# Handbook of CORROS ON ENGINEERING







THIRD EDITION

Pierre R. Roberge



# HANDBOOK OF CORROSION ENGINEERING

Pierre R. Roberge

**Third Edition** 



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ISBN: 978-1-26-011696-0 MHID: 1-26-011696-4

The material in this eBook also appears in the print version of this title: ISBN: 978-1-26-011697-7,

MHID: 1-26-011697-2.

eBook conversion by codeMantra Version 1.0

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# **PREFACE**

Corrosion is a natural process. Most structural materials in use today are basically engineered in an unstable state. Iron, chromium, nickel, titanium, aluminum, and most other metals naturally exist in the crust of the earth as oxides or sulfides. Given the first opportunity provided by the presence of a corrosive environment, these metals may rapidly revert to the initial state in which they were found in the earth. Corrosion is also a risk to safety, economy, and the normal operation of systems and equipment.

The information presented in this handbook is aimed at the practicing engineer and it should prove to be a valuable reference for the numerous facets of corrosion damage, from detection and monitoring to prevention and control. The intention in this third edition was to reorganize the material in a more explicit fashion and update the content with the most significant changes in the corrosion engineering world without changing the size of the handbook. That was an interesting challenge. The knowledge we have of corrosion processes and of the techniques to prevent and control these processes has not diminished over the past few years. In fact, there has been an exponential degree of discoveries and innovations in almost all aspects of science and technology associated with corrosion engineering.

This third edition follows the layout of the previous editions and contains 14 chapters that are relatively independent and may be consulted without reading previous chapters. The first six chapters introduce fundamental principles governing aqueous corrosion and the main environments where corrosion might be an issue. In Chapter 2 the behavior of metals and alloys, when exposed to indoor and outdoor environments, serves as a basis to discuss ways to test the resistance of metals to such environments, and to prevent or control corrosion damage.

The focus of Chapter 3 is on corrosion problems associated with water and seawater, a crucially important commodity for all aspects of modern life. What has been described as the Flint water crisis is used as an example to illustrate the complex difficulties in managing this precious asset. In Chapter 4, all aspects of corrosion in soils are discussed with a special emphasis on the tools at our disposal to evaluate the corrosivity of most soils.

Chapter 5 covers the corrosion processes that may degrade reinforced concrete, an extremely important construction material used around the world to build the most daring structures, sometimes with dire consequences such as the collapse of the Morandi bridge in the middle of Genoa in Italy on August 14, 2018.

Chapter 6 explores the mysterious world of microorganisms, which can turn otherwise benign environments into the most corrosive. This chapter also discusses the serious consequences the proliferation of microorganisms might have on the performance and durability of water handling equipment. Chapter 7 reviews the classic descriptions of some of the tools developed over the past century to transform the knowledge and understanding of corrosion processes into useful and practical life prediction tools greatly supported by tremendous advances in computer technologies.

Chapter 8 on corrosion failures has been extensively reworked to combine descriptions of the multiple forms of corrosion damage with methods to test these and prevent or control their occurrences and damaging effects. Chapter 9, the newest section of the book, introduces basic concepts of corrosion management before discussing corrosion management strategies in relation to more traditional maintenance and inspection practices. This chapter also describes in simple terms the advanced IMPACT corrosion management system recently introduced to support the critical decisions that need to be made on a daily basis when balancing conflicting operational requirements.

Chapter 10 starts with a review of the fundamental physical and chemical principles that may be used to monitor many aspects of progressing corrosion damage. The chapter then goes through a

detailed description of the many types of corrosion monitoring techniques available, from the most direct and intrusive to techniques used for offline measurements. Chapter 10 also describes many important considerations for the implementation of an efficient corrosion monitoring program, from data analysis and reporting to other aspects of corrosion monitoring such as probe design and positioning.

Chapter 11, the longest in the book, is particularly valuable for its detailed descriptions of the performance and maintenance considerations for the main families of engineering alloys based on aluminum, copper, nickel, chrome, magnesium, refractory metals, titanium, and zirconium, as well as cast irons, stainless steels, and other steels. This chapter is an important resource for any material selection problem where corrosion may be an issue.

The last three chapters provide elements for understanding the main practices and methods universally applied to protect exposed metal surfaces against the environment. Chapter 11 discusses basic aspects of protective coatings performance and their failures. The chapter then follows by providing detailed descriptions of many types of protective coatings and ways to inspect them in service or test them prior to service.

Chapter 13 describes another important tool used across a great variety of applications to reduce the corrosivity of an environment. Corrosion inhibitors have been added to protective coatings, to the strongest acidic cleaning solutions, and even to potable water to bring the aggressiveness of an environment to a manageable level. And finally, Chapter 14 provides a thorough coverage of the various techniques that have been developed to cathodically protect many structures such as ships, pipelines, oil drilling platforms, and many other components and systems exposed to most environments.

The first two appendices contain a periodic table of the elements and a table of appropriate SI units making references to most other types of units. A third appendix provides an introduction and some additional details on reference electrodes, a tool that is essential to measure the corrosion potential of any system. The designations and compositions of engineering alloys is the subject of a fourth appendix and a summary of the historical milestones in corrosion science and engineering is presented in a fifth appendix.

Chapter 14 and the appendices are available on the McGraw-Hill website by visiting the following URL: roberge/corrosion3e.

# **ACKNOWLEDGMENTS**

Many of the opinions expressed in the handbook have come from either work with collaborators or, more often, from determining work by many of the corrosion engineers and scientists that have made it possible to reach the level of understanding we have today. In this regard, I am particularly indebted to Professor David Hoeppner for the opportunity he has given me to teach with him the UCLA course on Corrosion of Aging Aircraft and for sharing his vast experiential knowledge on how catastrophic corrosion can be to flying machines and most moving pieces of equipment exposed to otherwise benign environments.

As many of my friends in the corrosion engineering community will attest, one gets better at solving corrosion problems as one gets older in the profession. In this respect, I am very grateful to the companies, firms, and agencies that have requested my services over the years. Each corrosion case has been an interesting challenge and an opportunity to grow better at recognizing the many subtleties that often culminate in a catastrophic failure or an embarrassing situation.

I would also like to take this occasion to express my love to the very close ones, and particularly to Diane whose endurance of my working habits is phenomenal.

# **ABOUT THE AUTHOR**

**Pierre R. Roberge, Ph.D.,** has worked as a research scientist, or engineer, on a variety of projects for the government and for many industries on subjects related to the performance of materials in service, corrosion engineering, and the production of energy with electrochemical power sources (fuel cells, batteries). Since the publication of his *Handbook of Corrosion Engineering* by McGraw-Hill in 2000 the focus of his research and consultancy has been mostly on corrosion-related issues. In 2011 he received the National Association of Corrosion Engineers International T.J. Hull Award and the Non-Atomic Military Research and Development Technical Cooperation Program Achievement Award from the Materials and Processing Technology Group.

# **CHAPTER 1**

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### 1.1 THE CONCEPT OF CORROSION IN HISTORY

To the great majority of people, corrosion means rust, an almost universal object of hatred. *Rust* is, of course, the name that has more recently been specifically reserved for the corrosion of iron, while *corrosion* is the destructive phenomenon that affects almost all metals. Although iron was not the first metal used by man, it has certainly been the most used, and must have been one of the first for which serious corrosion problems were faced. "Since the first day that man, through his ingenuity, contrived to reduce metallic ores to useful engineering materials, he has been constantly confronted and challenged by those fundamental laws of nature, that, through the process of corrosion tend to convert those useful metals back to the state in which they were first discovered." This citation from one of the first issues of the *Corrosion* journal still rings very true today.

The ancient Greek philosophers viewed the physical world as matter organized in the form of "bodies" having length, breadth, and depth that could act and be acted upon. They also believed that these bodies made up a material continuum unpunctuated by voids. Within such a universe, they speculated about the creation and destruction of bodies, their causes, the essence they consisted of, and the purpose they existed for. Surfaces did not fit easily into these ancient pictures of the world, even those painted by the Atomists, who admitted the existence of voids. The problem of defining the boundary or limit of a body or between two adjacent bodies led Aristotle (fourth century BC) and others to deny that a "surface" has any substance. Given Aristotle's dominance in ancient philosophy, his view of surfaces persisted for many centuries, and may have delayed serious theoretical speculation about the nature of solid surfaces.<sup>3</sup>

Perhaps the only ancient scientific account of surfaces is to be found in some passages of the great Roman philosopher Pliny the Elder (AD 23–79), who wrote at length about "ferrum corrumpitur," or spoiled iron, for by his time the Roman Empire had been established as the Western world's foremost

civilization, a distinction due partly to the extensive use of iron for weaponry and other artifacts that were, of course, highly subject to rust and corrosion.

Pliny described corrosion phenomena taking place at the surface of metals, as well as remedies for minimizing the effects of corrosion. His reference to the use of oil as a means of protecting bronze objects against corrosion, as well as of allowing the soldering of lead surfaces, has been unambiguously verified by modern chemical analysis of Roman artifacts. For example, according to Pliny, surfaces act as bodies that interact with each other and external agents. Pliny also speculated on the causes of metal corrosion (air and fire).

Numerous scientific and engineering discoveries have since been made, and the general understanding of corrosion mechanisms has progressed with these. Some of the discoveries that have improved the field of corrosion are listed in Appendix E. By the turn of the 20th century the basic processes behind the corrosion of iron and steel were relatively well understood. One of the first modern textbooks on corrosion prevention and control was published by McGraw-Hill in 1910. The following are some excerpts that illustrate the advanced state of knowledge when this landmark text came out.

On the Theory of Corrosion In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every iron ion that appears at a certain spot demands the disappearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyl ions inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarizing or dampening effect which prevents the solution of iron and the separation of hydrogen.

**Electrolytic Theory of Corrosion of Iron** From the standpoint of the electrolytic theory, the explanation of the corrosion of iron is not complicated, and so far has been found in accordance with all the facts. Briefly stated, the explanation is as follows: Iron has a certain solution tension, even when the iron is chemically pure and the solvent pure water. The solution tension is modified by impurities or additional substances contained in the metal and in the solvent. The effect of the slightest segregation in the metal, or even unequal stresses and strains in the surface, will throw the surface out of equilibrium, and the solution tension will be greater at some points than at others.

The points or nodes of maximum solution pressure will be electropositive to those of minimum pressure, and a current will flow, provided the surface points are in contact, through a conducting film. If the film is water, or is in any way moist, the higher its conductivity the faster iron will pass into solution in the electropositive areas and the faster corrosion proceeds. Positive hydrogen ions migrate to the negative areas, negative hydroxyls to the positives.

On the Effects of Cold Work A considerable body of evidence has been brought forward from time to time to show that in addition to the segregation of impurities in steel, the presence of scratches, sand pitholes, and, in fact, all indentations or wounds on the surface of steel will stimulate rusting by becoming centers of corrosion. Such marks or indentations are almost invariably electropositive to surrounding areas, and the depolarization which results in the rapid disengagement of hydrogen at these spots leads to stimulated pitting. This effect can be very prettily shown by means of the ferroxyl indicator.<sup>a</sup>

**On Puddle Iron**<sup>b</sup> **and Steel** Mr. J. P. Snow, Chief Engineer of the Boston and Maine Railroad, has called attention to a very significant case of corrosion in connection with the

<sup>&</sup>quot;The ferroxyl indicator is described in the next section.

<sup>&</sup>lt;sup>b</sup>Puddle iron is a type of wrought iron produced in a puddling furnace, a process invented at the end the eighteenth century. The process results with an iron that contains a slightly increased carbon content and a higher tensile strength compared to wrought iron. The puddling furnace also allows a better control of the chemical composition of the iron. The Eiffel Tower and many bridges were built with puddle iron.

destruction of some railroad signal bridges erected in 1894, and removed and scrapped in 1902. These structures were built at the time that steel was fast displacing puddled iron as bridge material.

The result was that the bridges were built from stock material which was partly steel and partly wrought iron. The particular point of interest in this case lies in the fact that while some of the members of the bridge structures rusted to the point of destruction in eight years, others were in practically as good condition as on the day they were erected.

Moreover, the tonnage-craze, from which the quality of product in so many industries is today suffering, is causing to be placed on the market a great mass of material, only a small proportion of which is properly inspected, which is not in proper condition to do its work: rails and axles which fail in service and steel skeletons for high buildings, which may carry in them the germs of destruction and death.

That the old, largely hand-worked metal of about 30 years ago is superior in rust-resisting quality to the usual modern steel and iron is attested by the recorded evidence of a large number of observers.

**On Paints and Corrosion Inhibitive Pigments** The many theories which have attempted to explain the rusting of iron, during the last century, have stimulated a large amount of original research on the relation of various pigments to the corrosion problems. In the course of the investigations undertaken, the subject of protective coatings for iron and steel was naturally brought into prominence and received a considerable amount of attention.

The study of protective coatings for iron has led many paint manufacturers, as well as scientific investigators, to make a closer study of the causes of corrosion. It is evident that the electrochemical explanation of corrosion must have a direct bearing on paint problems.

## 1.2 VISUALIZING CORROSION CELLS

The possibility to visualize corrosion cells by performing simple experiments to reveal the fundamentally dual nature of corrosion processes was probably the most determining turning point in the history of corrosion science. The color changes produced on chemical indicators by the corrosion processes were very helpful in the early days of corrosion science, allowing the study of the local interplay of local anodes and cathodes on apparently homogeneous steel surfaces exposed to a corrosive environment. As noted by Cushman and Gardner in their 1910 textbook, it is a matter of common observation that iron usually corrodes rapidly at certain weak points in an effect known as pitting.<sup>4</sup>

The interest in using color changes to reveal subtle corrosion mechanisms is still quite modern, as attested by two papers published in a reputed *Corrosion* journal. In one paper, the corrosion of Al and Al alloys in chloride-containing agar gels was studied by using a broad-range pH indicator.<sup>5</sup> Distinct changes in pH were observed at low-pH anodic sites and at high-pH cathodes. There was a definite edge effect that occurred when gels were placed directly on the metal, which dominated the pattern of corrosion. Wet-abraded surfaces initially showed a general type of corrosion, whereas dry-abraded surfaces showed localized corrosion under the gel.

In a second paper published recently, paint systems containing color-change or fluorescing compounds were found to be sensitive to underlying corrosion processes by reacting to the pH increase associated with the local cathodic reaction. The sensitivity of acrylic-based coating systems for detection of cathodic reactions associated with corrosion was determined by applying constant cathodic current and measuring the charge at which color change or fluorescence was detected.

The cathodic reaction in a corrosion process generally produces an increase in the concentration of hydroxyl ions as a result of removal of hydrogen ions or the reduction of oxygen. Phenolphthalein is a well-known indicator that develops a red color when the concentration of hydroxyl ions is increased. Therefore, if phenolphthalein turns red as corrosion proceeds, it will detect the existence of a cathode and reveal where it is.<sup>7</sup>

Similarly, potassium ferricyanide is a reagent that produces, as described in Eq. (1.1), a blue color by reaction with ferrous ions (Fe II) as they form at the anodic areas when iron corrodes. The appearance of this blue color, therefore, demonstrates the existence and location of anodes on iron.

$$3Fe^{2+} + 4[Fe(CN)_6]_{(yellow)}^{3-} \rightarrow Fe_4[Fe(CN)_6]_3 . 4H_2O_{(Prussian \, blue)} + 6CN^-$$
 (1.1) 
$$Fe^{3+} Fe^{2+} Fe^{2+}$$

The combination of these two reagents in a gelling agent to which sodium chloride is added is known as a ferroxyl solution. Cushman and Gardner made ample use of this medium to reveal local corrosion cells and supported their theories with many pictures in their 1910 textbook.

One classic example of a local cell revealed by the ferroxyl agent is the development and location of the anode and cathode in a cell established on a steel surface within a drop of ferroxyl gel. Oxygen from the air is more accessible to the periphery of the drop and sets up a cathode that becomes visible as a pink color. Simultaneously an anode that develops near the center of the drop, which is less accessible to oxygen, is revealed by the gel turning blue (Fig. 1.1).

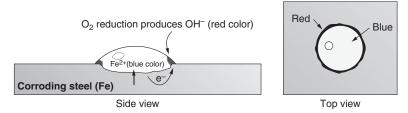
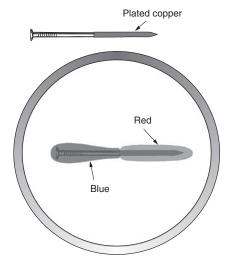


FIGURE 1.1 Ferroxyl drop experiment on a steel plate.

These color changing reagents have also been used to show the existence and location of anodes and cathodes created by joining dissimilar metals. For example, upon placing a steel nail with copper plated on the pointed half of it in a ferroxyl gel it will develop a pink area around the copper-plated portion and a blue area around the bare steel half (Fig. 1.2).<sup>7</sup> In this experiment, the colors become more intense with time. This shows that iron continues to corrode as an anode, and, at the same time, there is an increasing concentration of alkali at the copper cathode.

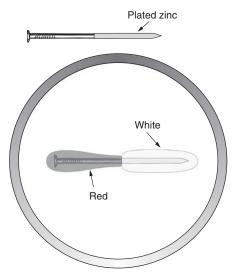
When a steel nail with zinc plated on the pointed end is placed in the same gel, the iron now acts as a cathode and the zinc as an anode (Fig. 1.3). Accordingly, the red color identifying the cathode develops at the iron half. No iron goes into solution on this area, and, therefore, no blue color develops. The zinc corrodes as an anode at the point and is consumed in providing protection to the iron. A white area develops around the zinc because the zinc corrosion products form a white substance in contact with the potassium ferricyanide reagent.

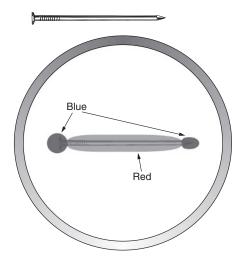


**FIGURE 1.2** Steel nail partially plated with copper with anode and cathode revealed by colors developed in a Petri dish containing a ferroxyl gel.

The local action cell on a single metal surface may be revealed by placing an ordinary steel nail in the ferroxyl gel (Fig. 1.4). After a short time, a pink area develops around the shank of the nail,

How to prepare 250 mL of ferroxyl gel containing 3% sodium chloride: Dissolve 7.5 g sodium chloride in 250 mL distilled water. Add 5 g powdered agar agar and boil the mixture until the agar is dispersed. Then add 0.5 g potassium ferricyanide and 5 mL of a 0.1% phenolphthalein solution.





**FIGURE 1.3** Location of anode and cathode areas on a steel nail partially plated with zinc.

**FIGURE 1.4** Location of local anodes and cathodes on a single steel nail.

indicating the formation of a cathode. Blue areas develop around the cold-worked head and point of the nail where the iron goes into solution, indicating that these areas are the anodes.

### 1.3 A SIMPLE CORROSION MODEL

All these observations, from those made by philosophers many centuries ago to discoveries made more recently by various researchers in the nineteen and twentieth centuries, have led to a simple corrosion model that can accommodate all the visualization experiments presented in the previous section.

In order to understand the corrosive nature of any aqueous environment, it is essential to discuss the electrochemical reactions that are taking place at the metallic surface exposed to the environment. An electrochemical reaction is defined as a chemical reaction involving the transfer of electrons. It is also a chemical reaction that involves oxidation and reduction. Since metallic corrosion is almost always an electrochemical process, it is important to understand the basic nature of electrochemical reactions. The discoveries that gradually evolved in modern corrosion science have, in fact, played an important role in the development of a multitude of technologies we enjoy today.

An important achievement early in the history of electrochemistry was the production of power sources, following the production of the first batteries by Alessandro Volta. Figure 1.5 illustrates the principle of a Daniell cell in which copper and zinc metals are immersed in solutions of their respective sulfates. The Daniell cell was the first truly practical and reliable electric battery; it supported many 19th-century electrical innovations such as the telegraph. In the process of the reaction, electrons can be transferred from the corroding zinc to the copper through an electrically conducting path as a useful electric current. Zinc more readily loses electrons than copper, so placing zinc and copper metals in solutions of their salts can cause electrons to flow through an external wire, which leads from the zinc to the copper.

Zinc anode: 
$$Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$$
 (1.2)

Copper cathode: 
$$Cu^{2+} + 2e^{-} \rightarrow Cu_{(s)}$$
 (1.3)

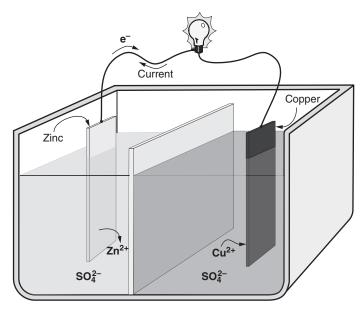


FIGURE 1.5 Schematic of a Daniell cell.

The difference in the susceptibility of two metals to corrode can often cause a situation that is called galvanic corrosion (see Chap. 8) named after Luigi Galvani, the discoverer of the effect. The purpose of the separator shown in Fig. 1.5 is to keep each metal in contact with its own soluble sulfates, a technical point that is critical in order to keep the voltage of a Daniell cell relatively constant. The same goal can be achieved by using a salt bridge between two different beakers as shown in Fig. 1.6.

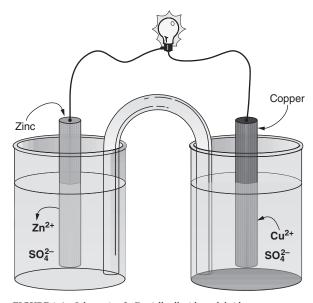


FIGURE 1.6 Schematic of a Daniell cell with a salt bridge.

The salt bridge, in that case, provides the electrolytic path that is necessary to complete an electrochemical cell circuit. This situation is common in natural corrosion cells where the environment serves as the electrolyte that completes the corrosion cell. The conductivity of an aqueous environment such as soils, concrete, or natural waters has often been related to its corrosivity.

The shorthand description in Eq. (1.4) is valid for both cells shown in Figs. 1.5 and 1.6. Such a description is often used to simplify textual reference to such cells.

$$(-)Zn/Zn^{2+}, SO_{4 (Conc_1)}^{2-} //Cu^{2+}, SO_{4 (Conc_2)}^{2-} /Cu(+)$$
 (1.4)

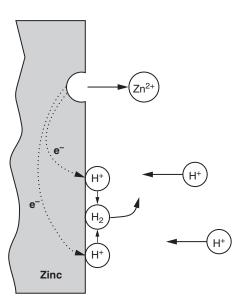
Conc<sub>1</sub> and Conc<sub>2</sub> in Eq. (1.4) indicate, respectively, the concentration of zinc sulfate and copper sulfate that may differ in the two half-cells while the two slanted bars (//) describe the presence of a separator. The same shorthand description also identifies the zinc electrode as the anode that is negative in the case of a spontaneous reaction and the copper cathode as positive.

The fact that corrosion consists of at least one oxidation and one reduction reaction is not always as obvious as it is in chemical power cells and batteries. The two reactions are often combined on a single piece of metal as it is illustrated schematically in Fig. 1.7. Figure 1.8 shows an actual experiment in which zinc rapidly corrodes in an acid solution while producing some hydrogen gas.

In these figures, a piece of zinc immersed in hydrochloric acid solution is undergoing corrosion. At some point on the surface, zinc is transformed to zinc ions, according to Eq. (1.5). This reaction produces electrons and these electrons pass through the solid conducting metal to other sites on the metal surface where hydrogen ions are reduced to hydrogen gas according to Eq. (1.6).

Anodic reaction: 
$$Zn_{(s)} \rightarrow Zn^{2+} + 2e^{-}$$
 (1.5)

Cathodic reaction: 
$$2H^+ + 2e^- \rightarrow H_{2_{(a)}}^{\uparrow}$$
 (1.6)



**FIGURE 1.7** Electrochemical reactions occurring during the corrosion of zinc in air-free hydrochloric acid.



**FIGURE 1.8** Bubbling, or "plating out of hydrogen" on zinc immersed in a 0.1 M sulfuric acid solution. (*Courtesy Kingston Technical Software.*)

During such a reaction, electrons are transferred, or, viewing it another way, an oxidation process occurs together with a reduction process. The overall corrosion processes are summarized in Eq. (1.7):

Overall corrosion reaction: 
$$Zn + 2H^+ \rightarrow Zn^{2+} + H_{2_{\omega}}^{\uparrow}$$
 (1.7)

In summary, for corrosion to occur there must be a formation of ions and release of electrons at an anodic surface where oxidation or deterioration of the metal occurs. There must be a simultaneous reaction at the cathodic surface to consume the electrons generated at the anode. These electrons can serve to neutralize positive ions, such as the hydrogen ions  $(H^+)$ , or create negative ions. The anodic and cathodic reactions must go on at the same time and at equivalent rates. However, what is usually recognized as the corrosion process occurs only at the areas that serve as anodes.

# 1.3.1 Anodic Processes

Let us consider in greater detail what takes place at the anode when corrosion occurs. For instance, reconsider Eq. (1.7). This reaction involves the reduction of hydrogen ions to hydrogen gas, according to Eq. (1.6). This hydrogen evolution reaction occurs with a wide variety of metals and acids, including hydrochloric, sulfuric, perchloric, hydrofluoric, formic, and other strong acids. The individual anodic reactions for iron, nickel, and aluminum are listed as follows:

Iron anodic reaction: 
$$Fe_{(a)} \rightarrow Fe^{2+} + 2e^{-}$$
 (1.8)

Nickel anodic reaction: 
$$Ni_{(s)} \rightarrow Ni^{2+} + 2e^{-}$$
 (1.9)

Aluminum anodic reaction: 
$$Al_{(s)} \rightarrow Al^{3+} + 3e^{-}$$
 (1.10)

Examining the above equations shows that the anodic reaction occurring during corrosion can be written in the general form:

General anodic reaction: 
$$M_{(s)} \rightarrow M^{n+} + ne^{-}$$
 (1.11)

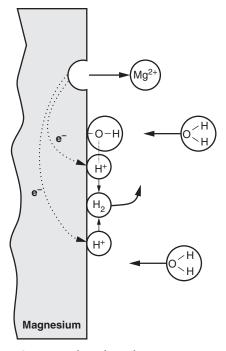
That is, the corrosion of metal M results in the oxidation of metal M to an ion with a valence charge of  $n^+$  and the release of n electrons. The value of n, of course, depends primarily on the nature of the metal. Some metals such as silver are univalent, while other metals such as iron, titanium, and uranium are multivalent and possess positive charges as high as 6. Equation (1.11) is general and applies to all corrosion reactions.

### 1.3.2 Cathodic Processes

When hydrogen ions are reduced at a cathodic surface to their atomic form, they often combine, as shown earlier, to produce hydrogen gas. This reduction of hydrogen ions at a cathodic surface will disturb the balance between the acidic hydrogen (H<sup>+</sup>) ions and the alkaline hydroxyl (OH<sup>-</sup>) ions and make the solution less acidic or more alkaline or basic at the corroding interface. In neutral waters, the anodic corrosion of some metals like aluminum, zinc, or magnesium develops enough energy to split water directly as illustrated in Fig. 1.9 and Eq. (1.12).

Water splitting cathodic reaction: 
$$2H_2O_{(1)} + 2e^- \rightarrow H_2^{\uparrow} + 2OH^-$$
 (1.12)

As illustrated in the previous section, the change in the concentration of hydrogen ions or increase in hydroxyl ions can be shown by the use of pH indicators that change color and thus can serve to demonstrate and locate the existence of surfaces on which the cathodic reactions in corrosion are taking place. There are several other cathodic reactions encountered during the corrosion of metals. These are listed as follows.



**FIGURE 1.9** Electrochemical reactions occurring during the corrosion of magnesium in neutral water.

Oxygen reduction:

(acid solutions) 
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 (1.13)

(neutral or basic solutions) 
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 (1.14)

Hydrogen evolution: 
$$2H^+ + 2e^- \rightarrow H_{2_{(g)}}^{\uparrow}$$
 (1.6)

Metal ion reduction: 
$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$
 (1.15)

Metal deposition: 
$$Cu^{2+} + 2e^{-} \rightarrow Cu_{(s)}$$
 (1.16)

Hydrogen ion reduction, or hydrogen evolution, has already been discussed. This is the cathodic reaction that occurs during corrosion in acids. Oxygen reduction [Eqs. (1.13) and (1.14)] is a very common cathodic reaction, since oxygen is present in the atmosphere and in solutions exposed to the atmosphere. Although less common, metal ion reduction and metal deposition can cause severe corrosion problems in special situations. One particular case worth mentioning here is the plating of copper ions, produced upstream in a water circuit, on the internal aluminum surface of a radiator, for example. The copper nodules being very good catalysts for the reduction of oxygen tend to greatly accelerate the localized corrosion of the surrounding aluminum surface. This particular form of corrosion, called deposition corrosion, is discussed in Chap. 8.

Note that all of the above reactions are similar in one respect, they consume electrons. All corrosion reactions are simply combinations of one or more of the above cathodic reactions, together with an anodic reaction similar to Eq. (1.11). Thus, almost every case of aqueous corrosion can be reduced to these equations, either singly or in combination.