

Corrosion Prevention and Protection Practical Solutions

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Mimoun Elboujdaini

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Preface

There are many books and monographs on corrosion, such as *Corrosion and Corrosion Control* by H. H. Uhlig and R. W. Revie; *Corrosion Engineering* by M. G. Fontana and N. D. Greene; *Principles and Prevention of Corrosion* by D. A. Jones; *An Introduction to Corrosion and Protection of Metals* by G. Wranglen; and *Corrosion for Science and Engineering* by K. R. Trethewey and J. Chamberlain. The present title differs from existing books in more ways than one, such as the chapters dealing with practical solutions. The title was chosen to reflect the content of the subject matter, which is presented in two parts.

The first chapter presents the historical development of corrosion concepts, such as the electrochemical theory of corrosion, the economic significance of corrosion and its impact, cathodic protection, Faraday's laws, the role of oxygen, passivity, inhibitors and their classification, the role of thermodynamics, the historical development of the corrosion literature, and the establishment of scientific organizations dealing with corrosion, and centres and laboratories for studies on corrosion phenomena, progressive development of the scientific literature on corrosion, safety and its impact. The role of thermodynamics and kinetics in corrosion, electrochemical principles of corrosion, Pourbaix diagrams, the Helmholtz double layer and its significance in corrosion, electrochemical polarization, Tafel plots, activation polarization, hydrogen overvoltage, mixed potential theory of corrosion, AC impedance and potential noise in corrosion phenomena, high-temperature corrosion, corrosion prevention strategies such as design factors, corrosion-based life prediction analysis of materials, corrosion inhibitors and their role in corrosion prevention, coatings and their role in corrosion control, cathodic protection and impressed current protection are presented.

The second chapter deals with corrosion testing for environmentally assisted cracking, atmospheric corrosion, galvanic corrosion, tests for degradation of polymeric materials, refractories and ceramic materials and corrosion inhibitors. This is followed by a discussion of corrosion detection and monitoring by methods such as visual examination, laser inspection, replication microscopy, radiographic inspection, neutron radiography, liquid penetrant method, eddy current method, ultrasonic testing, acoustic emission testing, finite element analysis, strain gage methods and thermal methods of inspection. Failure analysis consisting of various modes of failure by different damage mechanisms are presented, including microfractography, fracture mechanics, determination of

residual stress by X-ray diffraction, role of surface analysis techniques in failure analysis, including failure in polymeric and ceramic materials.

The next chapter deals with regulations, specification and safety. The regulations and specifications of materials used in industry are briefly discussed. This is followed by safety considerations to be observed both in the corrosion laboratory and field inspection. Hazard identification techniques at different stages of the project, a checklist for process hazard analysis, safety procedures in the corrosion laboratory, including a model chemical hygiene plan, guidelines in using radiation sources including lasers and safety considerations in the design stage and field plant inspection are presented.

Materials such as metals, alloys, steels and plastics form the theme of the fourth chapter. The behavior and use of cast irons, low alloy carbon steels and their application in atmospheric corrosion, fresh waters, seawater and soils are presented. This is followed by a discussion of stainless steels, martensitic steels and duplex steels and their behavior in various media. Aluminum and its alloys and their corrosion behavior in acids, fresh water, seawater, outdoor atmospheres and soils, copper and its alloys and their corrosion resistance in various media, nickel and its alloys and their corrosion behavior in various industrial environments, titanium and its alloys and their performance in various chemical environments, cobalt alloys and their applications, corrosion behavior of lead and its alloys, magnesium and its alloys together with their corrosion behavior, zinc and its alloys, along with their corrosion behavior, zirconium, its alloys and their corrosion behavior, tin and tin plate with their applications in atmospheric corrosion are discussed. The final part of the chapter concerns refractories and ceramics and polymeric materials and their application in various corrosive media.

Corrosion economics and corrosion management forms the theme of the fifth chapter. Discounted cash flow calculations, depreciation, the declining balance method, double declining method, modified accelerated cost recovery system and present worth calculation procedures are given, together with examples. In the second part, corrosion management, including the people factor in corrosion failure is briefly presented. Some of the expert systems presently available in the literature are briefly discussed.

The second part of the book consists of two chapters; namely the forms of corrosion and practical solutions. The chapter, 'Forms of Corrosion' consists of a discussion of corrosion reactions, corrosion media, active and active-passive corrosion behavior, the forms of corrosion, namely, general corrosion, localized corrosion, metallurgically influenced corrosion, microbiologically influenced corrosion, mechanically assisted corrosion and environmentally induced cracking, the types and modes of corrosion, the morphology of corroded materials along with some published literature on corrosion.

The last chapter is a collection of case histories or practical solutions the authors have provided to various clients. These solutions span a wide range of industrial problems in a variety of environments frequently encountered.

It is the experience of the authors that the material in the first part of the book can be covered in one semester lasting 12 weeks. The second part of the book can be covered in a subsequent semester lasting 12 weeks. It is also possible that some laboratory work can be carried out by the students when the instructor is teaching the second part of the book.

The authors have received their education in universities in North America and Europe and have a combined experience of approximately 100 years in corrosion and its mitigation. The present monograph is a product of this rich experience.

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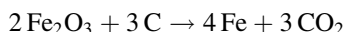
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Part I

1

Introduction and Principles of Corrosion

The term corrosion has its origin in Latin. The Latin term *rodere* means ‘gnawing’ and *corrodere* means ‘gnawing to pieces’. It is rather interesting to examine the historical aspects of the developments of corrosion. Metallic corrosion has no doubt been a problem since common metals were first put to use. Most metals occur in nature as compounds, such as oxides, sulfides, silicates or carbonates (very few metals occur in native form). The obvious reason is the thermodynamic stability of the compounds as opposed to the metals. The process of extraction of a metal from the ore is reduction.



In the extraction of iron, the oxide is reduced to metallic iron. On the other hand, the oxidation of iron to produce the brown iron oxide commonly known as rust is the opposite reaction to the production of the metal from the oxide. The extraction of iron from the oxide, must be conducted with utmost careful control of the conditions, such that the backward reaction is prevented.

During the Gupta Dynasty (320–480 A.D.) the production of iron in India achieved a remarkable degree of sophistication as attested by the Dhar Pillar, a seven-tonne, one-piece iron column made in the fourth century A.D. This implies that the production of metallic iron from the ores was a well-established process, and the people involved at that time were aware of the reverse reaction involving the oxidation of iron to produce the oxide (the familiar rusting of iron).

Other examples involve the use of copper nails coated with lead by the Greeks in the construction of lead-covered decks for ships.¹ They probably realized that metallic couples of common metals are undesirable in seawater. Protection of iron by bitumen, tar, etc., was known and practiced by the Romans.

The earliest published accounts of the causes of corrosion are the two publications by Robert Boyle (1627–1691) entitled ‘Of the Mechanical Origin of Corrosiveness’ and

'Of the Mechanical Origin of Corrodibility', which appeared in 1675 in London.² It was not until the turn of the 19th century^{3,4} that some of the basic principles were understood, soon after the discovery of the galvanic cell and Davy's theory on the close relationship between electricity and chemical changes.⁵

The impetus for further developments was the recognition of the economic significance of corrosion phenomenon during the 19th century that led the British Association for the Advancement of Science to sponsor corrosion testing projects such as the corrosion of cast and wrought iron in river and seawater atmospheres in 1837. Early academic interest in corrosion phenomenon (up to the First World War) was followed by industrial interest due to the occurrence of equipment failures. An example of this is the corrosion-related failure of condenser tubes as reported by the Institute of Metals and the British Non-ferrous Metals Research Association in 1911. This initiative led to the development of new corrosion-resistant alloys, and the corrosion related failure of condenser tubes in the Second World War was an insignificant problem.

Corrosion and its control mean the corrosion process and the measures taken to control or keep in check the corrosion process. Sometimes it is also referred to as corrosion, prevention and protection. Although the terms 'prevention' and 'protection' appear to be synonymous, prevention means measures taken to control corrosion to a limited extent while protection means extensive or more comprehensive measures taken to control the corrosion process. In more general terms preventive measures are knowledge-based while protection involves both known and unknown factors, such as natural disasters.

The heart of corrosion science has been identified as electrochemical science coupled with the thermodynamic and kinetic values. Other limbs are oxidation and high-temperature oxidation of metals, protective coatings, passivity, inhibitors, microbial-induced corrosion, corrosion fatigue, hydrogen embrittlement and corrosion-resistant alloys. Having identified the limbs of corrosion science, it is instructive to examine how the various aspects came into existence over a period of time.

The French chemist Louis Jacques Thenard first enunciated electrochemical nature of corrosion phenomenon explicitly in 1819. Some research activities that led to the firm electrochemical foundations of corrosion process are summarized below:

Sir Humphry Davy	1824	Principle of cathodic protection
Auguste de la Rive	1830	Established best quality of zinc for galvanic batteries
Michael Faraday	1834–1840	Provided relations between chemical action and generation of electric currents based on Faraday's laws
Svante Arrhenius	1901–	Postulated the formation of microcells
W.R. Whitney	1903	Confirmed the theory of microcells
A.S. Cushman	1907	
Walker	1907	Established role of oxygen in corrosion as a cathodic stimulator
Cederholm		
Bent		
William Tilden		
	1908	

Corey } Finnegan }	1939 }	Investigated attack of iron by oxygen-free water
Kay Thompson	1940 }	
A. Thiel } Luckmann }	1928	Investigated attack of iron by dilute alkali with liberation of hydrogen
Heyn and Bauer	1908	Corrosion studies of iron and steel, both alone and in contact with other metals, leading to the concept that iron in contact with nobler metal increased the corrosion rate, while in contact with a base metal resulted in partial or complete protection
Whitman and Russell	1924 }	Observed increased corrosion rate when a small anode is connected to a large cathode
U. Evans	1928 }	
G.V. Akimov	1935 }	

Other important and related phenomena in corrosion and their historical development are summarized below:

John Stewart MacArthur	1887	Process of cyanide dissolution of gold (gold is not soluble in hot acids)
P.F. Thompson	1947	Dissolution of gold in dilute cyanide solutions recognized as electrochemical process

Concept of passivity

James Keir	1790	Observed that iron in conc. nitric acid altered in its properties
Christian Friedrich Schönbein	1799–1868	Suggested the state of iron in conc. HNO_3 as passivity
W. Müller (Konopicky and Willi Machu)	1927	Posulated the mathematical basis of the mechanism of anodic passivation
Bengough (Stuart, Lee and Wormweil)	1927	Systematic and carefully controlled experimental work on passivity

Role of oxygen

~1900	Hydrogen peroxide was detected during the corrosion of metals
~1905	The view that acids are required for corrosion to occur was dispelled by the observation of rusting of iron in water and oxygen

Marianini	1830	The research work of these scientists indicated the electric currents due to the variations in oxygen concentrations
Adie	1845	
Warburg	1889	
V.A. Kistiakowsky	1908	
Aston	1916	
		Role of local differences in oxygen concentration in the process of rusting of iron
McKay	1922	Currents due to a single metal of varying metal ion concentrations
U.R. Evans	1923	Differential aerations and their role in metallic corrosion
Evans and co-workers	1931–1934	Electric currents due to corrosion of metal in salt solutions were measured and a quantitative electrochemical basis of corrosion was propounded. The oxygen-rich region becomes cathodic and the metal is protected, and the lower oxygen region, being anodic, is attacked

Inhibitors

Roman civilization	—	Protection of iron by bitumen, tar, extracts of glue, gelatin and bran to inhibit corrosion of iron in acid
Murangoni	1872	
Stephanelli		
Chyzewski	1938	Classified inhibitors as cathodic and anodic inhibitors
—	—	Distinction between inhibitive paints and mechanically excluding paints was made based on laboratory, and field tests
—	—	Development of paints containing zinc dust
John Samuel Frost	1930	Protective property of coating varied and depended on the rate of supply of oxygen to the surface
Roetheli and Brown		
Friend	1920	Colloidal solution of ferric hydroxide acts as an oxygen carrier, passing between ferrous and ferric states
Herzog	1936	Posulated that iron, on long exposure to water, becomes being covered by a magnetite overlaid with ferric hydroxide. Magnetite layer acts as cathode and ferric hydroxide is cathodically converted to hydrated

		magnetite. Hydrated magnetite may lose water and reinforce the pre-existing magnetite or absorb oxygen from air to give ferric hydroxide
V.S. Sastri	1990	Modern classification of inhibitors as hard, soft and borderline inhibitors (<i>11th International Corrosion Congress</i> , V. 3, p. 55)
V.S. Sastri	1988	Classification of corrosion inhibition mechanisms such as interface inhibition, interphase inhibition, intraphase inhibition and precipitation coating (<i>Corrosion</i> '88, Paper 155)
V.S. Sastri, J.R. Perumareddi and M. Elboujdaini	1994	Novel theoretical method of selection of inhibitors (<i>Corrosion</i> , 50 , 432, 1994)
V.S. Sastri, J.R. Perumareddi and M. Elboujdaini	2005	Sastri equation relating the percent inhibition to the fractional electronic charge on the inhibitor. (<i>Corrosion Eng. Sci. & Tech.</i> , 40 , 270, 2005)

High-temperature oxidation

Gustav Tammann	1920	Enumerated 'Parabolic Law' (i.e., rate of oxidation of metal decreases as oxide layer thickness increases)
	1922	Logarithmic law of oxidation of metals
N.B. Pilling and R.E. Bedworth	1923	Distinction between porous and non-porous oxide layer
Leonard B. Pfeil	1929	Concept of movement of metal outward rather than oxygen inward into the oxide layer
Portevin Prétet Jolivet	1934	Extensive studies on the oxidation of iron and its alloys
Carl Wagner	~1934	High-temperature oxidation involves passage of ions and electrons through the growing oxide layer. Postulated an equation relating oxidation rate with the electrical properties of the oxide layer
Hoar, Price	1938	Derivation of Wagner's equation
Mott, Cabrera	1939, 1948	Oxide film growth controlled by ions jumping from site to site over intervening energy barriers

Karl Houffe Ilschner	—	Significant work on the oxidation of alloys. Also criticism of Mott's theory
Tammann	1920–1926	Interference method of obtaining thickness of oxide films
Constable	1927	Spectroscopic method to obtain thickness of oxide film
Finch Quarrell	1933	X-ray and electron diffraction methods to study oxide films

Microbiological corrosion

R.H. Gaines	1910	Sulfate-reducing bacteria in soils produce H_2S and cause corrosion
Corrosion fatigue	~1900	Alternating stresses and chemical environment together cause corrosion fatigue
Stress–corrosion cracking	~1900	Applied stress and chemical environment causing stress–corrosion cracking

Hydrogen embrittlement

Haber–Bosch process for synthesis of ammonia	1916	Microcracks in the steel reactor were observed due to the reaction of hydrogen with carbon in the steel to produce methane. Mo and Cr were found to prevent hydrogen embrittlement
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Role of thermodynamics

—	—	Corrosion of metal obeys the laws of thermodynamics. This was recognized in the early development of corrosion science
Marcel Pourbaix	1940	Pourbaix diagrams involving pH and potential give regions of corrosion, immunity and passivity

Kinetics

Evans, Hoar	1932	Quantitative correlation of corrosion rates with measured electrochemical reaction rates
F. Habashi	1965	Validity of a single kinetic law irrespective of the metal, composition of aqueous phase, and evolution of hydrogen when no insoluble products, scales or films are formed

The number of published scientific papers through 1907–2003 illustrates development of the corrosion science in the form of published scientific literature as shown below:

Title	1907	1950	2000	2003
Corrosion	35	922	10985	10655
Corrosion and protection	3	122	1162	1050
Corrosion and prevention	3	320	1639	1358

The journals that came into existence are given below:

Title	Year
<i>Corrosion</i>	1945
<i>Corrosion Science</i>	1961
<i>British Corrosion Journal</i>	1965
<i>Werkstoffe und Korrosion</i>	1950
<i>Corrosion Prevention and Control</i>	1954
<i>Anti-corrosion Methods and Materials</i>	1962
<i>Materials Performance</i>	1962

Some of the leading organizations championing corrosion science, which were founded, are detailed below. This list does not include academic institutions.

American Society for Testing Materials (ASTM)	1898
American Society of Metals (ASM)	1913
Corrosion Division of the Electrochemical Society	1942
National Association of Corrosion Engineers	1943
Comité International de Thermodynamique et Cinétique Electrochimique (CITCE)	1949
International Society of Electrochemistry (ISE)	1971
International Corrosion Council	1961
The Corrosion Group of the Society of Chemical Industry	1951
Belgium Center for Corrosion Study (CEBELCOR)	1951
Commission of Electrochemistry	1952
National Corrosion Centre (Australia)	
Australian Corrosion Association	~1980
Chinese Society of Corrosion and Protection	~1980
National Association of Corrosion Engineers (in Canada)	—

Research groups, which became active in the field of corrosion in the early stages, are shown below. It is prudent to state that the list is by no means exhaustive.

Massachusetts Institute of Technology
National Bureau of Standards

Ohio State University
University of Texas
University of California, Los Angeles
National Research Council, Ottawa
Cambridge University
Technical University, Vienna

Industrial laboratories such as U.S. Steel, International Nickel company and Aluminum Company of America, DuPont have also initiated their own corrosion research.

The progress made in the scientific approach and the degree of sophistication attained over the years becomes evident from the following title papers:

1. A.S. Cushman, Corrosion of Iron as an Electrolytic Phenomenon, *U.S. Bur. Agr., Electrochemical Metallurgy Industry*, Vol. 5, No. 256, C.A., 1907, p. 2360.

Hydrogen ions are the primary cause of rusting and oxygen the secondary cause. Iron passes into solution in the form of ferrous ions as the result of galvanic action; the ferrous ions are then oxidized by the oxygen of the air to ferric ions. Alkaline solutions prevent rusting because they contain no hydrogen ions. Chromic acid and its salts prevent rusting because an oxygen film is formed, and the iron becomes polarized in the sense of becoming an oxygen electrode.

2. R.H. Brown, G.C. English and R.D. Williams, The Role of Polarization in Electrochemical Corrosion, *NACE Conference*, St. Louis, Missouri, USA, 4–7 April 1950.

In its most practical aspects as well as in its fundamental mechanisms electrochemical corrosion is almost always associated with irreversible electrode phenomena. The multitude of factors involved in these phenomena may be defined as electrochemical polarization. Idealized schematic as well as actual polarization diagrams are discussed. Methods of correlating polarization with corrosion data such as weight loss are shown. A method for obtaining the contribution made by the polarization of each electrode reaction to the total polarization observed at an electrode is described along with the implications, thereof in the evaluation of the true over-voltage values. In addition, other factors, which may fall within a broad definition of polarization, are treated. The relationship of the so-called IR drop or true ohmic resistance at metal liquid interfaces to polarization diagrams, and to over voltage concept is discussed.

3. R. Balasubramaniam, A.V. Ramesh Kumar, Corrosion Resistance of the Dhar Iron Pillar, *Corrosion Science*, 45, 2451–2465, 2003.

The corrosion resistance of the 950 year old Dhar iron pillar has been addressed. The microstructure of a Dhar pillar iron sample exhibited characteristics typical of ancient Indian iron. Intergranular cracking indicated P segregation to the grain boundaries. The potentiodynamic polarization behaviour of the Dhar pillar iron and mild steel, evaluated in solutions of pH 1 and 7.6, indicate that the pillar iron is inferior to mild steel under complete immersion conditions. However, the excellent atmospheric corrosion resistance of the phosphoric Dhar pillar iron is due to the formation of a protective passive film on the surface. Rust analysis revealed the presence of crystalline magnetite ($\text{Fe}_3\text{-xO}_4$), $\alpha\text{-Fe}_2\text{O}_3$ (hematite), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$) and phosphates, and amorphous $\delta\text{-FeOOH}$ phases. The rust cross-section revealed a layered structure at some locations.

The experimental techniques used are optical and scanning electron microscopes, electron microprobe, potentiodynamic polarization, X-ray diffraction, Fourier transform infrared spectroscopy and transmission Mössbauer spectroscopy.

Some significant titles, which are worth noting are shown below:

Gustav Tammann	Lehrbuch der Metallkunde	1914
	Die Aggregatzustände	1922
	Lehrbuch der heterogenen Gleichgewichte	1924
Ulick R. Evans	The Corrosion of Metals	1924
	Metallic Corrosion, Passivity and Protection	1937
	An Introduction to Metallic Corrosion	1948
	The Corrosion and Oxidation of Metals (first supplementary volume)	1960 1968
	(second supplementary volume)	1976
Marcel Pourbaix	Thermodynamics of Dilute Aqueous Solutions	
	Atlas of Electrochemical Equilibria in Aqueous solutions	
	Atlas of Chemical and Electrochemical Equilibria in the presence of Gaseous Phase	
	Lectures on Electrochemical Corrosion	
Herbert H. Uhlig		1948
	Uhlig's Corrosion Handbook (2nd edn)	2000
	Corrosion and Corrosion Control	1963
H.H. Uhlig, R.W. Revie	Corrosion and Corrosion Control (revised)	1986
Mars Guy Fontana	Corrosion	1957
N.D. Greene	Corrosion Engineering	1967
		1986
J.I. Bregman	Corrosion Inhibitors	1963
V.S. Sastri	Corrosion Inhibitors	1998
	Principles and Applications	
I.L. Rozenfeld	Corrosion Inhibitors	1982
H. Van Droffelaar	Corrosion and its Control	1995
J.T.N. Atkinson	An introduction to the subject	
Kenneth R. Trethewey	Corrosion	1988, 1995
	for Science and Engineering	
John Chamberlain	An introduction to Corrosion and	1972
	Protection of Metals	
D.A. Jones	Principles and Prevention of Corrosion	1992
P.R. Roberge	Handbook of Corrosion Engineering	1999
P.R. Roberge	Corrosion Doctor website on Internet	1999
K. Seymour Coburn	Corrosion	1984
L.S. Van Delinder	Corrosion Basics – an introduction	1984
A.R. Troiano	Hydrogen Embrittlement and Stress	1984
	Corrosion Cracking	

G. Charles Munger	Corrosion Prevention by Protective Coatings	1984, 1999
W.H. Ailor	Atmospheric Corrosion	1982
J. Yahalom	Stress Corrosion Cracking	1980
J.M. West	Basic Corrosion and Oxidation	1980
E. Mattsson	Basic Corrosion Technology for Scientists and Engineers	1989
F. Hine	Localized Corrosion	1988
J. Toucek	Theoretical Aspects of the Localized Corrosion of Metals	1985
P.A. Schweitzer	Encyclopedia of Corrosion Technology	1998
G. Welsch	Oxidation and Corrosion of Intermetallic Alloys	1996
J.B. Little	Microbiologically Influenced Corrosion	1997
Y.I. Kuznetsov	Organic Inhibitors for Corrosion of Metals	1996
P.A. Schweitzer	Encyclopedia of Corrosion Technology	1998
L.L. Shreir	Corrosion	1994
R.S. Munn	Computer Modeling in Corrosion	1992
R.H. Jones	Stress–Corrosion Cracking	1992
A.J. McEvily	Atlas of Stress–Corrosion and Corrosion Fatigue Curves	1990
G. Prentice	Perspectives on Corrosion	1990
A.S. Bradford	Corrosion Control	2001
R. Baboian	NACE Corrosion Engineer’s Reference Book	2002

1.1 Impact of Corrosion

There are three areas of concern when corrosion and its prevention are considered. The three major factors are economics, safety and environmental damage.

Metallic corrosion, although seemingly innocuous, indeed affects many sectors of a nation’s economy. The National Bureau of Standards (NBS) in collaboration with Battelle Columbus Laboratory (BCL) studied the costs of corrosion in USA using the input/output model.⁷ Some elements of the costs of corrosion used in the model are shown below:

Capital costs

- Replacement of equipment and buildings
- Excess capacity
- Redundant equipment

Control costs

- Maintenance and repair
- Corrosion control