

An Introduction to Metallic Corrosion and Its Prevention

Raj Narayan



AN INTRODUCTION TO METALLIC CORROSION AND ITS PREVENTION

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To
my wife
VIBHA

Preface

Corrosion is the deterioration of the useful properties of materials caused by the environment. Both direct and indirect losses due to corrosion are huge and will further increase with industrialisation. A substantial portion of the government and industrial funds are being spent all over the world for combating corrosion losses. The corrosion problem needs to be brought forcibly to the attention of engineers of all disciplines and in all fields of endeavour. The corrosion of metals is a matter as much of economic and technical concern. It affects economy, safety, product reliability, and people-oriented activities.

Engineers in all fields should have an appreciation of the possible causes of corrosion and methods of its prevention. In fact, corrosion offers an attractive field of interdisciplinary study. A course on fundamentals of corrosion and its prevention is offered in all the well-known universities of the world. In India too, a course on corrosion has been included in the undergraduate engineering curriculum of some universities, but the impact is far from satisfactory. One major reason for this is the non-availability of suitable textbooks on the subject.

This book has been written in order to meet the urgent need of a suitable textbook on corrosion. The main emphasis in this book has been laid on the principles of metallic corrosion and its prevention, rather than provide exhaustive data on the corrosion behaviour of different metals and alloys. Such data, if needed, can be obtained from standard corrosion handbooks. The subject matter of the book can be easily covered in one semester. Solved problems have been included to assist students in assimilating the information given. References to related literature have been provided to help the inquisitive reader. It should be emphasised that the list of references is not an exhaustive one in any way.

I am indebted to a number of colleagues and students who have gone through the notes and given many suggestions for improvement. I am grateful to Dr. K.P. Singh for his encouragement and interest.

I shall appreciate if omissions and mistakes are brought to my notice. I shall also welcome suggestions for any improvement.

*Kanpur
March, 1983*

RAJ NARAYAN

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Introduction

1.1. Definition

Corrosion can be defined in many ways. The one most preferred in literature is the loss of useful properties of a material as a result of chemical or electrochemical reaction with its environment. Loss due to purely mechanical forces is not called corrosion but is known as wear, fretting, etc. In some cases chemical or electrochemical attack may be accompanied by physical deterioration and is described by terms: corrosion-erosion, corrosive-wear or fretting-corrosion.

According to this general definition materials other than metals, such as ceramics, plastics or concrete, may also corrode. When no particular mention is made of the material, however, it is normally understood that a metal is being attacked. It is in this limited sense, unless otherwise stated, that the term corrosion shall be used in this book.

The well-recognized example of metallic corrosion is the rusting of iron and steel. Besides this there are numerous other familiar examples of corrosion reactions. Silver articles tarnish and finally go black in the atmosphere; here, the transformation of silver to its black sulphide does not amount to a serious loss of the costly metal, but steps have to be taken to restore the surface to its former lustre. A similar loss of appearance is involved in the dulling of brass and the fogging of nickel.

Corrosion engineering is the science and art to prevent or control corrosion economically and safely. The corrosion specialist is concerned with the study of corrosion mechanisms through which a better understanding is obtained of the causes of corrosion and the available means for preventing or minimizing its damage. He thus applies accumulated scientific knowledge to combat corrosion damage through practical and economical methods.

1.2. Cost of Corrosion

Losses due to corrosion could be direct or indirect. Direct losses may include:

- inability to use otherwise desirable materials.
- over-design to allow for corrosion.
- the cost of repair or replacement of the corroded component or equipment.
- cost of anti-corrosive painting or other protection methods.

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Indirect losses may be either economical or social. These may include

- contamination of the product.
- loss of valuable product from a container that has corroded through.
- damage of equipment adjacent to that in which corrosion failure occurs.
- loss of production.
- safety, e.g., sudden failure of equipment may cause fire, explosion or release of toxic product.
- appearance, e.g., corroded material is usually unpleasant to the eye.

The annual cost of corrosion in India and other countries is enormous (See Table 1.1).

Table 1.1. Cost of corrosion in different countries

Country	Cost
India	Rs. 600 crores [1]
USA	Rs. 28,000 crores [2]
UK	Rs. 2,300 crores [3]
Hungary	Rs. 265 crores [4]

1.3. Importance of Corrosion Studies

It is nowadays necessary to pay more attention to metallic corrosion than was done earlier due to

- increasing use of metals in all fields of technology.
- use of rare and expensive metals whose protection requires special precautions.
- use of new high strength alloys which are usually more susceptible to certain types of corrosive attack.
- increasing pollution of air and water resulting in a more corrosive environment.
- strict safety standards of operating equipment which may fail in a catastrophic manner due to corrosion.

Corrosion studies have also become important due to increasing awareness of the need to conserve the world's metal resources. A report prepared by the US Bureau of Mines in 1970, quoted the time left before some of the more important proven non-renewable metal resources would be exhausted. Assuming the present rate of consumption, the figures reported were 95 years for chromium, 93 years for iron and steel, 53 years for nickel and 13 years for mercury. Even though yet undiscovered reserves might yield a four-fold increase in these materials, the time left before resources of many important metals are exhausted is limited, and in the meantime their prices will become exorbitant. Rapidly diminishing metal resources will have far more profound effect on civilization than the much publicised energy crisis. Many energy resources are still available for commercial exploitation. However, as yet, there exist no practical substitutes to many commonly used metals and alloys whose specific engineering properties make them indispensable. Evidently more concern must be shown for conservation of metals by minimizing losses due to corrosion. This would necessitate that basic principles of corrosion and its prevention are included in the curriculum of all branches of engineering.

It has been argued by some that corrosion is unavoidable. However, through better appreciation of its basic principles the losses can be considerably reduced. For example, an

inexpensive sacrificial anode of magnesium could more than double the life of a pipeline. Regular washing, cleaning and maintenance painting programme prolongs component life and pays itself many times over.

In 1971 a Government sponsored Committee in UK estimated that by making proper use of existing products and techniques for corrosion prevention over 25% of the estimated annual loss due to corrosion could be easily saved. Assuming that such a saving can be made in India also the amount saved could be approximately Rs. 150 crores per year.

Despite the harmful effects of corrosion as outlined above, it is, however, desirable and beneficial in some cases. For example, metallographic examination of metallic structures will not be practicable unless corroding action of the etchants is used to reveal the grain boundaries, etc. Electrochemical machining is widely used to machine the hard and difficult-to-machine parts economically. Anodizing of aluminium is another beneficial corrosion process used for obtaining better appearance and corrosion resistance.

1.4. Classification of Corrosion

Corrosion has been classified in many different ways. One method divides it into high temperature and low temperature corrosion. Another classifies it into wet and dry corrosion. The preferred classification based on the mechanisms separates corrosion in the following two types.

1. *Electrochemical Corrosion* which involves an interface. It can be further separated into:

(a) *Separable anode/cathode type*: In these cases certain areas of the metal can be experimentally identified as predominantly anodic or cathodic. The distances of separation of these areas may be very small, of the order of fractions of a millimetre. There is a macroscopic flow of charge through the metal.

(b) *Interfacial anode/cathode type*: Here one entire interface will be cathode and the other will be anode. In this case the charge is transported through a film of reaction product on the metal surface.

(c) *Inseparable anode/cathode type*. Here the anodes and cathodes cannot be distinguished by experimental methods, though their presence is postulated by theory, e.g. the uniform dissolution of metal in fused salt non-aqueous solution, acid, alkaline or neutral solutions.

2. *Chemical Corrosion* which involves direct chemical reaction of a metal with its environment. There is no transport of electric charge and the metal remains film free. This would include corrosion in gaseous environments when the reaction product is volatile, corrosion in liquid metals, fused halides and organic liquids.

1.5. Expressions for Corrosion Rate

Throughout our studies we shall be comparing different materials on the basis of their corrosion resistance. Weight loss measurements are most commonly used to measure corrosion resistance. A specimen is cleaned, degreased, measured, weighed, exposed to the corrodent for a known time, removed, cleaned to remove the corrosion products and reweighed. The rate of metal

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removal due to corrosion is then calculated from:

$$R = KW/ATD \quad (1.1)$$

where R is the corrosion rate

K is a constant

W is the weight loss to the nearest 0.0001 g (corrected for any loss during cleaning)

A is the area of the specimen to the nearest 0.01 sq cm

T is the time of exposure to the nearest 0.01 hour

D is the density in g/cu cm

This method cannot be applied if the corrosion is highly selective, such as intergranular or preferential corrosion and deep pitting. In the first case the method cannot be used because it is difficult to remove the corrosion products, and in the second because the depth of pit may be an important factor which affects the strength of the metal more than loss in weight.

The accuracy of determination of corrosion resistance by weight loss depends on how completely corrosion products are removed from the specimens and how much of the noncorroded metal is dissolved in the cleaning reagent. To avoid or minimize the error it is necessary to carry out a control test, irrespective of the method used to remove the corrosion products. The amount of metal dissolved by the reagent used for cleaning the corrosion product must be determined. If the weight loss caused by cleaning is more than 10% of the average weight loss caused by corrosion, alternative method for removing the corrosion products should be used.

The method used for removing the corrosion product depends on properties of the metal and the corrosion product.

A variety of units have been used in the literature to express the corrosion rate. Using the units for T , A , W and D given in Eq. (1.1), corrosion rate can be calculated in different units with the appropriate value of K (Appendix A1). If desired, these constants may also be used to convert corrosion rates from one set of units to another. To convert corrosion expressed in units x to a rate in units y , multiply by K_y/K_x . For example, if R is 10 mpy, the rate in mm/yr would be

$$10 \left(\frac{8.76 \times 10^4}{3.45 \times 10^6} \right) = 0.254 \text{ mm/yr}$$

The unit commonly used in American and British literature is milligrams per square decimetre per day (mdd). It includes the effect of the exposed area and the duration of exposure. However, it has a serious disadvantage, it does not express corrosion resistance in terms of penetration. From an engineering viewpoint the rate of penetration, or the thinning of a structural component can be directly used to predict the life of a given component. The four expressions—*inches per year*, *inches per month*, *millimetres per year* and *mils per year*—express corrosion rate directly in terms of penetration. Since the corrosion rate of practically useful materials vary between 1 and 200 mpy, the use of this expression is preferred. Using this expression, it is possible to represent corrosion rate using small whole numbers. Appendix A2 gives constants to convert other units to mpy.

Densities of some commonly used metals and alloys are given in Appendix A3.

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2. M.G. Fontana, and N.D. Greene, Corrosion Engineering, McGraw-Hill, New York, pp. 377 (1978).
3. Anon., Anti-Corrosion, 26 (3), March (1979).
4. Anon., Current Titles in Electrochem., 11 (4), April (1979).

Corrosion Principles

2.1. Introduction

Corrosion resistance of a material depends on many factors. To understand corrosion principles one should have knowledge of several disciplines (Fig. 2.1).

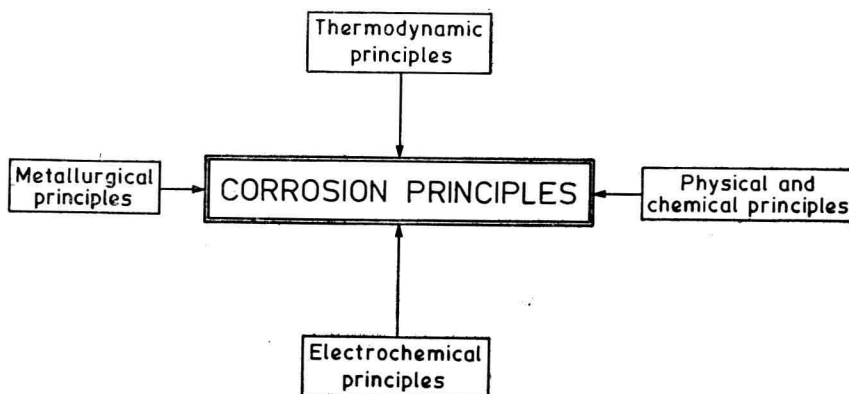


Fig. 2.1 Dependence of corrosion principles on other principles

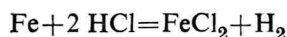
Thermodynamic principles can indicate the spontaneous direction of a chemical reaction. They can be used to determine whether or not corrosion is theoretically possible. Electrochemical principles including electrode kinetics can yield valuable information on the rate of different corrosion reactions. Metallurgical, physical and chemical principles also help to understand corrosion behaviour of a metal. In many cases the metallurgical structure of an alloy can be so changed as to improve its corrosion resistance. Since electrochemical and thermodynamic principles have the maximum importance in determining the corrosion behaviour of materials, we shall consider them in some detail.

2.2. Electrochemical Principles of Corrosion

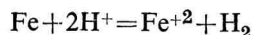
As stated in chapter 1 corrosion of metals can proceed either by a chemical or an electrochemical route, or by both taking place simultaneously. In wet corrosion, which usually occurs in electrically-conducting media (electrolytes), the electrochemical mechanism prevails to such a high extent that the purely chemical mechanism can be completely ignored.

The basic difference between the chemical and electrochemical mechanisms is in the overall reaction of metal with the environment. In the former case it takes place due to direct chemical reaction of a metal with the environment. The metal remains free and there is no transport of charge. In the latter case it takes place by two different processes, namely anodic and cathodic. The deteriorating or corroding metal leaves the metallic state at anodic areas as metallic cations which dissolve in the solution, that is, the metal is anodically converted to a solid compound. This anodic oxidation of metal is accompanied by a reduction of some constituent of the electrolyte at the cathodic areas. These anodes and cathodes may be of different metals as in the case of galvanic corrosion, or even of similar atoms perhaps only a few interatomic distances apart as in the case of corrosion of a single metal.

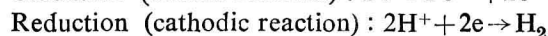
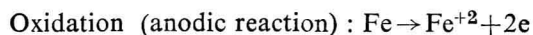
The electrochemical nature of corrosion can be illustrated by the attack of iron by hydrochloric acid. When iron is placed in dilute hydrochloric acid, a vigorous reaction occurs, as a result of which hydrogen gas is evolved and iron is dissolved. The reaction is:



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



Hence, iron reacts with the hydrogen ions of the acid solution to form iron ions and hydrogen gas. Thus the above reaction can be divided into two partial reactions:



The above anodic and cathodic reactions, known as partial reactions, 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 the conclusion that during metallic corrosion the rate of oxidation is equal to the rate of reduction (in terms of electron production and consumption). Corrosion occurs through formation of electrochemical cells in which the anode corrodes and the cathode is protected.

It should be emphasized here that until recently, corrosion theory has been usually based on the concept discussed in this chapter, of local cathodic and anodic areas. However, the modern mixed-potential theory based on electrode kinetic principles, described in later chapters, does not depend on assumptions regarding the distribution of local anodes and cathodes. In fact these two theories are not conflicting—they merely represent two different approaches to the subject of corrosion.

2.2.1. FARADAY'S LAWS

Electrochemical, including corrosion, reactions obey Faraday's laws of electrolysis. The basic laws discovered by Faraday in 1833 are as follows:

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Faraday's First Law: When a current is passing through a solution the amount of material going into or coming out of the solution is directly proportional to the amount of electricity (charge) passed through it. Thus, according to this law:

$$\begin{aligned} W &\propto It \\ W &= W_e It \end{aligned} \quad (2.1)$$

where W is the weight of the substance formed or dissolved at an electrode by the passage of current I amps for t seconds and W_e is its electrochemical equivalent. The electrochemical equivalent of a substance is defined as the mass which is liberated or dissolved by the passage of a constant current of a 1 amp for 1 second, i.e. 1 coulomb of electricity. If the current is not constant, we have

$$W = W_e \int_{t_1}^{t_2} I dt \quad (2.2)$$

Converse application of this law permits measurement of the quantity of electricity used by measuring the amount of the substance liberated or dissolved. The apparatus used for this purpose is called coulombmeter, since the quantity of electricity is measured in coulombs.

Appendix A4 gives electrochemical equivalents for different elements along with their valency.

Faraday's Second Law: The weights of various substances deposited or dissolved by one and same quantity of electricity are proportional to their respective equivalent weights. Thus, according to this law:

$$W \propto E$$

where W is the weight of the substance dissolved or deposited by the passage of certain quantity of electricity and E is the equivalent weight which is given by atomic weight A divided by the electrochemical valency n_e , i.e.

$$E = \frac{A}{n_e} \quad (2.3)$$

Thus H^+ , Ag^+ , $\frac{1}{2}Cu^{+2}$, $\frac{1}{2}Fe^{+2}$, $\frac{1}{3}Fe^{+3}$, $\frac{1}{2}(SO_4)^{-2}$, and $\frac{1}{4}Fe(CN_6)^{-2}$ have same equivalent weight. It follows that a given quantity of electricity will deposit twice the amount of metallic copper from a Cu^+ salt than from a Cu^{+2} salt.

From this law it follows that the same amount of electricity is required to dissolve or deposit 1 gm equivalent of a substance. This quantity is called Faraday and is denoted by symbol F . Recent experiments have established its value of 96483.7 coulombs per gram equivalent. (This value is based upon the modern scale of atomic weights in which the mass of nuclide C^{12} is taken to be exactly 12.) It is important to realize that 1 Faraday will produce each of the primary products of electrolysis. A primary product is one which is formed directly by the current rather than by subsequent chemical reaction.

The two laws can be combined in the following way. From second law, 1 Faraday will deposit or dissolve 1 gm-equivalent or A/n_e gm of a substance. Therefore, 1 coulomb will deposit or dissolve $A/n_e F$ gm of the substance. It has already been stated earlier that electrochemical

equivalent of a substance, W_e , is the mass of a substance deposited or dissolved by 1 coulomb. Therefore,

$$W_e = \frac{A}{n_e F} \quad (2.4)$$

Substituting this value in Eq. (2.1) we get

$$W = \frac{AIt}{n_e F} \quad (2.5)$$

The above equation representing the combined form of Faraday's first and second laws can be used to calculate the amount of a substance deposited or dissolved during electrolysis.

Faraday's laws are applicable to both fused and aqueous electrolytes, for initial step of the discharge of ions at the electrodes. However, deviations, which increase with temperature, are observed when these laws are tested experimentally. These deviations, which arise due to the following reasons, are usually more in fused salts than in aqueous electrolytes due to higher temperature of the former.

(i) *Recombination of primary products.* The cathodic products of electrolysis may combine with anodic products and form the original salt. This results in a loss of current. The possibility of this recombination is more in case of fused electrolytes due to their high temperature. By using salt mixtures which melt below the melting point of pure salts, this effect can be avoided.

(ii) *Discharge of other ions.* Loss of current occurs due to the discharge of impurities or even necessary components of electrolysis at the electrodes. For example, electrolysis of acidified zinc sulphate does not lead to the deposition of one equivalent of zinc at the cathode for each Faraday of current passed. This is due to the discharge of H^+ ions along with Zn^{+2} ions which account for loss of current. Similarly, in fused salt electrolytes decomposition of moisture may be responsible for current loss due to the evolution of hydrogen and oxygen.

(iii) *Formation of compound at the electrode.* It has been observed in certain cases that formation of compound at the electrode results in current loss. For example, in the electrolysis of fused $BiCl_2$, chlorine is liberated at the anode while no metal is formed at the cathode due to formation of a compound.

(iv) *Dissolution of the electrode.* Current loss can also occur due to dissolution of the electrode in the electrolyte. This factor is mainly present in fused electrolytes but can be neglected in aqueous electrolytes.

(v) *Mechanical loss.* There can be mechanical loss of substances formed at the electrode depending upon the structure of the deposit. This factor can be important in both fused and aqueous electrolytes.

(vi) *Evaporation losses.* This is present in salts of metals having high vapour pressure, e.g. in the electrolysis of NaCl. High temperature promotes the evaporation of the metal.

EXAMPLE 2.1

A Daniel cell is discharging at 1/10 amp. What is the rate of corrosion of zinc rod anode in inch/day and mpy. The anode is 1 cm diameter and is immersed to a depth of 15 cm in the electrolyte (Density of zinc = 7 gm/cc; electrochemical equivalent of zinc = 0.3387 mg/coulomb).