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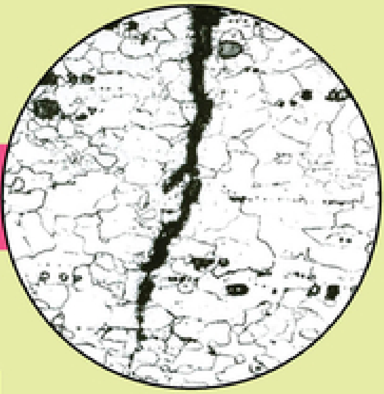
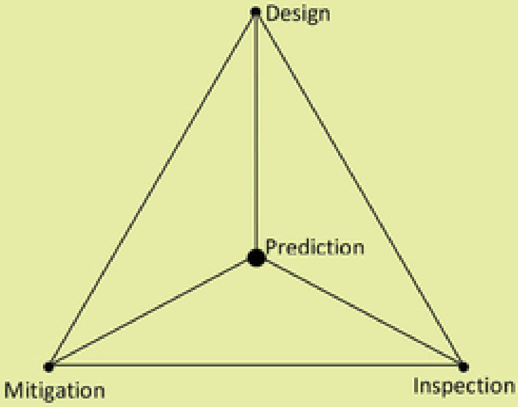
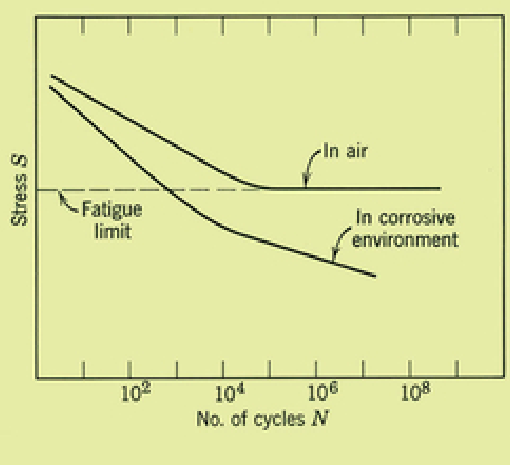


CORROSION AND CORROSION CONTROL

R. WINSTON REVIE ▪ HERBERT H. UHLIG





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FIFTH EDITION

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PREFACE

The great metallurgical achievements of the twentieth century must include the development (and subsequent commercialization) of alloys, such as stainless steels, nickel-base alloys, and others, to resist corrosion in specific environments. When the achievements of the twenty-first century are eventually assessed, the new approach to alloy development that has already resulted in multi-principal element alloys (MPEAs) will be a metallurgical highlight of this century. The development of these alloys, still in the early stages, has opened a universe of opportunity for meeting the challenges of materials performance and reliability in the most aggressive and corrosive environments, many of which are in the energy industry. These developments of materials science will be critical in achieving the transition to low-carbon energy and reduction of greenhouse gas emissions while maintaining energy security, enhancing industrial prosperity, and advancing public safety.

More than ever, the role of corrosion specialist is essential as the lifetime of critical infrastructure depends on materials reliability—achieved by a combination of materials selection, equipment design, periodic inspection during the many years of operation, and maintenance, with elements of corrosion control at every stage. Indeed, given the challenges that industry will face during the energy transition and the many demands of society at large, there has never been a greater need or a greater role for the corrosion specialist in helping to ensure materials reliability, energy security, environmental protection, and public safety.

Nor has there ever been a better time for all those who use and rely on materials to understand and appreciate the limitations that corrosion imposes as well as the opportunities that are possible through judicious application of basic corrosion knowledge and principles. Indeed, now is an opportune time for all those responsible for the use of materials to seize the body of corrosion knowledge that has been developed and use it to help reduce the global cost of corrosion, estimated to be about US$2.5 trillion annually*.

In this book, readers are able to explore the fundamentals of corrosion science and engineering, updated for the fifth edition. Following are revisions included in this new edition:

- Theories of passivity—Chapter 6
- Corrosion under insulation (CUI)—Chapter 7
- Texture as a variable to be considered in corrosion studies—Chapter 8
- Quantitative calculations of corrosion rates of alloys—Chapter 17
- Multi-principal element alloys—Chapter 17
- Benefits of copper surfaces to enhance public health by destroying bacterial, viral (including human coronavirus), and fungal species—Chapter 18
- Plastics as corrosion-resistant materials—Chapter 27

*NACE IMPACT Study, NACE International, Houston, TX, 2016. http://impact.nace.org/documents/Nace-International-Report.pdf.

- More problems, presented together at the ends of chapters
- Several problems included within the text and solved as examples to assist students with quantitative calculations

In addition, throughout the book, there are revisions to improve clarity or add new information.

I thank Michael Leventhal at the Wiley headquarters in Hoboken, NJ, as well as the staff throughout the global Wiley organization for their encouragement and support during the development of this new edition.

Lastly, I thank my wife, Viviane, for her understanding and encouragement of this initiative.

Ottawa, Ontario, Canada
September 2024

R. Winston Revie

PREFACE TO THE FOURTH EDITION

The three main global challenges for the twenty-first century are energy, water, and air; that is, sufficient energy to ensure a reasonable standard of living, clean water to drink, and clean air to breathe. The ability to manage corrosion is a central part of using materials effectively and efficiently to meet these challenges. For example, oil and natural gas are transmitted across continents using high-pressure steel pipelines that must operate for decades without failure, so that neither the ground water nor the air is unnecessarily polluted. In design, operation, and maintenance of nuclear power plants, management of corrosion is critical. The reliability of materials used in nuclear waste disposal must be sufficient so that the safety of future generations is not compromised.

Materials reliability is becoming ever more important in our society, particularly in view of the liability issues that arise when reliability is not assured, safety is compromised, and failures occur. Notwithstanding the many years over which university, college, and continuing education courses in corrosion have been available, high-profile corrosion failures continue to take place. Although the teaching of corrosion should not be regarded as a dismal failure, it has certainly not been a stellar success providing all engineers and technologists a basic minimum "literacy level" in corrosion that would be sufficient to ensure reliability and prevent failures.

Senior management of some organizations has adopted a policy of "zero failures" or "no failures." In translating this management policy into reality, so that "zero" really does mean "zero" and "no" means "no," engineers and others manage corrosion using a combination of well-established strategies, innovative approaches, and, when necessary, experimental trials.

One objective of preparing the fourth edition of this book is to present to students an updated overview of the essential aspects of corrosion science and engineering that underpin the tools that are available and the technologies that are used for managing corrosion and preventing failures. A second objective is to engage students, so that they are active participants in understanding corrosion and solving problems, rather than passively observing the smorgasbord of information presented. The main emphasis is on the quantitative presentation, explanation, and analysis wherever possible; for example, in this new edition, the galvanic series in seawater is presented with the potential range of each material, rather than only as a qualitative list. Considering the potential ranges that can be involved, the student can see how anodic/cathodic effects can develop, not only when different materials form a couple but also when materials that are nominally the same are coupled. In this edition, some new numerical problems have been added, and the problems are integrated into the book by presenting them at the ends of the chapters.

Since the third edition of this book was published, there have been many advances in corrosion, including advances in knowledge, advances in alloys for application in aggressive environments, and advances of industry in response to public demand. For example, consumer demand for corrosion protection of automobiles has led to a revolution of materials usage in the automotive industry. For this reason, and also because many students have a fascination with cars, numerous examples throughout this book illustrate advances that have been made in corrosion engineering of automobiles. Advances in protecting cars and trucks from corrosion must also be viewed in the context of reducing vehicle weight by using magnesium, aluminum, and other light-weight materials to decrease energy usage (increase the miles per gallon, or kilometers per liter, of gasoline) and reduce greenhouse gas emissions.

Although the basic organization of the book is unchanged from the previous edition, in this edition there is a separate chapter on Pourbaix diagrams, very useful tools that indicate the thermodynamic potential–pH domains of corrosion, passivity, and immunity to corrosion. A consideration of the relevant Pourbaix diagrams can be a useful starting point in many corrosion studies and investigations. As always in corrosion, and in this book, there is the dual importance of thermodynamics (In which direction does the reaction go?) and kinetics (How fast does it go?).

There are separate chapters on aluminum (Chapter 21), magnesium (Chapter 22), and titanium (Chapter 25) to provide more information on these metals and their alloys than in the previous editions. Throughout this book, environmental concerns and regulations are presented in the context of their impact on corrosion and its control; for example, the EPA Lead and Copper rule enacted in the United States in 1991. The industrial developments in response to the Clean Air Act, enacted in 1970, have had a major effect on reducing air pollution (Chapter 9) in the United States, so that air quality meets the requirements of the National Ambient Air Quality Standards.

This is primarily a textbook for students and others who need a basic understanding of corrosion. The book is also a useful reference and starting point for engineers, researchers, and technologists requiring specific information. The book includes discussion of the main materials that are available, including alloys both old and new. For consistency with current practice in metallurgical and engineering literature, alloys are identified with their UNS numbers as well as with their commonly used identifiers. To answer the question from students about why so many alloys have been developed and are commercially available, the contributions of individual elements to endow alloys with unique properties that are valuable for specific applications are discussed. Throughout the book, there are numerous references to further sources of information, including handbooks, other books, reviews, and papers in journals. At the end of each chapter, there is a list of currently available "General References" pertinent to that chapter, and most of these were published in 2000 and later.

This edition includes introductory discussions of risk (Chapter 1), AC impedance measurements (Chapter 5), Ellingham diagrams (Chapter 11), and, throughout the book, discussions of new alloys that have been developed to meet demands for increasing reliability notwithstanding the increased structural lifetimes that are being required in corrosive environments of ever-increasing severity. Perhaps nowhere are the demands for reliability more challenging than in nuclear reactors, discussed in Chapters 8 and 26. In the discussion of stainless steels (Chapter 19), the concept of critical pitting temperature (CPT) is introduced, and some CPT data are presented, as well as the information on critical pitting potential (CPP). The important problem of corrosion of rebar (reinforced steel in concrete) is discussed in Chapter 7 on iron and steel.

In addition to new technologies and new materials for managing corrosion, new tools for presenting books have become available; hence, this book is being published as an electronic book, as well as in the traditional print format. An instructor's manual is also being prepared.

Experience has been invaluable in using the book in a corrosion course in the Department of Mechanical and Aerospace Engineering at Carleton University in Ottawa, which Glenn McRae and I developed along with other members of the Canadian National Capital Section of NACE International.

It would be a delight for me to hear from readers of this book with their suggestions and ideas for future editions.

I acknowledge my friends and colleagues at the CANMET Materials Technology Laboratory, where it has been my privilege to work in the corrosion area for the past nearly 30 years. I also thank many organizations and individuals who have granted permission to use copyright material; acknowledgments for specific photographs and data are provided throughout the book. In addition, I thank Bob Esposito and his staff at John Wiley & Sons, Inc. for their encouragement with this book and with the Wiley Series in Corrosion.

I thank the Uhlig family for their generosity and hospitality during five decades, beginning when I was a student in the MIT Corrosion Laboratory in the 1960s and 1970s. In particular, I acknowledge Mrs. Greta Uhlig, who continues to encourage initiatives in corrosion education in memory of the late Professor Herbert H. Uhlig (1907–1993).

Lastly, I quote from the Preface of the first edition of this book:

> "If this book stimulates young minds to accept the challenge of continuing corrosion problems, and to help reduce the huge economic losses and dismaying wastage of natural resources caused by metal deterioration, it will have fulfilled the author's major objective."

Indeed, this remains the main objective today.

Ottawa, Ontario, Canada
September 2007

R. Winston Revie

ABOUT THE COMPANION WEBSITE

This book is accompanied by a companion website:

www.wiley.com/go/Revie/corrosioncontrol

The website includes:

- Solutions Manual for Instructors
- Guide for Instructors: PowerPoint Slides

1

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 electrochemistry is also important. Furthermore, since structure

*Nevertheless, a broader definition of corrosion, "destruction or deterioration of a material because of reaction with its environment," is also used [1].

Corrosion and Corrosion Control, Fifth Edition. R. Winston Revie and Herbert H. Uhlig.

Companion website: www.wiley.com/go/Revie/corrosioncontrol

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 the understanding of the causes of corrosion and the ways to prevent or at least minimized 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, and the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, etc. 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 repainting structures where prevention of rusting is the prime objective, and 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 study reported in 2002 [2]. In a more recent global study, the global cost of corrosion was estimated to be US$2.5 trillion, approximately 3.4% of the global GDP [3]. It has been estimated that between 15% and 35% of this total could be avoided if currently available corrosion technology were effectively applied [3].

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 [3, 4].

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, in most parts of the world, $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. In the U.S., improvements in the Lead and Copper Rule have been proposed to reduce the level of lead from 15 to 10 μg/L [5].

   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 [6] 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. Were the corrosion factor 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; i.e.,

$$R = P \times C$$

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, i.e., the total cost of a corrosion failure, including the cost of replacement, clean-up, repair, downtime, etc.

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

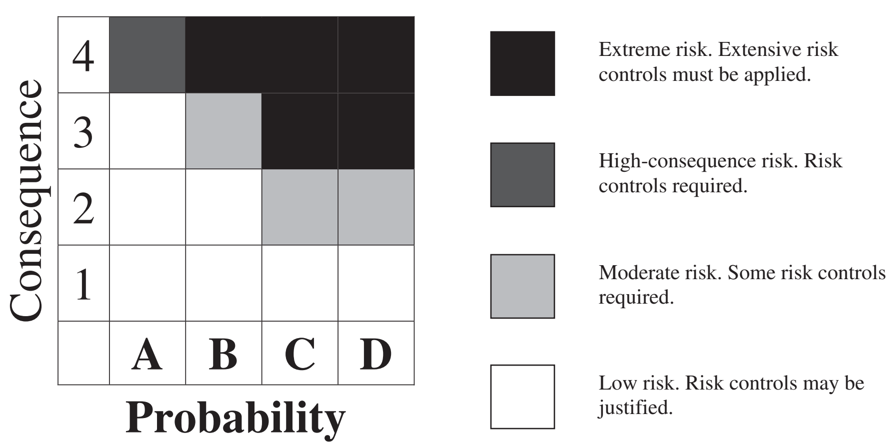

Figure 1.1. A simplified approach to risk management, indicating qualitatively the areas of high risk, where both consequence and probability are high.