CHAPTER 1

Introduction to Corrosion

1.1 Historical Background

'Lay not up for yourselves treasures upon earth where moth and rust doth corrupt and where thieves break-through and steal.'

(Mathew 6:14)

The word corrosion is as old as the earth, but it has been known by different names. Corrosion is known commonly as rust, an undesirable phenomena which destroys the luster and beauty of objects and shortens their life. A Roman philosopher, Pliny (AD 23–79) wrote about the destruction of iron in his essay 'Ferrum Corrumpitar.' Corrosion since ancient times has affected not only the quality of daily lives of people, but also their technical progress. There is a historical record of observation of corrosion by several writers, philosophers and scientists, but there was little curiosity regarding the causes and mechanism of corrosion until Robert Boyle wrote his 'Mechanical Origin of Corrosiveness.'

Philosophers, writers and scientists observed corrosion and mentioned it in their writings:

- Pliny the elder (AD 23–79) wrote about spoiled iron.
- Herodotus (fifth century BC) suggested the use of tin for protection of iron.
- Lomonosov (1743–1756).
- Austin (1788) noticed that neutral water becomes alkaline when it acts on iron.
- Thenard (1819) suggested that corrosion is an electrochemical phenomenon.
- Hall (1829) established that iron does not rust in the absence of oxygen.
- Davy (1824) proposed a method for sacrificial protection of iron by zinc.
- De la Rive (1830) suggested the existence of microcells on the surface of zinc.

The most important contributions were later made by Faraday (1791–1867) [1] who established a quantitative relationship between chemical action and electric current. Faraday's first and second laws are the basis for calculation of corrosion rates of metals. Ideas on corrosion control started to be generated at the beginning of nineteenth century. Whitney (1903) provided a scientific basis for corrosion control based on electrochemical observation. As early as in eighteenth century it was observed that iron corrodes rapidly in dilute nitric acid but remains unattacked in concentrated nitric acid. Schönbein in 1836 showed that iron could be made passive [2]. It was left to U. R. Evans to provide a modern understanding of the causes and control of corrosion based on his classical electrochemical theory in 1923. Considerable progress towards the modern understanding of corrosion was made by the contributions of Evans [3], Uhlig [4] and Fontana [5]. The above pioneers of modern corrosion have been identified with their well known books in the references given at the end of the chapter. Corrosion laboratories established in M.I.T, USA and University of Cambridge, UK, contributed significantly to the growth and development of corrosion science and technology as a multi disciplinary subject. In recent years, corrosion science and engineering has become an integral part of engineering education globally.

1.2 Definitions

Corrosion is a natural and costly process of destruction like earthquakes, tornados, floods and volcanic eruptions, with one major difference. Whereas we can be only a silent spectator to the above processes of destruction, corrosion can be prevented or at least controlled. Several definitions of corrosion have been given and some of them are reproduced below:

(A) Corrosion is the surface wastage that occurs when metals are exposed to reactive environments.
(B) Corrosion is the result of interaction between a metal and environments which results in its gradual destruction.
(C) Corrosion is an aspect of the decay of materials by chemical or biological agents.
(D) Corrosion is an extractive metallurgy in reverse. For instance, iron is made from hematite by heating with carbon. Iron corrodes and reverts to rust, thus completing its life cycle. The hematite and rust have the same composition (Fig. 1.1).
(E) Corrosion is the deterioration of materials as a result of reaction with its environment (Fontana).
(F) Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with the environment (Uhlig).

Despite different definitions, it can be observed that corrosion is basically the result of interaction between materials and their environment. Up to the 1960s, the term corrosion was restricted only to metals and their alloys and it did not incorporate ceramics, polymers, composites and semiconductors in its regime. The term corrosion now encompasses all types of natural and man-made materials including biomaterials and nanomaterials, and it is not confined to metals and alloys alone. The scope of corrosion is consistent with the revolutionary changes in materials development witnessed in recent years.

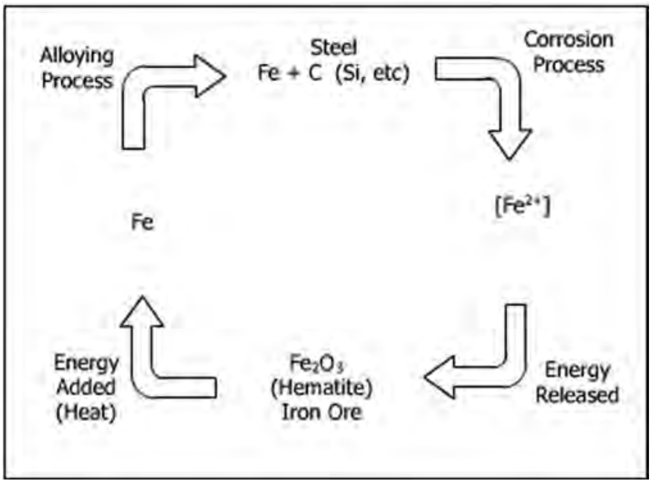

Figure 1.1 Refining-corrosion cycle

1.3 Corrosive Environment

Corrosion cannot be defined without a reference to environment. All environments are corrosive to some degree. Following is the list of typical corrosive environments:

(1) Air and humidity.
(2) Fresh, distilled, salt and marine water.
(3) Natural, urban, marine and industrial atmospheres.
(4) Steam and gases, like chlorine.
(5) Ammonia.
(6) Hydrogen sulfide.
(7) Sulfur dioxide and oxides of nitrogen.
(8) Fuel gases.
(9) Acids.
(10) Alkalies.
(11) Soils.

It may, therefore, be observed that corrosion is a potent force which destroys economy, depletes resources and causes costly and untimely failures of plants, equipment and components.

1.4 Consequences of Corrosion

Some important consequences of corrosion are summarized below:

- Plant shutdowns. Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.
- Loss of products, leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards. It is well known that at least 25% of water is lost by leakage.
- Loss of efficiency. Insulation of heat exchanger tubings and pipelines by corrosion products reduces heat transfer and piping capacity.
- Contamination. Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to the consumers.
- Nuclear hazards. The Chernobyl disaster is a continuing example of transport of radioactive corrosion products in water, fatal to human, animal and biological life.

The magnitude of corrosion would depend upon the sensitivity of a particular metal or alloy to a specific environment. For instance, copper corrodes rapidly in the presence of ammonia and it is a serious problem in agricultural areas. Many historical statues made from bronze have been destroyed by ammonia released from fertilizers. Environmental conditioning offers one method of controlling corrosion, such as the use of inhibitors and oil transmission pipelines.

1.5 Cost of Corrosion

In a study of corrosion cost conducted jointly by C. C. Technologies Inc., USA [6], Federal Highway Agencies (FHWA), USA [7] and National Association of Corrosion Engineers [8], the direct corrosion cost was estimated to be around 276 billion US dollars, approximately 3.1% of the national gross domestic product. Based on an extensive survey conducted by Battelle Columbus Laboratories, Columbus, Ohio, USA and National Institute of Standards and Technology (NIST), in 1975, the cost was estimated to be 82 billion US dollars, which would have exceeded 350 billion US dollars in view of price inflation over the last twenty-five years. Because of the long time involved in conducting cost structure, it is not possible to update the information every year. However, both studies show that corrosion costs are staggering and a figure of about 350 billion US dollars appears to be a reasonable estimate for another two to three years. At least 35% of the above amount could have been saved by taking appropriate corrosion control measures. In UK, the corrosion cost is estimated to be 4–5% of the GNP [4]. In Japan, the cost of corrosion is estimated to be 5258 trillion Yen per year. For most industrialized nations, the average corrosion cost is 3.5–4.5%

of the GNP. Below are some startling figures of corrosion losses:

- The corrosion cost of gas and liquid transmission pipelines in USA exceeds seven billion US dollars. The figure for the major oil producing countries in the Gulf region are not known, however the cost expected to be very high because of highly corrosive environment in the region [8].
- The corrosion-free life of automobiles in the coastal regions of Arabian Gulf is about six months only [9].
- Nearly 95% of concrete damage in the Arabian Gulf coastal region is caused by reinforcement corrosion and consequent spalling of concrete [10].
- It is estimated that 10% of all aircraft maintenance in USA is spent on corrosion remediation [11].
- Major annual corrosion losses to the tune of £350 million in transport, £280 million in marine, £250 million in buildings and construction and £180 million in oil and chemical industries, have been reported in UK [12]. These are uncorrected 1971 figures.
- About $120 billion is spent on maintenance of aging and deteriorating infrastructures in USA [13].
- Automotive corrosion costs 23.4 billion US dollars annually in USA [8].
- Every new born baby in the world now has an annual corrosion debt of $40.

1.6 Breakdown of Spending on Corrosion

The petroleum, chemical, petrochemical, construction, manufacturing, pulp and paper and transportation (railroad, automotive and aerospace) industries are the largest contributors to corrosion expenditure. The cost of corrosion differs from country to country. For instance in USA, the transportation sector is the largest sector contributing to corrosion after public utilities, whereas in the oil producing countries, such as the Arabian Gulf countries, petroleum and petrochemical industries are the largest contributor to corrosion expenditure. The highway sector in USA alone includes 4 000 000 miles of highways, 583 000 bridges, which need corrosion remediation maintenance [8]. The annual direct corrosion cost estimated to be 8.3 billion US dollars. The direct corrosion of transportation sector is estimated to be 29.7 billion US dollars. It includes the corrosion cost of aircraft, hazardous materials transport, motor vehicles, railroad car and ships [8]. In the oil sector, drilling poses severe hazards to equipment in the form of stress corrosion cracking, hydrogen induced cracking and hydrogen sulfide cracking [6]. In USA alone this sector costs more than 1.2 billion US dollars. The cost is very staggering in major oil producing countries, like Saudi Arabia, Iran, Iraq and Kuwait. The direct cost of corrosion to aircraft industry exceeds 2.2 billion US dollars [8].

Corrosion has a serious impact on defense equipment. In the Gulf War, a serious problem of rotor blade damage in helicopter was caused by the desert sand. The thickness of the blade was reduced to 2–3 mm in some instances. The desert erosion–corrosion offered a new challenge to corrosion scientists and engineers. The storage of defense equipment is a serious matter for countries with corrosive environments, such as Saudi Arabia, Malaysia and South-East Asia. Humidity is the biggest killer of defense hardware. Storage of defense equipment demands minimum humidity, scanty rainfall, alkaline soil, no dust storms, no marine environment and minimal dust particles.

From the above summary, it is observed that corrosion exists everywhere and there is no industry or house where it does not penetrate and it demands a state of readiness for engineers and scientists to combat this problem.

1.7 Corrosion Science and Corrosion Engineering

The term science covers theories, laws and explanation of phenomena confirmed by intersubjective observation or experiments. For instance, the explanation of different forms of corrosion, rates of corrosion and mechanism of corrosion is provided by corrosion science. Corrosion science is a 'knowing why' of corrosion. The term engineering, contrary to science, is directed towards an action for a particular purpose under a set of directions and rules for action and in a well-known phrase it is 'knowing how.' Corrosion engineering is the application of the principles evolved from corrosion science to minimize or prevent corrosion. Corrosion engineering involves designing of corrosion prevention schemes and implementation of specific codes and practices. Corrosion prevention measures, like cathodic protection, designing to prevent corrosion and coating of structures fall within the regime of corrosion engineering. However, corrosion science and engineering go hand-in-hand and they cannot be separated: it is a permanent marriage to produce new and better methods of protection from time to time.

1.8 Inter-disciplinary Nature of Corrosion

The subject of corrosion is inter-disciplinary and it involves all basic sciences, such as physics, chemistry, biology and all disciplines of engineering, such as civil, mechanical, electrical and metallurgical engineering.

1.9 Corrosion Education

The subject of corrosion has undergone an irreversible transformation from a state of isolated and obscurity to a recognized discipline of engineering. From the three universities in USA which offered courses in corrosion in 1946, corrosion courses are now offered by almost all major technical universities and institutions in USA, UK, Europe, South-East Asia, Africa and Japan. Corrosion is now considered as an essential component of design. Learned societies like National Association of Corrosion Engineers, European Federation of Corrosion, Japan Society of Corrosion Engineers and others are playing leading role in the development of corrosion engineering education. Detailed information on corrosion education, training centers, opportunities in corrosion can be found in various handbooks and websites. Some sources of information are listed in the bibliography. As a consequence of cumulative efforts of corrosion scientists and engineers, corrosion engineering has made quantum leaps and it is actively contributing to technological advancement ranging from building structures to aerospace vehicles.

1.10 Functional Aspects of Corrosion

Corrosion may severely affect the following functions of metals, plant and equipment:

(1) **Impermeability**: Environmental constituents must not be allowed to enter pipes, process equipment, food containers, tanks, etc. to minimize the possibility of corrosion.
(2) **Mechanical strength**: Corrosion should not affect the capability to withstand specified loads, and its strength should not be undermined by corrosion.
(3) **Dimensional integrity**: Maintaining dimensions is critical to engineering designs and they should not be affected by corrosion.
(4) **Physical properties**: For efficient operation, the physical properties of plants, equipment and materials, such as thermal conductivity and electrical properties, should not be allowed to be adversely affected by corrosion.
(5) **Contamination**: Corrosion, if allowed to build up, can contaminate processing equipment, food products, drugs and pharmaceutical products and endanger health and environmental safety.
(6) **Damage to equipment**: Equipment adjacent to one which has suffered corrosion failure, may be damaged.

Realizing that corrosion effectively blocks or impairs the functions of metals, plants and equipment, appropriate measures must be adopted to minimize loss or efficiency of function.

1.10.1 Health, Safety, Environmental and Product Life

These can involve the following:

(1) **Safety**: Sudden failure can cause explosions and fire, release of toxic products and collapse of structures. Several incidents of fire have been reported due to corrosion causing leakage of gas and oil pipelines. Corrosion adversely affects the structural integrity of components and makes them susceptible to failure and accident. More deaths are caused by accidents in old cars because of the weakening of components by corrosion damage. Corrosion has also been a significant factor in several accidents involving civil and military aircraft and other transportation vehicles. Corrosion failure involving bridges, ships, airports, stadiums are too numerous to be mentioned in detail in this chapter and recorded in the catalog of engineering disasters [11].

(2) **Health**: Adverse effects on health may be caused by corroding structures, such as a plumbing system affecting the quality of water and escaping of products into the environment from the corroded structures.

(3) **Depletion of resources**: Corrosion puts a heavy constraint on natural resources of a country because of their wastage by corrosion. The process of depletion outweighs the discovery of new resources which may lead to a future metal crisis similar to the past oil shortage.

(4) **Appearance and cleanliness**: Whereas anesthetics numb the senses, aesthetics arouse interest, stimulate and appeal to the senses, particularly the sense of beauty. A product designed to function properly must have an aesthetic appeal. Corrosion behaves like a beast to a beauty. It destroys the aesthetic appeal of the product and damages the product image which is a valuable asset to a corporation. Surface finishing processes, such as electroplating, anodizing, mechanical polishing, electro polishing, painting, coating, etching and texturing all lead to the dual purpose of enhancement of aesthetic value and surface integrity of the product.

(5) **Product life**: Corrosion seriously shortens the predicted design life, a time span after which replacement is anticipated. Cars have, in general, a design life of twelve years, but several brands survive much longer. A DC-3 aircraft has a design life of twenty years but after sixty years they are still flying. The Eiffel Tower had a design life of two years only, and even after one hundred years it is still a grand symbol of Paris. The reason for their survival is that the engineers made use of imaginative designs, environmental resistant materials and induction of corrosion-free maintenance measures. Distinguished and evocative designs always survive whereas designs of a transitory nature deteriorate to extinction with time. Design life is a process of imagination, material selection and corrosion-free maintenance.

(6) **Restoration of corroded objects**: Objects of outstanding significance to natural history need to be preserved. Many historical structures have been lost through the ravages of corrosion. One recent example is the call for help to restore the revolutionary iron-hulled steamships Great Britain built in 1843. It has been described as mother of all modern ships, measuring 3000 feet in length and weighing 1930 tons. A plea for £100 000 has been made for its restoration.

1.11 Five Good Reasons to Study Corrosion

(1) Materials are precious resources of a country. Our material resources of iron, aluminum, copper, chromium, manganese, titanium, etc. are dwindling fast. Some day there will be an acute shortage of these materials. An impending metal crisis does not seem

anywhere to be a remote possibility but a reality. There is bound to be a *metal crisis* and we are getting the signals. To preserve these valuable resources, we need to understand how these resources are destroyed by corrosion and how they must be preserved by applying corrosion protection technology.

(2) Engineering knowledge is incomplete without an understanding of corrosion. Aeroplanes, ships, automobiles and other transport carriers cannot be designed without any recourse to the corrosion behavior of materials used in these structures.

(3) Several engineering disasters, such as crashing of civil and military aircraft, naval and passenger ships, explosion of oil pipelines and oil storage tanks, collapse of bridges and decks and failure of drilling platforms and tanker trucks have been witnessed in recent years. Corrosion has been a very important factor in these disasters. Applying the knowledge of corrosion protection can minimize such disasters. In USA, two million miles of pipe need to be corrosion-protected for safety.

(4) The designing of artificial implants for the human body requires a complete understanding of the corrosion science and engineering. Surgical implants must be very corrosion-resistant because of corrosive nature of human blood.

(5) Corrosion is a threat to the environment. For instance, water can become contaminated by corrosion products and unsuitable for consumption. Corrosion prevention is integral to stop contamination of air, water and soil. The American Water Works Association needs US$ 325 billion in the next twenty years to upgrade the water distribution system.

Questions

Conceptual Questions

1. Explain how corrosion can be considered as extractive metallurgy in reverse.
2. List five important consequences of corrosion.
3. Which is the most common cause of corrosion damage, corrosion fatigue, stress corrosion cracking or pitting corrosion?
4. Describe with an example how corroded structures can lead to environmental pollution.
5. Does corrosion affect humans? If so, explain how.
6. Describe two engineering disasters in which corrosion played a leading role.
7. State two important corrosion websites.
8. How can corroded structures be injurious to human health?
9. Name three cities in South-East Asia and the Middle East which have the most corrosive environment.
10. What is the best way to minimize the corrosion of defense equipment during storage?
11. What is the relationship between depletion of natural resources and corrosion?

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