Preface

Originally, this book was written in Norwegian, primarily for the teaching of corrosion theory and technology for students at the faculties of mechanical engineering and marine technology and for other interested people at various faculties of the Norwegian Institute of Technology (NTH) in Trondheim, now being a part of the Norwegian University of Science and Technology (NTNU). The book has also been used at some other universities and engineering schools in Scandinavian countries, and as a reference book for engineers in industry.

The book was written with the aim of combining a description of practical corrosion processes and problems with a theoretical explanation of the various types and forms of corrosion. Relatively much attention was paid to the effects upon corrosion of factors such as flow, heat, materials selection, design, surface conditions, and mechanical loads and impacts, as well as their roles in the development of different corrosion forms. The scope of the book is wet corrosion in general. However, because of the vital position of the offshore industry in Norway, several cases and aspects dealt with are related to marine technology and oil and gas production.

In general, this edition is based on my own work on corrosion and related subjects at NTH/NTNU and its associated research foundation, SINTEF, during 35–40 years. Results and experience from our research and engineering activities at SINTEF Corrosion Centre have deliberately been included because this work was done with the same objective in mind as was the teaching: to solve practical corrosion problems by more extensive use of theoretical tools and understanding, combined with empirical knowledge. My approach in this direction was particularly inspired by professor Almar-Næss. He started the first modern teaching of corrosion for students at the faculty of mechanical engineering and other typical engineering students at NTH in the early 1960s, and stimulated to my own engagement in the discipline. Considering the further work, I will like to acknowledge my nearest co-workers during many years, including the permanent staff at SINTEF Corrosion Centre as well as many former students. These people have carried out much of the research and engineering work that I have referred to. I hope that the many references that are made to their contributions show how important they have been.. Results from ones own research milieu are valuable directly as well as by the personal engagement they contribute to the teaching. These contributions to the book have, however, been balanced with a major proportion of general knowledge

and research results from the world around. Several figures and tables are reproduced from external publications.

The preparation of the manuscript has been supported by a number of persons, with contributions such as comments to the content or language details of specific sections, assistance in providing literature and pictures, help in formatting the manuscript etc. Acknowledgement for the use of photographs is made in the captions. I wish to thank all for their kindness and help.

Particularly, I will take the opportunity to express my thanks to Detlef Blankenburg, head of Department of Machine Design and Materials Technology, NTNU, for permission to use the facilities of the department, and Siw Brevik for all her efforts and patience in preparing the manuscript. Last but not least, I will thank my wife, Liv, who originally typed the manuscript and who has supported me in many ways, my younger family members Eirunn and Sigmund Bardal, for, respectively, comments to the language, and indispensable computer expertise and efforts during the final preparation of the manuscript, and the rest of my family for their patience and understanding.

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July, 2003
Einar Bardal

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2. Wet Corrosion: Characteristics, Prevention and Corrosion Rate

Mighty ships upon the ocean
suffer from severe corrosion.
Even those that stay at dockside
are rapidly becoming oxide
Alas, that piling in the sea
is mostly Fe_2O_3.
And when the ocean meets the shore
You´ll find there´s Fe_3O_4,
´cause when the wind is salt and gusty
things are getting awful rusty.

T.R.B. WATSON

2.1   Description of a Wet Corrosion Process

The main features of corrosion of a divalent metal M in an aqueous solution containing oxygen are presented schematically in Figure 2.1. The corrosion process consists of an anodic and a cathodic reaction. In the anodic reaction (oxidation) the metal is dissolved and transferred to the solution as ions M^{2+}. The cathodic reaction in the example is reduction of oxygen. It is seen that the process makes an electrical circuit without any accumulation of charges. The electrons released by the anodic reaction are conducted through the metal to the cathodic area where they are consumed in the cathodic reaction. A necessary condition for such a corrosion process is that the environment is a conducting liquid (an electrolyte) that is in contact with the metal. The electrical circuit is closed by ion conduction through the electrolyte. In accordance with the conditions this dissolution process is called wet corrosion, and the mechanism is typically electrochemical.

In the example in Figure 2.1 the metal ions M^{2+} are conducted towards OH^- ions, and together they form a metal hydroxide that may be deposited on the metal surface. If, for instance, the metal is zinc and the liquid is water containing O_2 but not CO_2, the pattern in the figure is followed: Zn^{2+} ions join OH^- and form $Zn(OH)_2$. When

CO_2 is dissolved in the liquid a zinc carbonate is deposited. Corrosion of substances like iron and copper follow similar patterns with modifications: divalent iron oxide, $Fe(OH)_2$, is not stable, thus with access of oxygen and water it oxidizes to a trivalent hydrated iron oxide, $Fe_2O_3 \cdot nH_2O$, or an iron hydroxide, $Fe(OH)_3$, which also may be expressed as $FeOOH + H_2O$. FeOOH is the ordinary red (or brown) rust. If the access of oxygen is strongly limited, Fe_3O_4 is formed instead of the trivalent corrosion products. Fe_3O_4 is black (without water) or green (with water). Divalent copper hydroxide, $Cu(OH)_2$, is not stable either and tends to be dehydrated to CuO [2.1].
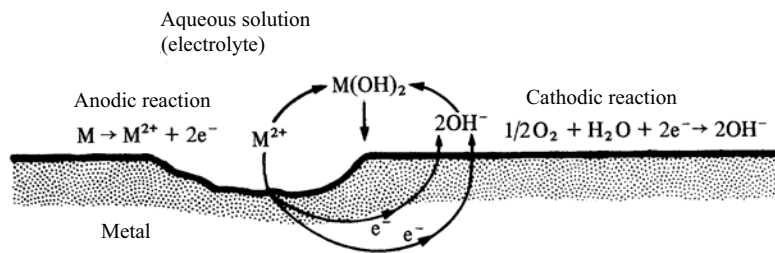

Figure 2.1 Wet corrosion of a divalent metal M in an electrolyte containing oxygen.

Reduction of oxygen is the dominating cathodic reaction in natural environments like seawater, fresh water, soil and the atmosphere. However, under certain conditions there are also other important cathodic reactions: the hydrogen reaction $2H^+ + 2e^- \Downarrow H_2$, reduction of carbonic acid (H_2CO_3) (in oil and gas production), reduction of metal ions etc. Various cathodic reactions are dealt with in Chapter 6.

Figure 2.1 illustrates an electrochemical cell, and the driving force for the electrochemical process (the corrosion) is the cell voltage, or in other words the potential difference between the anode and the cathode. This potential concept is developed further in Chapter 3.

2.2   Crucial Mechanisms Determining Corrosion Rates

It is seen that the corrosion process in Figure 2.1 depends on the availability of oxygen. When corrosion products, such as hydroxides, are deposited on a metal surface, they may cause a reduction in the oxygen supply because the oxygen has to diffuse through the deposits, which may form a more or less continuous layer on the metal surface. Since the rate of metal dissolution is equal to the rate of oxygen reduction (Figure 2.1), a limited supply and limited reduction rate of oxygen will also reduce the corrosion rate. In this case it is said that the corrosion is under cathodic control. This is a very widespread mechanism for corrosion limitation by

nature. If the corrosion products are removed from the metal surface by mechanisms such as the corrosion medium flowing at high velocity and corresponding strong fluid dynamical forces, the corrosion rate may be greatly increased (erosion corrosion, see Section 7.9).

In certain cases, the corrosion products form a dense and continuous surface film of oxide closely related to the crystallographic structure of the metal. Films of this type prevent the conduction of metal ions from the metal–oxide interface to the oxide–liquid interface to a great extent so that the corrosion rates may be very low (anodic control). This phenomenon is called passivation and is typical for materials like stainless steel and aluminium in many natural environments. Ordinary structural steels are also passivated in alkaline waters. Passivation is promoted by ample access of oxygen on the material surface, which is obtained by high oxygen concentration in the liquid and by efficient transport of oxygen as a result of strong convection (high flow rates). Conversely, passivation may be hindered – or a passive film may be broken down – by the lack of oxygen. This often happens underneath deposits and in narrow crevices that obstruct the oxygen supply (crevice corrosion, Section 7.5). Aggressive species like chlorides are other major causes of the local breakdown of passive films that occurs in crevice corrosion, pitting (Section 7.6) and other forms of corrosion.

When more and less noble materials are placed in contact, the more noble material offers an extra area for the cathodic reaction. Therefore the total rate of the cathodic reaction is increased, and this is balanced with an increased anodic reaction, i.e. increased dissolution of the less noble material (galvanic corrosion, Section 7.3). If the more noble material (the cathodic material) has a large surface area and the less noble metal (the anodic metal) has a relatively small area, a large cathodic reaction must be balanced by a correspondingly large anodic reaction concentrated in a small area. The intensity of the anodic reaction, i.e. the corrosion rate (material loss per area unit and time unit) becomes high. Thus, the area ratio between the cathodic and the anodic materials is very important and should be kept as low as possible. It should be mentioned that in a galvanic corrosion process, the more noble material is more or less protected. This is an example of cathodic protection, by which the less noble material acts as a sacrificial anode (see next section).

2.3   Corrosion Prevention Measures

Corrosion prevention aims at removing or reducing the effect of one or more of the conditions leading to corrosion using the following measures.:

1   Selecting a material that does not corrode in the actual environment.
2   Changing the environment, e.g. removing the oxygen or adding anticorrosion chemicals (inhibitors).
3   Using a design that will avoid corrosion, e.g. preventing the collection of water so that the metal surface can be kept dry.

4   Changing the potential, most often by making the metal more negative and thus counteracting the natural tendency of the positive metal ions to be transferred from the metal to the environment.
5   Applying coatings on the metal surface, usually in order to make a barrier between the metal and the corrosive environment.

Corrosion prevention is partly dealt with in connection with the various forms of corrosion in Chapter 7, and more generally in Chapter 10.

2.4   Expressions and Measures of Corrosion Rates

There are three main methods that are used to express the corrosion rate:

a)   Thickness reduction of the material per unit time.
b)   Weight loss per unit area and unit time.
c)   Corrosion current density.

Thickness reduction per unit time is the measure of most practical significance and interest. In the metric system this measure is usually expressed in mm/year. In some literature one can still find the unit mils per year (mpy) = 1/1000 inches per year, possibly also inches per year (ipy).

   Weight loss per unit area and unit time was commonly used in earlier times, mainly because weight loss was usually the directly determined quantity in corrosion testing. Here the test specimens were weighed before and after the exposure to the corrosion medium. On this basis one could calculate the thickness reduction as weight loss per unit area/density.

   From Figure 2.1 it can be understood that corrosion rate also can be expressed by corrosion current density. The dissolution rate (the corrosion rate) is the amount of metal ions removed from the metal per unit area and unit time. This transport of ions can be expressed as the electric current I_a per area unit, i.e. anodic current density i_a = corrosion current density i_{corr}.

   If it is preferred to express the local corrosion current density in the anodic area in Figure 2.1, one has $i_{corr} = i_a = I_a/A_a$, where A_a is the anodic area. However, usually the average corrosion current density over the whole surface area A is given, i.e. $i_{corr} = i_a = I_a/A$. The most suitable measure to employ for calculating the corrosion rate depends on which form of corrosion one is dealing with (Chapter 7).

   Corrosion current density is a particularly suitable measure of corrosion rate when treating corrosion theory and in connection with electrochemical corrosion testing. Current density is also directly applicable for cathodic and anodic protection (Sections 10.4 and 10.5). In corrosion testing the unit $\sigma A/cm^2$ is most often used. When dealing with cathodic protection the units mA/m^2 and A/m^2 are used for the cathode (structure to be protected) and the anode, respectively.

The relationship between thickness reduction per time unit ds/dt (on each corroding side of the specimen/component) and the corrosion current density i_{corr} is determined from Faraday's equations:

$$\frac{ds}{dt} = \frac{i_{corr}\, M}{z\, F} \quad cm/s \tag{2.1a}$$

or

$$\frac{s}{t} = 3268\, \frac{i_{corr}\, M}{z} \quad mm/year , \tag{2.1b}$$

where i_{corr} is given in A/cm^2;

> z = number of electrons in the reaction equation for the anodic reaction (dissolution reaction) (per atom of the dissolving metal);
> M = the mol mass of the metal (g/mol atoms) (the numerical value of M is the atomic weight of the metal);
> F = Faraday's constant = 96,485 coulombs/mole electrons = 96,485 $C/mol\ e^-$ = 96,500 $As/mol\ e^-$ [2.2];
> ψ = the density of the metal (g/cm^3).

Table 2.1 shows the conversion factors between the units of corrosion rates that are most frequently used in the literature. Note that, for most of the listed materials, a corrosion current density of 1 $\mu A/cm^2$ corresponds to a thickness reduction of roughly 0.01 mm/year. As an example of practical corrosion rates it can be mentioned that structural steels in seawater normally corrode by 0.1–0.15 mm/year = 10–15 $\mu A/cm^2$ on average. The corrosion rate can be a few times higher locally.

Table 2.1   Corrosion rate conversion factors.

Material/reaction	Corrosion current density	Weight loss per unit area and unit time	Average attack depth increment per unit time	
	$\mu A/cm^2$	mdd*	mm/year	mpy*
Fe ⇓ Fe^{2+} + $2e^-$	1	2.51	1.16 x 10^{-2}	0.46
Cu ⇓ Cu^{2+} + $2e^-$	1	2.84	1.17 x 10^{-2}	0.46
Zn ⇓ Zn^{2+} + $2e^-$	1	2.93	1.5 x 10^{-2}	0.59
Ni ⇓ Ni^{2+} + $2e^-$	1	2.63	1.08 x 10^{-2}	0.43
Al ⇓ Al^{3+} + $3e^-$	1	0.81	1.09 x 10^{-2}	0.43
Mg ⇓ Mg^{2+} + $2e^-$	1	1.09	2.2 x 10^{-2}	0.89

*   mdd = mg per dm^2 per day.
     mpy = mils per year (1/1000 inches per year).

2.5 Basic Properties That Determine if Corrosion Is Possible and How Fast Material Can Corrode

The corrosion process in Figure 2.1 is an example of a so–called spontaneous electrochemical cell reaction. The driving force of the reaction is a reversible cell voltage. The cell voltage can be expressed as the difference between the potentials of the two electrodes (anode and cathode). Reversible cell voltage and the corresponding reversible potentials of the electrodes are determined by *thermodynamic properties.* These properties, which are dealt with in Chapter 3, mainly provide a possibility to determine the spontaneous *direction* which a given reaction tends to have. Applied to corrosion, the thermodynamics can tell us if corrosion is theoretically possible or not under given conditions.

The driving voltage of the cell reaction must cope with various types of resistance: a) resistance against charge transfer between a metal and the adjacent electrolyte at the anode and cathode, respectively; b) resistance due to limited access of reactants or limited removal of reaction products at the electrodes; c) ohmic resistance in the liquid and possibly in the metal between the anode and the cathode. The driving voltage and the sum of the resistances will together determine how fast the reactions will proceed, i.e. how fast a given material will corrode. Resistances against the reactions and the resulting reaction rates are described and explained under *electrode kinetics* (Chapter 4). In other words by using kinetic relationships we can determine *how fast* a material will corrode under certain conditions. Thermodynamics and electrode kinetics make up the two main parts of corrosion theory. These are the key to understanding and explaining the majority of practical corrosion problems. It is normal to apply this corrosion theory in modern corrosion testing, and it provides a more rational basis for corrosion prevention and monitoring.

References

2.1   Pourbaix M. Lectures on Electrochemical Corrosion. New York–London: Plenum Press, 1973.
2.2   Zumdahl SS. Chemical Principles. Lexington, MA: D.C. Heath and Company, 1992.

EXERCISES

1.   Which reaction is the dominating cathodic reaction by corrosion in natural environments, such as seawater, fresh water, soil and condensation in the atmosphere? Write the reaction equation.

2. What types of corrosion products are usually deposited by corrosion in natural environments? What is rust? How can corrosion product deposits affect the corrosion rate?

3. Which property of the corrosion medium (the aqueous solution) is the most important prerequisite for electrochemical corrosion?

4. What can be said about the relationship between the anodic current I_a and the cathodic current I_c in a normal corrosion process?

5. A steel plate has corroded on both sides in seawater. After 10 years a thickness reduction of 3 mm is measured. Calculate the average corrosion current density. Take into consideration that the dissolution reaction is mainly $Fe \Downarrow Fe^{2+} + 2e^-$, and that the density and the atomic weight of iron are 7.8 g/cm^3 and 56, respectively.

6. What are the roles of thermodynamics and electrode kinetics in corrosion theory?