

Basrah University
Engineering College
Material Engineering Department

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Corrosion (I)



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Subject: Corrosion (I)
Code: MAE316/1st Semester
Class: 3rd Year
Units: 2

Theoretical: 2 hrs/wk
Tutorial: 1 hrs/wk

- The technology & evaluation of corrosion: Economics, safety, electrochemical nature of corrosion, the forms of corrosion and corrosion rate determination.
- Electrochemical thermodynamics and electrode potential: Electrode sign conventions, potential/pH diagrams, and experimental measurements.
- Electrochemical kinetics of corrosion: Faraday's Law, mixed potential theory, experimental methods, and instrumentation.
- Passivity and properties of passive films on metals: Alloy evaluation and experimental methods.
- Polarization methods for measuring corrosion rates: Tafel extrapolation & polarization resistance, instrumental methods and commercial corrosion monitoring devices.
- Galvanic, concentration cell, pitting and crevice corrosion: How to characterize the different forms of corrosion, their evaluation and prevention methods.

Chapter One: Introduction

1-1 DEFINITION OF CORROSION

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment.

In some instances, chemical attack accompanies physical deterioration, as described by the following terms: corrosion – erosion, corrosive wear, or fretting corrosion. Nonmetals are not included in this definition of corrosion.

“**Rusting**” applies to the corrosion of iron or iron - base alloys with formation of corrosion products consisting largely of hydrous ferric oxides. Nonferrous metals, therefore, corrode, but do not rust.

1-2 IMPORTANCE OF CORROSION

The **three main reasons** for the importance of corrosion are: **economics, safety, and conservation**. To reduce the economic impact of corrosion, corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, as well as the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on.

Corrosion can compromise the safety of operating equipment by causing failure (with catastrophic consequences) of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms. Safety is a critical consideration in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Loss of metal by corrosion is a waste not only of the metal, but

also of the energy, the water, and the human effort that was used to produce and fabricate the metal structures in the first place. In addition, rebuilding corroded equipment requires further investment of all these resources metal, energy, water, and human.

Economic losses are divided into (1) direct losses and (2) indirect losses.

Direct losses include the costs of replacing corroded structures and machinery or their components, such as condenser tubes, mufflers, pipelines, and metal roofing, including necessary labor. Other examples are (a) repainting structures where prevention of rusting is the prime objective and (b) the capital costs plus maintenance of cathodic protection systems for underground pipelines. Sizable direct losses are illustrated by the necessity to replace several million domestic hot - water tanks each year because of failure by corrosion and the need for replacement of millions of corroded automobile mufflers. Direct losses include the extra cost of using corrosion - resistant metals and alloys instead of carbon steel where the latter has adequate mechanical properties but not sufficient corrosion resistance; there are also the costs of galvanizing or nickel plating of steel, of adding corrosion inhibitors to water, and of dehumidifying storage rooms for metal equipment.

The economic factor is a very important motivation for much of the current research in corrosion. Losses sustained by industry and by government's amount to many billions of dollars annually, approximately \$ 276 billion in the United States, or 3.1% of the Gross Domestic Product (GDP), according to a recent study. It has been estimated that about 25 – 30% of this total could be avoided if currently available corrosion technology were effectively applied.

Studies of the cost of corrosion to Australia, Great Britain, Japan, and other countries have also been carried out. In each country studied, the cost of corrosion is approximately 3 – 4 % of the Gross National Product.

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 \$50,000 or more per hour in lost production. Similarly, replacement of corroded boiler or condenser tubes in a large power plant may require \$ 1,000,000 or more per day for power purchased from interconnected electric systems to supply customers while the boiler is down. Losses of this kind cost the electrical utilities in the United States tens of millions of dollars annually.

2. Loss of Product. Losses of oil, gas, or water occur through a corroded -pipe system until repairs are made. Antifreeze may be lost through a corroded auto radiator; or gas leaking from a corroded pipe may enter the basement of a building, causing an explosion.

3. Loss of Efficiency. Loss of efficiency may occur because of diminished heat transfer through accumulated corrosion products, or because of the clogging of pipes with rust necessitating increased pumping capacity. It has been estimated that, in the United States, increased pumping capacity, made necessary by partial clogging of water mains with rust, costs many millions of dollars per year. A further example is provided by internal - combustion engines of automobiles where piston rings and cylinder walls are continuously corroded by combustion gases and condensates. Loss of critical dimensions leading to excess gasoline and oil consumption can be caused by corrosion to an extent equal to or greater than that caused by wear. Corrosion processes can impose limits on the efficiencies of energy conversion systems, representing losses that may amount to billions of dollars.

4. Contamination of Product. A small amount of copper picked up by slight corrosion of copper piping or of brass equipment that is otherwise durable may damage an entire batch of soap. Copper salts accelerate rancidity of soaps and shorten the time that they can be stored before use. Traces of metals may similarly alter the color of dyes. Lead equipment, otherwise durable, is not permitted in the preparation of foods and beverages because of the toxic properties imparted by very small quantities of lead salts. The U.S. Bureau of Food and Drugs, for example, permits not more than 1 ppb of lead in bottled drinking water.

Similarly, soft waters that pass through lead piping are not safe for drinking purposes. The poisonous effects of small amounts of lead have been known for a long time. In a letter to Benjamin Vaughn dated July 31, 1786, Benjamin Franklin warned against possible ill effects of drinking rain water collected from lead roofs or consuming alcoholic beverages exposed to lead. The symptoms were called in his time “dry bellyache” and were accompanied by paralysis of the limbs. The disease originated because New England rum distillers used lead coil condensers. On recognizing the cause, the Massachusetts Legislature passed an act outlawing use of lead for this purpose.

Another form of contamination is spoilage of food in corroded metal containers. A cannery of fruits and vegetables once lost more than \$ 1 million in one year before the metallurgical factors causing localized corrosion were analyzed and remedied. Another company, using metal caps on glass food jars, lost \$ 0.5 million in one year because the caps perforated by a pitting type of corrosion, thereby allowing bacterial contamination of the contents.

5. Overdesign. Overdesign is common in the design of reaction vessels, boilers, condenser tubes, oil - well sucker rods, pipelines transporting oil and gas at high pressure, water tanks, and marine structures. Equipment is often designed many times heavier than normal operating pressures or applied stresses would require in

order ensuring reasonable life. With adequate knowledge of corrosion, more reliable estimates of equipment life can be made, and design can be simplified in terms of materials and labor. For example, oil - well sucker rods are normally overdesigned to increase service life before failure occurs by corrosion fatigue. If the corrosion factor were eliminated, losses would be cut at least in half. There would be further savings because less power would be required to operate a lightweight rod, and the expense of recovering a lightweight rod after breakage would be lower.

Indirect losses are a substantial part of the economic tax imposed by corrosion, although it is difficult to arrive at a reasonable estimate of total losses. In the event of loss of health or life through explosion, unpredictable failure of chemical equipment, or wreckage of airplanes, trains, or automobiles through sudden failure by corrosion of critical parts, the indirect losses are still more difficult to assess and are beyond interpretation in terms of dollars.

1-3 RISK MANAGEMENT

In general, risk, **R**, is defined as the probability, **P**, of an occurrence multiplied by the consequence, **C**, of the occurrence; that is,

$$\mathbf{R = P \times C}$$

Hence, the risk of a corrosion - related failure equals the probability that such a failure will take place multiplied by the consequence of that failure. Consequence is typically measured in financial terms that is, the total cost of a corrosion failure, including the cost of replacement, cleanup, repair, downtime, and so on.

Managing risk is an important part of many engineering undertakings today. Managing corrosion is an essential aspect of managing risk. Firstly, risk management must be included in the design stage, and then, after operation starts,

maintenance must be carried out so that risk continues to be managed. Engineering design must include corrosion control equipment, such as cathodic protection systems and coatings. Maintenance must be carried out so that corrosion is monitored and significant defects are repaired, so that risk is managed during the operational lifetime.

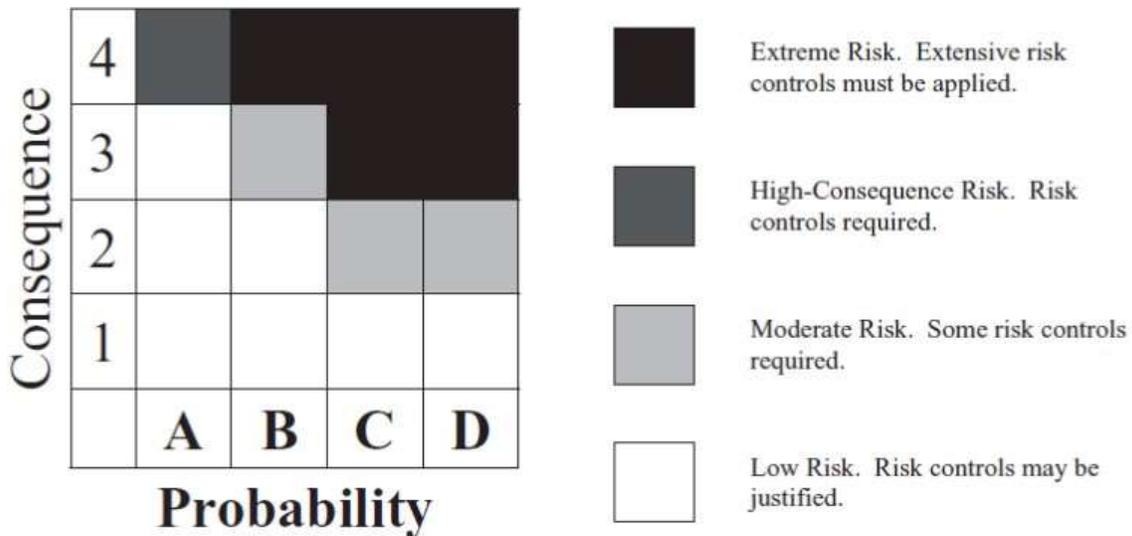


Figure 1.1. A simplified approach to risk management, indicating qualitatively the areas of high risk, where both consequence and probability are high.

1-4 TYPES OF CORROSION DAMAGE

Eight Forms of Corrosion

The idea of describing the various ways corrosion can damage metals by its appearance had been used by many before Fontana and Greene coauthored their famous book in 1967. McKay and Worthington were already discussing various forms of corrosion in their 1936 book on corrosion. However, the classification that follows seems to have gained the widest acceptance with subtle variations between authors.

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable. Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are:

- (1) Uniform, or general attack
- (2) Galvanic, or two-metal corrosion
- (3) Crevice corrosion
- (4) Pitting
- (5) Intergranular corrosion
- (6) Selective leaching, or parting
- (7) Erosion Corrosion
- (8) Stress corrosion.

This listing is arbitrary but covers practically all corrosion failures and problems. The forms are not listed in any particular order of importance. Below, the eight forms of corrosion are discussed in terms of their characteristics, mechanisms, and preventive measures. Hydrogen damage, although not a form of corrosion, often occurs indirectly as a result of corrosive attack, and is therefore included in this discussion.

1- Uniform Attack

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. For example, a piece of steel or zinc immersed in dilute sulfuric acid will normally dissolve at a uniform rate over its entire surface. A sheet iron roof will show essentially the same degree of rusting over its entire outside surface.

Uniform attack, or general overall corrosion, represents the greatest destruction of metal on a tonnage basis. This form of corrosion, however, is not of too great concern from the technical standpoint, because the life of equipment can be accurately estimated on the basis of comparatively simple tests. Merely immersing specimens in the fluid involved is often sufficient. Uniform attack can be prevented or reduced by (1) proper materials, including coatings, (2) inhibitors, or (3) cathodic protection.

2- Galvanic or Two-Metal Corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic, or two-metal, corrosion. It is electrochemical

corrosion, but we shall restrict the term galvanic to dissimilar-metal effects for purposes of clarity.

3- Crevice Corrosion

Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion.

4- Pitting

Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth.

Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and because the pits are often covered with corrosion products. In addition, it is difficult to measure quantitatively and compare the extent of pitting because of the varying depths and numbers of pits that may occur under identical conditions. Pitting is also difficult to predict by laboratory tests. Sometimes the pits require a long time—several months or a year—to show up in actual service. Pitting is particularly vicious because it is a localized and intense form of corrosion, and failures often occur with extreme suddenness.

5- Intergranular Corrosion

Grain boundary effects are of little or no consequence in most applications or uses of metals. If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive than the matrix. However, under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and/or loses its strength.

Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain-boundary areas. Small amounts of iron in aluminum, wherein the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion. It has been shown that based on surface tension considerations the zinc content of a brass is higher at the grain boundaries. Depletion of chromium in the grain-boundary regions results in intergranular corrosion of stainless steels.

6- Selective leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloys (dezincification). Similar processes occur in other alloy systems in which aluminum; iron, cobalt, chromium, and other elements are removed. Selective leaching is the general term to describe these processes, and its use precludes the creation of terms such as dealuminumification, decobaltification, etc. Parting is a metallurgical term that is sometimes applied, but selective leaching is preferred.

7- Erosion Corrosion

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Generally, this movement is quite rapid, and mechanical wear effects or abrasion are involved. Metal is removed from the surface as dissolved ions, or it forms solid corrosion products which are mechanically swept from the metal surface. Sometimes, movement of the environment decreases corrosion, particularly when localized attack occurs under stagnant conditions, but this is not erosion corrosion because deterioration is not increased.

Erosion corrosion is characterized in appearance by grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. In many cases, failures because of erosion corrosion occur in a relatively short time, and they are unexpected largely because evaluation corrosion tests were run under static conditions or because the erosion effects were not considered.

8- Stress-corrosion cracking

Stress-corrosion cracking refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. Many investigators have classified all cracking failures occurring in corrosive mediums as stress-corrosion cracking, including failures due to hydrogen embrittlement. However, these two types of cracking failures respond differently to environmental variables. To illustrate, cathodic protection is an effective method for preventing stress-corrosion cracking whereas it rapidly accelerates hydrogen-embrittlement effects. Hence, the importance of considering stress-corrosion cracking and hydrogen embrittlement as separate phenomena is obvious.

During stress-corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it. This cracking phenomenon has serious consequences since it can occur at stresses within the range of typical design stress. Exposure to boiling MgCl₂ at 310°F (154°C) is shown to reduce the strength capability to approximately that available at 1200°F.

The two classic cases of stress-corrosion cracking are "**season cracking**" of brass, and the "**caustic embrittlement**" of steel. Both of these obsolete terms describe the environmental conditions present which led to stress-corrosion cracking. Season cracking refers to the stress-corrosion cracking failure of brass cartridge cases. During periods of heavy rainfall, especially in the tropics, cracks were observed in the brass cartridge cases at the point where the case was crimped to the bullet. It was later found that the important environmental component in season cracking was ammonia resulting from the decomposition of organic matter.

1-5 Rate of Corrosion

The rate of corrosion is the speed at which any given metal deteriorates in a specific environment. The rate, or speed, is dependent upon environmental conditions as well as the type, and condition, of the metal.

Corrosion rates in the **US** are normally calculated using **mpy** (**Mils per year**). In other words, the corrosion rate is based on the number of millimeters (thousandths of an inch) it penetrates each year.

In order to calculate the rate of corrosion, the following information must be collected:

- ❖ Weight loss (the decrease in metal weight during the reference time period)
- ❖ Density (density of the metal)
- ❖ Area (total initial surface area of the metal piece)
- ❖ Time (the length of the reference time period)

Converting Corrosion Rates:

To convert corrosion rate between the mils per year and the metric equivalent millimeter per year (mm/y), you can use the following equation:

$$1 \text{ mpy} = 0.0254 \text{ mm/y} = 25.4 \text{ microm/y}$$

To calculate the corrosion rate from metal loss:

$$\text{CR (mm /y)} = 87.6 * (\text{W} / \text{DAT})$$

where:

W = weight loss in milligrams

D = metal density in g /cm³

A = area of sample in cm²

T = time of exposure of the metal sample in hours

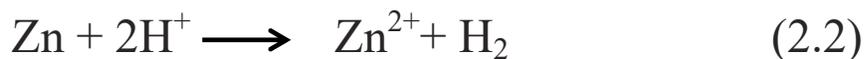
Chapter Two: Corrosion as a Chemical Reaction

2-1 Electrochemical Reaction

One of the common ways of generating hydrogen in a laboratory is to place zinc into a dilute acid, such as hydrochloric or sulfuric. When this is done, there is a rapid reaction in which the zinc is attacked or “dissolved” and hydrogen is evolved as a gas. This is shown in:



Noting that chloride ion is not involved in the reaction, this equation can be written in the simplified form:



Hence, zinc reacts with the hydrogen ions of the acid solution to form zinc and hydrogen gas. From the above we can see zinc is oxidized to Zn ions and hydrogen ions reduced to hydrogen gas. Therefore, these equations can be conveniently divided into:



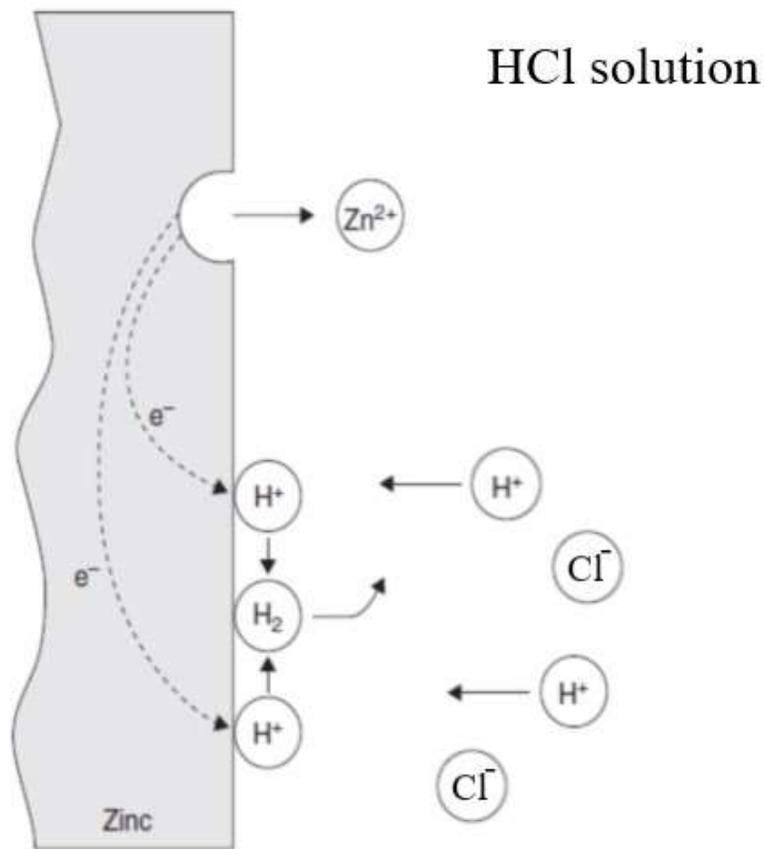


FIGURE Electrochemical reactions occurring during the corrosion of zinc in air-free hydrochloric acid.

Also, iron and aluminum are rapidly corroded by hydrochloric acid. The reactions are:



This hydrogen evolution reaction occurs with a wide variety of metals and acids, including hydrochloric, sulfuric, perchloric, hydrofluoric, formic, and other strong acids. All involve the hydrogen ion reduction and they differ only in their oxidation or anodic reactions. The individual anodic reactions for zinc, iron, and aluminum are listed as follows:





The anodic reaction occurring during corrosion can be written in the general form:



That is, the corrosion of metal **M** results in the oxidation of metal **M** to an ion with a valence charge of **n+** and the release of **n** electrons. The value of **n**, of course, depends primarily on the nature of the metal.

In neutral waters the anodic corrosion of some metals like aluminum, zinc, or magnesium develops enough energy to split water directly as illustrated in Eq. (2.11).



The change in the concentration of hydrogen ions or increase in hydroxyl ions can be shown by the use of pH indicators, which change color and thus can serve to demonstrate and locate the existence of surfaces on which the cathodic reactions in corrosion are taking place. There are several other cathodic reactions encountered during the corrosion of metals. These are listed below:

Oxygen reduction:



Hydrogen ion reduction, or hydrogen evolution, has already been discussed. This is the cathodic reaction that occurs during

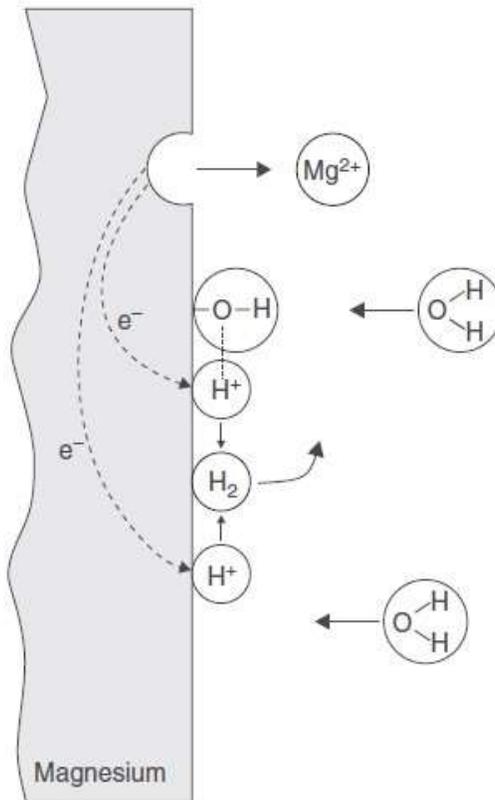
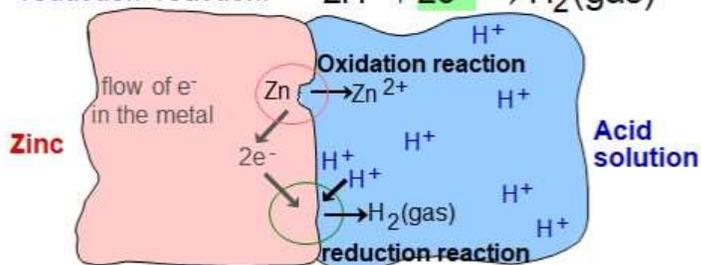


FIGURE Electrochemical reactions occurring during the corrosion of magnesium in neutral water.

Electrochemical Corrosion

Corrosion of zinc in an acid solution

- Two reactions are necessary:
 - oxidation reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
 - reduction reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{gas})$



- Other reduction reactions in solutions with dissolved oxygen:
 - acidic solution: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
 - neutral or basic solution: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4(\text{OH})^-$

2-2 Electrode sign conventions

Electrode: An electric conductor, the electrode metal and an ionic conductor, electrolyte solution, form an interface at which electrode process occurs. An electrochemical cell contains two electrodes (anode and cathode); a liquid-liquid junction separates two electrodes.

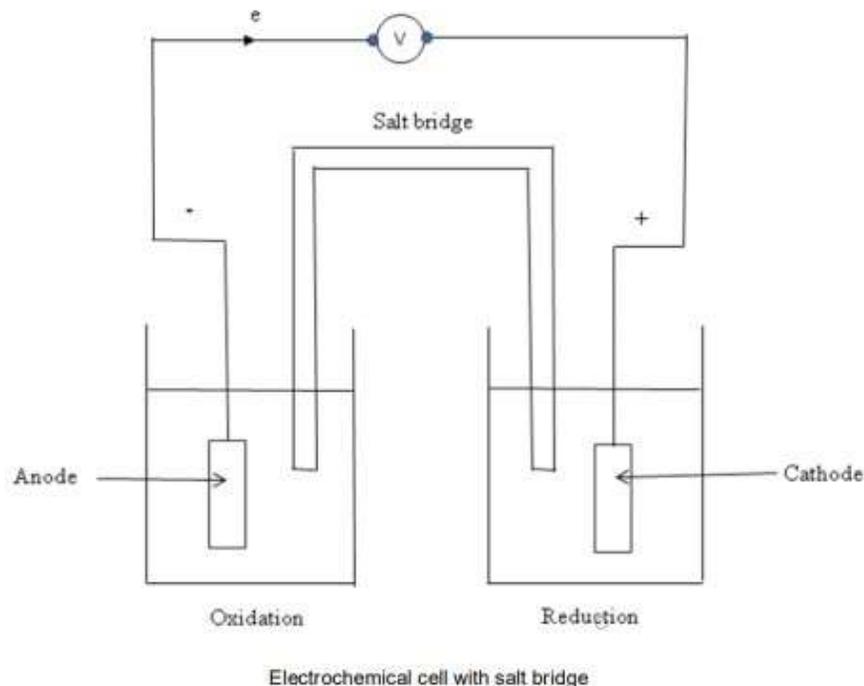
- Anode is the electrode where oxidation occurs.
- Cathode is the electrode where reduction occurs.

Electrochemical cell:

An electrochemical cell typically consists of:

- ❖ Two electronic conductors (also called electrodes)
- ❖ An ionic conductor (called an electrolyte)

Liquid Junction: Serves as galvanic contact between electrodes (can be a salt bridge or porous membrane). Salt bridge, very commonly used – an intermediate compartment filled with saturated Potassium chloride (KCl) solution and fitted with porous barrier at each end or agar solidified incorporating saturated KCl. Salt bridge minimizes liquid junction potential (diffusion potential) that develops when any two phases such as two solutions are contacted each other. This potential (if not corrected) introduces errors and interferences in the measured cell potentials. With introduction of a salt bridge, two liquid junction potentials are created; but they tend to cancel each other.



Reactions – half cell and overall:

At each electrode, an electrochemical reaction occurs. This reaction is called a half cell reaction (since there are two electrodes in a typical cell at which reactions occur)

The overall chemical reaction of the cell is given by combining the two individual half-cell reactions

Sign of the electrode potential, E^0

- is positive when the half – cell is spontaneous as cathode.
- is negative when the half – cell behaves as anode.
- is a measure of the driving force for the half – reaction.

E^0 is referenced to standard Hydrogen Electrode.



E^0 is independent of number of moles of reactant or product.

Positive means reaction is spontaneous with respect to Hydrogen electrode. In the present practice is to use reduction potentials.

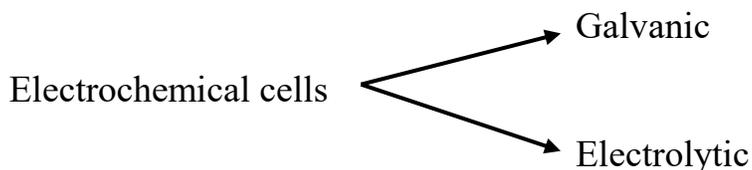
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Standard hydrogen electrode (SHE) is the reference point.

Table 1: Given below is a list of some reduction potentials

| | Half Reaction | E° (Volts) |
|--|--|---------------------|
|  Increasing tendency to get reduced | $\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$ | + 2.87 |
| | $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}(\text{aq})$ | + 2.01 |
| | $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$ | + 1.51 |
| | $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au}(\text{s})$ | + 1.42 |
| | $\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$ | + 1.07 |
| | $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$ | + 0.80 |
| | $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ | + 0.77 |
| | $\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$ | + 0.54 |
| | $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ | + 0.34 |
| | $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ | + 0.00 |
| | $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$ | - 0.25 |
| | $\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$ | - 0.40 |
| | $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$ | - 0.44 |
| | $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$ | - 0.76 |
| | $2\text{H}_2\text{O}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ | - 1.66 |
| | $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$ | - 2.37 |
| $\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$ | - 3.05 | |

Types of electrochemical cells:



| Galvanic | Electrolytic |
|--|--|
| Chemical energy to electrical energy Spontaneous/Reversible/Thermodynamic | Electrical to chemical energy Non spontaneous/Kinetic cell / irreversible |
| Cathode (+) | Cathode (-) |
| Anode (-) | Anode (+) |
| $E^0 \text{ cell} > 0$ | $E^0 \text{ cell} < 0$ |
| Eg: | Eg: |
| Dry cell | Electroplating |
| Daniel cell | Impressed current cathodic protection |

Why is the sign convention of the electrodes different in electrochemical cells and electrolysis?

In an electrochemical cell, two redox reactions occur spontaneously on the two electrodes. When connected through a wire, electrons flow from the side that is producing free electrons (where oxidation occurs) to the side that is consuming free electrons (where reduction occurs). Therefore, the flow of electrons in the external circuit is from electron donor (anode) to electron acceptor (cathode).

In an electrolytic cell, two redox reactions occur, but they require an external supply of energy to proceed. When connected to an external power source, electrons flow from the power source to the side that is consuming free electrons (where reduction occurs) through the solution to the side that is producing free electrons (where oxidation occurs) and back into the power source.

Therefore, the flow of electrons inside the electrolytic cell is from electron acceptor (cathode) to electron donor (anode).

In short, it's because the electrochemical cell is a source, so it produces high-energy electrons (on anode) and accepts low-energy ones (on cathode), whereas an electrolytic cell is a sink, so it consumes high-energy electrons (on cathode) and produces low-energy ones (on anode).

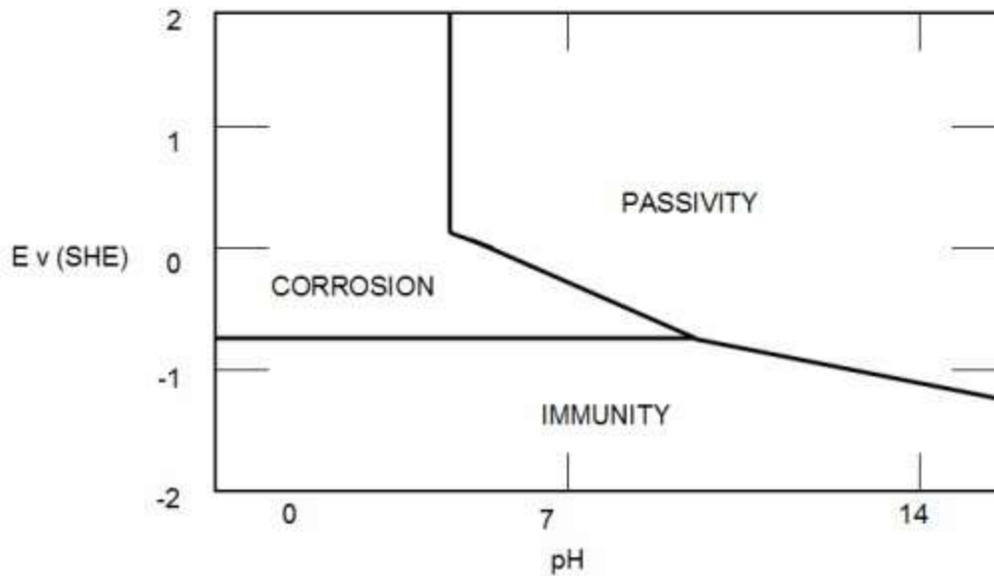
2-3 potential (pH) diagrams

Potential-pH diagrams are also called Pourbaix diagrams after the name of their originator, Pourbaix (1963), a Belgium electrochemist and corrosion scientist. These diagrams represent the stability of a metal as a function of potential and pH. At a particular combination of pH and potential, a stable phase can be determined from the Pourbaix diagram. In such diagrams, the redox potential of the corroding system is plotted on a vertical axis and the pH on a horizontal axis. These diagrams are constructed from calculations based on Nernst equations and solubility data for metal and its species, such as **Fe**, **Fe₂O₃**, **Fe(OH)₂**, **Fe₃O₄**, etc. in equilibrium. And we can identify the stability region (immunity, corrosion, and passivity), however these are only indications; actual rates cannot be derived from the diagrams. The information in the diagrams can be beneficially used to control corrosion of pure metals in the aqueous environment. By altering the pH and potential to the regions of immunity and passivation, corrosion can be controlled.

Thus, Pourbaix diagrams introduce the concept of the following three states of metals, depending on the potential in the given aggressive medium and the determination of its corrosion behavior: corrosion (active state), passivity (forming passive layers inhibiting the corrosion process on the surface of the metal, including thermodynamically active metals) and immunity (thermodynamic stability) of the metals. Further, it will be shown that these three metal states in aggressive media have a special value when corrosion action by an external current on the metal is considered and when methods and means of protection from electro corrosion are developed.

Characteristics of a Pourbaix Diagram

- 1) pH is plotted on the horizontal axis and redox potential E vs. SHE on the vertical axis.
- 2) The horizontal lines represent electron transfer reactions. They are pH - independent, but potential-dependent.
- 3) The vertical lines are potential-independent but pH-dependent and not accompanied by any electron transfer.
- 4) The sloping, straight lines give the redox potentials of a solution in equilibrium with hydrogen and oxygen, respectively. This equilibrium indicates electron transfer as well as pH.
- 5) The concentration of all metal ions is assumed to be 10^{-6} mol per liter of solution. At lower concentration, corrosion should not occur.
- 6) The diagram is computed for the equilibrium conditions at 25°C .
- 7) The upper end of the redox potential axis is the noble end and the lower end, the active end, meaning that the oxidizing power increase with increasing potential.
- 8) The hydrogen and oxygen lines are indicated in Pourbaix diagrams by dotted line.



The main objectives of the Pourbaix diagrams are:

- A.** To show the directions of the various reactions at given pH and potential.
- B.** To make a basis for estimation of the corrosion product compositions at various pH and potential combinations.
- C.** To show which environmental pH and potential changes will reduce or prevent corrosion.

Limitation of Pourbaix diagram

The validity of the diagrams is limited to reactions between pure metals, pure water and the species that can be formed from these. Small amounts of impurities and alloying elements in the metal and dissolved substances in the water do not necessarily influence strongly on the diagram, but in some cases they do.

- 1)** These diagrams are purely based on thermodynamic data and do not provide any information on the reactions.

- 2) Consideration is given only to equilibrium conditions in specified environment and factors, such as temperature and velocity are not considered which may seriously affect the corrosion rate.
- 3) The activity of species is arbitrarily selected as 10^{-6} gmol which is not realistic.
- 4) Pourbaix diagrams deal with pure metals which are not of much interest to the engineers.
- 5) All insoluble products are assumed to be protective which is not true, as porosity, thickness, and adherence to substrate are important factors.

Although the above disadvantages appear to be substantial, the advantages offered by the Pourbaix diagrams far outweigh their limitations

2-4 Faraday's Law

Faraday's law was discovered by Michael Faraday, one of the pioneers in electrochemistry during the 19th century. This law states that when current produced by anodic areas are known, it is possible to calculate the rate of corrosion penetration or corresponding mass loss.

This law relates to electrolysis and how the electrochemical reaction current is associated with the moles of elements under reaction. If the current generated by one of the anodic reactions expressed earlier was known, it would be possible to convert this current to an equivalent mass loss or corrosion penetration rate with a very useful relation. Faraday's empirical laws of electrolysis relate the current of an electrochemical reaction to the number of moles of the element being reacted and the number of moles of electrons involved.

Definition of Electrolysis

Electrolysis is the passage of electricity through an electrolyte, with cations moving to the cathode to get reduced, and anions moving towards the anode to get oxidized. An electrolyte is a liquid that conducts electricity.

The table below shows three different constants that we'll use during this lesson. Their details will be dealt with during the lesson.

| | |
|----------------------------|----------------------------------|
| The Faraday Constant, F | 96485C/mol |
| The Avogadro's Constant, L | 6.02×10^{23} |
| Electronic charge, e | $1.6023 \times 10^{-19}\text{C}$ |

Table showing values of constants

Let's first go through a few quantitative measures involved in electrolysis. Let's take a look at the relationship between current, charge, and time. How is a current produced? An electric current arises whenever there is a flow of charges (for example, electrons) and is defined as the rate at which charge flows. The formula is as follows:

$$\text{Current} = \text{Quantity of charge/Time, or } I = Q/t,$$

Where:

I is the current in Ampere (A), which is the flow of 1 Coulomb of charge per second, or C/s, t is time in seconds, and Q is quantity of electricity in Coulombs

Faraday's Constant

Do you know how much charge is carried by a single electron?

The answer is 1.6023×10^{-19} C.

What will then be the total charge carried by one mole of electrons?

1 mole of electrons is represented by the Avogadro's Number, $L = 6.022 \times 10^{23}$ electrons. Therefore, 6.022×10^{23} electrons carries a charge of $6.022 \times 10^{23} \times 1.6023 \times 10^{-19}$ C/mol = 96,485 C/mol.

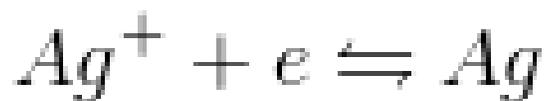
96,485 C/mol, or **one Faraday**, denoted by the symbol **F**, is the amount of electricity that is carried by one mole of electrons and is known as the Faraday constant.

Equivalent weight or equivalent mass is another quantity which is often used in electrolytic calculations and is given by:

Equivalent weight, or $E = \text{Atomic weight}/\text{Valency}$,

where atomic weight or atomic mass is in g/mol and the value is usually provided. Valency is an atom's ability to combine with other atoms, and equivalent weight or equivalent mass is measured in grams. Now let's take a look at some examples.

Example 1 - Find the equivalent weight for silver.



Atomic mass of Ag is given as 108.

Valency = 1, since only 1 mole of electron can be used to combine with another atom.

Equivalent weight = Atomic weight of silver/Valency of silver = $108/1 = 108$ g

Example 2 - Find the equivalent weight for aluminum



Atomic mass of Al is given as 27.

Valency = 3, since 3 moles of electrons can be used to combine with another atom.

Equivalent weight = Atomic weight of aluminum/Valency of aluminum

$$= 27/3 = 9 \text{ g}$$

Faraday's First Law of Electrolysis

The mass of the substance (m) deposited or liberated at any electrode is directly proportional to the quantity of electricity or charge (Q) passed. In the mathematical form, this law can be represented as follows:

$$m \propto Q$$

Removing the proportionality sign gives

$$m = ZQ$$

where

m is the mass in grams (g)

Q is measured in Coulombs (C)

Z is the proportionality constant in g/C (in grams per coulomb), is also known as the electrochemical equivalent,

Which is the mass of a substance produced at the electrode during electrolysis by one Coulomb of charge. Faraday further observed that 1 Faraday (96,485C) of charge liberates 1 gram equivalent of the substance at the electrodes.

This means that 1C will liberate one gram equivalent of a substance/96,485, which is the electrochemical equivalent (Z) of the substance. This goes to a relationship between electrochemical equivalent (Z) and equivalent weight or equivalent mass (E) of a substance, and this can be expressed as:

$$Z = \text{Equivalent weight}/96,485, \text{ or } Z = E/96,485$$

Moving back to the equation $m = ZQ$, it can alternately be written as:

$$m = Z \times I \times t \text{ (since } Q = I \times t \text{)}$$

$$m = E \times I \times t / 96,485 \text{ (since } Z = E/96,485 \text{)}$$

Let's now wrap up all what we've learned so far in two examples:

1. During an electrolysis of molten sodium chloride, a 4A current is passed through electrodes for 1 hour. Calculate the mass of sodium that is produced during this time.

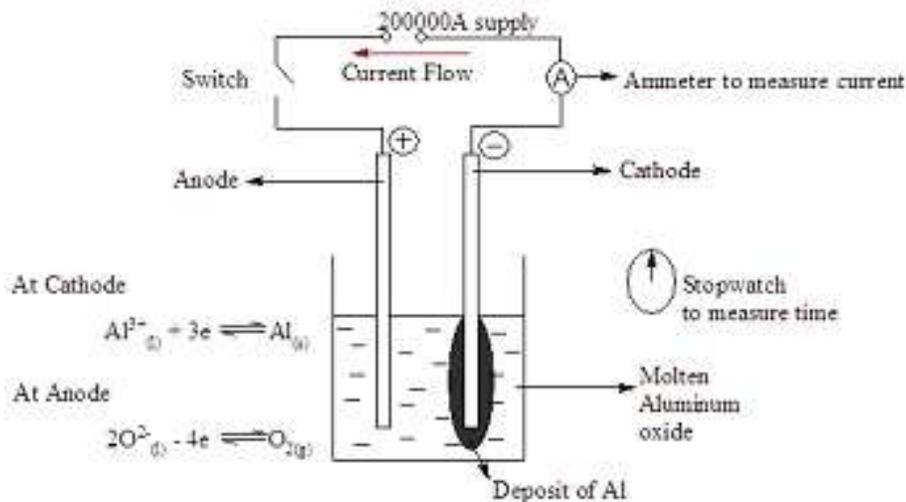
Given $I = 4\text{A}$, $t = 1 \times 60 \times 60 = 3,600\text{s}$, and E of sodium is $23/1 = 23\text{g}$

Mass of sodium produced = $E \times I \times t / 96,485$

$$= (23 \times 4 \times 3,600) / 96,485$$

$$= 3.43\text{g}$$

2. A plant to produce aluminum from molten aluminum oxide will use a current of 200,000A. A simplistic view of the plant is shown below:



Simplistic view of the aluminum plant

2-5 Factors Affecting Rate of Corrosion

This article describes about the different factors through which rate of corrosion can be affected. Read to know the various detail regarding the same.

1.Nature of the metals:

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum, and silver. Whereas metals with lower electrode potentials, readily undergo corrosion. E.g. metals like, zinc, magnesium, and aluminum. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For E.g., the potential difference between iron and copper is 0.78V which is more than that between iron and tin (0.3V). Therefore, iron corrodes faster when in contact with copper than that with tin. On this account, the use of dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should make of the same metal (or alloy) to avoid galvanic corrosion.

2. Ratio of cathodic to anodic region:

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated. Which are consumed at cathodic region. If cathodic region is larger the liberated electrons are rapidly consumed at cathode. This further enhances, the anodic reaction leading to increase in overall rate of corrosion. When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas.

3. Nature of the corrosion product:

The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non-porous. If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium. On the other hand if corrosion product is unstable, porous, and soluble, it further enhances corrosion.

Eg. in oxidizing environments, metals like aluminum, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments.

4. pH of the medium:

IN general rate of corrosion is higher in acidic pH that in neutral and alkaline pH. In case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion. Whereas at low pH severe corrosion takes place. But for metals like Aluminum, corrosion rate is high even at high pH.

5. Temperature:

Rate of corrosion increases with increase in temperature. This due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

6. Effect of oxygen:

Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place. The region which is less exposed to oxygen acts as anode hence undergoes corrosion and region exposed to high oxygen concentration acts cathode hence doesn't undergo corrosion.

7. Hydrogen over voltage:

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since at lower hydrogen over voltage, liberation of hydrogen gas is easy. Therefore cathodic reaction is very fast, which in turn makes anodic reaction very fast. Thus increasing rate of corrosion. Higher the over voltage lesser is the corrosion.

Chapter Three: Types of Corrosion

Introduction

The previous chapters provide an introduction to the general science of corrosion processes with some practical applications. In reality, the principles that govern these scientific concepts are rarely of interest to people facing corrosion problems.

It is convenient to classify corrosion by the forms, in which it manifests itself. The basis for this classification is the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment.

It is now widely accepted that much can be deduced from examination of materials which have failed in service and that it is often possible by visual examination to decide which corrosion mechanisms have been at work and what corrective measures are required. In another widely used NACE document (Statistical classification of economic activities in the European Community), **Paul Dillon** and his coauthors have **grouped the eight forms of corrosion** depicted graphically in Figure below in the following three categories:

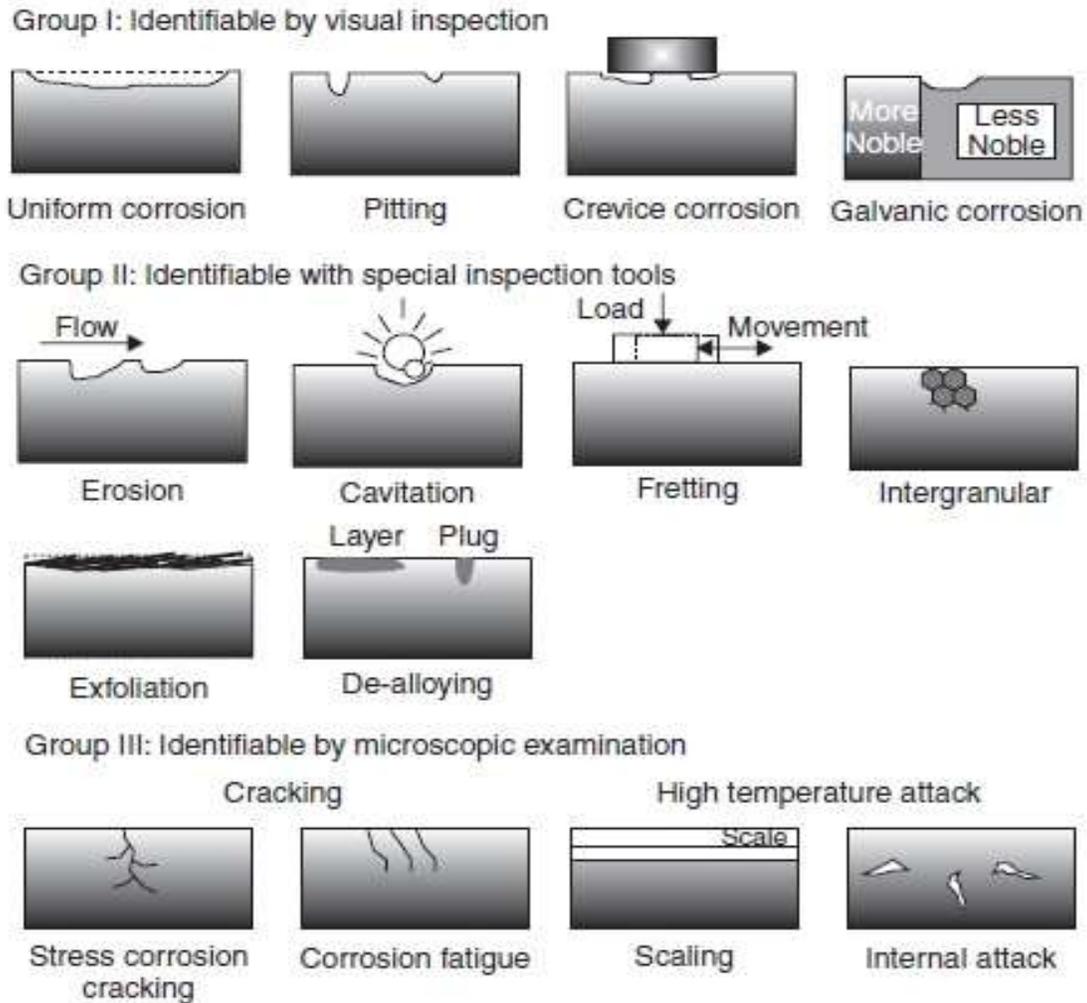


FIGURE Main forms of corrosion attack regrouped by ease of identification.

Group I: Corrosion problems readily identifiable by visual examination.

1. Uniform corrosion is characterized by an even, regular loss of metal from the corroding surface.
2. Localized corrosion during which all or most of the metal loss occurs at discrete areas. In this scheme crevice corrosion is said to be a particular form of pitting usually due to localized differences in the environment (pitting, crevice).
3. Galvanic corrosion occasioned by electrical contact between dissimilar conductors in an electrolyte.

Group II: Corrosion damage that may require supplementary means of examination for identification.

4. Velocity effects include erosion–corrosion, a form of attack caused by high velocity flow; cavitation caused at even higher flow by the collapse of bubbles formed at areas of low pressure in a flowing stream; and fretting that is caused by vibratory relative motion of two surfaces in close contact under load (erosion–corrosion, cavitation, fretting).

5. Intergranular corrosion at the grain boundaries in the metal structure (intergranular, exfoliation).

6. Dealloying corrosion due to the selective dissolution of one component of an alloy.

Group III: Corrosion specimens for these types should usually be verified by microscopy of one kind or another.

7. Cracking phenomena includes corrosion fatigue, a mechanical phenomenon enhanced by nonspecific corrosive environments, and environmental cracking, in which a brittle failure is induced in an otherwise ductile material under tensile stress in an environment specific for the alloy system (stress corrosion cracking, fatigue).

8. High-temperature corrosion (scaling, internal attack).

9. Microbial effects caused by certain types of bacteria or microbes when their metabolism produces corrosive species in an otherwise innocuous environment, or when they produce deposits which can lead to corrosion attack.

In this widely distributed guide, Paul Dillon acknowledged microbial effects as a ninth broad type of corrosion attack. It could also be argued that many of the forms in the previous list are more families or multiple forms of corrosion damage. It is obvious that pitting and crevice corrosion, for example, are quite distinct in how they occur, have very dissimilar triggering mechanisms, and would be prevented

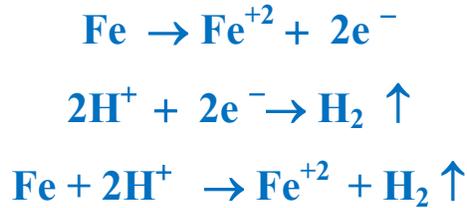
by totally different methods. Pitting and crevice corrosion were indeed treated as two distinct forms of corrosion by Fontana and Greene in their 1967 manual and by many others since then. Similarly the velocity effects group (erosion–corrosion, cavitation, and fretting corrosion) is a relatively artificial arrangement of corrosion types that are in fact quite different in appearance. So, if we count the actual forms of corrosion in Dillon’s document, we have a total closer to fifteen than to eight. If we add to these forms the ninth form of corrosion discussed in Fontana and Greene, that is, hydrogen damage either as blistering or embrittlement, we now have a total of seventeen corrosion forms. As Fontana indicated in 1967, “This listing is arbitrary but covers practically all corrosion failures and problems.” As this statement clearly acknowledged, the listing popularized by Fontana is an attempt to summarize all known corrosion types in recognizable category.

3-1 UNIFORM CORROSION

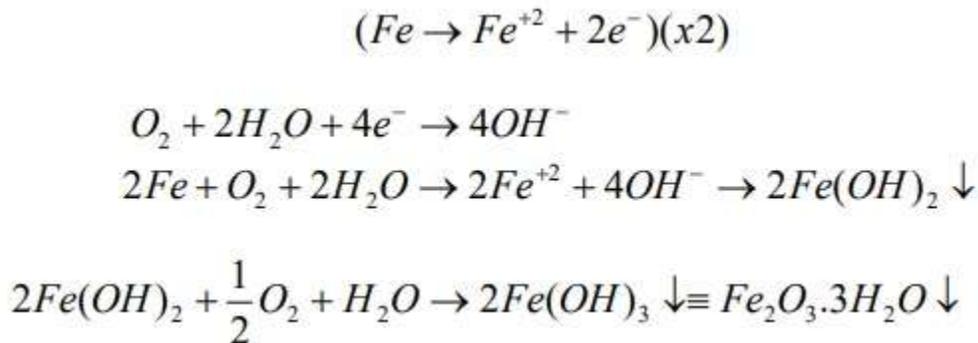
This is a uniform and general attack, in which the entire metal surface area exposed to the corrosive environment is converted into its oxide form, It is the uniform thinning of a metal without any localized attack, corrosion does not penetrate very deep inside, and the most familiar example is the rusting of steel in air. Uniform corrosion is assumed to be most common form of corrosion and particularly responsible for most the materials loss. Traditionally, however it is not recognized as dangerous form of corrosion, because:

- 1.** Prediction of thickness reduction rate can by means of simple tests. Corresponding corrosion allowance can be added taking into account strength requiring and lifetime.
- 2.** Available protection methods are usually so efficient that the corrosion rate is reduced to an acceptable level. Actual methods are application of coatings, cathodic protection or possibly change of environment or material.

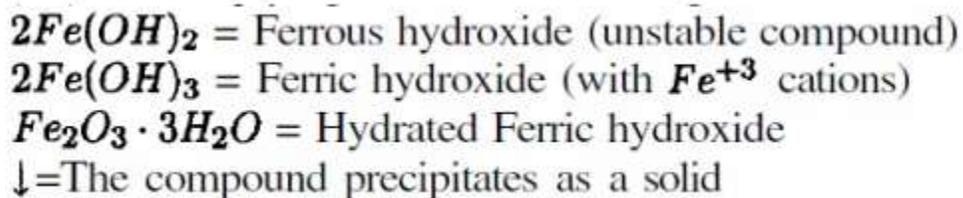
Aqueous corrosion of iron (**Fe**) in **H₂SO₄** solution is examples of uniform attack since **Fe** can dissolved (oxidize) at a uniform rate according to the following anodic and cathodic reactions, respectively.



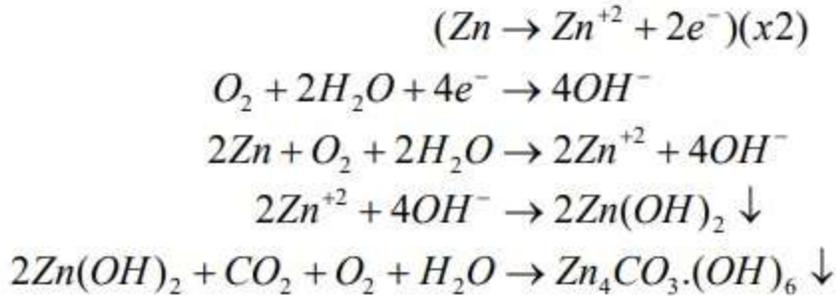
Atmospheric corrosion of a steel structure is also a common example of uniform corrosion, which is manifested as a brown-color corrosion layer on the exposed steel surface. This layer is a ferric hydroxide compound known as **Rust**. The formation of **Brown Rust** is as follows:



Where **(x2)**= Multiplying factor for balancing the number of electron

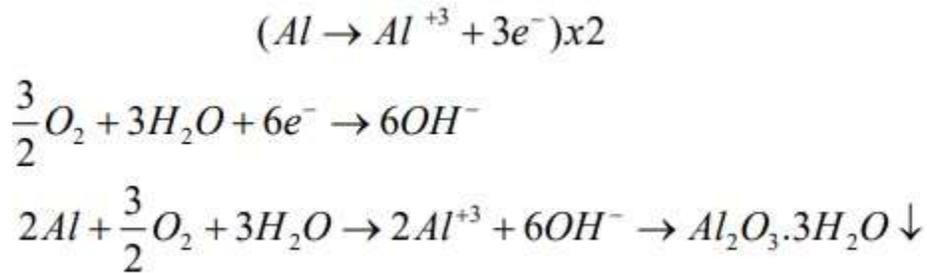


In addition, Zinc can uniformly corrode forming a White Rust according to the following reactions:



In fact, the compound or is $Zn_4CO_3 \cdot (OH)_6$ or $ZnCO_3 \cdot Zn(OH)_2$ is zinc carbonate or **white rust** or wet-storage stain (porous).

Atmospheric corrosion of aluminum is due to a passive oxide film formation instead of a porous layer. The gray/black-color film may form as follows:



Some factor effect on uniform corrosion

- 1) Effect of pollutants: corrosion can proceed in a dry environment without any moisture if trace of sulfur components or H_2S or other pollutants are present in the air. i.e. tarnishing of silver in dry air .the arte of corrosion in presence of SO_2 increase in the presence of moisture

