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DEFINITION AND IMPORTANCE OF CORROSION

1.1 DEFINITION OF CORROSION

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Deterioration by physical causes is not called corrosion, but is described as erosion, galling, or wear. In some instances, chemical attack accompanies physical deterioration, as described by the following terms: corrosion–erosion, corrosive wear, or fretting corrosion. Nonmetals are not included in this definition of corrosion. Plastics may swell or crack, wood may split or decay, granite may erode, and Portland cement may leach away, but the term corrosion, in this book, is restricted to chemical attack of metals.

"Rusting" applies to the corrosion of iron or iron-base alloys with formation of corrosion products consisting largely of hydrous ferric oxides. Nonferrous metals, therefore, corrode, but do not rust.

1.1.1 Corrosion Science and Corrosion Engineering

Since corrosion involves chemical change, the student must be familiar with principles of chemistry in order to understand corrosion reactions. Because corrosion processes are mostly electrochemical, an understanding of

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electrochemistry is also important. Furthermore, since structure and composition of a metal often determine corrosion behavior, the student should be familiar with the fundamentals of physical metallurgy as well.

The *corrosion scientist* studies corrosion mechanisms to improve (a) the understanding of the causes of corrosion and (b) the ways to prevent or at least minimize damage caused by corrosion. The *corrosion engineer*, on the other hand, applies scientific knowledge to control corrosion. For example, the corrosion engineer uses cathodic protection on a large scale to prevent corrosion of buried pipelines, tests and develops new and better paints, prescribes proper dosage of corrosion inhibitors, or recommends the correct coating. The corrosion scientist, in turn, develops better criteria of cathodic protection, outlines the molecular structure of chemical compounds that behave best as inhibitors, synthesizes corrosion-resistant alloys, and recommends heat treatment and compositional variations of alloys that will improve their performance. Both the scientific and engineering viewpoints supplement each other in the diagnosis of corrosion damage and in the prescription of remedies.

1.2 IMPORTANCE OF CORROSION

The three main reasons for the importance of corrosion are: economics, safety, and conservation. To reduce the economic impact of corrosion, corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, as well as the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on. Corrosion can compromise the safety of operating equipment by causing failure (with catastrophic consequences) of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms. Safety is a critical consideration in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Loss of metal by corrosion is a waste not only of the metal, but also of the energy, the water, and the human effort that was used to produce and fabricate the metal structures in the first place. In addition, rebuilding corroded equipment requires further investment of all these resources—metal, energy, water, and human.

Economic losses are divided into (1) direct losses and (2) indirect losses. Direct losses include the costs of replacing corroded structures and machinery or their components, such as condenser tubes, mufflers, pipelines, and metal roofing, including necessary labor. Other examples are (a) repainting structures where prevention of rusting is the prime objective and (b) the capital costs plus maintenance of cathodic protection systems for underground pipelines. Sizable direct losses are illustrated by the necessity to replace several million domestic hot-water tanks each year because of failure by corrosion and the need for replacement of millions of corroded automobile mufflers. Direct losses include the extra cost of using corrosion-resistant metals and alloys instead of carbon steel where the latter has adequate mechanical properties but not sufficient corrosion resistance; there are also the costs of galvanizing or nickel plating of steel, of adding corrosion inhibitors to water, and of dehumidifying storage rooms for metal equipment.

The economic factor is a very important motivation for much of the current research in corrosion. Losses sustained by industry and by governments amount to many billions of dollars annually, approximately $276 billion in the United States, or 3.1% of the Gross Domestic Product (GDP), according to a recent study [1]. It has been estimated that about 25–30% of this total could be avoided if currently available corrosion technology were effectively applied [1].

Studies of the cost of corrosion to Australia, Great Britain, Japan, and other countries have also been carried out. In each country studied, the cost of corrosion is approximately 3–4 % of the Gross National Product [2].

Indirect losses are more difficult to assess, but a brief survey of typical losses of this kind compels the conclusion that they add several billion dollars to the direct losses already outlined. Examples of indirect losses are as follows:

1. *Shutdown.* The replacement of a corroded tube in an oil refinery may cost a few hundred dollars, but shutdown of the unit while repairs are underway may cost $50,000 or more per hour in lost production. Similarly, replacement of corroded boiler or condenser tubes in a large power plant may require $1,000,000 or more per day for power purchased from interconnected electric systems to supply customers while the boiler is down. Losses of this kind cost the electrical utilities in the United States tens of millions of dollars annually.
2. *Loss of Product.* Losses of oil, gas, or water occur through a corroded-pipe system until repairs are made. Antifreeze may be lost through a corroded auto radiator; or gas leaking from a corroded pipe may enter the basement of a building, causing an explosion.
3. *Loss of Efficiency.* Loss of efficiency may occur because of diminished heat transfer through accumulated corrosion products, or because of the clogging of pipes with rust necessitating increased pumping capacity. It has been estimated that, in the United States, increased pumping capacity, made necessary by partial clogging of water mains with rust, costs many millions of dollars per year. A further example is provided by internal-combustion engines of automobiles where piston rings and cylinder walls are continuously corroded by combustion gases and condensates. Loss of critical dimensions leading to excess gasoline and oil consumption can be caused by corrosion to an extent equal to or greater than that caused by wear. Corrosion processes can impose limits on the efficiencies of energy conversion systems, representing losses that may amount to billions of dollars.
4. *Contamination of Product.* A small amount of copper picked up by slight corrosion of copper piping or of brass equipment that is otherwise durable

may damage an entire batch of soap. Copper salts accelerate rancidity of soaps and shorten the time that they can be stored before use. Traces of metals may similarly alter the color of dyes. Lead equipment, otherwise durable, is not permitted in the preparation of foods and beverages because of the toxic properties imparted by very small quantities of lead salts. The U.S. Bureau of Food and Drugs, for example, permits not more than 1 ppb of lead in bottled drinking water [3].

Similarly, soft waters that pass through lead piping are not safe for drinking purposes. The poisonous effects of small amounts of lead have been known for a long time. In a letter to Benjamin Vaughn dated July 31, 1786, Benjamin Franklin [4] warned against possible ill effects of drinking rain water collected from lead roofs or consuming alcoholic beverages exposed to lead. The symptoms were called in his time "dry bellyache" and were accompanied by paralysis of the limbs. The disease originated because New England rum distillers used lead coil condensers. On recognizing the cause, the Massachusetts Legislature passed an act outlawing use of lead for this purpose.

Another form of contamination is spoilage of food in corroded metal containers. A cannery of fruits and vegetables once lost more than $1 million in one year before the metallurgical factors causing localized corrosion were analyzed and remedied. Another company, using metal caps on glass food jars, lost $0.5 million in one year because the caps perforated by a pitting type of corrosion, thereby allowing bacterial contamination of the contents.

5. *Overdesign.* Overdesign is common in the design of reaction vessels, boilers, condenser tubes, oil-well sucker rods, pipelines transporting oil and gas at high pressure, water tanks, and marine structures. Equipment is often designed many times heavier than normal operating pressures or applied stresses would require in order to ensure reasonable life. With adequate knowledge of corrosion, more reliable estimates of equipment life can be made, and design can be simplified in terms of materials and labor. For example, oil-well sucker rods are normally overdesigned to increase service life before failure occurs by corrosion fatigue. If the corrosion factor were eliminated, losses would be cut at least in half. There would be further savings because less power would be required to operate a lightweight rod, and the expense of recovering a lightweight rod after breakage would be lower.

Indirect losses are a substantial part of the economic tax imposed by corrosion, although it is difficult to arrive at a reasonable estimate of total losses. In the event of loss of health or life through explosion, unpredictable failure of chemical equipment, or wreckage of airplanes, trains, or automobiles through sudden failure by corrosion of critical parts, the indirect losses are still more difficult to assess and are beyond interpretation in terms of dollars.

1.3 RISK MANAGEMENT

In general, risk, R, is defined as the probability, P, of an occurrence multiplied by the consequence, C, of the occurrence; that is,

$$R = P \times C$$

Hence, the risk of a corrosion-related failure equals the probability that such a failure will take place multiplied by the consequence of that failure. Consequence is typically measured in financial terms—that is, the total cost of a corrosion failure, including the cost of replacement, clean-up, repair, downtime, and so on.

Any type of failure that occurs with high consequence must be one that seldom occurs. On the other hand, failures with low consequence may be tolerated more frequently. Figure 1.1 shows a simplified approach to risk management.

Managing risk is an important part of many engineering undertakings today. Managing corrosion is an essential aspect of managing risk. Firstly, risk management must be included in the design stage, and then, after operation starts, maintenance must be carried out so that risk continues to be managed. Engineering design must include corrosion control equipment, such as cathodic protection systems and coatings. Maintenance must be carried out so that corrosion is monitored and significant defects are repaired, so that risk is managed during the operational lifetime.

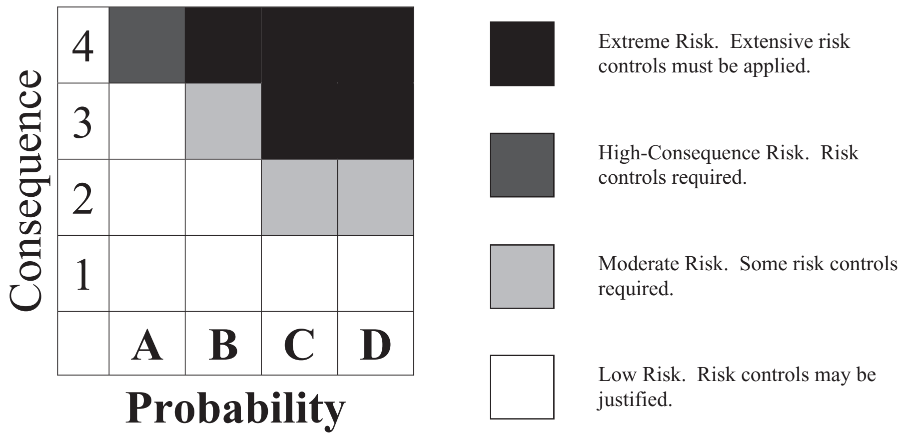

Figure 1.1. A simplified approach to risk management, indicating qualitatively the areas of high risk, where both consequence and probability are high.

1.4 CAUSES OF CORROSION

The many causes of corrosion will be explored in detail in the subsequent chapters of this book. In this introductory chapter, two parameters are mentioned: the change in Gibbs free energy and the Pilling–Bedworth ratio [5].

1.4.1 Change in Gibbs Free Energy

The change in Gibbs free energy, ΔG, for any chemical reaction indicates the tendency of that reaction to go. Reactions occur in the direction that lowers the Gibbs free energy. The more negative the value of ΔG, the greater the tendency for the reaction to go. The role of the change in Gibbs free energy is discussed in detail in Chapter 3.

1.4.2 Pilling–Bedworth Ratio

Although many factors control the oxidation rate of a metal, the Pilling–Bedworth ratio is a parameter that can be used to predict the extent to which oxidation may occur. The Pilling–Bedworth ratio is Md/nmD, where M and D are the molecular weight and density, respectively, of the corrosion product scale that forms on the metal surface during oxidation; m and d are the atomic weight and density, respectively, of the metal, and n is the number of metal atoms in a molecular formula of scale; for example, for Al_2O_3, $n = 2$.

The Pilling–Bedworth ratio indicates whether the volume of the corrosion product is greater or less than the volume of the metal from which the corrosion product formed. If $Md/nmD < 1$, the volume of the corrosion product is less than the volume of the metal from which the product formed. A film of such a corrosion product would be expected to contain cracks and pores and be relatively nonprotective. On the other hand, if $Md/nmD > 1$, the volume of the corrosion product scale is greater than the volume of the metal from which the scale formed, so that the scale is in compression, protective of the underlying metal. A Pilling–Bedworth ratio greater than 1 is not sufficient to predict corrosion resistance. If $Md/nmD >> 1$, the scale that forms may buckle and detach from the surface because of the higher stresses that develop. For aluminum, which forms a protective oxide and corrodes very slowly in most environments, the Pilling–Bedworth ratio is 1.3, whereas for magnesium, which tends to form a nonprotective oxide, the ratio is 0.8. Nevertheless, there are exceptions and limitations to the predictions of the Pilling–Bedworth ratio, and these are discussed in Chapter 11.

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PROBLEMS

1. A manufacturer provides a warranty against failure of a carbon steel product within the first 30 days after sale. Out of 1000 sold, 10 were found to have failed by corrosion during the warranty period. Total cost of replacement for each failed product is approximately $100,000, including the cost of environmental clean-up, loss of product, downtime, repair, and replacement.

(*a*) Calculate the risk of failure by corrosion, in dollars.
(*b*) If a corrosion-resistant alloy would prevent failure by corrosion, is an incremental cost of $100 to manufacture the product using such an alloy justified? What would be the maximum incremental cost that would be justified in using an alloy that would prevent failures by corrosion?

2. Linings of tanks can fail because of salt contamination of the surface that remains after the surface is prepared for the application of the lining. Between 15% and 80% of coating failures have been attributed to residual salt contamination. The cost of reworking a failed lining of a specific tank has been estimated at $174,000. [Reference: H. Peters, Monetizing the risk of coating failure, *Materials Performance* **45**(5), 30 (2006).]
(*a*) Calculate the risk due to this type of failure assuming that 20% of failures are caused by residual salt contamination.
(*b*) If the cost of testing and removal of contaminating salts is $4100, is this additional cost justified based on the risk calculation in (*a*)?
(*c*) Calculate the minimum percentage of failures caused by residual salt contamination at which the additional cost of $4100 for testing and removal of these salts is justified.