

Corrosion

Textbooks:

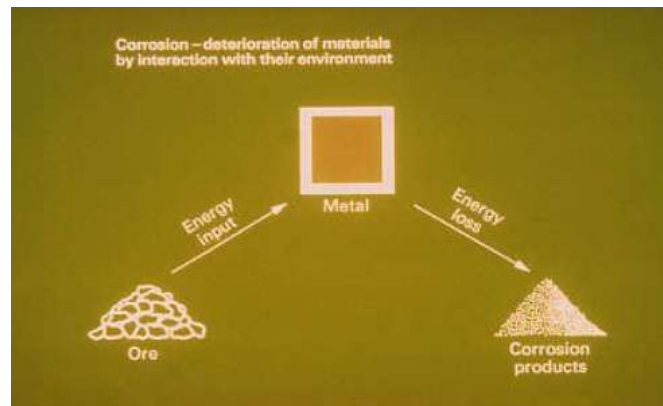
1. Marcus, P. (2011). *Corrosion Mechanisms in Theory and Practice* (3rd ed.). CRC Press.
2. Roberge, P. R. (2008). *Corrosion Engineering: Principles and Practice*. McGraw-Hill.
3. Philip A. Schweitzer, *Fundamentals of Corrosion*, 2010.
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5. R. Winston Revie, *Uhlig's corrosion handbook*, 3rd edition 2011.

Introduction to Corrosion

Definition

Corrosion is the destructive and unintentional attack of a material, usually a metal, through its chemical or electrochemical reaction with the environment. This process deteriorates the material's properties, leading to failure. While most prevalent in metals and alloys, non-metals like polymers, ceramics, and composites also undergo environmental degradation.

For Metals: Corrosion can be thought of as '*Extractive Metallurgy in Reverse*', where a refined metal returns to a more stable, oxidized state (e.g., iron ore → steel → rust).



What is Corrosion?

“The deterioration of a material or its properties due to a reaction of that material with its chemical and physical environment”. Corrosion is a general term used to describe various interactions between a material and its environment leading to degradation in the material properties.

The word corrosion is as old as the earth, but it has been known by different names. Corrosion refers to the degradation of metal by its environment other materials such as plastics, concrete, ceramics and composite materials all undergo deterioration when placed in some environment.

Corrosion is known commonly as rust, an undesirable phenomena which destroys the luster and beauty of objects and shortens their life. The word “rusting” applies to the corrosion of iron and plain carbon steel. Rust is a hydrated ferric oxide which appears in familiar color of red or dark brown see Figure 1.

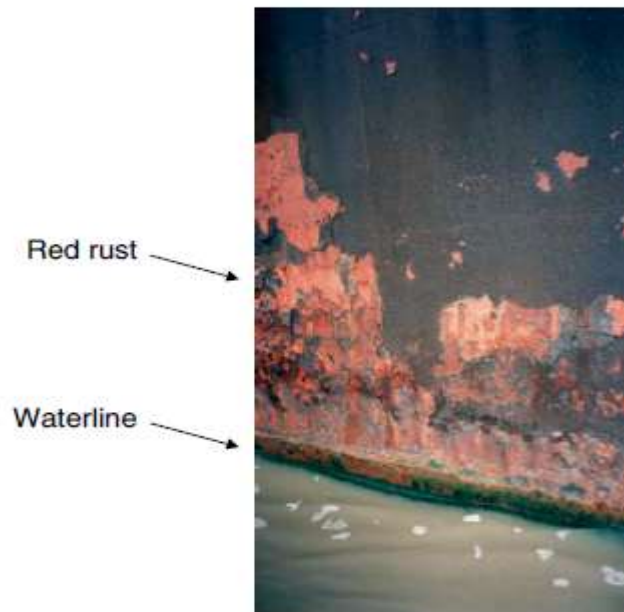


Figure 1: An example of red rust showing the corrosion of a ship near the waterline.

Thus, steel rusts (and corrodes), but non-ferrous metals such as aluminum, copper, and zinc corrode (but do not rust).

Why study Corrosion?

There are four main reasons to study corrosion. Three of these reasons are based on societal issues regarding (i) human life and safety, (ii) the cost of corrosion, and (iii) conservation of materials. The fourth reason is that corrosion is inherently a difficult phenomenon to understand, and its study is in itself a challenging and interesting pursuit.

Corrosion Losses

Corrosion costs could be divided into direct costs and indirect costs.



The following are some examples of *direct costs* listed below:

1. Capital costs – cost of replacement parts, eg., automobile mufflers, water lines, hot water, heaters, sheet metal roofs.
2. Control costs – maintenance, repair, and painting.
3. Design costs - extra cost of using corrosion resistance alloys, protective coatings, corrosion inhibitors.

Indirect losses are as follows:

1. Shutdown

Unplanned shutdowns because of the failure of equipment resulting from corrosion lead to loss of production and consequently loss of profit. Although the actual cost of maintenance work may be minimal, the value of the lost production can be considerable. If this type of occurrence is frequent, the cost is usually added to the cost of the product.

2. Loss of Product

Many times, corrosion is so severe that leakage will develop that permits loss of product. If this leakage occurs in a pipeline, it may go undetected for an extended period, during which time there is a continuous loss of product. If the leaking material itself is a corrosive material, it will attack its surroundings, thus causing additional loss. There have also been cases where leakage from underground tanks, such as gasoline, has contaminated the soil and even in some cases made the water in wells unsuitable for use.

3. Loss of Efficiency

Corrosion in a piping system can result in the buildup of a scale. This scale can cause a reduction in heat transfer as well as an increase in the power required to pump the fluid through the system. The efficient operation of other mechanical equipment can also be reduced by corrosion. This reduction in efficiency can cause an increase in operating costs as well as result in increased fuel consumption, lubricant loss, and reduced work output.

4. Contamination

During the corrosion of a metal, the fluid being transported, stored, processed, or packaged in a metallic component can pick up metallic salts. This metallic pick-up can be detrimental to the product; with soap products a shortened shelf life, with dyes a color alteration, and in some cases of intermediate products the inability to carry out succeeding process steps. For many years, lead pipes were used to transport water until it was determined that the lead pick-up in the water caused lead poisoning in humans.

5. Overdesign

In many instances when the corrosive effect of the system is known, additional thicknesses of vessel shells will be provided for in the design. This is known as corrosion allowance. Because this thickness is in addition to that required for the design conditions, an extra cost is involved. In some instances, the actual corrosive effect is not known and consequently, for safety reasons, a much thicker shell results.

6. Environmental Damage

Corrosion of equipment used to control atmospheric pollution resulting from processing operations can result in a decrease in efficiency. Such a decrease permits pollutants from the manufacturing operation to enter the atmosphere.



Figure 2: On December 15, 1967, the silver Bridge connecting Ohio and West Virginia over the Ohio River collapsed, and 46 people lost their lives. The case of the collapse was stress-corrosion.



Figure 3: An example of a harsh corrosive environment in which both the structural and electronic metals in the aircraft will be subject to corrosion.



Figure 4: (Top) Corrosion of vintage US automobiles. (Bottom) a view on the storage, recycling, and reclamation of used automobiles.



Figure 5: Photograph of a rust-covered outdoor work of art near Alexandria, VA.

Corrosion Science is an interdisciplinary area embracing chemistry, materials science, and mechanics as shown in Figure 7. The study of aqueous corrosion processes involves the interaction of chemistry and materials science. But the science of mechanics must be added to understand mechanically assisted corrosion processes, such as stress-corrosion cracking and corrosion fatigue.

Corrosion Engineering is the application of science and art to prevent or control corrosion damage economically and safely.

Corrosion Engineer is to protect corrosion of various metallic structures, e.g.: corrosion protection of Ships, Pipe Lines, Industries ...etc. Corrosion Engineering is supposed to have the knowledge of Metallurgy, Electro-Chemistry, Mechanical behaviors of Materials, Electrical Engineering, corrosion test, the nature of corrosive environments and the knowledge of Cost analysis.

What would be expected from Corrosion Scientist?

Several important timely challenges to the corrosion scientist can be listed

1. The development of protective surface treatments and corrosion inhibitors to replace inorganic chromates, which are environmentally objectionable.
2. An improved conservation of materials through the development of corrosion-resistant surface alloys which confine alloying elements to the surface rather than employing conventional bulk alloying.
3. The formation of a new generation of stainless steels containing replacement for chromium and other critical metals.

4. An improved understanding of passivity so as to use our fundamental knowledge to guide the development of alloys having improved corrosion resistance.
5. Understanding the mechanism of the breakdown of passive oxide films by chloride ions and subsequent pitting of the underlying metal.

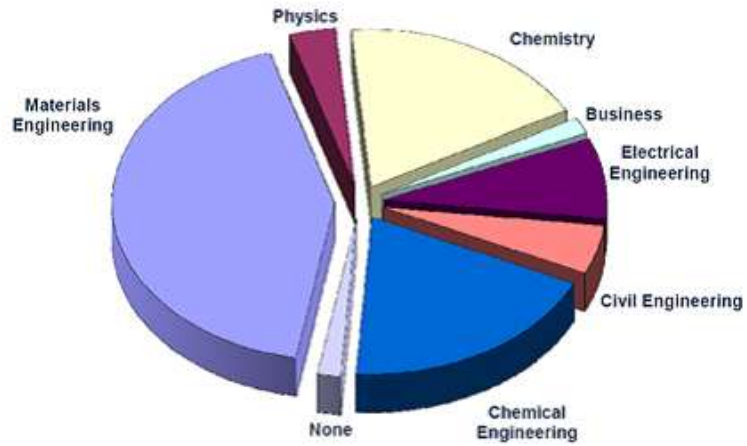


Figure 6: Distribution of disciplines in which active corrosion engineers have graduated

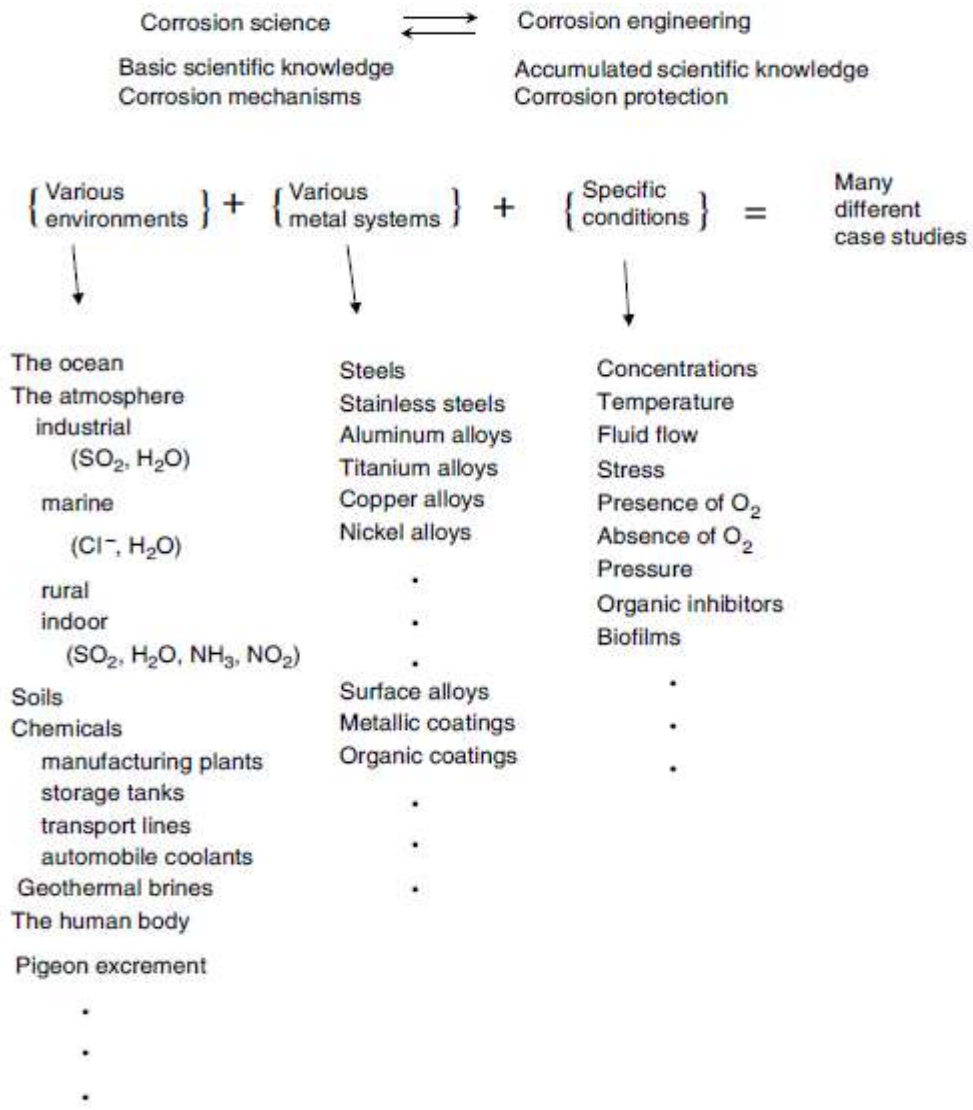
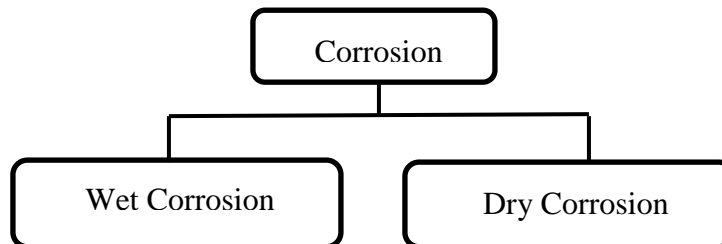
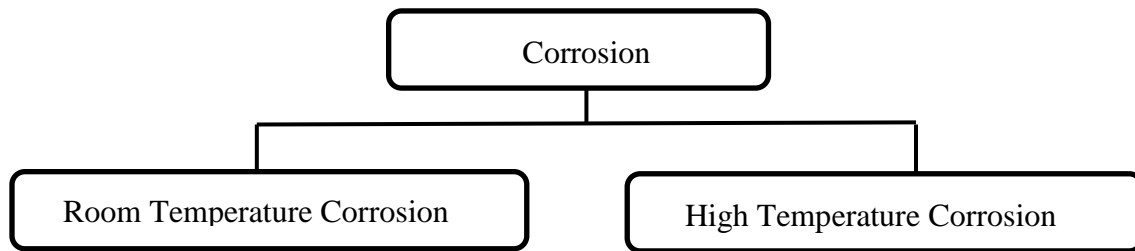


Figure 7: Various disciplines involved in corrosion science

Classification of Corrosion

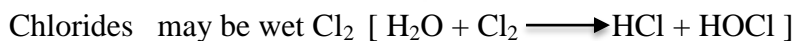
Corrosion may be classified in different ways





➤ **Wet & Dry Corrosion**

Wet / aqueous corrosion: is the major form of corrosion which occurs at or near room temperature and in the presence of water. This usually involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion by far. Wet Corrosion is a chemical reaction of a metal with the atmosphere in presence water like:



Salts like NaCl , MgCl , CaCl₂ , etc.



Corrosion by H₂O + O₂ at room temperature is about 1/20 to that of H₂O + chlorides

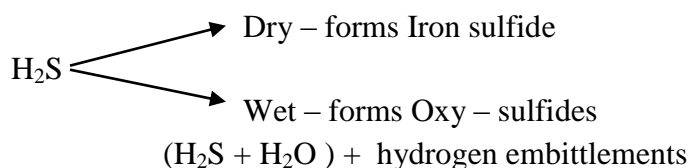
Dry / gaseous corrosion is significant mainly at high temperatures and it occurs in absence of a liquid phase or an above the dew point of the environment. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with high temperatures like:

Oxidation of metals



Dry chlorine is practically non-corrosive to ordinary steel, but moist chlorine dissolved in water, is extremely corrosive and attacks most of common metals and alloys. The reverse is true for Titanium – dry chlorine gas is more corrosive than wet chlorine.

Sulfides H₂S it is very highly corrosive substance.



SO₂: has no corrosion effect but in presence of moisture and oxygen at forms sulfides.

Differences between dry and wet corrosion

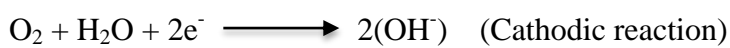
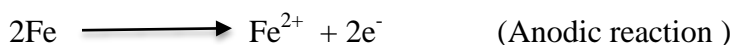
Wet corrosion	Dry corrosion
Corrosion occurs in presence of conducting medium.	Corrosion occurs in the absence of moisture.
It involves formation of electrochemical cells.	It involves direct attack of chemicals on the metal surface.
It is a rapid process	The process is slow.
Corrosion occurs at anode but rust is deposited at cathode.	Corrosion products are produced at the site of corrosion
It depends on the size of the anodic part of metal.	The process of corrosion is uniform.

Electro – Chemical Process:

There are two reactions taking place at the same time,

a) Anodic reaction (Oxidation).

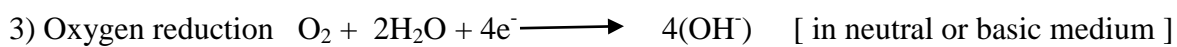
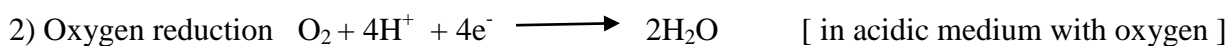
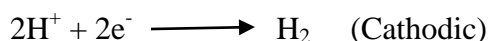
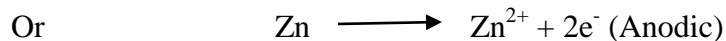
b) Cathodic reaction (Reduction).



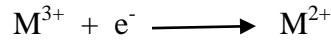
Anodic and Cathodic reaction have to take place at the same rate otherwise the rate of corrosion would become slow. Normally the Cathodic reaction is the rate controlling process. There are various types of cathodic reactions possible under different conditions:



Cathodic reactions:

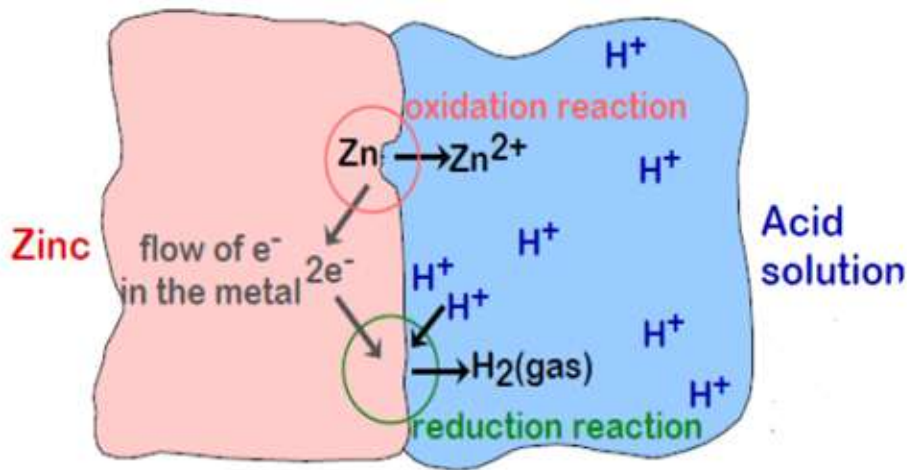


This is the most kind reaction happens



An overall electrochemical reaction must consist of at least one oxidation and one reduction reaction, and will be the sum of them; often the individual oxidation and reduction reactions are termed half-reactions. There can be no net electrical charge accumulation from the electrons and ions; that is, the total rate of oxidation must equal the total rate of reduction, or all electrons generated through oxidation must be consumed by reduction.

Example 1: Zinc metal immersed in an acid solution containing H^+



➤ Zinc will experience oxidation or corrosion according to,



➤ H^+ ions are reduced according to,

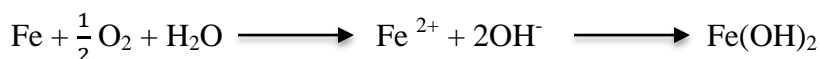


➤ The total electrochemical reaction

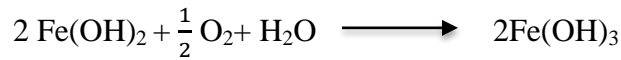


Example 2: Oxidation or rusting of iron in water, which contains dissolved oxygen, this process occurs in two steps:

➤ Fe is oxidized to Fe^{2+} [as $\text{Fe}(\text{OH})_2$]



➤ Fe²⁺ to Fe³⁺ [as Fe(OH)₃]



Rate of corrosion:-

The most common methods used are

1 – Weight loss in mg or gram.

2 – % weight change.

Poor – sample shape and exposure Time influence results.

3 – Milligram / sq. decimeter / day. (mdd).

4 – Grams / sq. decimeter / day.

5 – Grams / sq. centimeter / hour

6 – Grams / sq. meter / hour.

7 – Grams / sq. inch / hour.

8 – Moles / sq. centimeter / hour.

Good – but expressions do not give penetration rates.

9 - Inch / year.

10 - Inch / month.

11 – mm / year most common method .

Better – expressions give penetration rates.

12 – Mils per Year (MPY) . mil = 1/ 1000 .

Best – expresses penetration without decimals or large numbers.

$$MPY = \frac{534 W}{D A t}$$

Where W: weight loss in mg.

D: density of metal in g/cm³

A: area of specimen in sq in.

T: exposure time in hr.

Passivity:-

Passivity means the lack of activity under conditions where a metal would be expected to react readily. There are certain metals which are passive to certain corroding agents. For example; iron is passive to conc. HNO_3 . Aluminum has no action with conc. HNO_3 in absence of chlorides etc.

Metals which are susceptible to corrosion are made passive by alloying with one or more of metals which are passive or resist corrosion. For example; Iron is rendered passive by alloying it with any of the transition metals such as chromium, nickel and molybdenum.

The quantity of passive metal to be added depends upon the environments. For example; iron-chromium alloy, when the quantity of chrome added is from 12 to 20%, the alloy is passive to neutral salt solution but no concentration of chromium in iron makes the alloy passive to hydrochloric acid.

Passivity is defined as the reduction in chemical or electrochemical activity of a metal due to the reaction of metal with its environment so as to form a protective film on the metal surface.

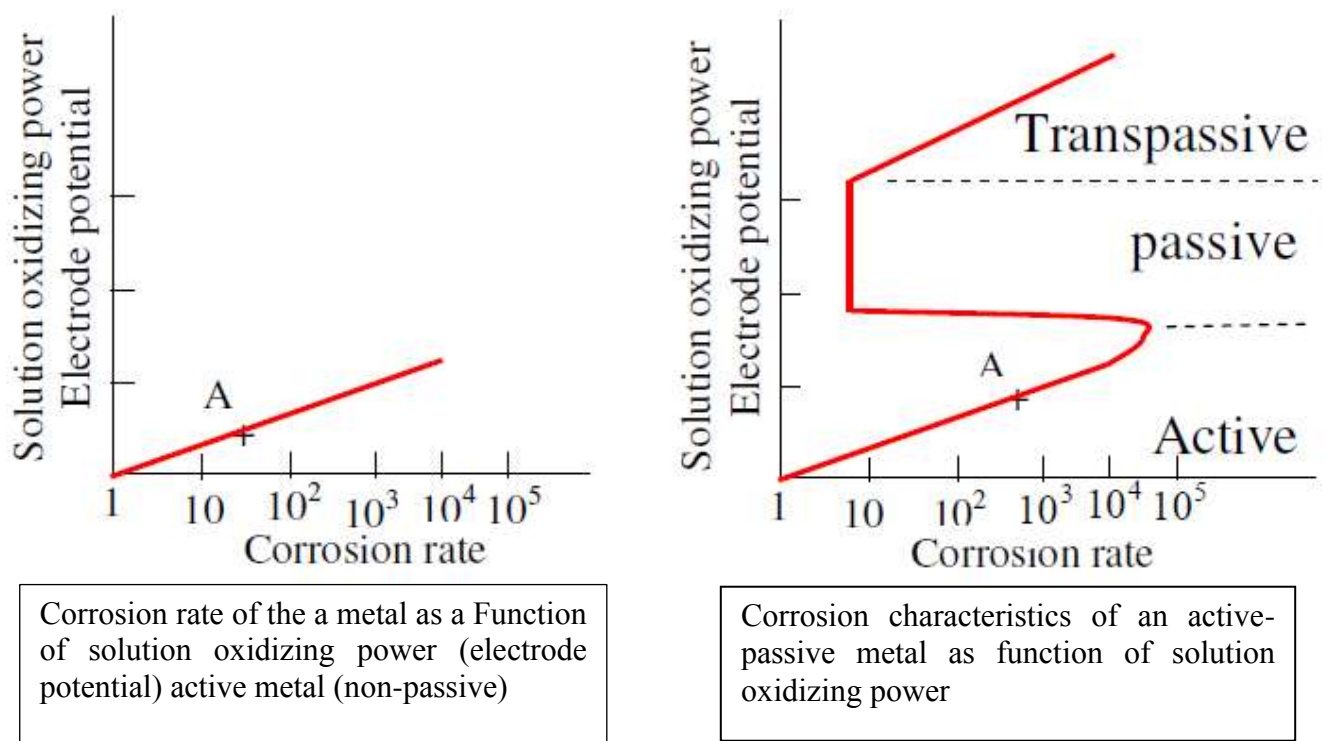


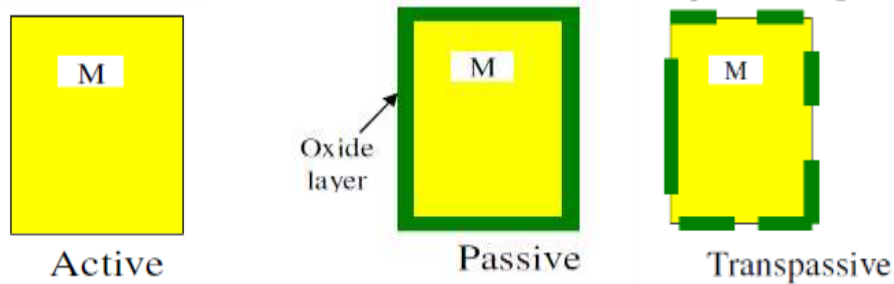
Figure 13: (First) refer to active metal in air-free acid solution it is corrode and corrosion rate increase by adding oxygen or ferric ions. (Second) illustrates the typical behavior of a metal of which demonstrates passive effects.

There are three regions, Active, Passive & Transpassive.

Active region: the behavior of a normal metal.

Passive region: If more oxidizing agent is added the corrosion rates suddenly decrease, this mean that this region begin.

Transpassive region: with further increase in oxidizing agents the corrosion rate again increase with increasing oxidizer power.



Factors Influencing Corrosion Rate:

The rate and extent of corrosion, depends on the following factors:

1. Nature of the metal:

- i. **Position in the galvanic series:** The greater the oxidation potential, when the metal is higher up in the galvanic series, greater is its tendency to become anodic and hence greater is the rate of corrosion.
- ii. **Purity of metal:** Lesser is the percentage purity of a metal, faster is the rate of corrosion. The impurities present in metal cause heterogeneity and thus tiny electrochemical cells are set up at the exposed part of the impurity and corrosion of metal around the impurity takes place due to local action.
- iii. **Physical state of the metal:** The rate of corrosion is influenced by physical state of metal. The smaller the grain size of the metal or alloy, the greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.
- iv. **Nature of the oxide film:** The ratio of the volumes of the metal oxide to the metal is known as "specific volume ratio". Greater the specific volume ratio, lesser is the oxidation corrosion rate.
- v. **Relative areas of the anode and cathode:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of the cathodic part and the anodic part. When cathodic area is smaller, the demand for electrons will be less and this result in the decreased rate of dissolution of metal at anodic regions.
- vi. **Solubility of corrosion products:** In the electrochemical corrosion, if the corrosion product is soluble in corroding medium, then corrosion proceeds at a faster rate. For

example, Pb in H_2SO_4 medium forms PbSO_4 which is insoluble in the corroding medium, hence corrosion proceeds at a smaller rate.

- vii. **Volatility of corrosion products:** Rapid and continuous corrosion of metal take place if corrosion product is volatile. This is due to the fact that as soon as corrosion product is formed, it volatilize, thereby leaving the underlying metal surface for further attack.

2. Nature of the corroding environment:

- i. **Temperature:** With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.
- ii. **Humidity of air:** The greater is humidity, the greater is the rate and extent of corrosion. This is due to the fact that moisture acts as a solvent for O_2 , H_2S , SO_2 and NaCl etc. to furnish the electrolyte essential for setting up a corrosion cell.
- iii. **Effect of pH:** Corrosions of that metal which are readily attacked by acids can be reduced by increasing the pH of the attacking environment.
- iv. **Presence of impurities in atmosphere:** Corrosion of metals is more in areas near to the industry and sea. This is due to the fact that corrosive gases like H_2S , SO_2 , CO_2 and fumes of H_2SO_4 and HCl in the industrial areas and NaCl of sea water leads to increased conductivity of the liquid layer in contact with the metal surface, thereby increase the corrosion rate.
- v. **Presence of suspended particles in atmosphere:** In case of atmospheric corrosion; (a) if the suspended particles are chemically active in nature [like NaCl , $(\text{NH}_4)_2\text{SO}_4$], they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion; (b) if the suspended particles are chemically inactive in nature (*e.g.*, charcoal), they absorb both sulphur gases, and moisture and slowly enhance corrosion rate.

Electro-Chemical Considerations:

For metallic materials, the corrosion process is normally electrochemical, that is a chemical reaction in which there is transfer of electrons from one chemical species to another. Metal atoms characteristically lose or give up electrons in what is called an oxidation reaction. The site at which oxidation takes place is called the anode; oxidation is sometimes called an anodic reaction.

The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed a reduction reaction. The location at which reduction occurs is called the cathode.

Corrosion Cell: For Corrosion to take place, the information of a corrosion cell is essential. A corrosion cell essentially comprised of the following four components.

1. Anode
2. Cathode
3. Electrolyte

4. Metallic path.

Anode (-ve of cell): One of the two dissimilar metal electrodes in an electrolytic cell. Electrons are released at anode, which is the more reactive metal. Electrons move through the wire in to the cathode.

Cathode (+ve of cell): The other Electrode in the electrolytic cell. Reduction takes place at cathode and electrons are consumed.

Electrolyte (e.g. salt solution): It is the electrically conductive solution for corrosion to occur. Positive electricity passes from anode to cathode through the electrolyte as cations.

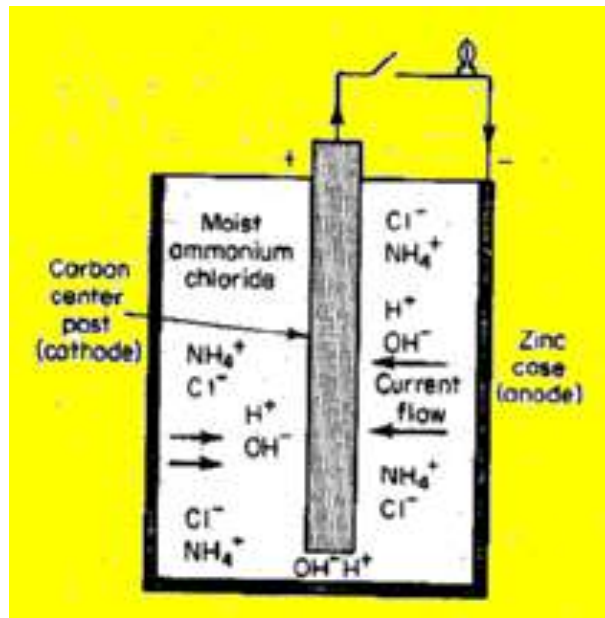
Metallic path: The two electrodes are connected externally by a metallic conductor. Current flow from (+) to (-) which really electrons flowing from (- e) to (+ e).

Current flow: Conventional current flows from anode (-) to cathode (+) as Zn^{++} ions through the solution. The circuit is completed by passage of electrons from the anode to the cathode through the wire (outer current).

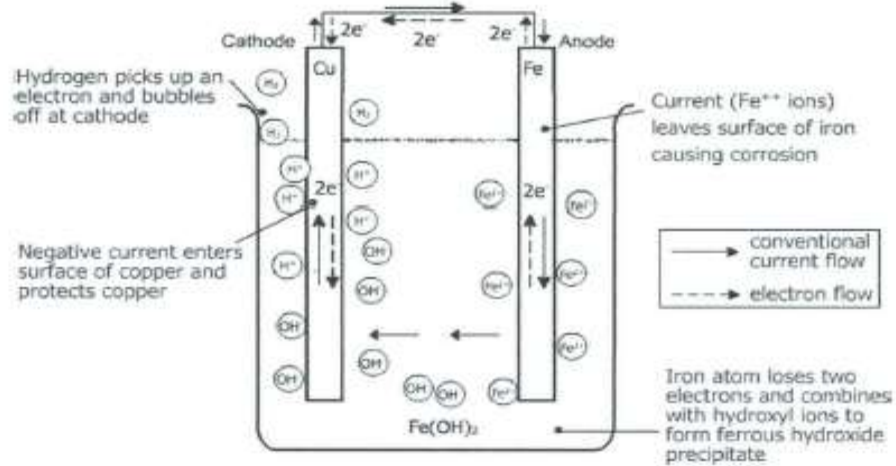
Electron Flow: The circuit is completed by negative ions (-) Which migrate from cathode (+) , through the electrolyte , towards the anode (-).

Example 4: In the dry Battery Zinc casing acts as anode. Carbon electrode acts as cathode.

Moist ammonium chloride acts as Electrolyte. e.g. Zn ions dissolve from a zinc anode and thus carry positive current away from it, through the aqueous electrolyte.



Anodic and Cathodic Reactions



Anodic reactions characteristics:

- (1) Oxidation of metal to an ion with a charge.
- (2) Release of electrons.
- (3) Shift to a higher valence state.

The process of oxidation in most metals and alloys represents corrosion. If oxidation is stopped, corrosion is stopped.

Cathodic reactions characteristics:

The Process of reductions which occur at the cathode represents protection. Electrons released by the anodic reactions are consumed at the cathode surface. Unlike an anodic reaction, there is a decrease in valence state. (Most common cathodic reactions mentioned above).

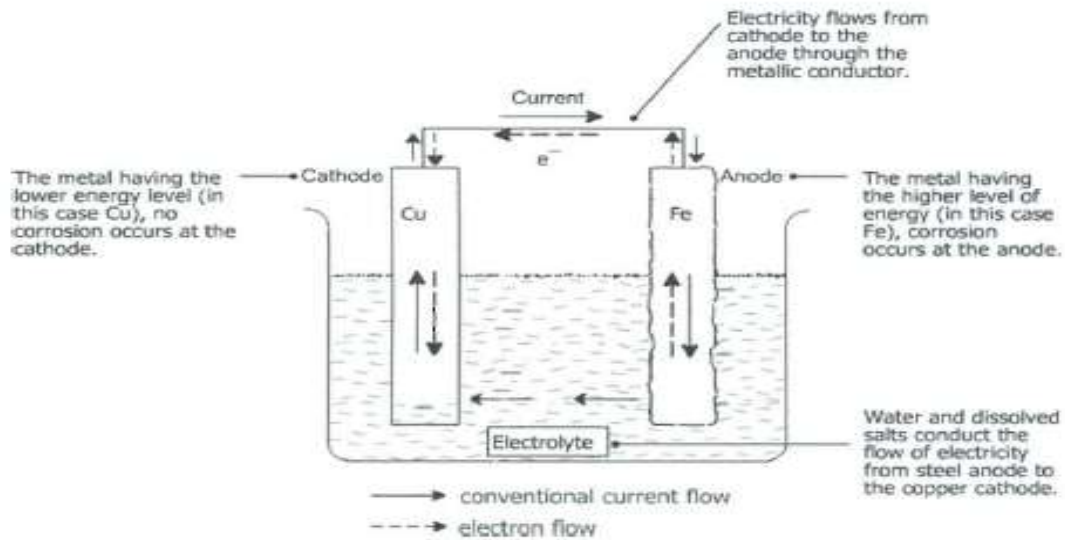
Types of Corrosion Cells:

There are several types of corrosion cells:

- (1) Galvanic cells.
- (2) Concentration cells.
- (3) Electrolyte cell.
- (4) Differential temperature cells.

(1) Galvanic cells:

The galvanic cell may have an anode or cathode of dissimilar metals in an electrolyte or the same metal in dissimilar conditions in common electrolyte.

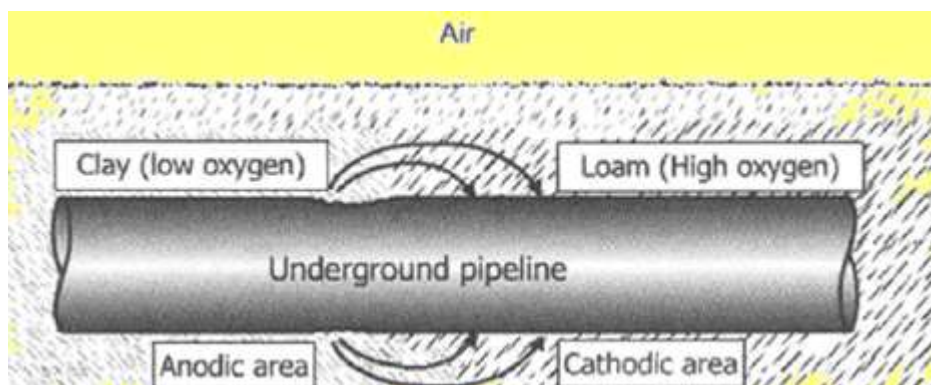


(2) Concentration Cells:

This is similar to galvanic cells except the anode and cathode are of same metals in a heterogeneous electrolyte. A pipe in soil, Concentration cells may be set up by:

- (a) Variation in the amount of oxygen in soils.
- (b) Differences in moisture content of soils.
- (c) Differences in compositions of the soil.

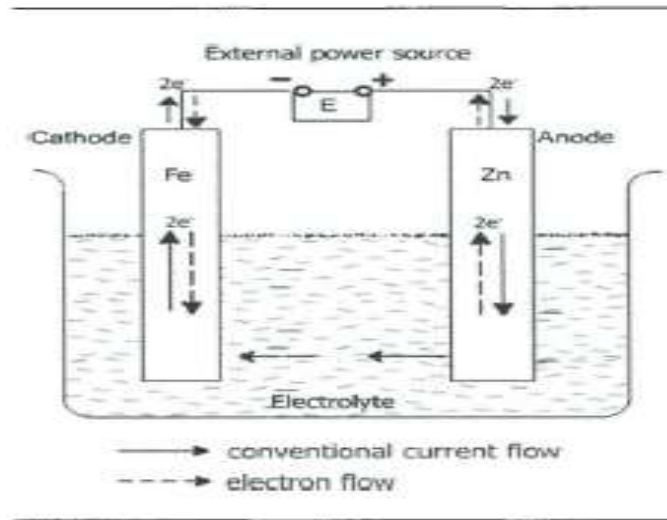
Concentration cells are commonly observed in underground corroding structures, such as buried pipes or tanks. The inequality of dissolved chemicals causes a potential difference which establishes anode in the more concentrated region and cathode in the less concentrated region.



(3) Electrolytic Cells:

This type of cell is formed when an external current is introduced into the system. It may consist of all the basic components of galvanic cells and concentration cells plus an external source of electrical energy.

Notice that anode has a (+) polarity and cathode has (-) polarity in an electrolytic cell, where external current is applied. This is the type of cell set up for electrically protecting the structures by cathodic protection.



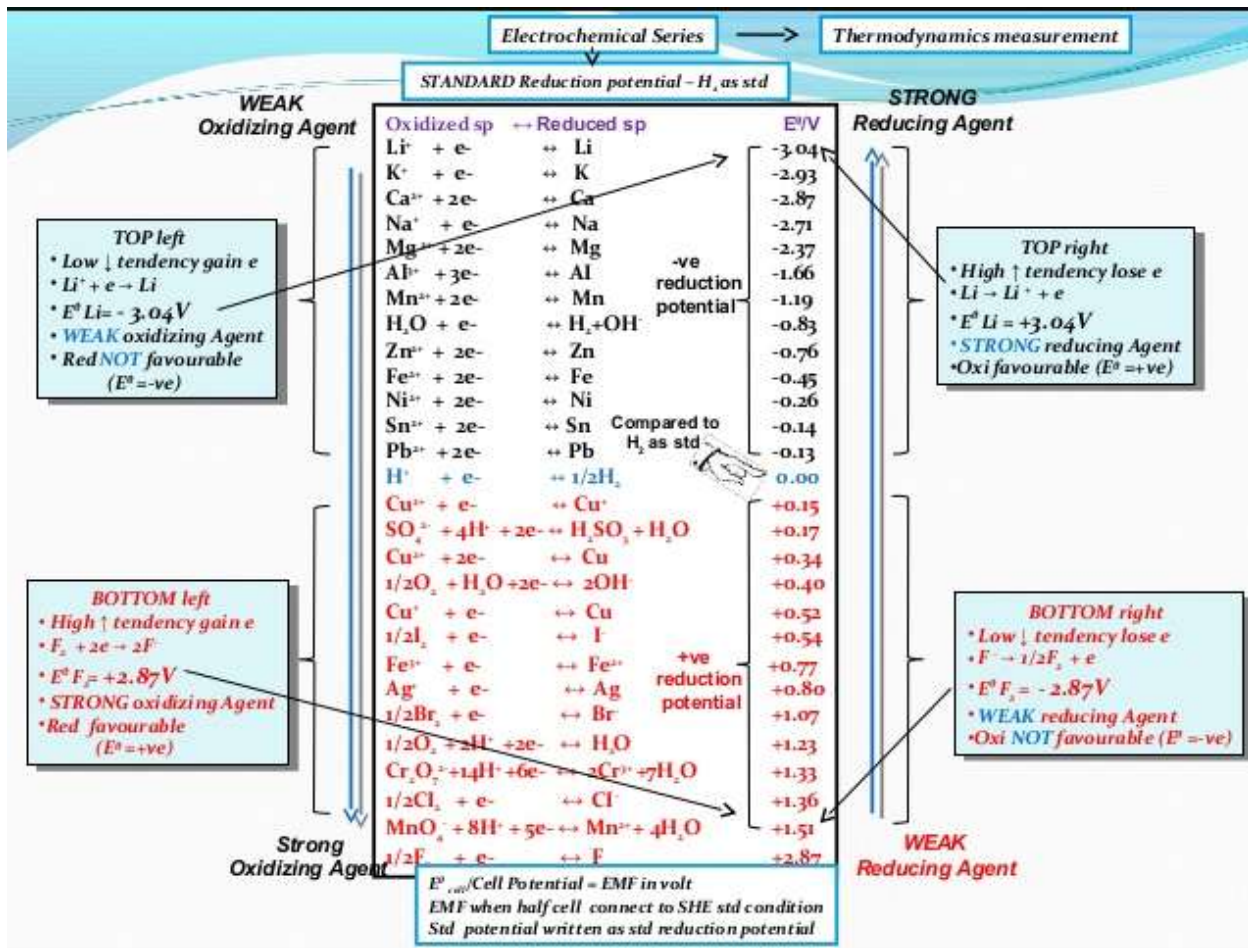
(4) Differential Temperature Cells:

This type of cell is formed when two electrode of same metals present in different temperatures, causing in different potential, high temp. Electrode will be the cathode and the lower temperature will be the anode. (e.g. heat exchangers & condensers).

The Electro Motive Series (EMF)

When a metal is immersed in an electrolyte, a dynamic equilibrium is established across the interface with a potential difference between the metal and electrolyte. If a metal is immersed in a solution of its own ions, such as Zn in ZnSO₄ solution, or copper in CuSO₄ the potential obtained is called the reversible potential (E_{rev}).

If the metals are in their standard states, such that activities of the metallic ions are equal to unity or gases are at 1 bar pressure, the potentials obtained are called “Standard Electrode Potentials”. A standard potential refers to the potential of pure metal measured with reference to a hydrogen reference electrode (H_2 / H^+) which is arbitrarily defined as Zero. It is not possible to establish a reversible potential for alloys containing two or more reactive components, so only pure metals are listed in table below.



The emf of the cell is the algebraic sum of the potentials of the half cells or '**Standard Electrode Potential**'

$$E_{cell} = E_{Zn/Zn^{2+}} + E_{Cu^{2+}/Cu}$$

The emf of any cell is, therefore given by

$$E_{cell} = E_{Oxidation} + E_{Reduction}$$

Galvanic series: In actual corrosion problems, galvanic coupling between metals in equilibrium with their ions rarely occurs. In general, the positions of metals and alloys in the galvanic series agree closely with their constituent elements in the emf series.

This represents the relative reactivity of a number of metals and commercial alloys in seawater.

Table 17.1 in Callister

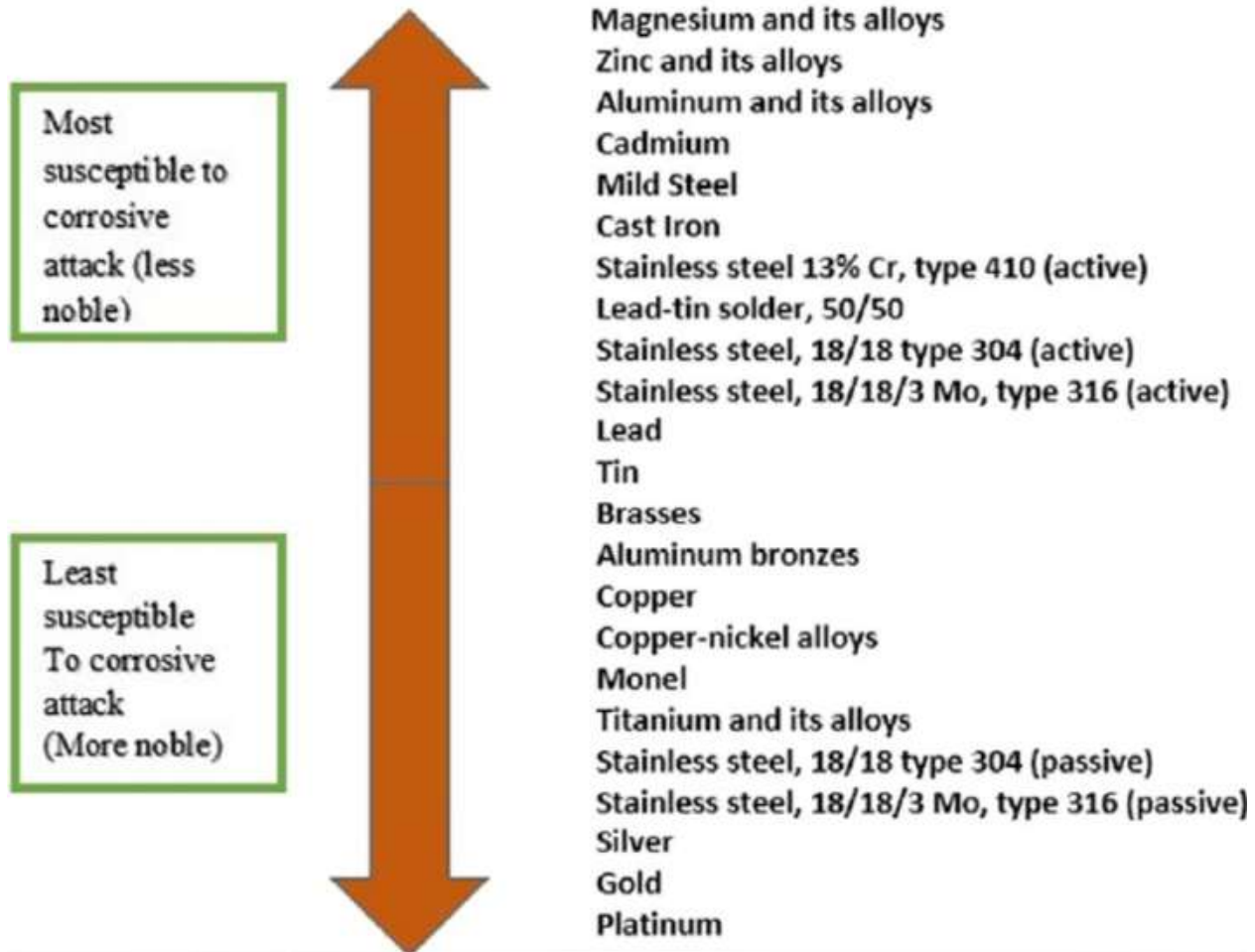
EMF Series

	<i>Electrode Reaction</i>	<i>Standard Electrode Potential, V^0 (V)</i>
	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.420
	$\text{O}_2 + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}$	+1.229
	$\text{Pt}^{2+} + 2e^- \longrightarrow \text{Pt}$	~+1.2
	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.800
	$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4(\text{OH}^-)$	+0.401
	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.340
	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^- \longrightarrow \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.440
	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.744
	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.662
	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.363
	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
	$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.924

↑
Increasingly inert
(cathodic)

↓
Increasingly active
(anodic)

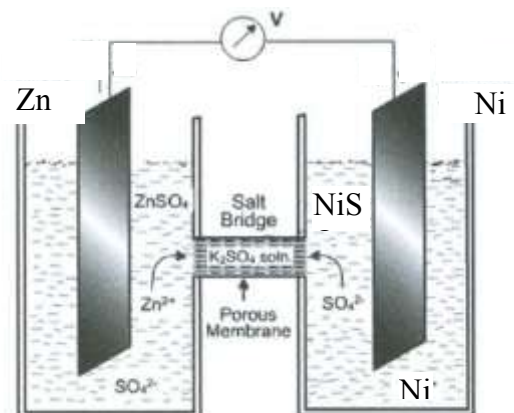
Corrosion Susceptibility of metals



Example 5 : A galvanic cell consist of (Zn) electrode in($ZnSO_4$) solution with (1 mole) concentration. The other is of (Ni) electrode in ($NiSO_4$) solution with (1 mole) concentration. The two electrodes are separated with porous partition to prevent mixing of the two solutions. The two electrodes are contacted with conductive wire.

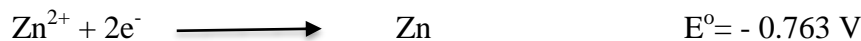
Find

- On which electrode the oxidation reaction will be.
- Which electrode will be the anode.
- Which electrode will corrode.
- What is the emf for this galvanic cell, circuit close.



Solution:

The half cells reactions are:

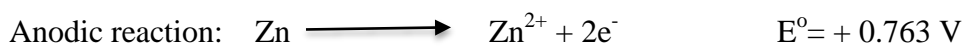


(a) Oxidation reaction will take place on Zn electrode .Because the potential difference in Zn half-cell more negative (- 0.763 V) compare with (-0.250 V) for Ni half Cell.

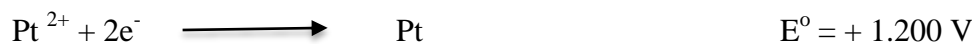
(b) From previous answer, Zn electrode is the anode, because the oxidation reaction takes place on anode electrode.

(c) In galvanic cell, the anode electrode is the corroded electrode, for that Zn electrode will corroded.

(d) Cell potential is the sum of the two half cells potential.



Example 6: if we connect Pt electrode with Cu electrode we get:

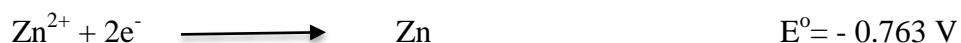


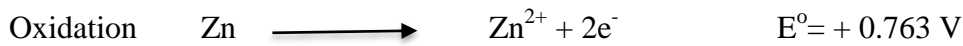
By subtraction the lower potential from the higher we get



$$E^{\circ}_{\text{cell}} = +0.8633 \text{ V}$$

Example 7: If the galvanic Cell contain two electrodes, One of them with (- ve) potential and the other with (+ ve), such as Zinc with Copper.





$$E^\circ_{\text{cell}} = + 1.100 \text{ V}$$

Example 8: Write the reactions of the anodic half cell (oxidation) and cathodic half cell (reduction). For the following electrodes and electrolytes, by using standards potential values:

- (a) Zinc and copper electrodes are immersed in dilute (CuSO_4).
- (b) Copper electrode is immersed in water saturated with oxygen.
- (c) Iron electrode is immersed in water saturated with oxygen.
- (d) Magnesium electrode is immersed in water saturated with oxygen.

a) Oxidation (Anodic reaction)

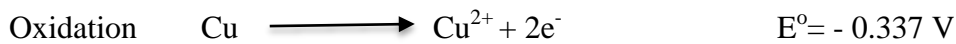


Reduction (Cathodic reaction)



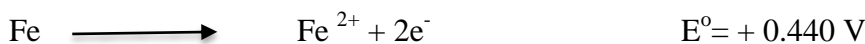
We observed that Zinc reaction possess more negative, so it is the anode and oxidation reaction occurred on it.

b) May be there is a low rate corrosion or maybe there is no corrosion , because the potential difference between Cu oxidation (0.337 V) and that formed in water from hydroxide ion (0.401 V) is very small.



c) Iron potential's difference is more negative, so it is the anode and oxidation reaction occurred on it.

Oxidation (Anodic reaction)



Reduction (Cathodic reaction)



d) Mg is more negative in potential, so it is the anode and oxidation reaction occurred on it.

Oxidation (Anodic reaction)



Reduction (Cathodic reaction)



Galvanic Cell not one molar with Electrolytes that are:-

Most of electrolyte solutions of the real galvanic cells are not to be (1 mole) .But they are always dilute solutions , which they are less than (1 mole) .If the ions concentrates in the electrolyte surround to the anode electrode is less than 1 mole , the reaction motive force to dissolve or corrode the anode will be higher .Because there is less concentrate of ions that causes the reverse reaction .There for it will be more negative of electro-chemical series on the anodic half-cell.



Truly the metal ion concentration effects (C_{ion}) on the standards potential of the electrochemical series (E°)at (25^o)Temperature are given by Nernst equation for the half anodic cell reaction .Where there is one kind of ions are produced . Nernst equation can be written as follow:

$$E = E^\circ - \frac{RT}{nF} \ln \left[\frac{a_{\text{products}}}{a_{\text{reactants}}} \right]$$

$$E = E^\circ - \frac{RT}{nF} \ln \left[\frac{a_{\text{M}^{z+}} a_{\text{e}^-}}{a_{\text{M}}} \right]$$

$$E = E^\circ - \frac{RT}{nF} \ln [a_{\text{M}^{z+}}]$$

Because a_{M} and $a_{\text{e}^-} = 1$

$$E = E^\circ - 2.303 \frac{8.314 \text{ J/K.mol} (25 + 273) \text{ K}}{n * 96500 \text{ coulomb}} \log [a_{\text{M}^{z+}}]$$

$$E = E^\circ - \frac{0.0591}{n} \log [a_{\text{M}^{z+}}]$$

Where:

E = New electrochemical potential for the half cell.

E° = standard electrochemical potential for the half cell.

n = No. of electrons transferred (the valence).

C_{ion} = molar concentrations of the ions.

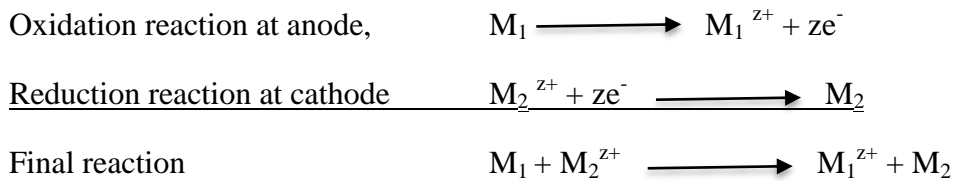
R = gas constant = 8.314 J/K^o/mole.

T = Temperature = 25 + 273 = 298 K^o.

F = Faraday constant = 96,500 coulomb.

Electrochemical cell potential for two standard half-cells that are electrically coupled

A corrosion reaction can be considered as composed of two half-cell reactions. One of the half-cell reactions corresponds to '*oxidation reaction*' taking place on the '*anode*,' and the other half cell reaction corresponds to '*reduction reaction*' taking place on the '*cathode*' of the cell. The contribution of each half cell reaction to the Nernst expression can be derived as follows:



$$E = E_1 + E_2$$

$$E = \left[E_1^o - \frac{RT}{nF} \ln \left(\frac{a_{M_1}^{z+}}{a_{M_1}} \right) \right] + \left[E_2^o - \frac{RT}{nF} \ln \left(\frac{a_{M_2}}{a_{M_2}^{z+}} \right) \right]$$

Where E^o = standard potential, $E^o = E_1^o + E_2^o$ as taken from the standard emf series.

$$\left. \begin{array}{l} E_1 = E_1^o - \frac{RT}{nF} \ln \left(\frac{a_{M_1}^{z+}}{a_{M_1}} \right) \\ E_2 = E_2^o - \frac{RT}{nF} \ln \left(\frac{a_{M_2}}{a_{M_2}^{z+}} \right) \end{array} \right]$$

Theses equations are Nernst equations for the half-cell reactions and

$$E = E^o - \frac{RT}{nF} \ln \left[\frac{a_{M_1}^{z+} a_{M_2}}{a_{M_1} a_{M_2}^{z+}} \right]$$

This equation is the Nernst equation for the complete cell reaction.

Since metal M_1 is oxidized, the sign of is opposite to that as it appears in Table of standard emf the two above equations yields and the cell potential E^o for this reaction to occur spontaneously, Must be positive; if it is negative, the spontaneous cell direction is just the reverse of equation. When standard half-cell are coupled together, the metal that lies lower in emf table will experience oxidation (i.e., corrosion), whereas the higher one will be reduced.

Influence of Concentration and Temperature on Cell Potential

Nernst equation electrochemical cell potential for two half-cells that are electrically coupled and for which solution ion concentrations are other than 1M.

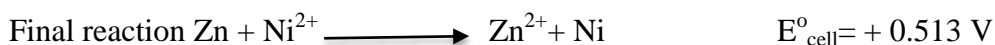
$$E = E^o - \frac{RT}{nF} \ln \left[\frac{a_{M_1}^{z+}}{a_{M_2}^{z+}} \right]$$

Simplified the equation for $T = 25^\circ\text{C}$ (room temperature).

$$E = E^o - \frac{0.0591}{n} \ln \left[\frac{a_{M_1}^{z+}}{a_{M_2}^{z+}} \right]$$

Example 9: A galvanic cell in (25 C^o) temperature it is formed from Zinc electrode in (0.10 mole ZnSO_4) solution, the other electrode is of Nickel in (0.05 mole NiSO_4) solution .The two electrodes are separated with porous wall and connected with external wire. What is the value of the cell potential, when the circle is connected.

Solution: First we suppose that the solutions are in (1 mole) concentrate. So the potentials of Zn & Ni are in standard value of EMF serious. Zn electrode will be the anode because it's potential (- 0.763 v) is more negative in the electrochemical cell of Zn – Ni than of Ni (- 0.250 v).



Then using Nernst equation to correct the potentials of the cell.

Anode reaction $E_A = 0.763\text{ V} - \frac{0.0591}{2} \log 0.1$
 $= 0.763\text{ V} + 0.0296\text{ V}$
 $= + 0.7926\text{ V}$

$$\begin{aligned}
 \text{Cathodic reaction} \quad E_C &= -0.250 \text{ V} - \frac{0.0591}{2} \log\left(\frac{1}{0.05}\right) \\
 &= -0.250 \text{ V} - 0.0385 \text{ V} \\
 &= -0.2885 \text{ V}
 \end{aligned}$$

$$\begin{aligned}
 \text{Emf of Cell} = E_A + E_C &= 0.7926 \text{ V} - 0.288 \text{ V} \\
 &= -0.5041 \text{ V}
 \end{aligned}$$

Example 10: two half-cell reactions are given below



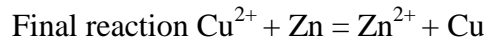
Their reduction potentials are given opposite to each. Calculate:

- The emf of the cell and
- Show the spontaneous cell reaction.

Solution: the left hand electrode (Zn) is the anode and the right hand electrode (Cu) is the cathode according to the convention we studied earlier on. Therefore, zinc will undergo oxidation and copper reduction as shown below. Hence:

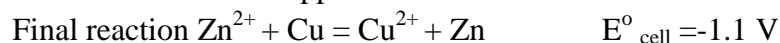
$$\begin{aligned}
 \text{(a)} \quad E_{cell}^\circ &= E_R^\circ + E_L^\circ \\
 E_{cell}^\circ &= E_{Cu}^\circ + E_{Zn}^\circ \\
 &= 0.337 + 0.763 \\
 &= +1.100 \text{ volts}
 \end{aligned}$$

(b) Spontaneous cell reaction is given by: cell reaction = cathodic reaction = anodic reaction



From the table of standard reduction potentials, the reduction potential of Cu is +0.337 volts and that of Zn is — 0.763 volts. The emf of the cell is positive. Hence the reduction is spontaneous and it should proceed from left to right.

If the position of the electrodes are now interchanged such that the copper electrode is placed on the left and the zinc electrode on the right, the sign of the cell emf will change. Here, zinc electrode being on the right is treated as cathode and the copper on the left as anode. Therefore:



The emf obtained is now negative which indicates that the reaction is not spontaneous and the current flows from right to left. The left hand electrode where the current originates is, therefore, the anode, and the right-hand electrode, the cathode. The polarity of the cell is, therefore, clearly established.

Example 11: calculate the reversible potential for a zinc electrode in contact with ZnCl₂ when the activity of zinc is $a_{Zn^{2+}} = 10^{-3}$.

Solution:

We write the half-cell reaction



Apply Nernst equation:

$$E_{Zn} = E_{Zn}^{\circ} - \frac{0.0591}{n} \log \left[\frac{1}{a_{Zn^{2+}}} \right]$$

$$E_{Zn} = -0.763 - \frac{0.0591}{n} \log \left[\frac{1}{10^{-3}} \right]$$

$$E_{Zn} = -0.8518 \text{ V}$$

Example 12: show that the reduction reaction given below:



Solution: the reaction is $2H^{+} + 2e^{-} \rightleftharpoons H_2$. Using Nernst equation we obtain for the above reaction:

$$E_{(H^{+}/H_2)} = E_{(H^{+}/H_2)}^{\circ} - \frac{RT}{nF} \ln \left[\frac{\text{Products}}{\text{reactants}} \right]$$

Changing to 2.303 log and substituting for

$$R = 8.314 \text{ J/(mol} \cdot \text{K)} \quad F = 96500 \text{ C,}$$

$$T = 298 \text{ }^{\circ}\text{K} \quad 2.303RT/F = 0.0591 \text{ V}$$

The Nernst expression above can, therefore, be written as:

$$E_{(H^{+}/H_2)} = E_{(H^{+}/H_2)}^{\circ} - 0.0591 \log [H^{+}]$$

Now substituting $\text{pH} = -\log (H^{+})$ in the above expression we get:

$$E_{H^{+}/H_2} = -0.0591 \text{ pH}$$

Example 13: Show that for the reaction: $O_2 + 2H_2O + 4e^{-} \rightleftharpoons 4(OH^{-})$,

$$E_{(O_2/OH^{-})} = E_{(O_2/OH^{-})}^{\circ} - 0.0591 \log a_{OH^{-}}$$

Solution:

The reaction is $O_2 + 2H_2O + 4e^{-} \rightleftharpoons 4(OH^{-})$, (in a basic solution), and

$$E_{(O_2/OH^-)} = E_{(O_2/OH^-)}^o - \frac{RT}{nF} \ln \frac{(a_{OH^-})^4}{a_{O_2}}$$

Note that O_2 is the oxidized state and OH^- is the reduced state, for the above reaction (from IUPAC-Nernst expression).

The activity (a_i) of an ion is defined by $a_i = M_i \gamma_i$, where M_i = molality (mol/kg) of ions in the solution, and a_i is the activity coefficient. The activity coefficient a_i for a given concentration can be found from a table of activity coefficients. In dilute solutions, the activity coefficient is taken to be unity.

If we take $a_{O_2} = \frac{P_{O_2}}{P^o} = 1$, when $P_{O_2} = P^o = 1 \text{ bar}$, standard state, and $R = 8.314 \text{ J/mol.K}$, $F = 96500 \text{ C (g.equiv.)}^{-1}$ and the term $2.303RT/F = 0.0591$, and substitute in the above expression, the oxygen electrode potential becomes:

$$E_{(O_2/OH^-)} = E_{(O_2/OH^-)}^o - 0.0591 \log a_{OH^-}$$

It can similarly be shown that in acid solution for a reaction, $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$, the oxygen electrode potential becomes:

$$E_{(O_2)} = E_{(O_2)}^o - \frac{RT}{4F} \ln \frac{a_{H_2O}^2}{(a_{O_2})(a_{H^+})^4}$$

Substituting the values for the constants as above, we get:

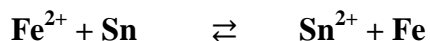
$$E_{(O_2)} = E_{(O_2)}^o - 0.0591 \log a_{H^+}$$

Or since $pH = -\log a_{H^+}$

$$E_{(O_2)} = E_{(O_2)}^o - 0.0591 pH$$

Exercise 1: calculate the potential of oxygen electrode at pH=14.0.

Exercise 2: In the cell reaction given below, what is the ratio of the activities of ionic species required to make the polarity reverse?



Exercise 3: The emf of a cell made of Zn (anode) and H_2 electrode (cathode) immersed in 0.7 M $ZnCl_2$ is +0.690 volts. What is the pH of the solution? Activity coefficient $\gamma = 0.6133$

Exercise 4: Calculate the theoretical tendency of nickel to corrode in deaerated water of pH = 8. Assume the corrosion products are H_2 and $Ni(OH)_2$ and the solubility product is 1.6×10^{-16} ?

Exercise 5: Calculate the pressure of H₂ required to stop corrosion of iron immersed in 0.1 M FeCl₂ and $\gamma=0.58$, pH = 4.

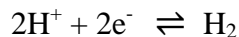
Exercise 6: Calculate if silver would corrode when immersed in 0.5 M CuCl₂ and $\gamma=0.42$ to form solid AgCl. What is the corrosion tendency?

Reference Electrodes

1) Hydrogen Electrode:

The hydrogen electrode is used as a reference for electrode potential measurements. Theoretically, it is the most important electrode for use in aqueous solutions. The reversible hydrogen electrode in a solution of hydrogen ions at unit activity exhibits a potential, which is assumed to be zero at all temperatures. The electrode consists of a platinum wire immersed in a solution containing hydrogen ions and saturated with hydrogen gas. Platinum is immersed completely in aqueous arsenic free hydrochloric acid and hydrogen gas free from oxygen and carbon monoxide is bubble and the reversible potential is achieved. Unfortunately, this electrode has some drawbacks. First the reversibility of hydrogen electrode cannot be maintained in oxidizing media. Second if a current is withdrawn from the electrode the electrode acts an anode, because of the ionization of gas molecules (Figure 14).

The electrode potential for hydrogen E_{H_2} can be determined as follows:



$$E_{(H^+/H_2)} = E_{(H^+/H_2)}^o - \frac{0.0591}{2} \log \frac{[P_{H_2}]}{[a_{H^+}]^2}$$

Where a_{H^+} is activity of hydrogen ions, and P_{H_2} is hydrogen partial pressure.

At one atmosphere pressure P_{H_2} , $a_{H^+} = 1$ and $E_{(H^+/H_2)}^o = 0$ by definition. Therefore,

$$E_{(H^+/H_2)} = 0.0591 \log(a_{H^+})$$

Or in term of pH,

$$E_{(H^+/H_2)} = -0.0591pH$$

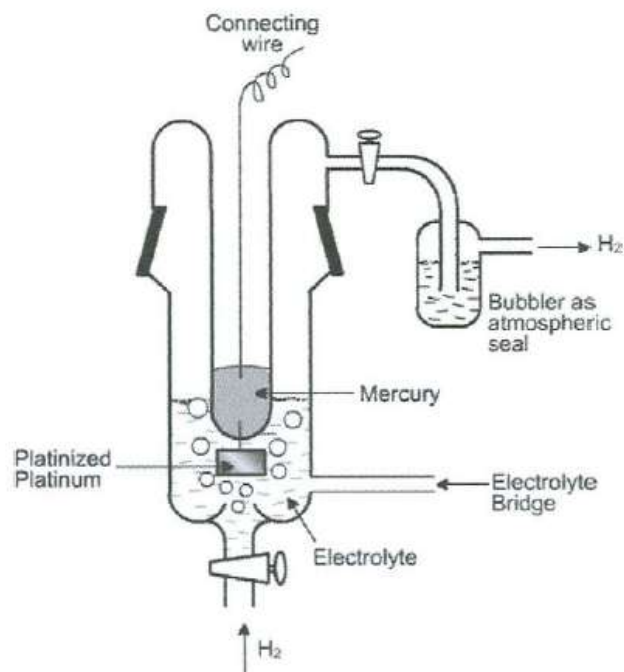
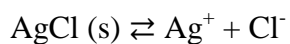


Figure 14: Hydrogen electrode

2) Silver – Silver chloride Electrode:

This electrode is composed of a silver chloride and immersed in a solution of chloride ions (Figure 15). The chloride equilibrium is given by:



Two other reactions involve a dynamic equilibrium between deposition and dissolution of silver together with solubility equilibrium between silver chloride and its ions. The metallic silver reaches equilibrium with silver ions according to the following reaction:



The overall electrode reaction is therefore given by:



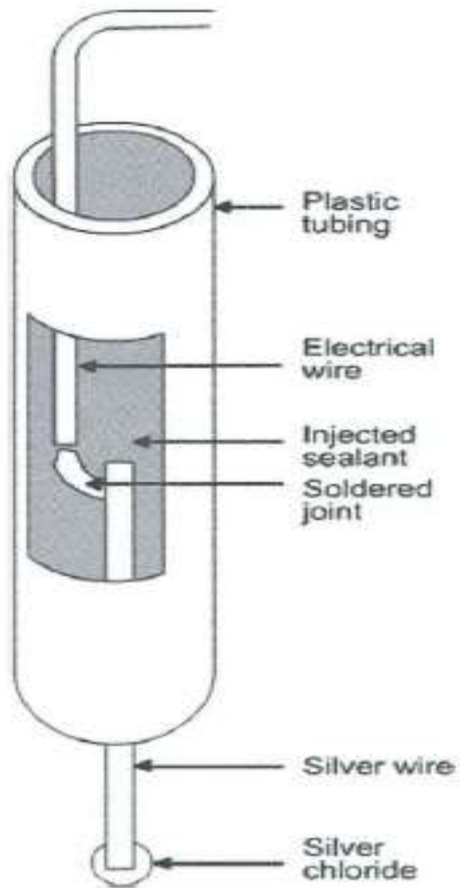


Figure 15: Silver-Silver chloride reference electrode

The electrode potential, $E_{AgCl/Ag}$, is given by :

$$E_{Ag/Cl} = E^o_{Ag/AgCl} - \frac{RT}{nF} \ln \frac{a_{Ag} a_{Cl^-}}{a_{AgCl}}$$

$$a_{Ag}=1, \quad a_{AgCl}=1$$

Therefore,
$$E_{Ag/Cl} = E^o_{Ag/AgCl} - \frac{2.303 RT}{nF} \log a_{Cl^-}$$

$$E_{Ag/Cl} = E^o_{Ag/AgCl} - 0.0591 \log a_{Cl^-}$$

The equation holds at 25°C. It can also be written in the following form:

$$E_{Ag/Cl} = 0.222 - 0.0591 \log a_{Cl^-}$$

At low concentration $\log a_{Cl^-}$ can be replaced by pH as Cl^- is provided by HCl acid, $[Cl^-] = [H^+]$ and hence $-\log a_{Cl^-}$ can be replaced by $-\log [H^+]$. Therefore, $-\log [H^+] = pH$

Hence,

$$E_{Ag/AgCl} = 0.222 - 0.0591pH$$

The following are the values of $E_{Ag/AgCl}$ for different HCl concentrations:

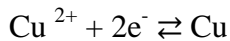
Concentration (M)	Electrode potential (Volts)
0.1	0.28
0.01	0.34
0.001	0.4

3) Copper – Copper Sulfate Electrode:

This is a reference electrode which is easy, robust and stable. It is used mainly in Cathodic protection measurements, such as the measurement of pipe – to – soil potential. It has lower accuracy than other electrodes used for laboratory work. It consists of copper metal placed in a solution containing copper sulfate and copper sulfate crystals placed in a non-conducting holder with a porous plug (Figure 16). The equation for the copper-copper sulfate electrode potential is given by:

$$E_{Cu-CuSO_4}^o = 0.316 + 0.0009(25\text{ }^\circ\text{C})\text{volts}$$

The reaction of the Cu-CuSO₄ half-cell is



And the electrode potential:

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu}^o - \frac{0.0591}{2} \log\left(\frac{1}{a_{Cu^{2+}}}\right)$$

Where

$a_{Cu^{2+}}$ = activity of copper which is unity,

$$E_{Cu^{2+}/Cu}^o = 0.34 \text{ V at } 25\text{ }^\circ\text{C}$$

A saturated solution of 1.47 M Cu-CuSO₄ at 25 °C is used.

$a_{Cu^{2+}}$ = [molarity (M) * activity coefficients γ]

$a_{Cu^{2+}} = 1.47 * 0.037$ (γ is found from the table of activity coefficients).

So $a_{Cu^{2+}} = 0.051$

Substituting in the above equation we obtain

$$E_{Cu^{2+}/Cu} = 0.34 - \frac{0.0591}{2} \log\left(\frac{1}{0.051}\right)$$

So $E_{Cu^{2+}/Cu} = 0.3$ Volts

$$E_{Cu^{2+}/Cu} = 0.316 + 0.009 (T \text{ } ^\circ\text{C}) \text{ volts}$$

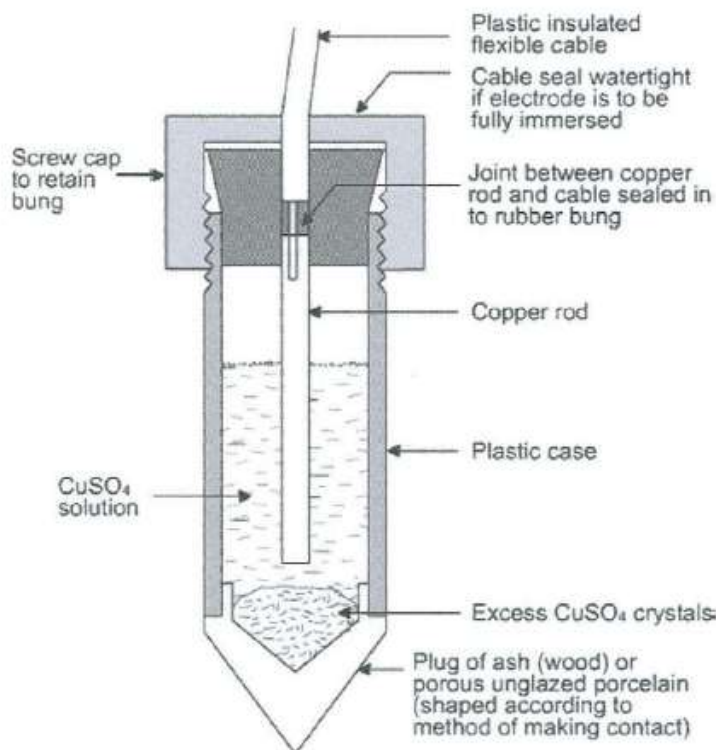


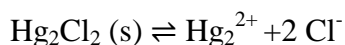
Figure 16: Reference copper-copper sulfate electrode

4) The Calomel Electrode:-

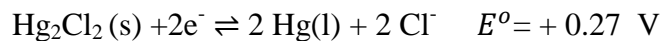
It is the most commonly used reference electrode. It has a constant and reproducible potential. The electrode basically consists of a platinum wire dipped into pure mercury which rests in a paste of mercurous chloride and mercury. The paste is in contact with a solution of potassium chloride (Figure 17).

The most commonly used concentrations of KCl are 0.1 N, 1.0 N and 3.5 N and saturated KCl. The saturated calomel is used when the liquid junction potential is to be kept low. The potential of electrode at 25°C is 0.241 V in saturated KCl solution.

Mercurous chloride is slightly soluble, and it is in equilibrium with mercurous ions according to:



The overall equilibrium is expressed by:



The mercurous chloride and mercury are at unit activity. Therefore, the electrode potential can be written as:

$$E_{\text{Calomel}} = E^\circ - \frac{RT}{2F} \ln a_{\text{Cl}^-}{}^2$$

$$E_{\text{Calomel}} = E^\circ - \frac{0.0591}{2} \log a_{\text{Cl}^-}{}^2$$

The of E° for the half-cell reaction of calomel electrode is 0.27 Thus, the electrode potential becomes:

$$E_{\text{Calomel}} = 0.27 - \frac{0.0591}{2} \log a_{\text{Cl}^-}{}^2$$

Electrode Potentials of Calomel Electrode

(Standard hydrogen electrode taken as reference)

Electrode	Potential (volts)
Hg/Hg ₂ Cl ₂ /KCl (Sat.)	0.244
Hg/Hg ₂ Cl ₂ /KCl (1.0 N)	0.267
Hg/Hg ₂ Cl ₂ /KCl (0.1 N)/Salt Bridge	0.3261

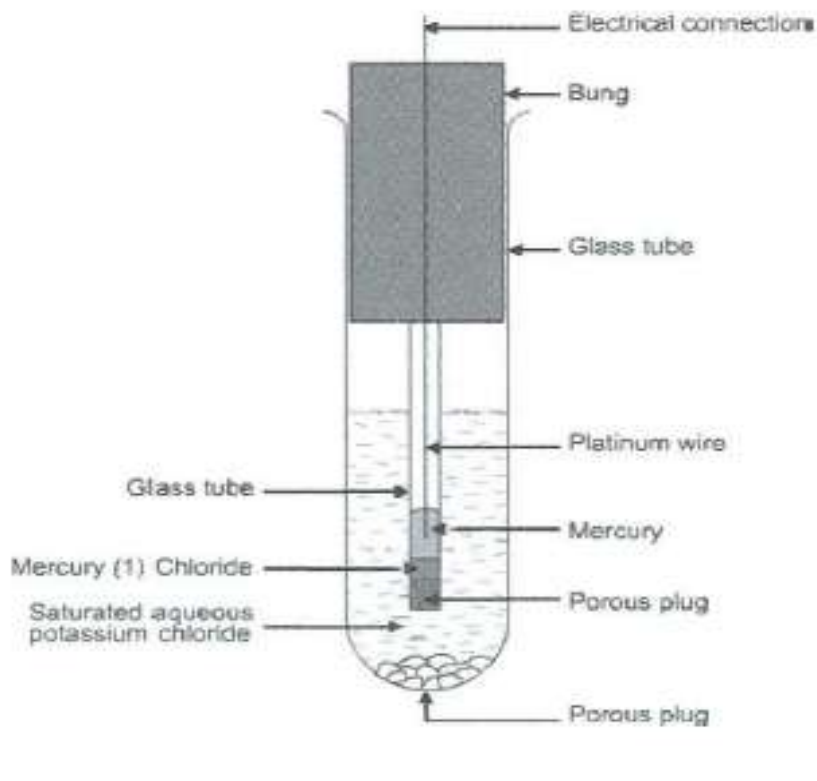


Figure 17: A saturated calomel reference electrode

Example 1: Convert -0.900 V (on SCE, Sat.) to the SHE scale.

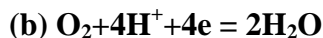
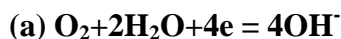
Solution:

$$\begin{aligned} -0.900\text{V (on SCE, Sat.)} &= -0.900 + 0.242\text{V (on SHE)} \\ &= -0.658\text{ V (on SHE)} \end{aligned}$$

Exercise 1: Convert -0.916 V (on SCE. 1.0 N) to the SHE scale.

Exercise 2: What is the potential on SHE scale, for an electrode which is at a potential of —0.920 V relative to a Ag/AgCl reference in 0.01 N KCl at 25° C.

Exercise 3: The following reduction reactions are given:



Show that the single electrode potential for each reaction at 25°C has the same potential dependence.

Types of Corrosion

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. 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. There are eight forms of corrosion.

1) Uniform or General Corrosion

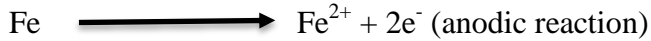
It is the uniform thinning of metal without any localized attack. This kind of corrosion happens mostly in one-phase materials and is unformed throughout the surface. Corrosion does not penetrate very deep inside. This kind of corrosion can happen in most environments, such as dry and wet atmospheres, acids, brines ... etc.

Uniform Attack is a form of electrochemical corrosion that occurs with equivalent intensity over the entire exposed surface and often leaves behind a scale or deposit.

Mechanism of uniform Corrosion

Corrosion mechanism in aqueous solution has been amply demonstrated. In atmospheric corrosion which also exemplifies uniform corrosion, a very thin layer of electrolyte is present. It is probably best demonstrated by putting a small drop of seawater on a piece of steel. On comparing the atmospheric corrosion with aqueous corrosion, the following differences are observed: On a metal surface exposed to atmosphere, only a limited quantity of water and dissolved ions are present, whereas the access to oxygen

present in the air is unlimited. Corrosion products are formed close to the metal surface, unlike the case in aqueous corrosion, and they may prevent further corrosion by acting as a physical barrier between the metal surface and environment, particularly if they are insoluble as in the case of copper or lead. The following is a simplified mechanism of aqueous corrosion of iron. At the anodic areas, anodic reaction takes place:



At the Cathodic areas, reduction of oxygen takes place:



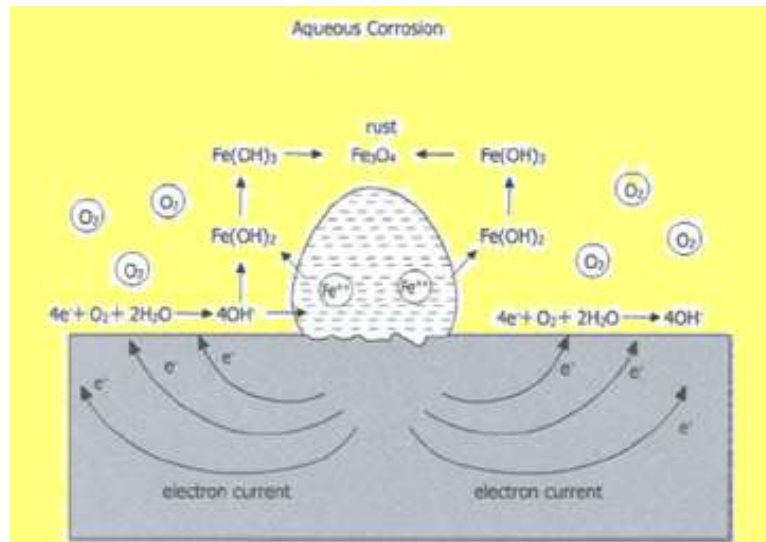
The OH ions react with the Fe⁺⁺ ions produced at the anode:



With more access to oxygen in the air, Fe(OH)₂ oxidizes to Fe(OH)₃ and later it loses its water:



Ferrous hydroxide is converted to hydrated ferric oxide or rust by oxygen.

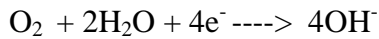


Rust (Fe₂O₃.H₂O) is a generic term to describe a series of different oxides, Fe(OH)₂, Fe(OH)₃, FeO(OH), Fe₂O₃.H₂O that forms when iron corrodes. The common form of Rust is a Red products:Fe₂O₃. Rust forms due to a reaction between the iron and water; either water condensing from air or rain.The oxygen in the air dissolves in the water and causes rust to form.There are always two distinct chemical reactions in a corrosion process, the basic is:

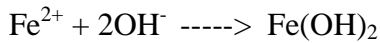
1)Anodic Dissolution of Metal (Iron) that goes into solution (water)



2)Cathodic Reduction of Oxygen dissolved in water



The final reaction is:

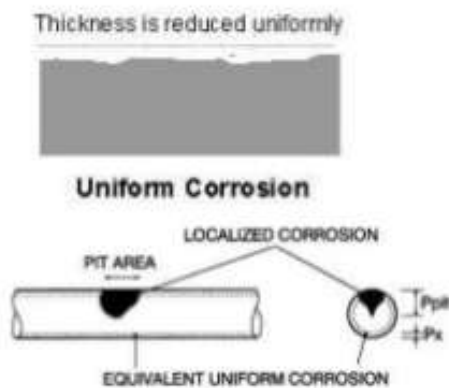


This oxide will then further reacts with oxygen to give the final red product: $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Uniform corrosion can be prevented or reduced by:-

- 1) Use paints or metallic coatings such as plating, galvanizing or anodizing
- 2) Use Corrosion inhibitors or modifying the environment.
- 3) Use thicker materials for corrosion allowance.

Examples include general rusting of steel and iron and the tarnishing of silverware. The life of equipment can be accurately estimated.



2) Galvanic or Two-Metal Corrosion

Galvanic corrosion occurs when two metals or alloys are electrically coupled while exposed to an electrolyte. The more reactive metal in the particular environment will experience corrosion, the more inert metal, will be protected from corrosion.

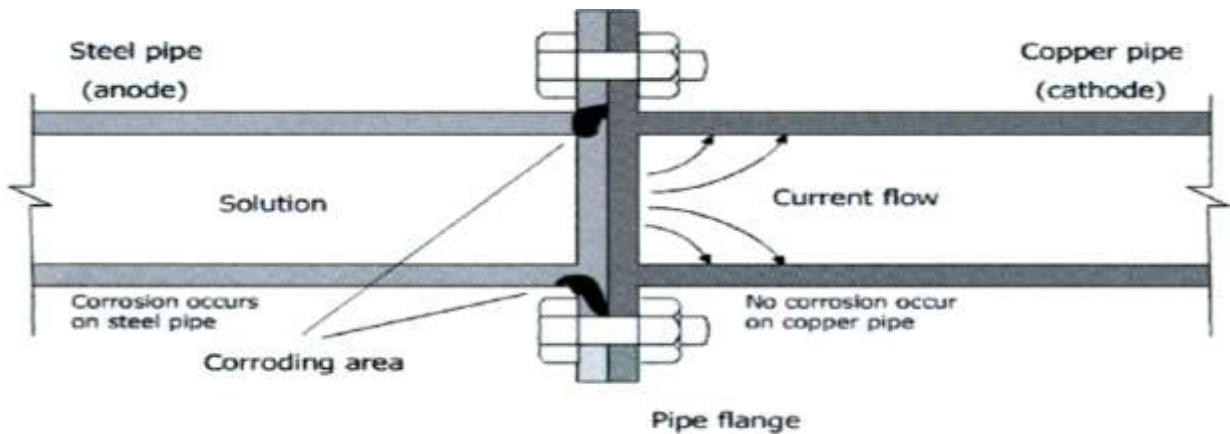
The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte. For a given cathode area, a smaller anode will corrode more rapidly than a larger one.

Mechanism of Galvanic corrosion

For the formation of a galvanic cell, the following components are required:

- 1) A cathode.
- 2) An anode.
- 3) An electrolyte.
- 4) A metallic path for the electron current.

In case of copper and steel pipe joint , Iron is more negative potential in the emf series (-0.440 V).It is the anode ,moisture acts an electrolyte and metal surface provides a metallic path for electron current to travel. A piece of copper is the cathode .Galvanic cell will form and galvanic corrosion proceeds.



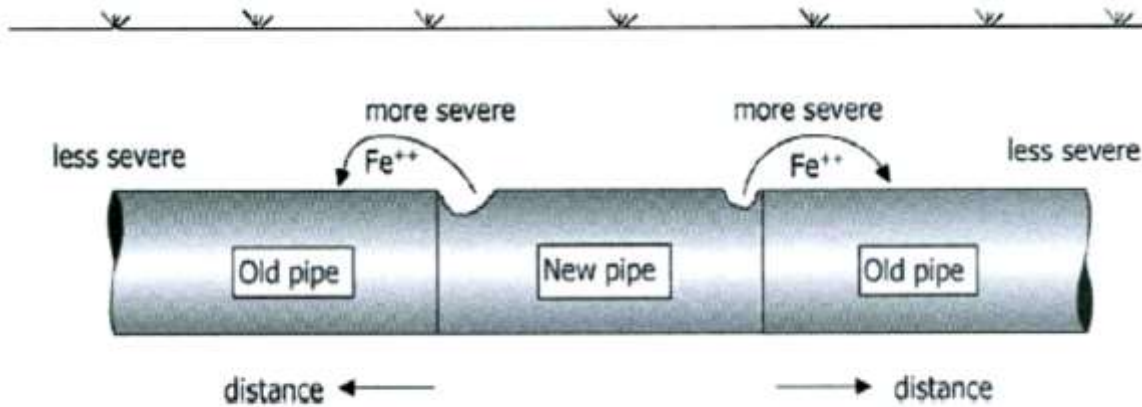
Factors affecting galvanic corrosion

The following factors significantly affect the magnitude of galvanic corrosion:-

- 1) **Position of metals in the Galvanic series:** For galvanic corrosion. The magnitude of galvanic corrosion primarily depends on how much potential difference exists between two metals. For a particular environment, the metals selected should be close to each other in galvanic series to minimize galvanic corrosion. (Al should not be joined to Fe).
- 2) **The Nature of Environment:** The environment that surrounds the metal must be considered. Water containing copper ions like seawater is likely to form galvanic cell on a steel surface of the tank. The marine environments, galvanic corrosion may be accelerated due to increased conductivity of the electrolyte. In cold climates, galvanic corrosion of buried material is reduced because of the increased resistivity of soil. In warm climates, on the other hand, it is the reverse because of the decreased resistivity of the soil.
Tantalum is very corrosion resistant metal. It is anodic to platinum and carbon, but the cell is active only at high temperatures. Zn is anode with respect to iron at room temperature with presence of water, but if the water temperature became higher ($60 - 75\text{ C}^{\circ}$). The polarity will reverse and iron will be anode (corroded).
- 3) **Area , Distance and Geometric Effects :**

Effect of Area: The anodic to Cathodic area is extremely important as the magnitude of galvanic corrosion is seriously affected by it .An unfavorable area ratio consists of a large cathode and a small anode .Corrosion of anodic area may be 100 or 100 times greater than if the anodic and Cathodic areas were equal in size .

Effect of Distance: It is a known principle that the solution conductivity varies inversely with the length of the conduction path. The greatest galvanic damage is likely to encounter near the junction of two metals and severity would be decreased with increased length.



Effect of Geometry: Geometry of components and their design also influence galvanic corrosion. As current does not flow around the corners, the geometry of the circuit affects the degree of galvanic corrosion. Any obstacle to polarization would accelerate galvanic corrosion.

Measures taken to reduce galvanic corrosion are:

- 1) If coupling of dissimilar metals is necessary, choose two that are close together in the galvanic series.
- 2) Avoid an unfavorable anode-to-cathode surface area ratio; use an anode area as large as possible.
- 3) Electrically insulate dissimilar metals from each other.
- 4) Electrically connect a third, anodic metal to the other two; this is a form of cathodic protection.

Examples:

- ♣ Plate and screw of different electrical potentials due to differences in processing
- ♣ Multiple component implant using different metals for each component
- ♣ Copper and steel tubing are Joined in a domestic water heater, the steel will corrode in the vicinity of the junction



Galvanic corrosion between stainless steel screw and Aluminium



Galvanic corrosion between Steel and Brass.

3) Crevice Corrosion

This is a localized form of corrosion, caused by the deposition of dirt, dust, mud and deposits on a metallic surface or by the existence of voids, gaps and cavities between adjoining surfaces. An important condition is the formation of a differential aeration cell for crevice corrosion to occur. This type of attack is usually associated with small volumes of stagnant solution.

Causes:

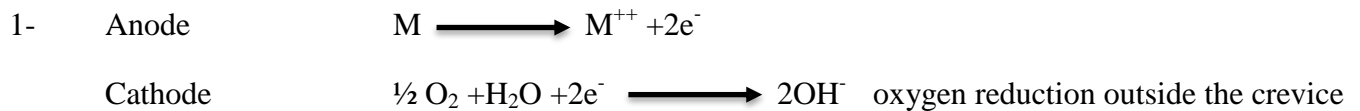
1. Presence of narrow spaces between metal-to-metal or non-metal to metal components.
2. Presence of cracks, cavities and other defects on metals.
3. Deposition of barnacles, befouling organisms and similar deposits.
4. Deposition of dirt, mud or other deposits on a metal surface.

Mechanism of Crevice Corrosion:

The phenomenon of crevice corrosion is extremely complex. Most of the mechanism is based on certain type of concentration cells.

- A difference in metal ions exists between the crevice and the outside, a corrosion cell is formed. The area with low metal concentration becomes the anode and the other cathode.
- A high concentration of oxygen on the surface outside the crevice and a low oxygen concentration inside a crevice create a differential aeration cell, which initiates crevice corrosion.

The mechanism is as follow:



2- After some time, the oxygen in the crevice is consumed, but the concentration of oxygen at the cathode remains unchanged, hence the reaction continues unchanged.

3- Within the crevice, the following processes continue to occur.



$Fe \longrightarrow Fe^{2+} + 2e^{-}$ To preserve electro-neutrality, the chloride ions are attracted by Cr^{3+} or Fe^{2+} ions and metallic chlorides are formed:



4- Hydrolysis of these chlorides takes place immediately which results in the production of acid conditions in the pit. Hydrolysis increases the level of acidity in the crevice. The geometry of a crevice

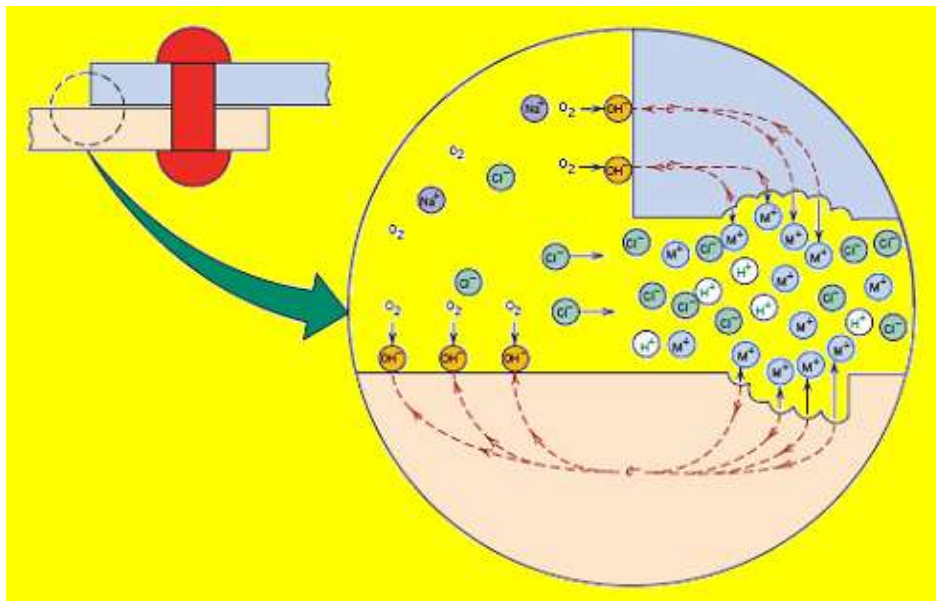
limits the exchange of solution between the structure and the crevice in the bulk, thus creating acid conditions in the pit. The above is generalized by:



In case of 18-8 stainless steel;



It can be observed that acid is produced and hence acid conditions are produced inside the crevice. The pH may attain a value of as low as 1.0 inside the crevice. Once the acid conditions are generated, the process continues until the reaction is terminated. The mechanism described above is self-generative and once it starts, it continues.



The above mechanism is, however purely qualitative and does not provide an explanation of the following:

- 1) Why crevice corrosion take place even in non-aggressive environments?
- 2) What is the critical concentration of chloride ions necessary to induce crevice corrosion?
- 3) The major emphasis is on the formation of a differential aeration cell, whereas other differential cells also may affect crevice corrosion.
- 4) The relationship of time, chloride concentration and passivity is not explained clearly.

Factors affecting crevice corrosion are:

- a) **Crevice Type:** Crevice type means whether the crevice is between metal- to-metal, metal to non-metal or a marine growth, like barnacles or other marine biofouling organisms, on the metal surface. It is important to know whether factors affecting crevice are man-made or natural in order to select appropriate methods for prevention.
- b) **Alloy Composition:** It is important to know whether or not the alloy is resistant to crevice corrosion. Example Hastelloy and Inconel were highly resistant to crevice corrosion in ambient and elevated temperature seawater. The alloying elements in various grade of steel affect both the electrochemical and chemical processes, such as hydrolysis, passive film formation, passive current density and metal dissolution.
- c) **Passive Film characteristics:** The type of passive film formed is important, as the breakdown of a passive film results in the onset of crevice corrosion.
- d) **Geometry of Crevice:** The magnitude of crevice corrosion also depends on the depth of the crevice, width of the gap, number of crevices and ratio of exterior to interior crevice.

And there are other factors such as

- e) **Effect of Temperature,**
- f) **Bulk Solution Composition,**
- g) **Mass Transfer in and out of Crevice, and**
- h) **Oxygen.**

Combating Crevice Corrosion:

Methods and procedures for combating or minimizing crevice corrosion are as follows:

1. Used welded butt joints instead of riveted or bolted joints in new equipment.
2. Close crevices in existing lap joints by continuous welding, caulking, or soldering.
3. Design vessels for complete drainage; avoid sharp corners and stagnant areas.
4. Inspect equipment and remove deposits frequently.
5. Remove solids in suspension early in the process or plant flow sheet, if possible.
6. Remove wet packing materials during long shutdowns.
7. Provide uniform environment, if possible as in the case of backfilling a pipeline trench.
8. Weld instead of rolling in tubes sheets.

Materials and Environment: The conventional steels, like SS304 and SS316, can be subjected to crevice corrosion in chloride containing environments, such as brackish water and sea water. Water chemistry plays a very important role.



4) Pitting Corrosion

It is a form of localized corrosion of a metal surface where small areas corrode preferentially leading to formation of cavities or pits, and bulk of the surface remains unattached. Metals which form passive films, such as aluminum and steel are more susceptible to this form of corrosion. It causes failure by penetration with only a small percent weight-loss of the entire structure.

Environment: Generally the most conducive environment for pitting is the marine environment. Ions such as Cl^- , Br^- and I^- in appreciable concentrations tend to cause pitting of steel. Thiosulfate ions also induce pitting of steels. Aluminum also pits in an same environments of steel. Present of dust or dirt particles in water may lead to pitting corrosion in copper pipes transporting seawater. With soft water pitting in copper occurs in the hottest part of system, whereas with hard waters pitting occurs in the coldest part of the system.

The following are the conditions for pitting to occur:-

The most important condition is that the metal must be in passive state for pitting to occur. Metals which become passive by film formation have a high resistance to uniform corrosion. The process of pitting destroys this protective film at certain sites resulting in the loss of passivity and initiation of pits on metal surface.

- 1) Breaks in the films or other defects .(lack of film homogeneity)
- 2) The presence of halogen ions, such as Cl^- , Br^- , and I^- and even S_2O_3^- .
- 3) Stagnant conditions in service. (Pumps serve in seawater with longer life than kept out of service).

Mechanism

In order for pitting to take place, the formation of anode is a prerequisite. With the formation of an anode, a local corrosion cell is developed. The anode may be formed as a result of:-

- 1) Lack of homogeneity at the metal corrosive interface, which caused by presence of impurities, grain boundaries, niches, rough surface, etc. The difference in the environments can cause formation of concentration cells on the metal surface.
- 2) Destruction of a passive film. Resulting to formation a small anode, results in several anode sites and the surrounding surface acts as cathode. Thus, an unfavorable area ratio results.
- 3) Deposit of debris or solids on the metal surface. This generally leads to the formation of anodic and cathodic sites.
- 4) Formation of an active – passive cell with a large potential difference.
- 5) The formation of small anode on the passive steel surface, leads to the formation of the above cell.

Conditions:-

- (1)The passive metal surrounding the anode is not subject to pitting as it forms the cathode and it is the site for reduction of oxygen.
- (2)The corrosion products which are formed at the anode cannot spread on to the cathode areas. Therefore, corrosion penetrates the metal rather than spread, and pitting is initiated.
- (3)There is a certain potential characteristic of a passive metal, below which pitting cannot initiate. This is called pitting potential (E_p).

Pitting Processes

- 1) The formation of anodic sites by disruption of the protective passive film on the metal surface.



This is balanced by the cathodic reaction of oxygen on the adjacent surface



- 2) Due to the continuing metal dissolution, an excess of positive ions (M^{+}) is accumulated in the anodic area. The process is self-stimulating and self-propagating. To maintain charge neutrality negative ions (anions), like chloride, migrate from electrolyte (for example seawater or a 5% NaCl solution).



(OH⁻) ions also migrate to neutralize the positive charges. This process is called hydrolysis.

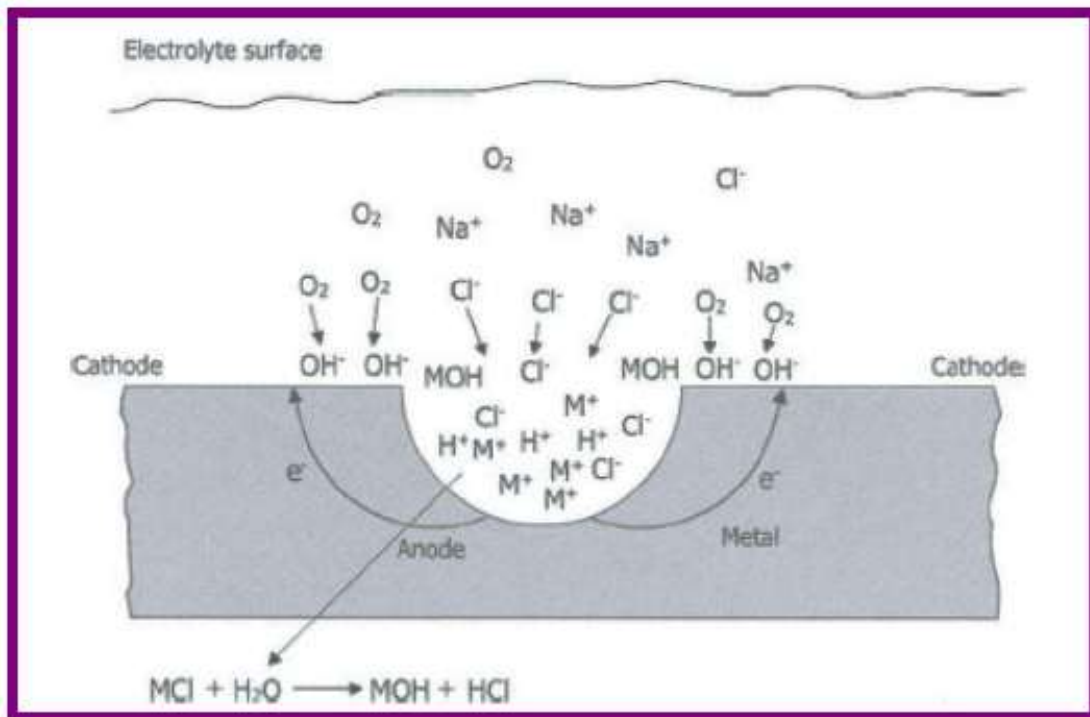
3) The presence of (H^+) ions and chloride content prevents repassivation. The above process generates free acid and the pH value at the bottom of pit is substantially lowered (1.5-1.0).

(4) The increase in the rate of dissolution at the anode increases the rate of migration of the chloride ions and the reaction becomes time dependent and continues, resulting in the formation of more and more M^+Cl^- , generation of more and more H^+Cl^- by hydrolysis.

(5) The process continues until the metal is perforated. The process is autocatalytic and it increases with time resulting in more and more dissolution.

(6) Finally, the metal is perforated and the reaction is terminated. As shown above, basically three processes are involved:

- 1 – Pitting Initiation.
- 2 – Pitting Propagation.
- 3 – Pitting Termination.





Corrosion Pits are the primary source of leaks in water handling systems

Prevention:

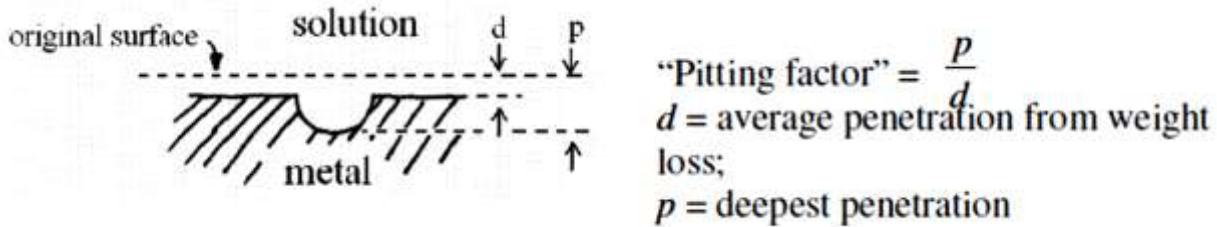
The methods suggested for combating crevice corrosion generally apply also for pitting. Or using inhibitors e.g Chromates $(\text{CrO}_4)^{-2}$, Phosphates $(\text{PO}_4)^{-3}$, Silicates $(\text{SiO}_4)^{-4}$



Pitting is an insidious and destructive form of corrosion:

- ❖ Difficult to detect (pits may be small on surface, but extensive below surface from undercutting; may be covered with deposit).
- ❖ Can cause equipment to fail (by perforation) with very little weight loss.

- ❖ Difficult to measure as pit depth and distribution vary widely under (nominally) identical conditions.
- ❖ “Incubation” period may be months or years.



Some alloys developed especially to resist pitting

Effects of alloying on pitting resistance of stainless steel alloys

<u>Element</u>	<u>Effect on pitting resistance</u>
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with Molybdenum
Titanium and niobium	Decreases resistance in FeCl ₃ , other mediums no effect
Sulfur and selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

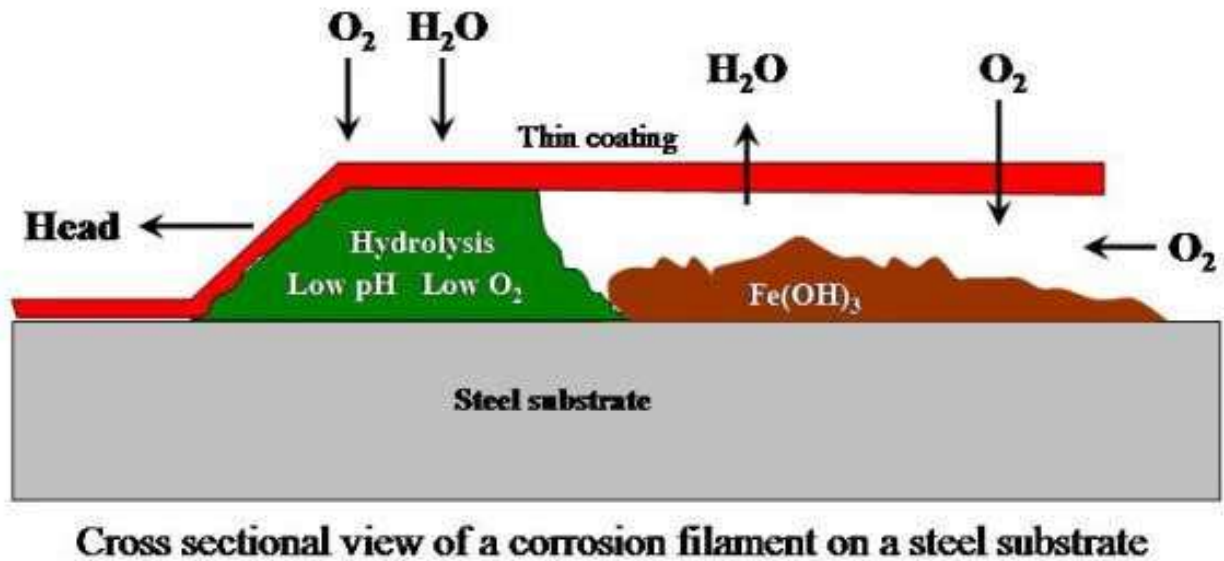
5) Filiform corrosion:

Filiform corrosion is a type of localized corrosion that is often associated with aluminum and magnesium alloys that have an organic coating. This type of corrosion has occurred on other coated metals such as zinc, iron and steel. Filiform corrosion tends to occur at high humidity, e.g. greater than about 75% and temperatures at or slightly above room temperature. The corrosion appears as thread-like filaments under the coating. The corrosion products cause the coating to bulge giving the surface the appearance akin to that of a lawn riddled with mole tunnels. The filaments proceed from points where the coating is no longer continuous. Numerous coating systems are susceptible. Condensates containing halides, sulfates, carbonates, or nitrates have been associated with Filiform corrosion. Damage to the metal tends to be limited but the effect on appearance tends to be detrimental.

Filiform corrosion occurs under surface layers such as paint. It depends on the relative moisture of the air and the quality of the surface treatment preparation prior to coating. Filiform corrosion has the appearance of thin threadlike attacks progressing along the surface beneath a surface layer. The mode of attack is similar to pitting corrosion in that the front of the attack is supported by moisture which penetrates the surface layer and becomes depleted of oxygen making the area anodic. Filiform corrosion

mainly has an aesthetic effect, but the corrosion products formed may cause deformation in narrow crevices or delimitation of surface treatment.

The mechanism of Filiform corrosion is shown in the figure below:-



The mechanism has a number of characteristics that are similar to Crevice corrosion, e.g. differential aeration and hydrolysis of metal ions resulting in increasing acidity in the region of dissolution. This type of corrosion has the following characteristics.

- 1) The coating allows oxygen and water to migrate through it.
- 2) The concentration of dissolved oxygen becomes highest at the back of the head near the region of the tail. This region becomes the cathode.
- 3) Oxygen becomes depleted at the head. This region becomes the anode.
- 4) Corrosion is driven by the potential difference between these regions, a potential difference which can rise to several tenths of a volt.
- 5) Metal ion formation and dissolution proceeds at the head while oxygen is reduced closer to the tail.

Thus, the worm-like or thread-like structure that is formed has two parts that participate in the corrosion process, the front of the head in which metal dissolves and the region behind the head in which oxygen is reduced. Farther back is an inactive region in which metal oxide and metal hydroxide have formed a precipitate. Hydrogen bubbles can be formed if the head becomes very acidic. The propagating head region continues to move under the coating into new areas leaving behind a thin tail of corrosion under the coating. The threads can measure less than 1 millimeter across. Multiple threads or worms can appear under the coating. When two propagating heads meet, the propagation tends to stop. When a propagating

head approaches the inactive tail it tends to be deflected. The corroding alloy can affect the appearance of the filament.

For example, Filiform corrosion of aluminum or magnesium can result in a whitish precipitate forming in the tail. Filiform corrosion of iron can result in a head containing a greenish fluid (Fe(II)) and a tail containing a redish precipitate (Fe(III)).

The occurrence of Filiform corrosion has been reported to be decreased by the following approaches

- Application of more than one layer of a coating.
- Use of a chromate containing conversion coating or primer on aluminum.
- Use of a zinc containing primer on steel.
- Reducing the relative humidity or maintaining a low relative humidity when storing items made of susceptible alloys

According to one recent investigation, a reduction of the Cu content in the aluminum alloy below 0.3% reduces Filiform corrosion substantially. The use of an inhibiting primer or a conversion coating can also be effective. However anodizing used as a pre-treatment seems to be the best solution.

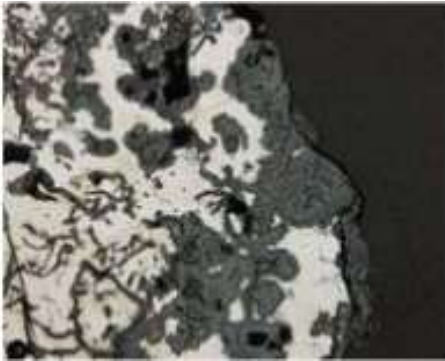


6) SELECTIVE LEACHING

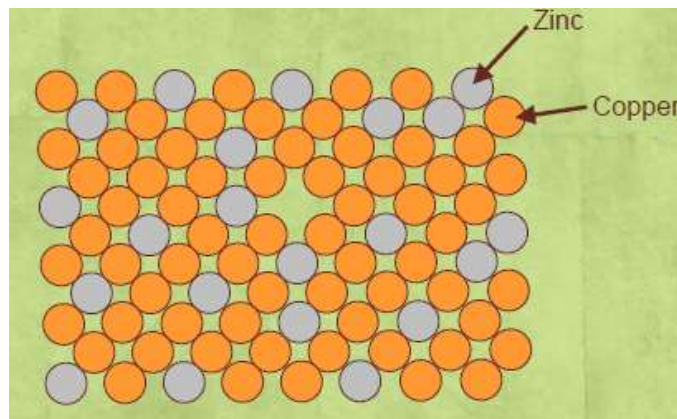
Selective leaching is also called de-alloying, parting, and selective corrosion.

De-alloying or **selective leaching** refers to the selective removal of one element from an alloy by corrosion processes. Corrosion in which one constituent of an alloy is preferentially removed, leaving behind an altered (weakened) residual structure, can occur in several systems.

A common example is the dezincification of brass, whereby a weakened, porous copper structure is produced, without modification of overall part dimensions.



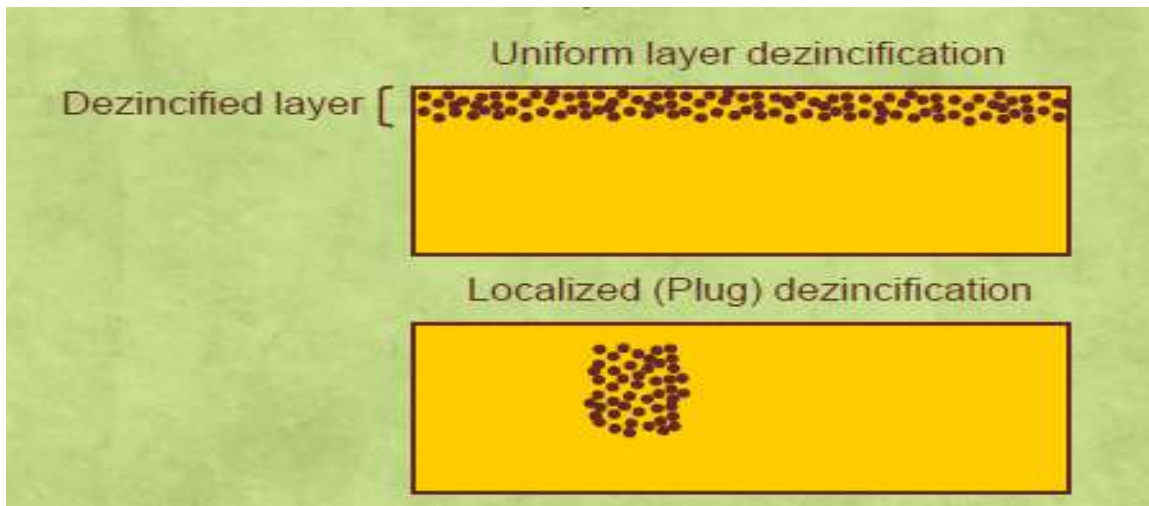
Dezincification: It is a form of corrosion in which zinc is selectively attacked in zinc- containing alloys, like brasses. Dezincification is a form of de-alloying. As the phenomenon was first observed in brass in which zinc separated by dissolution from copper occurs in brass alloys that contain more than 15% zinc.



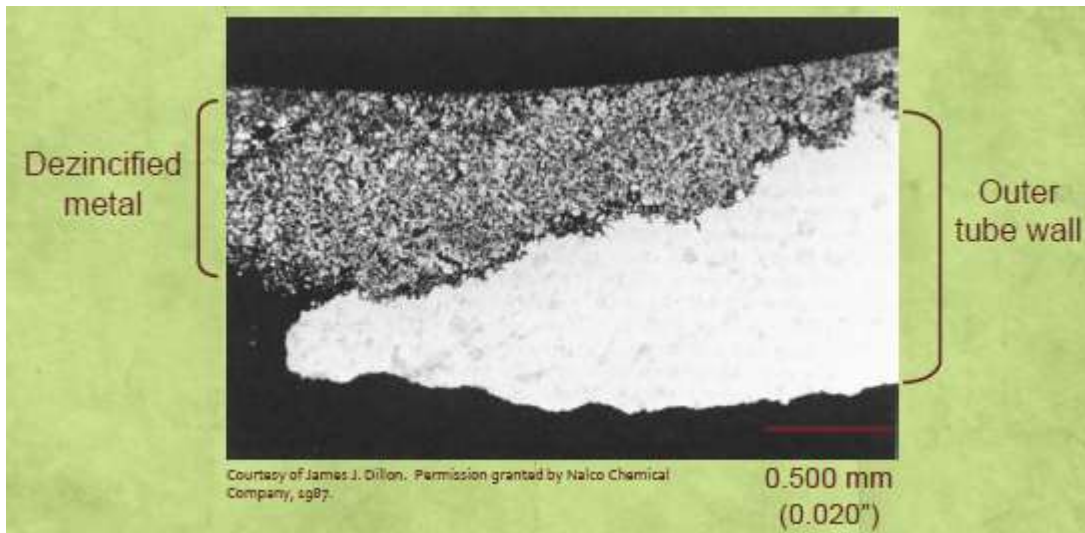
Zinc in solid solution within copper crystal lattice. Zinc atoms dissolve into electrolyte

Dezincification types:

Two forms of dezincification. Overall dimensions of the material do not change. Dezincified areas weakened or in some cases perforated



(1) Uniform type, like the potable water inside. In the uniform the active area is leached out over a broad area of the surface and it is not localized to certain point of the surface. Bulk electrolyte sufficiently corrosive to promote de-alloying.

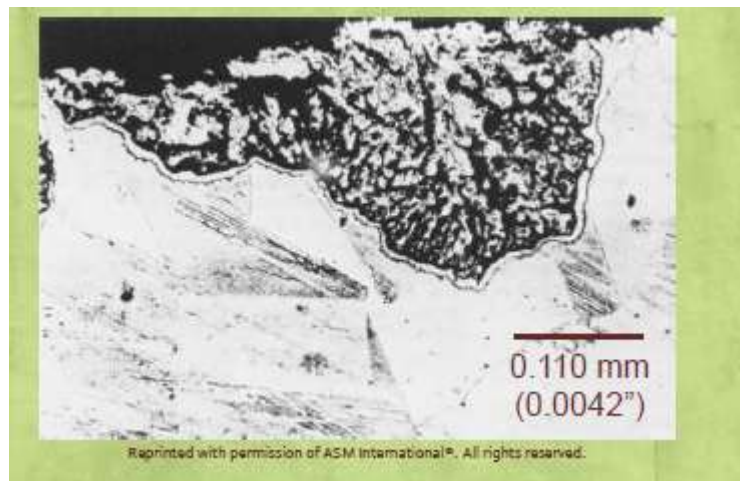


Uniform Layer dezincification in brass heat-exchanger tube.
Usually found in high brasses (high [Zn]), acid environments.

(2) Plug or localized type, like boiler water inside, combustion gases outside. The plug type of attack is localized, at a certain point on the surface and surrounding area remains unaffected. Caused by local increases in electrolyte corrosivity

Changes in electrolyte caused by

- Deposit on surface
- Local increase in temperature



Brass (Cu-30% zinc) exposed to room temperature salt solution for 80 days
 Usually found in low brasses, alkaline, neutral or slightly acid environments.

Mechanism:

Generally three mechanisms are proposed

1. Dissolution and re-deposition mechanism

- ❖ Entire alloy is dissolved first
- ❖ Active metal is leached away (eg. Zn in Brass)
- ❖ More noble metal is replated (eg. Cu in Brass)

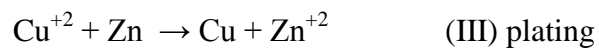
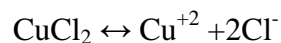
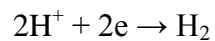
2. Selective dissolution

- ❖ One species is selectively dissolved from alloy leaving a porous residue of more noble metal behind

3. Combination of two methods

The basis of dissolution and re-deposition mechanism.

1) Zn atoms leave lattice sites . . . “are leached into the environment selectively”



Step I Dissolution of Cu and Zn (eq. I & II).

Step II Zinc stays in solution.

Step III Copper plates back (eq. III).

(2) Generally accepted . . .

- brass dissolves;
 - Zn stays in solution;
 - Cu re-deposits.
-
- Zinc is quite reactive to corrosive environment while copper is more noble metal.
 - Zinc can corrode slowly in corrosive environment and leaching of zinc occurs in brass which makes porous structure of copper. This mechanism is called dezincification.
 - The analysis of dezincified area shows 90 to 95% copper with present as copper oxide.
 - When oxygen is present then it also enters into cathodic reaction and increase rate of attack.
 - The material remaining is a copper-rich sponge with poor mechanical properties, and a color changed from yellow to red.
 - Dezincification can be caused by water containing sulfur, carbon dioxide, and oxygen. Stagnant or low velocity waters tend to promote dezincification.

Prevention:-

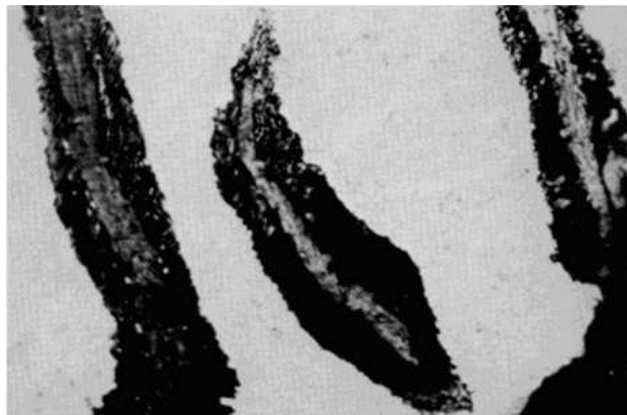
- ❖ Reducing the aggressiveness of the environment (i.e. Oxygen removal)
- ❖ Use less susceptible material:
 - 15% Zn (red brass)
 - Addition of 1%Sn in 70-30 brass which improve resistance towards dezincification.
 - Addition of As, Sb, P as ‘inhibitor’ (70%Cu, 29% Zn, 1% Sn, 0.04% As)
 - Cupronickel (70-90%Cu, 30-10%Ni) is used in severely corrosive environments.



Graphitization: is a form of material degradation occurring when the microstructure of some carbon and low alloy steels breaks down after long exposure to elevated temperatures (825 - 1300 F), causing the metal to weaken and be susceptible to cracking failures.

One common mistake in the books is to use the term graphitization rather than graphitic corrosion. Graphitization occurs when low alloy steel is subjected to high temperature for an extended time period. Graphitization results from the decomposition of pearlite into ferrite and carbon, whereas in graphitic corrosion the gray cast iron is selectively attacked. The presence of graphite is necessary for leaching to take place.

Gray cast iron sometimes shows the effect of selective leaching out of iron in mild corrosive environments. The surface layer of the iron becomes like graphite and it can be easily cut with a knife. Because of the attack, the iron or steel matrix is dissolved and an interlocking nobler graphite network is left. The graphite becomes cathodic to iron and a galvanic corrosion cell is formed. Iron is dissolved and a porous mass of voids and complex iron oxides is left behind. This graphitized cast iron loses its strength and other metallic properties, but to a casual view it looks dirty but unchanged in shape, which can lead to dangerous situations.



Micrograph of symmetrical envelopes of graphitically-corroded iron surrounding flakes of graphite.

Selective leaching of material depend on,

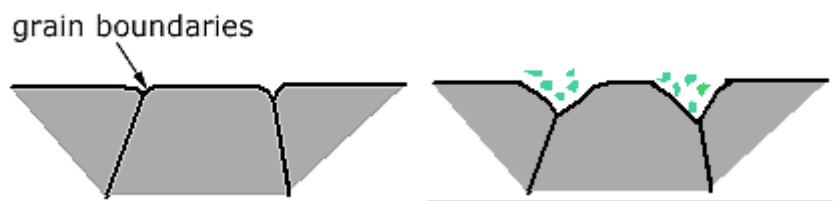
- a. Alloy composition
- b. Environment

Alloys subjected to leaching

Alloy Composition	Environment	Element removed
Brasses	Many waters, especially under stagnant conditions	Zinc (De-zincification)
Gray iron	Soils, many waters	Fe (graphite corrosion)
Aluminum bronzes	Hydrofluoric acid, acids containing chloride ions	Aluminum (De-aluminification)
Silicon bronzes	High-temperature steam and acidic species	Silicon
Tin bronzes	Hot brines or steam	Sn (De-stannification)
Copper-nickels	High heat flux and low water velocity (in refinery condenser tubes)	Ni (De-nickelification)
Copper-gold single crystals	Ferric chloride	Cu
Monels	Hydrofluoric and other acids	Cu in some acids, and Ni in others
Gold alloys with copper or silver	Sulfide solutions, human saliva	Copper, silver
High-nickel alloys	Molten salts	Cu, Ag, Cr, Fe, Mo and T
Medium and high-carbon steels	Oxidizing atmosphere, hydrogen at high temperatures	C (De-carburization)
Iron-chromium alloys	High-temperature oxidizing atmospheres	Cr, which forms a protective film
Nickel-molybdenum alloys	Oxygen at high temperature	Mo

7) Intergranular Corrosion

Intergranular corrosion (IGC), also known as **intergranular attack (IGA)**, is a form of corrosion where the boundaries of crystallites of the material are more susceptible to corrosion than their insides. This situation can happen in otherwise corrosion-resistant alloys, when the grain boundaries are depleted, known as **grain boundary depletion**, of the corrosion-inhibiting elements such as chromium by some mechanism.



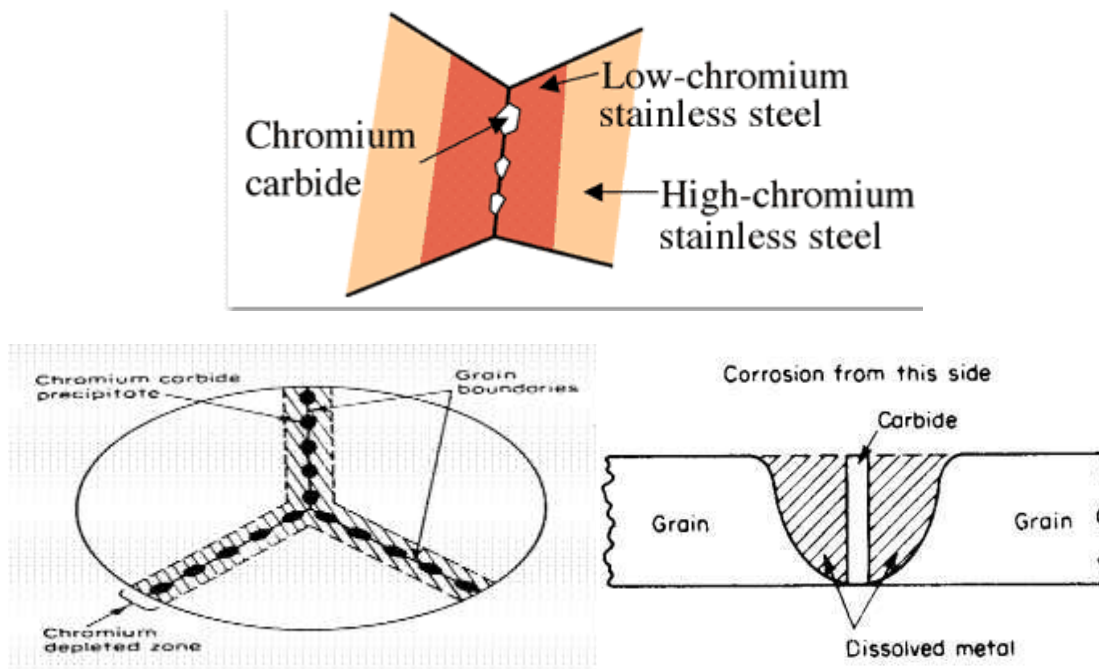
Causes of Intergranular Corrosion: Intergranular corrosion of an alloy may be caused by

- Impurities at the grain boundaries
- Enrichment of one of the alloying elements
- Depletion of one of the elements that affects its corrosion resistance in grain boundary areas.

The potential difference between the grain boundary regions and any precipitate, intermetallic phases, or impurities that form at the grain boundaries is responsible for higher dissolution rates at these regions.

Mechanism: The actual mechanism differs from one alloy system to another. Grain boundary precipitation, notably chromium carbides in stainless steels, is a well-recognized and accepted mechanism of intergranular corrosion.

This type of corrosion is a particular problem in stainless steels; however it can also occur in other metals. In stainless steels the problem occurs after the metal is heated to between 425°C and 870°C. During the heating, the chromium in the stainless steel reacts with carbon in the steel and forms particles of chromium carbide at the grain boundaries. The regions near the grain boundaries become depleted in chromium. This means that the regions around the grain boundaries are no longer protected by the chromium passivation, and therefore corrode intergranularly.



If the alloy is cut into a thin sheet and cross section of grain boundary area made, the corroded area would observe as a deep narrow trench when observe at low magnification.

Sensitization is the loss of alloy integrity. It results from chromium depletion in the vicinity of carbides precipitated at grain boundaries. This causes the steel or alloy to become susceptible to intergranular corrosion.

Sensitization requires specific combinations of:

- Temperature
- Time
- Composition

Sensitization happens when a stainless steel is held at a temperature of 425 - 815°C and chromium carbides precipitate at the grain boundaries. This precipitation happens because the carbides are insoluble at these temperatures. In order for the carbide to precipitate, it must obtain chromium from the surrounding metal. This means that there is a chromium-depleted zone around the grain boundaries.

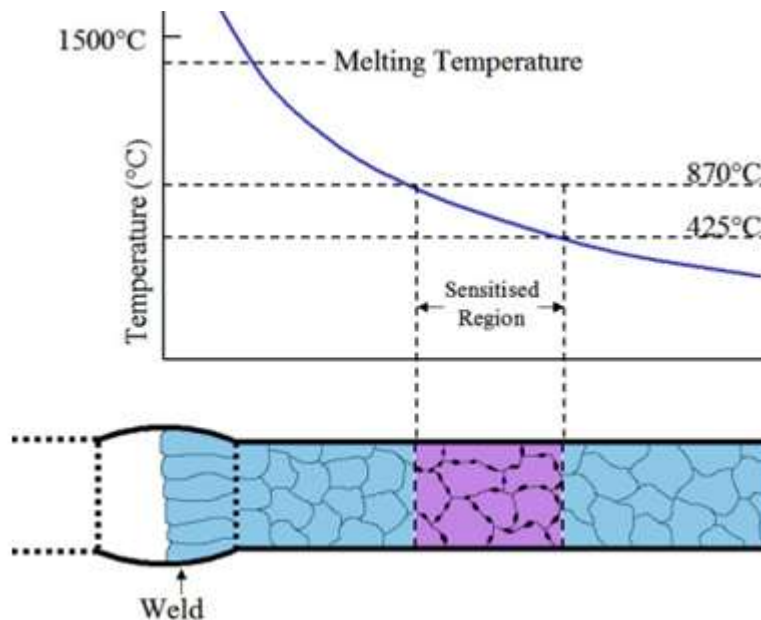
Sensitization can occur during welding or annealing after cold working. It can also occur in ferritic and duplex stainless steels, though the thermal profile that results in the formation of precipitates is different than for austenitic stainless steels.

Sensitization is particularly important in welded metals. This is because the welding zone experiences temperatures in the range that can cause sensitization, which causes localized intergranular corrosion at the weld site. If a sensitized alloy is exposed to a corrosive environment, the areas near the grain boundaries are preferentially attacked. As the corrosion proceeds, the grains fall out and the metal loses strength.

Sensitization can be prevented by:

- Reducing the carbon content
- Adding stabilizers such as niobium or titanium
- Reducing the time of exposure to the critical temperature range

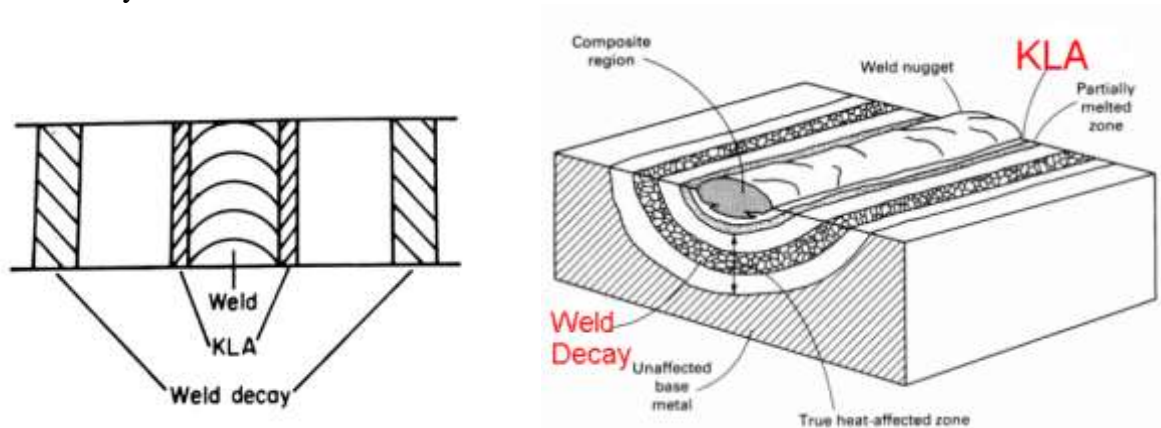
Non-sensitized austenitic stainless steels are resistant to intergranular attack in almost all environments.



Types of Intergranular Corrosion

There are two types of Intergranular corrosion:

- Knife line attack
- Weld Decay



Knife Line Attack: is a form of intergranular corrosion of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.

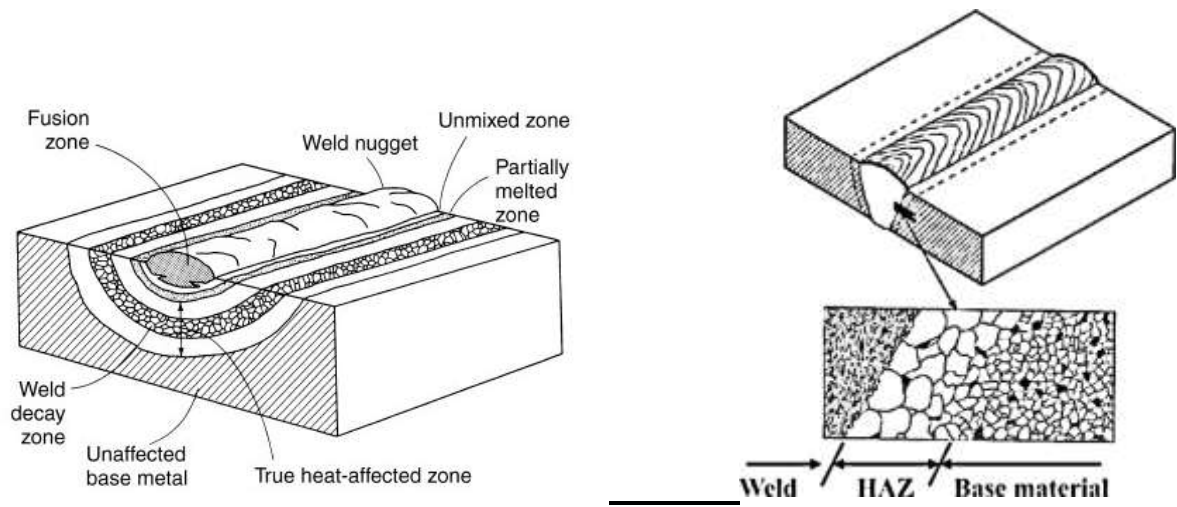
KLA is caused when, in stabilized alloys and steels, the carbon comes in contact with stabilizers such as niobium and titanium. In such, there will be no weld corrosion in the zones affected by heat during the welding process. However, when chromium carbide precipitates during subsequent welding or heat treatment, there is a possibility that the narrow band close to the fusion line undergoes a knifeline attack.

A good example of a knifeline attack is one involving steels that are stabilized by niobium, like stainless steel 347. Niobium and titanium, along with their associated carbides, can dissolve the steel at extremely high temperatures. With certain cooling systems, niobium does not undergo precipitation, so the steel acts like unstabilized steel, building chromium carbide as an alternative. This affects a very thin zone in the surrounding weld, making it difficult to notice the speed of corrosion. Materials that are made from steel should undergo heating at around 1950°F as the niobium carbide develops and the chromium carbide disbands. The cooling process after this treatment is not essential, since the carbon which is supposed to turn into chromium carbide is seized as niobium carbide.

Weld Decay: Weld decay is a corrosion process that mainly occurs as a result of sensitization (regions susceptible to corrosion) in the heat affected Zones (HAZ) of metal during welding operations. This process mostly occurs in stainless steels or certain nickel-based alloys. It is a form of intergranular corrosion.

During the welding process in nickel alloys and austenitic stainless steels, where chromium is added for corrosion resistance, local sensitized zones often develop. Sensitization is due to the formation of chromium carbide along grain boundaries, resulting in depletion of chromium in the region adjacent to the grain boundary. This chromium depletion produces localized galvanic cells. If this depletion drops the chromium content below the necessary 12 wt% that is required to maintain a protective passive film, the region will become sensitized to corrosion, resulting in intergranular attack.

This condition occurs when the material is heated to temperatures around 700°C (1290°F) for too long, and often happens during welding or an improper heat treatment. When such localized galvanic cells form due to welding, the resulting corrosion is known as weld decay.



Prevention of Knife line attack

- Heat treatment - heating the weld to 1065°C to re-stabilize the material.

Prevention of Weld Decay

- Using low carbon grade stainless steels alloyed with stabilized grades of titanium or niobium, which are strong carbide formers. They react with the carbon to form the corresponding carbides, thereby preventing chromium depletion.
- Use low carbon content grade stainless steel, e.g: 316L, 304L ~ 0.03 wt.%, so carbide formation is minimal.
- Heat treatment to re dissolve the carbides (post welding heat treatment)
- Weak corrosive conditions do not cause IGC
- Low acidity (high pH) will generally reduce the susceptibility to IGC

Difference in Weld Decay and Knife line attack

Knife line attack	Weld Decay
Knife line attack occurs in narrow band in the parent metal immediately adjacent to the weld.	Weld decay develops at the appreciable distance from the weld.
Knife line attack occurs in stabilized steel.	Weld decay occurs in non-stabilized steels.

Melting point, °F		°C
2250	Cr + Nb carbides dissolve	1230
1450	Cr carbide dissolves Nb carbide precipitates	790
950	Cr carbide precipitates	510
70	No reactions	20

Schematic chart showing solution and precipitation reactions in types 304 and 347 SS.

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Examples

- Intermetallic compound such as Mg₅Al₈, formation at the grain boundaries form a galvanic cell with an alloy matrix and in chloride environment severe intergranular type of corrosion occur.
- Intergranular corrosion can occur in many alloys systems such as stainless steel, nickel base and aluminum base alloys.

8) 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.

Erosion is the straightforward wearing away by the mechanical abrasion caused by suspended particles. e.g., sand-blasting, erosion of turbine blades by droplets

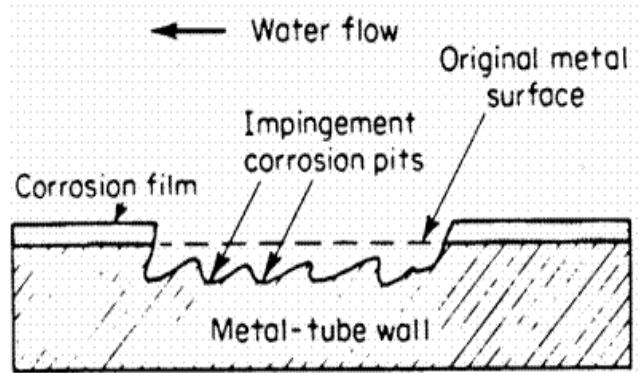
Erosion-corrosion also involves a corrosive environment the metal undergoes a chemical reaction.

Examples

- Many metals & alloys susceptible to erosion corrosion e.g. aluminum, lead, stainless steels, carbon steels
- All types of equipment exposed to fluid are susceptible to this type of corrosion such e.g. piping systems, elbows, tees, valves, pumps, blowers.
- Also centrifuges, propellers, impellers, agitators, heat exchangers tubing
- Measuring devices like orifices, turbine blades, ducts & all those equipment which are some way or the other exposed to fluids.

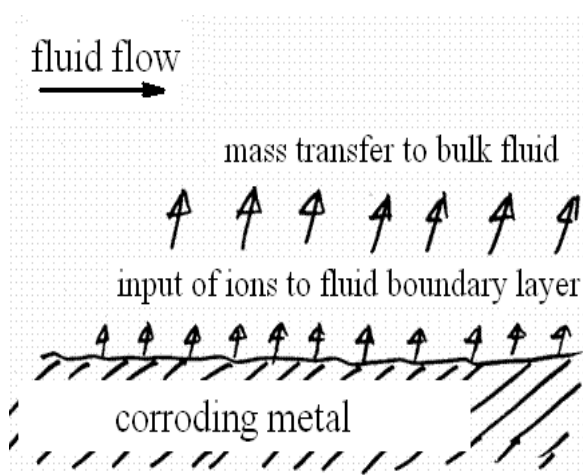
Appearance

- It appears in the form of grooves, gullies, waves, rounded holes & valleys. They typically show a directional pattern. This is figure showing erosion corrosion of condenser tube wall by water flow.



Erosion-corrosion of condenser tube wall

- Vulnerable equipment is that subjected to high-velocity fluid, to rapid change in direction of fluid, to excessive turbulence. viz equipment in which the contacting fluid has a very thin boundary layer
 - ❖ High mass transfer rates.



Vulnerable equipment includes:

Pipes (bends, elbows, tees)
Valves
Pumps
Blowers
Propellers, impellers
Stirrers
Stirrer vessel
HX tubing (heaters, condensers)

Flow-measuring orifices, ventureries
Turbine blades
Nozzles
Baffles
Metal-working equipment (scraper, cutters, grinders, mills)
Spray impingement components
etc.

Corrosive Medias

Many types of corrosive media could cause erosion corrosion. Gases, aqueous solutions, organic systems & liquid metals are some common corrosive medias that causes this type of corrosion.

Surface Films:

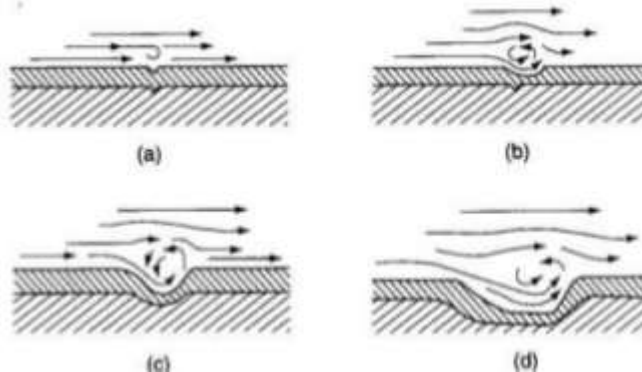
These are specially developed layers on the surface of metals which can protect the metal from metals. Such films develop due to the action of different environment on metals e.g. Al_2O_3 film developed on Al metal protect it from corrosion. There are two types of such films:

- ◆ Relatively thick porous diffusion barriers, formed on carbon steel (red rust) & copper (cuprous oxide). Diffusion barrier is formed by ionic dissolution followed by precipitation. It is more easily damaged & can be corroded.
- ◆ The thin invisible passive film on SS, Ni & Ti etc. Passive films are formed by direct oxidation & can withstand much more sever conditions.

Mechanism

Exact mechanism of erosion corrosion is less understood but it is believed it occurs due to:

- ❖ **Turbulent flow:** Turbulent flow is one of the major causes behind the occurrence of erosion corrosion. It causes agitation of the liquid at the metal surface. It results in more contact between metal & environment i.e. fluid. It is mostly confined to few inches at tubing inlet.



- ❖ **Impact of suspended solid particles:** Solid particles entrained in liquid flow damage both types of surface films explained above. Such particles can erode the metal as well & contribute to metal loss. This happens due to high impact of solid particles on the object through which fluid is passing.
- ❖ **Liquid droplets in gas flow:** Liquid droplet can cause erosion corrosion due to exposure of solid to repeated impact by droplets. It generates impulsive & destructive contact pressure. It is a problem with low pressure turbines & also rain erosion of aircrafts.
- ❖ **Impact of gas bubbles in aqueous flow:** Erosion corrosion of copper alloy heat exchanger is due to local damage of film by air bubbles. Nitrogen bubbles can also do the same damage.

Factors affecting on Erosion Corrosion:

1. Effect of flow velocity

Flow velocity plays an important role in erosion corrosion. Corrosion rate of steel may be high at high velocity as it may provide O₂, CO₂, H₂S in contact with metal surface. It may decrease corrosion rate & improve effectiveness of inhibitors by providing chemicals to the metal surface at higher rate e.g. less Sodium Nitrate is required to protect steel from tap water at high velocity. Suspended solid will damage the surface protection at high velocity.

2. Galvanic Effect

Two metal effect or galvanic effect influence corrosion if metals are dissimilar. This effect is nil if metals are in contact but in static conditions. But this effect is pronounced under moving conditions

3. Nature of metal & Alloy

Chemical composition, corrosion resistance & hardness can affect this type of corrosion. Composition tells us metal's corrosion resistance. Soft metals can easily be eroded by the action of fluid or other reagents favoring erosion corrosion. Hardness is best criteria to control the wear.

Prevention of Erosion-Corrosion

Methods are used to prevent erosion corrosion.

1. Design

- Design involves change the shape, geometry of part.
- Design of inlets & outlets should be streamlined to prevent turbulence.
- It also involves redesigning the flow of the fluid to ensure there is less turbulence.

2. Alteration of Environment

- Settling & filtration to remove solid particles.
- Temperature of environment should be reduced.

3. Coatings

- Coatings are utilized but they are not much effective.
- Welded overlays & hard facing are applied at times.
- Repair of attacked areas is done by welding.

4. Cathodic Protection

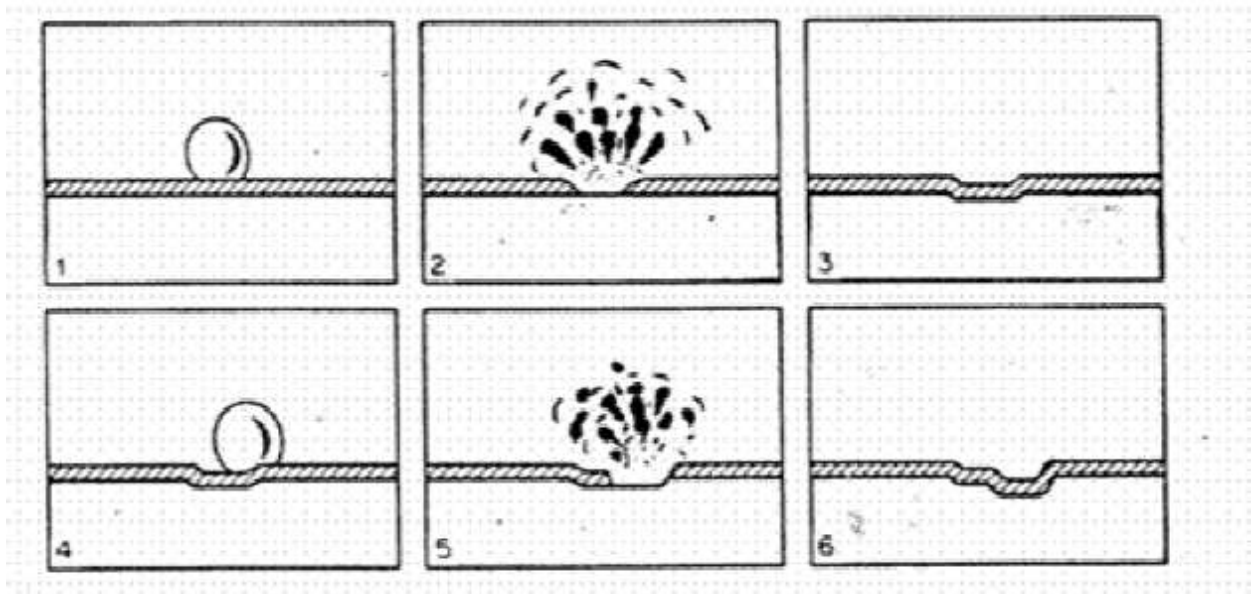
- Helps to reduce attack.
- Not much used in erosion corrosion.
- Steel plates are used on condenser head for cathodic protection.
- Zinc plugs are used for water pumps.

5. Better material

- Use that material which is more corrosion resistant than the previous one.
- It is an economical solution of erosion corrosion.

CAVITATION DAMAGE

It is the degradation of a solid body caused by cavitation. The damage appears in the form of loss of material, change in appearance, surface deformation or changes in properties. It takes place when the velocity becomes so high that its static pressure is lower than the vapor pressure of liquid. Similar effect to erosion corrosion mechanical removal of oxide film caused by collapsing vapor bubbles.



Cavitating propeller model in a water tunnel experiment.



Cavitation damage on a valve plate for an axial piston hydraulic pump.

High-speed pressure oscillations (pumps, etc.) can create shock waves $> 60,000$ psi. Surface attack often resembles closely-spaced pitting.

The most effective strategy for preventing cavitation damage is a holistic one:

1. Optimize System Design. Use CFD and proper engineering to maximize $NPSH_a$ and minimize $NPSH_r$. This is the most cost-effective long-term solution.
2. Select Resistant Materials. For components known to be at risk (e.g., impeller tips, valve trim), specify materials with high cavitation erosion resistance from the outset.

3. Apply Advanced Coatings. Use modern surface engineering techniques like laser cladding to protect critical components, especially in refurbishment.
4. Operational: Monitor and Adjust. Implement condition monitoring to detect incipient cavitation and adjust operating parameters (speed, temperature) to extend component life.

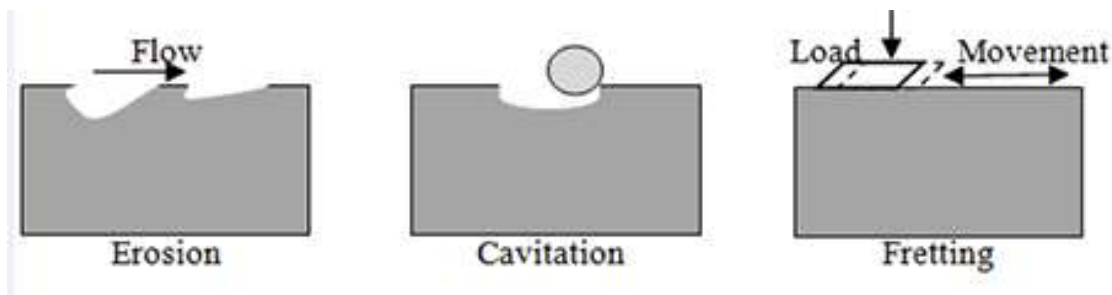
FRETTING CORROSION

Fretting corrosion refers to the deterioration at the interface between contacting surfaces as the result of corrosion and slight oscillatory slip between the two surfaces. Similar to Erosion corrosion but surface mechanical action provided by wear of another surface generally alternating

Example in which fretting corrosion occurs in bolted parts, engine components and other machineries.

Prevention of Fretting Corrosion

- Lubrication with oils or greases, to reduce friction and exclude oxygen from the interface.
- Increase in the hardness of one or both materials in contact.
- Increase relative motion to reduce attack severity.



9) Stress Corrosion Cracking (SCC):

In this type of corrosion loss due to corrosion effects is negligible, but the metal gets cracked after some time. It is a localized action caused by the presence of corrosion medium and the tensile stress conditions. The greater the stress on the material, the quicker it will crack.

Examples: The most common examples of SCC are:-

- Season cracking of brass
- Caustic embrittlements of CS
- Chloride

Season Cracking

Occurs where brass case is crimped onto bullet, i.e., in area of high residual stress. Common in warm, wet environments (e.g., tropics) Ammonia (from decomposition of organic matter, etc.) must be present.

Caustic Embrittlements

Early steam boilers (19th and early 20th century) of riveted carbon steel. Both stationary and locomotive engines often exploded.

Examination showed:

- Cracks or brittle failures around rivet holes.
- Areas susceptible were cold worked by riveting (i.e., had high residual stresses).
- Whitish deposits in cracked regions were mostly caustic (i.e., sodium hydroxide from chemical treatment of boiler water).
- Small leaks at rivets would concentrate NaOH and even dry out to solid. SCC revealed by dye penetrates.

Factors important in SCC:

- ☼ Environmental composition.
- ☼ Stress.
- ☼ Metal composition and microstructure.
- ☼ Temperature.

e.g., brasses crack in NH_3 , not in Cl^- ;
SSs crack in Cl^- , not in NH_3 ;
SSs crack in caustic, not in H_2SO_4 , HNO_3 , CH_3COOH , etc.

Prevention of SCC

- ❖ Choosing a material that is not susceptible to SCC in the service environment
- ❖ Residual stresses can be relieved by stress-relief annealing
- ❖ Similarly shot-peening or grit-blasting tend to introduce a surface compressive stress.
- ❖ Neutralizing the environment whenever possible, e.g. reducing chloride ion concentration.

10) Corrosion Fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion.

Where damage occurs:

- Water touched components especially the economizer
- Steam touched tubing containing condensate during operation transients
- Welded connection, bends and attachments with high thermally induced force and bending movements.



Locations

- Tube to header welds
- Scallop bar attachments
- U bend to drain line weld
- Riser and down comer tube

Corrosion Fatigue of Welded Joints



Corrosion Fatigue in Boiler Tubes

The Prevention of Corrosion Fatigue: As with most problems, there are always possible solutions. To prevent corrosion fatigue, what you need is through a reduction of different things, which include:

- Reduction of corrosion through the use of inhibitors and coatings to stall time before corrosion fatigue cracking starts
- Reduction of fatigue by controlling and bringing down the pressure and vibration fluctuations
- Reduction of corrosion through the use of high performance alloys which are resistant to corrosion fatigue

Stress Corrosion and Corrosion Fatigue are Not the Same Thing

Stress corrosion is crack initiation and crack development due to a residual stress. This is different from corrosion fatigue and both entities should not be confused with one another. While corrosion fatigue features transgranular cracks, stress corrosion usually features intergranular cracks. In addition, corrosion fatigue can be prone to most materials (especially high strength alloys); stress corrosion is rarely seen in technical materials.

11) Hydrogen Damage

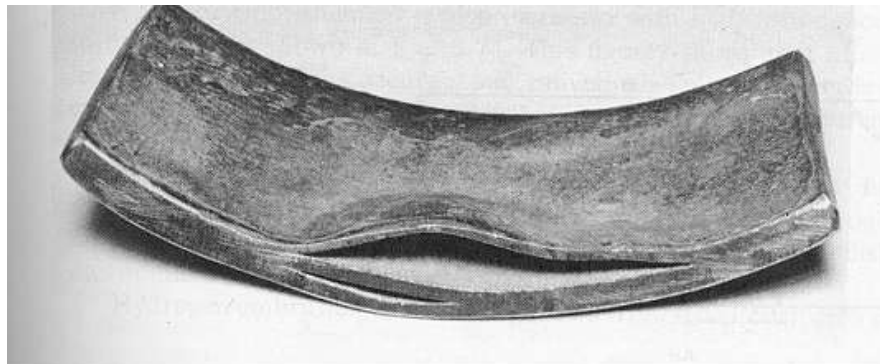
It is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen.

Hydrogen damage may be classified into four distinct types:-

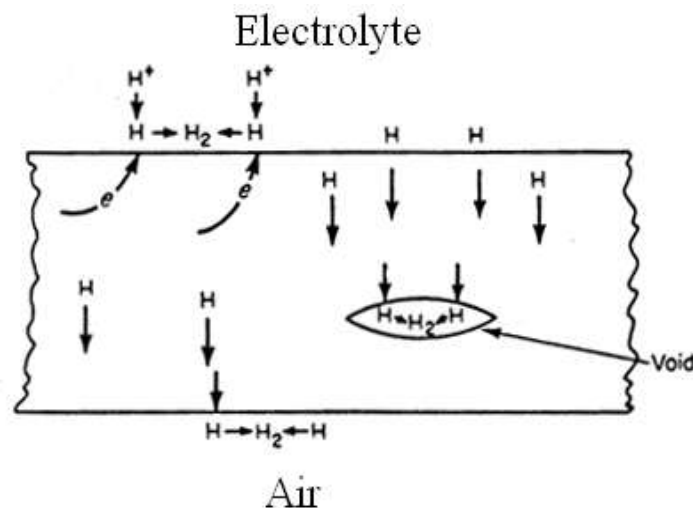
1) Hydrogen blistering.

Hydrogen enters the lattice of a metal, diffuses to voids, creates high internal stresses → blisters. Blistering may occur during exposure to:

- ❖ hydrocarbons;
- ❖ electroplating solutions;
- ❖ chemical process streams;
- ❖ pickling solutions;
- ❖ H-containing contaminants during welding;
- ❖ General corrosive environments.



Cross section of a carbon steel plate removed from a petroleum process stream showing a large hydrogen blister. Exposure time: 2 years.



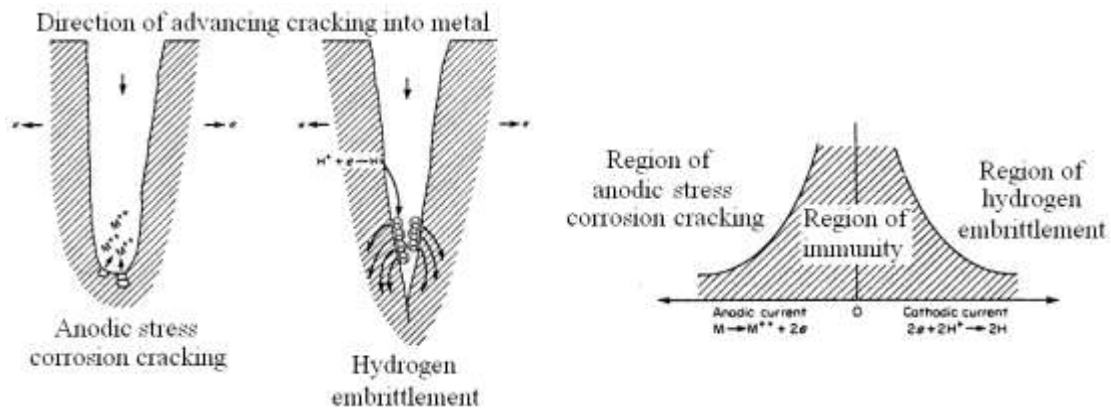
Schematic illustration showing the mechanism of hydrogen blistering.

Prevention of Blistering

- use steels with few or no voids; (Killed steel instead of rimmed)
- Use coatings; (Metallic, inorganic and organic coatings, cladding, rubber and plastic coating and brick linings).
- use inhibitors
- Remove poisons; (impurities that can promote hydrogen evolution . S^{2-} (particularly bad), As compounds , CN^- , etc.
- Use different materials (Ni-base alloys have low diffusion rates for hydrogen).

2) Hydrogen Embrittlements

Similar to blistering hydrogen enters metal lattice but interaction with metal lattice different. High-strength (and more brittle) steels are susceptible. H-embrittlements different from SCC in nature of cracks. stress-corrosion cracks usually propagate anodically

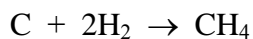


Prevention of Embrittlement

- Reduce corrosion rate (inhibitors, coatings, etc.).
- Change electroplating process to minimize H effects (voltage, current density, bath composition, etc.).
- Bake material to remove H; (200- 300 °F).
- Minimize residual stresses ;(annealing).
- Use less susceptible material ;(Alloying with Ni or Mb).
- Maintain clean conditions during welding. (Dry condition).

3) Decarburization and Hydrogen Attack

High temperature process - C or carbide in steels can react with gaseous hydrogen

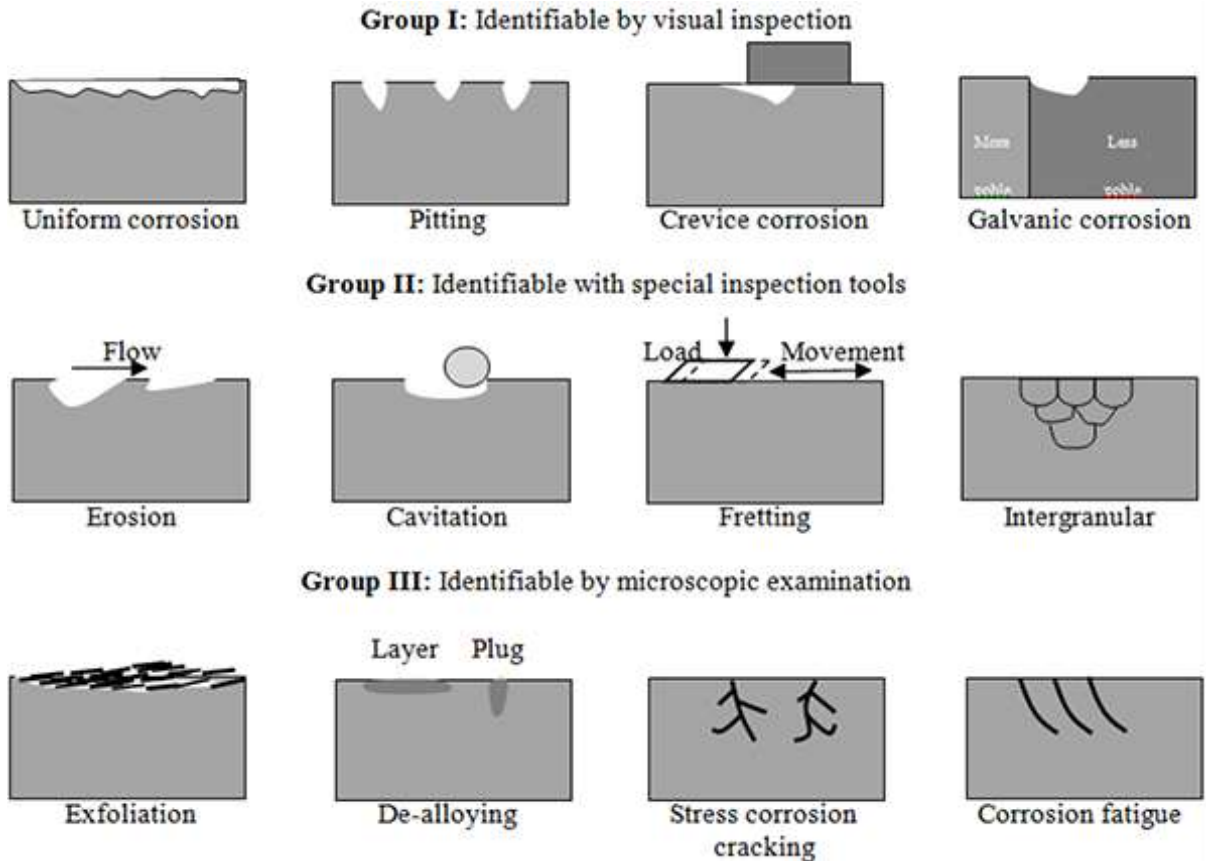


Note that the reaction can occur with atomic H in the metal lattice.



May crack the steel from high internal pressure.

May cause loss of strength as C disappears.



Modern Theory Principles

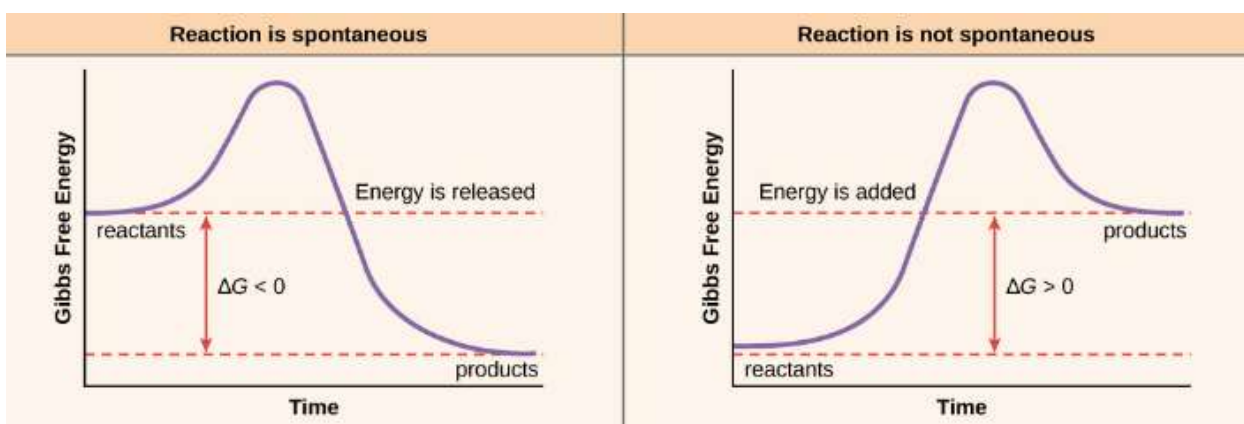
Modern Theory principles in Corrosion and their applications:-

Corrosion studies can be carried-out by two methods

- 1 – Thermodynamics or
- 2 – By electrode Kinetics

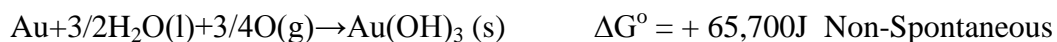
Thermodynamics give the change in energy state, also predicts the directions of a reactions. For spontaneous reactions, the systems must decrease their Free-energy and move to a lower energy state, e.g. Corrosion is a spontaneous reaction. For non-spontaneous reactions energy must be added to the system in order to facilitate the reaction.





By thermodynamic rate of reaction cannot be predicted.

Free Energy: Driving Force of a Chemical Reaction



Change in free-energy under equilibrium conditions is given as:

$$\Delta G = -nFE$$

ΔG : is Gibbs free energy in Joules

n : is the number of electrons involved in the reaction

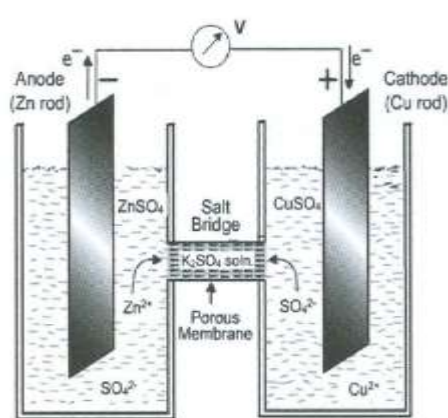
F : is the Faraday (96500 C/equivalent)

E : is emf in volts

For the Zn/ ZnSO₄ half cell and Cu/CuSO₄ half cell, Zn⁺² & Cu⁺² are in unit activity. A unit activity, Means 1gram atom of element salt (Zn salt; Cu salt) / 1 liter of Aqueous solution (electrolyte). As long as the Zn and Cu electrodes are not connected (short-circuited). There is no flow of current, but theoretically electrochemical reactions are occurs at individual electrodes, e.g.



If the Oxidant and Reducing species are at unit activity, then cell potential is calculated by Nernst equation.



$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{a_p}{a_R}$$

The change in free energy gives an idea of content of energy displacement .But it does not give the velocity or the rate of electro-chemical reaction. The other limitation equilibrium states, which are difficult to establish in corrosion reactions.

Free energy calculation has been used to determine:-

- 1 – Spontaneous direction of a reaction.
- 2 – Estimating the composition of corrosion products.
- 3 – Predicting the environment changes that will reduce the corrosion rate.

2 & 3 could be explained by the potential vs. pH diagram of a metal (also called pourbaix diagrams). e.g. iron in water. Redox potential or emf. series is a thermodynamic function – redox has been utilized to predict the corrosivity of metals in various environments. e.g. metals (-ve) to hydrogen electrode would corrode in acids but metals (+ve) to hydrogen electrode would not corrode in the absence of oxygen.

(-ve) such as (Fe or Zn) + Acid → Corrosion

(+ve) such as (Cu or Ag) + Acid → no corrosion

(Cu or Ag) + Acid + O₂ → Corrosion would happen in this case.

Cu + H₂SO₄ → No corrosion (Cu/Cu⁺² more than H₂/ H⁺)

Cu + H₂SO₄ + O₂ → 2CuSO₄ + 2H₂O (O₂/ H₂O more + than Cu/Cu⁺²)

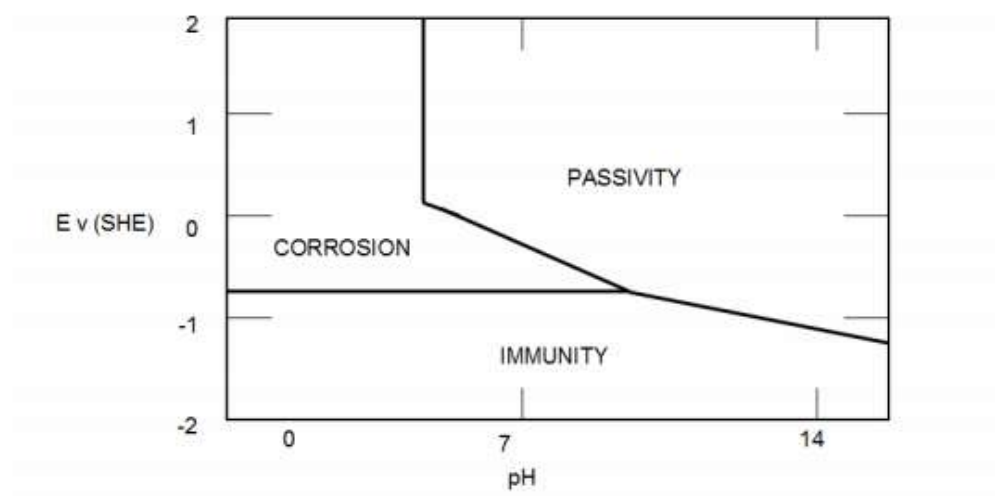
The corrosion rate of a metal decrease in presence of Oxygen in acids, with the increase in electro-positive character of a metal (e.g. Pt , Pb ,etc) are un-affected by containing O₂ .

Pourbaix Diagram:-

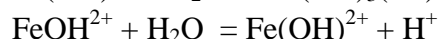
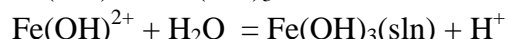
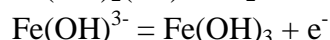
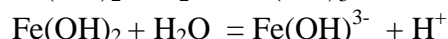
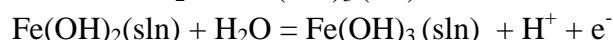
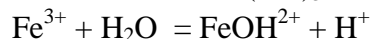
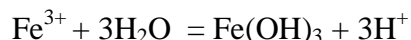
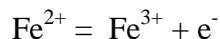
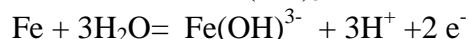
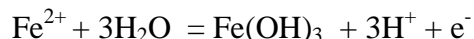
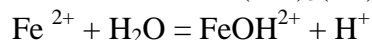
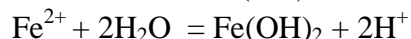
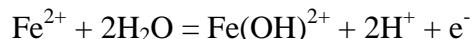
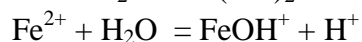
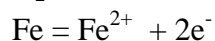
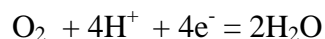
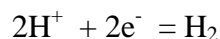
A Pourbaix diagram is a kind of phase diagram that shows the stability boundaries for a metal-aqueous interaction system. The phase boundaries are shown as a function of pH (acidity) and E (standard hydrogen electronic potential).

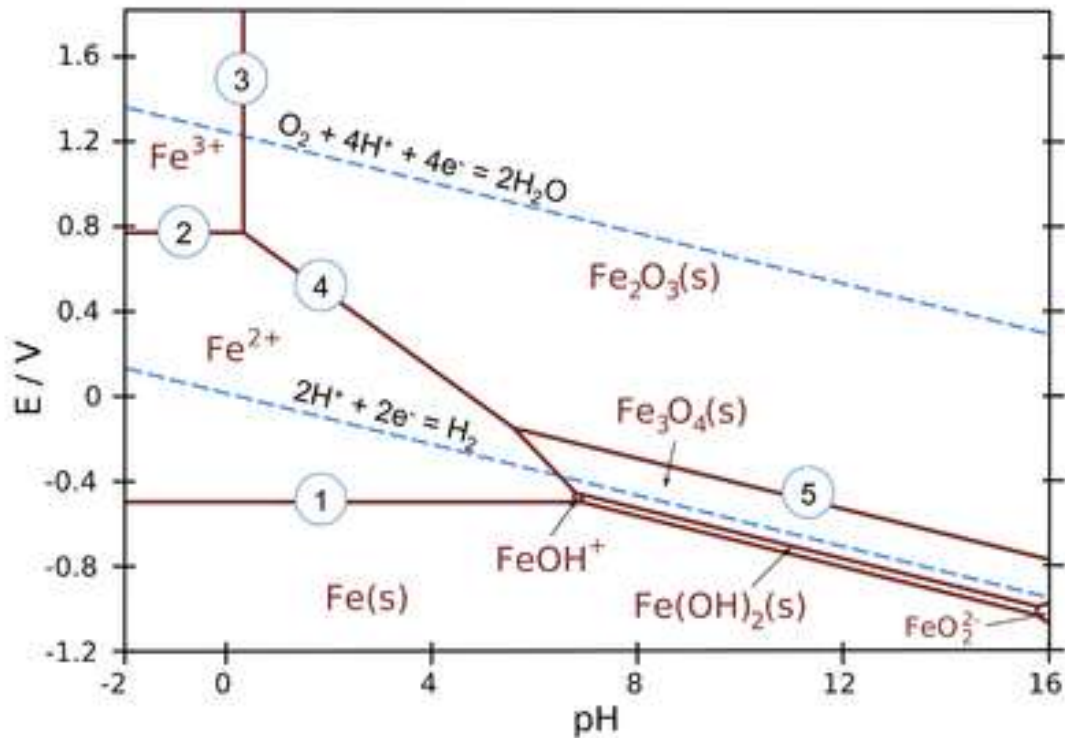
1. Marcel Pourbaix developed potential-pH diagrams to show the thermodynamic state of most metals in dilute aqueous solutions
2. With pH is plotted on the horizontal axis and potential on the vertical line, these diagrams have curves representing chemical and electrochemical equilibria between metal and aqueous environment

3. These diagrams ultimately show the conditions for immunity, corrosion or passivation.



Equilibrium Reactions of iron in Water





Benefits of Pourbaix Diagram

1. Pourbaix diagrams offer a large volume of thermodynamic information in a very efficient and compact format.
 2. The information in the diagrams can be 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. For example, on increasing the pH of environment in moving to slightly alkaline regions, the corrosion of iron can be controlled.
 - ◆ Changing the potential of iron to more negative values eliminate corrosion, this technique is called cathodic protection.
 - ◆ Raising the potentials to more positive values reduces the corrosion by formation of stable films of oxides on the surface of transition metals.

Limitations of Pourbaix Diagrams

1. These diagrams are purely based on thermodynamic data and do not provide any information on the reaction rates.
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. Pourbaix diagrams deal with pure metals which are not of much interest to the engineers

Electrochemical Polarization

Electrochemical polarization (usually referred to simply as “polarization”) is the change in electrode potential due to the flow of current. The rate of an electro-chemical reaction is limited by various physical and chemical factors. Hence an electro-chemical reaction is said to be polarized or retarded by these environmental factors.

There are two types of polarization:

- 1) **Activation Polarization:** is polarization caused by a slow electrode reaction.
- 2) **Concentration Polarization:** is polarization caused by concentration changes in reactants or products near an electrode surface.

Anodic and Cathodic polarization

Either an anode or a cathode can be polarized:

Anodic polarization is the displacement of the electrode potential in the positive direction so that the electrode acts more anodic.

Cathodic polarization is the displacement of the electrode potential in the negative direction so that the electrode acts more cathodic.

These processes are represented schematically in Figure 8

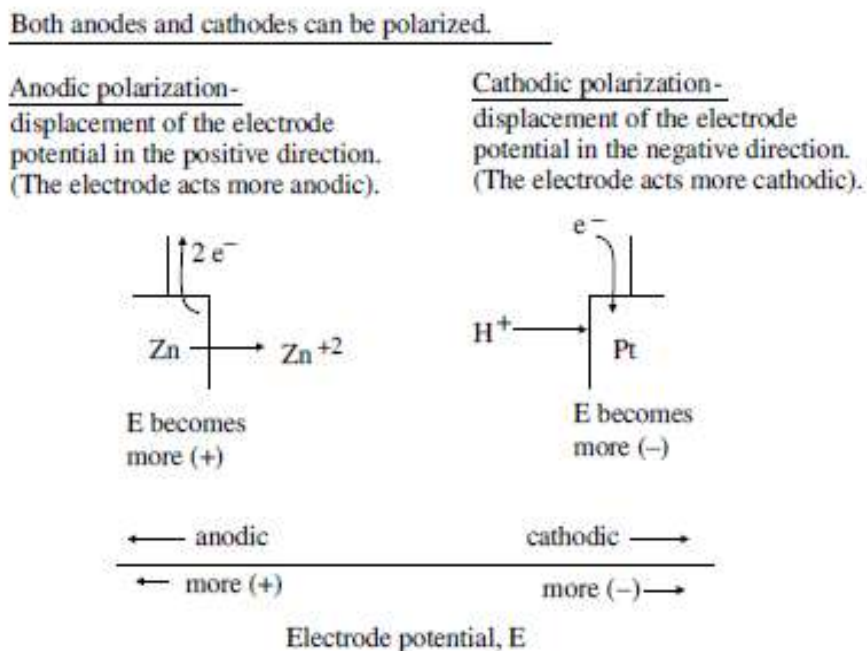


Figure 8: schematic representation of anodic and cathodic polarization.

Example 3: Consider the hydrogen evolution reaction occurring at a metal surface.

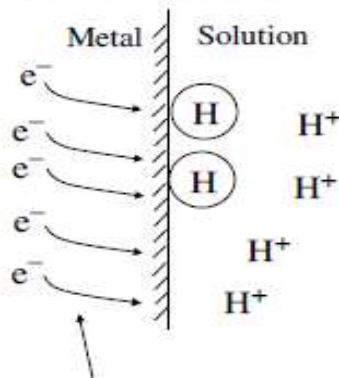
First: Hydrogen atoms are produced by the reduction reaction



This process of activation polarization involves a slow step in the electrode reaction. Suppose that electrons are supplied to the metal electrode faster than they can react to form H atoms, as represented in the Figure 9. Then the concentration of electrons is increased at the metal side of the interface. The result is that the electrode potential E becomes more negative, due to activation polarization.

Cathodic polarization (activation)

Suppose the reaction is slow.



Electrons are supplied to the metal faster than they can react.

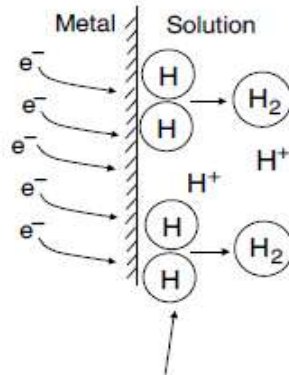
Thus, the concentration of e^- is increased at the metal side of the interface.

E becomes more (-) due to activation polarization .

Figure 9: Schematic representation of activation polarization for a cathode.

Suppose instead that there are concentration effects near the electrode surface for hydrogen reduction reaction. If reactant hydrogen H^+ are slow to diffuse to the electrode surface, as illustrated in Figure 10, then electrons again can accumulate at the metal side of the interface. The result is that the electrode potential E again becomes more negative, but this time due to concentration polarization.

Cathodic polarization (concentration)



Suppose H^+ ions are slow to move into the electrical double layer.

Then, electrons flow into the surface faster than they can be consumed.

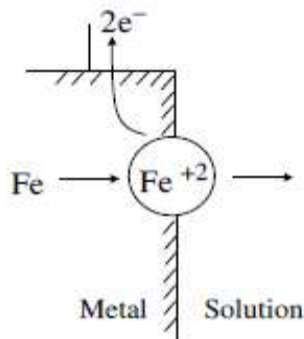
The concentration of e^- is again increased at the metal side of the interface.

E becomes more (-) due to concentration polarization.

Figure 10: Schematic representation of concentration polarization for a cathode.

Second: Suppose that the oxidation of Fe atoms to Fe^{2+} ions is slow. Then electrons exit the electrode faster than Fe atoms leave the metal matrix, as illustrated in Figure 11. This means that the electron concentration is decreased at the metal side of the interface. The electrode potential E thus becomes more positive due to activation polarization.

Anodic polarization (activation)



Suppose the reaction is slow.

Then, electrons exit from the surface faster than Fe atoms leave the matrix.

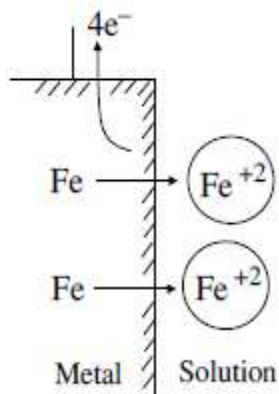
The concentration of e^- is decreased at the metal side of the interface.

E becomes more (+) due to activation polarization.

Figure 11: Schematic representation of activation polarization for an anode

Suppose next that the products of the anodic reaction, Fe^{2+} ions are slow to diffuse away from the metal surface, as represented in Figure 12. The surface becomes more positively charged due to the accumulation of Fe^{2+} ions. The electrode potential E again becomes more positive, but this time due to concentration polarization.

Anodic polarization (concentration)



Suppose the products are slow to diffuse away from the interface.

Again, the surface becomes more positively charged.

E becomes more (+) due to concentration polarization.

Figure 12: Schematic representation of concentration polarization for an anode

Electrode Kinetics:-

We are interested in what happens when cells such as shown in figure (3). In this short-circuited cell, a vigorous reaction occurs. The zinc Electrode rapidly dissolves in the solution and simultaneously a rapid evolution of hydrogen is observed at platinum electrode. Electrons released from the Zn dissolution and consumed in the hydrogen-reduction reaction.

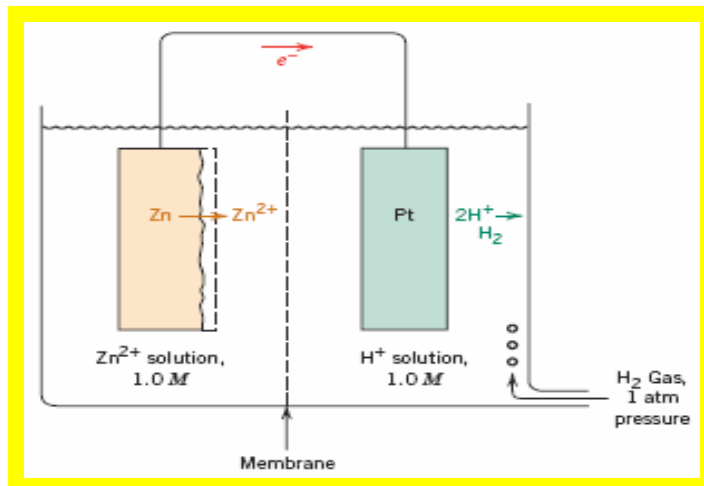


Figure (3) Electrochemical cell consisting of standard Zn & Hydrogen electrodes that has been short-circuited

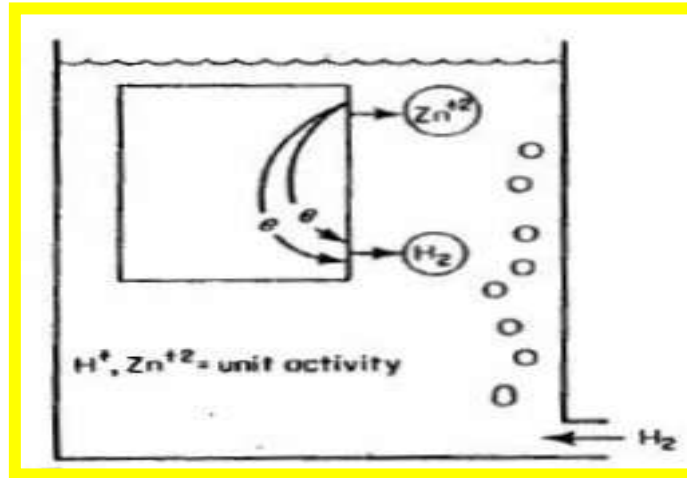


Figure (4) corroding Zn schematic

This process is the same of Fig.(4) ,In both the overall reaction is Zn dissolution and H₂ evolution. The potentials of these electrodes will no longer be at their equilibrium potential. This deviation from equilibrium potential is called *Polarization* (the displacement of electrode potential resulting from a net current). It is measured in terms of *overvoltage* (η). The overvoltage is stated in terms of volts plus or minus with respect to equilibrium potential.

By plotting electrode potential versus reaction rate, it is possible to establish a point corresponding to the platinum-hydrogen electrode. This point represents the particular exchange reaction rate of electrode expressed in terms of moles reacting per square centimeter per second , no net reaction (oxidation rate = reduction rate = exchange reaction rate). Exchange reaction rate can be expressed in terms of current density, and current density can be directly derived from Faraday's law:

$$r_{oxid} = r_{red} = \frac{i_o}{nF}$$

(i_o): Exchange current density depends on:

1. Redox potential of a metal.
2. Composition of electrode.
3. Temperature of the system.
4. The ratio of oxidized and reduced species.

Table (1) Exchange Current Densities .

Reaction	Electrode	Solution	i_0 , amp/cm ²
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Al	2N H_2SO_4	10^{-10}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Au	1N HCl	10^{-6}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Cu	0.1N HCl	2×10^{-7}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Fe	2N H_2SO_4	10^{-6}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Hg	1N HCl	2×10^{-12}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Hg	5N HCl	4×10^{-11}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Ni	1N HCl	4×10^{-6}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Pb	1N HCl	2×10^{-12}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Pt	1N HCl	10^{-3}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Pb	0.6N HCl	2×10^{-4}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Sn	1N HCl	10^{-3}
$\text{O}_2 + 4\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O}$	Au	0.1N NaOH	5×10^{-13}
$\text{O}_2 + 4\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O}$	Pt	0.1N NaOH	4×10^{-13}
$\text{Fe}^{+3} + \text{e} = \text{Fe}^{+2}$	Pt		2×10^{-3}
$\text{Ni} = \text{Ni}^{+2} + 2\text{e}$	Ni	0.5N NiSO_4	10^{-6}

Polarization means the reduction in corrosion rate either by slowing down the anodic or cathodic reaction. Activation Polarization: refers to the condition wherein the reaction rate is controlled by the one step in the series that occurs at the slowest rate. The term “activation” is applied to this type of polarization because an activation energy barrier is associated with this slowest, rate-limiting step.

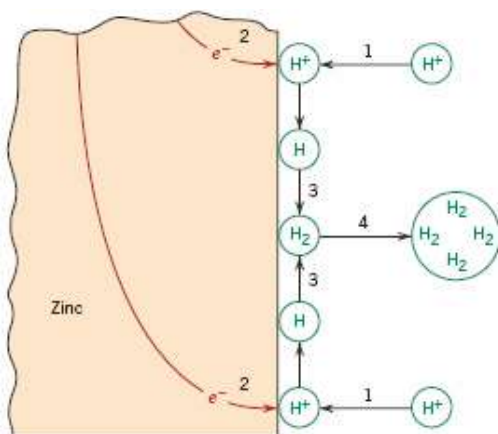
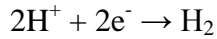


Figure (6) representation of possible steps in hydrogen reduction. The rate of which is controlled by Activation polarization.

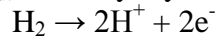
Considering the reduction of hydrogen ions to form bubbles of hydrogen gas on the surface of a zinc electrode. The slowest of these steps determines the rate of the overall reaction. For activation polarization, the relationship between overvoltage η and current density i is

$$\eta_a = \pm \beta \log \frac{i}{i_0}$$

Where β and i_0 are constants for the particular half-cell. The parameter i_0 is termed the *exchange current density*, which deserves a brief explanation. Equilibrium for some particular half-cell reaction is really a dynamic state on the atomic level. That is, oxidation and reduction processes are occurring, but both at the same rate, so that there is no net reaction. For example, for the standard hydrogen cell reduction of hydrogen ions in solution will take place at the surface of the platinum electrode according to



With a corresponding rate r_{red} . Similarly, hydrogen gas in the solution will experience oxidation as

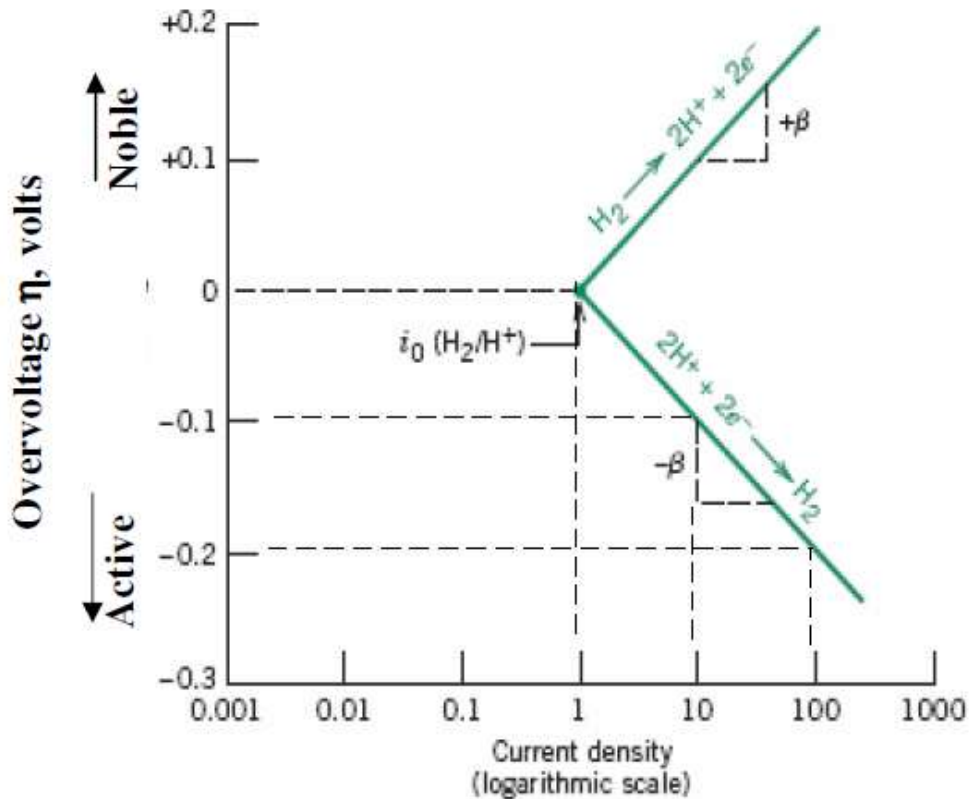


At rate r_{oxid} . Equilibrium exists when

$$r_{\text{red}} = r_{\text{oxid}}$$

This exchange current density is the current density at equilibrium, or

$$r_{\text{oxid}} = r_{\text{red}} = \frac{i_0}{nF}$$



Figure(8): For a hydrogen electrode, Plot of activation polarization overvoltage versus logarithm of current and reduction reactions.

Tafel equation is graphically illustrated in Figure (8). If a logarithmic scale is used, the relationship between overvoltage or potential and current density is linear function. The value of the slope called Tafel slope for electrochemical reactions. Both line segments originate at the exchange current density, and at zero overvoltage, since at this point the system is at equilibrium and there is no net reaction

Concentration polarization exists when the reaction rate is limited by diffusion in the solution.

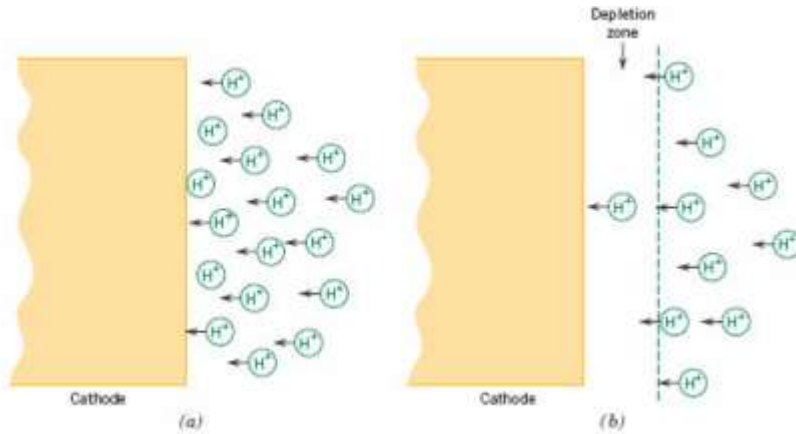


Fig.(9) For hydrogen reduction, schematic representation of the H⁺ distribution in the vicinity of the cathode for (a) low reaction rates and/or high concentrations, and (b) high reaction rates and/or low concentration wherein a depletion zone is formed that gives rise to concentration polarization.

In concentration polarization we calculate the *limiting diffusion current density* (i_L). It represent the maximum rate of reduction possible for a given system; the eq. expressing this parameter is

$$i_L = -\frac{nFD C_b}{\delta}$$

Where i_L = limiting diffusion current density.

D = diffusion coefficient of the reaction ions.

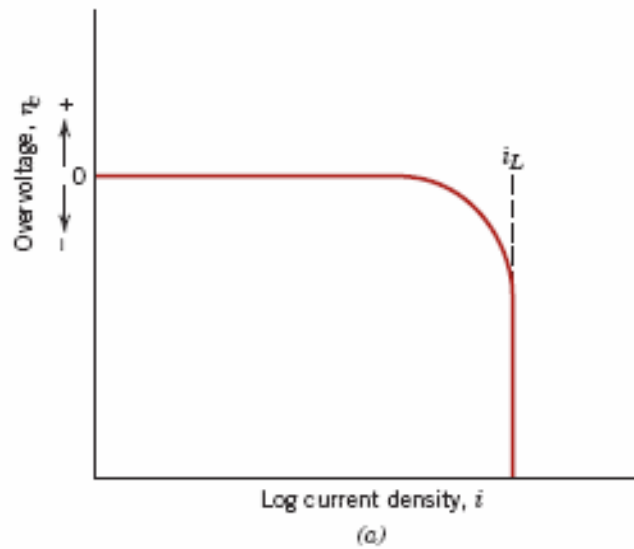
C_b = concentration of the reacting ions in the bulk solution.

δ = thickness of the diffusion layer.

The diffusion-layer thickness is influenced by the *shape* of the particular electrode, the *geometry* of the system, and by *agitation*. If we consider no activation polarization, then the equation for concentration polarization is:

$$\eta_c = 2.303 \frac{RT}{nF} \log \left(1 - \frac{i}{i_L} \right)$$

A graphical representation of the limiting diffusion current is shown in figure (10).



Figure(10) For reduction reactions. Schematic plots of overvoltage versus logarithm of current density for concentration polarization.

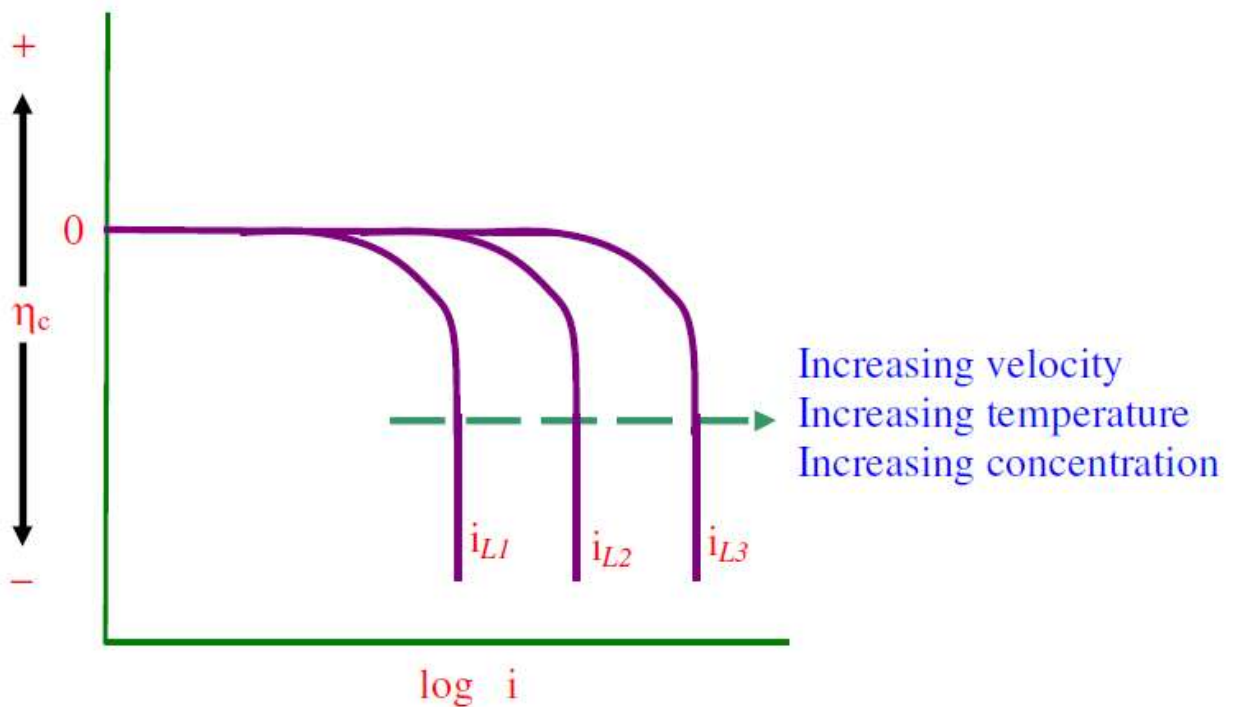


Fig.(11) Effect of environmental variables on concentration polarization curve.

The effects of changing limiting diffusion current on the shape of the polarization curve encountered during concentration polarization. As the solution velocity, concentration, or temperature are increased, limiting diffusion current increases since all of these factors exert an influence as indicated in equation of limiting current density.

$$i_L = -\frac{nFD C_b}{\delta}$$

Combined Polarization both activation and concentration polarization usually occur at an electrode. At low reaction rates, activation polarization usually controls, while at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contributions of activation polarization and concentration polarization.

Corrosion Rates from Polarization

$$\eta_T = \eta_a + \eta_c$$

Equation for the kinetic of anodic dissolution is given by

$$\eta_{oxd} = \beta \log \frac{i}{i_o}$$

$$\eta_{red} = -\beta \log \frac{i}{i_o} + 2.303 \frac{RT}{nF} \log \left(1 - \frac{i}{i_L} \right)$$

This equation is graphically illustrated in fig.(12).

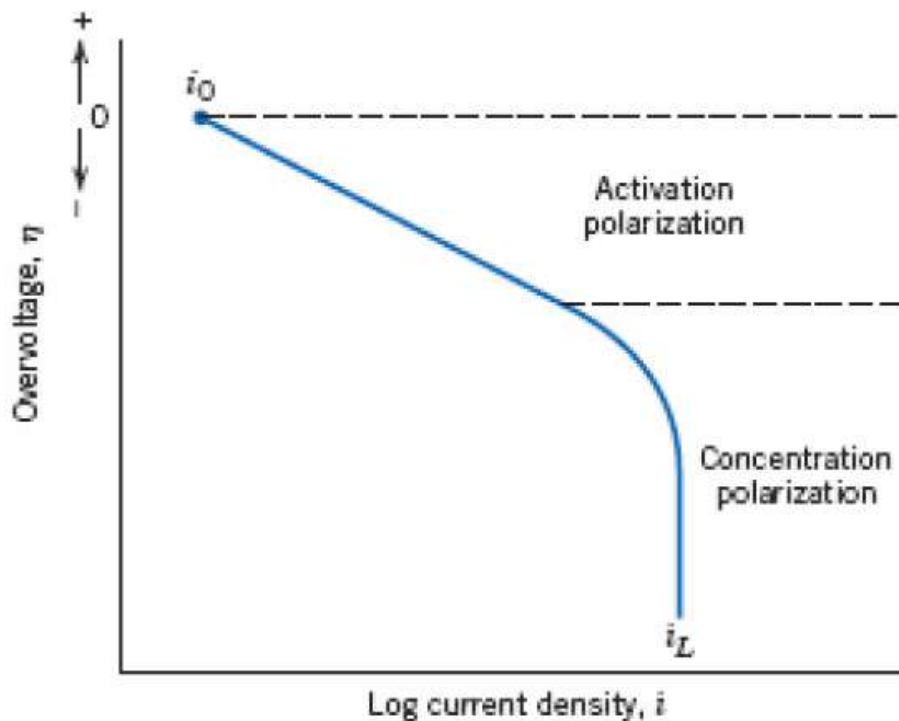


Fig.(12) For reduction reactions. Schematic plots of overvoltage versus logarithm of current density for combined activation-concentration polarization.

Mixed – potential Theory

The mixed – potential theory consist of two simple hypotheses:

- 1- Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.
- 2- There can be no net accumulation of electrical charge during an electrochemical reaction.

During the corrosion of an electrically isolated metal sample, the total rate of oxidation must equal the total rate of reduction. A mixed electrode is an electrode or metal sample which is in contact with two or more oxidation – reduction systems. Both oxidation and reduction reactions are rate limited by activation polarization.

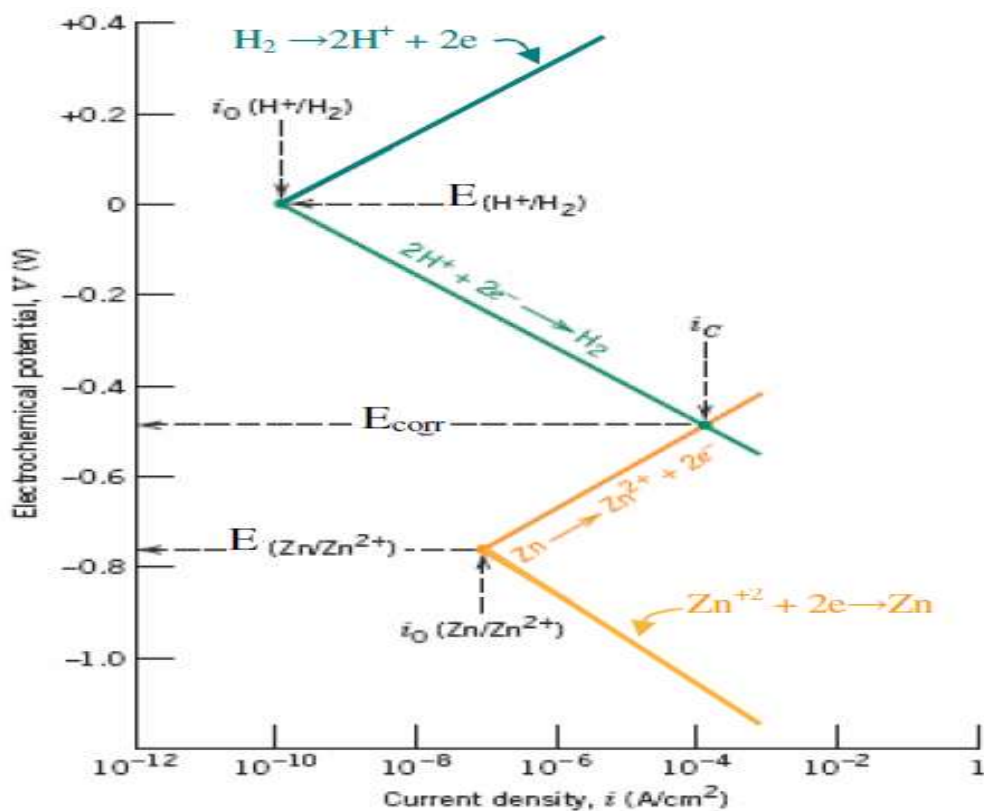


Figure (13) Electrode kinetic behavior of zinc in an acid solution.

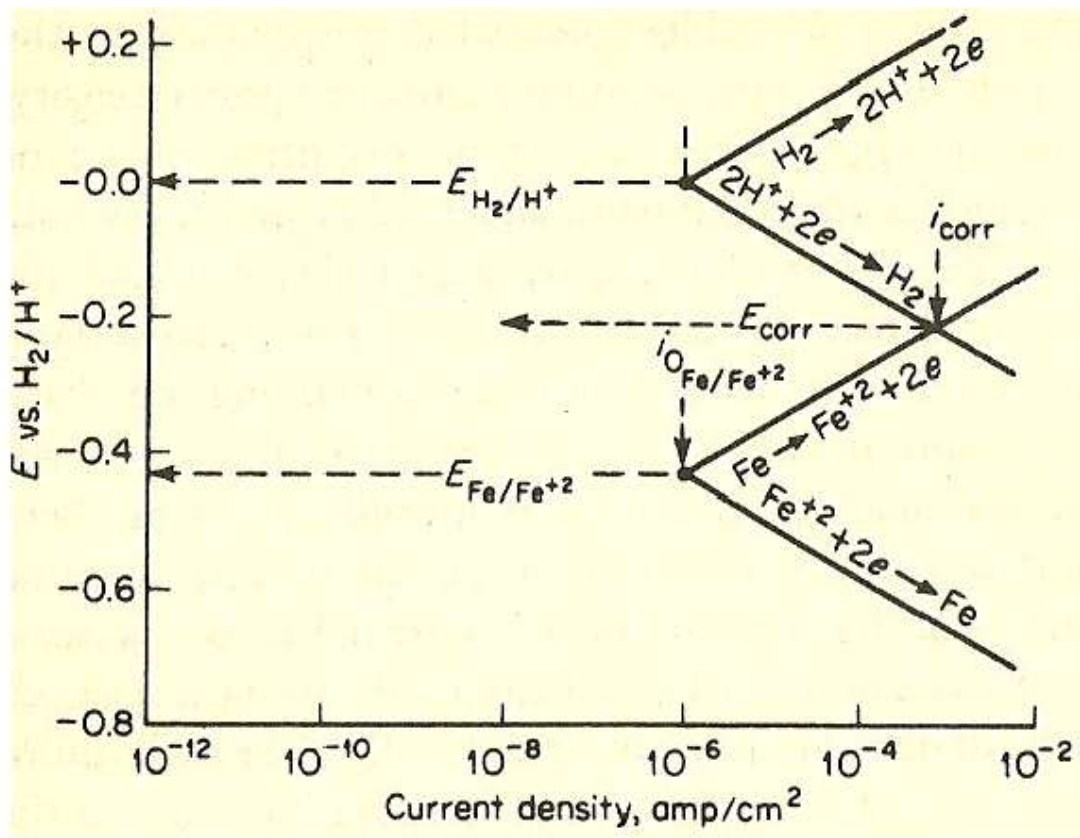


Figure (14) Corrosion behavior of Iron in dilute HCl acid solution. Electrode kinetic behavior of pure iron in acid solution schematic

In terms of loss of weight of a metal with time, from equation

$$\frac{dw}{dt} = \frac{M I}{n F}$$

The rate of corrosion is proportional to the current passed and to the molar mass. Dividing the equation by the exposed area of the metal in the alloy, we get

$$\frac{w}{A t} = \frac{M I}{n F A}$$

Corrosion rate can be written in terms of weight gain or loss

$$\frac{w}{A t} = \frac{M i}{n F}$$

The above equation has been successfully used to determine the rates of corrosion.

Where

w = the rate in weight gain or loss (g/cm²)

i = current density = $\frac{I}{A}$ (A / cm²).

t = exposure time (sec.)

M = Atomic weight of the metal (g / mole).

n = No. of electrons transferred (the valence).

F = Faraday's constant (96,500 coulomb's/mole or A.Sec./ mole).

I = Current (A).

A = Corroded surface area (cm²)

$$CR = C \cdot \frac{Mi}{n\rho}$$

where

ρ = density (g/cm³)

i = current density (A/cm²)

M = atomic weight (g / mol)

n = number of electrons involved

C = constant which includes F and any other conversion factor for units, for instance, C = 0.129 when corrosion rate is in mpy, 3.27 when in mm/year and 0.00327 when units are in mm³/year.

Example problem

Rate of Oxidation Computation, Zinc experiences corrosion in an acid solution according to the reaction $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ the rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Zn (in mol/cm².s) given the following activation polarization data:

$$E_{(Zn/Zn^{2+})} = -0.763 V$$

$$i_o = 10^{-7} A/cm^2$$

$$\beta = +0.09$$

$$E_{(H^+/H_2)} = 0.0 V$$

$$i_o = 10^{-10} A/cm^2$$

$$\beta = -0.08$$

b) Compute the value of the corrosion potential

Solution: (a) To compute the rate of oxidation for Zn, it is first necessary to establish relationships in the form of Tafel equation for the potential of both oxidation and reduction reactions. Next, these two expressions are set equal to one another, and then we solve for the value of I that is the corrosion current density, i_{corr} . Finally, the corrosion rate may be calculated using Equation (1). The two potential expressions are follows:

For hydrogen reduction

$$E_H = E_{rev.(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_o H}\right)$$

And for Zn oxidation

$$E_{Zn} = E_{rev.(Zn/Zn^{2+})} + \beta_{Zn} \log\left(\frac{i}{i_o Zn}\right)$$

Now setting $E_H = E_{Zn} = E_{corr}$ =leads to

$$E_{H^+/H_2} + \beta_H \log\left(\frac{i}{i_o H}\right) = E_{Zn/Zn^{2+}} + \beta_{Zn} \log\left(\frac{i}{i_o Zn}\right)$$

And solving for $\log i$ (i.e. $\log i_{\text{corr}}$) leads to

$$i_c = 1.19 \times 10^{-4} \text{ A/cm}^2$$

$$r_{\text{oxid}} = r_{\text{red}} = \frac{i_{\text{Corr}}}{nF}$$

$$= \frac{1.19 \times 10^{-4} \text{ C/s.cm}^2}{2 \times 96500 \text{ C/mol}} = 6.17 \times 10^{-10} \text{ mol/cm}^2 \cdot \text{s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential E_{Corr} . This is possible by using either of the above equations for E_{H} or E_{Zn} and substituting for I the value determined above for i_{Corr} . Thus using the E_{H} expression yields

$$E_{\text{Corr}} = E_{\text{H}^+/\text{H}_2}^{\circ} + \beta_{\text{H}} \log \left(\frac{i_{\text{Corr}}}{i_{\text{oH}}} \right)$$

$$E_{\text{H}} = 0 + (-0.08) \log \left(\frac{1.19 \times 10^{-4} \text{ A/cm}^2}{10^{-10} \text{ A/cm}^2} \right)$$

$$= -0.486 \text{ V}$$

This is the same problem that is represented and solved graphically in the voltage-versus logarithm current density plot of Figure (13). It is worth noting that the i_{Corr} and E_{Corr} we have obtained by this analytical treatment are in agreement with those values occurring at the intersection of the two line segments on the plot.

Exercise1: For the cell $[\text{Cu}/\text{Cu}^{2+}(1.0\text{M})]/[\text{Zn}^{2+}(1.0\text{M})/\text{Zn}]$, does the cell reaction $\text{Cu} + \text{Zn}^{2+} \rightarrow \text{Cu}^{2+} + \text{Zn}$ take place simultaneously? If E° for the reaction is -0.002 V .

Exercise2: Steel corrodes in an aqueous solution; the corrosion current is measured as 0.1 A/cm^2 .

Calculate the rate of weight loss per unit area in units of mdd.

Where: $M = 55.9 \text{ g/mol}$

$$i = 0.1 \text{ A/cm}^2$$

$$n = 2$$

Exercise3: Iron is corroding in seawater at a current density of $1.69 \times 10^{-4} \text{ A/cm}^2$. Determine the corrosion rate in mdd (milligrams per decimeter² day)

Exercise4: A sample of zinc corrodes uniformly with a current density of $4.2 \times 10^{-6} \text{ A/cm}^2$ in an aqueous solution. What is the corrosion rate of zinc in mm/year? Given current density, $i = 4.2 \times 10^{-6} \text{ A/cm}^2$, we know that for zinc atomic weight, $M = 65.38 \text{ g/mol}$, density, $\rho = 7.1 \text{ g/cm}^3$, $n = 2$, $F = 96500 \text{ coulombs/mole}$.

Exercise5: Consider the reaction $\text{M} \rightarrow \text{M}^{2+} + 2\text{e}$ on an electrode surface. An over potential of (-0.155 V) (η) is applied to the electrode. The exchange current density (i_0) at 25°C is $5 \times 10^{-7} \text{ A/cm}^2$, $\beta = -0.5$. Determine the current density, i , if the change in the oxidation state is one unity.

Exercise6: Suppose that a metal M has an oxidation-reduction exchange current density of $0.1 \mu\text{A}/\text{cm}^2$ at its reversible potential -0.160 V . The anodic Tafel slope is $+0.060 \text{ V}$ and the cathodic Tafel slope is -0.060 V for the system $\text{M}^+ + \text{e}^- \rightarrow \text{M}$. for hydrogen evolution on the surface of M, the anodic and the cathodic Tafel slopes $+0.100 \text{ V}$ and -0.100 V , respectively. The exchange current density for hydrogen evolution on the metal M is $1.0 \mu\text{A}/\text{cm}^2$ at the reversible potential of 0.00 V .

- Construct the individual polarization curves for the systems
- What is the corrosion potential?
- What is the corrosion rate?

Corrosion protection

1) Material selection

Metals and alloys: The most common method of preventing corrosion is the selection of the proper metal or alloy for a particular corrosive service.

Mediums and corrosion Resistant Metals

- 1) Very Oxidizing Medium nitric acid, (Stainless Steels).
- 2) Caustic Solutions, (Ni & Ni-alloys).
- 3) HCl, (Monel alloy).
- 4) Hot HCl, (Hastelloys –chlorimets).
- 5) Dilute H_2SO_4 , (lead).
- 6) Oxidizing mediums, (Al-alloy).
- 7) Distilled water, (Tin).
- 8) Hot strong oxidizing solutions, (Titanium).
- 9) For all conditions except for HF, (Tantalum).
- 10) Concentrated H_2SO_4 , (carbon steel).

Metal purification: The corrosion resistance of a pure metal is usually better than of one containing impurities or small amounts of other elements .However, pure metals are usually expensive and are relatively soft and weak.

Nonmetallic:-

Solid nonmetallic construction and sheet linings or coverings of substantial thickness (to differentiate from paint coatings) .They are

- 1- rubbers ,
- 2- plastics ,
- 3- ceramics ,
- 4- carbon and graphite ,
- 5- wood.

Rubbers & plastics are weaker, softer, and more resistant to chloride ions and hydrochloric acid than metals and alloys , but less resistant to sulfuric acid and nitric acid, less resistance to solvents, low temperature limitations.

Ceramics possess excellent corrosion and high temperature resistance but brittle and low tensile strength.

Carbons show good corrosion resistance, electrical and heat conductivity, but they are fragile.

Wood is attacked by aggressive environments.

2) Alteration of environment

1- Lowering temperature: In most cases the corrosion rate will be less or stop. But in some cases by reducing the temperature the corrosive will be faster, e.g. fresh water or seawater are less corrosive at high temperature because oxygen is removed from the water.

2- Decreasing velocity: Except for pitting and erosion corrosion all the other types of corrosion rate is reduced by reducing in velocity. Stress Corrosion Cracking stops with increasing medium velocity because pitting is stopped.

3- Removing oxygen or oxidizer from the system: - For most metals except for Stainless Steels and Al alloys corrosion would stop by removing oxygen. (Stainless steel and Al have protected oxide layer).

4- Reduction in concentration: - In all cases except in two cases (H_2SO_4 and H_3PO_4) the reduction in concentration reduces the corrosion rate. They passivated the surface of metal in concentrated form.

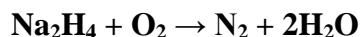
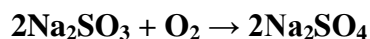
3) Inhibitors:-

An inhibitor is a substance which, when added in small concentrations to an environment, decreases the corrosion rate. There are numerous inhibitor types and compositions. Inhibitors can be classifying according to their mechanism and composition.

1-Adsorption – type inhibitors: - these represent the largest class of inhibiting substances these are organic compounds which adsorb on metal surface and suppress metal dissolution and reduction reactions Such as Organic amines.

2- Hydrogen – evolution poisons: - such as arsenic and antimony ions, specifically retard the hydrogen – evolution reaction (acidic solutions).

3- Scavengers: - These substances act by removing corrosive reagents from solution. Such as sodium sulfite and hydrazine, which remove dissolved oxygen from aqueous solutions



Oxygen reduction is controlling cathodic reaction; it is not effective in strong acid solutions.

4- Oxidizers: - Such substances as chromate, nitrate, ferric salts, they are primarily used to inhibit the corrosion of metals and alloys which demonstrate active – passive transitions, such as iron and its alloys and stainless steels.

5- Vapor – Phase Inhibitors: - These are very similar to the organic adsorption – type inhibitors and possess a very high vapor pressure. As a consequence, these materials can be used to inhibit atmospheric corrosion of metals without being placed in direct contact with metal surface. The vapor-phase inhibitors are usually only effective if used in closed spaces such as inside packages or on the interior of machinery during shipment.

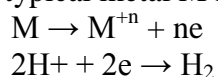
4) Design:

In designing a structure in corrosive environments the following considerations are essential:-

- i) Weld rather than rivet tanks and other containers. Riveted joints provide sites for crevice corrosion.
- ii) Design tanks and other containers for easy draining and easy cleaning. Tank bottoms should be sloped toward drain holes so that liquids cannot collect after the tank is emptied.
- iii) Design systems for the easy replacement of components that are expected to fail rapidly in service. Frequently, pumps in chemical plants are designed so that they can be readily removed from a piping system, since they fail frequently
- iv) There should be uniform stress distribution in the structure, otherwise Stress Corrosion Cracking or accelerated corrosion of higher stressed parts would occur.
- v) Two – metal contacts should be avoided, otherwise there would be Galvanic Corrosion at the joints.
- vi) A void sharp bends in the structure, otherwise there would be accelerated Erosion Corrosion.
- vii) There should be uniform distribution of air or oxygen in the system, otherwise galvanic effect would happen.
- viii) A void hot spots during heat –transfer operations. And a void heterogeneity, dissimilar metals, vapor spaces, uneven heat and stress distributions.

5) Cathodic and Anodic Protection

(I) Cathodic protection: The principles of Cathodic protection may be explained by considering the corrosion of a typical metal M in an acid environment.



Cathodic protection is achieved by supplying electrons to the metal structure to be protected. If current is considered to flow from (+) to (-), as in conventional electrical theory, then a structure is protected if current enters it from the electrolyte. Conversely, accelerated corrosion occurs if current passes from the metal to the electrolyte. There are two ways to cathodically protect a structure: (1) by an external power supply or, (2) by appropriate galvanic coupling.

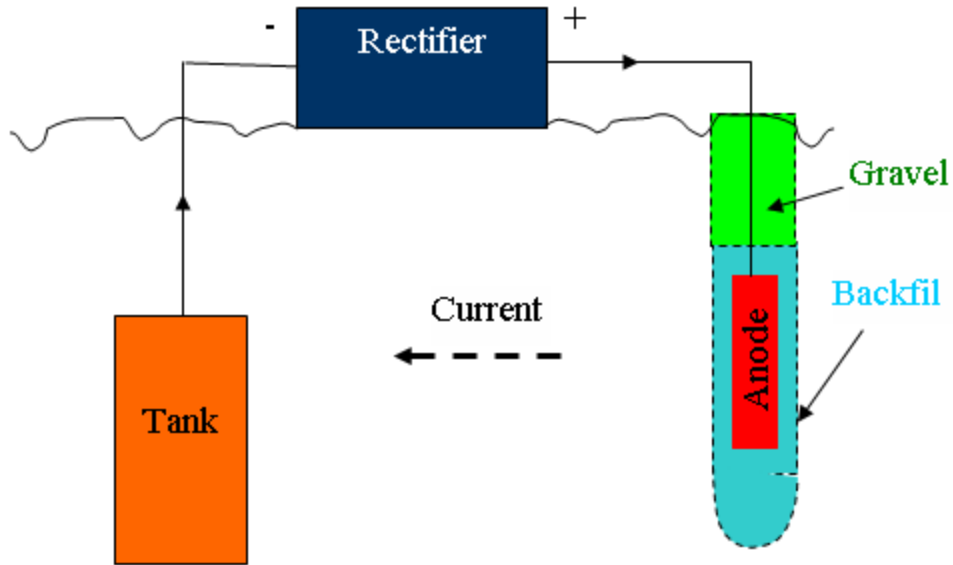


Figure (1) Cathodic protection of an underground tank using impressed
Ground level

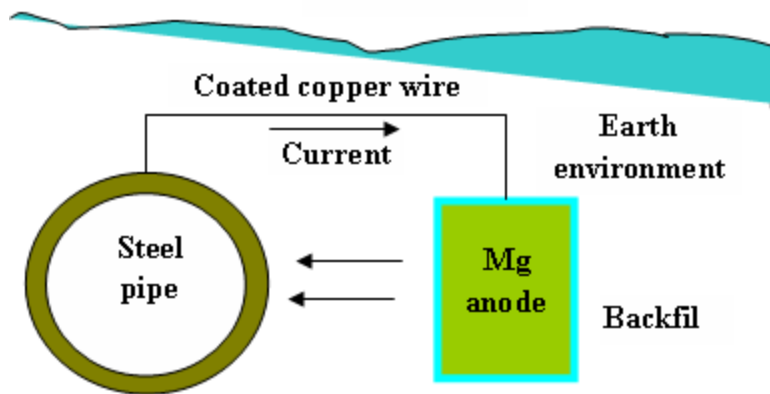


Figure (2) Protection of an underground pipeline with a magnesium anode.

Steel structures exposed to soils, fresh and brackish waters and sea water are protected if they are polarized to a potential of (-0.85 volt) versus copper/copper sulfate electrode. The potential of a structure is determined with a high-resistance voltmeter, during this measurement, the reference electrode is placed in ground or on sponge soaked in brine to make electric contact. The cathodic current density necessary to polarize the pipe to (-0.85 volt) can be readily determined. In case of sacrificial anodes (e.g. Mg, Zn) are used, this same measurement is used to indicate the number and size of anodes needed for full protection.

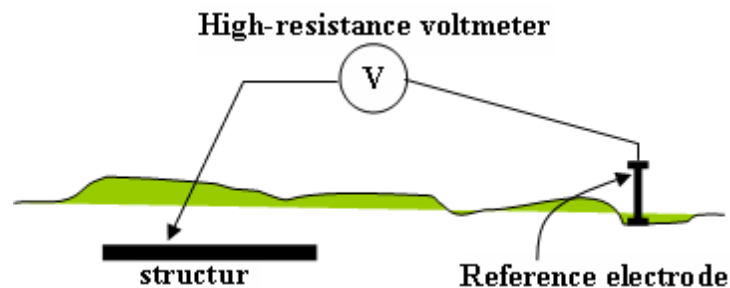


Figure (3) Pipe potential measurements with a reference electrode

(II) Anodic protection: - In contrast to cathodic protection, anodic protection is relatively new. Anodic protection is based on the formation of a protective film on metals by externally applied anodic currents. Metals with active-passive transitions such as Nickel, Iron, Chromium, Titanium, and their alloys. If carefully controlled anodic currents are applied to these materials, they are passivated and the rate of metal dissolution is decreased. To anodically protect a structure, a device called a potentiostat is required. As indicated in fig. (6) . In operation, potentiostat maintains a constant potential between the tank and the reference electrode. The optimum potential for protection is determined by electrochemical measurements.

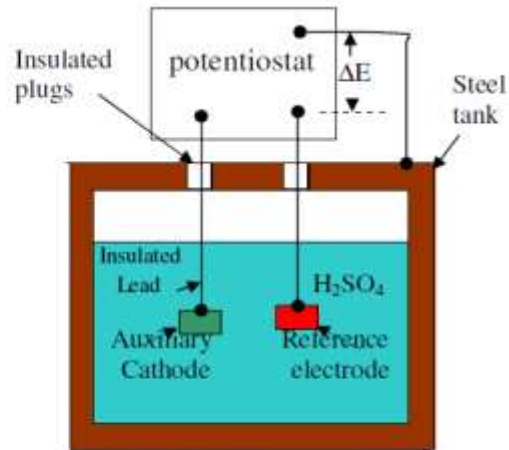
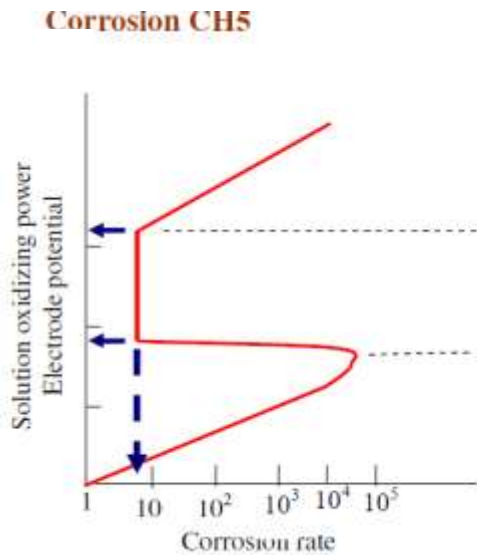


Fig. (6) Anodic protection of a steel storage tank containing H_2SO_4 .

Table (2) anodic protection of Austenitic stainless steel at 30 C (protected at 0.5 V vs. saturated Calomel Electrode)

Alloy type	Environment (air exposed)	Corrosion rate, mpy	
		unprotected	Anodically protected
304 (19Cr-9Ni)	N H_2SO_4 + 10^{-5} M NaCl	14	0.025
	N H_2SO_4 + 10^{-3} M NaCl	2.9	0.045
	N H_2SO_4 + 10^{-1} M NaCl	3.2	0.20
	10N H_2SO_4 + 10^{-5} M NaCl	1930	0.016
	10N H_2SO_4 + 10^{-3} M NaCl	1125	0.04
	10N H_2SO_4 + 10^{-1} M NaCl	77	0.21

Anodic protection can decrease corrosion rate substantially. (Table 2) lists the corrosion rates of austenitic stainless steel in sulfuric acid solutions containing chloride ions with and without anodic protection. Although anodic protection is limited to passive metals and alloys, most structural materials of modern technology contain these elements. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements.

Comparison of anodic and cathodic protection:

	Anodic protection	Cathodic protection
Applicability Metals	Active-passive metals only	All metals
Corrosion relative cost	Weak to aggressive	Weak to moderate
Insulation	High	Low
Operation	Very low	Medium to high
Throwing	Very high	Low
Signification of applied	Often a direct measure of protected corrosion rate	Complex-dose not indicate corrosion rate

6) Coatings

Corrosion protection of over-ground and underground structures by protective coatings is one of the most proven methods. Coatings must have the following characteristics for good corrosion resistance:

- (a) A high degree of adhesion to the substrate.
- (b) Minimum discontinuity in coating (porosity)
- (c) a high resistance to the flow of electrons.
- (d) a sufficient thickness (the greater the thickness , the more the resistance).
- (e) a low diffusion rate for ions such as Cl^- and for H_2O .

1) Metallic and Other Inorganic Coatings:-

Relatively thin coatings of metallic and inorganic materials can provide a satisfactory barrier between metal and its environment (sacrificial Zn coating).

Metal coating are applied by electro deposition, flame spraying, cladding, hot dipping, and vapor deposition. Inorganics are applied or formed by spraying , diffusion , or chemical conversion.

In both cases a complete barrier must be provided. Any porosity or other defects will accelerate localized attack. Examples of metal – coated galvanized steel, glassed steel tanks represent ceramic coating, also anodized aluminum and chromed steel.

1-Electro-deposition: - This process also called electro-plating, consists of immersing a part to be coated in a solution of the metal to be plated and passing a direct current between the part and another electrode. The character of the deposit depends on many factors including temperature, current density, time, and composition of the bath. For example an automobile bumper has an inner flash plate of copper (for good adhesion), an intermediate layer of nickel (for corrosion protection), and a thin top layer of chromium (primarily for appearance).

2)Flame Spraying :- This process , also called metallizing , consists of feeding a metal wire or powder through a melting flame so the metal , in finely divided liquid particles , is blown on to the surface to be protected. High melting metals may be deposited by plasma- jet spraying .The coatings are usually porous and not protective under severe wet corrosive conditions.

3) Cladding:- This involves a surface layer of sheet metal usually put on by rolling two sheets of metals together. For example 0.25 mm of nickel hot-rolled with 3 mm of steel to produce a composite sheet. Cladding present a great economic advantage in that the corrosion barrier on expansive material is relatively thin and is backed up by inexpensive steel.

4) Hot dipping :- Hot dipping coating are applied to metals by immersing them in a molten metal bath of low melting point metals, chiefly Zinc , Tin , Lead , and Aluminum. Galvanized steel is a popular example. Thickness of coating is much greater than electro-plating.

5) Vapor deposition: - This is accomplished in a high vacuum chamber. The coating metal is vaporized by heating electrically, and the vapor deposits on the parts to be coated. This method is more expensive than others and generally limited to critical parts. For example high – strength parts for missiles and rockets.

6) Diffusion: - Diffusion coatings involve heat treatment to cause alloy formation by diffusion of one metal into the other. This process is also termed (surface alloying). Parts to be coated are packed in solid materials or exposed to gaseous environments which contain the metal that forms the coating. Sherardizing (zinc coating), Chromizing (chromium), and Calorizing (aluminum) are examples. In case of calorizing, the surface is oxidized to form a protective layer of (Al_2O_3). Calorizing and chromizing are utilized mainly for resistance to high – temperature oxidation.

7) Chemical conversion: - Coating from chemical conversion is produced by "corroding" the metal surface to form an adherent and protective corrosion product. *Anodizing* consists of anodic oxidation in acid bath to build up an oxide layer. The surface layer is porous and provides good adherence for paints. The anodized surface can be "sealed" by exposing to boiling water. Additional examples are Bonderizing and Parkerizing (phosphatizing in a phosphoric acid bath), *chromatizing* (exposure to chromic acid and dichromate), and *oxide* or heat coatings for steel. Automobile bodies are the best known example of phosphatizing.

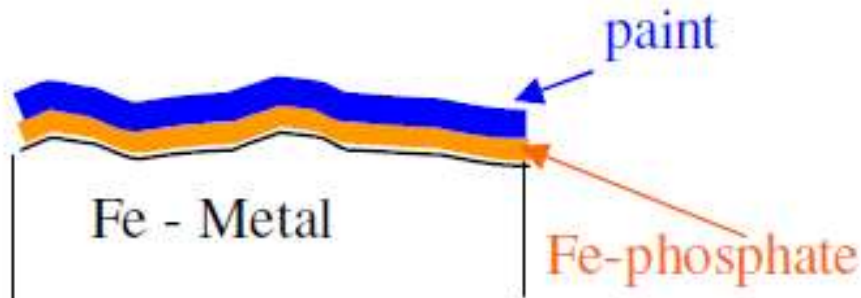
- ❖ *Glassed Steel* or glass-lined, e.g., hot water tanks. The smooth surface is an advantage when ease of cleaning is requirement or sticky materials such as latex, are being handled
- ❖ *Concrete* is utilized for many corrosion applications. Examples are encasing structural steel, concrete –lined pipe, and concrete vessels.

II) Organic Coatings: - These involve a relatively thin barrier between substrate material and the environment. Paints, Varnishes, Lacquers, and similar coatings doubtless protect more metal on a tonnage basis than any other method for combating corrosion. There are three main factors to consider for organic coating:-

- 1) Surface Preparation.
- 2) Selection of Primer or priming coat.
- 3) Selection of top coat or coats.

Top coat is an organic coat and the Fe- phosphate is the primer (prime coating) it has two purposes:-

- 1) Acts as an inhibitor if the top layer is damaged.
- 2) Provides bounding medium between the metal and top layer.
- 3) *Surface preparation* involves surface roughening to obtain mechanical bonding as well as removal of dirt, rust, mill scale, oil, grease, welding flux, crayon marks, wax and other impurities.



Corrosion Test

Methods used for corrosion testing.

- 1) Wt. increase or decrease during corrosion. (Measure the change in weight with time).
- 2) Electro-chemical method.
 - Measure current flow with time.
 - Measure change in potential with time.
- 3) Electrical resistance measurements with time.

Purpose of corrosion tests:

- ❖ To evaluate the metals and alloys in given environments for the manufacture of equipment or for industrial plants.
- ❖ To evaluate corrosion resistance of new alloys in various environments in order to specify their application.
- ❖ For corrosion control, e.g. effect of various inhibitors.
- ❖ To study the corrosion mechanism.

Tests are carried out at various levels for specific purposes.

- i. Laboratory tests. (100 – 150 hrs).
- ii. Pilot plant tests.
- iii. Tests of Industrial equipments in operation.
- iv. Field Tests, (3 – 20 yrs).

Before start of test , these steps are necessary.

1-Material and surface preparation

- ✦ Composition
- ✦ Heat-treatment or % cold work
- ✦ Fabrication method

2-Control of corrosion medium and temperature

3-If in moving environment (e.g. flowing liquid or gases then the velocity should be maintained constant).

4-Effect of surface area measurement