

CORROSION AND CORROSION CONTROL

An Introduction to Corrosion
Science and Engineering

Third Edition

HERBERT H. UHLIG

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PREFACE

During the past decade, the literature on corrosion science and its applications has expanded considerably. In the present edition, new information is integrated with that presented in the previous editions. Every chapter has been re-examined and brought up to date. The book benefits from the collaborative efforts that have evolved from a former professor-graduate student relationship.

A major change in this edition is the introduction of SI units, in line with their increasing use in the scientific and technical literature of all countries. In general, the ASTM "Standard for Metric Practice"¹ and "Condensed Metric Practice Guide for Corrosion"² are followed. Accordingly, corrosion rates are now reported in grams per square meter per day (gmd) and in millimeters penetration per year (mm/y). These units either replace or more often are cited in parallel with the units milligrams per square decimeter per day (mdd) and inches penetration per year (ipy), which are still commonly used in the United States. Current densities are expressed as amperes per square meter (A/m^2), except in some cases where mA/cm^2 or $\mu A/cm^2$ express the magnitude of experimental dimensions, and thereby provide the reader with a better visualization of the laboratory measurement. We now express electrode potentials in terms of their reduction reactions only; as before, the potential is designated by ϕ . The term E continues to be used for electromotive force (emf) of a cell. To avoid confusion, a differentiating symbol for the oxidation potential, equivalent to $-\phi$, is now discontinued.

In line with its fundamental importance, the discussion of polarization is now treated in further detail. A new section on fracture mechanics is included

¹ "Standard for Metric Practice," E380-82, in *1983 Annual Book of ASTM Standards*, Vol. 14.02, p. 315, American Society for Testing and Materials, Philadelphia, Pa., 1983.

² "Condensed Metric Practice Guide for Corrosion," in *1983 Annual Book of ASTM Standards*, Vol. 03.02, p. 496, American Society for Testing and Materials, Philadelphia, Pa., 1983.

in the chapter on stress. Critical potentials below which stress-corrosion cracking does not initiate are treated in further detail. Because failures by hydrogen cracking and delamination continue as a major engineering problem, this subject now receives greater emphasis. The discussion on the mechanism of corrosion fatigue is brought up to date. Corrosion of steel reinforcements in concrete is discussed as a separate topic, justified in our opinion by related continuing failures of concrete structures.

A new chapter on cobalt alloys is added; these alloys have recognized practical importance as surgical implant materials and in applications requiring unusual resistance to corrosion-erosion and to fretting corrosion.

The chapter on problems and answers has been updated. The derivation of the general equation applicable to the calculation of corrosion rates from polarization data, going beyond the limitations of the Stern-Geary equation, is given in the Appendix.

It is a pleasure to acknowledge helpful discussions and added information contributed by I. Matsushima, A. Asphahani, R. Pelloux, M. Vucich, J. Morgan, and M. Malhotra. For one of the authors (R.W.R.), support from his family—Terri, Julian, Kamilla, and aunt M. Audrey Dudley—was most helpful in completing the book.

HERBERT H. UHLIG
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Cambridge, Massachusetts
Ottawa, Canada
September 1984

PREFACE TO THE SECOND EDITION

Rapid advances in corrosion science and engineering since the publication of the first edition have made it necessary to update most chapters of the present book. The recently appreciated concept of a *critical pitting potential* and its useful application to practical situations are now described in detail. Similarly, appropriate space is given to the recognized importance of an analogous critical potential below which *stress corrosion cracking* does not occur, and a more detailed account of recent trends in proposed mechanisms of stress corrosion cracking is provided. The section on *corrosion fatigue* is rewritten in accord with new data and their corresponding interpretation; the chapter on *passivity*, which has benefited from several new and exciting experiments conducted in more than one laboratory, is also rewritten. The *intergranular corrosion of nonsensitized stainless steels* and related alloys is a new subject of special interest to the nuclear power industry. An elementary description of *Pourbaix diagrams* is included here in line with the availability of the extensive atlas published by Professor Pourbaix in 1966.

It has become plainly (and sometimes painfully) apparent by events of the past decade that all materials scientists as well as engineers in a broad cross section of professional activities should know something about environmental effects on properties of materials, including the corrosion behavior of metals and alloys. Where safety and economy of performance are vital considerations, the design of critical structures and their components employing modern materials requires more than the traditional attention to mechanical properties alone.

I am gratified that this book has been useful both to stimulate the teaching of corrosion to students in the universities and also to serve as a concise reference for experienced materials scientists and engineers who missed a

chance to learn something about the subject or who want to be brought up to date. To help in the necessary understanding of basic principles, additional problems have been added at the end of the book, and, in response to many requests, more answers to such problems are now provided.

Acknowledgment is due several persons who helped to clarify some of the discussions in the first edition, in particular to my former student Iwao Matsushima who, with Seigo Matsuda, also a former student of the Corrosion Laboratory, prepared the Japanese translation. I am indebted to Walter Hamer of the National Bureau of Standards for up-to-date values of reference electrode potentials, to J. Robinson of the Dow Chemical Company for statistical data on magnesium and aluminum production, to M. Vucich of the National Steel Company for production figures on chromium-plated container steel, and to H. Spähn, G. Cheever, and L. Brockway for various photographs.

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Cambridge, Massachusetts
June 1971

PREFACE TO THE FIRST EDITION

Corrosion research and the teaching of corrosion have a tradition of long standing at M.I.T. Professor W. R. Whitney, who later became the first Director of Research for the General Electric Company, initiated this tradition with his classic paper on "The Corrosion of Iron" published in 1903 in the *Journal of the American Chemical Society*. This paper stimulated the important researches on corrosion by Professor W. H. Walker, and later by Professor Walter Whitman and his associates in the Laboratory of Applied Chemistry, which Walker founded. Formal instruction in corrosion was apparently first presented in a subject entitled "Chemical Resistance of Materials," offered to students by Professor Walker in 1903. The title was changed in 1912 to "Materials of Construction" and was taught with the assistance of Professor W. K. Lewis, and later by Professor Lewis alone. The first M.I.T. subject under the name of "Corrosion" appeared in 1922 and was taught by Professor Whitman. It was subsequently offered by several other members of the Department of Chemical Engineering, including Professor Lewis. In 1931, Professor R. S. Williams of the Department of Metallurgy offered for the first time a subject entitled "Corrosion and Heat Resisting Alloys," which he taught until 1942. Beginning in 1938, I continued the organized lectures on corrosion previously presented by Professor Whitman. After the interruption caused by World War II, these lectures were resumed in the Department of Metallurgy and have continued up to the present time.

This book is based on the one-semester subject called "Corrosion," which I present to seniors and graduate students at M.I.T. The purpose is to introduce the student to the underlying science of corrosion and to the fundamentals of what is now known as corrosion engineering. In brief, the lectures are concerned with why metals corrode and what can be done about it. The subject

is treated as quantitatively as present knowledge permits, and, along these lines, problems are assigned which illustrate first principles and the application of these principles to practical situations. Some of the assigned problems are assembled in the latter part of this book. Answers to many of these are given, primarily to assist the professional engineer or the scientist who may use the book for background information on corrosion, and who finds that working out problems helps to obtain the necessary understanding. Better understanding is the justification for working out problems in any subject of instruction, and corrosion is no exception. It is assumed that the reader has familiarity with elementary physical chemistry; this subject is a prerequisite for the M.I.T. corrosion course. Background knowledge in physical metallurgy is also helpful, but not required.

Treatment of the subject is concise, consistent with time limitations for presentation of all the material within one semester. For this reason, only those literature references are cited which bear directly on the point under discussion. General references are added at the end of the various chapters. These references usually contain additional references if the reader is interested, but in no case is an attempt made to cite all the literature that might justifiably be mentioned. For a more complete guide to the literature, the reader should consult reference books such as *The Corrosion Handbook*, edited by the author, and *The Corrosion and Oxidation of Metals*, by U. R. Evans.

When more than one interpretation of the facts or more than one theory is current, I have tried to present both sides. At the same time, I have made my own preference clear on the premise that the reader is entitled to know my opinion. Corrosion rates are expressed as milligrams per square decimeter per day (mdd) and inches penetration per year (ipy), which are both in common use in the United States. The sign of electrode potential has always been a difficult matter to resolve in view of the opposite conventions followed by major groups in the United States and abroad. It is hoped that by defining *the potential* as opposite in sign to the oxidation potential, consistent with the use recommended by Lewis, Randall, Pitzer, and Brewer in *Thermodynamics*, 2nd edition, McGraw-Hill (1961), some degree of harmony is provided, or at least confusion is avoided.

I am indebted to many friends and colleagues for much of the information which has entered my lectures and is now contained here. Enlightened understanding of corrosion mechanisms in several instances was contributed through the patient effort of many students who sojourned in the Corrosion Laboratory and who searched with me for a critical experiment, or who laboriously accumulated decisive data.

Appreciation is expressed to those who read portions of the manuscript and made valuable suggestions, including Carl Wagner, Milton Stern, W. D. Robertson, Bruce Chalmers, G. T. Paul, G. Schikorr, H. S. Campbell, C. P. Larabee, W. W. Bradley, and J. P. Pemsler; and also to those who supplied photographs or sketches, in particular, F. L. LaQue, M. VanLoo, J. F. Seibald, and H. M. Bendler. A large part of the manuscript was written during a sab-

batical semester spent in Göttingen, West Germany. This opportunity was made possible by financial support provided by the John Simon Guggenheim Memorial Foundation and by the hospitality of Dr. Carl Wagner, Director of the Max Planck Institut für Physikalische Chemie.

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.

HERBERT H. UHLIG

Cambridge, Massachusetts
November 1962

1	Definition and Importance	1
2	Electrochemical Mechanisms	6
3	Corrosion Tendency and Electrode Potentials	16
4	Polarization and Corrosion Rates	35
5	Passivity	60
6	Iron and Steel	90
	Aqueous Environments	
	Metallurgical Factors	
7	Effect of Stress	123
	Cold Working, Stress Corrosion Cracking, Hydrogen Cracking, Radiation Damage, Corrosion Fatigue, Fretting Corrosion	
8	Atmospheric Corrosion of Iron and Other Metals	165
9	Corrosion of Iron and Other Metals in Soils	178
10	Oxidation and Tarnish	187
11	Stray-Current Corrosion	210
12	Cathodic Protection	217
	Anodic Protection	
13	Metallic Coatings	233
14	Inorganic Coatings	245
15	Organic Coatings	250
16	Inhibitors and Preservatives	263
17	Treatment of Water and Steam Systems	276
18	Alloying for Corrosion Resistance: Stainless Steels	287
		xii

CORROSION AND CORROSION CONTROL

DEFINITION

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 terms: corrosion-erosion, corrosive wear, or fretting corrosion. Nonmetals are not included in the present definition. Plastics may swell or crack, wood may split or decay, granite may erode, and Portland cement may leach away, but the term corrosion is presently restricted to chemical attack of metals.

"Rusting" applies to the corrosion of iron or steel to the extent with formation of rusted products consisting largely of hydrated ferric oxides. Nonferrous metals, therefore, corrode but do not rust.

Corrosion Science

Since corrosion involves chemical change, it is obvious that the student must be familiar with principles of chemistry in order to understand corrosion reactions. In particular, because corrosion processes are mostly electrochemical, an understanding of electrochemistry is important. Furthermore, since structure and composition of a metal often determine corrosion behavior, the student should also be familiar with fundamentals of physical metallurgy. Hence, both chemistry and metallurgy are basic to corrosion studies in the same sense as biology and chemistry are basic to the study of medicine.

The corrosion scientist is concerned with the study of corrosion mechanisms through which a better understanding is obtained of the causes of

CONTENTS

1	Definition and Importance	1
2	Electrochemical Mechanisms	6
3	Corrosion Tendency and Electrode Potentials	16
4	Polarization and Corrosion Rates	35
5	Passivity	60
6	Iron and Steel	90
	<i>Aqueous Environments</i>	
	<i>Metallurgical Factors</i>	
7	Effect of Stress	123
	<i>Cold Working, Stress Corrosion Cracking, Hydrogen Cracking,</i>	
	<i>Radiation Damage, Corrosion Fatigue, Fretting Corrosion</i>	
8	Atmospheric Corrosion of Iron and Other Metals	165
9	Corrosion of Iron and Other Metals in Soils	178
10	Oxidation and Tarnish	187
11	Stray-Current Corrosion	210
12	Cathodic Protection	217
	<i>Anodic Protection</i>	
13	Metallic Coatings	233
14	Inorganic Coatings	245
15	Organic Coatings	250
16	Inhibitors and Passivators	263
17	Treatment of Water and Steam Systems	278
18	Alloying for Corrosion Resistance; Stainless Steels	297

19	Copper and Copper Alloys	327
20	Aluminum and Magnesium	341
21	Lead	358
22	Nickel and Nickel Alloys	361
23	Cobalt and Cobalt Alloys	371
24	Titanium, Zirconium, and Tantalum	375
25	Silicon-Iron and Silicon-Nickel Alloys	389
26	Problems	392
27	Appendix	404
	Index	433

1	Definition and Importance	1
2	Electrochemical Mechanisms	2
3	Corrosion Tendency and Electrode Potentials	3
4	Polarization and Corrosion Rates	4
5	Passivity	5
6	Iron and Steel	6
	Aqueous Environments	
	Manufacturing Factors	
7	Effect of Stress	7
	Cold Working, Stress Corrosion Cracking, Hydrogen Cracking	
	Radiation Damage, Corrosion Fatigue, Fretting Corrosion	
8	Atmospheric Corrosion of Iron and Other Metals	8
9	Corrosion of Iron and Other Metals in Soils	9
10	Oxidation and Tarnish	10
11	Stagnant Current Corrosion	11
12	Cathodic Protection	12
	Anodic Protection	
13	Metallic Coatings	13
14	Inorganic Coatings	14
15	Organic Coatings	15
16	Inhibitors and Passivators	16
17	Treatment of Water and Steam Systems	17
18	Alloying for Corrosion Resistance, Stainless Steels	18

1 DEFINITION AND IMPORTANCE

DEFINITION

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The *corrosion scientist* is concerned with the study of corrosion mechanisms through which a better understanding is obtained of the causes of

2 DEFINITION AND IMPORTANCE

corrosion and the available means for preventing or minimizing resulting damage. The *corrosion engineer* applies accumulated scientific knowledge to the abatement of corrosion damage by practical and economical means. For example, the corrosion engineer employs cathodic protection on a large scale to prevent corrosion of buried pipelines, or tests and develops new and better paints, prescribes proper dosage of corrosion inhibitors, or recommends the correct metal 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 proper remedies.

Importance of Corrosion

The importance of corrosion studies is threefold. The first area of significance is *economic* including the objective of reducing material losses resulting from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on. The second area is *improved safety* of operating equipment which, through corrosion, may fail with catastrophic consequences. Examples are pressure vessels, boilers, metallic containers for toxic materials, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms. Safety is a prime consideration in the design of equipment for nuclear-power plants and for disposal of nuclear wastes. Third is *conservation*, applied primarily to metal resources—the world's supply of these is limited, and the wastage of them includes corresponding losses of energy and water reserves associated with the production and fabrication of metal structures. Not least important is the accompanying conservation of human effort entering the design and rebuilding of corroded metal equipment, otherwise available for socially useful purposes.

The economic factor is the prime motive for much of the current research in corrosion. Losses sustained by industry, by the military, and by municipalities amount to many billions of dollars annually.

Economic losses are divided into (1) direct losses and (2) indirect losses. By *direct* losses are meant 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 of structures where prevention of rusting is the prime objective and the capital costs plus upkeep of cathodically protected pipelines. Sizable direct losses are illustrated by the necessity to replace several million domestic hot-water tanks each year because of failure by corrosion or, similarly, 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, or of dehumidifying storage rooms for metal equipment. De-icing salt applications to roads and bridges have been estimated by one source to cause direct corrosion damage to motor vehicles in the order of \$2 billion (2×10^9) annually, and to roads and bridges in the order of \$0.5 million annually.¹ Cost of corrosion and its control experienced by one pulp and paper company was estimated to be \$20 million annually.² The total combined losses of this kind to the United States alone are estimated conservatively to be about \$70 billion annually, or 4.2% of the Gross National Product (GNP).³ It has been estimated that about 15% of this total could be avoided if currently available corrosion technology were effectively applied.³ Studies of the cost of corrosion to Australia,⁴ Great Britain,⁵ Japan,⁶ and other countries have also been carried out. In each country studied, the cost of corrosion is approximately 3–4% of the GNP.

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 \$20,000 per hour in lost production. Similarly, replacement of corroded boiler or condenser tubes in a large power plant may necessitate \$50,000 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.⁷

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.* This 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 is estimated

¹ J. Slater, *Mater. Perf.* 18(6), 34 (1979).

² R. Charlton, *Mater. Perf.*, 17(10), 27 (1978).

³ L. H. Bennett et al., *Economic Effects of Metallic Corrosion in the United States*, A Report to the Congress by the National Bureau of Standards, NBS Spec. Publ. 511-1, Washington, D.C., 1978.

⁴ R. Revie and H. Uhlig, *J. Inst. Engrs., (Australia)*, 46 (3–4), 3 (1974).

⁵ *Report of the Committee on Corrosion and Protection* (T. P. Hoar, Chairman), London, Her Majesty's Stationery Office, 1971.

⁶ *Boshoku Gijutsu*, 26, 401 (1977).

⁷ H. Klein and J. Rice, *Trans. Am. Soc. Mech. Eng. Ser. A*, 88, 232 (1966).

4 DEFINITION AND IMPORTANCE

that in the United States, e.g., increased pumping capacity, made necessary by partial clogging of water mains with rust, costs many millions of dollars per year.⁸)

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 is caused by corrosion to an extent often equal to or greater than that caused by wear. An additional illustration is provided by corrosion processes that impose limits on the efficiencies of energy conversion systems, representing a potential loss in the billions of dollars.^{9,10}

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 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.* Similarly, soft waters conducted through lead pipes are not safe for drinking purposes.†

Included in the category of contamination is spoilage of food in corroded metal containers. One cannery of fruits and vegetables 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 soon perforated by a pitting type of corrosion, thereby allowing bacterial contamination of the contents.

5. *Overdesign.* This factor is common in the design of reaction vessels, boilers, condenser tubes, oil-well sucker rods, buried pipelines, water tanks, and marine structures. Because corrosion rates are unknown or methods for corrosion control are uncertain, 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,

* Bureau of Foods and Drugs permit not over 1 ppm of lead in food.

† 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 Franklin¹¹ 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.

⁸ H. Jordan, American Water Works Association, private communication.

⁹ R. Rapp et al., *Mater. Sci. Eng.*, **50**, 1 (1981).

¹⁰ D. MacDonald et al., *Mater. Sci. Eng.*, **50**, 19 (1981).

¹¹ Benjamin Franklin's *Autobiographical Writings*, edited by Carl Van Doren, p. 671, Viking Press, New York, 1945.