UNIVERSITY OF DAIYLA
COLLEGE OF ENGINEERING
CHEMICAL ENGINEERING DEPARTMENT

(CORROSION)

For
Chemical Engineering Students

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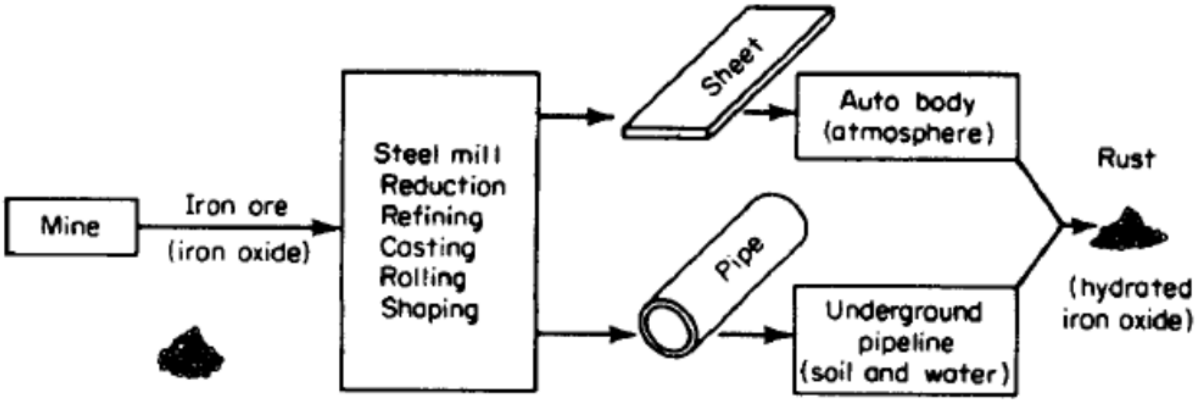
Chapter 1

Introduction

DEFINITION OF CORROSION

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Deterioration by physical causes is not called corrosion, but is described as erosion, galling, or wear. In some instances, chemical attack accompanies physical deterioration, as described by the following terms: corrosion – erosion, corrosive wear, or fretting corrosion. Nonmetals are not included in this definition of corrosion. Plastics may swell or crack, wood may split or decay, granite may erode, and Portland cement may leach away, but the term corrosion, in this book, is restricted to chemical attack of metals. “Rusting” applies to the corrosion of iron or iron - base alloys with formation of corrosion products consisting largely of hydrous ferric oxides. Nonferrous metals, therefore, corrode, but do not rust. Corrosion is a return of material to its origin.



(A) Four required components in an electrochemical corrosion cell:

1) An anode;

2) A cathode;

3) A conducting environment for ionic movement (electrolyte);

4) An electrical connection between the anode and cathode for the flow of electron current.

(B) If any of the above components is missing or disabled, the electrochemical corrosion

Process will be stopped.

IMPORTANCE OF CORROSION

The three main reasons for the importance of corrosion are:

1. Economics
2. Safety.
3. Conservation

Corrosion Science and Engineering

Corrosion science is the study of the chemical and metallurgical processes that occur during corrosion. Corrosion engineering is the design and application of methods to prevent corrosion. Ideally, science should be associated with engineering so as to invent new and better methods of prevention and apply existing methods more intelligently and effectively.

Classification of Corrosion

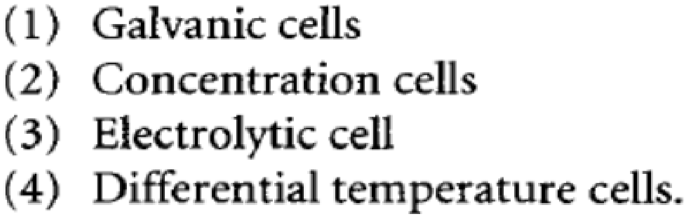
Corrosion has been classified in many different ways. One method divides corrosion into low-temperature and high – temperature corrosion. Another separates corrosion into direct combination (or oxidation) and electrochemical corrosion. The preferred classification here is (1) Wet corrosion and (2) Dry Corrosion.

(1) **Wet Corrosion**: Occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far. A common example is corrosion of steel by water.

(2) **Dry Corrosion**: occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with high temperatures. An example is attack on steel by furnace gases. The presence of even small amounts of moisture could change the corrosion picture completely. For example, dry chlorine is practically non corrosive to ordinary steel, but moist chlorine, or chlorine dissolved in water, is extremely corrosive and attacks of the common metals and alloys.

TYPES OF CORROSION CELLS

There are several types of corrosion cells

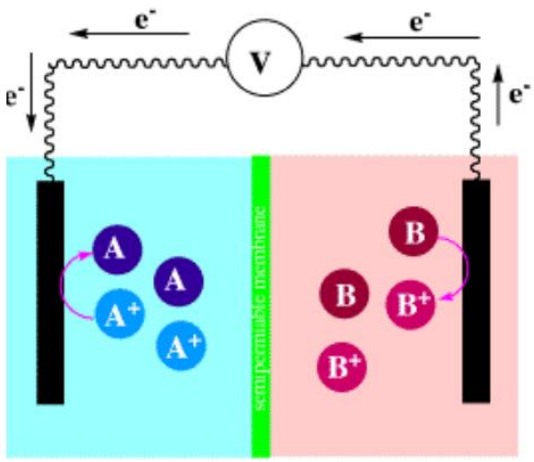


(1) Galvanic cells
(2) Concentration cells
(3) Electrolytic cell
(4) Differential temperature cells.

1.GALVANIC AND ELECTROLYTIC CELLS

A galvanic cell convert chemical energy to electrical energy.

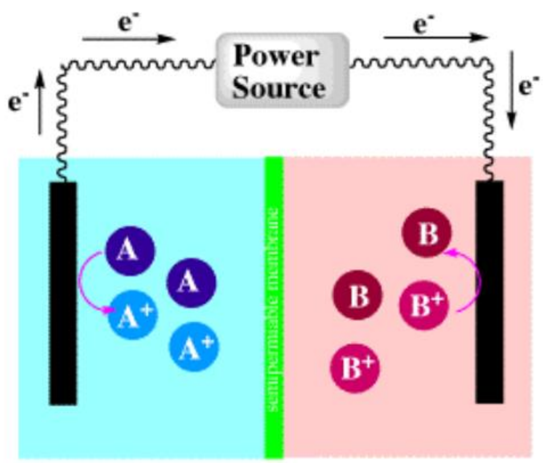
A electrolytic cell convert electrical energy to chemical energy.



Galvanic Cell

$A^+ + B \longrightarrow A + B^+$

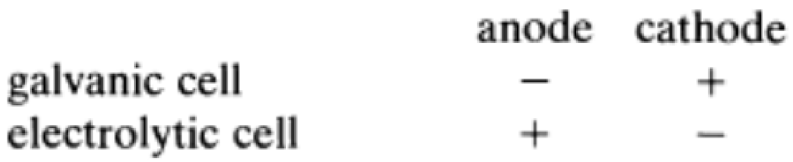
$E^0 = 0.10$ V



Electrolytic Cell

$A + B^+ \longrightarrow A^+ + B$

$E^0 = -0.10$ V



	anode	cathode
galvanic cell	−	+
electrolytic cell	+	−

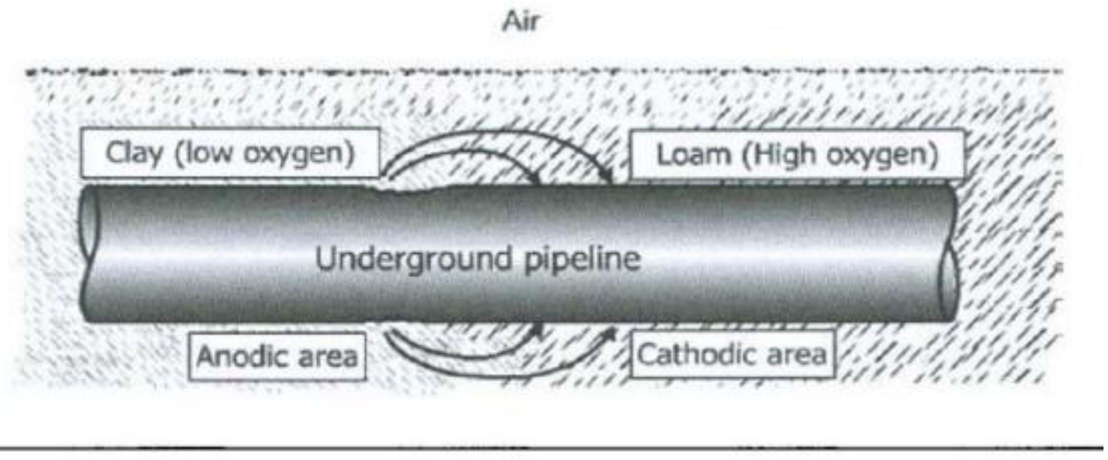
2. Concentration Cell

This is similar to galvanic cell except with an anode and cathode of the same metal in a heterogeneous electrolyte. Concentration cells may be set up by: Concentration Cell:

a- Variation in the amount of oxygen in soils.

b- Difference in moisture content of soils.

c- Difference in composition of the soils.



Concentration cell formation in an underground pipeline

3. Differential temperature cells

In electrolytic cells of the differential-temperature type, the anode and cathod consist of the same metal and differ only in temperature. If the anode and cathode are areas on a single piece of metal immerse in the same electrolyte, corrosion proceeds as in any short-circuited galvanic cell. For copper in aqueous salt solutions, the area of the metal at the higher temperature is the cathode and the area at the lower temperature the anode. In the preferential attack on the anode, copper dissolves from the cold area and deposits on the warmer area. Lead acts similarly, but for silver the polarity is reversed, with the warmer area being attacked preferentially.

DEFINITION OF ANODE AND CATHODE

A combination of two electrical conductors (electrodes) immersed in an electrolyte is called a galvanic cell in honor of Luigi Galvani, a physician in Bologna, Italy, who published his studies of electrochemical action in 1791. A galvanic cell converts chemical energy into electrical energy. On short - circuiting such a cell (attaching a low - resistance wire to connect the two electrodes), positive current flows through the metallic path from positive electrode to negative electrode. The electrode at which chemical reduction occurs (or + current enters the electrode from the electrolyte) is called the cathode.

Examples of cathodic reactions are

$$M^{+n} + ne \rightarrow M$$

Hydrogen evolution	$2H^{+} + 2e \rightarrow H_2$
Oxygen reduction (acid solutions)	$O_2 + 4H^{+} + 4e \rightarrow 2H_2O$
Oxygen reduction (neutral or basic solutions)	$O_2 + 2H_2O + 4e \rightarrow 4OH^{-}$
Metal ion reduction	$M^{3+} + e \rightarrow M^{2+}$

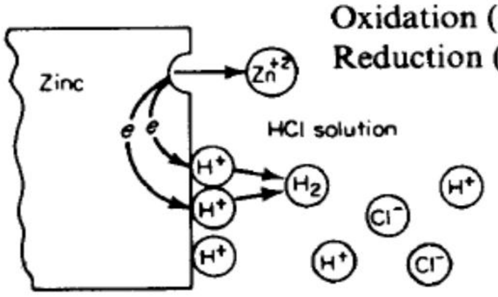
All of which represent reduction in the chemical sense. The electrode at which chemical oxidation occurs (or + electricity leaves the electrode and enters the electrolyte) is called the anode. Examples of anodic reactions are

$$M \rightarrow M^{+n} + ne$$

A few examples are:

$$Ag \rightarrow Ag^{+} + e$$
$$Zn \rightarrow Zn^{2+} + 2e$$
$$Al \rightarrow Al^{3+} + 3e$$

These equations represent oxidation in the chemical sense. Corrosion of metals usually occurs at the anode. In galvanic cells, the cathode is the positive pole, whereas the anode is the negative pole. Cations are ions that migrate toward the cathode when electricity flows through the cell (e.g., H + , Fe 2+) and are always positively charged whether current is drawn from or supplied to the cell. Similarly, anions are always negatively charged. Example of anodic – cathodic reaction is the corrosion of zinc in acid solution:



Oxidation (anodic reaction) $Zn \rightarrow Zn^{2+} + 2e$

Reduction (cathodic reaction) $2H^+ + 2e \rightarrow H_2$

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

TYPES OF CORROSION DAMAGE

1. General Corrosion, or Uniform Attack, Uniform or general corrosion, which is the simplest form of corrosion, is an even rate of metal loss over the exposed surface. It is generally thought of as metal loss due to chemical attack or dissolution of the metallic component into metallic ions. For handling chemical media whenever attack is uniform, metals are classified into three groups according to their corrosion rates and intended application. These classifications are as follows:

a. < 0.15 mm/y (< 0.005 ipy) — Metals in this category have good corrosion resistance to the extent that they are suitable for critical parts, for example, valve seats, pump shafts and impellors, springs.

b. 0.15 to 1.5 mm/y (0.005 to 0.05 ipy) — Metals in this group are satisfactory if a higher rate of corrosion can be tolerated, for example, for tanks, piping, valve bodies, and bolt heads

c. > 1.5 mm/y (> 0.05 ipy) — Usually not satisfactory.

2. Pitting. This is a localized type of attack, with the rate of corrosion being greater at some areas than at others. Depth of pitting is sometimes expressed by the pitting factor, the ratio of deepest metal penetration to average metal penetration as determined by the weight loss of the specimen. A pitting factor of unity represents uniform attack

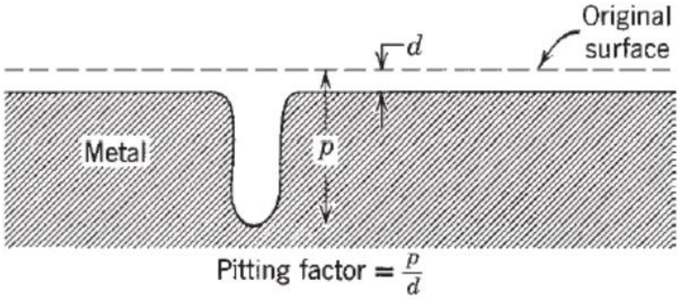
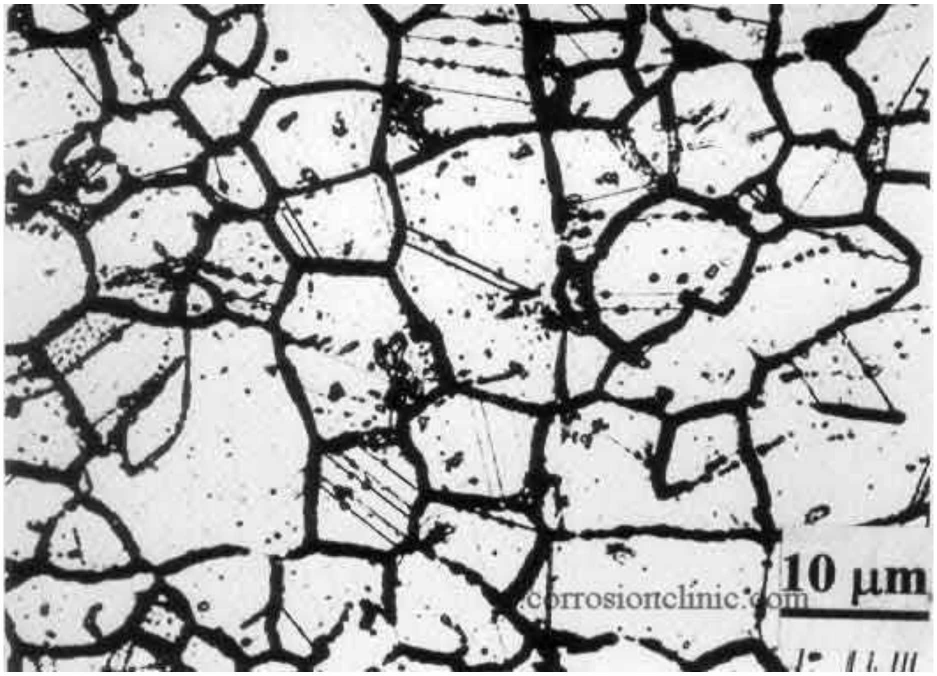


Figure Sketch of deepest pit in relation to average metal penetration and the pitting factor.

3. Dealloying and Dezincification. Dealloying is the selective removal of an element from an alloy by corrosion. One form of dealloying, dezincification, is a type of attack occurring with zinc alloys (e.g., yellow brass) in which zinc corrodes preferentially, leaving a porous residue of copper and corrosion products.

4. Intergranular Corrosion. This is a localized type of attack at the grain boundaries of a metal, resulting in loss of strength and ductility. Grain – boundary material of limited area, acting as anode, is in contact with large areas of grain acting as cathode.



5. Galvanic Corrosion, Dissimilar metals are physically joined in the presence of an electrolyte. The more anodic metal corrodes.

6. Stress Corrosion Cracking, SCC, A structure that has SCC sensitivity, if subjected to stresses and then exposed to a corrosive environment, may initiate cracks and crack growth well below the yield strength of the metal. Consequently, no corrosion products are visible, making it difficult to detect or prevent; fine cracks can penetrate deeply into the part.

7. Erosion-corrosion, Combined chemical attack and mechanical wear (e.g., pipe elbows).

8. Crevice corrosion refers to corrosion occurring in confined spaces to which the access of the working fluid from the environment is limited. These spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals.

CORROSION RTAE EXPRESSION

Corrosion can be expressed in different ways and different units.

1. Mils per year (mpy)

$$\text{mpy} = \frac{534W}{DAT}$$

where W = weight loss, mg
D = density of specimen, g/cm^3
A = area of specimen, sq. in.
T = exposure time, hr

2. Gram per square meter per day (gmd)

$$gmd = \frac{g}{m^2 .day} = \frac{W}{A.T}$$

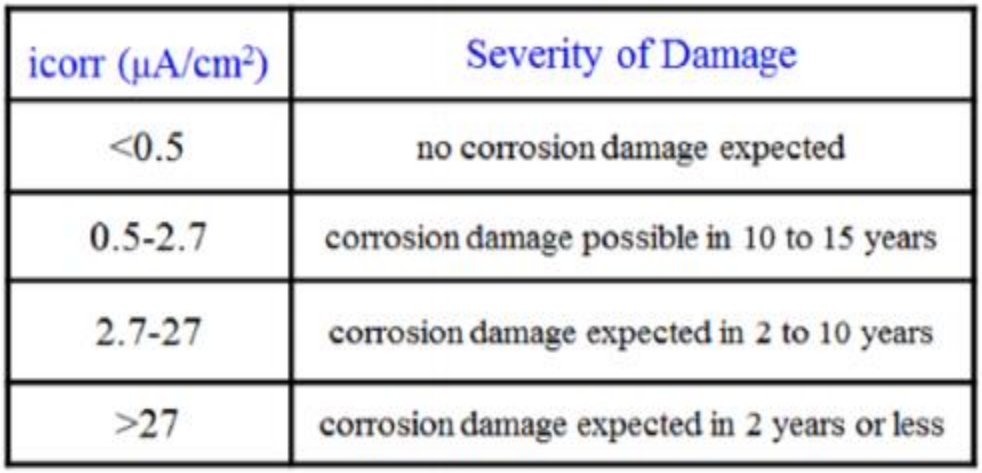
Multiply gmd by 0.365/density (g/cm^3) to obtain mm/y.

3. Milligrams per square decimeter per day (mdd).
4. Millimeters per year (mm/y). (mm/y)×2.74×density (g/cm^3) = gmd.
5. Inches per year (ipy). Multiply inches penetration per year (ipy) by 696 ×density to obtain milligrams per square decimeter per day (mdd). Multiply mdd by 0.00144/density to obtain ipy.
6. Current density (amperes per square area) equivalent to a corrosion rate. 1gmd = 1.117n /M amperes per square meter. $1\,gmd = \frac{1.117\,n}{M}(\frac{A}{m^2})$. where M is the gram atomic weight and n is number of electron.

For example, if the metal is steel or iron, n=2, M=55.85, density=7.88 g/cm^3.

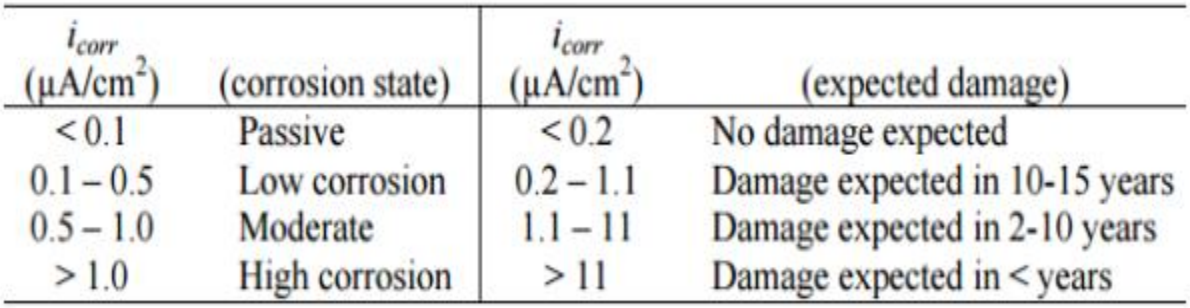
$$1\,gmd = \frac{1.117 \times 2}{55.85} = 0.04\,\frac{A}{m^2} = 4\,\frac{\mu A}{cm^2}$$

Corrosion rate can be used in predicting the severity of damage, for example:



icorr (μA/cm²)	Severity of Damage
<0.5	no corrosion damage expected
0.5-2.7	corrosion damage possible in 10 to 15 years
2.7-27	corrosion damage expected in 2 to 10 years
>27	corrosion damage expected in 2 years or less

Or another example for corrosion of *steel in concrete*:



i_{corr} (μA/cm²)	(corrosion state)	i_{corr} (μA/cm²)	(expected damage)
< 0.1	Passive	< 0.2	No damage expected
0.1 – 0.5	Low corrosion	0.2 – 1.1	Damage expected in 10-15 years
0.5 – 1.0	Moderate	1.1 – 11	Damage expected in 2-10 years
> 1.0	High corrosion	> 11	Damage expected in < years

ATMOSPHERIC CORROSION

INTRODUCTION

In the absence of moisture, iron exposed to the atmosphere corrodes at a negligible rate. For example, steel parts abandoned in the desert remain bright and tarnish - free for long periods of time. Also, the corrosion process cannot proceed without an electrolyte; hence, in climates below the freezing point of water or of aqueous condensates on the metal surface, rusting is negligible. Ice is a poor electrolytic conductor. Incidence of corrosion by the atmosphere depends, however, not only on the moisture content of air, but also on the particulate matter content and gaseous impurities that favor condensation of moisture on the metal surface.

Ambient air quality in the United States has improved dramatically since the Clean Air Act was enacted in 1970. The Environmental Protection Agency (EPA) monitors air quality and compares the data with the National Ambient Air Quality Standards (NAAQS), which have been established for ozone (O_3), carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), lead (Pb), and particulate matter (PM, airborne particles of any composition). Improvements in air quality help to mitigate atmospheric corrosion.

TYPES OF ATMOSPHERES

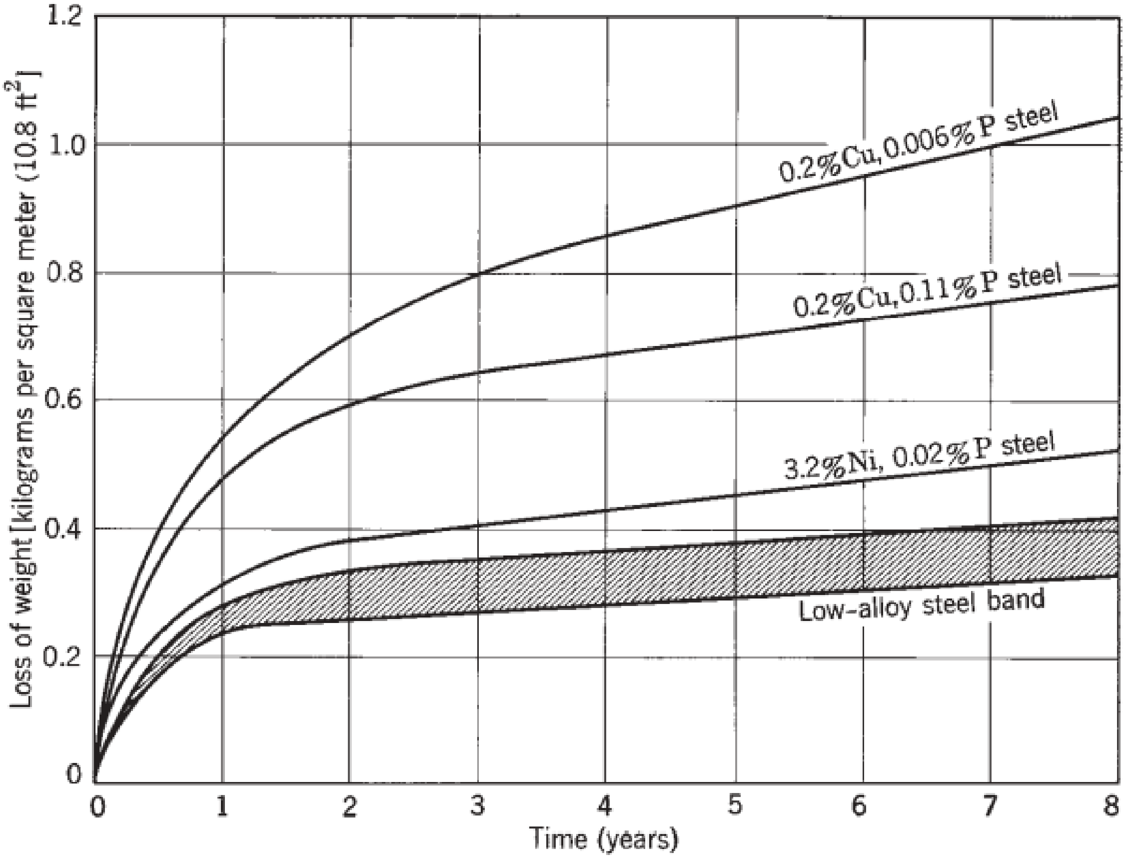
Atmospheres vary considerably with respect to moisture, temperature, and contaminants; hence, atmospheric corrosion rates vary markedly around the world. Approaching the seacoast, air is laden with increasing amounts of sea salt, in particular NaCl. At industrial areas, SO_2, H_2S, NH_3, NO_2 , and various suspended salts are encountered. Approximate concentration ranges of corrosive gases in urban areas are presented in Table below. Acids that can form from these gases include sulfuric acid (H_2SO_4), nitric acid (HNO_3), and organic acids, such as formic acid (HCOOH) and acetic acid (CH_3COOH).

A metal that resists corrosion in one atmosphere may lack effective corrosion resistance elsewhere; hence, relative corrosion behavior of metals changes with location; for example, galvanized iron performs well in rural atmospheres, but is relatively less resistant to industrial atmospheres. On the other hand, lead performs in an industrial atmosphere at least as well as, or better than, elsewhere because a protective film of lead sulfate forms on the surface. Recognition of marked differences in corrosivity has made it convenient to divide atmospheres into types.

The major types are marine, industrial, tropical, arctic, urban, and rural. There are also subdivisions, such as wet and dry tropical, with large differences in corrosivity. Also, specimens exposed to a marine atmosphere corrode at greatly differing rates depending on proximity to the ocean.

Atmospheric Corrosive Gases in Outdoor Urban Environments [1]

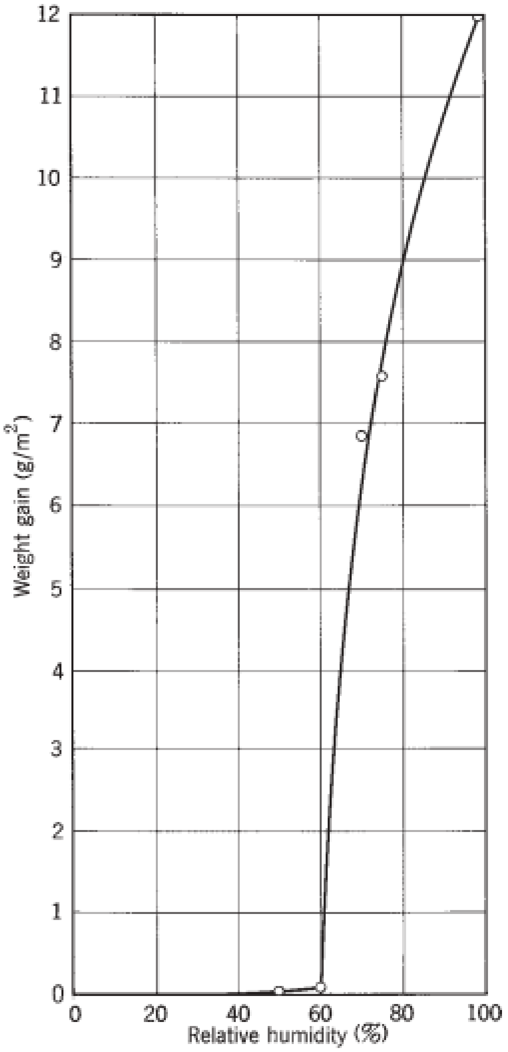
Gas	Approximate Concentration Range (ppbv)
H_2S	0.2–700
SO_2	3–1000
NH_3	1–90
HCl	0.5–100
NO_2	0.5–300
O_3	0.9–600
RCOOH	0.5–30



Atmospheric corrosion of steels as a function of time in an industrial environment

Moisture (Critical Humidity)

From previous discussions, it is apparent that, in an uncontaminated atmosphere at constant temperature, appreciable corrosion of a pure metal surface would not be expected at any value of relative humidity below 100%. Practically, however, because of normal temperature fluctuations (relative humidity increases on decrease of temperature) and because of hygroscopic impurities in the atmosphere or in the metal itself, the relative humidity must be reduced to values much lower than 100% in order to ensure that no water condenses on the surface. In very early studies, Vernon discovered that a critical relative humidity exists below which corrosion is negligible. Experimental values for the critical relative humidity are found to fall, in general, between 50% and 70% for steel, copper, nickel, and zinc. Typical corrosion behavior of iron as a function of relative humidity of the atmosphere is shown in Fig. below. In a complex or severely polluted atmosphere, a critical humidity may not exist.



Corrosion of iron in air containing 0.01% SO_2, 55 days' exposure, showing critical humidity

TYPES OF DRY or CHEMICAL CORROSION:

1. Corrosion by Oxygen or Oxidation corrosion
2. Corrosion by Hydrogen
3. Liquid Metal Corrosion

CORROSION BY OXYGEN or OXIDATION CORROSION:

Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

Mechanism:

1) Oxidation takes place at the surface of the metal forming metal ions

$$M2+ M \rightarrow M2+ + 2e-$$

2) Oxygen is converted to oxide ion ($O2^-$) due to the transfer of electrons from metal.

$$n/2\ O_2 + 2n\ e- \rightarrow n\ O2-\ 3)$$

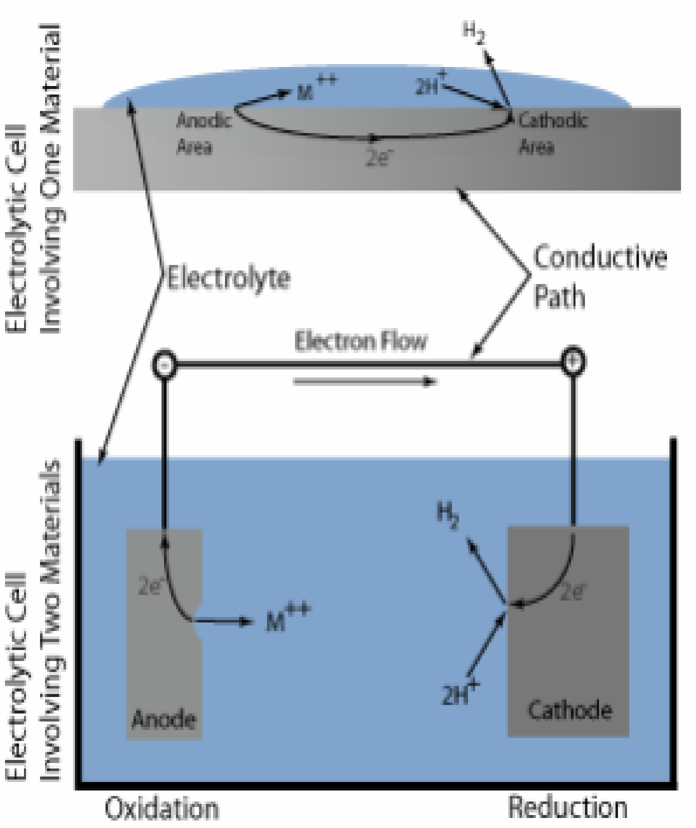
The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

$$2\ M + n/2\ O2 \rightarrow 2\ Mn+ + nO2-$$

The Nature of the Oxide formed plays an important part in oxidation corrosion process.

Metal + Oxygen → Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is



(i) **Stable layer**:

A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (ie., which cuts-off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable, tightly adhering and impervious in nature.

(ii) **Unstable oxide layer:**

This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) **Volatile oxide layer:**

The oxide layer film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO_3 is volatile in nature

(iv) Porous layer:

The layer having pores or cracks. In such a case, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

Corrosion by other gases (by hydrogen):

1) Hydrogen Embrittlement:

Loss in ductility of a material in the presence of hydrogen is known as hydrogen embrittlement.

Mechanism:

This type of corrosion occurs when a metal is exposed to hydrogen environment. Iron liberates atomic hydrogen with hydrogen sulphide in the following way.

$$\mathbf{Fe + H_2S \rightarrow FeS + 2H}$$

Hydrogen diffuses into the metal matrix in this atomic form and gets collected in the voids present inside the metal. Further, diffusion of atomic hydrogen makes them combine with each other and forms hydrogen gas.

$$\mathbf{H + H \rightarrow H_2\uparrow}$$

Collection of these gases in the voids develops very high pressure, causing cracking or blistering of metal.

2) decarburization:

The presence of carbon in steel gives sufficient strength to it. But when steel is exposed to hydrogen environment at high temperature, atomic hydrogen is formed.

$$H_2 \text{ Heat} \rightarrow 2H$$

Atomic hydrogen reacts with the carbon of the steel and produces methane gas.

$$C + 4H \rightarrow CH4$$

Hence, the carbon content in steel is decreases. The process of decrease in carbon content in steel is known as decarburization.

Collection of methane gas in the voids of steel develops high pressure, which causes cracking. Thus, steel loses its strength.

3) Liquid metal corrosion:

This is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occur in devices used for nuclear power. The corrosion reaction involves either:

(i) dissolution of a solid metal by a liquid metal or
(ii) Internal penetration of the liquid metal into the solid metal.

Both these modes of corrosion cause weakening of the solid metal.

Hydorgen Evolution Type:

All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen. It occurs in acidic environment. Consider the example of iron

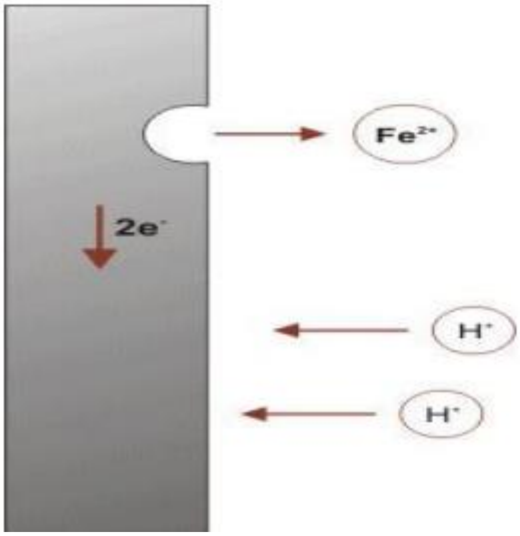
At anode: $Fe \rightarrow Fe^{2+} + 2e$

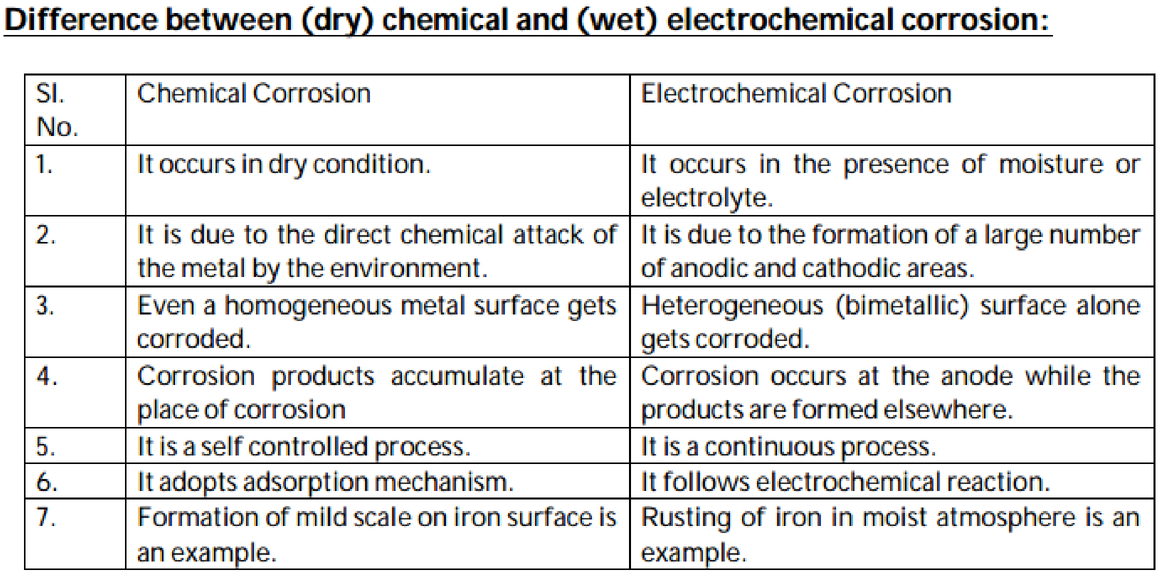
These electrons flow through the metal, from anode to cathode, where H+ ions of acidic solution are eliminated as hydrogen gas.

At cathode: $2\,H^+ + 2\,e^- \rightarrow H_2\uparrow$

The overall reaction is:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$





Difference between (dry) chemical and (wet) electrochemical corrosion:

Sl. No.	Chemical Corrosion	Electrochemical Corrosion
1.	It occurs in dry condition.	It occurs in the presence of moisture or electrolyte.
2.	It is due to the direct chemical attack of the metal by the environment.	It is due to the formation of a large number of anodic and cathodic areas.
3.	Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
4.	Corrosion products accumulate at the place of corrosion	Corrosion occurs at the anode while the products are formed elsewhere.
5.	It is a self controlled process.	It is a continuous process.
6.	It adopts adsorption mechanism.	It follows electrochemical reaction.
7.	Formation of mild scale on iron surface is an example.	Rusting of iron in moist atmosphere is an example.

Corrosion Prevention and Control

Four primary techniques are used for limiting corrosion rates to practical levels:

1. Material Selection
2. Coatings
3. Cathodic Protection
4. Chemical Corrosion Inhibitors

1. Material selection

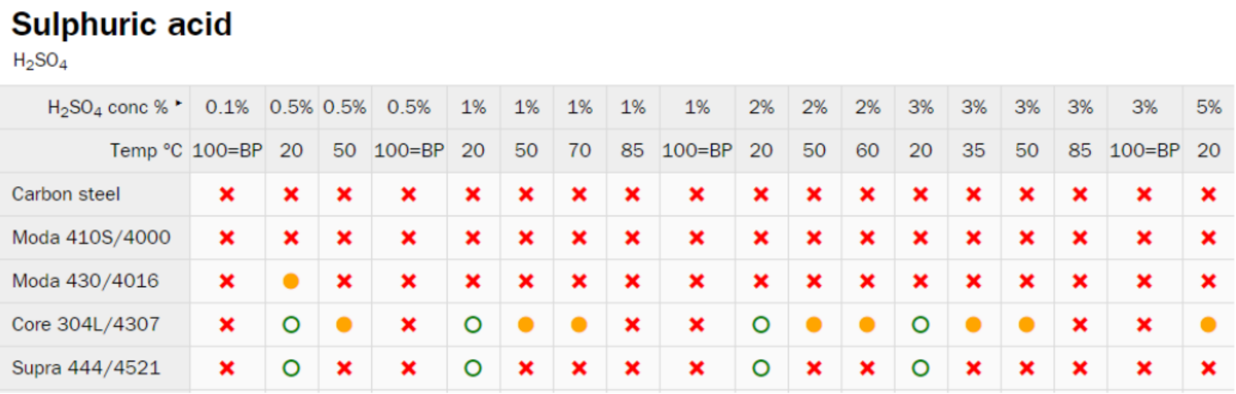
* entails picking an engineering material – either metal alloy or non-metal – that is inherently resistant to the particular corrosive environment and also meets other criteria.

* Variables that will affect corrosion are established along with materials that may provide suitable resistance for those conditions.

* Obviously other requirements such as cost and mechanical properties of the potential materials must be considered.

* Data needed to thoroughly define the corrosive environment include many of its chemical and physical characteristics plus application variables such as its velocity (or is it ever Stagnant?) And possible extremes caused by upset conditions.

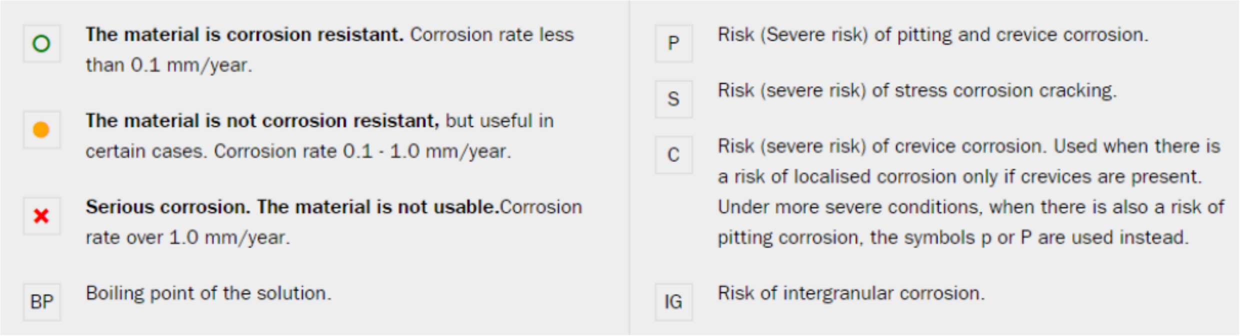
* Corrosion tables may be helpful tools for material selection in different environments. These tables are available in handbooks and internet.



Sulphuric acid

H_2SO_4

H_2SO_4 conc % ‣	0.1%	0.5%	0.5%	0.5%	1%	1%	1%	1%	1%	2%	2%	2%	3%	3%	3%	3%	3%	5%
Temp °C	100=BP	20	50	100=BP	20	50	70	85	100=BP	20	50	60	20	35	50	85	100=BP	20
Carbon steel	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖
Moda 410S/4000	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖
Moda 430/4016	✖	●	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖	✖
Core 304L/4307	✖	○	●	✖	○	●	●	✖	✖	○	●	●	○	●	●	✖	✖	●
Supra 444/4521	✖	○	✖	✖	○	✖	✖	✖	✖	○	✖	✖	○	✖	✖	✖	✖	✖



○	**The material is corrosion resistant.** Corrosion rate less than 0.1 mm/year.	P	Risk (Severe risk) of pitting and crevice corrosion.
●	**The material is not corrosion resistant,** but useful in certain cases. Corrosion rate 0.1 - 1.0 mm/year.	S	Risk (severe risk) of stress corrosion cracking.
✖	**Serious corrosion. The material is not usable.**Corrosion rate over 1.0 mm/year.	C	Risk (severe risk) of crevice corrosion. Used when there is a risk of localised corrosion only if crevices are present. Under more severe conditions, when there is also a risk of pitting corrosion, the symbols p or P are used instead.
BP	Boiling point of the solution.	IG	Risk of intergranular corrosion.

2. Coatings

* Are the most widely used method for controlling corrosion.

* The possibilities cover a wide range and include such things as paints of many types, Electroplating, weld overlays and bonding a thin, corrosion-resistant metal or non-metal onto a stronger substrate metal that is susceptible to corrosion.

* In many cases the coating simply acts as a barrier between the corrosive environment and the substrate material. In some cases such as in galvanized steel the coating (zinc in this case) provides a barrier but it also acts as a sacrificial anodic material to protect the steel below by preferentially corroding instead of the steel. This effect is cathodic protection.

* The coating selection, surface preparation, application and proper quality control throughout the process to attain an optimal coating for the given application requires special experience.

3. Cathodic protection

* Cathodic protection is a corrosion control technology with a long history. It functions due to a fundamental characteristic of corrosion, i.e., when the electrochemical process of corrosion occurs there is a flow of DC electric current from the surface being attacked.

* Cathodic protection (often known as CP) provides a flow of DC current onto the protected surface to counteract corrosion current flow. The resulting rate of corrosion is greatly reduced to allow practical, long-term use of the protected metal, e.g., for 10 to 20 years or more, although corrosion is not stopped. The amount of current necessary to be supplied to the surface to control the rate to practical levels depends on the area exposed. Thus CP is most often used in conjunction with some type of coating. This greatly lowers the current needed for protection. No coating is 100% free of small areas where the substrate is exposed. Using CP with a coating means current is only needed at these bare spots.

* There are two types of CP. One is the sacrificial anode (also called galvanic) type in which a metal more susceptible to corrosion in the given electrolyte is electrically connected to a less susceptible metal to be protected. The former metal becomes the anode and is consumed over time while the latter metal becomes the cathode in a galvanic corrosion cell. Thus the zinc on galvanized steel is the anode while the steel substrate – as the cathode – is protected.

* The second type of CP is impressed current CP. Here an electric power rectifier is used to lower the voltage of AC line voltage feed to it while changing the AC to DC current. The rectifier is connected to non-consumable anodes that supply DC current to the metal surface to be protected.

* Each type of CP has its separate advantages and disadvantages.

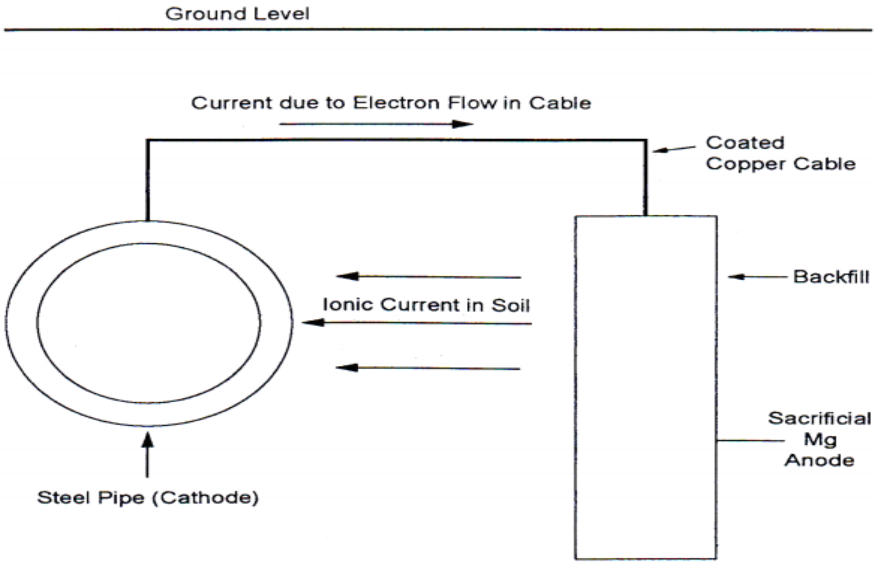


Fig. Principle of cathodic protection with sacrificial anodes

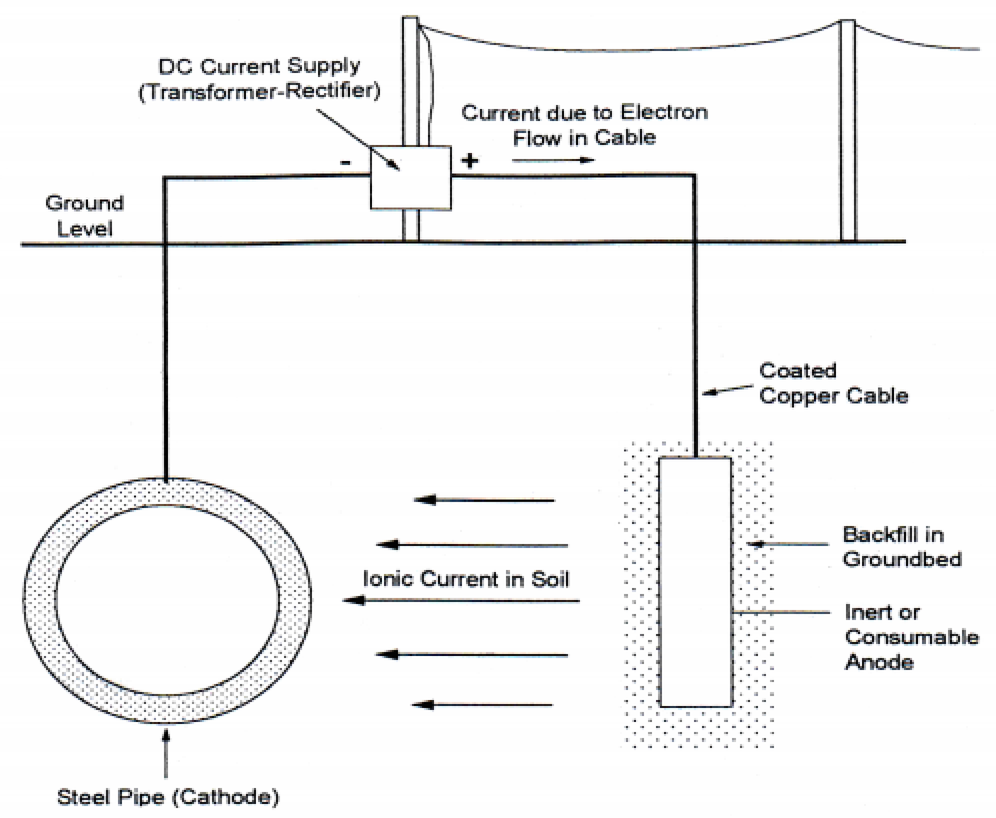


Fig. Principle of cathodic protection with impressed current

4. Chemical Corrosion Inhibitors

* Corrosion inhibitors are solid, liquid or gaseous compounds that are added in small quantities to the given corrosive environment to change its interaction with the metal to be protected.

* Corrosion is an electrochemical process that consists of an oxidation reaction on the anodic site (or sites) of the metal plus one or more reduction reactions on the cathodic site (or sites). These two types of reactions must always occur at the same rate. An effective inhibitor functions by chemically changing one or both of the two reactions so as to slow their rates. Thus the rate of the overall corrosion reaction is reduced to practical levels when a proper inhibitor is applied.

* using too much or too little can each have negative consequences.

* Inhibitors are most often used in circulating cooling water systems or to treat steam boiler feed water before usage in a boiler. Also can be used in acidic systems, such as, pickling and oil well acidifications.

4.1 Types of Corrosion Inhibitors:

Inhibitors can be classified, as described above, as:

A. Adsorption Inhibitors, which are generally organic compounds, their action is due to blanketing effect over the entire surface of metal, i.e. both anodic and cathodic areas, separating the metal surface from the action of aggressive ions in solution, sometimes cause a considerable reduction in corrosion rate.

B. Filming Forming Inhibitors, their action are appear to act by causing a barrier, or blocking film to be formed of material other than the actual inhibiting species itself, and as mentioned above, it may sub classified as

(a) Anodic film inhibitors, their function in neutral or alkaline solution and act by producing a passivating oxide film primarily at those parts of the surface where metal cations are formed, i.e. at the anodic sites.

(b) Cathodic film inhibitors, they act by inhibiting the cathodic regions without greatly affecting the anodic sites. They are operating by filming the cathodic areas.

C. Vapor Phase Inhibitors, these are substance of low but significant vapor pressure, the vapor of which has corrosion inhibiting properties. They are used to protect critical machine parts, such as ball bearings or other manufactured steel articles, temporarily against rusting by moisture during shipping or storage. On contact with the metal surface the inhibitor vapor condenses and forms the protective layer.

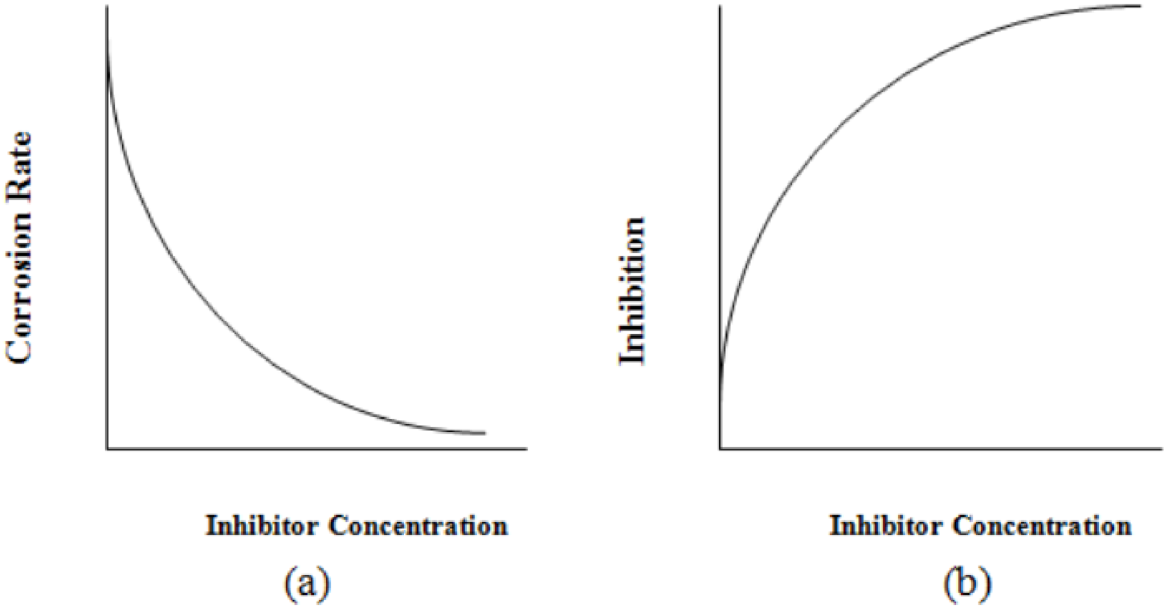


Fig. a- Typical Curves showing drop in corrosion rate as a function of inhibitor concentration.
b- Typical curves showing increased efficiency as a function of inhibitor concentration.

ELECTRODE POTENTIAL

* The absolute value of electrode potential cannot be measured.

* In order to measure the potential difference across the metal/solution interface of interest, we must choose one electrode as reference electrode.

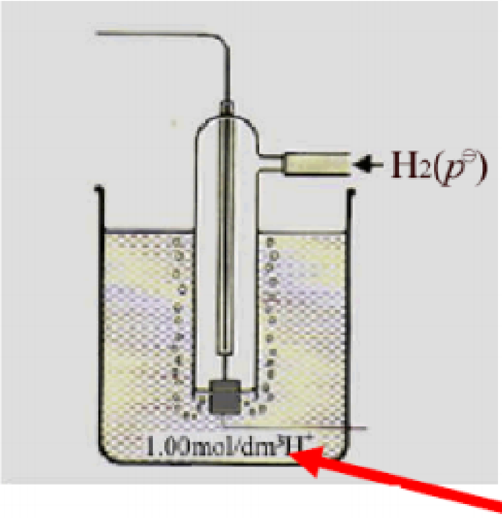
*The relative electrode potential can be obtained by measuring the electrode potential vs. a standard reference electrode.

* Internationally, a standard hydrogen electrode (SHE), which potential is defined to be zero, is used as a standard reference electrode.

There are several types of reference electrode:

① *Standard hydrogen electrode (SHE)*

$$\mathrm{Pt}\ |\ H_2\ (p=100\mathrm{kPa})\ |\ H^+\ (c=1\mathrm{mol{\cdot}L^{-1}})$$



$$2H^+(aq) + 2e \rightleftharpoons H_2$$

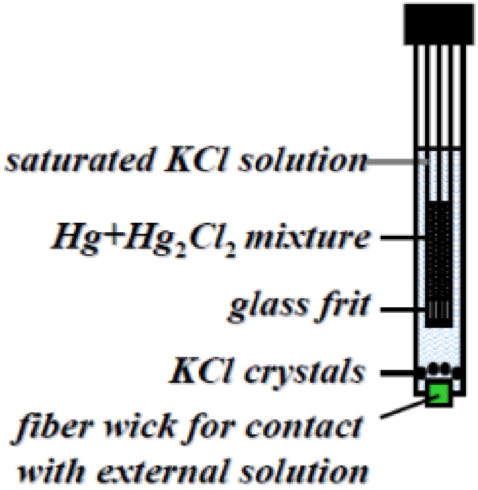
$$c = 1\ \mathrm{mol{\cdot}L^{-1}} \qquad p_{H2} = p^{\theta} = 100\ \mathrm{kPa}$$

Define: $\phi^{\theta}(H^+/H_2) = 0.0V$

Platinized Pt,

H_2 is constantly bubbled into a 1 M HCl solution

②Saturated calomel electrode (SCE)



$$Cl^-(c)\,|\,Hg_2Cl_2(s)\,|\,Hg(l)$$

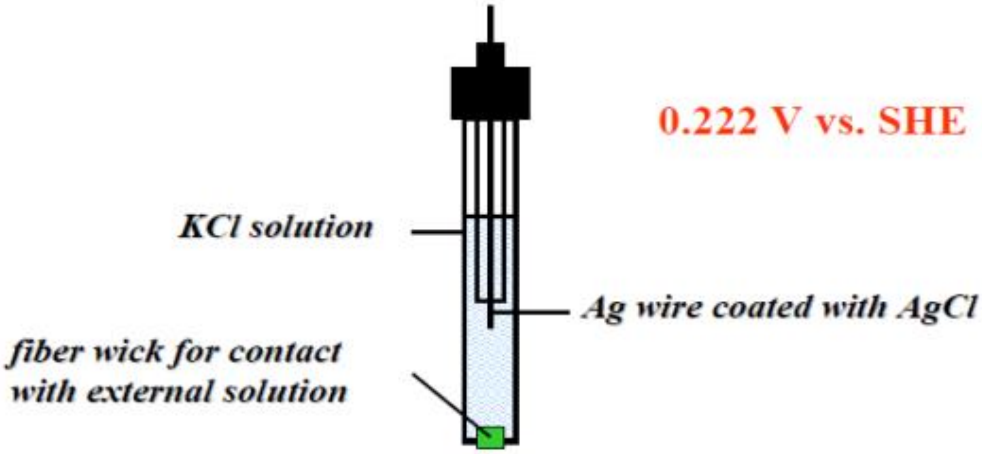
$$Hg_2Cl_2(s) + 2e^- = 2Hg(l) + 2Cl^-(aq$$

0.242 V vs. SHE

$$\phi\,(Hg_2Cl_2/Hg) = \phi^{\theta}(Hg_2Cl_2/Hg) - \frac{RT}{nF}\ln\frac{c(Cl^-)}{c^{\theta}}$$

③ Silver-silver chloride electrode

0.222 V vs. SHE



$$AgCl(s) + e^- = Ag(s) + Cl^-(aq)$$

$$\varphi(AgCl/Ag) = \varphi^{\theta}(AgCl/Ag) - \frac{RT}{nF}\ln\frac{c(Cl^-)}{c^{\theta}}$$

$$\varphi^{\theta}(AgCl/Ag) = 0.222\ V$$

Standard electrode potential

- The standard electrode potential (φ^o) is the potential under standard state conditions
- For an electrochemical cell, standard state conditions are:

- solutes at 1 M concentrations
- gases at 1 atm partial pressure
- solids and liquids in pure form

} **The activities of all these species are 1**

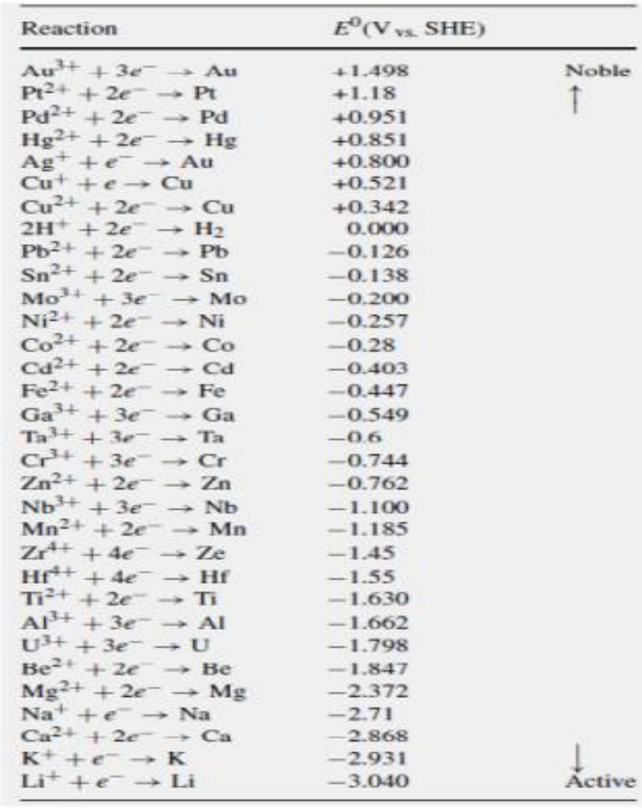
- all at some specified temperature, usually 298 K

The standard potential of most half cell reactions can be obtained in the handbook

The Electromotive Force Series

An ordered listing of the standard half-cell potentials is called the **electromotive force (emf) series**

The metals located near the top (positive end) of the emf series are more chemically stable than metals located near the bottom (negative end) . Said simply, metals near the top of the emf series are less prone to corrosion.



Reaction	$E^0(V_{vs.}\ SHE)$	
$Au^{3+} + 3e^- \rightarrow Au$	+1.498	Noble
$Pt^{2+} + 2e^- \rightarrow Pt$	+1.18	↑
$Pd^{2+} + 2e^- \rightarrow Pd$	+0.951	
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.851	
$Ag^+ + e^- \rightarrow Au$	+0.800	
$Cu^+ + e \rightarrow Cu$	+0.521	
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.342	
$2H^+ + 2e^- \rightarrow H_2$	0.000	
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126	
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.138	
$Mo^{3+} + 3e^- \rightarrow Mo$	−0.200	
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257	
$Co^{2+} + 2e^- \rightarrow Co$	−0.28	
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403	
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447	
$Ga^{3+} + 3e^- \rightarrow Ga$	−0.549	
$Ta^{3+} + 3e^- \rightarrow Ta$	−0.6	
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744	
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.762	
$Nb^{3+} + 3e^- \rightarrow Nb$	−1.100	
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.185	
$Zr^{4+} + 4e^- \rightarrow Ze$	−1.45	
$Hf^{4+} + 4e^- \rightarrow Hf$	−1.55	
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.630	
$Al^{3+} + 3e^- \rightarrow Al$	−1.662	
$U^{3+} + 3e^- \rightarrow U$	−1.798	
$Be^{2+} + 2e^- \rightarrow Be$	−1.847	
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372	
$Na^+ + e^- \rightarrow Na$	−2.71	
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868	
$K^+ + e^- \rightarrow K$	−2.931	↓
$Li^+ + e^- \rightarrow Li$	−3.040	Active

The limitations of emf series

The emf series is applied to pure metals in their own ions at unit activity. The relative ranking of metals in the emf series is not necessarily the same (and is usually not the same) in other media (such as seawater, groundwater, sulfuric acid, artificial perspiration).

The emf series is applied to pure metals only and not to metallic alloys. The relative ranking of metals in the emf series gives corrosion tendencies but provides no information on corrosion rates.

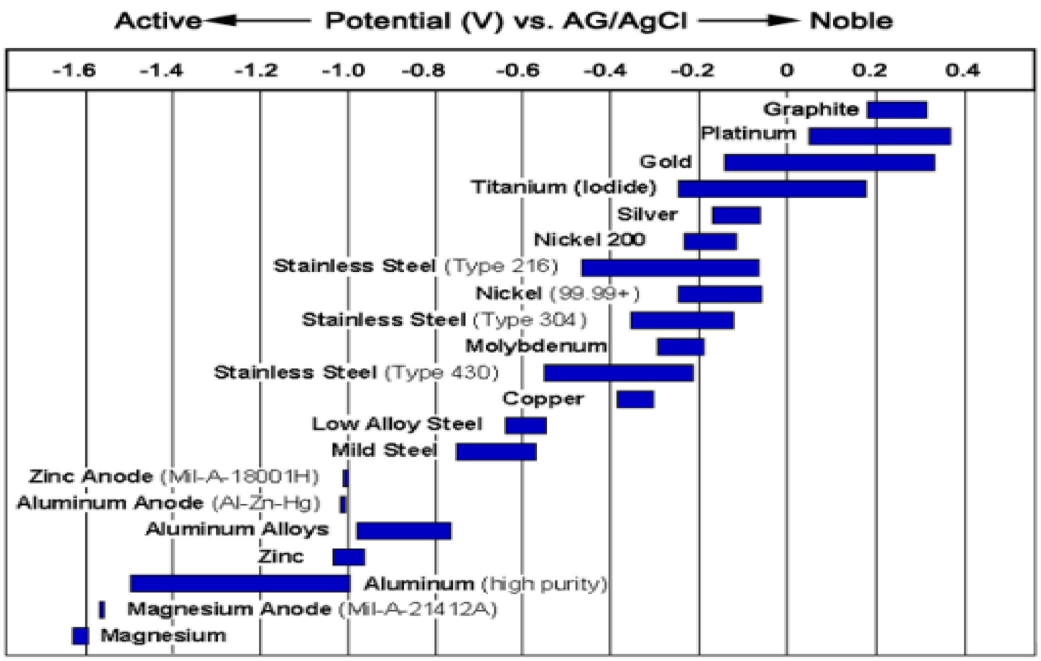
Galvanic Series

Because of the limitations of the Emf Series for predicting galvanic relations, and also because alloys are not included, the Galvanic Series has been developed.

*The Galvanic Series is an arrangement of metals and alloys in accord with their actual measured potentials in a given environment.

*The Galvanic Series for metals in seawater is given in Figure below.

* Some metals occupy two positions in the Galvanic Series, depending on whether they are active or passive, whereas in the Emf Series only the active positions are possible



MEASUREMENT OF pH

Hydrogen ion activity is commonly expressed, for convenience, in terms of pH, defined as

$$\mathrm{pH} = -\log(\mathrm{H}^+)$$

Hence, for the half - cell reaction, with the pressure of hydrogen equal to 1 atm, we have

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2$$

$$\phi_{\mathrm{H}_2} = -0.0592\,\mathrm{pH}$$

Example:

Consider a galvanic cell that uses the reaction:

$Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$

$[Fe^{3+}] = 1.0 \times 10^{-4}$ M $[Cu^{2+}] = 0.25$ M $[Fe^{2+}] = 0.20$ M

What is the potential of a cell at 25 °C that has the following ion concentrations? What is K, reaction quotient (equilibrium constant)?

Solution:

$$\mathrm{K} = \frac{[Cu^{2+}] \times [Fe^{2+}]^2}{[Fe^{3+}]^2} = \frac{(0.25) \times (0.20)^2}{(0.00010)^2} = 1.00 \times 10^6$$

Notice that solid copper is omitted.

Cell is not under standard conditions, so the Nernst Equation must be used:

$$E = E^o cell - \frac{0.0592}{n} \log \mathrm{K}$$

$E^o_{cell} = E^o cathode - E^o anode$ (What should it be under standard conditions)

$E^o_{cell} = 0.77\ V - 0.34\ V = 0.43\ V$

Total of 2 electrons transferred, n = 2

$$E = 0.43\,V - \frac{0.0592\,V}{2}\log(1.00 \times 10^6) = 0.43\,V - 0.0296\,V \times 6 = 0.25\,V$$

Example:

Calculate the EMF of the cell

$Zn(s) \mid Zn^{2+}\ (0.024\ M) \parallel Zn^{2+}\ (2.4\ M) \mid Zn(s)$

Solution

$Zn^{2+}\ (2.4\ M)\ +\ 2\ e\ =\ Zn$ Reduction

$Zn\ =\ Zn^{2+}\ (0.024\ M) +\ 2\ e$ Oxidation

$Zn^{2+}\ (2.4\ M)\ =\ Zn^{2+}\ (0.024\ M),\ \Delta E^{o} = 0$ Net reaction

Using the Nernst equation:

$$\Delta E = \Delta E^{o} - \frac{0.0592}{2}\log\frac{0.024}{2.4} = (-0.296)(-2) = 0.0592\ V$$

The Zn^{2+} ions try to move from the concentrated half-cell to a dilute solution. That driving force gives rise to 0.0592 V.

POURBAIX DIAGRAM

* Pourbaix diagram, also known as a potential/pH diagram, EH -pH diagram or a pE/pH diagram, maps out possible stable (equilibrium) phases of an aqueous electrochemical system.

* Pourbaix diagram can be read much like a standard phase diagram with a different set of axes.

* The Nernst equation forms the basis of developing thermodynamic “stability” of Pourbaix Diagrams

* Thus, a Pourbaix Diagram is constructed by looking at the thermodynamics of a system on

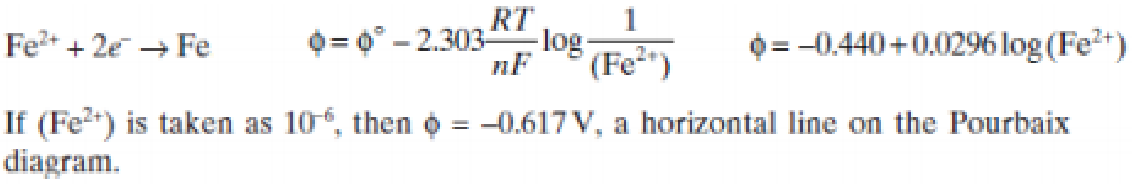
E vs pH axes.

* Pourbaix Diagram is a thermodynamic map of corrosion, passivity and nobility of a particular metal as a function of system pH and potential.

* In constructing Pourbaix diagrams, the concentration of the ionic species at the boundary between a solid substance and a dissolved substance is usually taken as a very low value, such as 10^{-6} M

POURBAIX DIAGRAM FOR IRON

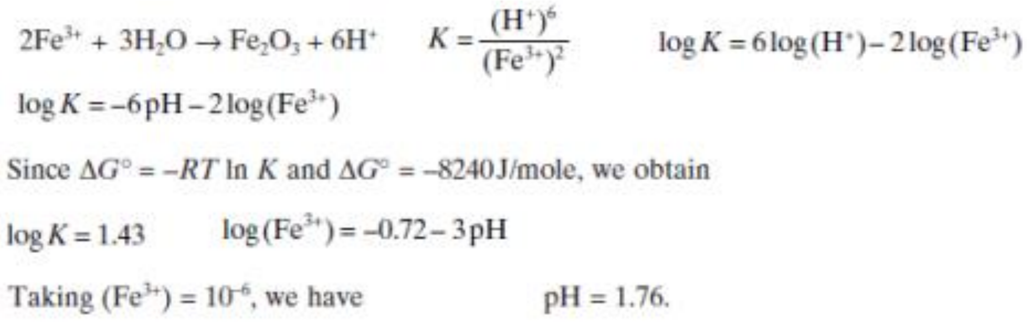
* A horizontal line represents a reaction that does not involve pH; that is, neither H +nor OH − is involved, as in the reaction, For this equilibrium, using the Nernst equation, we obtain A vertical line involves H + or OH -



$$Fe^{2+} + 2e^- \rightarrow Fe \qquad \phi = \phi^\circ - 2.303\frac{RT}{nF}\log\frac{1}{(Fe^{2+})} \qquad \phi = -0.440 + 0.0296\log(Fe^{2+})$$

If (Fe^{2+}) is taken as 10^{-6}, then $\phi = -0.617$ V, a horizontal line on the Pourbaix diagram.

*A vertical line involves H+or OH -, but not electrons. In Figure, the vertical line separating Fe3+ from Fe2 O3 corresponds to this reaction.



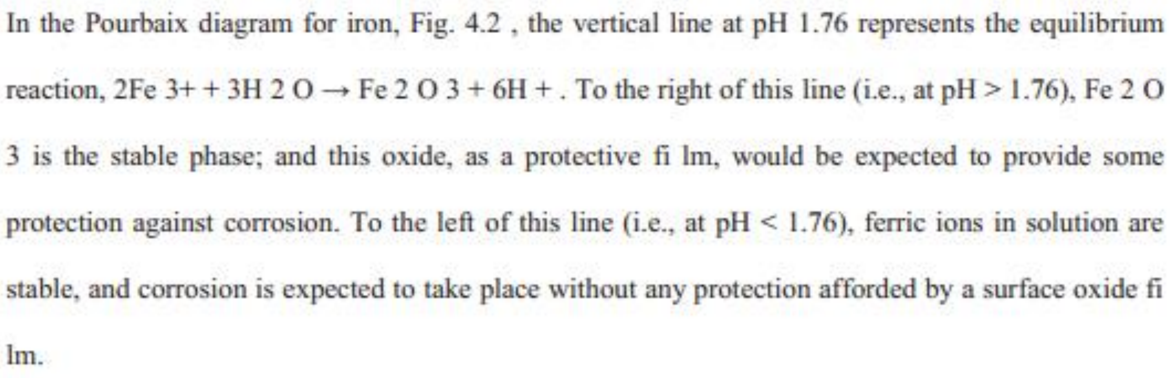
$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ \qquad K = \frac{(H^+)^6}{(Fe^{3+})^2} \qquad \log K = 6\log(H^+) - 2\log(Fe^{3+})$$

$$\log K = -6\,pH - 2\log(Fe^{3+})$$

Since $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = -8240$ J/mole, we obtain

$$\log K = 1.43 \qquad \log(Fe^{3+}) = -0.72 - 3pH$$

Taking $(Fe^{3+}) = 10^{-6}$, we have $pH = 1.76.$



In the Pourbaix diagram for iron, Fig. 4.2 , the vertical line at pH 1.76 represents the equilibrium reaction, 2Fe 3+ + 3H 2 O → Fe 2 O 3 + 6H + . To the right of this line (i.e., at pH > 1.76), Fe 2 O 3 is the stable phase; and this oxide, as a protective film, would be expected to provide some protection against corrosion. To the left of this line (i.e., at pH < 1.76), ferric ions in solution are stable, and corrosion is expected to take place without any protection afforded by a surface oxide film.

*A sloping line involves H +, OH -, and electrons.

$$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O \qquad \phi = \phi^\circ - 2.303\frac{RT}{nF}\log\frac{(Fe^{2+})^2}{(H^+)^6}$$

Since $\phi^\circ = 0.728$ V and $n = 2$, we get

$$\phi = 0.728 - 0.0296\,(Fe^{2+})$$

$$\phi = 0.728 - \frac{0.0592}{2}\log(Fe^{2+})^2 + \frac{0.0592}{2}\log(H^+)^6$$

$$\phi = 0.728 - 0.0592\log(Fe^{2+}) - 0.1776\,pH$$

Taking $(Fe^{2+}) = 10^{-6}$, we obtain

$$\phi = 1.082 - 0.1776\,pH$$

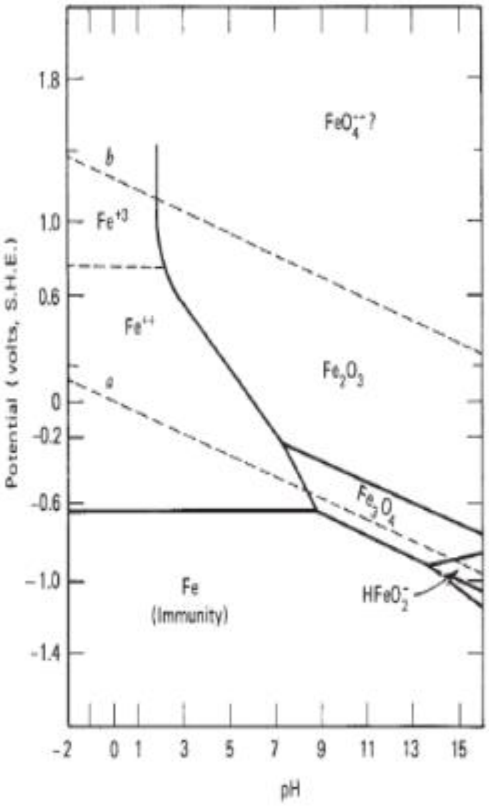


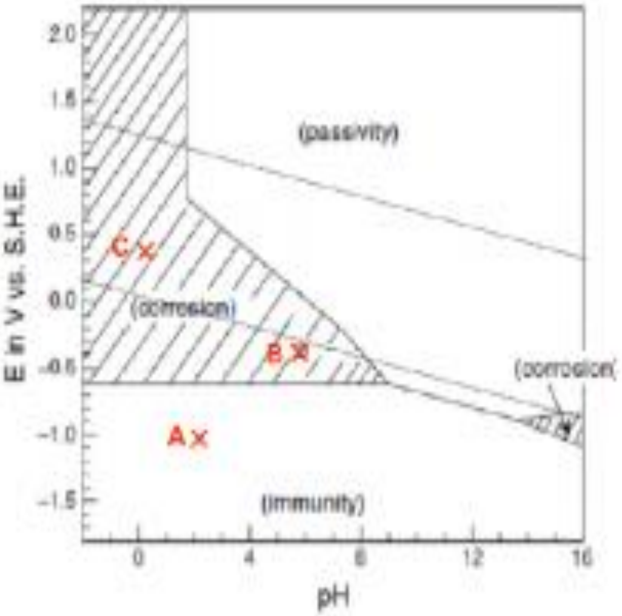
Figure Pourbaix diagram for the iron–water system at 25°C, considering Fe, Fe_3O_4, and Fe_2O_3 as the only solid substances.

Case study and application of Porbaix Diagram:

- **Point A:** Fe and H_2 are stable, Fe don't corrode.
- **Point B:** Fe^{2+} and H_2 are stable, Fe occur corrosion with evolution of H_2.

$$Fe = Fe^{2+} + 2e \text{ (anode)}$$

$$2H^+ + 2e = H_2 \text{ (cathode}$$

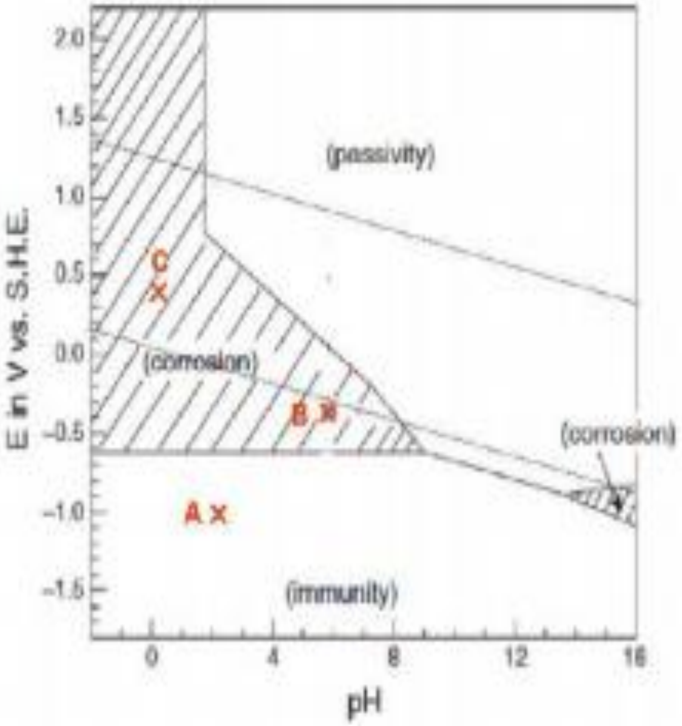


- **Point C:** Fe^{2+} and H_2O are stable, Fe occur corrosion with reduction of O_2.

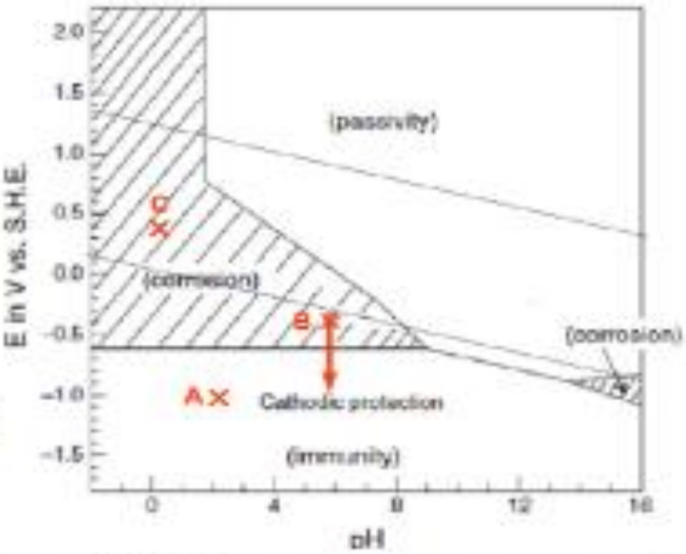
$$Fe = Fe^{2+} + 2e \text{ (anode)}$$

$$O_2 + 4H^+ + 4e = 2H_2O \text{ (cathode)}$$

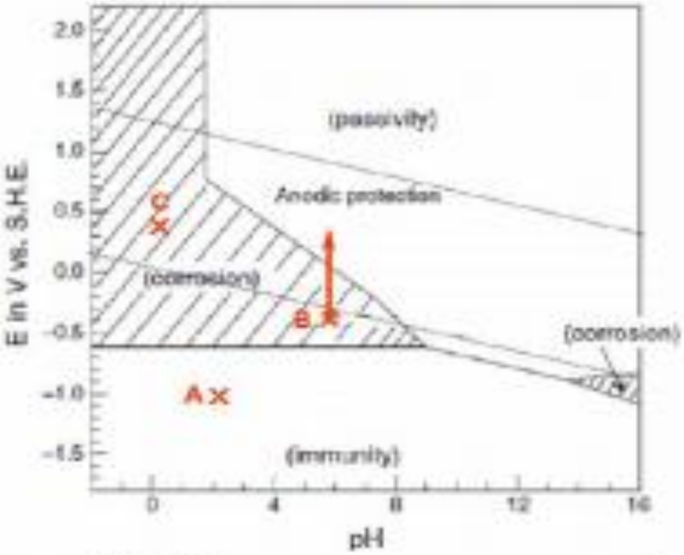
At Point B: a pH of 6.0 and an electrode potential of –0.4 V vs. SHE corresponds to a region of corrosion as Fe^{2+} ions.



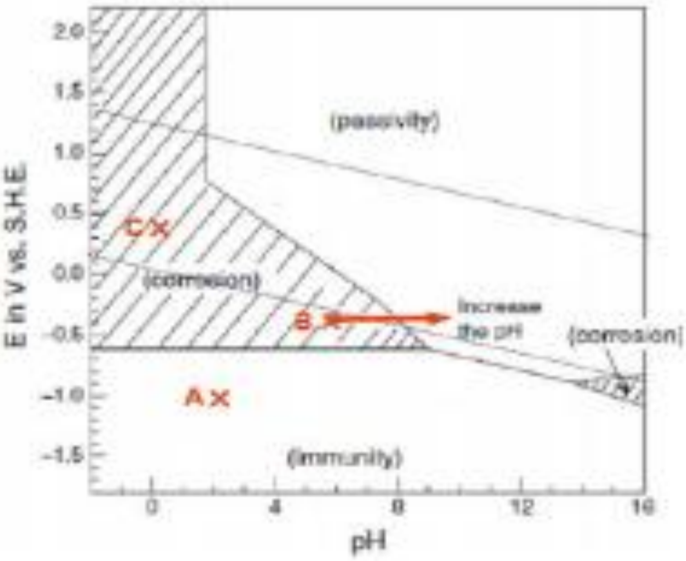
(1) Lower potential: If the electrode potential is changed in the negative direction to a value below –0.7 V SHE, the iron electrode is forced into a region of immunity. This process is called ***cathodic protection***



(2) Enhance potential: If the electrode potential is changed in the positive direction to values above approximately 0.0 V vs. SHE, the iron electrode is forced into a region of passivity. This process is called ***anodic protection***



(3) Increase pH: The third method of protection is to change the pH of the aqueous solution. If the pH is increased to approximately 8 or higher, the iron electrode will then also reside in a region of passivity



POLARIZATION AND CORROSION RATES

POLARIZATION

When there is no net current flows from an electrode, then this electrode is at equilibrium state and its potential is the equilibrium potential (E^0). When net current flows to or from its surface, the potential changes from E^0 to Ei , the electrode is then said to be polarized and the process is termed as polarization. Polarization is measured in volts as follows:

$$\eta = E_i - E^\circ \qquad (1)$$

Where:

η = The overvoltage, and E_i = The polarization potential

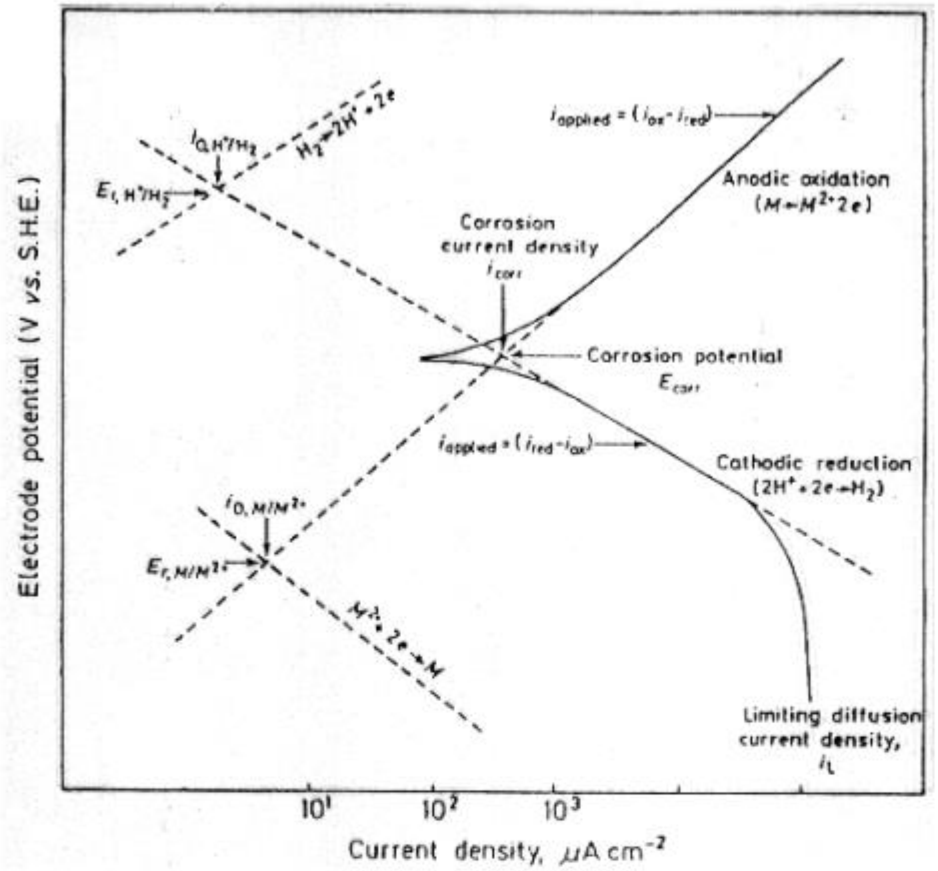


Fig. Electrode Kinetic Behavior of a Metal (M) in Reducing Acid

Above Figure shows polarization curves (E vs. log i) for the corrosion of metal in a reducing acid in which there are two exchange processes involving oxidation of M/M+and reducing H+/H2 .Polarization is divided into three main types:

1. ACTIVATION POLARIZATION (η_A):

This polarization is caused by a slow electrode reaction or stated in another way. The reaction at the electrode requires activation energy in order to go. The most important is that of hydrogen ion reduction at the cathode ; reaction might be considered as:

$$\underset{\text{Ions}}{2\,H^+} + 2e \xrightarrow[\text{Stage (1)}]{} \underset{\text{Absorbed on Metals}}{2\,H} \xrightarrow[\text{Stage (2)}]{} \underset{\text{Gas}}{H_2} \qquad (2)$$

Stage (1) occurs rapidly, whereas stage (2) is generally the slower and rate-controlling step.

The activation overpotential, and hence the activation energy varies exponentially with the rate of charge transfer per unit area of electrode surface, as defined by the well-known Tafel equation (70):

$$\eta_a = \pm\ \beta \log\left(\frac{i}{i_o}\right) \qquad (3)$$

Where:

i = The current density, and

β = The Tafel constant being equal to $\left(2.303\ \frac{R\ T}{\alpha\ Z\ F}\right)$

The Tafel constant (β) varies with the nature of the electrode process and with the nature of the solution. Thus (η_A) will be linearly related to (log i) at overpotential greater than 0.05 V and the position of the curve will be dependent on the equilibrium exchange current density (i_o), the transfer coefficient (α) and the number of electrons (z) involved in one act of the rate determining step. The Tafel equation for a cathodic process can be expressed in the form:

$$\boxed{\eta_{Ac} = \frac{R\ T}{\alpha\ z\ F}\ln i_o - \frac{R\ T}{\alpha\ z\ F}\ln i_c} \qquad (4)$$

Similarly for the anodic process:

$$\boxed{\eta_{act} = -\frac{R\,T}{(1-\alpha)\,z\,F}\ln i_o + \frac{R\,T}{(1-\alpha)\,z\,F}\ln i_a} \qquad (5)$$

HYDROGEN OVERPOTENTIAL

The polarization term that controls the corrosion rate of many metals in deaerated water and in nonoxidizing acids is hydrogen overpotential. In accord with the previously discussed definition of polarization, hydrogen overpotential is the difference of potential between a cathode at which hydrogen is being evolved, Ei , and a hydrogen electrode at equilibrium in the same solution; that is,

$$\eta_{H_2} = E_i - E^o_{H_2} = E_i - (-0.059\ pH) = E_i + 0.059\ pH$$

2. CONCENTRATION POLARIZATION (η_C):

Concentration polarization is obtained when the rate of an electrode reaction is dependent on mass transfer, i.e. the rate at which the reactant is transported to the surface of the electrode and the rate at which the product is transported away from the electrode. For concentration polarization reaction current is given by Fick's law:

$$|I| = z\,F\,D\,A\left(\frac{d\,C}{d\,x}\right) \qquad (6)$$

Or its equivalent

$$|I| = z\,F\,D\,A\left(\frac{C_b - C_s}{\delta}\right) \qquad (6.a)$$

The limiting current, i.e., the maximum current under diffusion control is obtained when $C_s = 0$.

$$|I_L| = z\,F\,D\,A\,\frac{C_b}{\delta} \qquad (6.b)$$

Or

$$|I_L| = z\,F\ A\ k\ C_b \qquad (7)$$

Where the mass transfer coefficient is defined as:

$$k = \frac{D}{\delta} \qquad (8)$$

The concentration polarization can also be expressed as:

$$\eta_c = \frac{R\,T}{z\,F}\ln\left(\frac{C_s}{C_b}\right) \quad (9) \qquad \text{Or} \qquad \boxed{\eta_c = \frac{R\,T}{z\,F}\ln\left(1-\frac{I}{I_L}\right)} \quad (10)$$

Where: F = Faraday's constant (columbs/mole), D = Diffusivity (cm^2/s), δ = Diffusion layer thickness (cm), C_b = Bulk concentration ($gmole/cm^3$), C_s = Surface concentration ($gmole/cm^3$), A = Surface area (cm^2). From equation (10) it can be seen that:

1. The term $\left(1-\frac{I}{I_L}\right)$ is equivalent to the term $\left(\frac{C_s}{C_b}\right)$ in equation (9).
2. When I is very small in comparison with I_L, the concentration polarization is negligible.
3. When I approach I_L in magnitude, concentration polarization approaches infinity.

3. RESISTANCE POLARIZATION *(η_R)*:

The resistance polarization is the ohmic potential drop through a portion of the electrolyte surrounding the electrode, through a metal reaction product film on the surface or both. An ohmic potential drop always occurs between the working electrode and the capillary tip of reference electrode. The ohmic (i.e., solution) IR drop is given by:

$$IR_{\text{soln.}} = i\,\rho\,l = i\,l/k \qquad (11)$$

Where: ρ = The specific resistance (i.e. resistivity) (Ω.cm), k = The conductivity ($\Omega^{-1}.cm^{-1}$) or ($S.cm^{-1}$); S = Siemens, *l* = The solution gap between the capillary tip and the working electrode (cm). Resistance polarization is important only at high current densities or in high resistance electrolyte solution. All of these three types of polarization will be present to a greater or less extent in most corrosion reactions.

$$\eta_{total} = \eta_A + \eta_c + \eta_R \qquad (12)$$

But if one is more influential than the others, then it will control the reaction rate.

HOW PLORIZATION MEASURED

Polarization can be measured using electrochemical corrosion cell and potentiostat as shown in figure 1. Electrical connections are shown in figure 2.

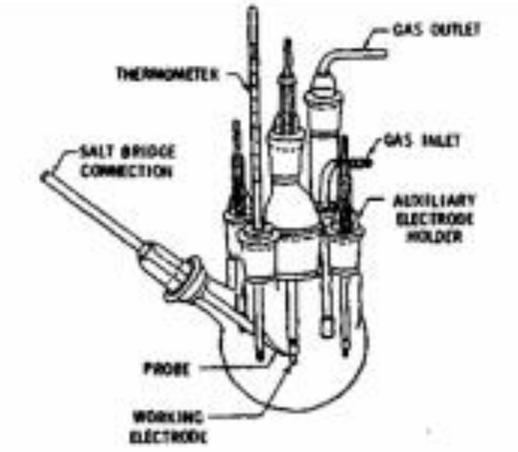


FIG. 1 Schematic Diagram of Polarization Cell (1)

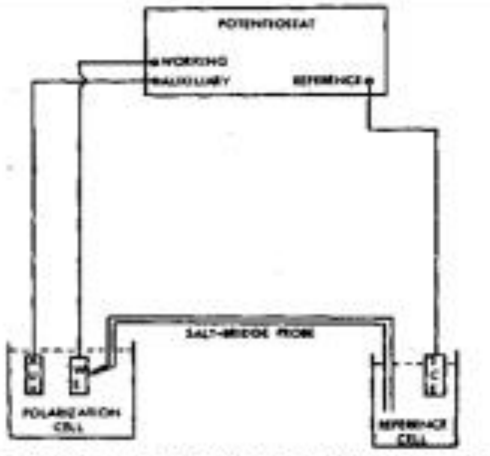


FIG. 2 Schematic Potentiostatic Anodic Polarization Wiring Diagram (2)

Polarization corrosion cell was equipped with several necks, which can be used according to the test conditions:

1. One for the working electrode (metal or test sample).
2. One for reference electrode (SCE, SHE, etc), for potential measurements.
3. One for thermometer, for temperature control.
4. Counter electrodes.

PASSIVITY

PASSIVITY

A passive metal is one that is active in the Emf Series, but that corrodes nevertheless at a very low rate. Passivity is the property underlying the useful natural corrosion resistance of many structural metals, including aluminum, nickel, and the stainless steels. Some metals and alloys can be made passive by exposure to passivating environments (e.g., iron in chromate or nitrite solutions) or by anodic polarization at sufficiently high current densities (e.g., iron in H2SO4).

Figure below illustrates the typical behavior of a metal that demonstrate passive eefects. The behavior of this metal or alloy can divided into three regions:

1. Active region: the behavior of this metal is identical to that of normal metal. Slight increase in oxidizing power (potential) of solution cause rapid increase in corrosion rate.

2. Passive region: if the oxidizing agent is added the corrosion rate shows sudden decrease.

3. Transpassive region: at very high concentration of oxidizing agent corrosion rate again increased with oxidizer power.

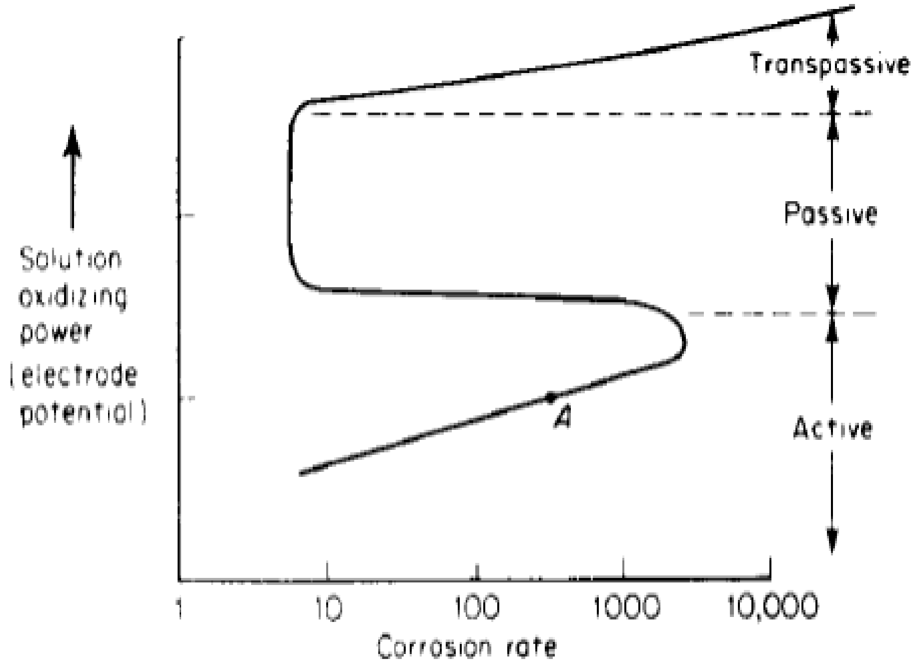


Figure Corrosion characteristics of an active-passive metal as a function of solution oxidi ing power (electrode potential).

CHARACTERISTICS OF PASSIVATION

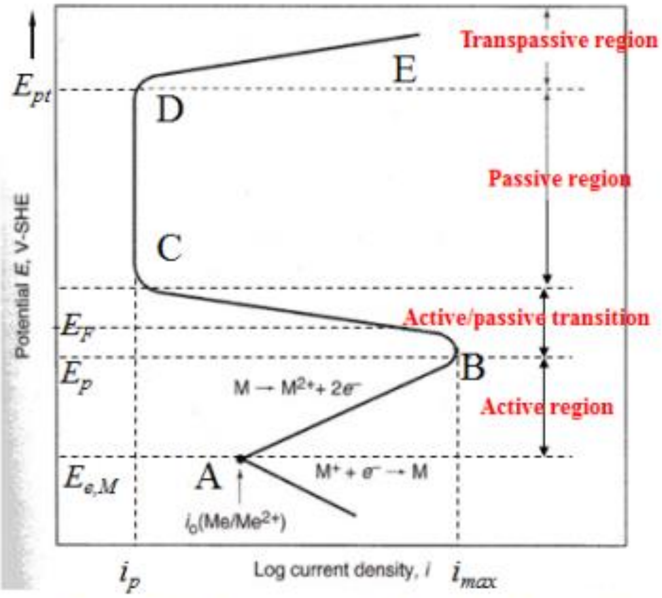
Theoretical anodic polarization curves of passivated metals

1. Four regions of the anodic polarization curve of passivated metal

(1)A-B section — active region

Metal is in anodic dissolution state. Polarization curve follows Tafel equation with the increase of potential.

$$Fe \rightarrow Fe^{2+} + 2e$$



Anodic polarization curve of passivated metal

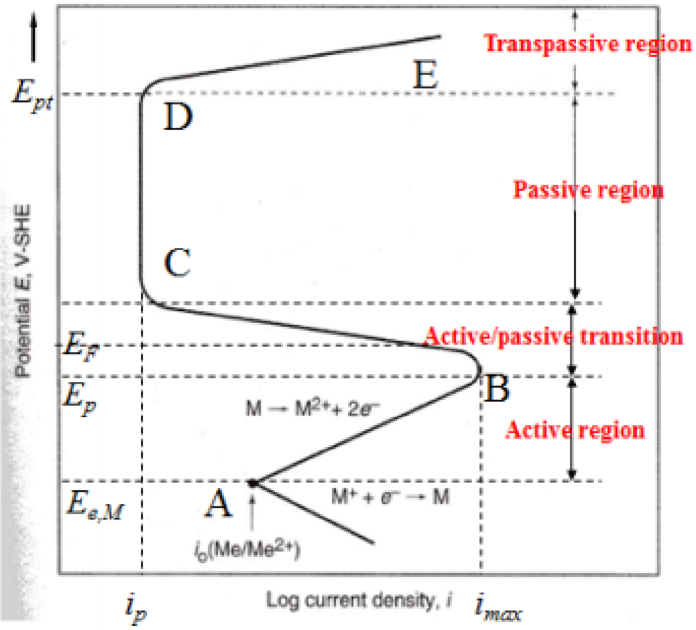
(2)B-C section — Active/passive transition

When the electrode potential increases to a critical value E_p, the passive film is formed on metal surface. The current density drops precipitously

E_p ⇨ passive potential

i_{max} ⇨ critical current density

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e$$



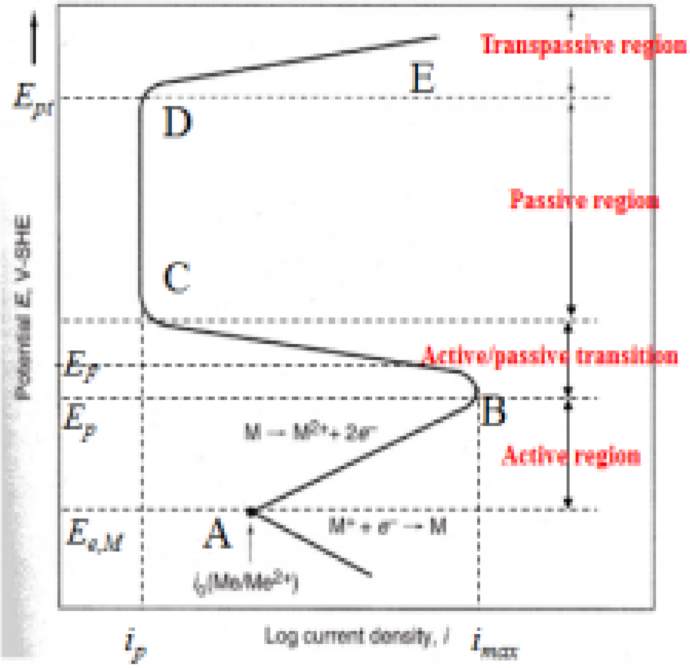
Anodic polarization curve of passivated metal

(3)C-D section —— passive region

The metal is in steady passivation state. Passive film is formed on metal surface. The current density is almost independent of the potential.

i_p ⇨ passive current density

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e$$



Anodic polarization curve of passivated metal

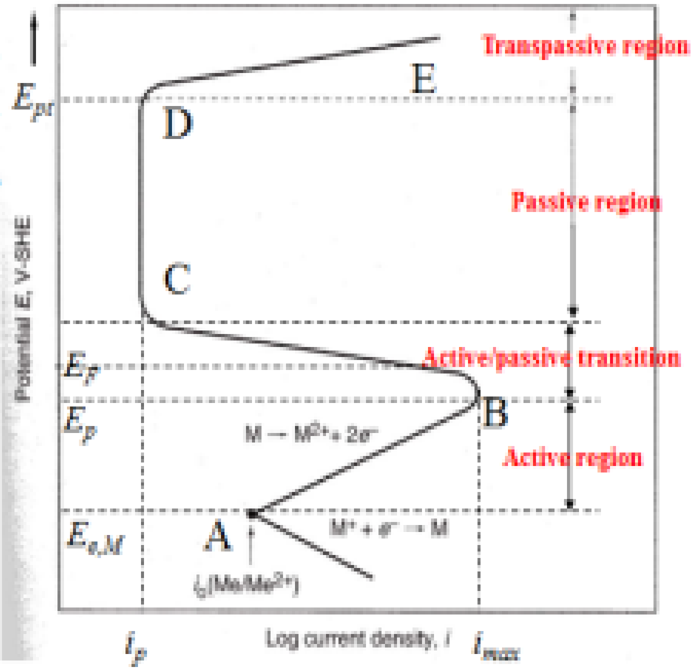
(4)D-E section —— transpassive region

When the potential is further increased, the current density increases. The passive film is damaged.

E_{pt} ⇨ tanspassive potential

$$M_2O_3 + 4H_2O \rightarrow M_2O_7^{2-} + 8H^+ + 6e$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$



Anodic polarization curve of passivated metal

CLASSIFICATION OF PASSIVITY

Chemical passivity	Passivity is caused by the reaction between metal and passivation agent
Electrochemical passivity	Passivity is caused by applying anodic current density (or positive shift of potential)

THEORIES OF PASSIVATION

Major theories that have been proposed are:

- Oxide film theory.
- Adsorption theory

The oxide theory attributes corrosion resistance of passive metals and alloys to the formation of a protective film on the metal surface; the film can be as a monolayer. A stable passive film is free from porosity and presents a protective barrier between the metal and the corrosive environment.

The adsorption theory is based on chemisorbed films. Oxygen adsorption on surfaces can reduce corrosion activity. Adsorbed oxygen atoms significantly decrease the exchange current density, thus increasing anodic polarization, favorable for passivation.

EFFECT OF ENVIRONMENTAL PARAMETERS ON CORROSION

EFFECT OF TEMPERATURE:

Temperature increases the rate of almost all-chemical reactions. An increase in temperature of a corroding system has four main effects:

1. The rate of chemical reaction is increased.
2. The solubility of gases in solution is decreased.
3. The solubility of some of the reaction products may change, resulting in a different corrosion reaction products; and
4. Viscosity is decreased, and many thermal differences will results in increased circulation.

When corrosion is controlled by diffusion of oxygen, the corrosion rate at a given oxygen concentration approximately doubles for every 30 ^{0}C rise in temperature. When corrosion is attended by hydrogen evolution, the rate increasing is more than double for every 30^{0}C rise in temperature. Arrhenius type equation:

$$Corrosion\ Rate\ (C.R.) = A\ Exp\left(-\frac{E}{R\,T}\right)$$

Where: A = Modified Frequency factor (pre-exponential factor), E = Activation energy (J/mole), R = Gas constant (8.314 J/mole.K), T = Absolute temperature (K).

Example:

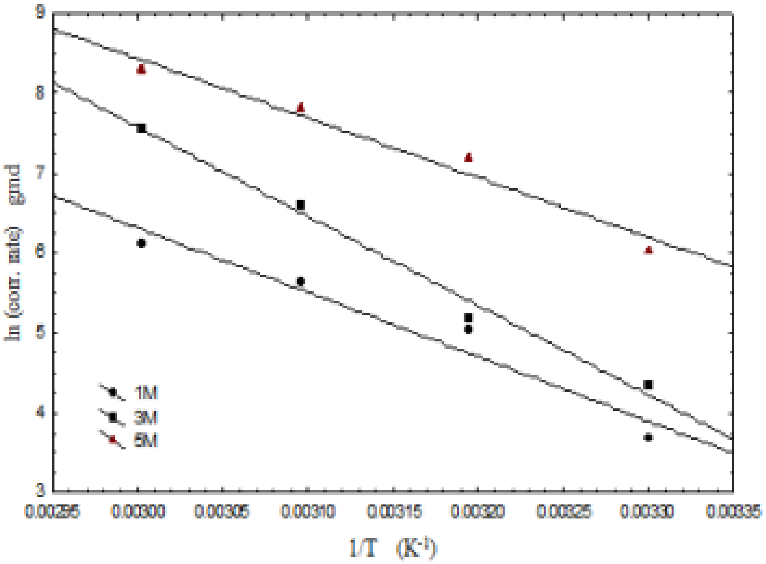
Following data for the corrosion rate (g/m^{2}day) of mild steel in HCl, estimate the values of Modified Frequency factor (pre-exponential factor) and E, Activation energy (J/mole).

HCl conc. M	Temperature °C			
	30	40	50	60
1	39.35	153.82	279.81	456.17
3	75.85	177.82	741.31	1905.46
5	602.55	1318.25	2454.71	3990.249

Solution:

The linear form of Arrhenius type equation is:

$$\ln(C.R.) = \ln A - \frac{E}{R\,T}$$ That can be drawn as ln (C.R.) vs 1/T.



Conc. M	E (kJ/mol)	A (day^{-1})
1	70.12	45.7×10^{12}
3	56.36	16.5×10^{12}
5	52.94	8.4×10^{12}

Arrhunis Plot for the Corrosion of Low Carbon Steel in HCl Acid

EFFECT OF VELOCITY

The effects of velocity on corrosion rate are like the effect of oxidizer addition, complex and depend on the characteristics of the metal and environment to which it is exposed. Increased the velocity may increase or reduce attack, depend on its effect on the corrosion mechanism involved. It may increase attack on metal by increasing the supply of oxygen in contact with the metal surface, or velocity may increase the diffusion or transfer of ions by reducing the thickness of the stagnant film at the surface. At the other end, a fast moving fluid generates turbulence that provides enhanced mass transfer. The mass transfer coefficient can be expressed in terms of the dimensionless Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers. These numbers are defined by:

$$Re = \frac{\rho u d_e}{\mu} \qquad Sc = \frac{\mu}{\rho D} \qquad Sh = \frac{k_d d}{D}$$

Where ρ is the density, u is the linear velocity, d is the inner tube diameter, μ is the dynamic viscosity, D is the diffusivity of oxygen in seawater, and k_d is the mass transfer coefficient. For single phase flow in a straight pipe, the correlation of Anederko can be used:

$$Sh = 0.0165\,\mathrm{Re}^{0.86}\,Sc^{0.33}$$

Example

Find the mass transfer coefficient as a function of Reynolds number. For flow of saline water in steel tube. The physical properties of seawater at 25° C and pH=7 are: ρ = 1.0311 g/cm^3, μ = 0.962×10^{-3} kg/m.s, D = 1.9×10^{-5} cm^2/s. solving of equations a yield the values of k$_d$. Figure below shows the variation of mass transfer coefficient, k_d, with *Re*. It can be seen that the k_d increases with increasing *Re*, that means the corrosion rate increases with increasing *Re*.

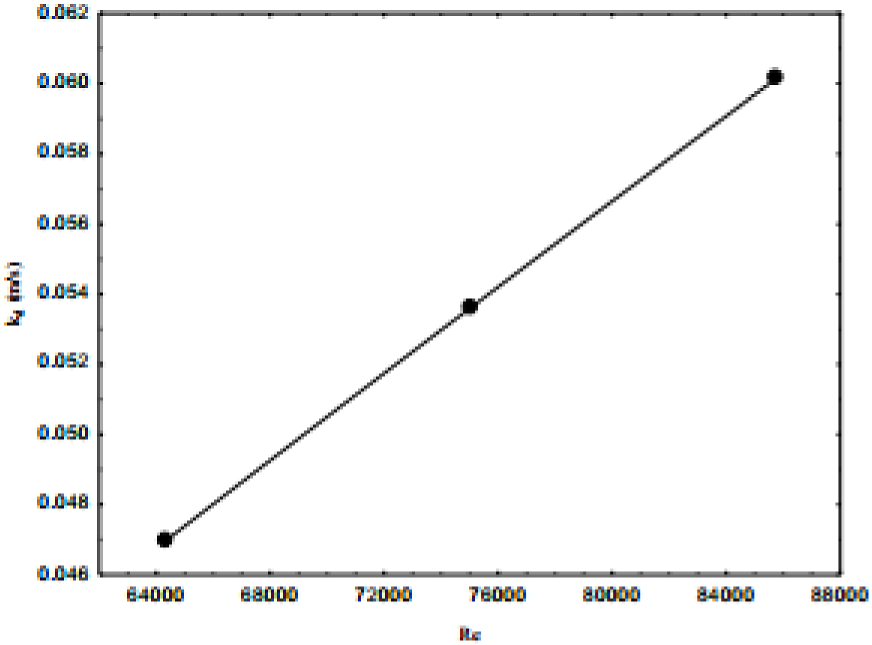


Fig. Effect of Reynold number on mass transfer coefficient for flow of 3.5% NaCl solution in mild steel pipe at 4%

Corrosion Petroleum Industries

Introduction:

Pipelines play an extremely important role through the world as a means of transporting gases and liquids over long distances from their sources to ultimate consumers. So that corrosion problems exist in the oil industry at every stage of production from initial extraction to refining and storage. Oilfield corrosion manifests itself in several forms, among which

* CO2 corrosion (sweet corrosion) and

* Hydrogen sulfide (H2 S) corrosion (sour corrosion) in the produced fluids

* Corrosion by oxygen dissolved in water injection

Corrosion of carbon steel is a significant problem in the oil & gas production and transportation systems, which causes:

* Significant economic loss. As a result of corrosion, rupture of the pipe wall frequently causes failure of petroleum and gas pipelines.

* The breakdowns are followed by large losses of the products.

* Environmental pollution and ecological disasters.

Sour Corrosion

* Presence of acidic gases, such as, CO2 and H2S produce a serious corrosion problems.

* Sour gas is any gas that specifically contains hydrogen sulfide in significant amounts, whereas an acid gas is any gas that contains significant amounts of acidic gases such as carbon dioxide (CO2) or hydrogen sulfide.

* Thus, carbon dioxide by itself is an acid gas, not a sour gas.

Corrosion types due to acidic or sour gases:

1. Stress Cracking Corrosion (SCC).
2. Sulfide Stress Cracking (SSC).
3. Hydrogen Induced Cracking (HIC).

Corrosion by H_2S:

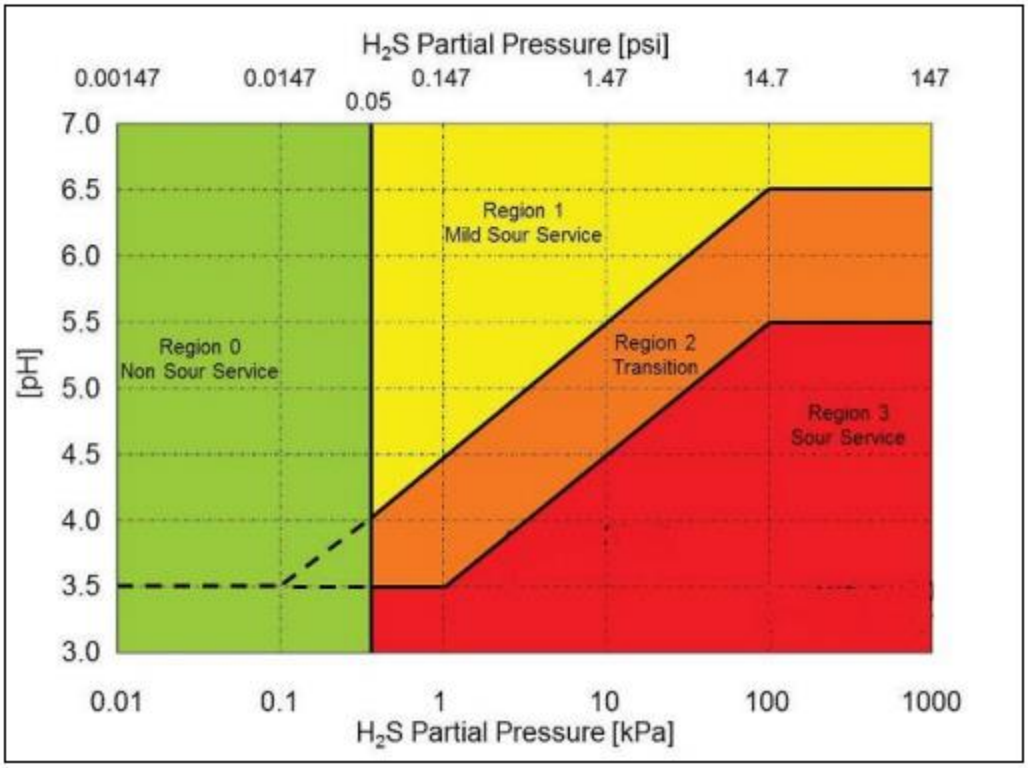
Corrosion increased with H_2S concentration.

$$P_{H_2S} < 0.3\ kPa \quad (0.05\ psi) \qquad Not\, sour\ service$$

$$P_{H_2S} \geq 0.3\ kPa \quad (0.05\ psi) \qquad sour\ service$$

According to NACE MR0175/ISO15156 corrosion by H_2S can related with pH according to figure below. The partial pressure of the gas can be calculated from mole fraction and total pressure as follows:

$$P_{H_2S} = P_T y_{H_2S}$$



Corrosion CO_2:

Corrosion increased with **CO_2** concentration.

$$P_{CO_2} < 7\ psi \quad (0.5\ bar) \qquad (No corrosion)$$

$$7\ psi \quad (0.5\ bar) < P_{CO_2} < 30\ psi \quad (2\ bar) \qquad (possible corrosion)$$

$$P_{CO_2} > 30\ psi \quad (2\ bar) \qquad (corrosion)$$

Empirical equation for calculation of corrosion rate by CO_2:

$$\log(\text{c.r., mm / y}) = 5.8 - \frac{1780}{T} + 0.67\log(pCO_2)$$

Where T in °C and P in bar.

Corrosion by combined effect of H_2S and CO_2:

Corrosion by sour and acidic gases depend on partial pressure

$$\frac{P_{CO_2}}{P_{H_2S}} > 500 \qquad CO_2\ corrosion$$

$$\frac{P_{CO_2}}{P_{H_2S}} < 20 \qquad H_2S\ corrosion$$

$$20 < \frac{P_{CO_2}}{P_{H_2S}} < 500 \qquad H_2S\ and\ CO_2\ corrosion$$

1. The charge of an electron is $1,58 \times 10^{-19}$ C.

   a) What is the charge of an Al ion?

   b) If 0,068 moles of Al^{+++} cross a given section in 1 hour, what is the current in amps?

Answer:

a) $3 \times 1,58 \times 10^{-19}$ $\quad C = 4,74 \times 10^{-19}$ C

b) 0,068 moles Al^{+++}

$$\text{charge} = 0,068 \text{ moles} \times 6,023 \times 10^{23} \text{ ion/mole} \times 3 \text{ ch/ion} \times 1,58 \times 10^{-19} \text{ C}$$

$$\text{charge} = 1,94 \times 10^{4} \text{ C}$$

$$I = \frac{1,94 \times 10^{4} \text{ C}}{3600 \text{ S}} = 5,39 \text{ A}$$

$$I = 5,39 \text{ A}$$

2. Compute the weight of one molecule of O_2.

Answer:

One mole of any molecular substance contains the same number of molecules, Avogadro's number:

$$N = 6,023 \times 10^{23} \text{ molecules/mole}$$

One mole of O_2 = 32 g.

$$\frac{32 \text{ g/mol}}{6,023 \times 10^{23} \text{ molecule/mol}} = 5,3 \times 10^{-23} \text{ g/molecule}$$

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