for use when in contact with magnesium alloys. Aluminum alloys 5052, 5056, and 6061 have been found to have the least galvanic effect on Mg alloys in a marine atmospheric environment.[75]

3.6.2.3 Stress Corrosion Cracking

The SCC susceptibility of magnesium is generally more severe in alloys containing Al and/or Zn. The addition of aluminum, above 0.15 to 2.5%, creates the highest susceptibility in Mg alloys.[75] The susceptibility increases with increasing Al content to a peak at about 6%, see Figure 38. The addition of zinc increases SCC susceptibility, but not to the extent as does Al containing alloys. Mg alloys absent of both Al and Zn are the most resistant to SCC.

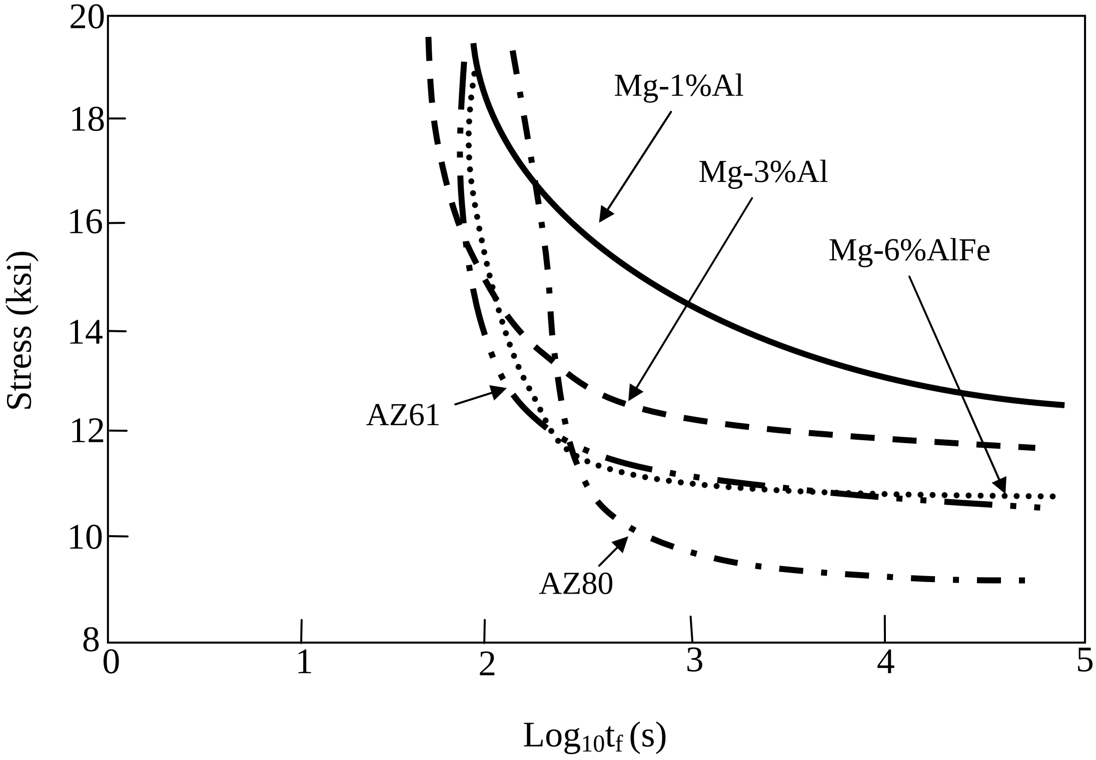


Figure 38 Stress versus Time to Failure for Mg-Al Alloys in a saltwater solution

3.6.3 Corrosion Resistance to Various Environments

Magnesium is susceptible to numerous environmental conditions. Only mild atmospheres and stagnant fresh water which do not break down the MgO surface layer on magnesium are acceptable for magnesium. Any agitation of the water environment or addition of salts into the environment will attack the protective coating and lead to corrosion of the magnesium. Humidity levels of 30% can produce mild corrosion with severe corrosion occurring at a level of

80%. All acids with the exception of hydrofluoric acid and H_2CrO_4 readily attack magnesium. Magnesium does resist corrosion in the presence of dilute alkalis. Organic acids, such as fruit juices and carbonated drinks severely attack magnesium. Other organic compounds do not affect magnesium at room temperatures but may lead to corrosion at elevated temperatures.

3.6.4 Corrosion Protection of Magnesium Alloys

Special care must be given to the fabrication of magnesium joints due to the high susceptibility of this metal. When joining two magnesium parts, a chemical conversion coating should be used, followed by one or more primer coats having alkali resistance such as an epoxy or vinyl resin. Fasteners for Mg-Mg joints include 5056 Al rivets, 6061 Al bolts, and cadmium or zinc plated steel bolts. For joining magnesium with a dissimilar metal, the surfaces must be insulated with an organic tape, sealing compound, or an alkali resistant paint. The joint should be fastened with cadmium plated steel bolts and nuts with a 5052 aluminum washer separating the steel and magnesium. Only 5056, 6061, and 6053 aluminum alloy bolts and screws can be used bare, to join magnesium. All other metal fasteners should be coated when used with magnesium. Some general procedures to limit corrosion in magnesium structures are listed in Table 40.

Table 40 Procedures to Limit Corrosion in Magnesium Structures

Procedure	**Method**
Eliminate areas where trapped moisture is held in contact with metal	Design them out in the first place by careful attention to design of structure details. Provide properly located drain holes. Minimum size about 3.2 mm to prevent plugging.
Choose nonabsorbent, nonwicking materials to contact magnesium	Determine water absorption qualities of materials to be used. Use epoxy and vinyl tapes and coatings, wax, or latex for protective barriers. Avoid use of wood, paper, cardboard, open cell foams, and sponge rubbers.
Protect all faying surfaces	Use proper sealing materials (tapes, films, sealing compounds) on all faying surfaces. Use primers. Lengthen continuous liquid path to reduce galvanic current.
Use compatible metals	For Mg-Al couples, 5000 and 6000 series Al alloys are most compatible For Mg-steel couples, plate steel with zinc, 80% Sn – 20% Zn, tin, or cadmium.
Select proper finishing systems	Choose chemical treatments, paints, plating on basis of service requirements. Service test system before setting up production run. Use past experience in similar applications as guide to choice.

3.7 Zinc and Its Alloys

Zinc is not commonly used without supplemental corrosion protection for corrosion resistant applications since zinc is located near magnesium on the Galvanic Series, and is thus very susceptible to corrosion. It is therefore very anodic to most metals, and will corrode preferentially when galvanically coupled with metals that are more cathodic. Often it is used as an anodic coating to protect steel from corrosion. It is also used as sacrificial anodes for ship hulls, pipelines and other applications. Furthermore, zinc can act as a barrier coating that is resistant to mechanical and electrochemical degradation.

Impurities have a significant impact on the corrosion resistance of zinc, as they often cause the surface to be more susceptible to corrosion. Some impurities, however, such as aluminum, may result in slight improvements in the corrosion resistance of zinc by forming a protective film on the surface.

3.7.1 Alloying for Corrosion Resistance

Neither alloying additions nor impurities significantly affect the corrosion resistance of zinc under normal conditions. Additions of antimony in amounts of 0.03 to 0.07 % do tend to increase the corrosion rate of zinc in atmospheric environments, while copper in amounts less than 0.06% may increase the corrosion resistance of zinc. Variations in the content of lead, cadmium and iron, on the other hand, have little affect on the corrosion resistance of zinc.

3.7.2 Resistance to Forms of Corrosive Attack

Severe pitting is rarely a problem for zinc, since most instances of corrosion takes place uniformly along the surface of the metal. Stress corrosion cracking and corrosion fatigue also rarely occur in zinc, but it is somewhat susceptible to crevice corrosion.

3.7.3 Corrosion Resistance in Various Environments

Zinc has a good resistance to all types of atmospheres, but moist and acidic environments can be problematic for zinc in terms of corrosion. Weak and strong acids and strong bases tend to attack zinc more readily, but it is generally resistant to weak bases. Industrial environments can be corrosive to zinc, especially if the contain sulfur dioxides. Zinc is susceptible to corrosion by sulfur dioxide, chlorides, and low-grade glycerin, but it is resistant to dry chlorine and hydrogen sulfide.

The corrosion rate of zinc is dependent on temperature, pH, and oxygen concentration. There seems to be a strong relationship between corrosion and oxygen content, as it increases with increasing oxygen content in the environment. Zinc is corroded 8 times faster in water with oxygen gas present than in water with no gases. In oxygen deficient environments, pitting tends to occur, while oxygen abundant environments lead to more uniform corrosion. The corrosion rate of zinc is temperature dependent, and it increases rapidly from room temperature to about 60°C, then decreases significantly at 100°C.

Zinc is susceptible to environments containing organic vapors, which tend to attack the metal’s surface. Organic substances therefore, may be very corrosive to zinc, if they produce organic vapors or other products such as sulfur or halogen compounds. Zinc does tend to be resistant, however, to anhydrous organic liquids with a neutral pH.

Zinc has a good resistance to water, but it is more susceptible to corrosion if oxygen or carbon dioxide is present, or if the water is at an elevated temperature, or if the water is strongly aerated or agitated. Furthermore, soft water attacks zinc more readily than hard water, and steam can also be damaging, if zinc is exposed to it in a continuous manner.

3.8 Cobalt and Its Alloys

Cobalt and cobalt-based alloys are very similar to nickel and nickel-based alloys in terms of corrosion resistance, but typically they are slightly more susceptible to corrosion compared to their nickel counterparts. Cobalt-based alloys have an inherent wear and corrosion resistance. Cobalt is not considered an oxidation resistant metal, especially since the oxidation rate is generally about 25 times that of nickel. Cobalt-based superalloys, however, are resistant to oxidation and hot corrosion. Furthermore, the cobalt superalloys are more resistant to hot corrosion than are the nickel superalloys. Nickel and cobalt superalloys have a similar resistance to aqueous corrosion at lower temperatures.

3.8.1 Alloys and Alloying Elements

3.8.1.1 Chromium

Chromium is typically alloyed with cobalt in significant amounts to improve various properties of the metal, including corrosion and oxidation resistance. Cobalt superalloys generally contain 20-30% chromium, which contributes to their good oxidation and hot corrosion resistance. It also provides resistance to corrosion at lower temperatures, as well as higher temperature resistance to oxidation and hot corrosion. Moreover, chromium additions provide enhanced protection of cobalt-based alloys against corrosion in dilute nitric acid environments, but may also decrease the resistance to corrosion in high concentrations of nitric acid. Cobalt-based alloys with a significant chromium content are susceptible to corrosion in chromic acid environments. Cobalt-chromium alloys with a high carbon content also have good wear resistance, but carbon can also inhibit the beneficial effects of the chromium additions.

3.8.1.2 Nickel

Nickel additions improve the resistance of cobalt to corrosion in mineral acids, such as sulfuric and phosphoric acids. It also improves the resistance to SCC. Furthermore, nickel additions provide improved resistance to corrosion in caustic environments.

3.8.1.3 Tungsten

Tungsten additions can improve the resistance of cobalt to corrosion in general, but may lead to corrosion problems at temperatures above 980°C. Tungsten may also increase the corrosion resistance of cobalt-based alloys in chromic acid.

3.8.1.4 Other Alloying Elements

Copper additions improve the resistance of cobalt to corrosion in sulfuric and phosphoric acid conditions. Molybdenum additions can improve the resistance of cobalt to corrosion in general. Additions of vanadium and niobium can be detrimental to the cobalt alloys in terms of corrosion resistance, while additions of manganese, iron, yttrium and lanthanum can improve the alloy.

3.8.2 Resistance to Forms of Corrosive Attack

Cobalt is susceptible to pitting and crevice corrosion, and is usually very resistant to SCC in many environments, but at higher temperatures (>150 °C) in acid chlorides and strong bases it may experience stress corrosion cracking.[77] Cobalt based alloys have an excellent resistance to erosion corrosion, especially from cavitation, and they also typically have outstanding resistance to high temperature corrosion. The resistance of cobalt alloys to oxidation and carburization at high temperatures is generally very good, and the resistance to sulfidation is better than that of nickel-based alloys. Furthermore, cobalt-based alloys tend to be more resistant to hydrogen embrittlement compared to their nickel counterparts.

3.8.3 Corrosion Resistance to Acids and Alkalis

Cobalt-based alloys are generally resistant to corrosion in aqueous environments. Cobalt-based alloys are very susceptible to corrosion in phosphoric acid, but are resistant to corrosion in acetic acid environments. The corrosion resistance of cobalt-based alloys is improved in sulfuric acid environments when oxidizing agents are present. Cobalt-based alloys are typically more resistant to nitric acid, but more susceptible to corrosion in caustic environments than their nickel counterparts.

3.9 Refractory Metals

Refractory metals have very high melting points, retain their strength at high temperatures, and accordingly are often used for jet engine and space applications. Several of the refractory metals and their corresponding melting points are given in Table 41. Refractory metals are typically susceptible to oxidation at high temperatures, but resistant to corrosion in many environments at lower temperatures.

Table 41 Melting Points of Several Refractory Metals

Metal	**Melting Point (°C)**
Tungsten	3410
Tantalum	2996
Molybdenum	2610
Niobium	2468
Zirconium	1852

3.9.1 Molybdenum

At high temperatures (approximately 700°C) in air, molybdenum forms a volatile oxide (MoO_3). It does not perform well in the presence of oxidizing agents at temperatures greater than 500°C, and requires protective coatings in order to be used practically in such environments. Molybdenum does, however, have a good resistance to hydrofluoric, hydrochloric and sulfuric acids without the presence of oxidizing agents. It has a good resistance to corrosion in low to moderate concentrations of sulfuric acid at low to moderate temperatures. Molybdenum is susceptible to oxidizers (e.g. nitric acid), and are generally resistant to alkaline solutions, although not in the presence of oxygen or oxidizing agents.

3.9.2 Tantalum

Tantalum is a fairly inert and expensive metal that is durable and long lasting with a very good resistance to corrosion in many environments including severe ones. Its corrosion resistance can be at least partially attributed to the thin, protective oxide film (usually Ta_2O_5) that forms when exposed to air or another oxidizing environment at 300°C. Its corrosion resistance, in general, is better than that of niobium. It is, however, embrittled in oxygen at temperatures greater than 350°C.

Tantalum is resistant to fresh water, mine water, deionized water and seawater; it is also resistant to steam at high pressures. It is highly resistant to most acids (e.g. sulfuric (H_2SO_4), nitric (HNO_3), hydrochloric (HCl), hydrobromic (HBr), etc.), chemical solutions, salts and salt solutions, and organic compounds including alcohols, ketones, alkaloids and esters, and is fairly resistant to dilute alkaline solutions.

Tantalum reacts with gaseous oxygen, nitrogen, and hydrogen at higher temperatures. It is susceptible to corrosion in hydrofluoric acid, hot concentrated phosphoric acid, sulfite (SO_3), strong alkalis, and strong sulfuric acid at higher temperatures. Tantalum is also susceptible to hydrogen embrittlement, if it is not protected from becoming cathodic in an electrochemical cell that produces atomic hydrogen. The reason for this is because tantalum will absorb hydrogen when it is galvanically coupled with anodic metals.

3.9.3 Niobium

Niobium is a refractory metal that has characteristics very similar to tantalum, which is located below it on the Periodic Table. It oxidizes readily, especially in air above 200°C, and forms a protective oxide film that provides good corrosion resistance.

Embrittlement of niobium is a problem in hydrogen, nitrogen, oxygen, or carbon at temperatures greater than 300°C. Niobium reacts with nitrogen at temperatures greater than 350°C, water vapor at temperatures greater than 300°C, chlorine at temperatures greater than 200°C, and hydrogen, carbon monoxide and carbon dioxide at temperatures greater than 250°C.

In general, niobium has a good resistance to both mineral and organic acids, but is susceptible to alkaline solutions. Specifically, it is resistant to hydrochloric, hydroiodic, hydrobromic, nitric, sulfuric and phosphoric acids; it is susceptible, however, to corrosion in hydrofluoric acid, and strong sulfuric and hydrochloric acids at higher temperatures. It is also less resistant to hot mineral acids compared to tantalum.

Niobium exhibits a good resistance to most gases at temperatures up to 100°C. It is also resistant to liquid and vaporous metals and molten salts. Furthermore, neither salt solutions nor seawater readily attack niobium.

3.9.4 Tungsten

Tungsten is extraordinary because it has the highest melting point of any metal. Besides its high temperature capability, it is resistant to corrosion in weak acids and alkalis at lower temperatures, but it is somewhat susceptible to strong acids at lower temperatures. Moreover, tungsten is susceptible to corrosion by alkalis and strong acids at high temperatures, and the attack can be accelerated or possibly more severe in the presence of oxidizing agents. Tungsten is highly resistant to atmospheric corrosion and to corrosion in water. Oxidation is insignificant in air below 595°C or in oxygen at temperatures less than 510°C.[9]

3.9.5 Zirconium

Zirconium is an expensive and fairly reactive metal that is similar to hafnium, which is below it on the Periodic Table. A self-healing oxide film forms readily on the surface of zirconium in environments with available oxygen; this film protects against corrosion and wear. Zirconium is generally resistant to water and water vapor at regular and higher temperatures, although prolonged exposure to hot water may lead to rapid corrosion of the metal. It is also resistant to salt solutions, seawater, and polluted water. More specifically, zirconium is resistant to uniform, pitting and crevice corrosion in seawater.

Zirconium is also resistant to many acids and bases, including most mineral and organic acids and strong alkalis. Specifically, it is resistant to hydrochloric, nitric, acetic, formic, citric, lactic, and tannic acids, among others. Zirconium is susceptible to hydrofluoric acid, chromic acid and strong hydrochloric and sulfuric acids at higher temperatures. Its resistance to alkalis remains, even at higher temperatures, and has only a moderate corrosion rate when exposed to fused alkalis and liquid sodium.

Ferric chloride ($FeCl_3$) and cupric chloride ($CuCl_2$) environments will often cause pitting to occur on the surface of zirconium, but it is resistant to some molten salts. In general, zirconium is resistant to oxidizers in the absence of halides, but it is susceptible to corrosion, for example, in a humidified chlorine gas. A further threat to zirconium is hydrogen embrittlement.

Impurities in the composition influence the corrosion resistance of zirconium. For example, impurities such as nitrogen, aluminum, titanium, and dissolved ferric and cupric chlorides) degrade the resistance of zirconium to water and steam. Nuclear grades of zirconium do not contain hafnium and have better corrosion resistance in water at higher temperatures.

3.10 Beryllium

Beryllium is used in the nuclear industry, jet and rocket propulsion systems, mirror and re-entry vehicle structures, and aircraft brakes. It is virtually unaffected in normal atmospheric conditions even at elevated temperatures. Condensation on Beryllium can pose a corrosive attack under certain circumstances.

3.10.1 Effect of Impurities

Beryllium is produced in several grades, although none include intentional alloy elements. The production of Beryllium is controlled to reduce impurities present. Commercial grade Beryllium typically contains between 1 and 4.5 % total impurity content. Impurities on the surface of Beryllium through fabrication, cleaning, and machining can increase rates of corrosion. Carbides (Be_2C), introduced through machining, as well as chlorides and sulfates, introduced during a drying process, have resulted in corrosive attack of Beryllium. Improper handling in the form of fingerprints left on dry Beryllium has also led to corrosion. It is essential to control the processing and handling of Beryllium to limit impurities in and on the surface of the finished product.

3.10.2 Resistance to Forms of Corrosive Attack

There is a limited amount of published literature on the corrosion of Beryllium with the following information found.

3.10.2.1 Pitting Corrosion

Pitting corrosion of Beryllium has been seen to occur in some components prompting an investigation of the source mechanisms. It was found that pitting occurred in areas rich in aluminum, silicon, and iron impurities on the material’s surface.

3.10.3 Corrosion Resistance in Various Environments

The susceptibility of Beryllium is primarily a result of corrosive chemicals, namely chlorides, sulfates, and nitrites present under humid conditions. A controlled humidity environment for storage has been found to be effective in limiting corrosion of Beryllium components.

3.10.4 Corrosion Protection of Beryllium

Coatings used on beryllium for corrosion resistance include anodic coatings, chromate, fluoride, and organic paints.[78] Anodic coatings, similar to those used in anodizing aluminum alloys, have been found to increase corrosion resistance in aqueous solutions and for elevated atmospheric temperature environments. Chromate coatings provide protection during storage and handling periods and in marine type environments for moderate periods. Fluoride coatings are used in distilled water and saltwater environments. Organic paints are used to provide an electrical insulation layer. This limits galvanic attack and has been observed to provide long term storage protection when deposited on top of a passivation type coating. Plated coatings have also been used on beryllium, providing electrical contacts, improved wear resistance, and better polishing surfaces.

3.11 Uranium

Depleted uranium is primarily used in weapon systems for its high density. With some alloying, the corrosion resistance is increased in various environments. Two forms of corrosion of which uranium alloys have showed a higher susceptibility, are galvanic and stress corrosion cracking. Protective measures used for uranium alloys have been oxide coatings, organic films, and metal platings.

3.11.1 Alloys and Alloying Elements

The corrosion resistance of uranium is increased with the addition of some alloying elements. The most common alloying elements are titanium, molybdenum, niobium, and zirconium. The addition of these elements promotes the formation of γ-phase (cubic) rather than the α-phase (orthorhombic) of unalloyed uranium, which increases the corrosion resistance.

3.11.2 Resistance to Forms of Corrosive Attack

3.11.2.1 Galvanic Corrosion

A measure of the electrode potentials of a few uranium alloys was obtained in both seawater and 0.1 N HCL. These values are used to determine the potential for galvanic corrosion in similar environments, when in contact with dissimilar metals as covered in Section 2.2. Table 42 gives the values measured in the two environments.

Table 42 Electrode Potentials of Uranium Alloys in Seawater and HCl[79]

Alloy	**0.1 N HCl Electrode Potential (mV)**		
	Oxygen Saturated (25ºC)	**Air-equilibrated**	
		(25ºC)	**(70ºC)**
Unalloyed Uranium	-740	-755	-790
U-4.5Nb	-465	-475	-600
U-6Nb	-395	-420	-465
U-8Nb	-375	-400	-445
U-7.5Nb-2.5Zr	-305	-340	-410
U-10Mo	-170	-190	-240

Alloy	**Seawater Electrode Potential (mV)**	
	Oxygen Saturated (25ºC)	**Air-equilibrated (25ºC)**
Turballoy (Depleted Uranium)	-770	-795
U-4.5Nb	-525	-530
U-6Nb	-470	-460
U-8Nb	-430	-415
U-7.5Nb-2.5Zr	-370	-
U-10Mo	-300	-

3.11.2.2 Stress Corrosion Cracking

Stress corrosion cracking has been found to be problematic with uranium alloys. The U-0.75Ti alloy has the highest susceptibility, with SCC also occurring for the U-Mo and U-Nb alloys. The study of U-0.75Ti alloy in varying environments showed water to be the primary variable responsible for SCC with oxygen deterring SCC. The U-Mo alloys revealed susceptibility for Mo concentrations of 0.6-12%. From 0.6 to ~5%, metastable materials were produced containing the α-phase, showing greater susceptibility to SCC. Above 5%, oxygen is the primary variable responsible for SCC, just the opposite as for the U-0.75Ti alloy. Increasing carbon content in the U-Mo alloys also produces increased susceptibility. Heat treating quenched alloys produced a more equilibrium microstructure, proving to be less susceptible. Uranium-niobium alloys showed water induced susceptibility for the lower content Nb alloys (2.3 and 4.5%) and oxygen induced susceptibility for the higher content alloys (6 and 8%). Water vapor further increases the rate of attack for the U-6Nb and U-9Nb materials in an oxygen environment. The U-7.5Nb-2.5Zr alloy has been observed to form intergranular cracking which is easily propagated in the presence of oxygen, water, and chloride. Transgranular cracking has also been seen for U-7.5Nb-2.5Zr in oxygen environments, but propagates slowly. The standard aging temperature for this alloy is 150ºC, showing the slowest crack propagation rates.

3.11.3 Corrosion Resistance in Various Environments

The methods to study corrosion of uranium alloys have primarily been through the thermodynamics and kinetics of corrosion science as covered in Section 6.0. There has been some limited corrosion testing on uranium, such as in seawater environments.

3.11.3.1 Atmospheric Environments

Corrosion of uranium and uranium alloys will react in humid air environments by the reaction:

$$U + (2+x)\ H_2O \rightarrow UO_{2+x} + (2+x)H_2 \qquad \text{Equation 12}$$

where $0 \le x \le 0.1$. The generation of hydrogen of various uranium alloys in a 100% relative humidity, 75ºC environment, is presented in

Figure 39.

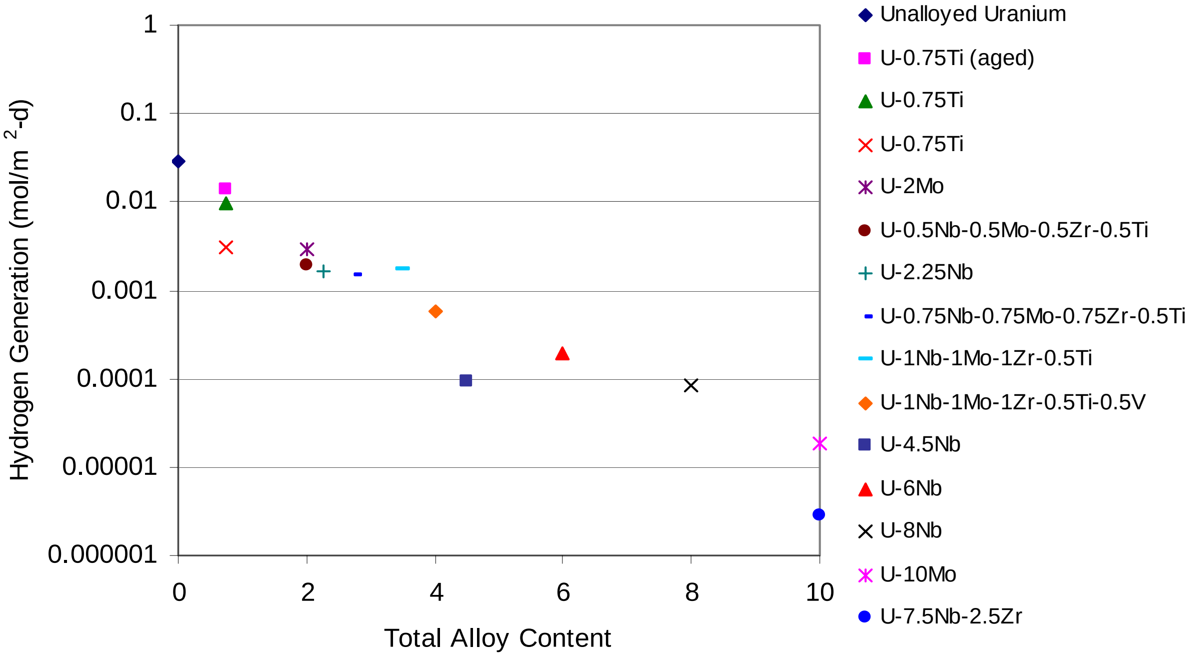


Figure 39 Hydrogen Generation of Various Uranium Alloys[79]

3.11.3.2 Water Environments

A similar dependence of alloying effect on the corrosion of uranium in water environments takes place. Measurements of the uniform corrosion rates of some uranium alloys and unalloyed uranium in seawater at 20ºC is shown in Figure 40.

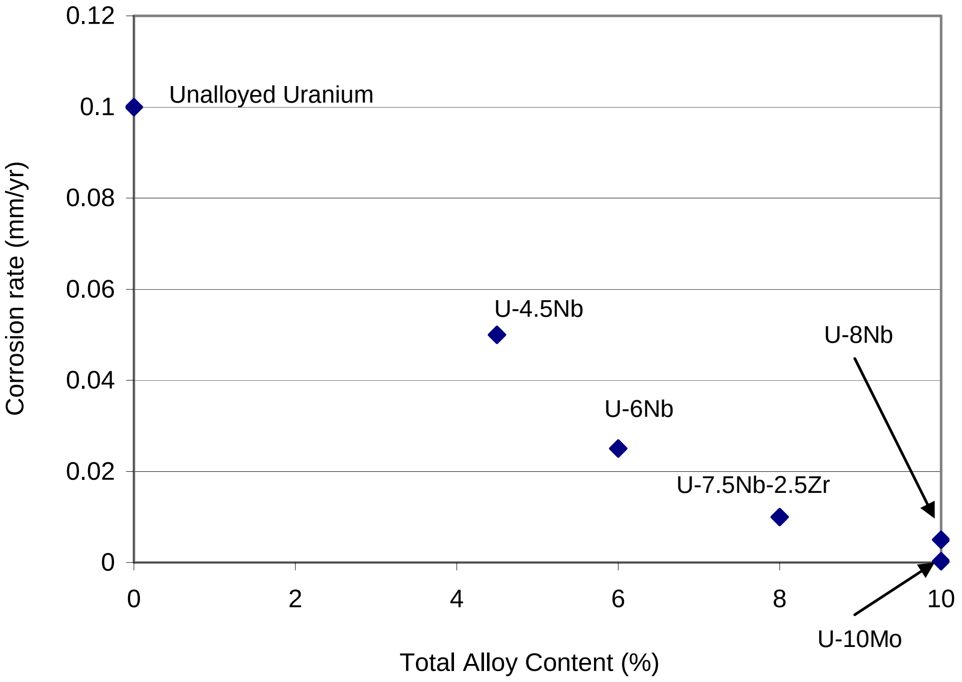


Figure 40 Uranium Alloy Uniform Corrosion Rates in Seawater[79]

3.11.3.3 Chemical Environments

The uranium-binary alloys show active-passive behavior in a number of chemical environments. The ion U^{3+} forms an active region, while UO_2^{2+} forms the passive region near the corrosion potential. Anodic polarization methods are used to study the active-passive transitions in uranium. The transition from active to passive generally represents a decrease in corrosion rate on the order of 10^4 to 10^6.

3.11.4 Corrosion Protection of Uranium

Materials and methods to provide corrosion protective coatings on uranium were studied primarily on unalloyed uranium. Ceramic oxides, organic films and metal platings have all been studied. The ceramic oxides and organic coatings tested have shown a minimal decrease up to increased uniform corrosion rates over unalloyed uranium. Metal platings, namely electroplated nickel and ion-plated aluminum have been found to decrease uniform corrosion rates in short-term slightly elevated temperature tests.

3.12 Cast Irons

Cast iron generally consists of alloying with >2% carbon and >1% silicon with various additional alloying elements dependent upon the application. Cast irons are among the lowest cost metals as they have low raw material costs and are more easily manufactured into product forms. They may be alloyed for corrosion resistance obtaining levels similar to that of stainless steels and nickel-based alloys.

3.12.1 Alloying for Corrosion Resistance

Cast irons can be classified by the degree of alloying into unalloyed gray, ductile, malleable, and white cast irons, low to moderately alloyed cast irons, and high-nickel, high-chromium, and high-silicon cast irons. The unalloyed irons consist of ≤3% of carbon, ≤3% silicon, with no additional intentional alloying. The corrosion resistance of this class is slightly higher than that of the unalloyed steels. The low to moderate alloyed irons include additions of chromium, nickel, copper, and/or molybdenum. They typically have two to three times the corrosion resistance of the unalloyed irons. The high alloyed cast irons have a high corrosion resistance to certain acid and alkali environments. High alloying for corrosion resistance may however compromise other material properties, such as a lower strength.

Alloying with silicon, nickel, chromium, copper, molybdenum, and to lesser extent, titanium and vanadium, will increase corrosion resistance. The alloying elements along with their associated effects on corrosion resistance are presented in Table 43.

Table 43 Cast Iron Alloying Elements and Their Effects[8]

Alloying Element	**Effect**
Silicon	▪ 3 – 14% results in some increased corrosion resistance ▪ > 14% results in a significant increase in corrosion resistance but with a decrease in strength and ductility ▪ >16% results in brittleness and manufacturing difficulties
Nickel	▪ Up to 4% in combination with chromium results in increased corrosion resistance and strength ▪ Corrosion resistance to both acids and alkalis increases ▪ ≥ 12% needed for optimal corrosion resistance ▪ ≥ 18% austenitic irons are practically immune to alkali and caustics, with increased SCC.
Chromium	▪ Small additions result in increased resistance to seawater and weak acids ▪ 15 – 30% increases resistance to oxidizing acids such as nitric acid ▪ High additions decrease ductility
Molybdenum	▪ Added to high silicon cast irons for increased resistance especially effective against hydrochloric acid ▪ 3 – 4% optimal concentration
Copper	▪ 0.25 – 1% increases resistance to dilute acetic, sulfuric, and hydrochloric acids, as well as acid mine water. ▪ ≤10% made to high nickel/chromium cast irons to further increase corrosion resistance.

3.12.2 Resistance to Forms of Corrosion

Cast irons will exhibit the same forms of corrosion as other metals. Notable susceptibilities found in the literature, specific to cast irons will be covered in the following sections.

3.12.2.1 Uniform Corrosion

The corrosion resistance of unalloyed cast irons slightly exceeds that of unalloyed cast steels, with increased resistance dependent upon the extent of higher alloying content. Figure 41 depicts the uniform corrosion rates of some cast irons in relation to a cast steel alloy.

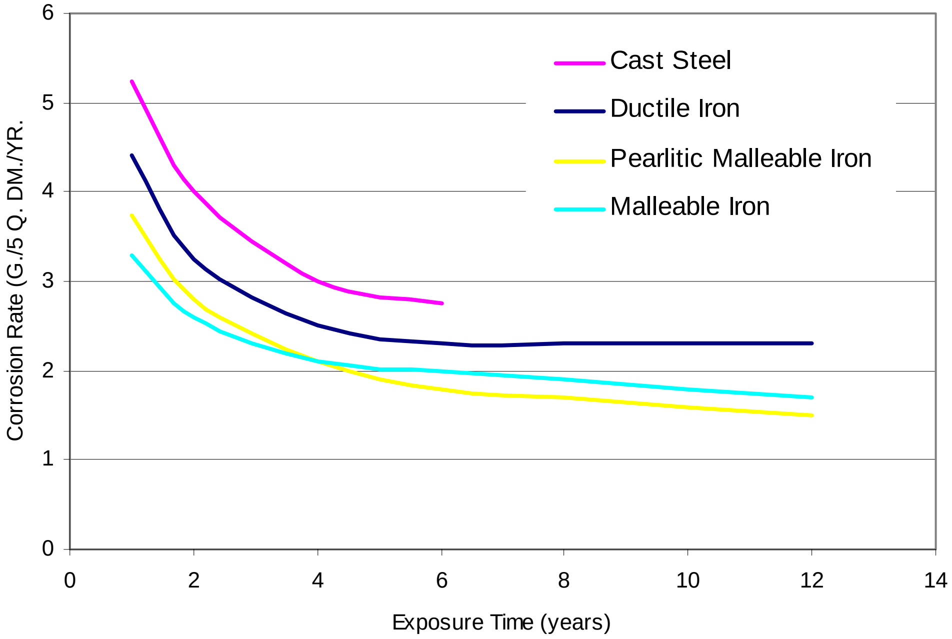


Figure 41 Uniform Corrosion Rates for Ferrous Metals Exposed for Twelve Years[80]

3.12.2.2 Galvanic Corrosion

Gray irons have microstructures conducive to galvanic attack in mild environments. The attack has been termed "graphitic corrosion" and has been classified as both galvanic corrosion and selective leaching. Graphite is cathodic to iron which leads to a localized galvanic cell within gray irons, which in turn leads to selective leaching of the iron. This form of attack only occurs in mild environments as more severe environments produce a more uniform corrosion where the graphite is also removed from the surface of the gray iron.

3.12.2.3 Fretting Corrosion

Fretting corrosion has been observed in a number of metals when in contact with cast irons. Table 44 summarizes field experience in fretting resistance of cast irons to other various materials.

Table 44 Fretting Resistance of Cast Irons to Various Materials[81]

Poor	Average	Good
Aluminum Magnesium Chrome plate Laminated plastic Bakelite Tin plate Shellac coated cast iron	Cast iron Copper Brass Zinc Silver plate Copper plate Amalgamated copper plate	Phosphate coated cast iron Rubber cement coated cast iron Tungsten sulfide coated cast iron Rubber gasket with cast iron Molykote lubricant with cast iron Molykote lubricant with stainless steel

3.12.2.4 Pitting Corrosion

Pitting of cast irons has been reported for environments that included chlorides, dilute alkylaryl sulfonates, antimony trichloride, and calm seawater. High silicon cast irons, especially those containing chromium and/or molybdenum have been found to exhibit a higher resistance to pitting. Nickel additions to cast irons increase pitting resistance for calm seawater environments.

3.12.2.5 Crevice Corrosion

The presence of chlorides in crevice areas of cast irons will increase the rate of crevice corrosion. High silicon cast irons with chromium and/or molybdenum provide higher resistances to crevice corrosion.

3.12.2.6 Intergranular Corrosion

Intergranular attack in cast irons is rare. The only instance found involves an attack of unalloyed cast iron by ammonium nitrate.

3.12.2.7 Erosion Corrosion

The resistance of cast irons to erosion corrosion may be enhanced by increasing the hardness and/or increasing some alloying elements. In relatively non corrosive environments, increasing the hardness through solid-solution or phase transformation induced hardening can increase erosion corrosion resistance. Higher alloying content combined with a higher hardness will increase resistance in more corrosive environments.

3.12.2.8 Stress Corrosion Cracking

Cast irons generally have less susceptibility to SCC due to their fabrication process which limits stresses in the material compared to other processes. However, cast irons still exhibit SCC in a number of environments. The flake graphite structure, found in gray irons and high silicon irons have been found to be more susceptible than other cast irons in the presence acid environments. The acids diffuse into the iron along graphite boundaries and the corrosive byproducts eventually produce enough pressure to crack the iron. Environments found to increase SCC in cast irons include the following:[82]

- Sodium hydroxide solutions
- Calcium nitrite solutions
- Ammonium nitrate solutions
- Sodium nitrate solutions
- Mercuric nitrate solutions
- Hydrogen sulfide solutions
- Oleum (fuming hydrogen sulfide)
- Mixed acids
- Hydrogen cyanide solutions
- Seawater
- Molten sodium-lead alloys
- Acid chloride solutions

3.12.3 Corrosion Resistance in Various Environments

Cast irons find many applications in various environments, and are selected based upon the anticipated chemicals present. Unalloyed and low-alloy cast irons corrosion rates are increased by exposure to sulfur dioxide and similar industrial type atmospheres. They are also readily attacked by chlorides, typical in marine environments. In soils, increased rates of corrosion can be expected in poorly drained areas and where corrosive chemicals are present. The addition of ~3% nickel has been used to increase corrosion resistance of cast irons in poorly drained soils. The corrosion of unalloyed cast irons in water is lower for hard water conditions, where a protective scale of calcium carbonate will develop. Protective scales do not develop well in soft and deionized waters for unalloyed cast irons, resulting in some expected corrosion. Lower pH levels will increase the rate of attack while higher pH levels reduce corrosive effects. High alloy cast irons are not typically used in these environments as their increased cost versus performance does not warrant their use. High-nickel austenitic cast irons have been used for their resistance to pitting in calm seawater conditions. High-silicon cast irons have been used for anodic protection in seawater and brackish water environments.

Cast irons also find applications in many of the common acid and alkali solutions used. They are generally attacked more in mineral acids than the organic acids. The cast irons find uses for varying concentration levels and temperatures, but impurities present can severely degrade their corrosion resistance. The resistance to mineral acids is summarized in Table 45. Unalloyed and low-alloyed cast irons have fair resistance to alkali solutions, but should be kept below 80ºC and 70% concentrations and are highly susceptible to hot solutions of ≥30% concentration levels. The addition of 3-5% nickel increases corrosion resistance to alkali solutions. The high-silicon cast irons have generally the same corrosion resistance as the unalloyed cast irons. They may be used only when impurities are present which reduce the resistance of the unalloyed irons. High-chromium cast irons are more susceptible to alkali solutions and are therefore not recommended.

Table 45 Cast Iron Acid Resistance Properties

Cast Iron	**Environment**
Unalloyed, low-alloyed	H_2SO_4: Limited to low-velocity, low-temperature concentrated acid (>70%) HNO_3: Limited to low-velocity, low-temperature concentrated acid. Rapid corrosion occurs in dilute to medium concentration at any temperature. HCl: Unsuitable in any concentration. H_3PO_4: May be used for concentrated solutions only, although the presence of fluorides, chlorides, or sulfuric acid will significantly reduce corrosion resistance.
High-nickel austenitic	H_2SO_4: Acceptable for room temperature and slightly elevated service in all concentrations HNO_3: Limited to low-velocity, low-temperature concentrated acid. Rapid corrosion occurs in dilute to medium concentration at any temperature. HCl: Some resistance at room temperature and below. H_3PO_4: May be used for all concentration levels and for slightly elevated temperatures. The presence of impurities will significantly reduce corrosion resistance.
High-silicon	H_2SO_4: Best resistance among cast irons. Resistant at all concentrations up to boiling. Rapidly attacked by SO_3. Slow initial passivation results in rapid attack for the first couple days, after which a slow steady corrosion rate develops. HNO_3: Good resistance to all concentrations and temperatures except dilute hot acids HCl: Best resistance among cast irons. With ~4-5% Cr, suitable for all concentrations up to 28ºC. Higher Si content with Cr and Mo can increase temperature service. However, at acid concentrations >20%, Oxidizers will attack the alloy. Initial rapid corrosion occurs for the first couple days, after which a slow steady corrosion rate develops. H_3PO_4: good resistance to all concentration levels and temperatures. The presence of fluorides makes this cast iron unacceptable for use.
High chromium	HNO_3: >20% Cr addition has good resistance, especially for dilute acids. Attacked by high temperature solutions. HCl: Unsuitable for any concentrations H_3PO_4: generally acceptable up to a 60% concentration level

3.12.4 Corrosion Protection of Cast Irons

Metal, organic, conversion, and enamel coatings are used to protect unalloyed and low-alloyed cast irons. High-alloyed irons are rarely coated. Metal coatings may be anodic to iron, providing a sacrificial protection, while other metals may be barrier type coatings. The remaining coating material types are all barrier coatings. The various coatings and applicable environments are listed in Table 46.

Table 46 Coating Materials for Cast Irons[82]

Coating Material Class	Coating Material	Environmental Application
Metals	Zinc	Rural and arid atmospheres
	Cadmium	Rural and arid atmospheres
	Tin	Food handling equipment
	Aluminum	Corrosives of sulfur fumes, organic acids, salts, nitrate-phosphate compounds
	Lead and lead-tin	H_2SO_4 and H_2SO_3
	Nickel-phosphorus	Barrier coating reaching corrosion resistance levels of stainless steels
Organics	Corrosion preventive compounds	Atmospheric protection
	Rubber-based (chlorinated neoprene and hypalon)	Used for their mechanical properties
	Bituminous paints	Water environments (low permeability coating)
	Asphaltic compounds	Alkalis, waste water, acids, tap water
	Thermosets and thermoplastics	Fluids
	Fluorocarbons	Industrial service to 205ºC.
Conversion Coatings	Phosphates	Sheltered atmospheric protection
	Oxides	Sheltered atmospheric protection
	Chromates	Sheltered atmospheric protection, sometimes used with cadmium plating
Inorganic	Enamels	Acids except HF

3.13 Tin

Tin is commonly used as a coating for metals (tin plate) to provide corrosion resistance. It is a relatively inert metal that is ductile and has a low strength, which degrades significantly with increasing temperature.

Oxygen or other oxidizers readily attack tin, but it has an excellent resistance to water having a high purity, and a good resistance to salt solutions and water containing carbon dioxide. A good resistance to atmospheric corrosion is also characteristic of tin. Tin is resistant to weak acids, but is very susceptible to corrosion in alkalis, strong acids and oxidizing acids. Tin is particularly susceptible to sulfuric, hydrochloric and nitric acids.

3.14 Cadmium

Cadmium is used mostly as an electroplated coating, especially on high-strength steels in aircraft, since it improves the resistance to corrosion fatigue. It has a favorable resistance to alkalis, but is susceptible to hydrogen embrittlement.

3.15 Lead and Its Alloys

In general, lead has a very good resistance to corrosion in a number of environments including atmospheric, aqueous, and other chemical environments. Atmospheric corrosion poses almost no threat to lead due to its excellent resistance to corrosion in most types of atmospheric environments including those containing industrial pollutants (e.g. SO_2, SO_3, CO_2, H_2S, etc.). Lead's inherent corrosion resistance is mostly due to the protective film on its surface, which can form in a wide variety of environments including those containing oxides, sulfates, carbonates, and chromates. An added benefit of this film is that it is insoluble in the corrosive medium in which it is formed, which consequently results in long-term protection in that environment.

Lead is generally resistant to corrosion in fresh water and seawater, except in those water environments containing dissolved oxygen. In soil, lead also typically has a good resistance to corrosion. The presence of organic acids in the soil from wood, usually results in an increased rate of attack. Acetic, nitric and formic acids attack lead readily, but it has a good resistance to sulfuric, sulfurous, chromic and phosphoric acids and adequate resistance to hydrochloric and hydrofluoric acids. The presence of oxygen in acidic and soft water environments causes a significant increase in the corrosion rate. In the presence of most alkaline environments, lead only has a fair resistance to corrosion. Table 47 lists a number of corrosive media and lead's corresponding resistance to corrosion.

Lead is a very ductile metal with low strength and hardness properties, and due to its softness, it is especially susceptible to erosion corrosion. The corrosion resistance of lead does not vary much between the pure form and its alloys. Therefore, alloys are commonly chosen over pure lead based solely on strength properties. For instance, lead with 3-18% antimony has twice the strength of pure lead, but the strength does decrease rapidly with temperature.

3.16 Noble Metals

The corrosion resistance of the noble metals is considered excellent although there are some discrepancies in corrosion testing results of these materials. A practical upper limit on the uniform corrosion rates of noble metals is generally set at about 2 mils/yr due to their high costs. Some of the corrosion rates in various environments may extend higher than this "acceptable" limit as will be discussed. The high cost of the noble metals limits their use in functional devices to small scale applications such as electrical contacts due to their good conductivity and corrosion resistant linings where the combination of their properties make them cost effective.

Table 47 Resistance of Lead to Specific Corroding Agents[83]

Corrosive Agent	Resistance
Acetone	**Resistant**
Acetylene	**Resistant**
Acid, acetic	**Moderate general attack**
Acid, chromic	**Resistant**
Acid, citric	**Moderate general attack**
Acid, hydrochloric	**Moderate general attack**
Acid, hydrofluoric	**Resistant**
Acids, mixed	**Resistant**
Acid, nitric	**Severe general attack**
Acid, phosphoric	**Resistant**
Acid, sulfuric	**Resistant**
Acid sulfurous	**Resistant**
Acid, tartaric	**Moderate general attack**
Air	**Resistant**
Alcohol, ethyl	**Resistant**
Alcohol, methyl	**Resistant**
Ammonium sulfate	**Resistant**
Ammonia	**Resistant**
Ammonium azide	**Resistant**
Ammonium chloride	**Resistant**
Ammonium hydroxide	**Resistant**
Ammonium phosphate	**Resistant**
Benzol	**Resistant**
Bromine	**Resistant**
Carbon dioxide	**Resistant**
Carbon tetrachloride	**Resistant**
Chlorine	**Resistant**
Dyestuffs	**Generally resistant**
Formaldehyde	**Moderate general attack**
Magnesium chloride	**Severe general attack**
Magnesium sulfate	**Resistant**
Motor fuel	**Resistant**
Nickel sulfate	**Resistant**
Oxygen	**Resistant**
Phenols	**Resistant**
Photographic solutions	**Generally resistant**
Sodium carbonate	**Resistant**
Sodium chloride	**Resistant**
Sodium hydroxide	**Resistant**
Sodium Sulfate	**Resistant**
Sulfur dioxide	**Resistant**
Water, chlorinated	**Resistant**
Water, sea	**Resistant**

3.16.1 Silver

Silver is a ductile material, easily processed, with good corrosion resistance making it applicable as a coating material for corrosion protection in some environments. It is used throughout the food and pharmaceutical industries for lining processing equipment as it maintains the products purity without imparting a metallic flavor to the product.[84]

Low alloying is done to improve the mechanical properties and has little effect on the corrosion resistance of silver. Sterling silver contains ≥ 92.5% Ag with some Cu addition. The copper addition results in a duplex structure for most sterling silvers which can be a source of galvanic attack in strong electrolyte environments. The copper can also be selectively oxidized in elevated temperature environments. The corrosion resistance of silver in various environments is listed in Table 48.

Table 48 Susceptibility of Silver to Various Acids[84]

Environment	**Corrosion Resistance**
HCl	May be used under ambient conditions, but can be attacked under strong aerating conditions especially with high HCl concentrations and increased temperatures.
HI	Only should be used at room temperature with dilute HI.
HNO_x	Attacked by nitric and nitrous acids
H_2SO_4	Attacked by 95% concentrations at room temperature and hot (~60%) concentrations.
Cl, Br	Resistant to chlorine and bromine
I, F	Attacked by iodine and fluorine unless cathodically protected

3.16.2 Gold

The high cost of gold in combination with its susceptibility to corrosion from halogens severely limits its use for corrosion properties. Gold is readily attacked by hot mixtures of HNO_3 and H_2SO_4, aqua regia, hydrogen cyanide, mixtures of HBr, HCl, HI, and HNO_3. Gold has been used as an autoclave lining for handling phosphate mixtures up to 500ºC and in the chemical industry for lining equipment used in hydrochlorinations and hydrofluorinations.

3.16.3 Platinum

Platinum has excellent corrosion resistance properties including resistance to industrial type atmospheres containing sulfur compounds. Like other noble metals, platinum finds uses as electrical contacts and for lining process equipment. Alloying platinum with rhodium, iridium, and ruthenium slightly increase corrosion resistance. A 10% rhodium addition increases the susceptibility of platinum to corrosion from dilute HCl at slightly elevated temperatures. Alloying with palladium has essentially no effect on the corrosion resistance while large additions of silver and gold will degrade corrosion resistance to certain chemicals. Platinum is more apt to be used as an alloying element to other materials such as titanium increasing their resistance to some acids. Table 49 gives the general corrosion susceptibilities of platinum to various chemicals.

Table 49 Chemicals that Attack Platinum[84]

Chemical	Resistance
Aqua regia	Readily attacked
HBr, HI	Attacked at room temperature and increasing with elevated temperatures
HCl	Attacked by 36% HCl at 100ºC
HNO_3	Attacked by 70% HNO_3 at room temperature

3.16.4 Palladium

Palladium is similarly used as other noble metals in electrical contact and as a coating in process equipment. Palladium has been extensively researched as an alloying element to titanium as well as other metals to increase corrosion resistance to acids such as HCl, HNO_3, and $FeCl_3$ salts.

Palladium is generally resistant to single acids and alkalis, and to most salt solutions. The susceptibilities of Pd are to the following compounds:[84]

- Nitric acid, hydroiodic acid
- $FeCl_3$ and hypochlorite solutions
- Iodine (very slightly)
- Potassium cyanide
- Hot sulfuric acid
- Chlorine and bromine
- Aqua regia
-

3.16.5 Ruthenium

Applications of ruthenium are limited due to the difficulty in producing wrought forms. Ruthenium is used as an alloying element to platinum and palladium as a hardening agent and to titanium for corrosion resistance. It has excellent resistance to acids at room temperature and at 100ºC, including aqua regia. Chlorine, bromine, and iodine solutions will attack ruthenium.

3.16.6 Rhodium

Rhodium is primarily used as an alloying element to palladium, platinum, and nickel. It hardens these materials as well as providing increased corrosion resistance. Platinum containing rhodium is used in crucibles, furnace windings, thermocouples, and oxidation catalysts for HNO_3 and ammonia production. Thin coatings of rhodium have been used on glass to produce high reflectivity mirrors and gray filters. Rhodium is slowly attacked by sodium hypochlorite solutions at room temperature but is resistant to most all other solutions including aqua regia and concentrated acids. At 100ºC, it is attacked by sulfuric and bromic acids.

3.16.7 Osmium

Osmium is the rarest of the noble metals with a worldwide annual production usually in the range of a few thousand ounces.[84] It is alloyed in conjunction with ruthenium to other noble metals for use in electrical contacts, non-rusting pivots for small instruments, and fountain pen tips. Osmium's corrosion resistance is lower than most other noble metal, being attacked by halogens, some salt solutions, and hot acids. Osmium powder will slowly oxidize at room temperature to form osmium tetroxide.

3.16.8 Iridium

Iridium may be fabricated using conventional powder metallurgy techniques, although it is primarily used as an alloying element. Pure iridium is used in high performance spark plugs and very high temperature crucibles for single crystal preparation. It is used as a hardener and for increased corrosion resistance when added to palladium and platinum. Iridium containing 30% platinum have been used in chemical handling equipment for extremely corrosive materials and for electrical contacts in severe environments. Iridium is the most corrosion resistant metal known. It is highly resistant to virtually all acids at room temperature and at 100ºC. Iridium is slightly attacked by fused sodium, potassium hydroxides, fused sodium bicarbonate, and aqueous potassium cyanide. It has the highest resistance of the noble metals to halogen compounds, with a measured susceptibility only to moist bromine. Iridium can be dissolved in a hot aqua regia solution.

4.0 Corrosion Protection and Control Methods

Even with the proper selection of base metals and well-designed systems or structures, there is no absolute way to eliminate all corrosion. Therefore, corrosion protection methods are used to additionally mitigate and control the effects of corrosion. Corrosion protection can be in a number of different forms/strategies with perhaps multiple methods applied in severe environments. Forms of corrosion protection include the use of inhibitors, surface treatments, coatings and sealants, cathodic protection, and anodic protection. This section discusses many of the various forms of corrosion protection methods.

4.1 Inhibitors

Inhibitors are chemicals that react with the surface of a material decreasing the material's corrosion rate, or interact with the operating environment to reduce its corrosivity. Inhibitors may be introduced into the environment in which the material is operating as solutions or dispersions to form a protective film. For instance, they can be injected into a completely aqueous recirculating system (e.g. automobile radiators) to reduce the corrosion rate in that system. They may also be used as additives in coating products, such as surface treatments, primers, sealants, hard coatings, and corrosion preventive compounds (CPCs). Furthermore, some inhibitors can be added to water that is used to wash a vehicle, system or component.

Corrosion inhibitors interact with the metal, slowing the corrosion process by:

- shifting the corrosion potential of the metal's surface toward either the cathodic or anodic end
- preventing permeation of ions into the metal
- increasing the electrical resistance of the surface

The corrosion potential of a metal is shifted toward the anodic end by inhibiting the cathodic process. This is accomplished by using chemicals that inhibit the corrosion reactions taking place at the cathodic site of the corrosion cell, for example, blocking the hydrogen ions at the metal's surface from combining to form hydrogen gas. Likewise, the corrosion potential of a metal is shifted toward the cathodic end by inhibiting the anodic process. This is accomplished by using chemicals that inhibit the corrosion reactions taking place at the anodic site of the corrosion cell for example, by keeping the metal from dissociating into ions.

Preventing the permeation of ions into the metal is accomplished by forming a protective film or layer on the metal surface. Inhibitors can form a protective barrier film, which effectively isolates the metal from the corrosive environment, or they can induce the formation of precipitates that block the corrosive agents from accessing the metal. Inhibitors can also increase the electrical resistance of the metal by passivating the surface.

Inhibitors are usually grouped into five different categories: passivating, cathodic, organic, precipitation, and vapor phase. Each of these groups is discussed separately in the following sections.

4.1.1 Passivating Inhibitors

Passivating inhibitors are the most common type of inhibitors mainly because they are very effective in reducing the rate of corrosion. They protect the material by aiding in the formation of a thin, inert film on the surface of a metal, thereby moving its corrosion potential toward the noble region, which effectively passivates the metal. This shift in corrosion potential can be significant, and sometimes on the order of a 100 mV.[3] Passivating inhibitors can be either oxidizing, which do not require oxygen to be present, or nonoxidizing, which do require oxygen to be present in the environment. Oxidizing inhibitors include nitrites and nitrates, and chromates were one of the most widely used inhibitors. Although chromate inhibitors are some of the most effective, they are currently being phased out by regulations from the Environmental Protection Agency in the United States due to health and environmental concerns. Nonoxidizing inhibitors include phosphates and molybdates. These can only be used for applications which encounter oxygen-containing environments. The primary disadvantage to passivating inhibitors is that they can actually accelerate localized corrosion on the material being protected if the concentration of inhibitors falls below a critical concentration. Therefore it may be necessary to periodically reapply the corrosion inhibitor or monitor the inhibitor concentration.[10]

4.1.2 Cathodic Inhibitors

Cathodic inhibitors specifically target the cathodic region of the metal or electrochemical cell and provide protection by inhibiting the rate of the cathodic reaction. This is generally accomplished by building a barrier layer to obstruct the corrosive agents from accessing the metal surface or by preventing the reagents in the cathodic process from forming their normal products (e.g. hydrogen gas). For example, certain inhibitors can precipitate on selected cathodic areas of the metal to form a barrier, effectively isolating the metal from the environment. Also, other inhibitors can preemptively occupy or react with hydrogen or oxygen, for example, and keep them from forming hydrogen gas or, in the case of oxygen, keep it from oxidizing the metal. Calcium bicarbonate, zinc compounds, and polyphosphates are some examples of cathodic inhibitors.

4.1.3 Organic Inhibitors

Unlike cathodic inhibitors, organic inhibitors tend be active over the entire metal by adsorbing to the surface to form a thin, water-displacing film. The strength of the adsorptive bond between the metal and the film is a key factor in determining the level of protection the inhibitor will provide. This bonding strength is primarily dependent on the relative ionic charge between the metallic surface and the organic inhibitor. Anionic inhibitors (inhibitors with a negative ionic charge), such as sulfonates, are used for positively charged metal. Cationic inhibitors (inhibitors with a positive ionic charge), such as amines, are used for a negatively charged metal.[10]

4.1.4 Precipitation Inhibitors

Precipitation inhibitors are chemicals that can induce the formation of precipitates on a metal. The precipitates tend to cover the entire surface of the metal and act as somewhat of a barrier to the corrosive environment. Examples of precipitation inhibitors are silicates (e.g. sodium silicate) and phosphates.[10]

4.1.5 Vapor Phase Inhibitors

Vapor phase inhibitors are also known as volatile corrosion inhibitors are carried by a vapor phase product, such as water vapor, to the surface of the metal to be protected. When it reaches the metal surface it the vapor phase condenses, causing a release of the inhibitor ions.

4.1.6 Inhibitor Compounds

Inhibitors may be inorganic or organic materials. Inorganic inhibitors are usually crystalline salts including sodium chromates, phosphates and molybdates. The negative ions of these materials are responsible for reducing corrosion. Organic inhibitors include sodium sulfonates, phosphonates, mercaptobenzotriazole (MBT), and aliphatic or aromatic compounds containing positively charged amine groups. Inhibitors may be produced into liquids, solids including hard and soft materials, or vapors to be used in numerous applications. Their greatest use comes in systems involved with liquid heating or cooling systems. Inhibitors are introduced into the liquid media and the concentration and/or the corrosion rate of the system monitored to maintain an optimal concentration level. Vapor phase inhibitors including morpholine and hydrazine are introduced into steam environments such as boilers, to increase the pH level in the system. The selection of inhibitors will depend upon the metal requiring protection, as well as the operating environment. Various inhibitors used to protect metals in some environments are listed in Table 50.

4.2 Surface Treatments

A surface treatment is the modification of a material’s surface using various means to improve some characteristic of the material, in this case the corrosion resistance. Conversion coatings and anodizing involves a chemical reaction to create an improved corrosion resistant oxide film layer on the metal’s surface. Shot peening is a mechanical process to induce compressive residual stresses improving resistance to SCC and corrosion fatigue. Laser treatment uses heat to modify surface structure, aid a chemical reaction in modifying the surface, or to induce compressive residual stresses within a metal to increase its resistance to SCC and corrosion fatigue.

4.2.1 Conversion Coatings

Conversion coatings are used as a protective, or sometimes decorative, coating which is produced in-situ by a chemical reaction of a metal’s surface with a chosen environment.

4.2.2 Anodizing

Anodizing is an electrochemical process, most frequently used on aluminum, although it can be used with other metals, such as magnesium and titanium alloys. An electric current is passed through an electrolyte (usually chromic, phosphoric, or sulfuric acid) causing the surface of the anodic metal to form an oxide film. This film can be significantly thicker than the naturally occurring one, and thus can provide better corrosion protection. An advantage of anodizing over coating deposition methods is that the resultant coating is an integral part of the substrate rather than being a layer that is bonded to the substrate. Anodized coatings are, however, typically brittle and susceptible to strong acids and bases.

Table 50 Some Inhibitors Used to Protect Various Systems/Metals[6]

System	Inhibitor	Metal	Concentration
	Acids		
HCl	Ethylaniline	Fe	0.5%
	MBT		1%
	Pyridine + phenylhydrazine		0.5% + 0.5%
	Rosin amine + ethylene oxide		0.2%
H_2SO_4	Phenylacridine		0.5%
H_3PO_4	NaI		200 pm
Others	Thiourea		1%
	Sulfonated castor oil		0.5–1.0%
	As_2O_3		0.5%
	Na_3AsO_4		0.5%
	Waters		
Potable	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Polyphosphate	Fe, Zn, Cu, Al	5–10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	10 ppm
	Na_2SiO_3		10-20 ppm
Cooling	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Na_2CrO_4	Fe, Zn, Cu	0.1%
	$NaNO_2$	Fe	0.05%
	NaH_2PO_4		1%
	Morpholine		0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate		10 ppm
	Morpholine	Fe	Variable
	Hydrazine		O_2 scavenger
	Ammonia		Neutralizer
	Octadecylamine		Variable
Engine Coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1-1%
	$NaNO_2$	Fe	0.1-1%
	Borax		1%
Glycol/water	Borax + MBT	All	1% + 0.1%
Oil field brines	Na_2SiO_3	Fe	0.01%
	Quarternairies		10-25 ppm
	Imidazoline		10-25 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH dependent
	$NaH_2PO_4 + NaNO_2$	Fe	10 ppm + 0.5%

4.2.3 Shot Peening

Shot peening is a cold working process originally implemented to increase fatigue strength. A stream of shot is used to bombard a metal's surface, inducing compressive stresses and relieving tensile stresses within the material.[85] The depth of the shot peening effect is typically about 0.13 to 0.25 mm below the surface. The altering of residual stresses on the metal's surface results in a higher fatigue resistant material, and also a higher resistance to corrosion fatigue and stress corrosion cracking.

4.2.4 Laser Treatment

There a four uses of laser technology to modify the surface properties of metals. One method is to harden the surface using laser heating which enhances thermal diffusion at the surface.[86] A second technique is to use laser heating to melt the surface which is then rapidly quenched to modify the surface structure. A third method uses a laser to melt the surface and alloying elements are added to the surface melt effectively creating a different material at the surface. The fourth method makes use of a laser's shock effect to induce compressive stresses within a metal's surface.[87] This has the same effect as shot peening with the major difference that it can produce residual compressive stresses to a depth of approximately 1.0 mm, resulting in higher fatigue lives. This method is referred to as "laser peening" or "laser shock processing."

4.3 Coatings and Sealants

Metallic, inorganic and organic coatings are used frequently for providing long-term corrosion protection of metals in various types of corrosive media. There are two main types of coatings: barrier coatings and sacrificial coatings. A barrier coating acts as a shield and protects the metal from the surrounding environment, whereas a sacrificial coating functions as a sacrificial anode and thus, corrodes preferentially. Barrier coatings are typically unreactive, resistant to corrosion, and protective against wear. Sacrificial coatings provide cathodic protection by supplying electrons to the base metal. Sealants provide corrosion protection by completely securing the component from moisture penetration.

4.3.1 Metallic

Metallic coatings provide enhanced corrosion resistance of metals as either barrier coatings or sacrificial coatings. They are durable, usually easy to form, but sometimes porous, which can result in accelerated corrosion of the substrate metal. Some of the common metals used as coatings are nickel, lead, zinc, copper, cadmium, tin, chromium, and aluminum. Methods for applying metallic coatings include cladding, electrodeposition (electroplating), electroless plating, spraying, hot dipping, diffusion, chemical vapor deposition (CVD), and ion vapor deposition.

4.3.1.1 Nickel

Nickel is used as a coating for corrosion protection applications, and is also used as an undercoat for other coatings. Electrodeposition is the common method for applying nickel, but electroless plating can also be used. When nickel is used as a coating for steel, copper is sometimes used as an intermediate layer. Nickel is also used as an intermediate layer between steel and microcracked chromium to prevent the corrosion of steel. Nickel-phosphorous coatings have a superior corrosion resistance compared to nickel coatings, and can be electrodeposited or electrolessly deposited.

4.3.1.2 Aluminum

Hot-dipping, spraying, cementation, and ion vapor deposition processes are used to deposit aluminum coatings on steel. Hot-dipped aluminum coatings are used to protect the metal substrate from atmospheric corrosion and oxidation at elevated temperatures. Sprayed aluminum coatings are sometimes sealed with organic coatings to provide more uniform and impermeable protection. Ion vapor deposited aluminum coatings are soft and formable. Aluminum coatings have a minimum thickness of approximately 8-25 μm.[6]

4.3.1.3 Lead

Electrodeposition and hot dipping are usually employed to apply lead coatings on steel, with tin sometimes added to improve bonding. Of course, lead compounds are toxic and therefore, the use of lead coatings is limited.

4.3.1.4 Copper

Copper is susceptible to atmospheric corrosion, and thus, it is not very useful as a protective coating when used alone. It is, however, useful when used in conjunction with subsequent coatings, as it has a low porosity and can work as a barrier coating with porous, corrosion resistant coating to protect the base metal from corrosion. In addition corrosion inhibitors, such as benzotriazole, can also improve the performance of copper coatings.[88]

4.3.1.5 Cadmium

Cadmium is usually a preferred coating for the corrosion protection of steel in moist and marine environments; it is anodic to steel and therefore, will act as a sacrificial anode on steel. Cadmium coatings are smooth and conductive, and resist fretting and fatigue, but have been known to cause solid metal embrittlement of steel and titanium and exfoliation of susceptible aluminum alloys. Furthermore, the corrosion products of cadmium are toxic, so it should be avoided in applications that may contaminate the environment. There are alternatives to cadmium coatings however, such as zinc and tin coatings. Cadmium coatings are applied mostly by the electrodeposition process and are good for electrical applications. Minimum coating thickness is approximately 5 – 25 μm.[6]

4.3.1.6 Zinc

Galvanization denotes the application of a zinc coating to the surface of a metal by any method. Hot dipping, electrodeposition, and spraying are a few methods used to galvanize a metal. Zinc is less expensive than cadmium, and is generally the preferred coating in industrial environments.

4.3.1.7 Chromium

Chromium coatings are hard and provide good wear resistance, but are typically used in conjunction with other coatings such as copper and nickel for corrosion protection applications.

4.3.1.8 Tin

Tin is another very common material used in coating applications and it provides good corrosion resistance to the metal substrates, either as a barrier or sacrificial coating. It is often used to coat steel and sometimes copper. Tin coatings are typically thin and porous; therefore, to achieve corrosion protection they should act as a sacrificial coating. Tin coatings are widely used in the food industry as coatings on steel containers.

4.3.1.9 Gold

Gold is often coated over other coatings to provide enhanced appearance or improved electrical properties. Gold coatings are used mostly for electrical applications (and jewelry) as they have a low contact resistance.

4.3.2 Ceramic

Ceramic coatings are inorganic, nonmetallic coatings that act as a barrier between the corrosive environment and the base material being protected. They often consist of an oxide film that is formed on the surface of a metal by chemical reaction, which can occur naturally on some metals; however, more effective corrosion resistant coatings can be produced. Ceramic coatings are especially useful for providing high temperature corrosion protection. Examples of ceramic coatings include chromate films and phosphate coatings.

4.3.2.1 Chromate Films

Although chromate films provide a significant improvement in the corrosion resistance of a metal substrate, it is mainly used as a precursor to other coatings and paints. Chromate coatings are often used on steel, copper, aluminum, magnesium, nickel, silver, tin, and cadmium substrates.[89] Thin chromate films can be applied by immersion, spraying, or brushing.

4.3.2.2 Phosphate Films

Metal phosphate coatings, which form on the surface of a metal when subjected to the appropriate environment by chemical reaction, are used mainly for corrosion protection, but in addition, they provide a good surface for other coatings to adhere to. When combined with corrosion inhibitors or other coatings, the corrosion protection is improved significantly. Phosphate coatings are usually applied either by spraying for larger components or by immersion in solution baths. Immersion is the preferred method as a more homogeneous coating is produced.

4.3.3 Organic

Organic coatings are widely used for corrosion protection applications on exterior surfaces and also for interior coatings and linings. In fact, organic coatings are used more for corrosion protection than any other protection method available; they can also provide enhanced appearance of a previously dull or unattractive metal. There are several types of organic coatings, which include paints, varnishes, enamels, and lacquers, and numerous organic materials to choose from for corrosion protection applications. The types of coatings are defined below in Table 51.

Table 51 Organic Coating Types and Definitions[9]

Coating Type	Definition
Paint	A pigmented composition of liquid consistency which after application as a thin layer is converted to solid, adherent, tough film.
Oil Paint	A paint that contains drying oil or oil varnish as the basic film-forming vehicle
Water Paint	A paint that contains a water emulsion or dispersion as the basic ingredient
Enamel	A paint that is characterized by an especially smooth surface film.
Varnish	A liquid composition which after application as a thin layer is converted to a transparent or translucent solid film. Varnish is generally a clear liquid combining a drying oil and a fortifying resin, air-drying by oxidation of the oil.
Lacquer	A film-forming liquid composition containing polymeric esters or ethers and plasticizers as the basic film-forming ingredients in a solvent, and which dries by evaporation of the solvent. Lacquer may be constituted with or without resins.
Baking Finish	A paint or varnish that requires baking above 66 °C (150 °F) for the development of the desired properties.

Organic coatings have three basic methods of protecting a metal substrate from corrosion: 1) by preventing the attacking agents from penetrating through to the metal (impermeability), 2) by inhibiting attacking agents, and 3) by functioning as a cathodically protective material. An impermeable coating will protect the metallic substrate from having to face otherwise harmful environments that contain corrosive agents. Organic coatings containing inhibitors can neutralize the attacking corrosive agents by reacting with them and possibly forming a protective film on the metallic substrate. Cathodically protective organic coatings contain additives which decreases the corrosion potential between the metal and the surrounding corrosive environment.

An organic coating system will often have three components: 1) a primer, 2) an intermediate coat, and 3) a topcoat. The primer is very important to the integrity of the coating system. It is the fundamental layer of the system and thus provides the basic adhesion between the metal substrate and the intermediate or subsequent layer of the coating system, as well as corrosion protection. The intermediate coat provides corrosion resistance and thickness to the coating system. The top-coat is also very important since it provides the first level of protection against corrosion and acts as a seal over the intermediate coat and primer. Typically it is thinner than the priming coat, has good wear and abrasion resistance, and usually determines the appearance of the organic coating system.

Proper coating selection is clearly one of the most important aspects in protecting the metal from corrosion. There are, however, three other important factors that should be given proper consideration along with selecting the proper organic coating in order to provide the optimal service life. The first (1) is surface preparation, which is important for providing a strong bond between the coating and the substrate. The second (2) is proper selection and application of a priming coat, which should have good adherence to the substrate and should be compatible with the coating. Poor adhesion or incompatibility could lead to coating failure. The third (3) important factor is the proper selection of a topcoat; however, the topcoat is unimportant if the surface is prepared poorly or an improper primer is selected since the coating will fail anyway.

The ingredients of organic coatings usually include volatile and non-volatile components. The volatile components serve as thinners, while the non-volatile components act as the film-forming ingredients (e.g. resin, oil, wax etc.) and sometimes include pigments and plasticizers.[9] The pigments have several functions; they provide protection against moisture penetration, resist corrosion, protect against sunlight, and add consistency and color to the coating. Plasticizers are used to keep the coating from cracking.

Organic coatings have some advantages and disadvantages when compared to metallic coatings.[9] For instance, they are usually more economical, can be applied on top of metallic and inorganic coatings, come in various colors and have a broad range of physical characteristics. They are, however, more susceptible to mechanical damage, and they don’t offer any anodic protection to areas of the substrate that are exposed.

Table 52 provides a summary of various organic materials used in coating systems. The table shows the advantages and disadvantages of the different resin materials, including properties and characteristics, compatibility with other materials, as well as their performance and compatibility in certain environments.

Table 52 Advantages and Limitations of Principal Organic Coating Materials[90]

Resin Type	Advantages	Limitations	Comments
Alkyds	Good resistance to atmospheric weathering and moderate chemical fumes; not resistant to chemical splash and spillage. Long oil alkyds have good penetration but are slow drying; short oil alkyds are fast drying. Temperature resistant to 105 °C (225 °F)	Not chemically resistant; not suitable for application over alkaline surfaces, such as fresh concrete or for water immersion.	Long oil alkyds make excellent primers for rusted and pitted steel and wooden surfaces. Corrosion resistance is adequate for mild chemical fumes that predominate in many industrial areas. Used as interior and exterior industrial and marine finishes.
Epoxy esters	Good weather resistance; chemical resistance better than alkyds and usually sufficient to resist normal atmospheric corrosive attack	Generally the least resistant epoxy resin. Not resistant to strong chemical fumes, splash or spillage. Temperature resistance: 105 °C (225 °F) in dry atmospheres. Not suitable for immersion service	A high quality oil-base coating with good compatibility with most other coating types. Easy to apply. Used widely for atmospheric resistance in chemical environments on structural steel, tank exteriors, etc.
Vinyls	Insoluble in oils, greases, aliphatic hydrocarbons, and alcohols. Resistant to water and salt solutions. Not attacked at room temperature by inorganic acids and alkalis. Fire resistant: good abrasion resistance.	Strong polar solvents redissolve the vinyl. Initial adhesion poor. Relatively low thickness (0.04 to 0.05 mm, or 1.5 to 2 mils) per cost. Some types will not adhere to bare steel without primer. Pinholes in dried film are more prevalent than in other coating types.	Tough and flexible, low toxicity, tasteless, colorless, fire resistant. Used in potable water tanks and sanitary equipment; widely used industrial coating. May not comply with Volatile Organic Compound (VOC) regulations.

Table 52, continued - Advantages and Limitations of Principal Organic Coating Materials

Resin Type	Advantages	Limitations	Comments
Chlorinated rubbers	Low moisture permeability and excellent resistance to water. Resistant to strong acids, alkalis, bleaches, soaps and detergents, mineral oils, mold, and mildew. Good abrasion resistance.	Redissolved in strong solvents. Degraded by heat (95 °C, or 200 °F, dry; 60 °C or 140 °F wet) and ultraviolet light, but can be stabilized to improve these properties. May be difficult to spray, especially in hot weather.	Fire resistant, odorless, tasteless, and nontoxic. Quick drying and excellent adhesion to concrete and steel. Used in concrete and masonry paints, swimming pool coatings, industrial coatings, marine finishes.
Coal tar pitch	Excellent water resistance (greater than all other types of coatings); good resistance to acids, alkalis, and mineral, animal, and vegetable oils.	Unless cross linked with another resin, is thermoplastic and will flow at temperatures of 40 °C (100 °F) or less. Hardens and embrittles in cold weather. Black color only will alligator and crack upon prolonged sunlight exposure, although still protective.	Used as moisture-resistant coatings in immersion and underground service. Widely used as pipeline exterior and interior coatings below grade. Pitch emulsions used as pavement sealers. Relatively inexpensive.
Polyamide-cured epoxies	Superior to amine-cured epoxies for water resistance. Excellent adhesion, gloss, hardness impact, and abrasion resistance. More flexible and tougher than amine-cured epoxies. Temperature resistance: 105 °C (225 °F) dry; 65 °C (150 °F) wet.	Cross linking does not occur below 5 °C (40 °F). Maximum resistances generally require 7-day cure at 20 °C (70 °F). Slightly lower chemical resistance than amine-cured epoxies.	Easier to apply and topcoat, more flexible, and better moisture resistance than amine-cured epoxies. Excellent adhesion over steel and concrete. A widely used industrial and marine maintenance coating. Some formulations can be applied to wet or underwater surfaces.
Coal tar epoxies	Excellent resistance to saltwater and freshwater immersion. Very good acid and alkali resistance. Solvent resistance is good, although immersion in strong solvents may leach the coal tar.	Embrittles upon exposure to cold or ultraviolet light. Cold weather abrasion resistance is poor. Should be topcoated within 48 h to avoid intercoat adhesion problems. Will not cure below 10 °C (50 °F). Black or dark colors only. Temperature resistance: 105 °C (225 °F) dry; 65 °C (150 °F) wet.	Good water resistance. Thicknesses to 0.25 mm (10 mils) per coat. Can be applied to bare steel or concrete without a primer. Low cost per unit coverage.
Polyurethanes (aromatic or aliphatic)	Aliphatic urethanes are noted for their chemically excellent gloss, color, and ultraviolet light resistance. Properties vary widely, depending on the polyol coreactant. Generally, chemical and moisture resistances are similar to those of polyamide-cured epoxies, and abrasion resistance is usually excellent.	Because of the versatility of the isocyanate reaction, wide diversity exists in specific coating properties. Exposure to the isocyanate should be minimized to avoid sensitivity that may result in an asthmatic-like breathing condition upon continued exposure. Carbon dioxide is released upon exposure to humidity, which may result in gassing or bubbling of the coating in humid conditions Aromatic urethanes may darken or yellow upon exposure to ultraviolet radiation	Aliphatic urethanes are widely used as glossy light-fast topcoats on many exterior structures in corrosive environments. They are relatively expensive, but extremely durable. The isocyanate can be combined with other generic materials to enhance chemical, moisture, low-temperature, and abrasion resistance.

Table 52, continued - Advantages and Limitations of Principal Organic Coating Materials

Resin Type	Advantages	Limitations	Comments
Asphalt pitch	Good water resistance and ultraviolet stability. Will not crack or degrade in sunlight. Nontoxic and suitable for exposure to food products. Resistant to mineral salts and alkalis to 30 % concentration.	Black color only. Poor resistance to hydrocarbon solvents, oils, fats and some organic solvents. Do not have the moisture resistance of coal tars. Can embrittle after prolonged exposure to dry environments or temperatures above 150 °C (300 °F), and can soften and flow at temperatures as low as 40 °C (100 °F).	Often used as relatively inexpensive coating in atmospheric service, where coal tars cannot be used. Relatively inexpensive. Most common use is as a pavement sealer or roof coating.
Water emulsion latex	Resistant to water, mild chemical fumes, and weathering. Good alkali resistance. Latexes are compatible with most generic coating types, either as an undercoat or topcoat.	Must be stored above freezing. Does not penetrate chalky surfaces. Exterior weather and chemical resistance not as good as solvent or oil-base coatings. Not suitable for immersion service.	Ease of application and cleanup. No toxic solvents. Good concrete and masonry sealers because breathing film allows passage of water vapor. Used as interior and exterior coatings.
Acrylics	Excellent light and ultraviolet stability, gloss, and color retention. Good chemical resistance and excellent atmospheric weathering resistance. Resistant to chemical fumes and occasional mild chemical splash and spillage. Minimal chalking, little if any darkening upon prolonged exposure to ultraviolet light.	Thermoplastic and water emulsion acrylics not suitable for any immersion service or any substantial acid or alkaline chemical exposure. Most acrylic coatings are used as topcoats in atmospheric service. Acrylic emulsions have limitations described under “Water emulsion latex.”	Used predominantly where light stability, gloss, and color retention are of primary importance. With cross linking, greater chemical resistance can be achieved. Cross-linked acrylics are the most common automotive finish. Emulsion acrylics are often used as primers on concrete block and masonry surfaces. Also useful for protecting aluminum alloys and other non-ferrous alloys.
Amine-cured epoxies	Excellent resistance to alkalis, most organic and inorganic acids, water, and aqueous salt solutions. Solvent resistance and resistance to oxidizing agents are good as long as not continually wetted. Amine adducts (formed by an addition reaction) have slightly less chemical and moisture resistance.	Harder and less flexible than other epoxies and intolerant of moisture during application. Coating will chalk on exposure to ultraviolet light. Strong solvents may lift coatings. Temperature resistance: 105 °C (225 °F) wet; 90 °C (190 °F) dry. Will not cure below 5°C (40 °F); should be topcoated within 72 h to avoid intercoat delamination. Maximum properties require curing time of about 7 days.	Good chemical and weather resistance. Best chemical resistance of epoxy family. Excellent adhesion to steel and concrete. Widely used in maintenance coatings and tank linings.
Phenolics	Greatest solvent resistance of all organic coatings described. Excellent resistance to aliphatic and aromatic hydrocarbons, alcohols, esters, ethers, ketones, and chlorinated solvents. Wet temperature resistance to 95 °C (200 °F). Odorless, tasteless, and nontoxic; suitable for food use.	Must be baked at a metal temperature ranging from 175 to 230 °C (350 to 450 °F). Coating must be applied in a thin film (approximately 0.025 mm or 1 mil) and partially baked between coats. Multiple thin coats are necessary to allow water from the condensation reaction to be removed. Cured coating is difficult to patch due to extreme solvent resistance. Poor resistance to alkalis and strong oxidants.	A brown color results upon baking, which can be used to indicate the degree of cross linking. Widely used as tank lining for alcohol storage and fermentation and other food products. Used for hot water immersion service. Can be modified with epoxies and other resins to enhance water, chemical, and heat resistance.

Table 52, continued - Advantages and Limitations of Principal Organic Coating Materials

Resin Type	Advantages	Limitations	Comments
Organic zinc-rich	Galvanic protection afforded by the zinc content, with chemical moisture resistance similar to that of the organic binder.	Generally have lower service performance than inorganic zinc – rich coatings, but ease of application and surface preparation tolerance make them increasingly popular.	Widely used in Europe and the Far East, while inorganic zinc-rich coatings are most common in North America. Organic binder can be closely tailored to topcoats (for example, epoxy topcoats over epoxy-zinc-rich coatings) for a more compatible system. Organic zinc-rich coatings are often used to repair galvanized or inorganic zinc-rich coatings.
Inorganic zinc-rich	Provides excellent long-term protection against pitting in neutral and near-neutral atmospheric, and some immersion, services. Abrasion resistance is excellent, and dry heat resistance exceeds 370 °C (700 °F). Water-base inorganic silicates are available for confined and VOC compliance.	Inorganic nature necessitates thorough blast-cleaning surface preparation and results in difficulty when topcoating with organic topcoats. Zinc dust is reactive outside the pH range of 5-10, and topcoating is necessary in chemical fume environments. Somewhat difficult to apply; may mudcrack (irregular fracture formed by shrinkage caused by drying) at thicknesses in excess of 0.13 mm (5 mils).	Ethyl silicate zinc-rich coatings require atmospheric moisture to cure and are the most common type. Widely used as a primer on bridges, offshore structures, and steel in the building and chemical-processing industries. Used as a weldable preconstruction primer in the automotive and shipbuilding industries. Use eliminates pitting corrosion.

4.3.3.1 Corrosion Preventive Compounds (CPCs)

The organic coating system is typically expected to be a longer-term protection method for metals, but there are temporary protective organic materials that can provide short-term protection against corrosion. These are called corrosion preventive compounds (CPCs). CPCs are generally separated into two categories: water displacing and non-water displacing compounds. They are often used on places where the protective coating has been damaged and the metal substrate is exposed until the coating can be reapplied. CPCs can be used on both interior and exterior surfaces for corrosion protection. Although some CPCs may appear to be a permanent film, they can usually be removed with an appropriate solvent, and are not expected to be a long-term solution to corrosion.

The water displacing compounds are usually clear or translucent, soft, oily compounds, however some form hard, dry films. These can fill cracks and crevices and form a thin protective layer that is less than 1 mm thick.[91] Non-water displacing compounds are typically thick, colored, and can be either hard or soft and are usually used for longer periods than the water displacing compounds. Generally, CPCs are applied as fluids by wiping, brushing, spraying or dipping.[6]

Three of the most common CPCs are described in military specifications. These are MIL-C-16173, MIL-C-81309, and MIL-C-85054. MIL-C-16173 is a soft, water-displacing CPC that is sprayed on as a brown film. MIL-C-81309 is a very thin compound which forms a soft film after drying. MIL-C-85054, which is also known as Amlguard, forms a hard, clear film after drying and is of the most commonly used CPCs due to its superior protection capability. Some of the more common CPCs are categorized in Table 53.

Table 53 List of Some Common CPCs[10]

Water Displacing (Soft)	**Water Displacing (Hard)**	**Non-Water Displacing (Soft)**	**Non-Water Displacing (Hard)**
ACF-50	AV-8	Fluid Film NAS	Ardrox 3322
Ardrox 3107	AMLGUARD (AML-350)	LPS-3 Heavy Duty Inhibitor	Dinol AV-30
Ardrox 3961	Cor-Ban 35		Dinol AV-40
Boeshield T-9	VCI-368		LPS Procyon
Cor-Ban 22			ZipChem ZC-029
CorrosionX			
CRC Protector 100			
CRC 3-36			
Dinitrol AV8			
Mobilarma 245			
LPS-2			
LPS-3			
WD40			

4.3.3.2 Rubber

Rubber is not like most other organic coatings, since it is usually used as a lining material on pipes or tanks. They provide an excellent resistance to water.

4.3.4 Coating Processes

There are a number of methods, ranging from simple to sophisticated, that are used to apply coatings, and there are advantages and disadvantages to each method. The quality of the application of a coating is critical because any defect or significant porosity in the coating can result in severe localized corrosion. Selection of a coating application method is usually based on the type of coating (i.e. metallic, ceramic, organic), the type of substrate to be coated, the amount of surface area that will be coated, and whether there are any environmental regulations or restrictions. Application methods for metallic coatings include cladding, electrodeposition (electroplating), flame spraying, vapor deposition, and hot dipping. Application methods for ceramic coatings include diffusion, spraying, and chemical conversion.[12] Application methods for organic coatings include brushing, rolling, and spraying. Materials and application methods of metallic, inorganic, and organic coatings will be described below.

4.3.4.1 Hot-Dipping

Hot dipping designates the coating application process of immersing a metal substrate in a molten metal bath, which is usually aluminum, zinc, tin, or lead. Since the applied coating consists of a molten metal, the melting temperature of the metal coating should be relatively low. Hot dipping can be either a continuous or batch process. Hot-dip galvanizing is the most common metal coating method; it involves the application of a thin layer of zinc to carbon steel. The zinc layer provides cathodic protection of the steel thereby protecting the steel from corrosion. Figure 42 shows the service life of hot-dip galvanized steel in different environments.

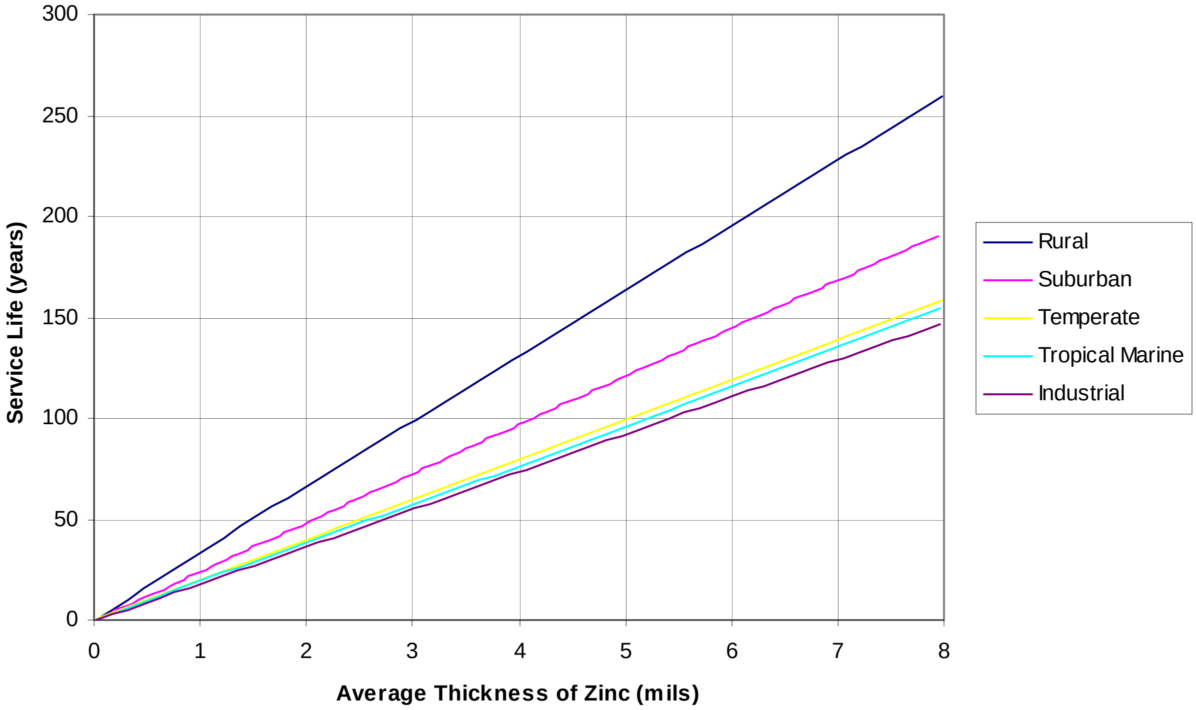


Figure 42 Service Life[2] for Hot-Dip Galvanized Coatings[92]

4.3.4.2 Electrodeposition

Electrodeposition, also called electroplating, is a process where a thin metal layer is deposited on a metal substrate in order to enhance the surface properties, including its corrosion resistance. The metal substrate is placed in an electrolytic solution containing dissolved metal ions, which will ultimately become the coating. An electrical current is passed through the solution, between two electrodes, causing the ions to deposit on the cathode (metal substrate) resulting in a metallic coating.

Characteristics of the coating are dependent on control of the processing parameters including temperature, current density, residence time and composition of the solution.[12] The physical and mechanical properties of these coatings can be altered by varying the processing parameters. They can be made to be thick or thin, hard or soft, or have a layered composition.

A variety of metals are available for use as electrodeposited coatings and include aluminum, chromium, iron, cobalt, nickel, copper, zinc, rhodium, palladium, silver, cadmium, indium, tin, rhenium, platinum, gold, lead, brass, bronze and a number of other alloys. As with all coating application methods, electrodeposition has its advantages and disadvantages.

4.3.4.3 Electroless Plating

Electroless nickel plating is similar to the electrodeposition process except that it does not require an external electrical current to be applied. It is a chemical reduction process where

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[2] Service Life is defined as the time to 5% corrosion of the steel surface

nickel ions are driven to the surface of the substrate metal by a reducing agent which is also present in the host solution. If processing conditions are properly maintained and the composition of the aqueous solution is uniform, the deposition of the nickel should be uniform over the entire surface of the substrate, even if it has a complex geometry.

4.3.4.4 Cladding

Metal claddings typically provide corrosion protection by acting as a barrier and a sacrificial coating. The cladding method involves a thin metal layer that is installed on the metal substrate by pressing, rolling or extrusion. This produces a metal layer with essentially zero porosity. An advantage is that this allows a thin piece of expensive, corrosion resistant material to be used on an inexpensive thicker piece of metal that is susceptible to corrosion instead of using the corrosion resistant material as the entire piece.

4.3.4.5 Thermal Spraying

Thermal spraying is a coating process in which a material feed is melted by a flame and sprayed by compressed gas onto a substrate; when the molten droplets/particles hit the substrate they flatten and adhere to the surface to form a coating. The process involves the build-up of these flattened particles which melt to form a cohesive coating that adheres to the substrate and covers the entire surface, while filling irregularities on the surface. Bonding between the coating and substrate usually results from mechanical interlock or diffusion and alloying. Therefore, surface preparation of the substrate is an important aspect in the quality of the coating. Often, it is required for the surface to be roughened in order to promote good mechanical adhesion between the coating and substrate. Thermal spraying can be performed using flame spraying, electric arc, or plasma arc.

4.3.4.6 Physical Vapor Deposition

There are several coating application methods which are subsets of the physical vapor deposition category. These include sputtering, evaporation, and ion plating. PVD processes involve plasma bombardment to deposit the metal over the entire area of the substrate.

4.3.4.7 Sputtering

Sputtering is the process where a target material is bombarded by gas ions causing atoms to be ejected and consequently deposited onto the substrate. Some advantages and disadvantages of this process are given in Table 54.

4.3.4.8 Evaporation

Evaporation is a relatively simple process that involves the vaporization of a metal, which is subsequently deposited on a substrate. The adhesion of coatings deposited by this method is only marginal and uniformity is difficult to achieve. Therefore, the evaporation method is not typically used for corrosion prevention applications.

4.3.4.9 Ion Plating

Ion plating is a process in which ions are driven from a plasma by an electrical bias on the substrate where they are deposited. Alternatively, the coating can be applied using an ion beam deposition technique, where plasma ions bombard the substrate to create nucleation sites for a neutral ion species. The neutral species can then deposit onto the nucleation sites, resulting in the formation of a coating.

4.3.4.10 Laser Surface Alloying

Laser surface alloying involves feeding the metal to be deposited into a laser beam. The laser beam melts the metal and deposits it on the surface of the substrate, where heat is transferred and a strong metallurgical bond is formed.

4.3.4.11 CVD

Chemical vapor deposition processes involve coating a substrate by chemical means, namely by reacting a precursor gas on the metal substrate. The gas is mixed in a chamber causing it to become reactive and is then sent to another chamber to be deposited onto the substrate. The gas mixture reacts at the surface of the substrate, which is heated in order to drive the endothermic reaction, to ultimately form the coating. It is important in this process to maintain a non-contaminated system. Table 55 lists some of the advantages and disadvantages corresponding to the various coating application methods.

4.3.4.12 Brushing

Brushing is perhaps the most intuitive coating application process, and is used to apply organic based coatings. It is a manual application method, and there are numerous types of brushes that can be used. It is very important to select the appropriate type of brush with the proper bristles in order to produce a high quality coating. The brush size, shape, and bristle type are all important considerations when selecting a brush for a specific coating application. This is because poor brush selection can lead to uneven or discontinuous coating application, runs, drips, or other unfavorable coating characteristics. A standard wall brush is often used for applying coatings to structural steel or similar surfaces. Oval-shaped brushes are used for other structural and marine applications, and are also used to apply coatings near rivets, boltheads, piping, railings and other difficult to reach areas.[64]

Brushes are made with either synthetic, typically nylon, or natural fibers for bristles. The advantage to using a brush with synthetic bristles is that it has a very good resistance to abrasion and are good to use on rough surfaces such. Brushes with synthetic bristles are also less expensive than those employing natural fibers. One of the primary disadvantages to synthetic bristles is that they may be susceptible to strong solvents such as ketones. Natural bristles are more expensive and sensitive to water, but they have a good resistance to strong solvents and are capable of a much finer, uniform coating application.[64]

An advantage to the application method of brushing is the ability to perform what’s called striping. Striping is used to apply the coating around irregular areas that cannot be easily or properly coated through a spraying or other coating technique. Areas that typically require striping include edges, rivets, fasteners, corners, boltheads, and welds. It is a recommended procedure because it can provide the proper coating thickness around these irregular areas, which would not be able to be achieved otherwise. Striping is not used, however, for coatings that have a solute that must remain in suspension, such as zinc-rich coatings. The brushing application method can also achieve complete coating penetration in particularly porous surface areas on a substrate.[64]

A disadvantage of the brushing application method is that it is time consuming as opposed to the spraying methods. Also when applied over a large surface area it is very difficult to maintain a uniform coating thickness through brushing, and therefore it is not a practical method for components or systems with large areas. Furthermore, after the coating dries the surface may have brush marks or slight grooves left over from the bristles. This usually is only a detriment to the appearance rather than the functionality. Another disadvantage to using the brushing method is that it is a difficult technique to use for coatings containing a high solid content and also for fast drying coatings.[64]

Brushing is most commonly used for applying oil-based or water-based coatings to surfaces with small or irregular areas. There are proper techniques in applying the coating that give the best results in the end product. Either an experienced professional or a well-trained technician should be used to apply coatings on critical assets or components.[64]

4.3.4.13 Rolling

Rolling is another manual coating application process, and it requires a roller assembly consisting of a core roller and a cover to absorb and apply the coating material. The assembly can vary in diameter as well as length, and there are also various cover materials. Common cover materials are polyester, nylon, mohair, and lambskin. Of course, the cover material is usually selected to suit the type of surface to be coated.[64]

There are three types of roller cores: pipe rollers, fence rollers, and pressure rollers. Pipe rollers are used just as the name suggests: for coating surfaces such as pipes. The surfaces usually are contoured and need the roller to flex and cover the surface. Fence rollers use roller covers that have an extra long fiber length, which enables them to simultaneously coat both sides of a surface such as fence wire. Pressure rollers are more sophisticated and have a feed line that moves the coating material to the inside of the roller core from a pressurized tank. The core is a porous material which allows the coating to pass through to the surface of the cover, and thus pressure rollers can provide continuous application of the coating.[64]

Rolling is a good application method for coating large, flat surfaces. A disadvantage is that it is much more difficult to achieve coating penetration into porous or cracked surfaces using the rolling coating application method, and is therefore not recommended for rough or irregular surfaces. Rolling does provide a fine quality finished surface on smooth surfaces. Rolling is a faster process than brushing, but is slower than other coating methods such as spraying.[64]

The roller coating application method is typically used to apply oil-based and water-based coatings, and can also be used to apply epoxy and urethane coatings. This method is not recommended for applying coatings containing a high solids content, zinc rich coatings, or high performance coatings and linings. As with the brushing application method there are proper techniques that result in uniform and quality application of the coating on the substrate.[64]

4.3.4.14 Spraying

There are several variations of the spray coating application method, including high volume-low pressure spraying, airless spray, air-assisted airless spray, plural component spray, and electrostatic spray. Conventional spraying simply uses compressed air to atomize coating particles and propel them toward the substrate. Though simple, the efficiency with which the coating successfully reaches the intended surface is low: ~ 25-30%. Conventional spraying is used to apply coatings such as latex paints, lacquers, stains, sealers, zinc-rich mixtures, alkyds, and epoxies.[64]

An advantage of the spray application technique is that it requires significantly less time than brushing and rolling, and therefore it can be used to coat large surface areas. It also results in a smooth, uniformly coated surface compared to brushing and rolling, and does not leave brush or speckle marks or a textured appearance. Spraying equipment can also be used to clean off the surface prior to applying the coating. Spraying can produce a high quality, smooth surface.[64]

A low efficiency for the amount of coating that is deposited on the substrate is one disadvantage to the spray application method. Spraying can be a slower process than other coating methods. It also is sometimes difficult to coat hard to reach areas, such as edges corners, and irregular surfaces with spraying. Since the equipment required for spraying is more expensive than that used for other coating methods, it must be cleaned after each use and properly maintained to ensure durability of the equipment.[64]

High volume low pressure spraying is a spraying technique that uses approximately the same amount of compressed air as conventional spraying but requires less pressure to atomize the coating material. This results in a lower velocity air/coating stream and consequently improves the transfer efficiency from ~30% to up to 70%. This effectively reduces the coating costs by preserving more coating material. The negative side of high volume low pressure spraying is that the application time needed to coat an equivalent surface area compared to conventional spraying is increased. Furthermore, this spraying technique may not be suitable for applying more viscous coatings due to the low pressure requirement.[64]

Airless spraying is another spraying technique that uses a fluid pump to pressurize and propel the coating material onto the substrate. Advantages to using this technique include good surface penetration (e.g. cracks, porous surfaces), better irregular surface coverage (e.g. corners, edges), quick film buildup, rapid area coverage, and higher viscosity coating materials. The coating material transfer efficiency is usually between 30 and 50%. One of the disadvantages to airless spraying is that it is difficult to adjust and change the equipment configurations (e.g. nozzles, orifices) while in the field. It also does not atomize the coating material as well as the conventional spraying method. Poor application techniques using this particular method can result in coating deficiencies such as solvent entrapment, voids, runs, sags, pinholes, and wrinkles.[64]

A variation of the airless spraying method is the air-assisted airless spray, which incorporates the advantages of the airless spray method and the conventional spray method. For instance, it combines the fine atomization abilities of the conventional spray with the improved production and surface penetration characteristics of the airless spray. This method allows the coating material to be joined with a compressed air jet after it has been atomized in the absence of air. This results in a further atomization of the coating material before it reaches the substrate. This combined method is useful for applying fillers, glazes, lacquers and polyurethanes.[64]

Plural component spraying is a complex application method that mixes coating components immediately before the coating is propelled to the substrate. This method is used for high-solids coatings and for coatings with a short cure time, such as epoxies. This method can be performed by any of the spraying methods mentioned above. This method is used to apply polyesters, polyurethanes, vinyl esters, and epoxies.[64]

Electrostatic spraying is also a coating application process that utilizes the various atomization methods mentioned above (i.e. conventional, airless, air assisted airless). It utilizes an electrostatic, high voltage supply to direct the atomized particles to the substrate by electrostatic attraction. This technique is used to coat irregularly shaped substrates such as cables, piping, and fencing. The advantages of this coating method are that it improves the coating material transfer efficiency, has a good rate of application, and has good atomization properties. A disadvantage to this method is that it has a tendency for non-uniform deposition of the coating near irregular shaped objects on a surface. Furthermore, it requires special formulation of the coating material.[64]

Proper application techniques are critical when using spraying techniques in order to achieve a high quality, uniform coating on the substrate. Therefore, it is very important that the applicator have either the necessary experience or training in order to produce acceptable coating results.

Table 55 Advantages and Disadvantages of Coating Application Methods[6, 64, 88]

Coating Method	Advantages	**Disadvantages**
Electrodeposition	Can choose from a variety of coatings Versatility of application – can be used on components for many different applications Common coating method Coatings are electrically conductive Can be sacrificial or barrier coating Coatings can be weldable and solderable Coating thickness can be controlled Substrate can be more formable with electrodeposited coating compared to other coating methods	▪ Color limitations ▪ Some substrates may not be receptive to coating ▪ Coating application may be limited by geometry and very large parts.
Electroless Plating	▪ Uniform deposition ▪ Low porosity ▪ Less hydrogen absorption compared to electroplated nickel and hard chrome ▪ No (or compressive) residual stress ▪ Coatings have lubricity ▪ Coatings are weldable and solderable ▪ Higher hardness than electroplated coatings	
Cladding	▪ Essentially zero porosity	▪ Limited to simple geometries
Hot Dipping	▪ Can coat difficult geometries ▪ Resistant to mechanical damage	▪ Coating metal must have relatively low melting temperature

Table 55, continued - Advantages and Disadvantages of Coating Application Methods

Coating Method	Advantages	**Disadvantages**
Sputtering	▪ Can produce thin films ▪ Good adhesion ▪ Highly automatic process ▪ High quality ▪ Uniform deposition	▪ Limited thickness ▪ High cost ▪ Difficult to coat substrate uniformly
Evaporation	▪ Used with most metals	▪ Difficult to coat substrate uniformly ▪ Adhesion is marginal
CVD	▪ Can deposit thick, dense films ▪ High quality ▪ Good Adhesion ▪ Generally costs less than PVD	▪ May have residual stresses ▪ May require high temperatures for deposition ▪ May contain impurities ▪ Limited number of coatings available
Thermal Spraying	▪ Excellent long-term corrosion resistance ▪ Minimal maintenance ▪ Can apply thick coatings ▪ Excellent paintability ▪ No heat distortion ▪ Can apply coatings on-site	
Brushing	▪ Inexpensive equipment ▪ High quality coating near irregular surface areas ▪ Good surface penetration	▪ Time consuming ▪ Difficult to maintain uniformity over large surface areas ▪ May leave brush marks or slight grooves on surface
Rolling	▪ Can be used for large surface areas ▪ Faster application compared to brushing	▪ Poor surface penetration ▪ Relatively slow process ▪ May leave speckled texture on surface
Spraying	▪ Faster application than brushing and rolling ▪ Can be used for large surface areas ▪ Results in a smooth, uniform coating ▪ Can have good surface penetration	▪ Low coating transfer efficiency ▪ Requires experienced technicians to apply coatings

4.4 Cathodic Protection

Cathodic protection (CP) is a widely used electrochemical method for protecting a structure or important components of a system from corrosion. A CP system is essentially an electrochemical cell and must have a cathode, an anode, an electrical connection between them and an electrolyte. The principle behind CP is that dissolution of a metal (cathode) can be suppressed by supplying it with electrons, and in effect, controlling the corrosion. Corrosion is then targeted on the anode instead of the metal. Since an electrolyte is required for this method of protection, CP is not effective for systems in air or other environments that resist current flow between the anode and cathode.

There are two main classes of CP: active and passive. Active cathodic protection, also called impressed-current, requires the use of an external power supply. In this type of protection, the negative terminal of the power supply is connected to the metal to be protected, and the positive terminal is connected to an inert anode. The anode, however, is often not more anodic to the metal, and can be even more cathodic than the metal. The impressed-current ensures that current flows such that the metal acts as the cathode and is therefore protected from corrosion. Moreover, the anodes are not typically consumed by corrosion in impressed-current CP systems, since they do not undergo the typical corrosion reactions. It is possible to overprotect a system using impressed-current CP. If the voltage is too high, the metal can experience hydrogen embrittlement (e.g. steel) or possibly accelerated corrosion (e.g. aluminum). Therefore, proper conditions for the system should be determined in order to optimize the protection.

Passive CP systems are simpler than impressed-current systems and involve the galvanic coupling of the metal to be protected to a sacrificial anode, which corrodes preferentially. The anode in this type of system must be more anodic than the metal and must also readily corrode without passivation in order for the system to be successful. In some instances the sacrificial anode must be replaced after it has been consumed to ensure protection of the structure. A comparison of the characteristics of the active and passive CP systems is provided in Table 56.

Table 56 Comparison between Sacrificial Anode and Impressed-Current Cathodic Protection Systems[93]

Passive Cathodic Protection	**Active Cathodic Protection**
Simple………………………………………	Complex
Low/no maintenance……………………….	Requires maintenance
Works best in conductive electrolytes……...	Can work in low-conductivity electrolytes
Lower installation costs for smaller installations…………………………………	Remote anodes possible
Higher capital investment for large systems.	Low capital investment for large systems
	Can cause the following problems: ▪ Stray current corrosion ▪ Hydrogen embrittlement ▪ Coating debonding ▪ Cathodic corrosion of aluminum

There are several anodes that are available for use in cathodic protection applications. For passive CP systems magnesium, aluminum and zinc are commonly used. Characteristics of some sacrificial anodes are given in Table 57. Furthermore, there is a variety of anodes available for active CP systems. These include high-silicon cast iron, graphite, polymers, precious metals, lead alloys, and ceramics. Table 58 gives a comparison of the consumption rate between various sacrificial and impressed-current anodes.

Table 57 Characteristics of Sacrificial Anodes[11]

Sacrificial Anode Type	Density (lb/in^3)	Half Cell Potential vs. SCE (V)	Consumption Rate (lb/amp. yr.)	Theoretical Current Capacity (Amp. Hrs./lb)	Actual Current Capacity (Amp. Hrs/lb)	Efficiency (%)
Zinc	0.256	-1.04	25	372	355	95
Aluminum/Mercury	0.100	-1.04	6.8	1,352	1,280	95
Aluminum/Indium	0.100	-1.08	7.6	1,352	1,150	85
Aluminum/Tin	0.100	-1.05	7.4	1,352	1,176	87

Table 58 Comparison of Sacrificial and Impressed-Current Anodes for Cathodic Protection[12, 93]

Anode	Consumption Rate (lb/A-yr)
Sacrificial Anodes	
Magnesium	18
Zinc	25
Aluminum-Tin	16-20
Aluminum-Zinc-Tin	7.4-20.8
Aluminum-Zinc-Indium	8-11.5
Aluminum-Zinc-Mercury	6.8-7
Impressed-Current Anodes	
Scrap Steel	20
Aluminum	10-12
Graphite	0.25-5
High-Silicon Iron and Si-Cr Iron	0.25-1
Lead	0.1-0.25
Platinized Titanium	0
Pb-6Sb-1Ag	0.1-0.2

Impressed current cathodic protection is sometimes not practical, such as when the metal is in an extremely corrosive environment, which would require a prohibitively high current. Therefore, CP is sometimes used in conjunction with other protection methods in order to enhance the level of protection and avoiding an impractical system. It is common for pipelines, for example, to be coated with an organic coating, and CP is used to protect the structure from corrosion where there are weaknesses or defects in the coating, known as holidays.

A notable disadvantage of CP, specifically active CP, is the resulting stray-current effects it may impose on nearby systems or structures. Stray currents can be picked up by metallic components or structures that are in close proximity to the CP system, potentially resulting in accelerated corrosion of that metal component or system, as depicted in Figure 43.

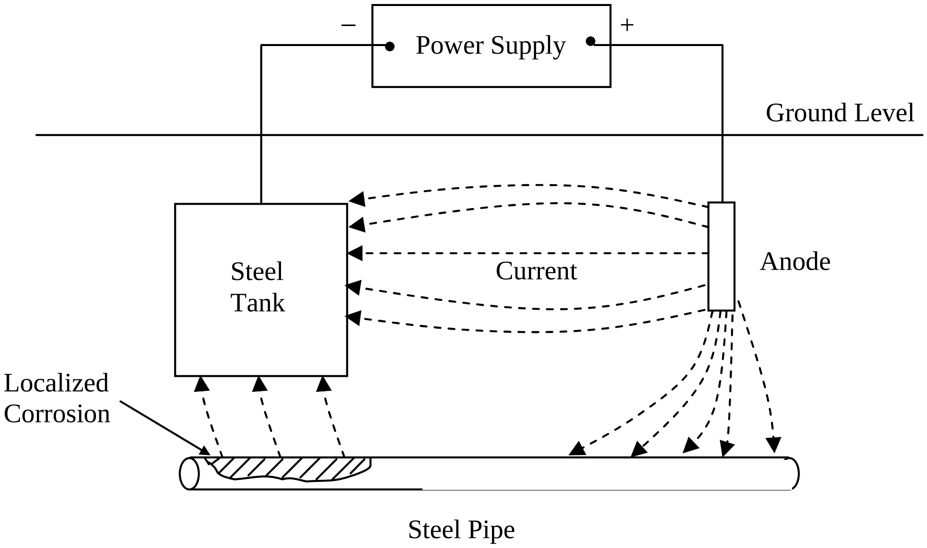

Figure 43 Stray Currents Resulting from Cathodic Protection[12]

Cathodic protection systems are usually designed and implemented by a company that specializes in this field. Choosing the right system and then designing it is not a straightforward process, and usually requires expert knowledge to determine what is best for a specific system in a specific environment. Therefore, it is generally recommended that an expert company be contracted or at least consulted to do such work.

4.5 Anodic Protection

Anodic protection is a method of corrosion control that was developed more recently than cathodic protection, but it is used less frequently. As its name implies, anodic protection shields the anodic electrode in the system from corrosion rather than the cathodic electrode as in CP. The principle behind anodic protection, however, is not quite analogous to that of CP. Essentially, instead of shifting corrosion potential from the metal to be protected to an anodic material as in CP, anodic protection involves passivation of the metal to be protected. A passive film forms on the surface of the metal with the application of an electrical current. Once this film is formed, it acts to protect the metal from dissolution, and the film itself is nearly insoluble in the environment which it formed. Passivation causes metals to become very non-reactive and consequently very resistant to corrosion. The limitation of this type of corrosion control is that not every metal can be protected this way; only certain metals in specific environments can be anodically protected. These include the metals and solutions shown in Table 59.

Table 59 Metals and Solutions Capable of Being Anodically Protected[94]

Solutions	**Metals**
Sulfuric acid	Steels
Phosphoric acid	Stainless steels
Nitric acid	Nickel
Nitrate solutions	Nickel alloys
Aqueous ammonia	Chromium
Organic acids	
Caustic solutions	

Anodic protection requires three electrodes, a potential controller (potentiostat), and a power source. The necessary electrodes are a cathode, a reference electrode and an anode, which is by definition the metal to be protected. The reference electrode monitors the voltage on the anode, and is very important since it is necessary to maintain proper protection and avoid accelerated corrosion. The cathode should be resistant to dissolution; it can be platinum on brass, steel, silicon cast iron, copper, stainless steel, or nickel-plated steel, among others. The potential controller actively controls the potential on the anode.

A notable advantage of anodic protection is that after the passive film has formed, the amount of current required to maintain this protective film is very small. A further advantage is that the applied current is equal to the corrosion rate of the protected metal. This allows the instantaneous corrosion rate to be measured, which is not the case for CP. Moreover, anodic protection is effective in weak and strong corrosive media. Furthermore, the operating conditions for anodic protection systems can be determined accurately by laboratory-scale experiments, whereas, to do so for CP is hardly a scientific procedure. A general comparison of anodic protection and cathodic protection methods is provided in Table 60.

Table 60 Comparison of Anodic and Cathodic Protection

	Anodic Protection	**Cathodic Protection**
Applicability		
Metals	Active-passive metals only	All metals
Corrosives	Weak – aggressive	Weak – moderate
Relative Cost		
Installation	High	Low
Operation	Very low	Medium to high
Throwing Power	Very high	Low
Significance of applied current	Often a direct measure of protected corrosion rate	Complex – does not indicate corrosion rate
Operating Conditions	Can be accurately and rapidly determined by electrochemical measurements	Must usually be determined by empirical testing

Throwing power indicates the distribution uniformity of the current density that is required. To achieve uniform protection, for example, electrodes need to be placed close together if the throwing power is low. On the other hand, if the throwing power is high, the electrodes can be placed farther apart. In anodic protection, for instance, a single cathode can protect a wider area of metal because it has a high throwing power.

5.0 Corrosion Monitoring and Inspection Technologies

There are numerous methods that may be used to monitor or inspect components for corrosion and corrosion related damage. The following section is aimed only at introducing available technologies and their applicability to the various forms of corrosion. Corrosion monitoring involves methodologies to assess the corrosivity of a system which may or may not be continuous (real-time monitoring) and to continuously monitor systems for defect formation. Corrosion inspection is the periodic checking of a system for corrosion and corrosion related defects. Since corrosion fatigue and stress corrosion cracking involves the formation and propagation of cracks, monitoring and inspection techniques to look for surface and subsurface cracks have been included.

5.1 Corrosion Monitoring

Corrosion monitoring is used to predict component wear out and to manage the corrosivity of the environment. There are a couple different methodologies used in the field of corrosion monitoring. One method uses probes (sensors) to monitor the chemical or electrochemical nature of the environment. The data collected is then used to relate to corrosion rates of materials, which is not always a direct method. Furthermore, probes can be adversely affected under certain conditions leading to erroneous corrosion rate determinations. A corrosion coupon is a second method, providing a low technology method to measure corrosion rates of materials. Acoustic emission is used to detect the formation of surface and subsurface damage in materials.

5.1.1 Coupon Testing

Coupon testing involves placing a sample within a system. The sample is removed periodically for inspection and weight loss measurements. Coupon testing is a simple procedure but is often overlooked as it is an old and low technology method. However, coupons provide the most reliable evidence, whereby information on the forms and location of corrosion on the samples, the average rate of corrosion, and the corrosion byproducts can be obtained. The downfalls are that it is time consuming and does not provide real time data.

5.1.2 Electrical Resistance Probes

Electrical resistance probes measure the change (increase) in electrical resistance due to a reduced cross-sectional area of the sensing element as a result of corrosion. The sensitivity of the sensor increases with a decrease in thickness of the sensing element; however this also results in a reduced lifetime. Any build up of deposits on the sensing element will affect the electrical resistance readings from the probe. Electrical resistance probes are also temperature dependent requiring an additional shielded probe for proper corrosion rate adjustments. They may be permanently installed within a system for continuous monitoring or potable for periodic measurements.

5.1.3 Inductive Resistance Probes

Inductive resistance probes measure a reduction in sensing element thickness by changes in the inductive resistance of a coil in the probe. By using sensing elements with a high magnetic permeability, the magnetic field around the coil is intensified. Any change in thickness of the elements will change the magnetic field encompassing the coil, and thus the corrosion rate may be obtained. Inductive resistance probes require a temperature adjustment similar to electrical resistance probes. The sensitivity of induction resistance probes is higher than with the electrical resistance probes.

5.1.4 Linear Polarization Resistance

The linear polarization resistance (LPR) monitoring method is an electrochemical method used to measure instantaneous rates of uniform corrosion and is widely applied under full immersion aqueous environments. A small potential, about 5-20mV, is applied to a sensor electrode with the direct current being measured. The solution resistance should be measured independently and subtracted from the measured resistance for accuracy. The polarization resistance obtained is inversely proportional to the corrosion rate. This method has been used for more than thirty years in virtually all types of water-based environments.

5.1.5 Electrical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS), like LPR, uses the polarization of electrodes to measure corrosion rates. The difference is that EIS uses alternating currents and measures the resulting phase shift relative to the applied current. The applied frequency is about 0.1 Hz to 100 kHz with more than one frequency required to obtain useful data. Typically, two frequencies are used; however, full frequency measurements may be used, producing the best data to identify the corrosion processes taking place.

5.1.6 Electrochemical Noise

The electrochemical noise method measures changes in the electric potential and current between freely corroding electrodes. Highly sensitive instrumentation is required as the fluctuations are on such a small scale. Three electrodes are needed to simultaneously measure both the potential and current noise. Different corrosion processes will produce different noise signatures. This data may be used to identify pit initiation and growth before visible detection. However, the interpretation of signals is complex, with different strategies developed to help interpret results. Although this method is proven and can detect different corrosion processes, there is skepticism over the accuracy of corrosion rates derived from the measurements.

5.1.7 Zero Resistance Ammetry

Zero resistance ammetry is the measure of galvanic currents between two materials. This is accomplished by placing samples of the materials into a sensor unit, which is placed in the system environment. Deviation from actual component materials may occur due to slight differences in composition, heat treatment, surface condition and applied stresses. This technique can be used to monitor changes to the environment by using the same material for both sensor elements.

5.1.8 Thin Layer Activation

Thin layer activation involves inducing radioactive species on the surface layer of a material, and subsequently measuring gamma ray emission to determine the corrosion rate. A high energy beam of charged particles is used to bombard a material's surface, producing radioactive elements in the surface area. One example is the formation of Co^{56} within steel. This isotope will decay into Fe^{56}, emitting gamma rays in the process. The change in gamma ray emission is used to determine the rate of material loss. A radioactive surface may be induced on system components or sample materials to be placed within the system.

5.1.9 Electric Field Method

This technique is used to look for corrosion across large structures by applying an electric current across the structure and measuring the resulting voltage distribution. Arrays of pins for the measurements are placed in specific areas across the structure. Increasing the distance between pins reduces the ability to detect localized corrosion. This method is widely used to detect corrosion on the interior of pipelines.

5.1.10 Corrosion Potential

Measuring the corrosion potential to determine the risk of corrosion is a direct result of corrosion kinetics (Appendix A). The corrosion potential of a material is measured relative to a reference electrode. This method is widely used to assess the corrosion of steel rebar in concrete and underground pipes incorporating cathodic protection. It is also used for structures containing anodic protection.

5.1.11 Hydrogen Probes

Hydrogen probes can be used to measure corrosion rate and to detect the diffusion of atomic hydrogen into materials. Many corrosion processes involve atomic hydrogen as a product of the corrosion reaction. Thus, by measuring the atomic hydrogen present, a corrosion rate may be determined. Hydrogen probes are more often used to detect the diffusion of atomic hydrogen into adjacent materials, such as pipe walls, as hydrogen-induced cracking may result. Hydrogen monitoring has been highly beneficial in oil refining and petrochemical industries due to the presence of hydrogen sulfide in such plants.

5.1.12 Chemical Analysis

Chemical analysis involves the inspection of materials, usually fluids, from a system for corrosion reaction by-products. This method is widely used to monitor the health of emergency generators through routine oil analysis. Particles in the waste oil are identified and quantified to monitor any abnormal wear and/or corrosion within the system.

5.1.13 Acoustic Emission

Acoustic emission is a monitoring technique where elastic waves are generated by the release of energy built up in stressed materials revealing the formation of a defect. The elastic waves must be continuously recorded for interpretation. This method is complicated by the normal emission of waves produced by thermal or mechanical stresses exhibited on the system. The interpreter must therefore be experienced to dismiss such "background noise" and diagnose abnormal events. This technique can be used to detect the formation of defects such as crack growth, material corrosion, surface rubbing, and leaking fluids. A summary of the corrosion monitoring methods is provided in Table 61.

Table 61 Advantages and Disadvantages of Corrosion Monitoring Methods[6]

Monitoring Techniques	**Advantages**	**Disadvantages**
Corrosion Coupons	▪ Low cost ▪ Many forms of corrosion may be monitored ▪ Applicable to all corrosive environments	▪ Erosion and heat transfer effects not easily simulated ▪ Long exposure times required for meaningful data collection (not real-time) ▪ Labor intensive ▪ Removal of coupons from the system for examination and cleaning will affect the corrosion rate if the coupon is reused.
Electrical Resistance	▪ mature technology with several commercial suppliers ▪ probes do not have to be removed from the system to obtain weight loss data	▪ Only suitable to measure uniform corrosion ▪ The sensitivity lacks the ability for real-time data collection with short durations going undetected. ▪ Gives erroneous results in the presence of conductive products or deposits on the probe
Inductive Resistance	▪ Better sensitivity and less affected by temperature changes than electrical resistivity probes.	▪ A more recent technology with commercial products largely applicable to uniform corrosion only
Linear Polarization Resistance	▪ The sensitivity allows real-time measurements in appropriate environments	▪ Based on uniform corrosion only ▪ An environment with a relatively high ionic conductivity is required for this method ▪ Unstable corrosion potentials will produce erroneous measurements ▪ Electrode surface colors in long-term surface have been observed to be different than freely corroding surfaces. Idealized theoretical conditions are assumed which is not always the case in practice ▪ Conductive species may cause short circuiting of the electrodes, producing erroneous results
Electrochemical Impedance Spectroscopy	▪ More suited to low-conductivity environments than DC polarization ▪ Can provide information on the state of organic coatings ▪ Detailed characterization of the corroding surface is possible	▪ The instrumentation and interpretation of results is complex ▪ Usually limited to uniform corrosion, although may used to detect pitting corrosion in certain systems ▪ Full frequency analysis is rarely used in the field ▪ The corrosion potential has to be stable to obtain useful data at low frequencies ▪ The applied potential perturbation may affect the corroding sensor element, especially for long-term, repeated use conditions.

Table 61, continued - Advantages and Disadvantages of Corrosion Monitoring Methods

Monitoring Techniques	Advantages	Disadvantages
Electrochemical Noise	▪ Highly sensitive and performs well under limited conductivity, such as thin-film corrosion ▪ One of the few techniques with the ability to detect localized corrosion including pitting damage and certain submodes of stress corrosion cracking	▪ The data analysis requirements are complex with substantial experience needed for interpreting noise signals
Zero Resistance Ammetry	▪ Simple method to monitor galvanic corrosion and the effects of treatments to prevent it	▪ The measured currents may not accurately represent galvanic corrosion since it is highly dependent upon the anode: cathode area ratio ▪ An increase in current readings is not always related to an increase in galvanic corrosion
Thin Layer Activation	▪ Desirable for direct measurements of actual components ▪ Small areas may be irradiated for monitoring such as weld zones ▪ May be used to monitor erosion corrosion	▪ The instrumentation used is only applicable to small components ▪ The results are only meaningful if the radioactive species are removed from the material’s surface during the corrosion process. ▪ Low sensitivity
Electrical Field Signature Method	▪ Corrosion damage is monitored in actual components ▪ Once instruments are installed, monitoring may be performed over several years with minimal maintenance	▪ Does not distinguish between internal and external flaws ▪ The interpretation of voltage signals for localized corrosion is complex ▪ Not highly sensitive, especially for small areas
Acoustic Emission	▪ Applicable to a wide range of materials including non-conducting ones ▪ Monitoring may be performed over larger areas rather than at specific points of interest	▪ Only detects actively growing defects ▪ Does not detect defect size ▪ Requires a high level of skill for interpretation of results
Corrosion Potential	▪ The method and instrumentation are relatively simple	▪ Only an indication of corrosion behavior and not a measurement of corrosion rate
Hydrogen Probes	▪ The attachment of probes on external surfaces for hydrogen diffusion measurements is convenient and can be easily changed	▪ Measurements are restricted to a small area ▪ Restricted to systems where hydrogen is produced in the cathodic reaction ▪ Guidelines that correlate hydrogen uptake to actual damage has not been established
Chemical Analysis	▪ In well characterized systems, it may be possible to perform cost effective monitoring with such techniques ▪ Provides useful supplementary information, to the direct measurement methods, for identifying and solving corrosion problems	▪ Does not measure corrosion rates ▪ Many chemical analysis methods require outside laboratory evaluations so that immediate information is not available

5.2 Corrosion Inspection

Corrosion Inspection Methods are periodic checks of materials and material systems to detect corrosion and corrosion related defects including cracks. The success of many of these methods lies with the operator and their experience with locating and identifying corrosion. Low technology methods are limited to surface damage only. They include visual inspection, liquid penetrant inspection, and magnetic particle inspection. High technology methods are used to detect subsurface defects, damage to hidden areas, and damage too small for visual inspection. These methods usually induce some form of energy into the material of interest, such as x-rays, sound waves, or heat, and measure the absorption/reflection of the energy. The data collected is then used to "map" defects found in the material. Experience with the various equipment/methods and second or third inspection methods may be required to identify exactly what type of defect has been detected.

5.2.1 Visual

Visual Inspection involves the observation of light reflected from the surface of an object to the human eye. Although not a highly technical method, it's the most widely used technique for corrosion inspection. The quality of inspection is directly related to the experience of the inspector with the equipment and environmental conditions. Corrosion products are sometimes visible, which can lead to the identification of the corrosion problem. The appearance of corrosion products from several alloys is provided in Table 62.

5.2.2 Enhanced Visual

Borescopes and fiberscopes provide a means to inspect interior areas of critical and corrosion prone components. A borescope is a thin rod shaped optical device that transmits an image from the components interior to the inspector's eye. Critical areas are designed with access ports for borescope inspections. Fiberscopes work in the same way as borescopes, but they are flexible so that a wider area may be observed. Video imaging may also be incorporated into these devices so that the images can be viewed on a video monitor.

5.2.3 Liquid Penetrant Inspection

Liquid penetrant inspections provide a low cost option for locating surface cracks too small to be seen by visual inspection. An ultraviolet reflective liquid is first sprayed or wiped onto the surface of the material. After a period of time, the liquid will enter cracks via capillary action. The excess liquid is wiped from the surface and a powder is then applied. The powder draws the liquid back out of the crevices to the surface. An ultraviolet light is then used to illuminate the surface revealing the remaining liquid. The area of the liquid will be larger than the crack size.

5.2.4 Magnetic Particle Inspection

Magnetic particle inspection is used to find surface defects in ferromagnetic materials such as steel and iron. Magnetic particles, which may be dry or suspended in a liquid and colored or fluorescent, are dispersed over the material's surface. A magnetic field is then induced in the material which produces flux lines which will be distorted by defects. Care must be taken in surface preparation as scratches and irregularities will also distort magnetic flux lines.

Table 62 Corrosion of Metals – Nature and Appearance of Corrosion Products[95]

Alloys	Type of Attack to which Alloy is Susceptible	Appearance of Corrosion Product
Aluminum Alloys	Surface pitting, intergranular and exfoliation.	White or gray powder.
Titanium Alloys	Highly corrosion resistant. Extended or repeated contact with chlorinated solvents may result in degradation of the metals structural properties.	No visible corrosion products.
Magnesium Alloys	Highly susceptible to pitting.	White powdery snow-like mounds, and white spots on surface.
Low Alloy Steels (4000-8000 series)	Surface oxidation, pitting, and intergranular.	Reddish-brown oxide (rust).
Corrosion Resistant Steel (CRES) (300-400 series)	Intergranular corrosion (due to improper heat treatment). Some tendency to pitting in marine environment (300 series more corrosion resistant than 400 series). Stress corrosion cracking.	Corrosion evidenced by rough surface; sometimes by red, brown or black stain.
Nickel-Based Alloys (Inconel)	Generally have good corrosion-resistant qualities. Sometimes susceptible to pitting.	Green powdery deposit.
Copper-Based Alloy, Brass, Bronze	Surface and intergranular corrosion.	Blue or blue-green powder deposit.
Cadmium (used as a protective plating for steel)	Good corrosion resistance. If attack occurs, will protect steel from attack.	White, powdery corrosion products.
Chromium (used as a wear-resistant plating for steels)	Subject to pitting in chloride environments.	Chromium, being cathodic to steel, does not corrode itself, but promotes rusting of steel where pits occur in the coating.

5.2.5 Eddy Current Inspection

Eddy currents are used to detect defects on and below the surface of a material. An alternating magnetic field is applied to the surface of the material. This induces eddy currents in the material producing a magnetic field which opposes the applied magnetic field. The measured impedance is used to map the defects in the material. Low frequency eddy current, roughly 100 Hz – 50 kHz, is used to penetrate deeper into a material.

5.2.6 Ultrasonic Inspection

Ultrasonic inspection uses high frequency sound waves transmitted through the material of interest. The transmitted sound wave will be reflected back to the source by both defects in the material and once the wave has reached the other side of the material. The recorded sound wave is then used to map defects in the material and also to measure the thickness of the material. The identification of defects found in a material is left up to operator experience and/or additional inspection methods. Ultrasonic inspection is costly compared with other methods requiring large equipment and operator experience.

5.2.7 Radiography

Radiography is a method whereby x-rays, gamma rays, or neutrons are transmitted into a material and the absorption data recorded is then used to find any defects within the material. Again, the identification of defects is left up to operator experience or aided with the used of additional inspection methods. Neutron radiography is the most sensitive/most costly of these techniques.

5.2.8 Thermography

Thermography is a measure of the infrared radiation a material system emits. The underlying principal is that a good mechanical bond between materials is also a good thermal bond. It may be used to detect corrosion, debonding, cracking, thinning, water absorption, among other defects. Thermography is not widely used due to its cost and limitation to surface defect detection. A comparison between various nondestructive inspection techniques is given in Table 63.

Table 63 Nondestructive Inspection Methods[3]

Technology	Advantages	Disadvantages	Primary Defects
Visual	▪ Relatively inexpensive ▪ Large area coverage ▪ Portability	▪ Highly subjective ▪ Measurements not precise ▪ Limited to surface inspection ▪ Labor intensive	Surface, exfoliation, pitting, and intergranular corrosion
Enhanced Visual	▪ Large area coverage ▪ Very fast ▪ Very sensitive to lap joint corrosion ▪ Multi-layer	▪ Quantification difficult ▪ Subjective – requires experience ▪ Requires surface preparation	Same as visual except enhanced through magnification or accessibility
Eddy Current	▪ Relatively inexpensive ▪ Good resolution ▪ Multiple layer capability ▪ Portability	▪ Low throughput ▪ Interpretation of output ▪ Operator training ▪ Human factors (tedium)	Surface and subsurface flaws such as cracks, exfoliation corrosion around fasteners and corrosion thinning
Ultrasonic	▪ Good resolution ▪ Can detect material loss and thickness	▪ Single-sided ▪ Requires couplant ▪ Cannot assess multiple layers ▪ Low throughput	Corrosion loss and delaminations, voids in laminated structures
Radiography	▪ Best resolution (~ 1%) ▪ Image interpretation	▪ Expensive ▪ Radiation safety ▪ Bulky equipment	Surface and subsurface corrosion flaws
Thermography	▪ Large area scan ▪ Relatively high throughput	▪ Complex equipment ▪ Layered structures are a problem	Surface corrosion

5.3 Corrosion Inspection Devices

Corrosion inspection devices that incorporate more than one inspection technique have been developed to improve the reliability of accurate detection of corrosion defects. These devices must be hand held for ease of use and cost effective. The two following devices have been developed for aircraft inspections to identify cracks and hidden corrosion by scanning the device across surface areas of the aircraft.

5.3.1 Mobile Automated Ultrasonic Scanner

The Mobile Automated Ultrasonic Scanner (MAUS) incorporates ultrasonic pulse-echo, ultrasonic resonance, and eddy current technologies into one unit for nondestructive inspection. MAUS IV is the forth generation device which is portable and applicable for detecting cracks and defects in materials for various components. The MAUS was developed for aircraft inspections, especially for lap joint evaluations.

5.3.2 Magneto-Optic Eddy Current Imaging

Magneto-optic eddy current imaging (MOI) is an inspection method which measures induced eddy currents using a Faraday magneto-optic sensor and displays the measurements on a video monitor. The images may be viewed in real time or recorded. The device is small enough to be hand held and may be easily moved about to scan large areas.

6.0 Electrochemistry, Kinetics, and Thermodynamics of Typical Corrosion Processes

Corrosion is a process involving the deterioration of a material and is regulated by chemical or electrochemical reactions with the surrounding environment; consequently, it also results in a degradation of the material’s properties. The corrosion process occurs spontaneously when the environmental conditions thermodynamically favor a metal to be in its oxidized state. Therefore, thermodynamics is commonly used to determine the tendency of a material to corrode. To describe the chemical process of corrosion, however, electrochemistry and kinetics are used.

6.1 Electrochemistry and Kinetics

The principles of corrosion, based on electrochemistry, can be illustrated by an electrochemical cell, as shown in Figure 44. There are four necessary elements in order for corrosion to occur:

- Anode
- Cathode
- Electrolyte
- An electrical conducting path between the anode and cathode

Since corrosion requires all four of the elements listed above, it is readily obvious that corrosion prevention or control necessitates the elimination of just one of these elements and not necessarily all four.

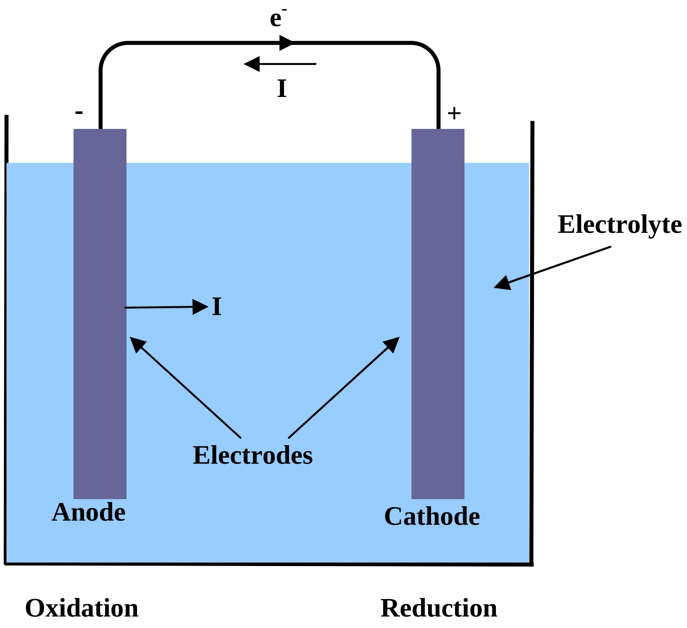

Figure 44 Electrochemical Cell Showing Principles of Corrosion

The electrochemical process of corrosion involves the transfer of electrons between the two electrodes resulting in a flow of electrical current (indicated as “I” in Figure 44, which is necessary to sustain the chemical reactions. These electrochemical reactions occur at both the anode and cathode and are oxidation-reduction reactions. The anode is host to the oxidation reaction, which generates electrons. This anodic (oxidation) reaction is described by Equation 13.

$$M \rightarrow M^{n+} + ne \qquad \text{Equation 13}$$

where

M – represents a metallic element

e – represents an electron

For the electrons to be transferred between the anode and cathode there must be an electrically conductive path, since the electrons are simultaneously consumed at the cathodic site where the reduction reaction takes place. An example of this cathodic reaction (reduction) is the evolution of a hydrogen gas from the reduction of hydrogen ions as shown in Equation 14. An example of the oxidation-reduction process is illustrated in Figure 45.

$$2H^{+} + 2e \rightarrow H_2 \qquad \text{Equation 14}$$

Consumption of the electrons generated in Equation 1 could also occur by other mechanisms, as shown in Table 64.

Table 64 Other Possible Cathodic/Reduction Reactions

Metal Deposition	$M^{n+} + ne \rightarrow M$
Metal Ion Reduction	$M^{n+} + e \rightarrow M^{(n-1)+}$
Reduction of Dissolved Oxygen (Neutral or Basic Solution)	$O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Reduction of Dissolved Oxygen (Acidic Solution)	$O_2 + 4H^+ + 4e \rightarrow 2H_2O$
Reduction of Water	$2H_2O + 2e \rightarrow H_2 + 2OH^-$

An electrolyte is also necessary to sustain the electrochemical reactions, given by Equation 13 and Equation 14, because it contains the ions that aid in driving the reactions. The reactions shown in Equation 13 and Equation 14 are only partial reactions, and thus, together they occur simultaneously and at the same rate.

Of course, it is not necessary to always have two distinct and separate electrodes for corrosion to occur. In fact, the most common form of corrosion occurs in the presence of one metal. It is still necessary, however to have the two electrodes (i.e. the anode and the cathode). In this case, localized cells or electrodes exist on the surface of the metal, where there is a relatively small difference in electrical potential). This is usually the case where there is compositional dissimilarities on the metal surface, for example, different metal phases, different crystal orientations, crystal imperfections, grain boundaries, etc.[96] An example of this is given in the following section. Furthermore, it is not necessary that the electrolyte be in the form of a liquid. Instead, it may exist as ions in some vaporous media.

6.1.1 Example

A good example of the electrochemical corrosion process can be illustrated with the corrosion of zinc in a hydrochloric acid environment. Zinc is removed from the surface of the metal and enters the electrolytic solution in ionic form, as shown in Equation 15 and illustrated in Figure 45.

$$Zn \rightarrow Zn^{2+} + 2e \qquad \text{Equation 15}$$

Simultaneously, the two electrons released from zinc are transferred to the hydrogen ion, which is supplied from the dissociation of the acid as shown in Equation 16. Equation 14 shows the association of hydrogen ions to form hydrogen gas upon the transfer of electrons from the zinc.

$$2HCl \rightarrow 2H^{+} + 2Cl^{-} \qquad \text{Equation 16}$$

The overall reaction of zinc with a hydrochloric acid solution can be described as in Equation 17.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \qquad \text{Equation 17}$$

The corrosion process for other metals in like solutions is similar to that illustrated in this example; however there are other corrosion mechanisms for metals in different types of environments.

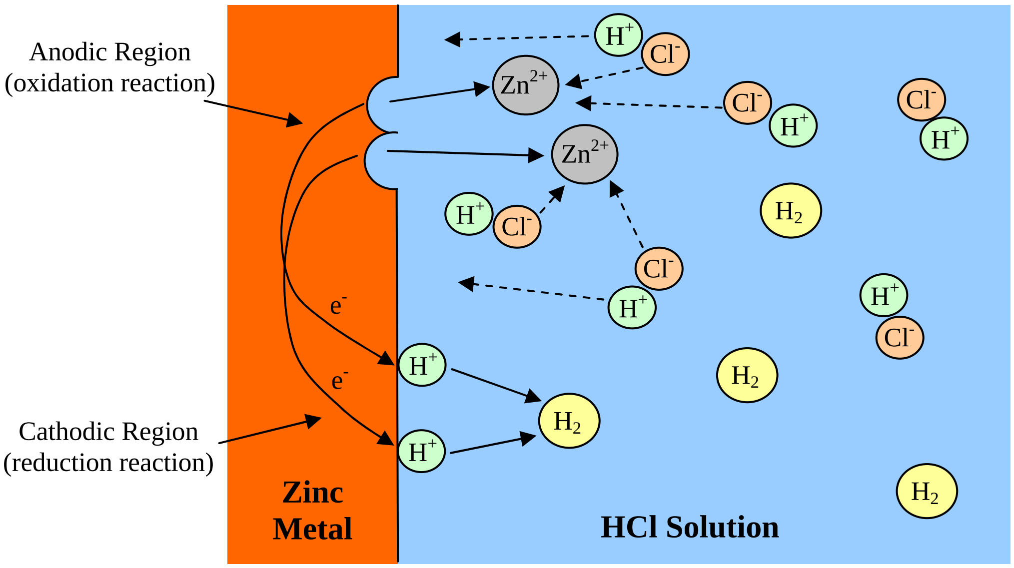

Figure 45 Illustration of the Oxidation-Reduction Process

6.2 Thermodynamics

The electrochemical reactions causing the physical corrosion of a material are spontaneous with no external driving forces, and thus, are driven only by nature’s tendency to seek lower energy states, as described by the Second Law of Thermodynamics. In other words, the electrochemical reactions occur to reduce the energy in the system. The surrounding system may, however, influence these reactions to occur at accelerated rates. For example, in an environment with an elevated temperature there is additional energy (from the heat) to drive the reactions at a faster rate. Thermodynamics, however, does not provide an indication of the rate of reaction, since it is independent of which path the reaction will take.

Thermodynamics is used primarily to determine, mathematically, the tendency for corrosion to occur, and can also be used to predict whether a metal will not experience corrosion. It cannot, however, be used to determine whether a metal will, in fact, experience corrosion or to what extent corrosion will occur.

Thermodynamics essentially quantifies the chemical stability of a system in terms of the Gibbs free energy. The amount of Gibbs free energy in a system represents the proximity of the system to equilibrium. That is, the lower the free energy, the closer the system is to equilibrium and conversely, the higher the free energy, the less stable the system is. (The free energy is at a minimum when the system is in equilibrium.) Gibbs free energy, G, at constant temperature, is given in terms of enthalpy, H, absolute temperature, T, and entropy, S as shown in Equation 18.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation 18}$$

where

ΔG – Change in the Gibbs free energy
ΔH – Change in the enthalpy
ΔS – Change in the entropy

At equilibrium, when the free energy is at a minimum, the system has no tendency to undergo chemical change, and the free energy can be represented by Equation 19.

$$\Delta G^{o} = -RT \ln K_{eq} \qquad \text{Equation 19}$$

where

ΔG^{o} – Gibbs free energy at standard state
R – gas constant
K_{eq} – equilibrium constant

The equilibrium constant of a reaction can be determined for a range of conditions given the standard state free energy, which is commonly available or can be determined from the free energy of formations of the products.

The potential of an electrochemical cell can be given by Equation 20, if the system is thermodynamically reversible, and if the activities of the reactants and products remain approximately constant.

$$\Delta G^{o} = -nFE^{o} \qquad \text{Equation 20}$$

where

n – number of electrons/atom of the species involved in the reaction
F – Faraday Constant (electric charge of 1 mole of electrons)
E^{o} – electrochemical cell potential at standard state

The electrochemical cell potential (E) is derived from Equation 21. The greater the difference between the electrochemical potentials of the electrodes (anode and cathode) the greater is the driving force for the corrosion reaction.

$$E = E_c - E_a \qquad \text{Equation 21}$$

where

Ec – electrochemical potential of the cathode
Ea – electrochemical potential of the anode

Combining Equation 19 and Equation 20 gives

$$\ln K_{eq} = \frac{nFE^{\circ}}{RT} \qquad \text{Equation 22}$$

Ultimately, Equation 22 provides the means to predict the potential of an electrochemical cell. The more negative the cell potential, the more reactive the material, and thus the material is more susceptible to corrosion. Conversely, if the cell potential is less negative or even positive, then the material is less susceptible to corrosion.

1. **Which of the following atmospheric environments would generally be the least corrosive?**

   ○ a. Rural
   ○ b. Urban
   ○ c. Industrial
   ○ d. Marine

2. **Under what conditions would atmospheric contaminants be the most severe? (Ref. Table 3, page 3)**

   ○ a. Rural, Summer
   ○ b. Industrial, Winter
   ○ c. Rural, Winter
   ○ d. Industrial, Summer

3. **True or False? Regarding soil environments, lower resistivity equates to higher corrosivity.**

   ○ True
   ○ False

4. **What is the correct equation for uniform corrosion? (p=corrosion rate, t=exposure time, A/B=constants, dependent upon material and environment)**

   ○ a. p = At*(-B)
   ○ b. p = At^(-B)
   ○ c. p = AB^(t)
   ○ d. p = A*t*B

5. **Which of following metals should be used as a sacrificial anode?**

   ○ a. Hastelloy, Bronze
   ○ b. Naval brass, Lead
   ○ c. Cast iron, Aluminum
   ○ d. Magnesium, Zinc

6. **What type of corrosion can be one of the most dangerous forms of corrosion because it is difficult to anticipate and prevent, relatively difficult to detect, occurs very rapidly, and penetrates a metal without causing it to lose a significant amount of weight?**

   ○ a. Galvanic
   ○ b. Crevice
   ○ c. Pitting
   ○ d. Intergranular

7. **Adding plates to protect welded areas from a fluid stream is a mitigation effort for which type of corrosion?**

   ○ a. Corrosion Fatigue
   ○ b. Dealloying
   ○ c. Intergranular
   ○ d. Erosion Corrosion

8. **True or False? Regarding Stress-Corrosion Cracking (SCC), Most cracks tend to propagate in a direction that is perpendicular to the direction of applied stress.**

   ○ True
   ○ False

9. **Regarding Microbiological Corrosion (MIC), which of the following are true?**

   ○ a. MIC may be misdiagnosed as conventional chloride induced corrosion
   ○ b. MIC is actually not a form of corrosion, but rather is a process that can influence and even initiate corrosion
   ○ c. MIC can accelerate most forms of corrosion
   ○ d. All of the above

10. **Which of the following applications must MIC corrosion be considered?**

    ○ a. Fuel tanks
    ○ b. Fire sprinkler systems
    ○ c. Cooling systems
    ○ d. All of the above

11. **For carbon steels, ____________ additions of 0.01 to 0.05% have the greatest effect for increasing general corrosion resistance.**

    ○ a. copper
    ○ b. nickel
    ○ c. chromium
    ○ d. zinc

12. **What stainless steel alloy has the lowest corrosion resistance of all stainless steels?**

    ○ a. 316
    ○ b. 409
    ○ c. 405
    ○ d. 630

13. **All stainless steel alloys will exhibit pitting when exposed to ______ velocity seawater.**
    - ○ a. high (more than five feet per second)
    - ○ b. low (less than five feet per second)
    - ○ c. any
    - ○ d. All of the above

14. **_____________ excellent resistance to corrosion can usually be attributed to the rapid formation of an oxide film on the metal's surface, which acts as a barrier to corrosive environments.**
    - ○ a. Stainless steel's
    - ○ b. High-carbon steel's
    - ○ c. Brass's
    - ○ d. Aluminum's

15. **What is the most common type of corrosion found in aluminum and its alloys?**
    - ○ a. Pitting
    - ○ b. Galvanic
    - ○ c. Hydrogen embrittlement
    - ○ d. Stress corrosion cracking

16. **True or False? Copper is a high-cost alternative to stainless steels and nickel-base alloys when selecting a material for a corrosion resistant application.**
    - ○ True
    - ○ False

17. **Brass is a ____________ alloy with a significant ___________ content.**
    - ○ a. aluminum, manganese
    - ○ b. nickel, chromium
    - ○ c. copper, zinc
    - ○ d. magnesium, cobalt

18. **If designing for an application in a severe corrosive environment and cost is not an issue, which of the following materials should be chosen?**
    - ○ a. Stainless Steel
    - ○ b. Nickel
    - ○ c. Aluminum
    - ○ d. Cast Iron

19. **Which of the following are alloys of nickel with excellent corrosion resistance?**

○ a. Monel
○ b. Hastelloy
○ c. Inconel
○ d. All of the above

20. **What metal typically should not be used in any application where corrosion is a concern?**

○ a. Zinc
○ b. Titanium
○ c. Magnesium
○ d. Tungsten

21. **True or False? Cast irons may be alloyed for corrosion resistance obtaining levels similar to that of stainless steels and nickel-based alloys.**

○ True
○ False

22. **What coating material should be applied to cast iron for only atmospheric protection? (Ref. Table 46, page 112)**

○ a. Zinc
○ b. Bituminous paint
○ d. Organic corrosion preventive compound
○ c. Enamel

23. **Which inhibitors can induce the formation of precipitates on a metal which covers the entire surface of the metal and act as somewhat of a barrier to the corrosive environment?**

○ a. Organic inhibitors
○ b. Precipitation inhibitors
○ c. Vapor Phase inhibitors
○ d. Passivating inhibitors

24. **What is the preferred coating for the corrosion protection of steel in moist and marine environments.**

○ a. Cadmium
○ b. Copper
○ c. Lead
○ d. Aluminum

25. What coatings are used more for corrosion protection than any other protection method available?

○ a. Organic coatings
○ b. Metallic coatings
○ c. Inorganic coatings
○ d. None of the above

26. Which coating has a brown color resulting from baking which can be used to indicate the degree of cross linking? (Ref. Table 52, page 127)

○ a. Asphalt pitch
○ b. Acrylics
○ c. Phenolics
○ d. Chlorinated rubbers

27. ____________ is widely used to detect corrosion on the interior of pipelines.

○ a. Linear Polarization Resistance
○ b. Electric Field Method
○ c. Electrical Resistance Probes
○ d. Zero Resistance Ammetry

28. Which nondestructive inspection method will detect surface and subsurface flaws such as cracks, exfoliation corrosion around fasteners and corrosion thinning? (Ref. Table 63, page 148)

○ a. Visual
○ b. Enhanced visual
○ c. Eddy Current
○ d. Thermography

29. Regarding the principles of corrosion, how many elements are necessary for corrosion to occur, and how many elements need to be eliminated for corrosion prevention?

○ a. Two elements required for corrosion. eliminate one element to prevent
○ c. Four elements required for corrosion. eliminate one element to prevent
○ d. Four elements required for corrosion. eliminate four elements to prevent
○ b. Two elements required for corrosion. eliminate two elements to prevent

30. True or False? Thermodynamics is used primarily to determine, mathematically, the tendency for corrosion to occur, and can also be used to predict whether a metal will not experience corrosion.

○ True
○ False