

CHAPTER **1**

Introduction and Overview of Electrochemical Corrosion

Definition and Examples of Corrosion

The deterioration of materials due to reactions with their environments is the currently accepted broad definition of corrosion. From a practical standpoint, the term *materials* refers to those substances used in the construction of machines, process equipment, and other manufactured products. These materials include metals, polymers, and ceramics. The environments are liquids or gases, although under special circumstances certain solid-solid reactions might be included as corrosion. The breadth of this definition can best be appreciated by considering examples, starting with cases that are usually recognized as corrosion and proceeding to those that are less obvious or are not generally recognized as corrosion:

- Rusting of steel and cast iron in water, including humid air, as occurs with domestic and industrial water tanks and supply piping, automobiles, and exposed steel structures
- Corrosion of copper, aluminum, and cast iron in automotive cooling systems

- Corrosion of iron-base, copper-base, nickel-base, etc. alloys in the chemical process industry
- Corrosion of automobile exhaust systems by direct reaction of the metal with high-temperature gases and by condensation of water and absorption of the oxides of sulfur and nitrogen to produce aqueous acid environments
- Corrosion of turbine blades in gas turbines by hot combustion gases
- Corrosion of metallic surgical implant materials used in orthopedic, cardiovascular, and dental devices resulting in the release of metal ions to tissues, and degradation of the physical properties of polymeric implant materials due to interactions with tissue fluids and/or blood
- Corrosion of iron-base and nickel-base alloys by liquid metals used as heat transfer agents (e.g., liquid sodium, potassium, and lithium)
- Enhanced deterioration of structural concrete and stone by interaction with condensed moisture and acidic contaminants in the air, such as the oxides of sulfur and nitrogen
- Stress-corrosion cracking (SCC) of gold and brass by mercury
- SCC and pitting of stainless steel in sea water

The Need to Control Corrosion

The need to control corrosion almost always reduces to considerations of safety and economics. Machines, equipment, and functional products may fail due to corrosion in such a manner as to result in personal injury. Because the choice of materials, enforcement of manufacturing procedures, and control of products to minimize personal injury all involve economic considerations, implementation of safety measures not only involves humanitarian concerns but also economics. With all economic decisions, the basis for action is a compromise between the benefits generated by a certain level of corrosion control versus the costs that would result if that level of control were not maintained. Examples of economic decisions involving considerations of the consequences of corrosion include the following:

- Within limits of health and safety, materials should not be selected for individual products, or components of more complex products, if the corrosion resistance would permit the life of the part to be significantly longer than the life actually realized because of other factors. Thus, the muffler of an automobile could be made of materials that would permit it to outlast the use of some large fraction of all automobiles manufactured at a given time. Because driving habits

have a major influence on muffler life, and reasonable performance and ease of replacement can be realized by using relatively inexpensive materials, it is not economical to use more highly corrosion-resistant materials. This choice also is favored by the fact that the muffler is not a critical component from the safety standpoint. For example, a different set of criteria would be required for critical components of the steering mechanism.

- Design for corrosion resistance may be almost exclusively for appearance when favorable appearance is an economic advantage. Stainless steel and aluminum are frequently used for architectural applications and in food service largely for appearance. They also are used for trim on automobiles for the same reason.
- On the other hand, materials exhibiting very low corrosion rates may be selected for reasons of both health and appearance in the processing of foods, pharmaceuticals, and cosmetics. Even if health is not involved, corrosion products producing objectionable color or particles of foreign material are not acceptable to the consumer. For example, such product contamination in paint obviously can lead to totally unacceptable products.
- In some cases, severely corrosive environments are contained by metals such as gold and platinum, which, in spite of high costs, are required because of their inertness. The initial cost, however, is countered by the ease of recovery of the metals following use and their high recycle value.
- A major economic factor in designing for corrosion resistance is the avoidance of interruption of plant production. Failure due to corrosion of critical components such as pumps and heat exchangers may necessitate large sections of a process or entire plants to become inoperative, leading to costs associated with lost production far in excess of the cost of replacement of the failed component. Process design and materials selection to minimize plant outage is a major engineering consideration.

Corrosion Mechanisms

Particularly under the broad definition of corrosion as the deterioration of materials by reaction with the environment, the number of mechanisms whereby deterioration occurs is large. In general, a mechanism of corrosion is the actual atomic, molecular, or ionic transport process that takes place at the interface of a material. These processes usually involve more than one definable step, and the major interest is directed toward the slowest step that essentially controls the rate of the overall

reaction. In corrosion, of course, this rate should be as slow as possible. Because these processes cannot be observed directly on an atomic scale, it is necessary to infer possible mechanisms from indirect measurements and observations. Examples are the rate of change in weight or dimensions, the rate of buildup of corrosion products in the environment, changes in surface appearance examined by optical or electron microscopy, or changes in mechanical or physical properties. When electrochemical corrosion is occurring, mechanisms may be inferred from measurements of electrical potential and current.

Considering engineering materials as metals, polymers, and ceramics, transport of mass across the interface to the environment may be broadly considered as electrochemical, chemical, or physical. Since electrochemical corrosion involves the release of ions to the environment and movement of electrons within the material, this mechanism can occur only if the environment can contain ions and the material can conduct electrons. The most important case of electrochemical mechanisms is the simple corrosion of metals in aqueous solutions, where atoms at the surface of the metal enter the solution as metal ions and electrons migrate through the metal to a site where, to sustain the reaction, they are consumed by species in contact with the metal. In more complicated cases, the metal ions move into solution by forming complex ions, or they combine with other species in the solution and precipitate compounds such as hydroxides, oxides, or sulfides. At sufficiently high temperatures, metals corrode in gases, particularly oxygen to form oxides. Whereas the mechanism in this case appears to be one of direct chemical attack, the mechanism may still be electrochemical in nature, with ions and electrons moving in the oxide which acts as the electrolyte supporting the electrochemical mechanism.

Polymeric and ceramic materials generally do not support electron conduction and hence corrode by either direct chemical or physical mechanisms. Chemical attack of polymers breaks bonds responsible for the properties of these materials, resulting in changes of molecular structure, possible transfer of material to the environment, and degradation of properties. In the case of chemical attack of ceramic materials, the composition of the environment may cause the ceramic or components in the ceramic to either become soluble or to be changed into soluble corrosion products. An example is the attack of sulfurous and sulfuric acid on limestone. Corrosion by direct chemical attack often results in the material being transported into the environment—polymers in certain organic solvents or metals in liquid metals. Direct physical attack often is the result of the mechanical action of the environment, which can remove protective films or actually disintegrate the material by intense local forces. Thus, cavitation corrosion results from the forces of collapsing vapor bubbles in a liquid impinging on the surface

of the material. If the environment contains suspended matter, abrasive wear may cause a form of failure classified as erosion-corrosion.

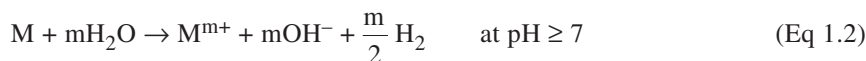
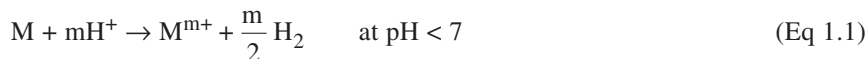
In the present treatment, the fundamental mechanisms involved in aqueous electrochemical corrosion of metals and alloys and the effects of direct chemical and physical processes will be emphasized.

Electrochemical Corrosion Processes and Variables

Before examining in detail the theories of aqueous corrosion processes and the bases for making quantitative calculations of corrosion rates, it will be useful to develop qualitatively the major phenomena involved. The following sections review several general types of metal/corrosive-environment combinations, the chemical reactions involved, idealized mechanisms for the transfer of metal ions to the environment, and the electrochemical processes occurring at the interface between the metal and the aqueous environment.

Uniform Corrosion with pH as the Major Variable

For metals, M, that are thermodynamically unstable in water, the simplest corrosion reactions are:



Thus, the metal passes from the metallic state to ions of valence m in solution with the evolution of hydrogen. The reaction is considered to be directly with hydrogen ions in acid solution and progressively with water molecules as the pH increases to neutral and alkaline conditions. Two processes are involved in the reaction, with each involving a change in charge: M to M^{m+} and mH^+ to $m/2 H_2$ (in acid solution). The changes in charge are accomplished by electron transfer from M to H^+ . Because the metallic phase is an electron conductor, it supports the electron transfer, allowing the two processes to occur at separate sites on the metal surface. In limiting cases, these processes occur within a few atom diameters on the surface with the sites constantly changing with time, thus producing uniform corrosion. Otherwise, the corrosion is nonuniform. Uniform corrosion supported by pH is represented schematically in Fig. 1.1. In this example, oxygen is excluded by a nitrogen gas purge and overblanket.

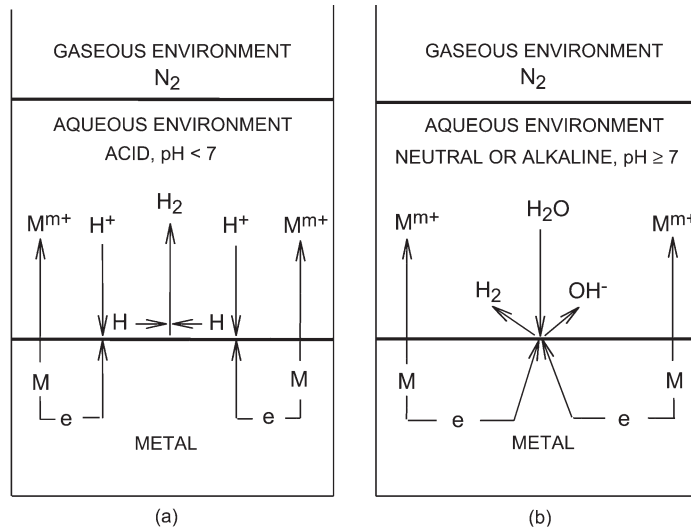


Fig. 1.1 Uniform corrosion supported by controlled pH (oxygen excluded, deaerated). (a) Acid, pH < 7. (b) Neutral or alkaline, pH ≥ 7

Uniform Corrosion with pH and Dissolved Oxygen as Variables

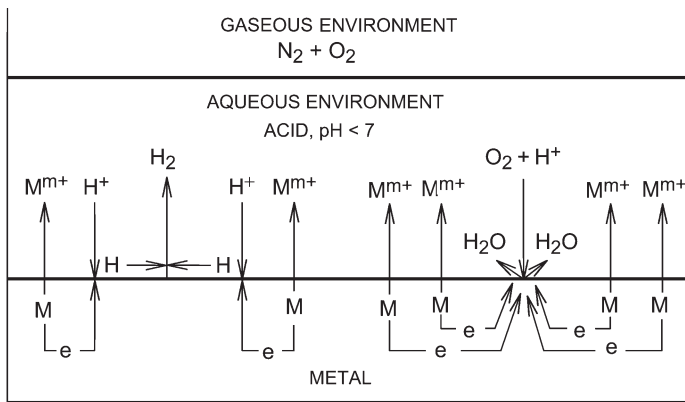
When dissolved oxygen is present in the solution, usually from contact with air (aerated environment), the following reactions apply *in addition* to those just considered:



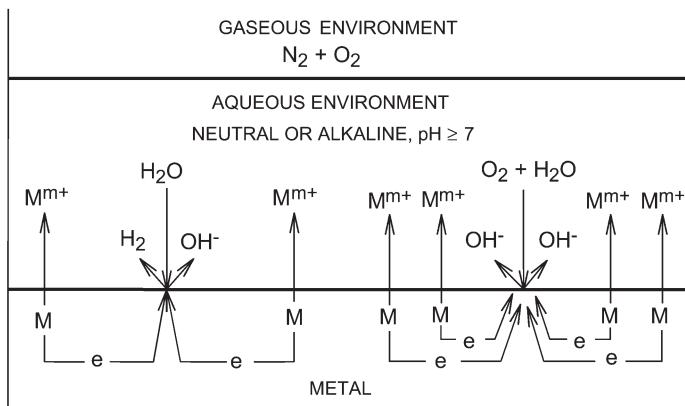
Uniform corrosion supported by dissolved oxygen and pH is represented schematically in Fig. 1.2. Since electrons are now consumed by two reactions, the rate of corrosion of the metal increases. In the case of iron, dissolved oxygen is more important in supporting corrosion than the presence of hydrogen ions when the pH is greater than approximately 4. This is an initial illustration of the role of dissolved oxygen (aeration of solutions) in corrosion.

Uniform Corrosion with Corrosion Product Formation

An example of corrosion product formation is the rusting of iron as illustrated in Fig. 1.3. When the pH is greater than approximately 4, and under aerated conditions, a layer of black Fe₃O₄, and possibly Fe(OH)₂, forms in contact with the iron substrate. In the presence of the dissolved oxygen, an outer layer of red Fe₂O₃ or FeOOH forms. The adherence



(a)



(b)

Fig. 1.2 Uniform corrosion supported by pH and dissolved oxygen (aerated). (a) Acid, $\text{pH} < 7$. (b) Neutral or alkaline, $\text{pH} \geq 7$

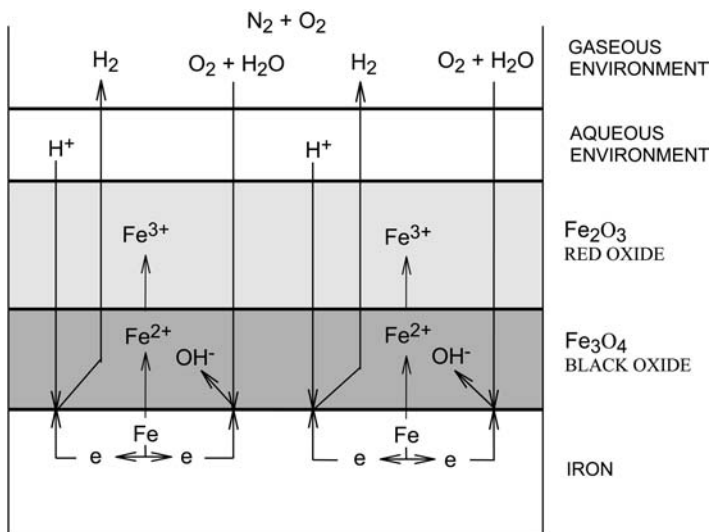


Fig. 1.3 Uniform corrosion with solid corrosion product deposit. Details of the formation of oxide species are not considered at this point.

and porosity of these layers change with time and can be influenced by other chemical species in the environment, such as chloride and sulfate ions. In any case, the formation of the corrosion product layer influences the corrosion rate by introducing a barrier through which ions and oxygen must diffuse to sustain the corrosion process.

Some Basic Terminology, Reactions, and Variables in Aqueous Corrosion

The basic corrosion process is represented in Fig. 1.4. In the simplest case, the corrosion reaction is the transfer of metal atoms from the solid to the solution where they exist as ions (i.e., $M \rightarrow M^{m+} + me$). Because there is a loss of electrons from the metal atom in this transfer, the metal has undergone oxidation. The oxidation is sustained by the consumption of the electrons by another reaction, generalized in this case as $X^{x+} + xe \rightarrow X$. The oxidation occurs at a site on the metal surface referred to as the anodic reaction site and is the location of the loss of metal by corrosion. The electrons are picked up at a cathodic reaction site. The areas over which the anodic and cathodic reactions occur individually vary greatly and may extend from positions a few atom distances apart on the surfaces to microscopic areas, and even to macroscopic areas extending to hundreds of square meters. When the sites are so close together that they cannot be distinguished, and when the sites undergo changes and reversals with time, uniform corrosion is said to occur. With resolvable areas and/or with anodic and cathodic sites that do not change with time, the corrosion will be largely identified by the anode areas only, and localized corrosion is said to occur. Obviously, there are large differences in interpretation of what is uniform corrosion and what is localized corrosion. It frequently depends on the scale of obser-

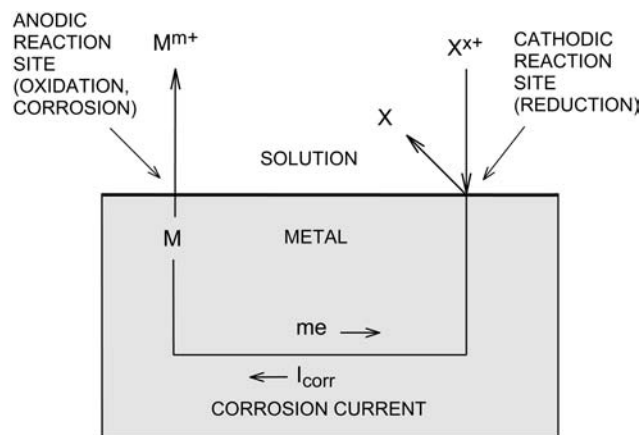
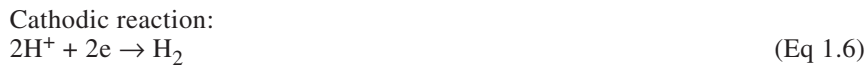
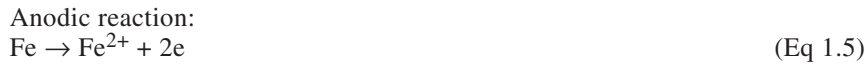


Fig. 1.4 The basic corrosion process

vation, or the magnitude of the difference in corrosion rate between areas that are predominantly anodic and areas that are predominantly cathodic because both reactions often occur over the entire surface. If the two processes are occurring on a microscale, then the anodic and cathodic areas are considered the same and equal to the total area, A . If the two processes are occurring over separate areas, an anodic reaction area, A_a , is distinguished from a cathodic reaction area, A_c .

For a specific example, such as the corrosion of iron in an aerated acid solution, the net reaction due to acidity is:



and the reaction due to dissolved oxygen is:



To show that these reactions actually proceed to the right (i.e., to show that corrosion actually occurs), it is necessary to calculate the Gibbs free-energy change and find that it is negative. To make this calculation requires quantitative information on the activity or effective concentration of iron ions ($a_{\text{Fe}^{2+}}$) in the solution, the acidity, or pH, and the concentration of dissolved oxygen that is related to the partial pressure of the oxygen, P_{O_2} , in contact with the solution. It is demonstrated in the following chapter that the change in the Gibbs free energy is negative for these reactions at all values of pH, and hence, iron tends to corrode at all pH values. The rate of corrosion, however, depends on factors influencing the kinetic mechanisms of the several processes involved in the transport of ions from metal to solution and in the supporting cathodic reactions. In addition to the species in solution relating directly to the above reactions (Fe^{2+} , H^+ , and O_2), other species in solution can affect both the tendency to corrode in terms of thermodynamic driving forces and the kinetics of the several steps involved. For example,

complexing agents reacting with metal ions in solution reduce the concentration of free metal ions and make it more favorable thermodynamically for metal ions to pass into solution, thereby increasing the corrosion rate. Conversely, if species in solution can form precipitates with metal ions and form protective diffusion barriers at the interface, corrosion rates may be decreased significantly.

The important processes, terminology, and variables associated with the anodic and cathodic reactions, and which characterize the environment, are summarized in Table 1.1.

Table 1.1 Summary of processes, terminology, and variables associated with aqueous corrosion(a)

Anode

Area, A_a
 Reactions (oxidation)
 General, $M \rightarrow M^{m+} + me$
 Reduced state \rightarrow oxidized state
 Example, $Fe \rightarrow Fe^{2+} + 2e$

Cathode

Area, A_c
 Reactions (reduction)
 General, $X^{x+} + xe \rightarrow X$
 Oxidized state \rightarrow reduced state
 Examples
 Deaerated
 Acid, $H^+ + e \rightarrow \frac{1}{2}H_2$
 Neutral or alkaline
 $H_2O + e \rightarrow \frac{1}{2}H_2 + OH^-$
 Aerated (additive to above)
 Acid, $O_2 + 4H^+ + 4e \rightarrow 2H_2O$
 Neutral or alkaline
 $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Aqueous phase variables

Acidity
 H^+ concentration
 C_{H^+} , molal concentration
 a_{H^+} , activity
 $pH = -\log a_{H^+}$
 $(a_{H^+})(a_{OH^-}) = 10^{-14}$
 Dissolved gases
 $H_2, C_{H_2} \propto P_{H_2}$
 $O_2, C_{O_2} \propto P_{O_2}$

Other dissolved species

Fe^{2+}, Cl^-, SO_4^{2-} , etc., with activities $a_{Fe^{2+}}$, etc.

Note: C_z = Molal concentration of species Z; a_z = Activity or effective concentration of species Z; P_z = Partial pressure of species Z. (a) Figure 1.4 shows a schematic representation of the interrelationships of the processes characterized in this table.

The Elementary Electrochemical Corrosion Circuit*

Aqueous corrosion is most readily understood in terms of a “dead-shortened” battery or electrochemical cell consisting of two half cells (Fig. 1.5). In comparison with the battery, the solution or electrolyte above the corroding metal is the battery fluid, and the metallic path between the anodic site (exposed metal) and the cathodic site (for example, an area of adherent-conducting oxide) is the external circuit. At the anodic site, the net oxidation reaction is $M \rightarrow M^{m+} + me$, and at the cathodic site, the generalized net reduction reaction is $X^{x+} + xe \rightarrow X$. As a consequence of the transfer of ions and electrons at each interface, differences in electrical potential, $\Delta\phi_a$ and $\Delta\phi_c$, develop between the metal and the solution at the anodic and cathodic sites, respectively, where

$$\Delta\phi_a = \phi_{M,a} - \phi_{S,a} \quad (\text{Eq 1.11})$$

$$\Delta\phi_c = \phi_{M,c} - \phi_{S,c} \quad (\text{Eq 1.12})$$

The subscripts a and c designate the anodic and cathodic sites, and the subscripts M and S designate the metal and solution phases. These differences in potential, coupled as shown, constitute the electrochemical cell in which electrons are caused to flow from the anodic to the cathodic site in the metal; conventional electrical current (positive charge) flows in the opposite direction. In the solution, current flows from the anodic to the cathodic site as a consequence of the potential in the solution being

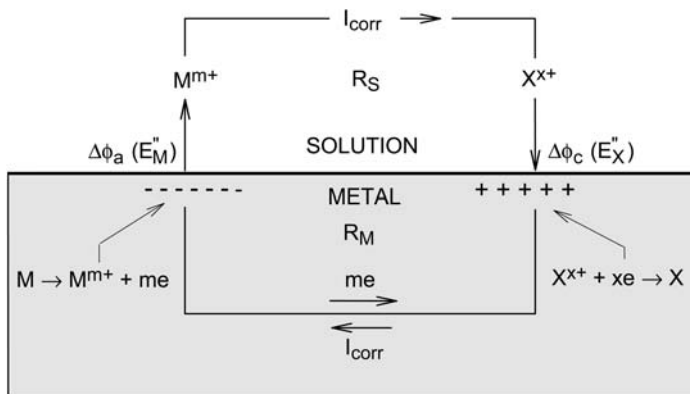


Fig. 1.5 The elementary electrochemical corrosion circuit

* The following section provides a qualitative insight into the essentials of the corrosion process. Important factors such as current distributions, nonuniform metal and environment compositions, and finite resistance of the metal are considered later in the text.

higher above the anodic site than above the cathodic site; that is, $\phi_{S,a} > \phi_{S,c}$. This current is defined as a positive quantity for the spontaneous corrosion process represented in Fig. 1.5. In practice, individual interface differences in potential, $\Delta\phi$, are assigned values relative to the standard hydrogen electrode as discussed in the next chapter. In this text, these values are designated by E for the general case, by E' for the case of no current passing, and by E'' for the case of a corrosion current passing the interface. If the potential of the standard reference electrode is taken as zero, then for the general case, $\Delta\phi_a = E_M$ and $\Delta\phi_c = E_X$.

The driving potential for the current in the solution, $\Delta\phi_S$, is:

$$\Delta\phi_S = \phi_{S,a} - \phi_{S,c} = (\phi_{M,a} - \Delta\phi_a) - (\phi_{M,c} - \Delta\phi_c) \quad (\text{Eq 1.13})$$

If it is assumed that the metal path is a good conductor (as is the general case), then the potential difference in the metal will be small, and $\phi_{M,a} \approx \phi_{M,c}$. The driving potential for the current in the solution, using Eq 1.13, is then:

$$\Delta\phi_S = \Delta\phi_c - \Delta\phi_a = E''_X - E''_M \quad (\text{Eq 1.14})$$

where the E s are now double primed to emphasize their values associated with the corrosion current. Recognizing that Ohm's law must apply, the corrosion current is given by:

$$I_{\text{corr}} = (E''_X - E''_M) / (R_S + R_M) \quad (\text{Eq 1.15})$$

where R_S and R_M are the resistances of the solution and metal paths of the current. This current is called the corrosion current, I_{corr} , and when the area of the anode through which the current flows is taken into consideration, the corrosion penetration rate can be calculated, for example, in micrometers or mils (0.001 in.) per year. The total path resistance, $R_S + R_M$, is obviously an important variable in determining the corrosion rate. In addition, if high-resistance interface films form, the total circuit resistance, $R_S + R_M + R_{\text{interface}}$, increases, and the corrosion rate decreases.

The relative sizes and locations of anodic and cathodic areas are important variables affecting corrosion rates. As stated previously, these areas may vary from atomic dimensions to macroscopically large areas. In Fig. 1.6, areas have been depicted over which the anodic and cathodic reactions occur, designated as A_a and A_c . If the current is uniformly distributed over these areas, then the *current densities*, $i_a = I_a/A_a$ and $i_c = I_c/A_c$, may be calculated.* The current density is fundamentally more

* Actually, the current will not be uniformly distributed. Rather, the current density near the anode/cathode junction will be higher, and hence, the corrosion rate will be higher because resistance of a current path is smaller here and increases with distance from the junction.

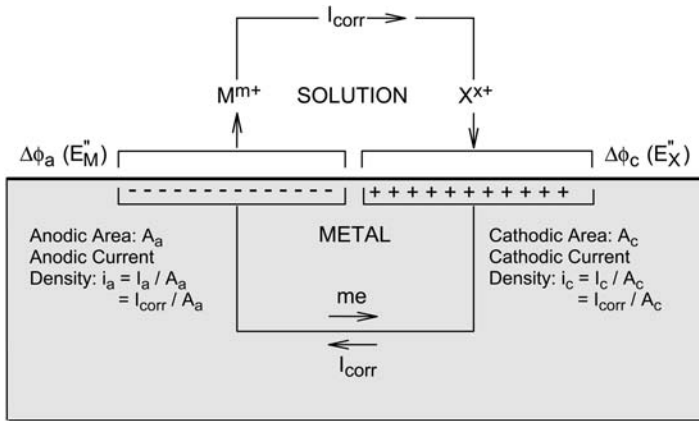


Fig. 1.6 Relationships between anodic and cathodic areas, current densities, and potentials

important than the current for two reasons. First, through Faraday's law, the anodic current density, i_a , relates directly to *corrosion intensity* as mass loss per unit time per unit area, or to *corrosion penetration rate* as a linear dimension loss per unit time. Second, it is observed that interface potentials, E , are functions of current density, $E(i)$, of the form:

$$E_X(i_c) = E'_X + \eta_X(i_c) = E'_X + \eta_X(I_c / A_c) \quad (\text{Eq 1.16})$$

$$E_M(i_a) = E'_M + \eta_M(i_a) = E'_M + \eta_M(I_a / A_a) \quad (\text{Eq 1.17})$$

In these expressions, E_X and E_M become the potentials E'_X and E'_M if the current is zero and, therefore, relate to the potential differences across the individual interfaces at equilibrium (i.e., no net transport of ions or electrons). These limiting potentials are referred to as *equilibrium half-cell potentials*, and when conditions of concentration and temperature are standardized, they characterize the *standard equilibrium half-cell reactions* to which they relate. Equations 1.16 and 1.17, therefore, indicate that the existing potential with current flow is the equilibrium value plus a term, $\eta(i)$, representing the shift in potential resulting from the current density. This shift is referred to as *overpotential* (or overvoltage) and increases in magnitude with increasing current density. During corrosion, the anodic current must equal the cathodic current, $I_a = I_c$, and this current is the corrosion current, I_{corr} . Thus, Ohm's law can be written as:

$$I_{corr} = \frac{E''_X - E''_M}{R_{total}} = \frac{[E'_X + \eta_X(I_{corr} / A_c)] - [E'_M + \eta_M(I_{corr} / A_a)]}{R_{total}} \quad (\text{Eq 1.18})$$

where E''_X and E''_M are now the potentials when the cathodic and anodic reactions are coupled. If theoretically or experimentally based expressions for the polarized potentials, Eq 1.16 and 1.17, are available, the Ohm's law equation can be solved for the corrosion current, I_{corr} . I_{corr} is a measure of the *total* loss of metal from the anode surface during corrosion. The anodic current density during corrosion, $i_{\text{corr}} = I_{\text{corr}}/A_a$, is a measure of the corrosion intensity from which the corrosion penetration rate can be calculated.

Criteria for Metal/Aqueous-Environment Reactions: Corrosion

For the current to flow in the direction shown in Fig. 1.6, corresponding to the corrosion of M, E''_X must be greater than E''_M . Because η_X is always negative and η_M always positive (as shown in Chapter 4), E'_X must be greater than E'_M , and because these equilibrium potentials can be calculated from tables of standard equilibrium half-cell potentials, these tables are useful for establishing whether corrosion can occur. The corrosion rate, however, is also strongly dependent on both η_X and η_M ; η_X is a function of the kinetic mechanisms of the physical, chemical, and electrochemical processes occurring at the cathode surface; η_M relates to kinetic processes at the anode surface. It is essential, therefore, to realize that processes of corrosion, particularly the rate of corrosion, depend on both the anodic and cathodic reactions. In some cases, the anodic process will control, and in other cases, the cathodic process will control the corrosion rate. Conversely, in attempting to control corrosion by additives called corrosion inhibitors, control may be directed selectively to either the cathodic or anodic, or both, kinetic mechanisms. Obviously, it is important to understand the steps in each process as completely as possible.

Comments on Cathodic Reactions

The corrosion of a metal, a process of oxidation or loss of electrons, is supported by a cathodic reactant or oxidizing agent, which is reduced in performing the cathodic reaction. In general, the stronger the oxidizing reaction is, thermodynamically and kinetically, the greater the induced corrosion rate will be.

The cathodic reaction has been generalized in the form $XX^+ + xe \rightarrow X$. Representative specific cathodic reactions are classified in Table 1.2 along with the standard equilibrium half-cell potentials, E° , relative to the standard hydrogen electrode (SHE), where $E^\circ_{\text{H}_2, \text{H}^+} \equiv 0$. The variables that must be set to correct the standard potentials, E° , to values

Table 1.2 Cathodic reactions and equilibrium potentials

Examples of cathodic reactions	Standard equilibrium half-cell potentials(a), E° (mV vs. SHE)	Variables required for correction of E° to E'
Oxidation due to H⁺ ions or water		
H ⁺ + e = ½ H ₂ pH < 7	0	a _{H⁺} (pH), P _{H₂}
H ₂ O + e = ½ H ₂ + OH ⁻ pH ≥ 7	-820	a _{OH⁻} (pH), P _{H₂}
Oxidation due to dissolved oxygen		
O ₂ + 4H ⁺ + 4e = 2H ₂ O pH < 7	+1,229	a _{H⁺} (pH), P _{O₂}
O ₂ + 2H ₂ O + 4e = 4OH ⁻ pH ≥ 7	+401	a _{OH⁻} (pH), P _{O₂}
Oxidation due to change in valence of ionic species		
Fe ³⁺ + e = Fe ²⁺	+771	a _{Fe³⁺} , a _{Fe²⁺}
Oxidation due to reaction to the metallic state		
Cu ²⁺ + 2e = Cu	+342	a _{Cu²⁺}
Oxidation due to "oxidizing" anion radical		
Dichromates		
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 4e = 2Cr ³⁺ + 7H ₂ O	+1,333	a _{Cr₂O₇²⁻} , a _{Cr³⁺} , a _{H⁺} (pH)
Nitrites		
NO ₂ ⁻ + 8H ⁺ + 6e = NH ₄ ⁺ + 2H ₂ O	+890	a _{NO₂⁻} , a _{NH₄⁺} , a _{H⁺} (pH)
Nitric acid:		
2H ⁺ + NO ₃ ⁻ + 2e = NO ₂ ⁻ + H ₂ O	+940	a _{NO₃⁻} , a _{NO₂⁻} , a _{H⁺} (pH)

(a) It should be noted that all of these potentials, except for the reduction of water, are relatively positive, which reflects that they tend to be oxidizing and involve oxidizing agents that are reduced by the reaction. These standard values correspond to 25° C and to unit activity of the species and would need to be corrected for the actual temperature and activities.

that they would have under the actual equilibrium conditions, E', are also given.

Comments on Anodic Reactions

The anodic or corrosion half-cell reaction has been generalized as M → M^{m+} + me. The previously presented schematic representations of anodic corrosion processes immediately raise three questions:

- What is the particular metal or alloy constituting the anode?
- What governs the positions on metal surfaces at which metal ions transfer from the metallic phase to the solution phase?
- What governs the rate at which the transfer occurs?

A pure metal can be anodic only if its equilibrium half-cell potential, E'_M, is less than the half-cell potential of some cathodic reaction, E'_X, such that the total cell potential (E''_X - E''_M) causes current to flow as in Fig. 1.6, that is, current away from the anode area as ions in the solution. A few representative anodic reactions are listed in Table 1.3 along with their standard equilibrium half-cell potentials.

For any specific pure metal, the physical state or condition may also influence the tendency for the metal to become anodic and corrode.

Table 1.3 Anodic reactions and equilibrium potentials

Examples of anodic reactions	Standard equilibrium half-cell potentials(a), E° (mV vs. SHE)
$Zn = Zn^{2+} + 2e$	-763
$Fe = Fe^{2+} + 2e$	-440
$Pb = Pb^{2+} + 2e$	-126
$Cu = Cu^{2+} + 2e$	+342
$Ag = Ag^{+} + e$	+799

(a) These standard values correspond to 25 °C and unit activity of the metal ions and would need to be corrected for the actual temperature and activity to determine E' .

These variables include the amount of general or localized cold working (e.g., scratches); the presence of imperfections such as dislocations and grain boundaries, the latter making grain size a variable; and crystal orientation. The latter becomes a variable because different crystal faces exposed to the environment have different arrangements of atoms and, hence, different tendencies to react with the environment.

When metals are combined to form alloys, it is no longer possible to define a unique half-cell potential, nor to calculate whether corrosion is possible, to the same extent that this calculation can be made for pure metals. Obviously, the response of an alloy to a corrosive environment depends on the kinds and amounts of alloying elements added to a given base metal. Solid-solution-type alloys tend to segregate alloying elements during solidification, and as a consequence, cast shapes, ingots, and even fabricated products, such as pipe and plates, may corrode in localized regions. Solidification segregation may be a particular problem leading to the corrosion of weldments. In most of these cases, heat treatments to remove the segregation are uneconomical. In multiphase alloys, different phases may act as relative anodes and cathodes. For all alloys, conditions affecting the physical state, such as cold work and grain boundaries, also may be significant.

Corrosion Considerations Based on Relative Cathodic and Anodic Equilibrium Potentials

The initial consideration in analyzing an existing or proposed metal/environment combination for possible corrosion is determination of the stability of the system. According to Eq 1.18, the criterion is whether the equilibrium half-cell potential for an assumed cathodic reaction, E'_{X} , is greater than the equilibrium half-cell potential for the anodic reaction, E'_{M} . A convenient representation of relative positions of equilibrium half-cell potentials of several common metals and selected possible corrodent species is given in Fig. 1.7. To the left is the scale of potentials in millivolts relative to the standard hydrogen electrode (SHE). The solid vertical lines identified by the name of the metal give

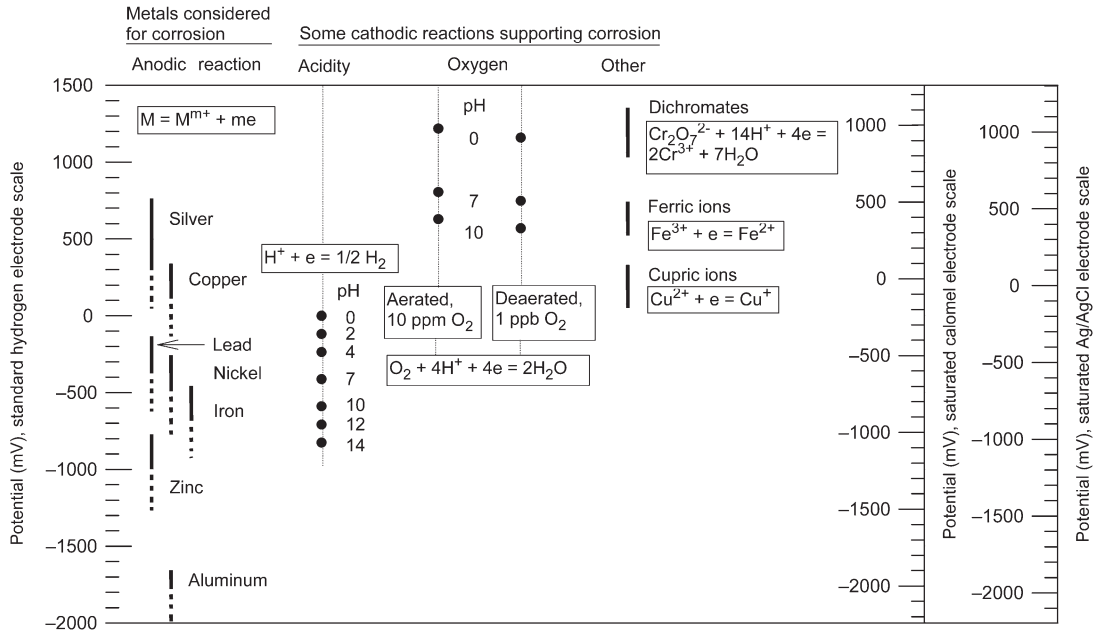


Fig. 1.7 Ranges of half-cell potentials of some electrochemical reactions of importance in corrosion. Vertical bars represent metal ion concentration of 1 molal (approximately 10%) down to 1 ppm. Dashed extensions may apply with precipitated and complexing species. The hydrogen and oxygen reactions depend on both pH and pressure of the gases. Values for the hydrogen are at one atmosphere pressure. Values for oxygen are for water in contact with air (aerated) giving 10 ppm dissolved oxygen and for water deaerated to 1ppb dissolved oxygen.

the range of half-cell potentials for the metal, extending from the potential at unit concentration of metal ions (1 mole per 1000 g of water) at the top to a concentration of about 1 ppm by weight at the bottom of the solid line. The dotted extensions to lower potentials apply when precipitating or complexing agents are present that reduce the metal ion concentration below 1 ppm. Reactions that might support corrosion involve hydrogen ions, dissolved oxygen, and ferric, cupric, and dichromate ions. The potential of the hydrogen ion reaction depends on pH and is given for the pH range of 0 to 14. The potential of the oxygen reaction depends on pH and dissolved oxygen concentration. Potentials are given for pH values of 0, 7, and 10 at 10 ppm dissolved oxygen, the approximate concentration of an aqueous solution in contact with air, and 1 ppb dissolved oxygen, an approximation to the deaerated condition. The other ions will have a range of potentials depending on concentration as shown by the solid vertical lines on the right.

The information in Fig. 1.7 allows quick estimation of the stability of a metal/environment combination. Thus, if the potential for a possible cathodic reaction is determined and found to be greater than that for the half-cell reaction of the metal being examined, then $[E'_X - E'_M]$ is positive,

and according to Eq 1.18, the current flow induced will be positive and, therefore, corrosion will be expected. An example would be iron in contact with a completely deaerated aqueous environment at pH = 2 (all oxygen excluded; values can be found under the column “Acidity”) and containing Fe²⁺ ions at a concentration of 1 ppm. The difference in potential will be $[E'_X - E'_M] = -120 - (-670) = +550$ mV, and iron should undergo corrosion at pH = 2, as in fact it does.

It is emphasized that while following the above procedure to determine whether a metal/environment combination is susceptible to corrosion, no information is provided on the rate of corrosion, the physical nature of the attack (i.e., uniformity of attack), the influence of corrosion products, or factors relating to the environment, such as fluid velocity and uniformity of fluid composition.

Importance of Solid Corrosion-Product Formation: Corrosion Acceleration Versus Passivation

The formation of solid corrosion products may be a dominant factor in controlling corrosion. These products form when the metal ions passing into solution (corrosion) reach a critical concentration, causing precipitation with some species in the environment. Since the metal-ion concentration is greatest at the surface where transfer is occurring across the metal-solution interface, the precipitate tends to form at or near the surface of the metal. Common solid corrosion products are hydroxides, oxides, sulfides, or complex mixtures of these. If the precipitate does not adhere to the surface, and the solubility is very small, the precipitation process will maintain the metal-ion concentration at a low value, and the corrosion rate will be high due to the continual removal of metal ions from solution and the resulting driving force to compensate for this removal by transfer of ions from the metal to the solution.

In contrast to the above, precipitates that adhere to the metal surface as continuous, nonporous films greatly reduce corrosion rates because the controlling mechanism becomes the slow solid-state diffusion of ions through the films. Further, if the film is a poor conductor of electrons, then the oxidation (corrosion) reaction is retarded because electrons have difficulty reaching the solution interface to enter into the cathodic reaction.

As discussed at some length in this introduction, metals corrode as a consequence of species in solution supporting a cathodic reaction (i.e., accepting electrons released at the corrosion sites where metal ions are discharged into the solution). The cathodic reactant is acting as an oxidizing agent oxidizing the metal from M⁰ to M^{m+} with the transfer of electrons to the cathodic reactant, which is reduced. The more positive

the cathodic-reactant half-cell potential (Fig. 1.7) and the greater the concentration, the greater is the oxidizing power of the environment and, therefore, the tendency for corrosion to occur. However, for those metals capable of forming protective corrosion-product films, such films are observed to form at critical oxidizing conditions, and once formed, the corrosion rate may decrease by several orders of magnitude. When this occurs, the metal is described as having undergone *passivation*. That is, it becomes passive to its environment rather than, as might be expected, progressively more active with increasingly aggressive properties of the environment. The phenomenon can be represented by a schematic plot of corrosion rate as a function of oxidizing power of the environment as shown in Fig. 1.8. The shape and position of the curve depends on the particular metal or alloy and a number of environmental factors, such as acidity (pH), temperature, and the presence of a number of nonoxidizing anions, particularly the chloride ion. Obviously, a metal or alloy should be selected that will form a passive protective film in the environment in which it is used. Consideration also should be given to adjustments in the environmental conditions to provide oxidizing conditions that will form the passive film on the metal surface.

For some materials in some environments, it is not possible to form passive films for corrosion protection. In this case, the corrosion rate continues to increase with increasing oxidizing conditions, and satisfactory use of materials of this type depends upon maintaining acceptably low oxidizing conditions and, therefore, acceptably low corrosion

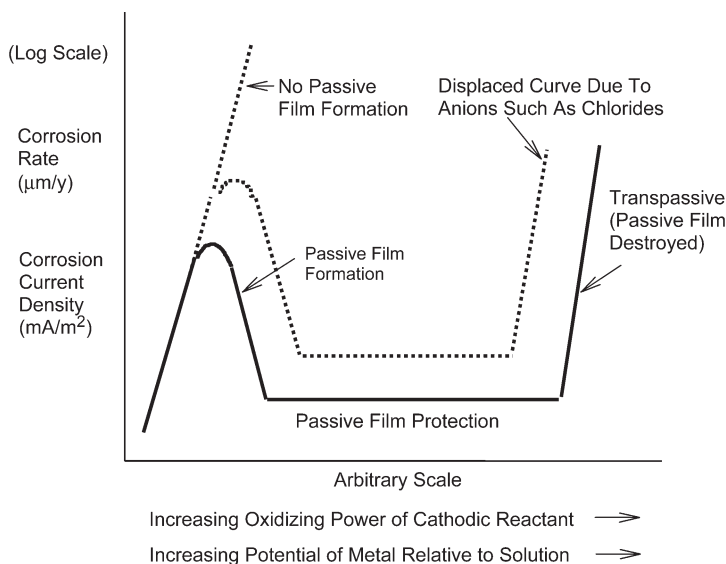


Fig. 1.8 Schematic representation of the effect of increasing oxidizing power of the environment on the corrosion of an active-passive type alloy such as stainless steel

rates. The best example of corrosion control based on these general observations is the deaeration of water in heat transfer loops to reduce the dissolved oxygen, which is the principal cathodic reactant.

Iron does not passivate in most environments and, therefore, performs best when the oxidizing power of the environment is as low as possible, for example, by deaeration as mentioned above. In contrast, a large class of industrially important alloys depend upon sufficiently oxidizing conditions to produce a protective passive film if they are to perform satisfactorily. These alloys include stainless steels, nickel-base alloys, titanium and its alloys, and many others.

Chapter 1 Review Questions

1. Give four examples of the economic significance of the control of corrosion.
2. Show schematically the processes involved in the corrosion of a metal, M , in a simple acid ($\text{pH} < 7$) and in a neutral or alkaline ($\text{pH} \geq 7$) environment in both deaerated and aerated conditions.
3. For the case of an aerated alkaline environment, list the reasonably possible electrochemical, chemical, and physical (diffusion, electron conduction) steps in the total corrosion process.
4. Under what circumstances can the formation of insoluble corrosion products (a) increase corrosion and (b) decrease corrosion?
5. The current given by the Ohm's law expression (Eq 1.18) is the total current referred to as I_{corr} . Later in the course, considerable significance is given to the fact that $I_{\text{corr}} = I(\text{cathode}) = I(\text{anode})$. Why will it always be necessary to equate $I_c = I_a$?
6. In calculating corrosion rates, the anodic current density should be evaluated as $i_a = I_{\text{corr}}/A_a$. Why?
7. Relative to question 6, give another reason why current density is fundamentally more important than current.
8. In a corroding system involving distinguishable anodic and cathodic areas, which is more desirable, (a) a large A_a/A_c area ratio or (b) a small A_a/A_c area ratio? Explain.
9. In Eq 1.18, for corrosion to occur, I_{corr} must be positive, or E'_X must be greater than E'_M . On this basis, which of the cathodic reactions listed in Table 1.2 should support the corrosion of copper (see Table 1.3)? Assume standard conditions such that $E' = E^0$.
10. As discussed in the text, in reacting electrochemical systems (corroding), the values of E''_X and E''_M depend upon current density (Eq 1.18).
 - a. When corrosion is occurring, is it desirable for η_M and η_X to be weak or strong functions of the current density? Explain.

- b. Comment on “a” for electrochemical reactions in a battery.
11. List at least eight conditions relating to a metal or alloy and/or its environment that could cause localized regions on the surface to become anodic and result in localized corrosion.
 12. Plain carbon steels may be heat treated to have dispersions of small, round, isolated iron carbides in the continuous iron matrix. The amount of carbide is usually less than 10% of the structure. With two-phase alloys such as this, the carbide may become anodic in some environments and cathodic in others. Predict the progress of corrosion if the carbide is (a) anodic and (b) cathodic. Be reasonably specific in describing changes at the surface.
 13. With reference to question 12, predict the corrosion behavior if the carbide is in the form of a continuous thin film between the grains.
 14. If an alloy can be passivated, is it generally desirable to have oxidizing conditions in the environment? Explain.
 15. If an alloy does not form passive films, is it generally desirable to have minimum oxidizing conditions in the environment? Explain.



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