CHAPTER
ONE

INTRODUCTION

1-1 Cost of Corrosion

Estimates of the annual cost of corrosion in the United States vary between \$8 billion and \$126 billion. I believe \$30 billion is the most realistic figure. In any case, corrosion represents a tremendous economic loss and much can be done to reduce it. These large dollar figures are not surprising when we consider that corrosion occurs, with varying degrees of severity, wherever metals and other materials are used. Several examples follow.

According to the *Wall Street Journal* (Sept. 11, 1981) cost to oil and gas producers is nearly \$2 billion. Costs are increasing because of deeper wells and more hostile environments—higher temperatures and corrosive sulfur gases (e.g., 500°F and hydrogen sulfide).

Corrosion of bridges is a major problem as they age and require replacement, which costs billions. The collapse (because of stress corrosion) of the Silver Bridge into the Ohio River cost 40 lives and millions of dollars. Corrosion of bridge decks costs about \$500 million. Proper design and use of cathodic protection reduces costs substantially. One large chemical company spent more than \$400,000 per year for corrosion maintenance in its sulfuric acid plants, even though the corrosion conditions were not considered to be particularly severe. Another spends \$2 million per year on painting steel to prevent rusting by a marine atmosphere. A refinery employing a new process developed a serious problem after just 16 weeks of operation; some parts showed a corrosion loss of as much as 1/8 inch. The petroleum industry spends a million dollars per day to protect underground pipelines. The paper industry estimates corrosion increases the cost of paper \$6 to \$7 per ton. Coal conversion to gas and oil involves high temperatures, erosive particles, and corrosive gases, thus presenting severe problems that must be solved.

Corrosion costs of automobiles—fuel systems, radiators, exhaust systems, and bodies—are in the billions. I personally incurred costs of $500 in refurbishing an automobile fuel system in which water had been mixed with gasoline! (A photograph of the gasoline tank is on the cover of *Materials Performance*, March 1982.) Approximately 3 million home water heaters are replaced every year. Corrosion touches all—inside and outside the home, on the road, on the sea, in the plant, and in aerospace vehicles.

Total annual costs of floods, hurricanes, tornadoes, fires, lightning, and earthquakes are less than the costs of corrosion. Costs of corrosion will escalate substantially during the next decade because of worldwide shortages of construction materials, higher energy costs, aggressive corrosion environments in coal conversion processes, large increases in numbers and scope of plants, and other factors.

"Political" considerations are also a factor. We depend largely on foreign sources for some metals: 90 percent for chromium (the main alloying element for stainless steel) and 100 percent for columbium (niobium) used in high-temperature alloys. Our sources could be shut off or the prices boosted. For example, during a recent crisis the price per pound of columbium jumped from $5 to $50.

Production of metals used for corrosion resistance and to replace corroded parts require large amounts of energy, thus compounding the nation's energy problems.

The most comprehensive study of the annual cost of *metallic* corrosion in the United States was conducted by the National Bureau of Standards (NBS) and Battelle Memorial Institute in response to a congressional directive. Results are published in a seven-part series. The first is, "NBS-Battelle Cost of Corrosion Study ($70 Billion) Part 1—Introduction," by J. H. Payer, W. K. Boyd, D. B. Dippold, and W. H. Fisher of Battelle (*Materials Performance*, May 1980). The other six parts appeared in subsequent issues of *Materials Performance* (June–November 1980). The figure of $70 billion* covers corrosion (in 1975) of metals (nonmetallics not included) and are costs incurred if corrosion *did not exist*; this amount has no practical significance, but it does emphasize the *magnitude* of the problem. Unfortunately, $70 billion has been simply stated as the "cost of corrosion" in later literature and is misleading (implying that $70 billion could be saved) because nothing can be done *economically* to reduce most of these costs. It is somewhat like asking how much you could save on your food budget if you *stopped eating*. However, the report states that about $10 billion could be saved if best, and presently known, practices to combat

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*The U.S. Department of Commerce stated, "Corrosion will cost the United States an estimated 126 billion dollars in 1982." (*Materials Performance*, 57, Feb. 1983).

corrosion were applied. Chemical industry efforts involve high costs, but this industry is in the forefront with regard to utilizing corrosion control practices.

In fact our economy would be drastically changed if there were *no* corrosion. For example, automobiles, ships, underground pipelines, and household appliances would not require coatings. The stainless steel industry would essentially disappear and copper would be used only for electrical purposes. Most metallic plants, as well as consumer products, would be made of steel or cast iron.

Although corrosion is inevitable, its cost can be considerably reduced. For example, an inexpensive magnesium anode could double the life of a domestic hot water tank. Washing a car to remove road deicing salts is helpful. Proper selection of materials and good design reduce costs of corrosion. A good maintenance painting program pays for itself many times over. Here is where the *corrosion engineer* enters the picture and is effective—his or her primary function is to combat corrosion.

Aside from its direct costs in dollars, corrosion is a serious problem because it definitely contributes to the depletion of our natural resources. For example, steel is made from iron ore, and our domestic supply of high grade directly smeltable iron ore has dwindled. Another important factor concerns the world's supply of metal resources. The rapid industrialization of many countries indicates that the competition for and the price of metal resources will increase. The United States is no longer the chief consumer of mineral resources.

1-2 Corrosion Engineering

Corrosion engineering is the application of science and art to prevent or control corrosion damage economically and safely.

In order to perform their function properly, corrosion engineers must be well versed in the practices and principles of corrosion; the chemical, metallurgical, physical, and mechanical properties of materials; corrosion testing; the nature of corrosive environments; the availability and fabrication of materials; computers*; and design. They also must have the usual attributes of engineers—a sense of human relations, integrity, the ability to think and analyze, an awareness of the importance of safety, common sense, a sense of organization, and, of prime importance, a solid feeling for economics. In solving corrosion problems, the corrosion engineer must select the method that will maximize profits. One definition of economics is simply—"there is no free lunch."

The following articles offer insight into applications of computer

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*See Chapter 4 for the revolution brought about by the introduction of electronic instrumentation in corrosion science and engineering.

technology in corrosion engineering: Thinking Machines (Artificial Intelligence) and the CPI, *Chem. Eng.* 45–51 (Sept. 20, 1982), which describes several examples including prediction of stress corrosion cracking; S. N. Smith and F. E. Rizzo, Computer Assisted Corrosion Engineering, *Materials Performance*, **19**:21–23 (Oct. 1980); and C. Edeleanu, The Effect of the Microprocessors on Corrosion Technology, *Materials Performance*, **22**: 82–83 (Oct. 1983).

In the past, relatively few engineers received educational training in corrosion. Most of the people then engaged in this field had chemical, electrical, or metallurgical backgrounds. Fortunately this picture has changed. From only three in 1946, now 65 U.S. universities and colleges (including the author's) offer formal courses in corrosion.* *Corrosion Engineering* is a popular textbook for these courses. What this all means is that now there are hundreds of engineers in the field who have had a formal course in corrosion. In the past, and even today, corrosion is often regarded as a "necessary evil" to be tolerated. *Ignorance* is the cause of many premature, unexpected, and expensive failures—ignorance even by people who should know better. For example, two vendors of sacrificial anodes describe their systems as anodic protection! Actually it is cathodic protection, which is completely different.

1-3 Definition of Corrosion

Corrosion is defined as the destruction or deterioration of a material because of reaction with its environment. Some insist that the definition should be restricted to metals, but often the corrosion engineers must consider both metals and nonmetals for solution of a given problem. For purposes of this book we include ceramics, plastics, rubber, and other nonmetallic materials. For example, deterioration of paint and rubber by sunlight or chemicals, fluxing of the lining of a steelmaking furnace, and attack of a solid metal by another molten metal (liquid metal corrosion) are all considered to be corrosion.

Corrosion can be fast or slow. Sensitized 18-8 stainless steel is badly attacked in hours by polythionic acid. Railroad tracks usually show slight rusting—not sufficient to affect their performance over many years. The famous iron Delhi Pillar in India was made almost 2000 years ago and is almost as good as new. It is about 32 feet high and 2 feet in diameter. It should be noted, however, that it has been exposed mostly to arid conditions.

Corrosion of metals could be considered as extractive metallurgy in reverse as illustrated by Fig. 1-1. Extractive metallurgy is concerned primarily with the winning of the metal from the ore and refining or alloying the metal

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*I took a corrosion course in 1932 at the University of Michigan. If readers know of an earlier college course, I would like to hear about it.

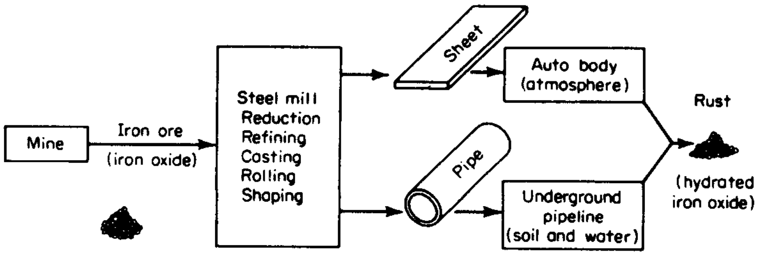

Figure 1-1 Metallurgy in reverse.

for use. Most iron ores contain oxides of iron, and rusting of steel by water and oxygen results in a hydrated iron oxide. *Rusting* is a term reserved for steel and iron corrosion, although many other metals form their oxides when corrosion occurs.

1-4 Environments

Practically all environments are corrosive to some degree. Some examples are air and moisture; fresh, distilled, salt, and mine waters; rural, urban, and industrial atmospheres; steam and other gases such as chlorine, ammonia, hydrogen sulfide, sulfur dioxide, and fuel gases; mineral acids such as hydrochloric, sulfuric, and nitric; organic acids such as naphthenic, acetic, and formic; alkalies; soils; solvents; vegetable and petroleum oils; and a variety of food products. In general, the "inorganic" materials are more corrosive than the "organics." For example, corrosion in the petroleum industry is due more to sodium chloride, sulfur, hydrochloric and sulfuric acids, and water, than to the oil, naphtha, or gasoline.

The trend in the chemical process industries toward higher temperatures and pressures has made possible new processes or improvements in old processes—for example, better yields, greater speed, and lower production costs. This also applies to power production, including nuclear power, missiles, and many other methods and processes. Higher temperatures and pressures usually involve more severe corrosion conditions. Many of the present-day operations would not have been possible or economical without the use of corrosion-resistant materials.

1-5 Corrosion Damage

Some of the deleterious effects of corrosion are described in the next few paragraphs. However, corrosion is beneficial or desirable in some cases. For example, *chemical machining* or chemical milling is widely used in aircraft and other applications. Unmasked areas are exposed to acid and excess metal is dissolved. This process is adopted when it is more economical or when the parts are hard and difficult to machine by more conventional methods. Anodizing of aluminum is another beneficial corrosion process used to obtain better and more uniform appearance in addition to a protective corrosion product on the surface.

Appearance Automobiles are painted because rusted surfaces are not pleasing to the eye. Badly corroded and rusted equipment in a plant would leave a poor impression on the observer. In many rural and urban environments it would be cheaper to make the metal thicker in the first place (corrosion allowance) than to apply and maintain a paint coating. Outside surfaces or trim on buildings are often made of stainless steel, aluminum, or copper for the sake of appearance. The same is true for restaurants and other commercial establishments. These are examples where service life versus dollars is not the controlling factor.

Maintenance and operating costs Substantial savings can be obtained in many types of plants through the use of corrosion-resistant materials of construction. One example is classic in this respect. A chemical plant effected an annual saving of more than $10,000 merely by changing the bolt material on some equipment from one alloy to another more resistant to the conditions involved. The cost of this change was negligible. In another case a waste acid recovery plant operated in the red for several months until a serious corrosion problem was solved. This plant was built to take care of an important waste disposal problem. Application of cathodic protection can cut leak rates in existing underground pipelines to practically nil with attendant large savings in repair costs. Maintenance costs are scrutinized because the labor picture accents the necessity for low-cost operation.

Close cooperation between the corrosion engineer and process and design personnel *before* a plant is built can eliminate or substantially reduce maintenance costs in many cases. Slight changes in the process sometimes reduce the corrosiveness of plant liquors without affecting the process itself, thus permitting the use of less expensive materials. These changes can often be made after the plant is in operation, but original preventive measures are more desirable. Corrosion difficulties can often be "designed out" of equipment, and the time to do this is in the original design of the plant.

When I started working for Du Pont in 1934, we had to write a report every month and indicate the dollars saved through our efforts. After a year or so we convinced management that *preventive* action was necessary and economical. The design people and the corrosion engineers collaborated at the inception of the project and much corrosion was "designed out" of the equipment. It is easier and cheaper to erase lines on a drawing than to repair or replace failed equipment in a plant.

Plant Shutdowns Frequently plants are shut down or portions of a process stopped because of unexpected corrosion failures. Sometimes these shutdowns are caused by corrosion involving no change in process conditions, but occasionally they are caused by changes in operating procedures erroneously regarded as incapable of increasing the severity of the corrosive conditions. It is surprising how often some minor change in process or the addition of a new ingredient changes corrosion characteristics completely. The production of a chemical compound vital to national defense is an example. To increase its production, the temperature of the cooling medium in a heat-exchanger system was lowered and the time required per batch decreased. Lowering the temperature of the cooling medium resulted, however, in more severe thermal gradients across the metal wall. They, in turn, induced higher stresses in the metal. Stress corrosion cracking of the vessels occurred quickly, and the plant was shut down with production delayed for some time.

Corrosion monitoring of a plant process is helpful in preventing unexpected corrosion failure and plant shutdown. This can be done by periodically examining corrosion specimens that are continually exposed to the process or by using a corrosion probe that continuously records the corrosion rate. Periodic inspection of equipment during scheduled downtimes can help prevent unexpected shutdown.

Contamination of product In many cases the market value of the product is directly related to its purity and quality. Freedom from contamination is a vital factor in the manufacture and handling of transparent plastics, pigments, foods, drugs, and semiconductors. In some cases a very small amount of corrosion, which introduces certain metal ions into the solution, may cause catalytic decomposition of a product, for example, in the manufacture and transporting of concentrated hydrogen peroxide or hydrazine.

Life of the equipment is not generally an important factor in cases where contamination or degradation of product is concerned. Ordinary steel may last many years, but more expensive material is used because the presence of rust is undesirable from the product standpoint.

Loss of valuable products No particular concern is attached to slight leakage of sulfuric acid to the drain, because it is a cheap commodity. However, loss of a material worth several dollars per gallon requires prompt corrective action. Slight losses of uranium compounds or solutions are hazardous and can be very costly. In such cases, utilization of more expensive design and better materials of construction are well warranted.

Effects on safety and reliability The handling of hazardous materials such as toxic gases, hydrofluoric acid, concentrated sulfuric and nitric acids, explosive and flammable materials, radioactive substances, and chemicals at high temperatures and pressures demands the use of construction materials that minimize corrosion failures. Stress corrosion of a metal wall separating the fuel and oxidizer in a missile could cause premature mixing, which could result in a loss of millions of dollars and in personal injury. Failure of a small component or control may result in failure or destruction of the entire structure. Corroding equipment can cause some fairly harmless compounds to become explosive. Economizing on materials of construction is not desirable if safety is risked.

Other health considerations are also important such as contamination of potable water. Corrosion products could make sanitizing of equipment more difficult. An interesting example here involves milk and other dairy product plants. The straight chromium stainless steels are satisfactory in old plants where much of the equipment is disassembled and sanitized by "dishpan" techniques. Newer plants use in-place cleaning and sanitizing which require more corrosive chemicals, particularly with regard to chloride ions and pitting. These solutions are circulated through the system without taking it apart thus saving many labor hours. These advances require use of more pit-resistant stainless steels, such as type 316 containing nickel and molybdenum.

Corrosion also plays an important part in medical metals used for hip joints, screws, plates, and heart valves. Reliability is, of course, of paramount importance here.

An *unusual* experience (*Chem. Eng.*, 28, March 19, 1984) emphasizes the importance of safety considerations. A large carbon steel vessel was cleaned, washed, and entered for maintenance. A workman was asphyxiated and died because the air became oxygen-deficient (about 1% O_2)—a situation "created by rapid rusting" of the empty steel vessel. If a second manhole had been opened, a natural draft would have changed the air.

Product liability There is an important and disturbing trend in this country toward putting the blame and legal responsibility on the producers or manufacturer of any item or piece of equipment that fails because of corrosion or for any other reason. The U.S. Department of Commerce has issued a report on the increase of product liability claims that points out that such claims have far outstripped inflation and are approaching medical malpractice insurance claims. One estimate indicates an average loss in 1965 from a product liability claim was $11,644. By 1973 this figure was $79,940, an increase of 686 percent. Lack of "contract," or "negligence," is no longer a defense.

A ridiculous example (to make the point) would be blaming the auto manufacturer if your car corroded because you drove it through a lake of hydrochloric acid! The car could be made of tantalum, but the cost would be astronomical, nobody would buy it, and then a disclaimer would have to be filed stating that hydrofluoric acid must not be present!

What this all means is that the manufacturer or producer of a product must make sure that it is made of proper materials, under good quality control, to a design that is as safe as possible, and the inspection must be critical. The corrosion engineer must be doubly sure that failure will not occur in the actual environment and should also be aware of the legal liability aspects. Passage of time is not a precluding factor; lawsuits resulted from failure of a bridge that had been in use for about 40 years.

The numbers listed in the third paragraph above have escalated tremendously (*Chem. Eng. Progr.*, p. 146, Mar. 1984). In the product liability area *alone*, jury awards "are now approaching $100 *billion* dollars per year." Corporate legal costs to defend suits are about $50 billion. One reason for this escalation is that there are roughly 600,000 attorneys in this country or about one lawyer for every 400 citizens. In Japan the corresponding number is one lawyer for every 16,000 people. In 1984 American law schools graduated about 35,000 lawyers—a number higher than the *total* number of American graduate students "in engineering, chemistry, physics and biology, combined!"

We are indeed a litigious society today.

1-6 Classification of Corrosion

Corrosion has been classified in many different ways. One method divides corrosion into low-temperature and high-temperature corrosion. Another separates corrosion into direct combination (or oxidation) and electrochemical corrosion. The preferred classification here is (1) *wet* corrosion and (2) *dry* corrosion.

Wet corrosion occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far. A common example is corrosion of steel by water. Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with high temperatures. An example is attack on steel by furnace gases.

The presence of even small amounts of moisture could change the corrosion picture completely. For example, dry chlorine is practically noncorrosive to ordinary steel, but moist chlorine, or chlorine dissolved in water, is extremely corrosive and attacks most of the common metals and alloys. The reverse is true for titanium—dry chlorine gas is more corrosive than wet chlorine.

1-7 Future Outlook

The future will place greater and greater demands on corrosion engineers. They must meet the challenge with their expertise and must exercise ingenuity to solve new problems. Energy considerations, materials shortages, and political aspects are relatively new complicating factors. The abnormal conditions of today will be normal tomorrow. In the past the emphasis has been on the development of "bigger and better alloys" and other materials; in the future, acceptable substitutes may be emphasized. For example, a Fe-6Cr-6Al alloy might be used instead of 18Cr-8Ni where the full corrosion resistance of the latter is not essential. New research tools are now available and better ones will be available later to aid in the study and understanding of corrosion and its prevention. Closer collaboration between corrosion engineers and corrosion scientists is a must. Greater collaboration between countries will occur.

Closer collaboration between corrosion engineers (and materials engineers) and design engineers is a must. The corrosion engineer must be a part of the design team from the beginning of the project. He should "sign off" on drawings and specifications. The corrosion and design engineers must understand fracture mechanics aspects and also inspection techniques including nondestructive examination.

There is a greater national awareness today than a decade ago. Witness the corrosion cost study resulting from a congressional directive (Sec. 1-1). This awareness will increase.*

M. H. Van de Voorde in "Materials for Advanced Energy Technologies —A European Viewpoint" (*J. Metals*, 19–23, July 1983) emphasizes the importance of many points made in this section and this chapter. For example, "Investment in materials research may be crucial for the survival of European energy supply and industrial innovation." Also, "Materials science must be reassessed and its great potential as a future profession must be acknowledged."

The Materials Technology Institute of the Chemical Process Industries was established in 1977. Consumers and producers alike are contributing funds for study of procedures to mitigate corrosion losses in areas of mutual interest. Some of the results are described later in this book. Other industry groups should form similar organizations. These combined efforts are more cost effective and productive than individual efforts.

A large number of plants using corrosive processes will be built in the future. These include coal conversion, power, refineries, synthetic fuel plants, oil and gas wells, thousands of miles of pipelines, and many other process plants. The number of environmental control systems will mushroom at great cost. In many cases corrosion problems will increase in severity.

There is a great clamor for universities and colleges to provide training in the field of corrosion. Closer alliance between universities and industries

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*The federal budget for 1985 calls for over $1 billion for R and D in materials science and engineering (*Materials Performance*, 63, May 1984).

should occur. The best way to reduce corrosion costs is to have more practicing corrosion engineers.

The prospects of an interesting and rewarding career look bright for the corrosion engineer.

CHAPTER

TWO

CORROSION PRINCIPLES

2-1 Introduction

To view corrosion engineering in its proper perspective, it is necessary to remember that the choice of a material depends on many factors, including its corrosion behavior. Figure 2-1 shows some of the properties that determine the choice of a structural material. Although we are primarily concerned with the corrosion resistance of various materials, the final choice frequently depends on factors other than corrosion resistance. As mentioned in Chap. 1, the cost and the corrosion resistance of the material usually are the most important properties in most engineering applications requiring high chemical resistance. However, for architectural applications, appearance is often the most important consideration. Fabricability, which includes the ease of forming, welding, and other mechanical operations, must also be considered. In engineering applications, the mechanical behavior or strength is also important and has to be considered even though the material is being selected for its corrosion resistance. Finally, for many highly resistant materials such as gold, platinum, and some of the super-alloys, the availability of these materials frequently plays a deciding factor in whether or not they will be used. In many instances the delivery time for some of the exotic metals and alloys is prohibitive.

The engineering aspects of corrosion resistance cannot be overemphasized. Complete corrosion resistance in almost all media can be achieved by the use of either platinum or glass, but these materials are not practical in most cases.

Corrosion resistance or chemical resistance depends on many factors. Its complete and comprehensive study requires a knowledge of several fields of scientific knowledge as indicated in Fig. 2-2. Thermodynamics and

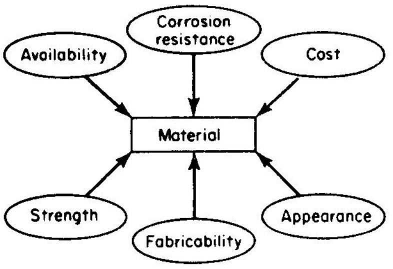

Figure 2-1 Factors affecting choice of an engineering material.

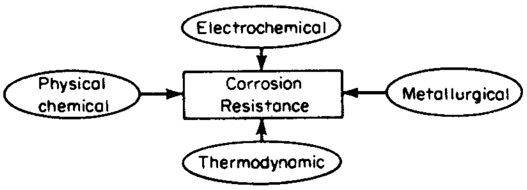

Figure 2-2 Factors affecting corrosion resistance of a metal.

electrochemistry are of great importance in understanding and controlling corrosion.

Thermodynamic studies and calculations indicate the spontaneous direction of a reaction. In the case of corrosion, thermodynamic calculations can determine whether or not corrosion is theoretically possible. Electrochemistry and its associated field, electrode kinetics, are introduced in this chapter and discussed in considerable detail in Chaps. 9 and 10.

Metallurgical factors frequently have a pronounced influence on corrosion resistance. In many cases the metallurgical structure of alloys can be controlled to reduce corrosive attack. Physical chemistry and its various disciplines are most useful for studying the mechanisms of corrosion reactions, the surface conditions of metals, and other basic properties.

In this chapter and the ones that follow, all of these disciplines that are important for the understanding and controlling of corrosion will be utilized. Since the rate of corrosion is of primary interest for engineering application, electrochemical theory and concepts will be considered in greater detail.

2-2 Corrosion Rate Expressions

Throughout this book, metals and nonmetals will be compared on the basis of their corrosion resistance. To make such comparisons meaningful, the rate of attack for each material must be expressed quantitatively. Corrosion rates have been expressed in a variety of ways in the literature; such as percent weight loss, milligrams per square centimeter per day, and grams per square inch per hour. These do not express corrosion resistance in terms of penetration. From an engineering viewpoint, the rate of penetration, or the thinning of a structural piece, can be used to predict the life of a given component.

The expression *mils per year* is the most desirable way of expressing corrosion rates and will be used throughout this text. This expression is readily calculated from the weight loss of the metal specimen during the corrosion test by the formula given below:

$$\text{mpy} = \frac{534W}{DAT}$$

where W = weight loss, mg
D = density of specimen, g/cm^3
A = area of specimen, sq. in.
T = exposure time, hr

This corrosion rate calculation involves whole numbers, which are easily handled.

Section 4-13 in Chap. 4 describes corrosion rate expressions in greater detail, including the metric system.

ELECTROCHEMICAL ASPECTS

2-3 Electrochemical Reactions

The electrochemical nature of corrosion can be illustrated by the attack on zinc by hydrochloric acid. When zinc is placed in dilute hydrochloric acid, a vigorous reaction occurs; hydrogen gas is evolved and the zinc dissolves, forming a solution of zinc chloride. The reaction is:

$$\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2 \qquad (2.1)$$

Noting that the chloride ion is not involved in the reaction, this equation can be written in the simplified form:

$$\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \qquad (2.2)$$

Hence, zinc reacts with the hydrogen ions of the acid solution to form zinc ions and hydrogen gas. Examining the above equation, it can be seen that during the reaction, zinc is oxidized to zinc ions and hydrogen ions are reduced to hydrogen. Thus Eq. (2.2) can be conveniently divided into two reactions, the oxidation of zinc and the reduction of hydrogen ions:

Oxidation (anodic reaction)* $\quad Zn \rightarrow Zn^{2+} + 2e \quad (2.3)$

Reduction (cathodic reaction) $\quad 2H^{+} + 2e \rightarrow H_2 \quad (2.4)$

An oxidation or anodic reaction is indicated by an increase in valence or a production of electrons. A decrease in valence charge or the consumption of electrons signifies a reduction or cathodic reaction. Equations (2.3) and (2.4) are partial reactions—both must occur simultaneously and at the same rate on the metal surface. If this were not true, the metal would spontaneously become electrically charged, which is clearly impossible. This leads to one of the most important basic principles of corrosion: *during metallic corrosion, the rate of oxidation equals the rate of reduction* (in terms of electron production and consumption).

The above concept is illustrated in Fig. 2-3. Here a zinc atom has been transformed into a zinc ion and two electrons. These electrons, which remain in the metal, are immediately consumed during the reduction of hydrogen ions. Figure 2-3 shows these two processes spatially separated for clarity. Whether or not they are actually separated or occur at the same point on the surface does not affect the above principle of charge conservation. In some corrosion reactions the oxidation reaction occurs uniformly on the surface, while in other cases it is localized and occurs at specific areas. These effects are described in detail in following chapters.

The corrosion of zinc in hydrocholoric acid is an electrochemical process. That is, any reaction that can be divided into two (or more) partial reactions of oxidation and reduction is termed electrochemical. Dividing corrosion or other electrochemical reactions into partial reactions makes them simpler to understand. Iron and aluminum, like zinc, are also rapidly

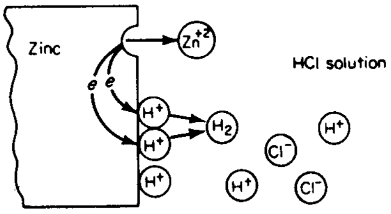

Figure 2-3 Electrochemical reactions occurring during corrosion of zinc in air-free hydrochloric acid.

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*Until recently, corrosion theory usually has been based on the concept of local anode and cathode areas on metal surfaces. However, descriptions of corrosion phenomena based on modern electrode kinetic principles (mixed-potential theory) are more general since they apply to any corroding system and do not depend on assumptions regarding the distribution of anodic and cathodic reactions. It should be emphasized that these two methods of treating corrosion are not conflicting—they merely represent two different approaches. In this text, we have used electrode kinetic descriptions because of their greater simplicity and more general application.

corroded by hydrochloric acid. The reactions are:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \tag{2.5}$$

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2 \tag{2.6}$$

Although at first sight these appear quite different, comparing the partial processes of oxidation and reduction indicates that reactions (2.1), (2.5), and (2.6) are quite similar. All involve the hydrogen ion reduction and they differ only in their oxidation or anodic reactions:

$$Zn \rightarrow Zn^{2+} + 2e \tag{2.3}$$

$$Fe \rightarrow Fe^{2+} + 2e \tag{2.7}$$

$$Al \rightarrow Al^{3+} + 3e \tag{2.8}$$

Hence, the problem of hydrochloric acid corrosion is simplified since in every case the cathodic reaction is the evolution of hydrogen gas according to reaction (2.4). This also applies to corrosion in other acids such as sulfuric, phosphoric, hydrofluoric, and water-soluble organic acids such as formic and acetic. In each case, only the hydrogen ion is active, the other ions such as sulfate, phosphate, and acetate do not participate in the electrochemical reaction.

When viewed from the standpoint of partial processes of oxidation and reduction, all corrosion can be classified into a few generalized reactions. The anodic reaction in every corrosion reaction is the oxidation of a metal to its ion. This can be written in the general form:

$$M \rightarrow M^{+n} + ne \tag{2.9}$$

A few examples are:

$$Ag \rightarrow Ag^{+} + e \tag{2.10}$$

$$Zn \rightarrow Zn^{2+} + 2e \tag{2.3}$$

$$Al \rightarrow Al^{3+} + 3e \tag{2.8}$$

In each case the number of electrons produced equals the valence of the ion.

There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common are:

Hydrogen evolution	$2H^{+} + 2e \rightarrow H_2$	(2.4)
Oxygen reduction (acid solutions)	$O_2 + 4H^{+} + 4e \rightarrow 2H_2O$	(2.11)
Oxygen reduction (neutral or basic solutions)	$O_2 + 2H_2O + 4e \rightarrow 4OH^{-}$	(2.12)
Metal ion reduction	$M^{3+} + e \rightarrow M^{2+}$	(2.13)

Metal deposition $M^+ + e \rightarrow M$ (2.14)

Hydrogen evolution is a common cathodic reaction since acid or acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of producing this reaction Metal ion reduction and metal deposition are less common reactions and are most frequently found in chemical process streams. All of the above reactions are quite similar—they consume electrons.

The above partial reactions can be used to interpret virtually all corrosion problems. Consider what happens when iron is immersed in water or seawater which is exposed to the atmosphere (an automobile fender or a steel pier piling are examples). Corrosion occurs. The anodic reaction is:

$$Fe \rightarrow Fe^{2+} + 2e \qquad (2.7)$$

Since the medium is exposed to the atmosphere, it contains dissolved oxygen. Water and seawater are nearly neutral, and thus the cathodic reaction is:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (2.12)$$

Remembering that sodium and chloride ions do not participate in the reaction, the overall reaction can be obtained by adding (2.7) and (2.12):

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2\downarrow \qquad (2.15)$$

Ferrous hydroxide precipitates from solution. However, this compound is unstable in oxygenated solutions and is oxidized to the ferric salt:

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \qquad (2.16)$$

The final product is the familiar rust.

The classic example of a replacement reaction, the interaction of zinc with copper sulfate solution, illustrates metal deposition:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad (2.17)$$

or, viewed as partial reactions:

$$Zn \rightarrow Zn^{2+} + 2e \qquad (2.3)$$

$$Cu^{2+} + 2e \rightarrow Cu \qquad (2.18)$$

The zinc initially becomes plated with copper and eventually the products are copper sponge and zinc sulfate solution.

During corrosion, more than one oxidation and one reduction reaction may occur. When an alloy is corroded, its component metals go into solution as their respective ions. More importantly, more than one reduction reaction can occur during corrosion. Consider the corrosion of zinc in aerated hydrochloric acid. Two cathodic reactions are possible: the evolution of hydrogen and the reduction of oxygen. This is illustrated schematically in Fig. 2-4. On the surface of the zinc there are two electron-consuming

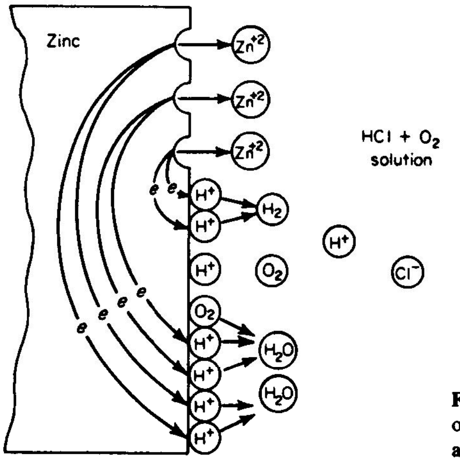


Figure 2-4 Electrochemical reactions occurring during corrosion of zinc in aerated hydrochloric acid.

reactions. Since the rates of oxidation and reduction must be equal, increasing the total reduction rate increases the rate of zinc solution. Hence, acid solutions containing dissolved oxygen will be more corrosive than air-free acids. Oxygen reduction simply provides a new means of "electron disposal." The same effect is observed if any oxidizer is present in acid solutions. A frequent impurity in commercial hydrochloric acid is ferric ion, present as ferric chloride. Metals corrode much more rapidly in such impure acid because there are two cathodic reactions, hydrogen evolution and ferric ion reduction:

$$Fe^{3+} + e \rightarrow Fe^{2+} \tag{2.19}$$

Since the anodic and cathodic reactions occuring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rates of either reaction. In the above case of impure hydrochloric acid, it can be made less corrosive by removing the ferric ions and consequently reducing the total rate of cathodic reduction. Oxygen reduction is eliminated by preventing air from contacting the aqueous solution or by removing air that has been dissolved. Iron will not corrode in air-free water or seawater because there is no cathodic reaction possible.

If the surface of the metal is coated with paint or other nonconducting film, the rates of both anodic and cathodic reactions will be greatly reduced and corrosion will be retarded. A corrosion inhibitor is a substance that when added in small amounts to a corrosive reduces its corrosivity. Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. Many of these inhibitors are organic compounds; they function by forming an impervious film on the metal surface or by interfering with either the anodic or cathodic reactions. High-molecular-weight amines retard the hydrogen evolution reaction and subsequently reduce corrosion rate. It is obvious that good conductivity must be maintained in both the metal and the electrolyte during the corrosion reaction. Of course, it is not practical to increase the electrical resistance of the metal, since the sites of the anodic and cathodic reactions are not known, nor are they predictable. However, it is possible to increase the electrical resistance of the electrolyte or corrosive and thereby reduce corrosion. Very pure water is much less corrosive than impure or natural waters. The low corrosivity of high-purity water is primarily due to its high electrical resistance. These methods for increasing corrosion resistance are described in greater detail in following chapters.

2-4 Polarization

The concept of polarization is briefly discussed here because of its importance in understanding corrosion behavior and corrosion reactions. The following discussion is simplified, and readers desiring a more comprehensive and quantitative discussion of this topic are referred to Chaps. 9 and 10.

The rate of an electrochemical reaction is limited by various physical and chemical factors. Hence, an electrochemical reaction is said to be polarized or retarded by these environmental factors. Polarization can be conveniently divided into two different types, activation polarization and concentration polarization.

Activation polarization refers to an electrochemical process that is controlled by the reaction sequence at the metal-electrolyte interface. This is easily illustrated by considering hydrogen-evolution reaction on zinc during corrosion in acid solution. Figure 2-5 schematically shows some of the possible steps in hydrogen reduction on a zinc surface. These steps can also be applied to the reduction of any species on a metal surface. The species must first be adsorbed or attached to the surface before the reaction can proceed according to step 1. Following this, electron transfer (step 2) must occur, resulting in a reduction of the species. As shown in step 3, two hydrogen atoms then combine to form a bubble of hydrogen gas (step 4). The speed of reduction of the hydrogen ions will be controlled by the slowest of these steps. This is a highly simplified picture of the reduction of hydrogen; numerous mechanisms have been proposed, most of which are much more complex than that shown in Fig. 2-5.

Concentration polarization refers to electrochemical reactions that are controlled by the diffusion in the electrolyte. This is illustrated in Fig. 2-6 for the case of hydrogen evolution. Here, the number of hydrogen ions in solution is quite small, and the reduction rate is controlled by the diffusion of hydrogen ions to the metal surface. Note that in this case the reduction rate is

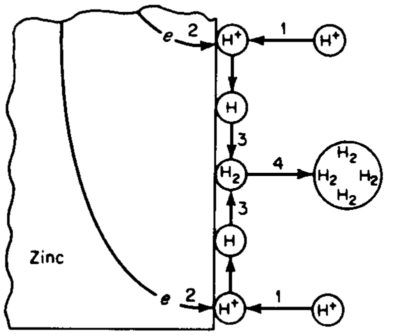


Figure 2-5 Hydrogen-reduction reaction under activation control (simplified).

controlled by processes occurring within the bulk solution rather than at the metal surface. Activation polarization usually is the controlling factor during corrosion in media containing a high concentration of active species (e.g., concentrated acids). Concentration polarization generally predominates when the concentration of the reducible species is small (e.g., dilute acids, aerated salt solutions). In most instances concentration polarization during metal dissolution is usually small and can be neglected; it is only important during reduction reactions.

The importance of distinguishing between activation and concentration polarization cannot be overemphasized. Depending on what kind of polarization is controlling the reduction reaction, environmental variables produce different effects. For example, any changes in the system that increase the diffusion rate will decrease the effects of concentration polarization and hence increase reaction rate. Thus, increasing the velocity or agitation of the corrosive medium will increase rate *only* if the cathodic process is controlled

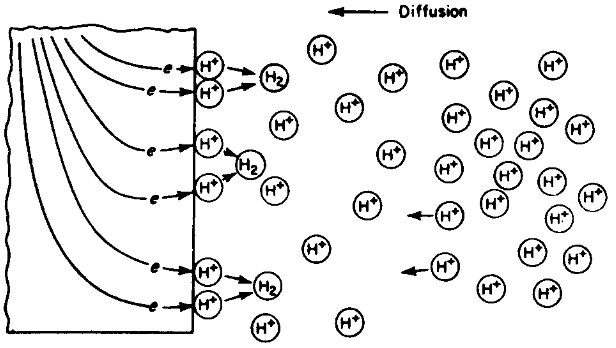


Figure 2-6 Concentration polarization during hydrogen reduction.

by concentration polarization. If both the anodic and cathodic reactions are controlled by activation polarization, agitation will have no influence on corrosion rate. These and other differences are discussed in detail below and also in Chaps. 9 and 10.

2-5 Passivity

The phenomenon of metallic passivity has fascinated scientists and engineers for over 120 years, since the days of Faraday. The phenomenon itself is rather difficult to define because of its complex nature and the specific conditions under which it occurs. Essentially, passivity refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. That is, certain metals and alloys become essentially inert and act as if they were noble metals such as platinum and gold. Fortunately, from an engineering standpoint, the metals most susceptible to this kind of behavior are the common engineering and structural materials, including iron, nickel, silicon, chromium, titanium, and alloys containing these metals. Also, under limited conditions other metals such as zinc, cadmium, tin, uranium, and thorium have also been observed to exhibit passivity effects.

Passivity, although difficult to define, can be quantitatively described by characterizing the behavior of metals which show this unusual effect. First, consider the behavior of what can be called a normal metal, that is, a metal which does not show passivity effects. In Fig. 2-7 the behavior of such a metal is illustrated. Let us assume that we have a metal immersed in an air-free acid solution with an oxidizing power corresponding to point *A* and a corrosion rate corresponding to this point. If the oxidizing power of this solution is increased, say, by adding oxygen or ferric ions, the corrosion rate of the metal will increase rapidly. Note that for such a metal the corrosion rate increases as the oxidizing power of the solution increases. This increase in rate is exponential and yields a straight line when plotted on a semilogarithmic scale as in Fig. 2-7. The oxidizing power of the solution is controlled by both the specific oxidizing power of the reagents and the

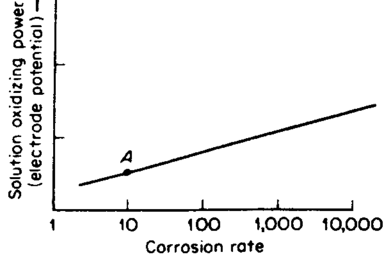


Figure 2-7 Corrosion rate of a metal as a function of solution oxidizing power (electrode potential).

concentration of these reagents. As will be described in Chaps. 9 and 10, oxidizing power can be precisely defined by electrode potential, but this is beyond our present discussion.

Figure 2-8 illustrates the typical behavior of a metal that demonstrates passivity effects. The behavior of this metal or alloy can be conveniently divided into three regions: active, passive, and transpassive. In the active region the behavior of this material is identical to that of a normal metal. Slight increases in the oxidizing power of the solution cause a corresponding rapid increase in the corrosion rate. If more oxidizing agent is added, the corrosion rate shows a sudden decrease. This corresponds to the beginning of the passive region. Further increases in oxidizing agents produce little, if any, change in the corrosion rate of the material. Finally, at very high concentrations of oxidizers or in the presence of very powerful oxidizers the corrosion rate again increases with increasing oxidizer power. This region is termed the transpassive region.

It is important to note that during the transition from the active to the passive region, a 10^3 to 10^6 reduction in corrosion rate is usually observed. The precise cause for this unusual active-passive-transpassive transition is not completely understood. It is a special case of activation polarization due to the formation of a surface film or protective barrier that is stable over a considerable range of oxidizing power and is eventually destroyed in strong oxidizing solutions. The exact nature of this barrier is not understood. However, for the purposes of engineering application, it is not necessary to understand the mechanism of this unusual effect completely since it can be readily characterized by data such as are shown in Fig. 2-8.

To summarize, metals that possess an active-passive transition become passive or very corrosion resistant in moderately to strongly oxidizing environments. Under extremely strong oxidizing conditions, these materials

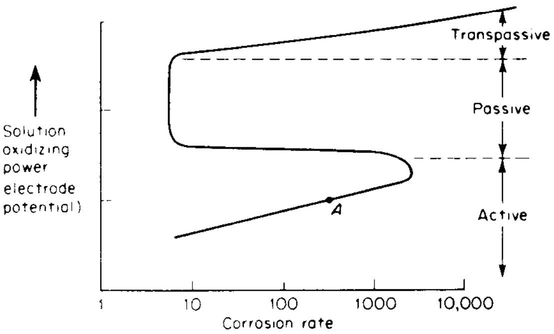


Figure 2-8 Corrosion characteristics of an active-passive metal as a function of solution oxidizing power (electrode potential).

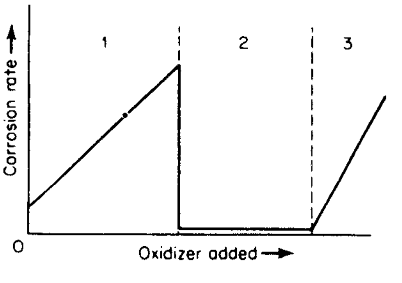
lose their corrosion-resistance properties. These characteristics have been successfully used to develop new methods of preventing corrosion and to predict corrosion resistance. These applications are described in detail in succeeding chapters.

ENVIRONMENTAL EFFECTS

Frequently in the process industries, it is desirable to change process variables. One of the most frequent questions is: What effect will this change have on corrosion rates? In the following section, some of the more common environmental variables are considered on the basis of the concepts developed above.

2-6 Effect of Oxygen and Oxidizers

The effect of oxidizers and oxidizing power was discussed above in connection with the behavior of active-passive metals. The effect of oxidizers on corrosion rate can be represented by the graph shown in Fig. 2-9. Note that the shape of this graph is similar to that of Fig. 2-8 and that this figure is divided into three different sections. Behavior corresponding to section 1



Examples

1: Monel in $HCl + O_2$
Cu in $H_2SO_4 + O_2$
Fe in $H_2O + O_2$

1-2: 18Cr-8Ni in $H_2SO_4 + Fe^{+3}$
Ti in $HCl + Cu^{+2}$

2: 18Cr-8Ni in HNO_3
Hastelloy C in $FeCl_3$

2-3: 18Cr-8Ni in $HNO_3 + Cr_2O_3$

1-2-3: 18Cr-8Ni in concentrated $H_2SO_4 + HNO_3$ mixtures at elevated temperatures

Figure 2-9 Effect of oxidizers and aeration on corrosion rate.

is characteristic of normal metals and also of active-passive metals when they exist only in the active state. For metals that demonstrate active-passive transition, passivity is achieved only if a sufficient quantity of oxidizer or a sufficiently powerful oxidizer is added to the medium. Increasing corrosion rate with increasing oxidizer concentrations as shown in section 1 is characteristic of Monel and copper in acid solutions containing oxygen. Both of these materials do not passivate. Although iron can be made to passivate in water, the solubility of oxygen is limited, and in most cases it is insufficient to produce a passive state as shown in Fig. 2-8.

An increase in corrosion rate, followed by a rapid decrease, and then a corrosion rate that is essentially independent of oxidizer concentration is characteristic of such active-passive metals and alloys as 18Cr-8Ni stainless steel and titanium.

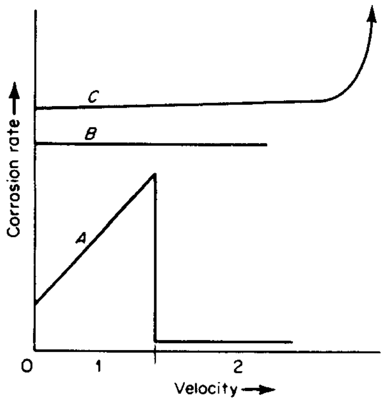
If an active-passive metal is initially passive in a corrosive medium, the addition of further oxidizing agents has only a negligible effect on corrosion rate. This condition frequently occurs when an active-passive metal is immersed in an oxidizing medium such as nitric acid or ferric chloride. The behavior represented by sections 2 and 3 results when a metal, initially in the passive state, is exposed to very powerful oxidizers and makes a transition into the transpassive region. This kind of behavior is frequently observed with stainless steel when very powerful oxidizing agents such as chromates are added to the corrosive medium. In hot nitrating mixtures containing concentrated sulfuric and nitric acids, the entire active-passive-transpassive transition can be observed with the increased ratios of nitric to sulfuric acid.

It is readily seen that the effect of oxidizer additions or the presence of oxygen on corrosion rate depends on both the medium and the metals involved. The corrosion rate may be increased by the addition of oxidizers, oxidizers may have no effect on the corrosion rate, or a very complex behavior may be observed.

By knowing the basic characteristics of a metal or alloy and the environment to which it is exposed it is possible to predict in many instances the effect of oxidizer additions.

2-7 Effects of Velocity

The effects of velocity on corrosion rate are, like the effects of oxidizer additions, complex and depend on the characteristics of the metal and the environment to which it is exposed. Figure 2-10 shows typical observations when agitation or solution velocity are increased. For corrosion processes that are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate as illustrated in curve *B*. If the corrosion process is under cathodic diffusion control, then agitation increases the corrosion rate as shown in curve *A*, section 1. This effect generally occurs



Examples

Curve A :
1 : Fe in $H_2O + O_2$
Cu in $H_2O + O_2$
1-2 : 18Cr-8Ni in $H_2SO_4 + Fe^{+3}$
Ti in HCl + Cu^{+2}

Curve B : Fe in dilute HCl
18Cr-8Ni in H_2SO_4

Curve C : Pb in dilute H_2SO_4
Fe in concentrated H_2SO_4

Figure 2-10 Effect of velocity on corrosion rate.

when an oxidizer is present in very small amounts, as is the case for dissolved oxygen in acids or water.

If the process is under diffusion control and the metal is readily passivated, then the behavior corresponding to curve *A*, sections 1 and 2, will be observed. That is, with increasing agitation, the metal will undergo an active-to-passive transition. Easily passivated materials such as stainless steel and titanium frequently are more corrosion resistant when the velocity of the corrosion medium is high.

Some metals owe their corrosion resistance in certain mediums to the formation of massive bulk protective films on their surfaces. These films differ from the usual passivating films in that they are readily visible and much less tenacious. It is believed that both lead and steel are protected from attack in sulfuric acid by insoluble sulfate films. When materials such as these are exposed to extremely high corrosive velocities, mechanical damage or removal of these films can occur, resulting in accelerated attack as shown in curve *C*. This is called erosion corrosion and is discussed in Chap. 3. In the case of curve *C*, note that until mechanical damage actually occurs, the effect of agitation or velocity is virtually negligible.

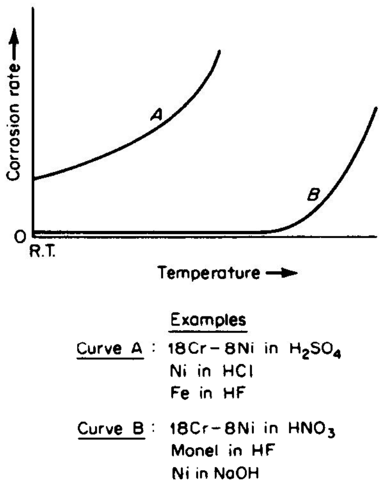


Figure 2-11 Effect of temperature on corrosion rate.

2-8 Effect of Temperature

Temperature increases the rate of almost all chemical reactions. Figure 2-11 illustrates two common observations on the effect of temperature on the corrosion rates of metals. Curve *A* represents the behavior noted above, a very rapid or exponential rise in corrosion rate with increasing temperature. Behavior such as noted in curve *B* is also quite frequently observed. That is, an almost negligible temperature effect is followed by a very rapid rise in corrosion rate at higher temperatures. In the case of 18-8 stainless steel in nitric acid, this effect is readily explained. Increasing the temperature of nitric acid greatly increases its oxidizing power. At low or moderate temperatures, stainless steels exposed to nitric acid are in the passive state very close to the transpassive region. Hence, an increase in oxidizing power causes a very rapid increase in the corrosion rate of these materials. A similar sort of mechanism may explain the behavior of Monel and nickel, as noted in Fig. 2-11. However, it is possible that curves such as *B* in many instances erroneously represent actual behavior. If the corrosion rate at low temperature is very low, and increases exponentially, linear plots will appear as curve *B*. That is, corrosion rate increases rapidly with temperature; this is not evident in the usual plots of corrosion rate versus temperature because of the choice of scales.

2-9 Effects of Corrosive Concentration

Figure 2-12 shows schematically the effects of corrosive concentration on corrosion rate. Note that curve *A* has two sections, 1 and 2. Many materials that exhibit passivity effects are only negligibly affected by wide changes in

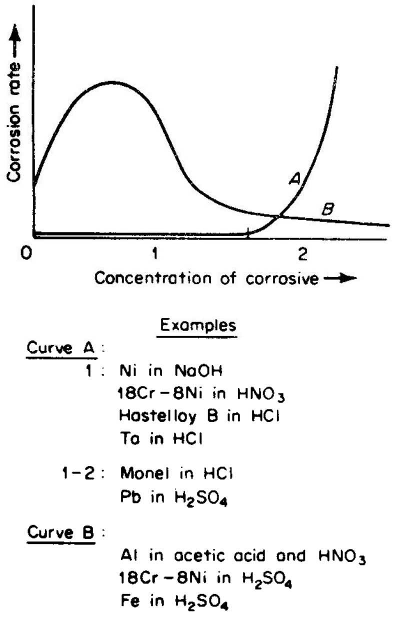


Figure 2-12 Effect of corrosive concentration on corrosion rate.

corrosive concentration, as shown in curve *A*, section 1. Other materials show similar behavior except at very high corrosive concentrations, when the corrosion rate increases rapidly as shown in curve *A*, sections 1 and 2. Lead is a material that shows this effect, and it is believed to be due to the fact that lead sulfate, which forms a protective film in low concentrations of sulfuric acid, is soluble in concentrated sulfuric acid. The behavior of acids that are soluble in all concentrations of water often yield curves similar to curve *B* in Fig. 2-12. Initially, as the concentration of corrosive is increased, the corrosion rate is likewise increased. This is primarily due to the fact that the amount of hydrogen ions, which are the active species, are increased as acid concentration is increased. However, as acid concentration is increased further, corrosion rate reaches a maximum and then decreases. This is undoubtedly due to the fact that at very high concentrations of acids ionization is reduced. Because of this, many of the common acids—such as sulfuric, acetic, hydrofluoric, and others—are virtually inert when in the pure state, or 100% concentration, and at moderate temperatures.

2-10 Effect of Galvanic Coupling

In many practical applications the contact of dissimilar materials is unavoidable. In complex process streams and piping arrangements, different metals and alloys are frequently in contact with each other and the corrosive medium. The effects of galvanic coupling will be considered in detail later

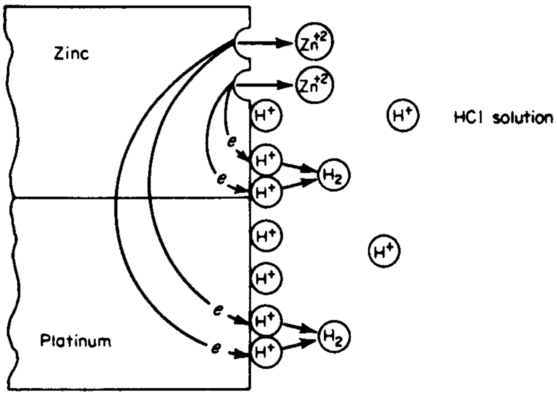


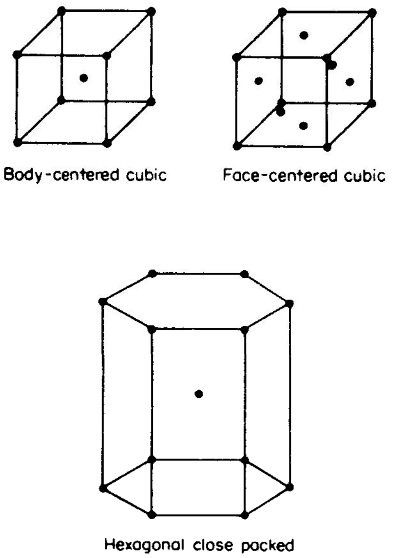
Figure 2-13 Electrochemical reactions occurring on galvanic couple of zinc and platinum.

and are only briefly mentioned here. Consider a piece of zinc immersed in a hydrochloric acid solution and contacted to a noble metal such as platinum (Fig. 2-13). Since platinum is inert in this medium, it tends to increase the surface at which hydrogen evolution can occur. Further, hydrogen evolution occurs much more readily on the surface of platinum than on zinc. These two factors increase the rate of the cathodic reaction and consequently increase the corrosion rate of the zinc. Note that the effect of galvanic coupling in this instance is virtually identical to that of adding an oxidizer to a corrosive solution. In both instances, the rate of electron consumption is increased and hence the rate of metal dissolution increases. It is important to recognize that galvanic coupling does not always increase the corrosion rate of a given metal; in some cases it decreases the corrosion rate. These specialized cases will be discussed in later chapters.

METALLURGICAL AND OTHER ASPECTS

2-11 Metallic Properties

Metals and alloys are crystalline solids. That is, the atoms of a metal are arranged in a regular, repeating array. The three most common crystalline arrangements of metals are illustrated in Fig. 2-14. Iron and steel have a body-centered cubic structure, the austenitic stainless steels are face-centered cubic, and magnesium possesses a hexagonal, close-packed lattice structure. Metallic properties differ from those of other crystalline solids such as ceramics and chemical salts. They are ductile (can be deformed plastically without fracturing) and are good conductors of electricity and heat. These



Body-centered cubic Face-centered cubic

Hexagonal close packed

Figure 2-14 Metallic crystal structures.

properties result from the nondirectional bonding of metals; that is, each atom is bonded to many of its neighbors. Hence, the crystal structures are simple and closely packed as shown in Fig. 2-14. Ductility is probably the most important property of metals. Their ductility permits almost unlimited fabrication. Further, when highly stressed, metals usually yield plastically before fracturing. This property is, of course, invaluable in engineering applications.

When a metal solidifies during casting, the atoms, which are randomly distributed in the liquid state, arrange themselves in a crystalline array. However, this ordering usually begins at many points in the liquid, and as these blocks of crystals or grains meet, there is a mismatch at their boundary. When the metal has solidified and cooled, there will be numerous regions of mismatch between each grain. These regions are called grain boundaries. Figure 2-15 shows this using a two-dimensional representation of a grain boundary. Since the most stable configuration of the metal is its particular crystal lattice, grain boundaries are high-energy areas and are more active chemically. Hence, grain boundaries are usually attacked slightly more rapidly than grain faces when exposed to a corrosive. Metallographic etching, in many cases, depends on this difference in chemical reactivity to develop contrast between grains. Figure 2-16 shows a magnified view of 18-8 stainless steel that has been etched in acid solution. The grain boundaries appear dark because they have been more severely attacked than the grains.

Alloys are mixtures of two or more metals or elements. There are two

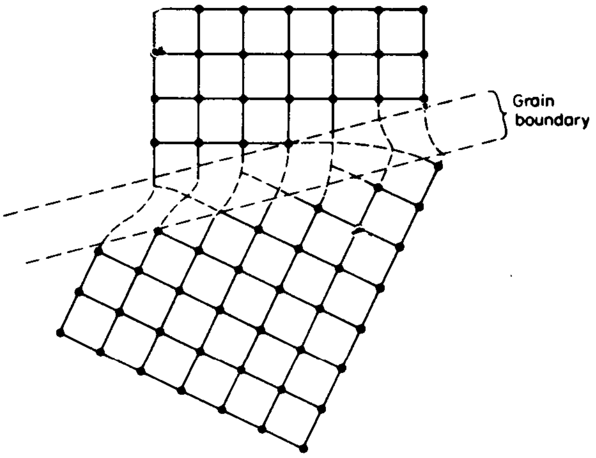


Figure 2-15 Grain boundary in a polycrystalline metal (two-dimensional representation).

kinds of alloys—homogeneous and heterogeneous. Homogeneous alloys are solid solutions. That is, the components are completely soluble in one another, and the material has only one phase. An example of a homogeneous or solid-solution alloy is 18-8 stainless steel (Fig. 2-16). The iron, nickel, chromium, and carbon are dissolved completely, and the alloy has a uniform composition. Heterogeneous alloys are mixtures of two or more separate phases. The components of such alloys are not completely soluble and exist as separate phases. The composition and structure of these alloys are not uniform. Figure 2-17 shows a photomicrograph of low-carbon steel. The carbon combines with some of the iron to form iron carbide, which usually appears in a lamellar form. Each type of alloy has advantages and disadvantages. Solid-solution alloys are generally more ductile and have lower strength than heterogeneous alloys. The choice between these two

Figure 2-16 Photomicrograph of 18Cr-8Ni stainless steel etched to reveal grain boundaries (100 ×).

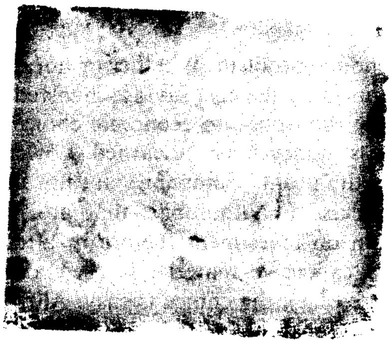


Figure 2-17 Photomicrograph of carbon steel etched to reveal iron carbide platelets (600 ×).

types depends on the mechanical properties desired. Solid-solution alloys are usually more corrosion resistant than alloys with two (or more) phases, since galvanic coupling effects are not present. However, there are important exceptions to this generalization and they are described in the following chapters.

Alloys are quite similar to aqueous solutions. Some substances can be dissolved, whereas others are insoluble. Solubility usually increases rapidly with increasing temperature. For example, iron carbide is completely soluble in iron at high temperatures; hence steel becomes a solid solution when heated to a high temperature. Precipitation of a phase can occur from supersaturated solid solutions as it does in the case of liquid solutions. As noted above, grain boundaries are high-energy areas, so precipitation frequently begins at the grain interfaces.

Other differences in the metal can be chemical, metallurgical, or mechanical in nature. Examples are impurities such as oxides and other inclusions, mill scale, orientation of grains, dislocation arrays, differences in composition of the microstructure, precipitated phases, localized stresses, scratches, and nicks. Highly polished surfaces are used in only special cases. Very pure metals are more corrosion resistant than commercial materials. For example, very pure and smooth zinc will not corrode in very pure hydrochloric acid, yet their commercial counterparts react rapidly. However, pure metals are expensive, and they are usually weak—one would not build a bridge of pure iron.

The following shows the effect of purity of aluminum on corrosion by hydrochloric acid:

% aluminum	Relative corrosion rate
99.998	1
99.97	1,000
99.2	30,000

Differences in the environment will be discussed in Chap. 3.