

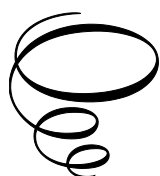
The Corrosion Characteristics of Alloys in Simulated Physiological Fluids

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Edited by

Susai Rajendran, Abdulhameed Al-Hashem, Branimir N. Grgur,
T. Uma Sankareswari, A. Krishnaveni and S. Johnson Raja

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This book first published 2026

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

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ISBN: 978-1-0364-6504-9

ISBN (Ebook): 978-1-0364-6505-6

TABLE OF CONTENTS

Acknowledgements.....	viii
-----------------------	------

Section A: Fundamental elements of corrosion

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
Professor T Umamathi, Dr Abdulhameed Al-Hashem

Chapter 1.....	2
Corrosion and rusting of iron	
Chapter 2.....	9
Effects of corrosion	
Chapter 3.....	12
Corrosion rate and factors influencing corrosion rate	
Chapter 4.....	19
Theories of corrosion	
Chapter 5.....	23
Electro chemical corrosion	
Chapter 6.....	32
Methods of corrosion control	
Chapter 7.....	38
Corrosion inhibitors	

Section B: Body fluids and their roles

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
Dr. Branimir N. Grgur

Chapter 1.....	46
Saliva	
Chapter 2.....	48
Serum	
Chapter 3.....	50
Tears	

Chapter 4.....	54
Urine	

Section C: Corrosion resistance of orthodontic wires in simulated saliva

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
V Velkannan, Professor R Saranya, Dr Abdulhameed Al-Hashem

Chapter 1	60
The corrosion characteristics of orthodontic wires in simulated saliva examined both in the absence and presence of green extract	

Chapter 2.....	66
The resistance to corrosion of the SS18/8 alloy and the 18 Karat Gold alloy evaluated in simulated saliva containing Suda Mittai (Premium Peppermint)	

Chapter 3.....	77
Is it permissible for individuals with Ni-Cr orthodontic wire to consume vodka orally?	

Section D: Corrosion resistance of alloys in synthetic sweat

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
Dr. Branimir N. Grgur

Chapter1	88
The corrosion characteristics of alloys in synthetic sweat	

Chapter 2.....	93
Corrosion resistance of ornaments in artificial sweat	

Section E: Corrosion resistance of alloys in simulated tears

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
Professors Shabnam Dan, Amit Chatree, Mahima Luther, Sam Higginbottam,
Dr Abdulhameed Al-Hashem

Chapter 1	104
Tears	

Chapter 2.....	107
The impact of elevated levels of glucose and sodium chloride on the corrosion characteristics of Nickel-Titanium alloy in artificial tears	

Chapter 3.....	120
The resistance to corrosion of Nickel -Chromium alloy in artificial tears (AT) when exposed to elevated levels of glucose and sodium chloride.	

Section F: The corrosion characteristics of alloys in artificial urine

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
Professor R Nagalakshmi

Chapter 1	128
The resistance of alloys to corrosion in simulated urine environments	
Chapter 2	133
The resistance to corrosion of SS 316 L in artificial urine containing bile salt	

Section G: Corrosion behavior of alloys in simulated Ringer's solution

Authors:

Professor Dr Susai Rajendan, A Grace Baby, A Mariya Agnes Deena, I Suganya Vinnarasi,
Professor S Agiladevi, Dr. Branimir N. Grgur

Chapter 1	142
Ringer's solution	
Chapter 2	146
Corrosion behaviour of alloys in Ringer's solution	
Chapter 3	151
Influence of glucose on corrosion resistance of Ni-Ti alloy in simulated Ringer's solution	

ACKNOWLEDGEMENTS

The Editors express their gratitude to their respective managements for their assistance and support. They extend their appreciation to the Research Students who have significantly contributed to the development of this book. They are also deeply grateful to the Publishers and Reviewers for their invaluable help and support.

SECTION A

FUNDAMENTAL ELEMENTS OF CORROSION

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Abstract: Corrosion refers to the degradation of materials resulting from chemical interactions with their surrounding environment. While the term is predominantly associated with metals, it can also pertain to the deterioration of plastics, concrete, and wood. This phenomenon is a natural process that transforms refined metals into more chemically stable compounds, including oxides, hydroxides, carbonates, or sulfides. Corrosion involves the gradual breakdown of materials through chemical and/or electrochemical reactions with their environment. This section will explore the causes of corrosion, prevention methods, various forms of corrosion, and its effects.

Keywords: Corrosion, definition, causes, effects, theories, methods of controlling corrosion.

This section is organized into the subsequent chapters.

1. Corrosion and rusting of iron
2. Effects of corrosion
3. Corrosion rate and factors influencing corrosion rate
4. Theories of corrosion
5. Electro chemical corrosion

Types of electrochemical corrosion

6. Methods of corrosion control
7. Corrosion inhibitors

CHAPTER 1

CORROSION AND RUSTING OF IRON

Abstract

This chapter provides a definition of corrosion, explores the rusting process of iron, and examines the various causes of corrosion. The roles of the anode, cathode, and electrolyte are crucial to the corrosion process. Additionally, the presence of oxygen and water is essential for the corrosion of metals. These elements are discussed in detail within this chapter.

Keywords: corrosion, rusting of iron, causes of corrosion, corrosion triangle

Corrosion

Corrosion can be defined in many ways.

Corrosion is the deterioration of materials by chemical interaction with their environment. The expression corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but normally refers to metals.

Corrosion is a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide, carbonate or sulfide. It is the steady devastation of materials by chemical and/or electrochemical reaction with their environment.

Corrosion is the decline and loss of a material and its critical properties due to chemical, electrochemical and other reactions of the exposed material surface with the surrounding environment.

Corrosion of metals and nonmetals takes place due to the gradual environmental interaction on the material surface. The structures and facilities of different materials are affected by this interaction. Even the ambient air, laden with moisture and oxygen, can start this process, known as rusting, on steel surfaces.

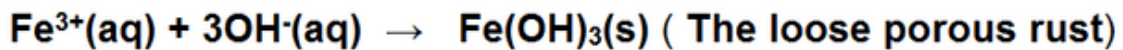
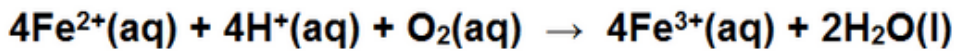
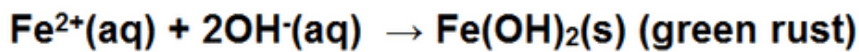
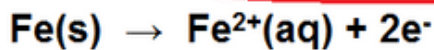
Rusting of iron

Rusting is the simplest instance of corrosion. Rusting is concerned with iron only and not with other metals and alloys.

Rust has been called “the great destroyer” and “the evil.” It is called as “the pervasive menace.” It destroys cars, fells bridges, sinks ships, sparks house fires, and nearly brought down the Statue of Liberty. Rust costs America more than \$400 billion per year—more than all other natural disasters shared.

Rusting of iron consists of the formation of hydrated oxide, $\text{Fe}(\text{OH})_3$, $\text{FeO}(\text{OH})$, or even $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It is an electrochemical process which requires the presence of water, oxygen and an electrolyte. In the absence of any one of these rusting does not occur to any noteworthy extent. In air, a relative humidity of over 50% provides the necessary amount of water and at 80% or above corrosion of bare steel is worse.

Formation of Rust- "the pervasive menace."

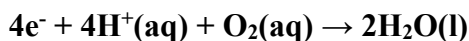


$\text{Fe(OH)}_3(\text{s})$ (The loose porous rust) \rightarrow $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ crystallized red-brown stuff "rust"

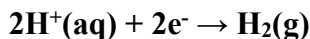
Since these processes involve hydrogen ions or hydroxide ions, they will be affected by changes in pH.

With limited O_2 , magnetite is formed (Fe_3O_4).

The electrons are rapidly consumed by hydrogen ions from water (H_2O) and dissolved oxygen or $\text{O}_2(\text{aq})$ at the edge of the droplet to create water:

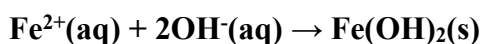


More acidic water increases corrosion. If the pH is very low the hydrogen ions will consume the electrons anyway, making hydrogen gas as a substitute of water:

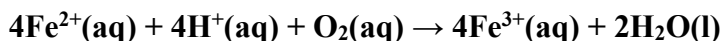


But where's the rust? The equations above tell only a small part of the story.

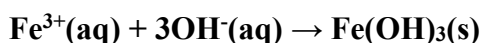
Hydrogen ions are being consumed by the process. As the iron corrodes, the pH in the droplet rises. Hydroxide ions (OH^{-}) appear in water as the hydrogen ion concentration falls. They react with the iron(II) ions to produce insoluble iron(II) hydroxides or green rust:



The iron(II) ions also react with hydrogen ions and oxygen to produce iron(III) ions:



The iron(III) ions react with hydroxide ions to produce hydrated iron(III) oxides (also known as iron(III) hydroxides):



The loose porous rust or Fe(OH)_3 can gradually transform into a crystallized form written as $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ the common red-brown stuff that is called "rust" forming tubercles as shown here. Since these processes involve hydrogen ions or hydroxide ions, they will be affected by changes in pH. With incomplete O_2 , magnetite is formed (Fe_3O_4).

Process of Corrosion

- Corrosion is a natural, spontaneous and thermodynamically favourable process.
- Metals decompose when they come in contact with environment especially air (oxygen) and moisture.
- Corrosion is the expression of desire of the metal to go back to its original state (ore).
- Man is born to live happily and then to die.
- Metal is produced to live and to undergo decay finally.
- Our death is sure.
- We can postpone death, we can't avoid it.
- Metal corrosion can be controlled but cannot be prevented.

Pure metal is in high energy state. It is unstable. During corrosion process it undergoes oxidation. Energy is released. Ore is produced. For instance, metal oxide. It is in low energy state. It is more stable. During metallurgy, the ore undergoes reduction in presence of energy. It is a reduction process. Pure metal in high energy state is produced (Figure1).

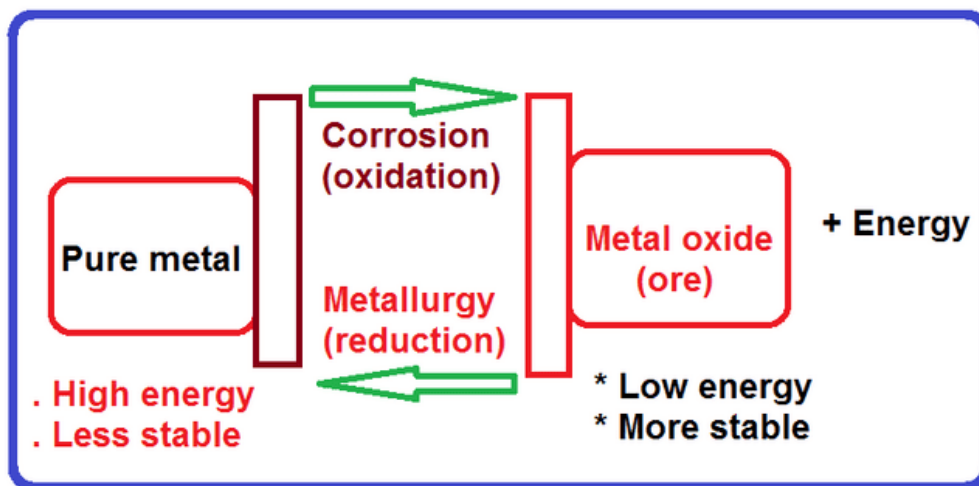


Figure 1: Pure metal and ore

Causes of Corrosion

The causes of corrosion are complex and vary across industries. Some examples common to specific industries are listed below:

- Corrosion in construction frequently occurs due to metals being exposed to outdoor elements and tremendous temperatures
- Underground mining is typified by an acidic water environment (often with chlorides and sulfates), combined with high humidity and temperature
- Forestry corrosion often takes place in remote locations, with equipment parked on grass or soil surfaces which draw up huge amounts of moisture overnight; this can corrode onboard mechanical systems and components.

Environmental conditions will also affect corrosion rates and spread. Where humidity is present, this generates moisture – causing a reaction where metals corrode much more rapidly than they would in dry conditions.

One or more of the following factors will often be present in a corrosive environment (Figure 2): Humidity, Extreme temperature, Surface moisture, Airborne particles, Salt and Industrial lubricants.

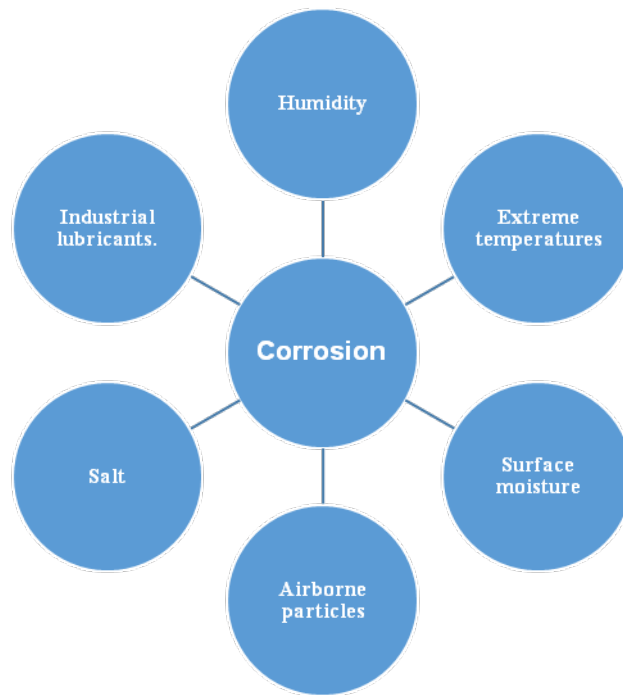


Figure 2: Causes of corrosion

Corrosion triangle

Corrosion triangle:

- 1) For steel (iron) to undergo corrosion, air (oxygen) and moisture (water) are necessary (Figure 3).
- 2) Corrosion takes place when anode and cathode are connected through an electrolyte (Figure 4).

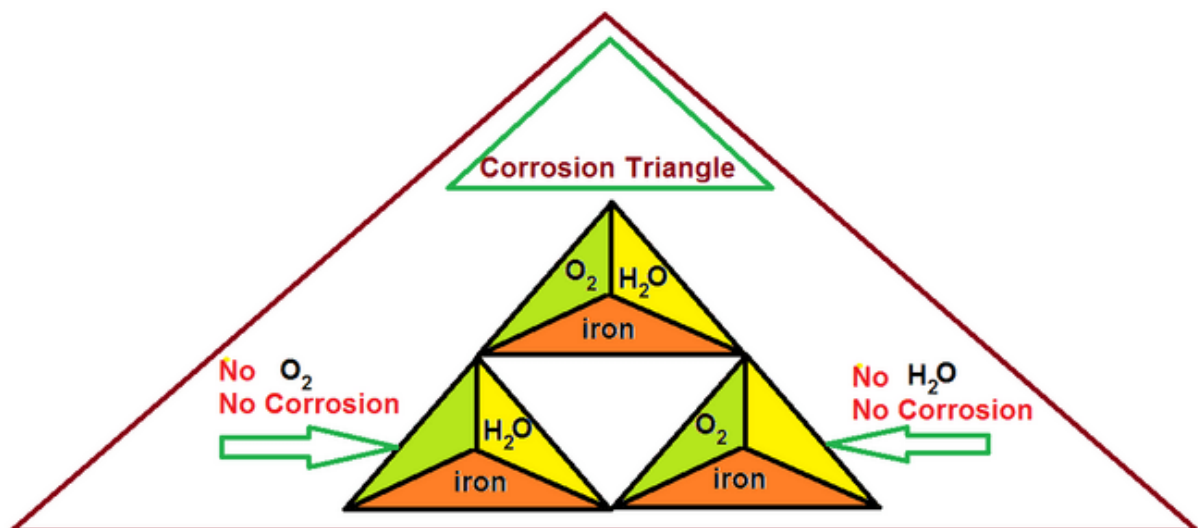


Figure 3: Oxygen and water corrosion triangle

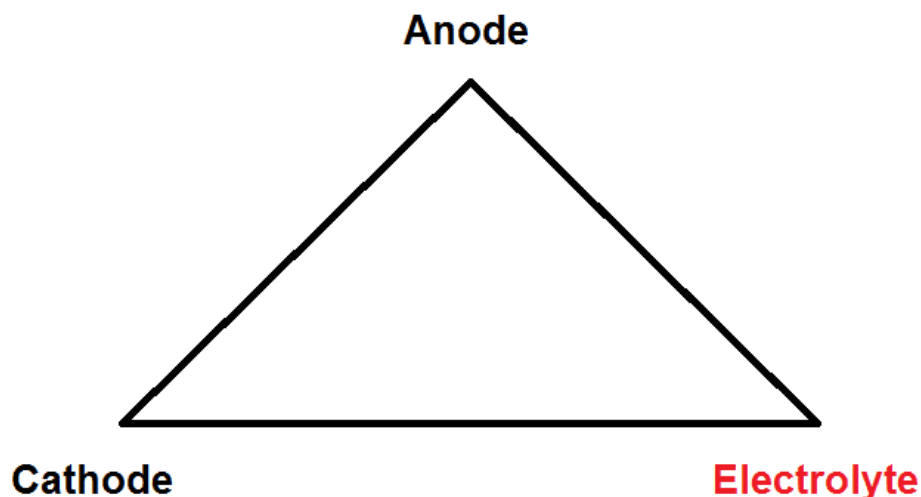


Figure 4: Anode, cathode, electrolyte: corrosion triangle

Experiment to show the need of oxygen and water for metals to undergo corrosion

For corrosion to take place, air (oxygen) and water are essential. This is proved by easy experiments (Figure 5).

Experiments:

Take four glass test tubes. Iron nails are introduced into them.

Test tube 1: It contains air and water (unboiled)

Test tube 2: It contains water (boiled) but no air

Test tube 3: It contains air but no water (water removed by anhydrous calcium chloride)

Test tube 4: It contains air + water + sodium chloride

Test tube	Observation	Inference (due to)
1	Corrosion	Presence of air and water. Therefore corrosion
2	no corrosion	No air. No corrosion
3	no corrosion	No water. No corrosion
4	more corrosion	Presence of air + water + Sodium Chloride (Cl ⁻) More corrosion

Conclusion

Presence of air and water are essential for metals to undergo corrosion.

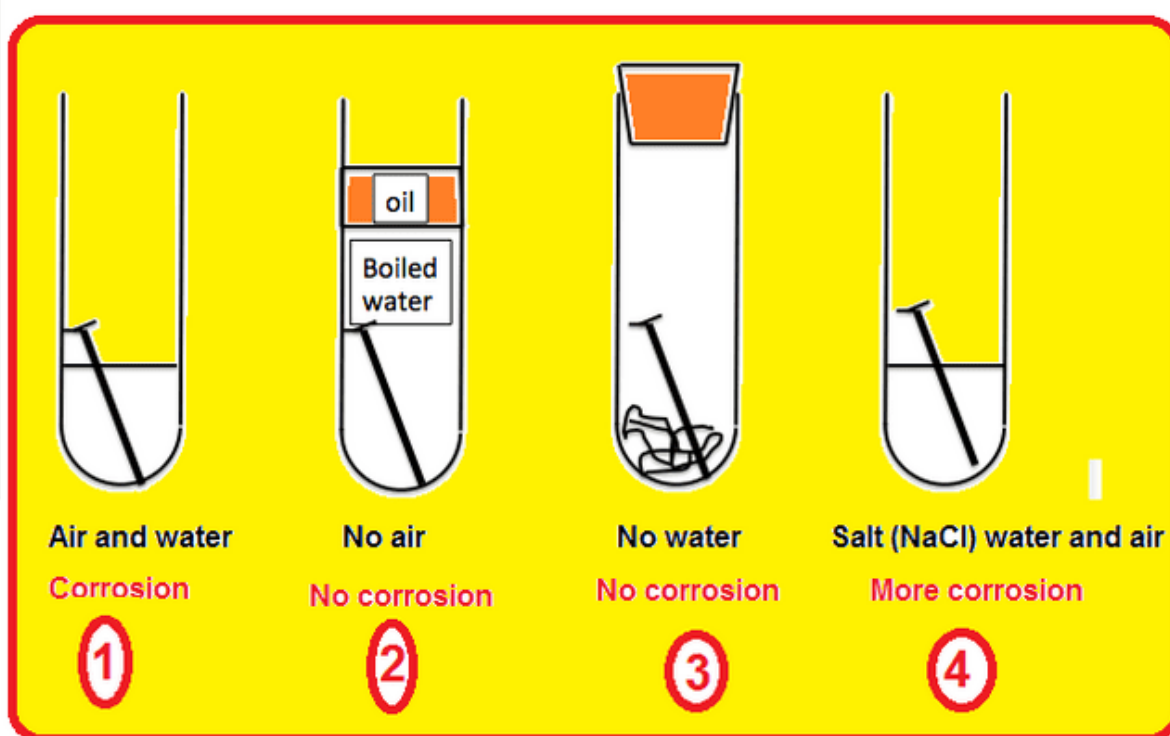


Figure 5: Presence of air and water are necessary for metals to undergo corrosion

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CHAPTER 2

EFFECTS OF CORROSION

Abstract

Corrosion affects our economy and human life in many ways. Collapse of bridges, air crafts, ships and loss of human life are some examples. Corrosion has many serious economic, health, safety, technological, and cultural consequences to our society. The annual corrosion costs ranged from about 1 to 5 percent of the Gross National product (GNP) of each nation. These aspects are discussed in this chapter.

Keywords: economic, health, safety, technological, and cultural consequences, Gross National product

Effects of corrosion

Corrosion affects our economy and human life in many ways. Some of them are as follow.

1. Collapse of bridges, air crafts, ships
2. Loss of human life
3. Shut down of factories
4. Over design of equipment
5. Loss of efficiency
6. Bopal tragedy is due to corrosion
7. Corrosion sank titanic ship

Consequences of Corrosion

Corrosion has many serious economic, health, safety, technological, and cultural consequences to our society (Fig. 1).

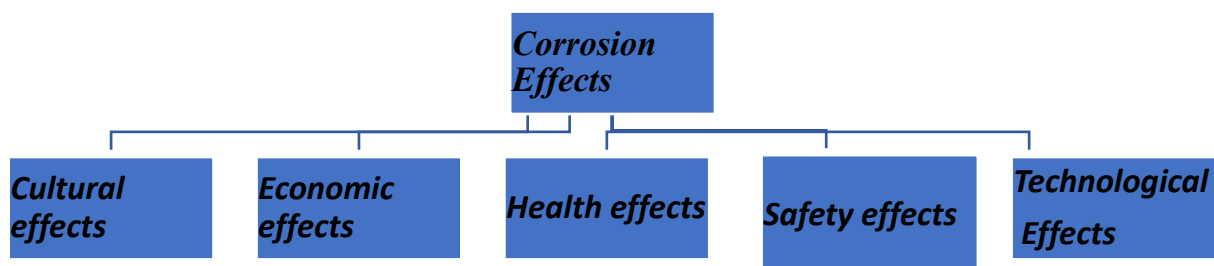


Figure 1. Corrosion effects

Cultural effects

Inside the world's museums conservators and restorers work to protect cultural resources against the negative effects of corrosion or to get rid of its traces from creatively or culturally significant artifacts.

Economic effects

Studies in a number of countries have attempted to resolve the national cost of corrosion. The most wide of these studies was the one carried out in the United States in 1976 which recognized that the overall annual cost of metallic corrosion to the U.S. economy was \$70 billion, or 4.2% of the gross national product.

Health effects

Recent years have seen an increasing use of metal prosthetic devices in the body, such as pins, plates, hip joints, pacemakers, and additional implants. New alloys and better techniques of implantation have been developed, but corrosion continues to generate problems. The situation has enhanced in recent years, so that hip joints which were at first limited to persons over 60 are now being used in younger persons, because they will last longer.

Safety effects

An even more important problem is corrosion of structures, which can result in harsh injuries or even loss of life. Security is compromised by corrosion contributing to failures of bridges, aircraft, automobiles, gas pipelines etc., the whole complex of metal structures and devices that make up the current world. Silver bridge collapse and Titanic corrosion are some of the examples.

Technological effects

The economic consequences of corrosion affect technology. An immense deal of the development of new technology is held back by corrosion problems because materials are necessary to withstand, in numerous cases simultaneously, higher temperatures, higher pressures, and more highly corrosive environments. Examples are solar energy systems and drilling for oil. The drilling for oil in the sea and on land, involves overcoming such corrosion problems as sulfide stress corrosion, microbiological corrosion, and the enormous display of difficulties involved in working in the highly corrosive marine environment. In many of these instances, corrosion is a limiting factor preventing the development of economically or even technologically workable systems.

Cost of corrosion

Corrosion is documented as one of the most serious problems in our modern societies and the resulting losses each year are in the hundreds of billions of dollars. Cost of corrosion studies have been undertaken by quite a lot of countries including, the United States, the United Kingdom, Japan,

Australia, Kuwait, Germany, Finland, Sweden, India, and China. The studies have ranged from formal and extensive efforts to informal and modest efforts. The ordinary finding of this studies was that the annual corrosion costs ranged from about 1 to 5 percent of the Gross National product (GNP) of each nation. India loses Rs.2 lakh crore every year due to corrosion.

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CHAPTER 3

CORROSION RATE AND FACTORS INFLUENCING CORROSION RATE

Abstract

Loss of material per unit time is called corrosion rate. It is expressed in various units such as corrosion current (mA cm^{-2}), mass loss ($\text{g m}^{-2} \text{day}^{-1}$) and penetration rates (mm y^{-1} or mpy) for all metals or for steel. Several factors such as nature of metal and nature of environment influence the rate of corrosion. They are discussed in this chapter.

Keywords: corrosion rate, factors influencing, mdd, mpy, nature of metal, nature of environment.

Corrosion rate and factors influencing corrosion rate

Corrosion Rate

Loss of material per unit time is called corrosion rate (CR)

Units: It is expressed in various units such as millimetre per year, mills per year and milligram per decimetre square per day (mdd).

$\text{Mdd} = (\text{weight loss in mg}) / (\text{surface area of metal in dm}^2 \times \text{immersion period in days})$

Corrosion Rate Conversion

Corrosion rate can be expressed in different units.

The following Tables 1 and 2 provide a simple way to convert data between the most common corrosion units in usage, i.e. corrosion current (mA cm^{-2}), mass loss ($\text{g m}^{-2} \text{day}^{-1}$) and penetration rates (mm y^{-1} or mpy) for all metals or for steel.

where:

- mpy = milli-inch per year
- n = number of electrons freed by the corrosion reaction
- M = atomic mass
- d = density

Table 1. Table of conversion of corrosion rates

	mA cm^{-2}	mm year^{-1}	mpy	$\text{g m}^{-2} \text{day}^{-1}$
mA cm^{-2}	1	3.28 M/nd	129 M/nd	8.95 M/n
mm year^{-1}	0.306 nd/M	1	39.4	2.74 d
Mpy	0.00777 nd/M	0.0254	1	0.0694 d
$\text{g m}^{-2} \text{day}^{-1}$	0.112 n/M	0.365 /d	14.4 /d	1

Note: one should read the Table from left to right, i.e.:

$$1 \text{ mA cm}^{-2} = (3.28 \text{ M/nd}) \text{ mm y}^{-1} = (129 \text{ M/nd}) \text{ mpy} = (8.95 \text{ M/n}) \text{ g m}^{-2} \text{ day}^{-1}$$

For example, if the metal is steel or iron (Fe), $n=2$, $M = 55.85 \text{ g}$ and $d = 7.88 \text{ g cm}^{-3}$ and the Table of conversion becomes:

Table 2. Table of conversion of corrosion rates in various units [1].

	mA cm⁻²	mm year⁻¹	mpy	g m⁻² day⁻¹
mA cm⁻²	1	11.6	456	249
mm year⁻¹	0.0863	1	39.4	21.6
Mpy	0.00219	0.0254	1	0.547
g m⁻² day⁻¹	0.00401	0.0463	1.83	1

Note: one should read the Table from left to right, i.e.:

$$1 \text{ mA cm}^{-2} = 11.6 \text{ mm y}^{-1} = 456 \text{ mpy} = 249 \text{ g m}^{-2} \text{ day}^{-1}$$

Corrosion calculators are also available [2,3].

Corrosion rate is also known as corrosion ratio [4].

The weight loss of a corrosion coupon after exposure to a corrosive environment, expressed as mils (thousandths of an inch) per year penetration. Corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupon. $\text{mpy} = (\text{weight loss in grams}) * (22,300) / (A \cdot d \cdot t)$ mpy = corrosion rate (mils per year penetration) A = area of coupon (sq. in.) d = metal density of coupon (g/cm^3) t = time of exposure in corrosive environment (days). It is significant to note that the calculated values using this formula are not representative in cases of severe pitting. Consequently, a complete report, including a visual inspection, is required to determine either the type of attack or the suitable corrosion control program. Corrosion rate is also known as corrosion ratio.

The following formula can be used to calculate corrosion rate from metal loss data [5]:

$$R_{corr} (\text{mm/yr}) = 87.6 \times (W/DAT)$$

where:

W = weight loss in milligrams

D = metal density in g/cm^3

A = area of sample in cm^2 $3.2T$ = time of exposure of the metal sample in hours

Factors Influencing rate of corrosion

Corrosion:

Corrosion is defined as the gradual destruction or deterioration of metals or alloys by the chemical or electrochemical reaction with its surroundings

Ex: Rusting of iron and steel.

Factors influencing the rate of corrosion:

1. Nature of metal
2. Nature of the environment

1. Nature of the metal

a. Position in emf series

The extent of corrosion depends upon the metal in the emf series. The metal above the hydrogen in emf series (Lower the reduction potential and high negative reduction potential) gets greater corroding nature vigorously.

b. Relative areas of the anode and cathode

The rate of corrosion will be more, when the area of cathode is larger and the area of anode is smaller.

c. Purity of the metal

The metal should be pure in state. Impurities present in the metal support galvanic corrosion. For example, the presence of minute amount of iron in zinc metal causes galvanic corrosion.

% purity of zinc	99.999	99.99	99.95
Corrosion rate	1	2650	5000

d. Over voltage (or) Over potential

Corrosion rate is inversely proportional to the over voltage of a metal in the corrosive environment
 Corrosion rate \propto 1/Over voltage of metal

- Example**

The over voltage of hydrogen is 0.7 V when zinc metal is placed in 1 M sulphuric acid and the rate of the corrosion is low. When we add a little amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33 V. This results in the increased rate of corrosion of zinc metal.

e. Nature of the corrosion product

The nature of the oxide film formed on the metal surface which can be decided by pilling –Bedworth rule.

- Alkali and alkaline earth metals such as Mg, Ca, etc. form, whose volume is less than the volume of the metal. Hence the oxide film will be porous and non – protective and bring about further corrosion.
- Heavy metals like Al, Cr, etc. form oxide, whose volume greater than that of the metal. Hence the oxide film will be non-porous and protective and prevents additional corrosion.

f. Nature of the corrosion product

If the corrosion product is soluble in the corroding medium, the corrosion rate will be faster. Likewise, if the corrosion product is volatile (like MoO₃ on Mo surface), the corrosion rate will be faster.

2.) Nature of the environment**a.) Temperature**

As temperature increases, rate of corrosion increases.

b.) Humidity

As humidity in the environment increases corrosion rate increases.

c) Presence of corrosive gases

The acidic gases like, CO₂, SO₂, H₂S and fumes of HCl, H₂SO₄ etc., produces electrolytes and thus accelerates the electrochemical corrosion.

d.) Presence of suspended particles

Particles like, NaCl along with moisture act as powerful electrolytes and thus accelerate the electrochemical corrosion.

e.) Effect of pH

Normally, acidic medium favours the corrosion reaction than alkaline (or) neutral media.

(f). Pourbaix diagram

- It explains the conditions (pH and electrode potentials) under which a metal undergoes corrosion.
- Example: Let us consider pourbaix diagram of iron system
- pH is plotted against electrode potential.
- Let us consider the situation of iron at points A, B, C and Z
- at A: metal undergoes corrosion
- at B: immunity (no corrosion)
- at C: passive (no corrosion)

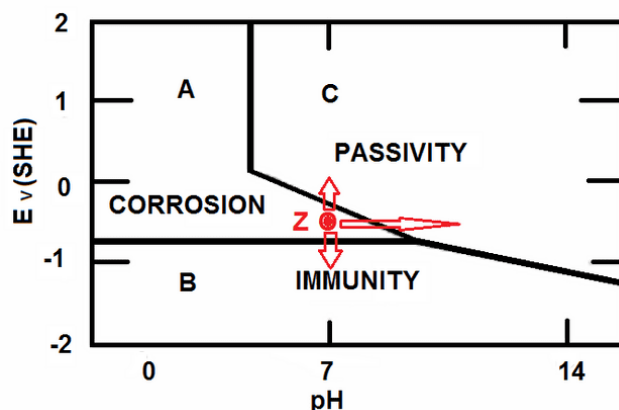


Figure 1. Pourbaix diagram

At Z: Corrosion.

Corrosion at Z can be prevented by

- Increasing the electrode potential
- Decreasing electrode potential
- Increasing pH value
 - This is explained in the Pourbaix diagram
 - This diagram is obtained by plotting pH of the medium on x axis and electrode potential on the axis.
 - Pourbaix diagram for iron system is shown in the figure
 - Depending on experimental conditions (pH and electrode potential), iron will be passive or undergo corrosion.

Example:

At A: Corrosion
 B: Immunity
 C: Passive

Summary

The above discussions on “factors influencing corrosion rate” are summarized in Figures 2 and 3.

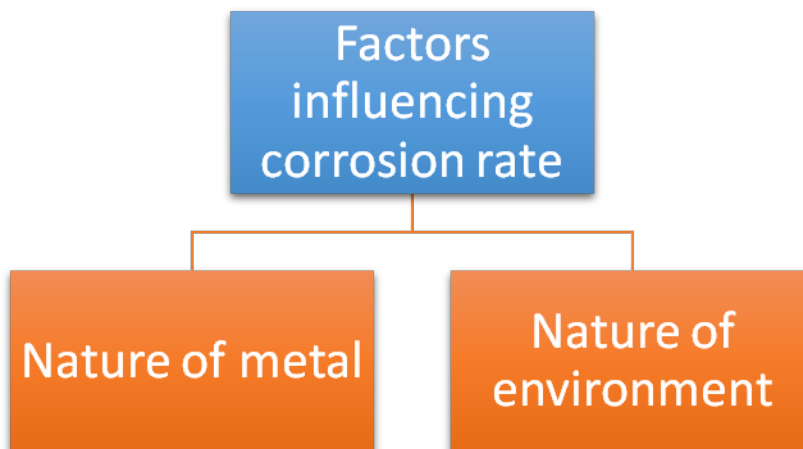


Figure 2: Factors influencing corrosion rate

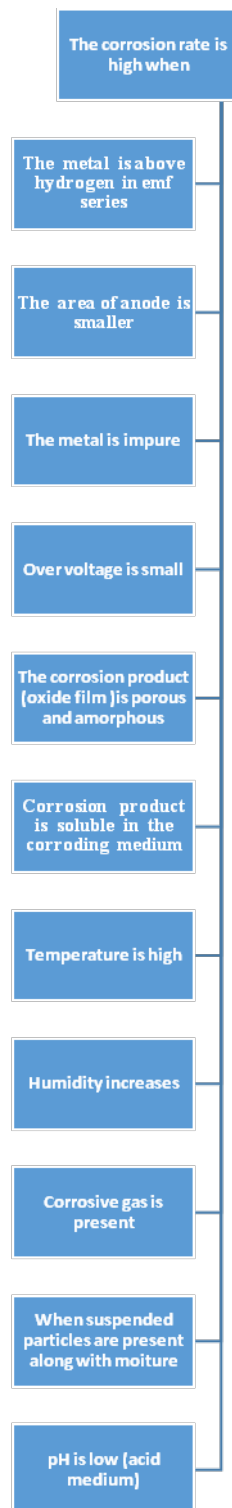


Figure 3: Corrosion rate is high when...

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CHAPTER 4

THEORIES OF CORROSION

Abstract

There are several theories of corrosion. One of them classifies corrosion as dry corrosion and wet corrosion. They are explained briefly in this chapter. Dry corrosion is further classified into oxidation corrosion, corrosion by hydrogen and liquid –metal corrosion. Due to the presence of moisture or a liquid medium, wet corrosion takes place.

Keywords: theories of corrosion, dry corrosion, wet corrosion, chemical corrosion, electrochemical corrosion

Theories of Corrosion

There are numerous theories of corrosion. One of them classifies corrosion as Dry corrosion and Wet Corrosion. They are explained briefly in this section.

DRY CORROSION (Chemical corrosion):

- Dry corrosion is due to the attack of metal surfaces by the atmospheric gases such as oxygen, hydrogen sulphide, sulphur dioxide, nitrogen, etc.
- It takes place in the absence of moisture

There are 3 main types of dry corrosion.

- (a) Oxidation corrosion (or) corrosion by oxidation
- (b) Corrosion by hydrogen
- (c) Liquid –metal corrosion.

(a) Oxidation corrosion (or) corrosion by oxidation:

Oxidation corrosion is the direct attack of oxygen at low or high temperatures on metal surface in the absence of moisture.

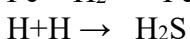
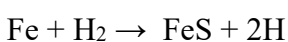
Mechanism of dry corrosion;

- i. Formation of metal ions (M^{2+})
 $M \rightarrow M^{2+} + 2e^-$ (oxidation)
- ii. Formation of oxide ions (O^{2-})
 $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$ (reduction)
- iii. Formation of metal – oxide film (over all reaction)
 $M + \frac{1}{2} O_2 \rightarrow M^{2+} + O^{2-} = MO$ (metal-oxide film)

Meal oxide formation;

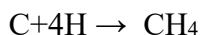
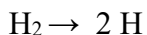
(b) Corrosion by hydrogen

(i) Hydrogen embrittlement (at ordinary temperature)



“The process of formation of cracks and blisters on the metal surface, due to high pressure of hydrogen gas is called hydrogen embrittlement”.

(ii) Decarburization (at higher temperature)



“The removal of carbon from the alloy or steel is known as decarburization”

DECARBURIZATION

(c) Liquid- metal corrosion

This is due to the chemical reaction of liquid metal at high temperature.

The corrosion reaction involves.

Dissolution of a solid metal by a liquid metal. (or)

Liquid metal may go into the solid metal.

WET CORROSION (or) (Electro Chemical Corrosion):

Due to the presence of moisture or a liquid medium, wet corrosion takes place.

Conditions for the wet corrosion to take place:

1. Availability of two different metals (electrodes) partially or completely immersed in a solution (electrolyte).
2. Availability of conducting medium (electrolyte) or presence of atmospheric moisture.

Principle:

Surface of the metal is non-uniform (i.e no plain surface)

They have ‘ups’ (crest) and downs (trough)

Crests are releasing electrons so they are called as anode.

Troughs are absorbing electrons. So they are called as Cathode.

Electron flow from crest to trough

Mechanism of wet corrosion

Under the above conditions,

- One part of the metal acts as anode
- Another part of the metal acts as cathode

(i) At anode:

In anodic part, oxidation (or) dissolution of metal occurs takes place,

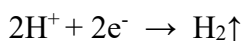


(ii) At cathode:

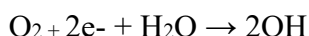
In cathodic part reduction occurs, which depends on nature of the corrosive environment.

(a) Acidic environment

Hydrogen evolution occurs at cathodic part

**(b) Natural environment (or) slightly alkaline**

Hydroxide ion forms at cathodic part.

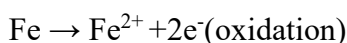
**(a) Hydrogen evolution type corrosion**

“All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen gas”.

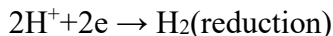
Example

When iron metal contacts with acid like HCl, H₂ evolution occurs.

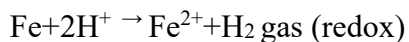
At anode



At cathode



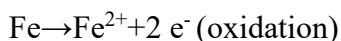
Overall reaction

**(b) Absorption of oxygen (or) formation of hydroxide ion type corrosion**

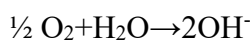
When a metal piece (iron) is placed in a basic (OH⁻ ions) medium (or) neutral medium (NaCl solution) oxygen absorption reaction takes place. The neutral medium is changed to a base medium, due to the formation of OH⁻ ion

Example;

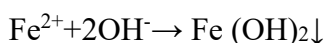
When iron metal contacts with a neutral solution of an electrolyte in presence of oxygen, OH⁻ ions are formed.

Formation of hydroxide ion type corrosion at anode

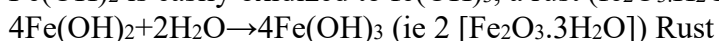
At cathode



Over all reaction



Fe(OH)₂ is easily oxidized to Fe(OH)₃, a rust (Fe₂O₃.H₂O).



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