

# MANUAL OF INDUSTRIAL CORROSION STANDARDS AND CONTROL

ASTM SPECIAL TECHNICAL PUBLICATION 534

F. H. Cocks

# MANUAL OF INDUSTRIAL CORROSION STANDARDS AND CONTROL

Sponsored by ASTM Committee G-1  
on Corrosion of Metals

ASTM SPECIAL TECHNICAL PUBLICATION 534  
F. H. Cocks, editor

List price \$16.75  
04-534000-27



AMERICAN SOCIETY FOR TESTING AND MATERIALS  
1916 Race Street, Philadelphia, Pa. 19103

© BY AMERICAN SOCIETY FOR TESTING AND MATERIALS 1973  
Library of Congress Catalog Card Number: 73-75375

**NOTE**

The Society is not responsible, as a body,  
for the statements and opinions  
advanced in this publication.

Printed in Baltimore, Md.  
November 1973

## Foreword

The *Manual of Industrial Corrosion Standards and Control* has been prepared and sponsored by the members of ASTM Committee G-1 on Corrosion of Metals. Dr. Franklin H. Cocks was responsible for the organization of this material.

## **Related ASTM Publications**

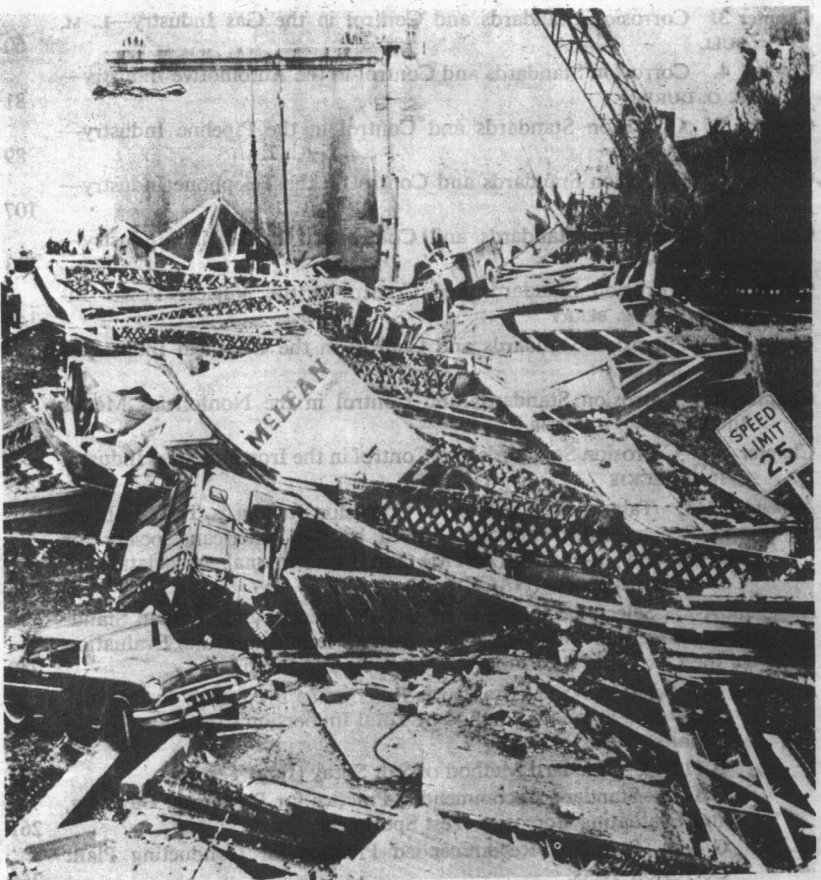
**Metal Corrosion in the Atmosphere, STP 435 (1968),  
\$27.00 (04-435000-27)**

**Localized Corrosion—Cause of Metal Failure, STP  
516 (1972), \$22.50 (04-516000-27)**

**Stress Corrosion Cracking of Metals—A State of the  
Art, STP 518 (1972), \$11.75 (04-518000-27)**

# Contents

Introduction	1
Chapter 1. Introduction to Corrosion—R. H. COOK	3
Chapter 2. Corrosion Standards and Control in the Petroleum Industry—A. S. COOPER	42



G 15-71—Standard Definitions of Terms Relating to Corrosion and Corrosion Testing	279
G 15-71—Standard Recommended Practices for Applying Standards to Analysis of Corrosion Data	281

Frontispiece: Photograph of U.S. 33 Highway Bridge, Point Pleasant, W. Va., taken after its collapse on 12 Dec. 1967. Courtesy National Transportation Safety Board.

# Contents

<b>Introduction</b>	1
<b>Chapter 1.</b> Introduction to Corrosion—F. H. COCKS	3
<b>Chapter 2.</b> Corrosion Standards and Control in the Petroleum Industry— A. S. COUPER	42
<b>Chapter 3.</b> Corrosion Standards and Control in the Gas Industry—L. M. BULL	60
<b>Chapter 4.</b> Corrosion Standards and Control in the Automotive Industry— C. O. DURBIN	81
<b>Chapter 5.</b> Corrosion Standards and Control in the Pipeline Industry— A. W. PEABODY	89
<b>Chapter 6.</b> Corrosion Standards and Control in the Telephone Industry— G. SCHICK	107
<b>Chapter 7.</b> Corrosion Standards and Control in the Marine Industry— B. F. BROWN	133
<b>Chapter 8.</b> Corrosion Standards and Control in the Nuclear Power In- dustry—W. E. BERRY	144
<b>Chapter 9.</b> Corrosion Standards and Control in the Chemical Industry— L. W. GLECKMAN	164
<b>Chapter 10.</b> Corrosion Standards and Control in the Nonferrous Metals Industry—W. H. AILOR	194
<b>Chapter 11.</b> Corrosion Standards and Control in the Iron and Steel Industry —H. P. LECKIE	209
<b>Appendix A-1.</b> Tabulated list of Current Corrosion Standards, Test Methods, and Recommended Practices Issued by the American Society for Testing and Materials (ASTM) and the National Association of Corrosion Engineers (NACE)	236
<b>Appendix A-2.</b> Selected Tabulation of British, French, and German Stand- ards Concerned with Corrosion Testing Methods and the Evaluation of the Corrosion Resistance of Materials and Products	240
<b>Appendix B.</b> Selected ASTM Standards Referred to Frequently in Book:	
A 279-63—Standard Method of Total Immersion Corrosion Test of Stainless Steels.	245
B 117-73—Standard Method of Salt Spray (Fog) Testing.	253
G 1-72—Standard Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.	261
G 4-68—Standard Recommended Practice for Conducting Plant Corrosion Tests.	266
G 15-71—Standard Definitions of Terms Relating to Corrosion and Corrosion Testing.	279
G 16-71—Standard Recommended Practice for Applying Statistics to Analysis of Corrosion Data.	281

---

**Frontispiece:** Photograph of U.S. 35 Highway Bridge, Point Pleasant, W.Va. taken after its collapse on 15 Dec. 1967. Courtesy National Transportation Safety Board.

# Introduction

This manual is a working source book of procedures, equipment, and standards currently being used to solve industrial testing and control problems. It is intended as a guide to those in university and government, as well as in industrial laboratories, who are faced with combatting corrosion problems or developing more corrosion resistant materials. The aim throughout is to combine a brief discussion of fundamental principles with clear descriptions of concomitant techniques and methods as well as the types of problems to which these have been and are being applied.

Although corrosion problems are common to all industries, the test methods and control procedures that have been developed to deal with them are diverse. By combining descriptions of major corrosion problem areas together with discussions of the approaches that have been evolved for controlling them, more effective means for reducing corrosion losses may be fostered. Thus, this manual is organized so that the first chapter provides a concise introduction to basic corrosion science, while subsequent chapters, each written by a leader in his field, review the application of these principles in practice. Emphasis is placed on the explanation of proven methods and standards, as well as on suggestions for procedures which might well become standards in the future. These chapters are followed by two appendices. The first provides abstracts and sources for existing corrosion standards, while the second appendix includes six ASTM standards referred to most frequently in the text.

Within the past decade it has become clear to an increasing number of diverse scientific and industrial groups that more emphasis on the standardization of corrosion tests and the means for interpreting data derived from them is both necessary and valuable. It is often difficult, however, when faced with a specific corrosion problem, to know which of several different testing procedures and standards should be utilized or where information directly relevant to a particular situation might be obtained. It is hoped that this manual will assist in resolving this difficulty.

*Franklin H. Cocks*

Duke University  
School of Engineering  
Durham, N.C. 27706





## Chapter 1

# Introduction to Corrosion

*F. H. Cocks<sup>1</sup>*

---

Webster [1]<sup>2</sup> defines corrosion as "the action or process of corrosive chemical change . . . a gradual wearing away or alteration by a chemical or electrochemical essentially oxidizing process as in the atmospheric rusting of iron." This definition does not restrict corrosion to any one class of materials, nor to any one environment. It does, however, imply a degradation in properties through the reaction of a material with its surroundings. This environment may be liquid, gaseous, or even solid as in the case of the reaction of filaments of SiC with an aluminum matrix they are intended to reinforce. Although many such new corrosion reactions are being encountered as more complex materials are applied in increasingly varied and unusual situations, the problems associated with far more mundane and widespread corrosion reactions have by no means been satisfactorily solved. The formation of oxides on iron exposed to the atmosphere at both ambient and elevated temperatures, for example, in automobile mufflers, year after year continues to extract a cost of hundreds of millions of dollars. Considerable progress has been and continues to be made, however, in reducing these corrosion losses. It is to the further control and reduction of practical and industrially important corrosion problems that this manual is directed.

Corrosion studies and the development of improved methods of corrosion prevention and control are of enormous practical industrial importance. It has been estimated that in the United States alone, the costs attributable to corrosion amount to more than 10 billion dollars annually [2]. While some corrosion losses may appear inevitable, the proper selection of materials and the application of known principles and protection methods can be expected to reduce these losses greatly.

In this introductory chapter, the basic principles of corrosion science are reviewed as a guide to subsequent chapters which each provide a discussion of how this knowledge can be applied in industrial practice to achieve the desired goal—the minimization of the economic burden imposed by corrosion. The unifying theme throughout these chapters is the use of

<sup>1</sup> Duke University, School of Engineering, Durham, N.C. 27706.

<sup>2</sup> Italic numbers in brackets refer to references listed at the end of this chapter.

standards which accurately detail the testing methods and control procedures now carried out in major industries. It is to be hoped that the information provided will contribute not only to the more effective and widespread use of available standards but to the development of additional corrosion standard test methods and control procedures as well.

The attack on metals by their environment can take many forms, ranging from uniform general attack and tarnishing to more complex reactions such as pitting, filiform corrosion, corrosion fatigue, stress corrosion, and other specific forms of damage discussed later in this chapter. The type of property degradation that will occur depends not only on the nature of the metallic material, and its physical state and conditions of use, but on the composition of the environment as well. The specific chemical species present in this environment, their concentration, and the temperature can determine whether attack will be general or localized or whether it will be fast or slow, accelerated or inhibited. The physical structure of many metals of a given composition can be enormously altered by heat treatment or cold working, and this structure in many cases will determine whether attack will be catastrophic or relatively mild.

In evaluating and correcting an existing or potential corrosion situation there are several fundamental choices to be considered. Does the metal or alloy being considered represent an optimum choice both from the point of view of economics as well as corrosion resistance? What will the environmental conditions this alloy is exposed to be and is it feasible to consider modifying this environment? What limits are imposed on the design of the structure being considered and how can this design be changed to minimize corrosive effects? Can protective coatings be used to isolate the whole structure, or critical parts of it, from the environment? The design engineer, too, can influence corrosion processes, not only directly through the specification of materials but also by providing material and environment configurations that minimize corrosive effects. Such designs can only be optimized if the processes that might lead to damage are understood.

While the range of possible corrosion situations is so large that a description of even a small fraction of them is not practical, a surprisingly few basic principles are sufficient to understand the detailed mechanisms of each case. Once the mechanism of damage is understood, the likelihood of making the correct choice to eliminate or minimize this damage is greatly improved.

In the following section, these underlying principles of corrosion processes are described before going on to consider important special forms of corrosion attack and methods of corrosion protection and control.

### Basic Corrosion Principles

The conversion of elemental metals or alloys into ions in an electrolyte (any electrically conducting solution, for example, seawater) is an essentially electrochemical process. The electrochemical character of corrosion has

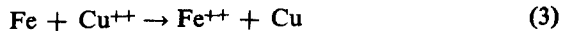
long been firmly established, and a concise review of the early experimental proofs of the electrochemical basis of corrosive action is available [3]. When a metal is placed in an electrolyte it acquires an electrical potential which is a measure of the tendency for that metal to dissolve as positive ions in solution. Since the solution must remain electrically neutral, an equivalent number of some other positive ions must be removed as the metal corrodes. A sample of iron placed into a solution of copper sulfate, for example, will begin to corrode (dissolve as iron ions) while at the same time copper ions are plated out of solution forming copper metal on the surface of the iron. The dissolution of the iron can be written as



and is said to be an anodic reaction because the solid iron (Fe) is being increased in oxidation state to form iron ions ( $\text{Fe}^{++}$ ), by the removal of two electrons ( $2e^{-}$ ) per iron atom. The copper reaction can be written as



and is said to be a cathodic reaction because copper ions are being reduced in oxidation state through the gain of electrons, to form copper metal. The combination of reactions 1 and 2 gives



as the overall electrochemical reaction. This corrosion reaction is self-stifling, however, because the deposited copper acts as a barrier between

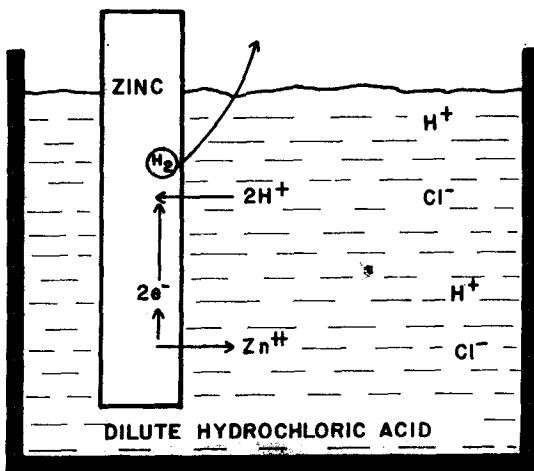


FIG. 1—Schematic drawing showing the corrosion of zinc in dilute hydrochloric acid.

the iron and the solution, thus preventing further reaction. In the case of zinc immersed into acid solutions, it is hydrogen which is plated out from solution in order to maintain electrical neutrality, as shown in Fig. 1. Here, the electrons released by the zinc as it ionizes and goes into solution travel through the remaining solid zinc to the points on the surface where hydrogen ions are neutralized to form hydrogen atoms. Two such neutralized atoms must then combine to form a molecule of hydrogen gas. Since the hydrogen gas can be removed as bubbles, the reaction is not a self-limiting one, and the formation of zinc chloride is not stifled.

In both corrosion reactions just described, the flow of electrons occurs within the specimen of corroding metal itself. This current flow could just as well pass through an external wire to neutralize ions at some other point, as for example, at a piece of copper immersed elsewhere in the solution as shown in Fig. 2. In such a case, the corroding sample (zinc) is defined as the anode and the copper sample, which does not corrode, as the cathode.

The tendency for zinc to enter the solution is dependent upon the concen-

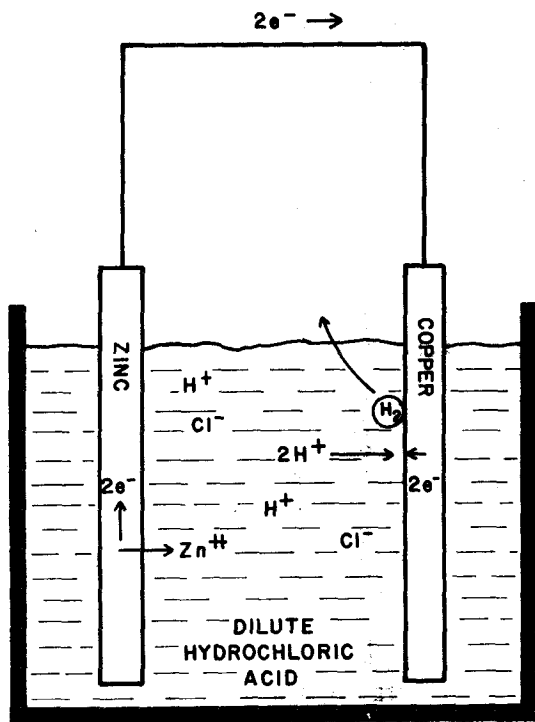


FIG. 2—Schematic drawing showing the separation of anodic and cathodic relations when strips of zinc and copper in hydrochloric acid are electrically connected.

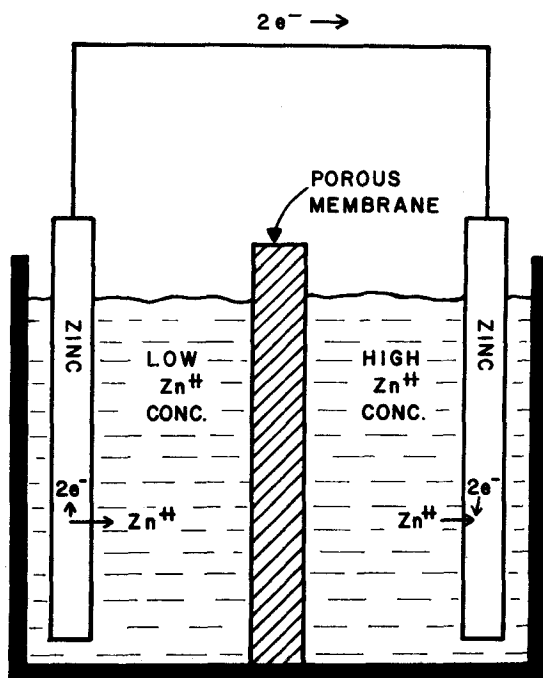


FIG. 3—Schematic drawing of a metal-ion concentration corrosion cell.

tration of zinc ions already present in this solution. For example, one could construct a corrosion cell as shown in Fig. 3, by placing two zinc specimens in solutions containing different concentrations of zinc ions. In this case the zinc sample which is immersed in the less concentrated zinc solution will corrode while the zinc specimen immersed in the more concentrated zinc solution will have additional zinc plated on it. This process is an example of concentration cell corrosion and illustrates the point that corrosion can occur even if the metals making up the anode and the cathode are identical.

The electrical potential reached by a metal immersed in an aqueous solution thus depends on the concentration of its ions already present in solution. The electromotive force series shown in Table 1 lists the potentials acquired by different metals when each is in contact with an aqueous solution of its ions at unit activity (approximately 1 mole/1000 g of water at 25 C) [4]. The zero potential assigned to hydrogen is selected arbitrarily and thus constitutes the reference potential against which the others have been measured. Very reactive metals such as sodium and magnesium appear at the negative or less noble end of the list, while inert metals such as platinum or gold appear at the more noble or positive end.

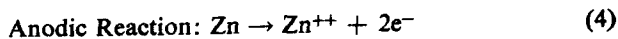
TABLE 1—Standard electromotive force series (emf) at 25 C [4].

Reaction	Standard Electrode Potential, volts	
$\text{Au}^{+++} + 3\text{e}^- = \text{Au}$	+1.50	Noble (more cathodic)
$\text{Ag}^+ + \text{e}^- = \text{Ag}$	+0.7991	
$\text{Cu}^{++} + 2\text{e}^- = \text{Cu}$	+0.337	
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.00	
$\text{Pb}^{++} + 2\text{e}^- = \text{Pb}$	-0.126	
$\text{Sn}^{++} + 2\text{e}^- = \text{Sn}$	-0.136	
$\text{Ni}^{++} + 2\text{e}^- = \text{Ni}$	-0.250	
$\text{Cd}^{++} + 2\text{e}^- = \text{Cd}$	-0.40	
$\text{Fe}^{++} + 2\text{e}^- = \text{Fe}$	-0.440	
$\text{Cr}^{+++} + 3\text{e}^- = \text{Cr}$	-0.74	
$\text{Zn}^{++} + 2\text{e}^- = \text{Zn}$	-0.763	
$\text{Al}^{+++} + 3\text{e}^- = \text{Al}$	-1.66	
$\text{Mg}^{++} + 2\text{e}^- = \text{Mg}$	-2.37	Active (more anodic)

As an example of how such a scale can be used, one can imagine a corrosion cell constructed as shown in Fig. 4. Here one compartment contains a specimen of zinc in a solution of zinc ions at unit activity (approximately 1 mole of zinc ions per 1000 g of water). The other compartment contains a specimen of silver in a solution of silver ions also at unit activity. A voltmeter connected between these two metal specimens would read 1.562 V as would be expected from their relative position in Table 1. Then, when the voltmeter is replaced by a copper wire, the more active zinc will be found to corrode, while the less active silver is plated from solution. As this process continues, the voltage measured between the zinc and silver specimens would decrease as the concentration of zinc ions increased while that of silver ions decreased. Thus, corrosion cell potentials depend on both the electrode material and the electrolyte composition.

In addition to the standard emf series of Table 1 it is also useful to know cell potentials obtained using a single common electrolyte. Such a listing is called a galvanic series and the relative position shown by a group of metals and alloys immersed in seawater as the standard electrolyte is shown in Table 2. If a pair of metals selected from this list are immersed in seawater and connected together electrically, the metal lower on the list will be found to corrode. The farther apart the metals of this pair are, the greater will be the tendency for the lowermost one to corrode. It must be remembered that this list applies only to a specific electrolyte—seawater—and a much different sequence could result if some electrolyte other than seawater were chosen.

As illustrated for the case of zinc in hydrochloric acid, corrosion reactions can be divided into two parts. In the case of zinc in hydrochloric acid, the anodic (corrosion) reaction is that involving zinc entering solution.



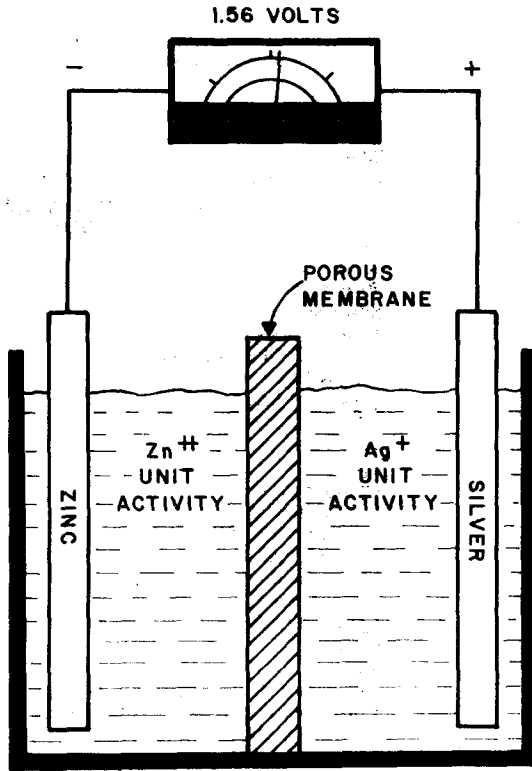
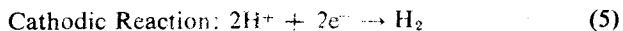


FIG. 4—Schematic drawing showing the voltage developed between two standard half cells.

The second part is the cathodic reaction of the hydrogen required for electrical neutrality of the solution.



There are not many practical situations, however, in which metals are used in sufficiently acid solutions that hydrogen gas evolution occurs. In many service environments corrosion is decreased by the formation of a thin film of hydrogen gas on the cathodic surfaces which decreases the current flow and hence the corrosion rate. This situation is known as hydrogen polarization. If this film of hydrogen is destroyed or prevented from forming, the corrosion rate will be increased. The presence of dissolved oxygen can lessen hydrogen polarization by shifting the potential to more active values and reacting with the hydrogen to form water.

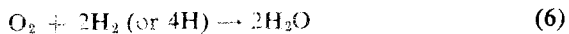




TABLE 2—*Galvanic series of metals and alloys.*

Noble (more cathodic)	Platinum
	Gold
	Graphite
	Silver
	Chromium Nickel Stainless Steel Type 304 (passive)
	Chromium Nickel Stainless Steel Type 316 (passive)
	13% Chromium Steel Type 410 (passive)
	Titanium
	Monel
	70-30 Cupro-Nickel
	Silver Solder
	Nickel (passive)
	76Ni-16Cr-7Fe Alloy (passive)
	Yellow Brass
	Admiralty Brass
	Aluminum Brass
	Red Brass
	Copper
	Silicon Bronze
	Nickel (Active)
	76Ni-16Cr-7Fe Alloy (active)
	Muntz Metal
	Manganese Bronze
	Naval Brass
	Lead Tin Solders
	Lead
	Tin
	Chromium Nickel Stainless Steel Type 304 (active)
	Chromium Nickel Stainless Steel Type 316 (active)
	Chromium Stainless Steel Type 410 (active)
	Mild Steel
	Wrought Iron
	Cast Iron
	Aluminum (2024)
	Cadmium
	Aluminum (6053)
	Alclad
	Zinc
	Magnesium Alloys
Active (more anodic)	Magnesium

It is also possible for dissolved oxygen to participate directly in the cathodic reaction by being reduced to hydroxyl ions.



In either case the presence of dissolved oxygen acts to depolarize the cathodic reaction and leads to an increased rate of corrosion by increasing the rate at which metal ions can enter the solution.

During corrosion, more than one oxidation process and more than one reduction process may occur simultaneously. This situation would be expected, for example, if the corroding metal were an alloy containing two