

CORROSION AND ITS CONTROL

2nd edition

An
Introduction
to the
Subject

Van Droffelaar
Atkinson



Corrosion and its Control An Introduction to the Subject

H. Van Droffelaar and J.T.N. Atkinson

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In memory of my friend, Dr. Jim A. Atkinson

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Preface

The second edition of *Corrosion and Its Control* has been marred by the untimely passing of my friend and co-author, Dr. Jim Atkinson, on April 15, 1991. Jim is sadly missed by his many friends, colleagues, and his family.

This book developed from the notes used by the authors for more than two decades in their course, "The Corrosion and Protection of Metals" taught to junior and senior students in various branches of engineering at Queen's University, Kingston, Ontario, Canada. The students have good backgrounds in basic science and engineering. The reader will find some background in chemistry, material science, and strength of materials of construction helpful.

The intention of the authors has been to emphasize the engineering aspects of corrosion and its control in ways that will be helpful to the practicing engineer. Therefore, chapters are included on corrosion economics, detecting and monitoring corrosion, regulations, specifications, safety, and a major section on the selection and use of materials of construction with special emphasis on the use and corrosion of stainless steels.

To the second edition we have added more than 100 pages of text distributed over the 17 chapters. We have placed particular emphasis on updating chapters on corrosion monitoring, corrosion fundamentals, and materials of construction, including plastics and failure analysis. We also have introduced a new chapter 18 dealing with an introduction of "The Use of the Computer in the Practice of Corrosion." We trust the reader will find the introduction to computers and a description of the "corrosion expert system" helpful and stimulating.

No attempt has been made to provide extensive coverage of corrosion data that can readily be found elsewhere, trusting the text will provide the engineer with the information to make critical use of such data.

In a book that developed in the fashion described, there have been numerous helpful discussions with the authors' colleagues at Queen's University; DuPont Canada, Inc.; Atomic Energy of Canada, Ltd. (AECL); and with members of the corrosion community in general. Specific mention of R.D. Watson of AECL for information on stretch oxidation and to T.R.B. Watson of Corrosion Services, Ltd. for permission to extract from his work on economics. Furthermore, we wish to express our appreciation to Dr. W. Thompson, Royal Military College, for providing data on computerized Pourbaix diagrams and to J. J. Lamoureux of L. Ecole Polytechnique, Montreal, for information on his "Corrosion Expert System." A special thanks to DuPont Canada, Inc. for their encouragement of the authors and their contribution of data and illustrations used in this book. And last, but not least, to Mrs. Shirley Donnelly of Queen's University for her assistance with the preparation of the book and to Cicely Wynne of NACE for her expedient and competent completion of the book manuscript.

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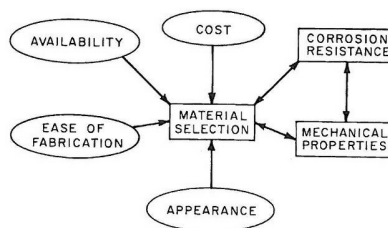
Introduction

Corrosion and its control is an important, but often neglected, element in the practice of engineering. Of necessity, it is a pragmatic subject since the proper solution to any corrosion problem is the most economical one, provided safety is assured. This solution is not always the most aesthetic; rust has to be tolerated whenever it is the least costly alternative. Of course, all cost elements, both direct and indirect, have to be considered. The proper solution to a corrosion situation often involves the use of low-cost, low-performance materials, such as carbon steel, with regular replacement as necessary.

Corrosion engineering seeks to minimize corrosion costs for a particular owner or operator. Because of the distorting influence of taxation on these costs, it does not necessarily minimize total corrosion costs for society as a whole. Nor does it necessarily minimize the energy requirement that results from the various anticorrosion strategies. Such considerations are outside the scope of this work.

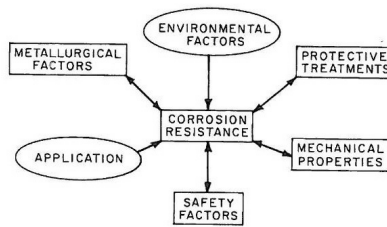
Selection of a material for use in a corrosion situation must be based on sound economics. Both the cost of the material and the ongoing cost of preventive measures must be included. Sound judgment about materials must include the recognition that the relative corrosion resistance of materials and the cost of supplementary protective measures can change significantly from one corrosive medium to another. For example, weathering steels have much better corrosion resistance than carbon steels in an unpolluted atmosphere. However, where chlorides are found, much of this advantage is lost; for immersion in chloride contaminated waters, weathering steels show no corrosion advantage at all.

The interrelationships in material selection are shown in Figure 1. Factors that influence material selection are distinguished from those that interact in a more complex fashion. For example, ease of fabrication influences selection because weldability, workability, etc. will define whether the material can be used for the intended application. On the other hand, mechanical properties are not uniquely defined for all environments. If the material is to be used at low temperatures (e.g., in the Arctic), embrittlement can be a serious problem. At high ambient pressure on the deep ocean floor, brittle behavior related to tensile stresses is much less of a problem. The endurance limit for corrosion fatigue can vary dramatically from one corrosive environment to another. Corrosion resistance is even more complicated, as indicated in Figure 2.



Factors affecting material selection: ○ direct influences; □ interactive factors.

Figure 1



Factors affecting corrosion resistance of a material: ○ direct influences; □ interactive factors.

Figure 2

The interactions between metallurgical factors and corrosion resistance are straightforward. Less obvious are the interactions with the application. For example, a system to contain drinking water or a pharmaceutical product, where contamination is stringently limited, can call for a more resistant material than would be specified on economic grounds alone. Protective treatments are viewed as a means of extending the use of a particular material; they carry an inevitable associated cost.

The performance level of the typical engineer in fighting corrosion has been seriously deficient. Enough surveys have been conducted to show that every developed country is spending about 4% of its gross national product on metallic corrosion, with close to 25% of this total being preventable by the application of appropriate known technology (Chapter 11). There also are serious cost and safety hazards associated with deterioration of nonmetallic structures. Creep and ultraviolet degradation are the prime culprits for plastics. A nonproductive expenditure of the magnitude indicated is more than the various national economies should have to bear. Strong action is needed.

The purpose of this text is to help equip the engineer with the knowledge to make appropriate choices in the struggle against corrosion through recognition and evaluation of all relevant factors. The public certainly is entitled to better protection than it has been getting.

Electrochemical Background of Corrosion

Virtually all known instances of metallic corrosion are electrochemical in nature, including high-temperature oxidation reactions. For this reason, a solid background in electrochemistry is essential with emphasis on the potential to current relationships when there is a departure from equilibrium. Most older texts are inadequate in this area; one of the best modern texts for self-study by a non-expert is Bockris and Reddy's *Modern Electrochemistry*.¹ Those who start with a better background in electrochemistry may prefer the more compact treatment in Bockris and Drazic's *Electrochemical Science*.²

Suppose a clean and pure electrode of each common metal is immersed in a 1N solution of one of its salts. Under these conditions, each metal will eventually assume its own unique potential. This potential cannot be measured directly because the available measuring devices can measure only a difference in potential. To overcome this limitation, we add a standard hydrogen electrode (SHE) to the system by means of a suitable salt bridge. The difference between the SHE and the electrode of the metal of interest can now be measured. Since the potential of the SHE is (by arbitrary definition) zero, the difference in potential between the SHE and the metal electrode gives the potential of the latter on the hydrogen scale thus defined.

Choice of a sign convention for whether the differences are plus or minus is arbitrary. However, it is convenient to assign positive potentials to metals such as copper and gold that are cathodic with respect to hydrogen, and negative potentials to metals such as iron and zinc that are anodic with respect to hydrogen. The collected values of these potentials are termed the electromotive series (Table 1.01). Additional data referring to redox potentials are given in Table 1.02.

Data from Table 1.01 permit the determination of the potential differences between any set of two metals, each immersed in a 1N solution of one of its own salts, with the electrolytic path completed by a salt bridge.

For example, the Daniell cell potential is correctly predicted as the copper potential minus the zinc potential (+0.337 minus -0.763 volts) for an overall potential difference of 1.1 volts. The classic form of the Daniell cell is a copper electrode in a copper sulfate solution, contained in a porous pot sitting in a larger container of zinc sulfate solution that contains a zinc electrode.

TABLE 1.01 The Electromotive Series

Electrode	Cell Reaction	E° (volts)
Li ⁺ ½ Li	½ H ₂ + Li ⁺ = Li + H ⁺	-3.025
K ⁺ ½ K	½ H ₂ + K ⁺ = K + H ⁺	-2.925
Ca ²⁺ ½ Ca	½ H ₂ + ½ Ca ²⁺ = ½ Ca + H ⁺	-2.870
Na ⁺ ½ Na	½ H ₂ + Na ⁺ = Na + H ⁺	-2.714
Mg ²⁺ ½ Mg	½ H ₂ + ½ Mg ²⁺ = ½ Mg + H ⁺	-2.370
Al ³⁺ ½ Al	½ H ₂ + 1/3 Al ³⁺ = 1/3 Al + H ⁺	-1.660
Zn ²⁺ ½ Zn	½ H ₂ + ½ Zn ²⁺ = ½ Zn + H ⁺	-0.763
Fe ²⁺ ½ Fe	½ H ₂ + ½ Fe ²⁺ = ½ Fe + H ⁺	-0.440
Cd ²⁺ ½ Cd	½ H ₂ + ½ Cd ²⁺ = ½ Cd + H ⁺	-0.402
Ni ²⁺ ½ Ni	½ H ₂ + ½ Ni ²⁺ = ½ Ni + H ⁺	-0.250
Sn ²⁺ ½ Sn	½ H ₂ + ½ Sn ²⁺ = ½ Sn + H ⁺	-0.136
Pb ²⁺ ½ Pb	½ H ₂ + ½ Pb ²⁺ = ½ Pb + H ⁺	-0.126
H ⁺ ½ H ₂ , Pt	½ H ₂ = H ⁺ + e	0.000
Cu ²⁺ ½ Cu	½ H ₂ + ½ Cu ²⁺ = ½ Cu + H ⁺	+0.337
Ag ⁺ ½ Ag	½ H ₂ + Ag ⁺ = Ag + H ⁺	+0.799
Au ⁺ ½ Au	½ H ₂ + Au ⁺ = Au + H ⁺	+1.680

In general: ½ H₂ + (Oxidized State) = H⁺ + (Reduced State).

TABLE 1.02 Selected Standard Redox Potentials

Reaction	E _o (volts)
Fe + S ²⁻ = FeS + 2e	-1.000
Ni + S ²⁻ = NiS (α) + 2e	-0.860
Cu + 2CN ⁻ = Cu(CN) ₂ ⁻ + e	-0.780
Cu + S ²⁻ = CuS + 2e	-0.760
Pb + SO ₄ ²⁻ = PbSO ₄ + 2e	-0.560
Ag + 2CN ⁻ = Ag(CN) ₂ ⁻ + e	-0.290
Cu + 4NH ₃ = Cu(NH ₃) ₄ ²⁺ + 2e	-0.050
Fe ²⁺ = Fe ³⁺ + e	+0.771
PbSO ₄ + 2H ₂ O = PbO ₂ + SO ₄ ²⁻ + 2e	+1.685

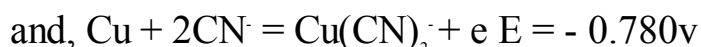
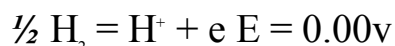
From Table 1.02, it is possible to draw further inferences. The presence of Fe³⁺ at the cathode of a corrosion cell where it can be reduced to Fe²⁺ can give a potent cathodic reaction.

The 0.771v associated with this reaction adds algebraically to the voltages corresponding to whatever other reactions are occurring. It is no surprise then that the presence of an ion in solution that can be in more than one valence state can have a powerful effect on corrosion reactions.

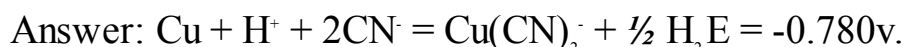
If we now consider the standard electrode potential for copper, i.e., +0.337v, as shown in Table 1.01, we see that copper does not replace hydrogen in a standard acid solution. The corrosion of copper can only proceed if there is a concurrent reaction with Cu²⁺ or H₂ to force the reaction to continue by providing more energy than is represented by the 0.337v barrier noted above.

Example 1.01 Determine the standard potential for the dissolution of copper in cyanide solution.

Solution: The basic data is given by entries in Tables 1.01 and 1.02, i.e.,



Reversing the first of these and adding, we have:



We can see the strong tendency for copper to pass spontaneously into solution with the evolution of

hydrogen. In addition to being soluble in hydrocyanic acid, copper also is soluble in solutions of cyanide salts, such as NaCN or KCN.

In addition to using a complexant for copper as a facilitator for dissolving copper in acids, anything that has an energetic reaction with hydrogen will have the same effect. Atmospheric oxygen or an oxidizing agent such as nitric acid qualify in this sense.

In general then we would say that copper, despite being noble to hydrogen, can be expected to corrode in solutions containing complexants and/or oxidizing agents. Silver and gold behave somewhat similarly. For example, gold can be dissolved in a dilute solution of sodium cyanide that also contains dissolved oxygen from the air. Such generalizations are helpful in understanding corrosion phenomena.

So far, the SHE has been considered the reference electrode of choice. In the practice of corrosion, other electrodes often are more convenient. A number of such reference electrodes and their voltage relation to the SHE are shown in Table 1.03.

TABLE 1.03 Common Reference Electrodes

Designation	Composition	Electrode Reaction	Potential Relative to SHE (volts)	Temp. Coefficient (mV/C°)
Saturated Calomel Electrode (SCE)	Hg, Hg ₂ Cl ₂ (s)/ KCl (saturated)	Hg ₂ Cl ₂ + 2e ⁻ = 2Hg + 2Cl ⁻	+ 0.2446	- 0.76
0.1 M Calomel Electrode	Hg, Hg ₂ Cl ₂ (s)/ KCl (0.1 M)	Hg ₂ Cl ₂ + 2e ⁻ = 2Hg + 2Cl ⁻	+ 0.3338	- 0.07
0.1 M Silver Chloride Electrode	Ag, AgCl(s)/ KCl (0.1 M)	AgCl + e ⁻ = Ag + Cl ⁻	+ 0.2881	- 0.65
1 M Mercury Sulfate Electrode	Hg, Hg ₂ SO ₄ (s)/ K ₂ SO ₄ (1 M)	Hg ₂ SO ₄ + 2e ⁻ = 2Hg + SO ₄ ²⁻	+ 0.6600	- 0.80
Saturated Copper Sulfate Electrode	Cu/CuSO ₄ (saturated solution)	Cu ⁺ + 2e ⁻ = Cu	+ 0.3200	

If two different portions of a piece of metal are exposed to two different concentrations of a solution of one of its salts, a current will tend to flow in the direction that will decrease the concentration difference. The metal exposed to the low concentration will become the anode and corrode, and there will be a plating out on the cathode from the solution of higher concentration [Equation (1.01)].

$$-\Delta G = nFE = RT \ln \frac{C_1}{C_2} \quad (1.01)$$

Where ΔG is the change in Gibbs Free Energy associated with the reaction:



where: n is the valence of the metallic ion in solution; F is Faraday's constant (96,500 joules/volt equivalent); E is the potential difference associated with the reaction; R is the gas constant (8.3125 joules/ degree); T is the absolute temperature; C₁ is the concentration (or activity) of metallic ion in solution in the more concentrated solution; and C₂ is the concentration (or activity) of metallic ion in

solution in the less-concentrated solution.

The corrosion cells that occur in practice often can be regarded as a combination of the two metals in question from Table 1.01 modified by concentration cell terms, as calculated by Equation (1.01). A different form of concentration cell also is significant in some types of corrosion—the oxygen concentration cell. In the cell, the anode reaction is:



While the cathode reaction is:



or some similar reaction-consuming oxygen.

Note that the location where the oxygen concentration is high becomes the cathode while the anodic corrosion occurs at the oxygen-depleted site. The potential of the oxygen concentration cell is given in Equation (1.04), a modified form of Equation (1.01).

$$nFE = RT \ln \frac{PO_2}{P'O_2} \quad (1.04)$$

where: PO_2 is the vapor pressure of oxygen at the cathode; and $P'O_2$ is the vapor pressure of oxygen at the anode.

This type of corrosion cell is characteristic of pitting, crevice corrosion, and pipelines passing from aerated to nonaerated soil (e.g., clay). In this case, O_2 is consumed at the cathode, and the O_2 -starved area suffers anodic corrosion.

A Closer Look at Electrode Processes

When a clean and pure metal is immersed in a solution of one of its salts, it reaches a state of dynamic equilibrium in which the rates of reactions are equal. Equation (1.05) will correspond to an anodic current flow, and Equation (1.06) will correspond to a cathodic current flow.



The electrical circuit is completed by the electrolytic conductivity of the salt solution and the electronic conductivity of the metal. Each equal current flowing both ways at equilibrium is called the exchange current, and the potential of the system is the equilibrium potential associated with the system under study. Unfortunately, it is not possible to measure this equilibrium potential directly. As before, a reference electrode, such as the SHE, is needed.

At equilibrium, Equations (1.05) and (1.06) will occur at local anodes and cathodes, respectively. With the exchange current flowing, there will be a vanishingly small potential difference between the two types of site. The oxidation or corrosion reaction at the anode will be exactly balanced by a reduction reaction (in this case, plating out) at the cathode. If there is a small disturbance from the equilibrium potential, currents (i_{an} and i_{cath}) corresponding to Equations (1.05) and (1.06) will no longer be equal, and the net current will follow the applied disturbance in potential.

If the exchange current is designated as i_{ex} , the situation at equilibrium will be:

$$i_{ex} = i_{an} = i_{cath} \quad (1.07)$$

If there is a shift in potential in the cathode direction, the net current flowing, i , will be given by:

$$i = i_{\text{cath}} - i_{\text{an}} \quad (1.08)$$

And if the shift in potential is in the anode direction:

$$i = i_{\text{an}} - i_{\text{cath}} \quad (1.09)$$

The net current is directly measurable.

If the value of the exchange current is large, there will be a large change in i for a given change in potential. In practice, this means the electrode for which the exchange current is high will exhibit a potential that is stable and difficult to disturb significantly. The electrode with the highest exchange current known in aqueous solution is the platinized platinum electrode at which hydrogen is the reacting species. Such an electrode, in which the gaseous hydrogen is at a pressure of (strictly fugacity) and hydrogen ion is in 1N concentration (strictly activity), is known as the SHE and is the primary reference electrode. It is assigned the arbitrary potential of exactly zero at 298 K.

On the other hand, if the exchange current is small, large differences in potential from equilibrium can lead only to small net restoring currents, and the electrode is said to be readily polarized. The difference between the equilibrium potential and the actual potential is referred to as the overvoltage or overpotential of the electrode. The relationship between net current and overvoltage is of prime importance in the study of corrosion. A reasonable model of the current to overvoltage relationship leads to the Butler-Volmer Equation (Equation 1.10). Traditionally, the interest in electrochemistry has focused on equilibrium processes, particularly since these are amenable to accurate measurement and interpretation. However, for the study of electrochemical processes that occur at significant rates, including corrosion, there has to be more emphasis on the actual rate of particular reactions, though the data may be somewhat imprecise.

Equilibrium and Nonequilibrium Aspects of Electrochemistry

Thus far, only the equilibrium case has been considered. The potential is a guide for showing which way a reaction tends to go, but can offer no conclusion as to whether the reaction will be significantly rapid and cause significant corrosion. Therefore, the rates of corrosion must be examined, as measured by the corrosion current flowing and changes in potential associated with current flow. Polarization is the term used to denote the change in voltage that results from the passage of current. This is the difference between the equilibrium potential, as studied earlier, and the actual case of the working corrosion cell.

There are various kinds of polarization, ranging from the inevitable resistive iR drop (because a current i flows through a resistance R) to specific effects at anode and cathode. The terms “overvoltage” and “overpotential” refer to polarization effects at a specific electrode.

One of the most significant types of polarization is activation polarization. When this controls the rate of an electrochemical reaction, the activation energy of the reaction is the “bottleneck” limiting the rate of reaction. A theoretical model of the current/overvoltage reaction can be drawn up in the form of the Butler-Volmer Equation 1.10 (Figure 1.01).

$$i = i_{\text{ex}} \{ \exp[(1 - \beta)F\eta/RT] - \exp(-\beta F\eta/RT) \} \quad (1.10)$$

This can be related to absolute reaction rate theory. For example, in Glasstone, Laidler, and Eyring, where i_{ex} is the exchange current as before (β is the symmetry factor (usually 0.5), and η is the overpotential.³