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

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

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/cm^2)
i = current density = $\dfrac{I}{A}$ (A / cm^2).
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 (cm^2)

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

where
ρ = density (g/cm^3)
i = current density (A/cm^2)
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 mm^3/year.

Example problem

Rate of Oxidation Computation, Zinc experiences corrosion in an acid solution according to the reaction Zn + 2H$^+$ →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/cm^2.s) given the following activation polarization data:

$E_{(Zn/Zn^{2+})} = -0.763\ V$ $E_{(H^+/H_2)} = 0.0\ V$
$i_o = 10^{-7} A/cm^2$ $i_o = 10^{-10} A/cm^2$
$\beta = +0.09$ $\beta = -0.08$

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

$$E^o_{H^+/H_2} + \beta_H \log\left(\frac{i}{i_{o\,H}}\right) = E^o_{Zn/Zn^{+2}} + \beta_{Zn} \log\left(\frac{i}{i_{o\,Zn}}\right)$$

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

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

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

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

(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

$$E_{Corr} = E^o_{H^+/H_2} + \beta_H \log\left(\frac{i_{Corr}}{i_{o\,H}}\right)$$

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

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

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 $[Cu/Cu^{2+}(1.0M)]//[Zn^{2+}(1.0M)/Zn]$, does the cell reaction $Cu + Zn^{2+} \text{------>} Cu^{2+} + Zn$ take place simultaneously? If E^o 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 g/mol
$$i = 0.1 \text{ A/cm}^{-2}$$
$$n = 2$$

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

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

Exercise5: Consider the reaction $M \text{---->>} M^{2+} + 2e$ on an electrode surface. An over potential of (-0.155 V) (η) is applied to the electrode. The exchange current density (i_o) at 25°C is $5x10^{-7} A/cm^2$, $\beta = -0.5$. 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 $\mu A/cm^2$ at its reversible potential -0.160 V. The anodic Tafel slope is +0.060 V and the cathodic Tafel slope is -0.060 V for the system M+ + e- $\rightarrow$ M. for hydrogen evolution on the surface of M, the anodic and the cathodic Tafel slopes +0.100 V and -0.100 V, respectively. The exchange current density for hydrogen evolution on the metal M is 1.0 $\mu A/cm^2$ at the reversible potential of 0.00 V.
(a) Construct the individual polarization curves for the systems
(b) What is the corrosion potential?
(c) 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

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

$$Na_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$
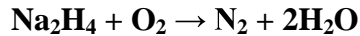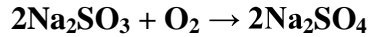
Oxygen reduction is controlling cathodic reaction; it is not effective in strong acid solutions.

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 uniforms 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.

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

$$2H^+ + 2e \rightarrow H_2$$
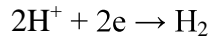
Cathodic protection is achieved by supplying electrons to the metal structure to be protected. If current is considered to flow from (+) to (-), as in conventional electrical theory, then a structure is protected if current enters it from the electrolyte. Conversely, accelerated corrosion occurs if current 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.
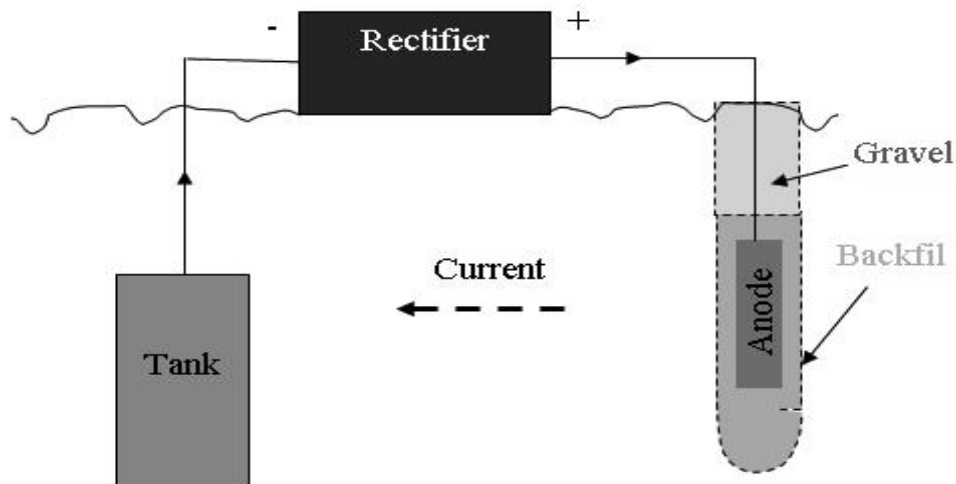

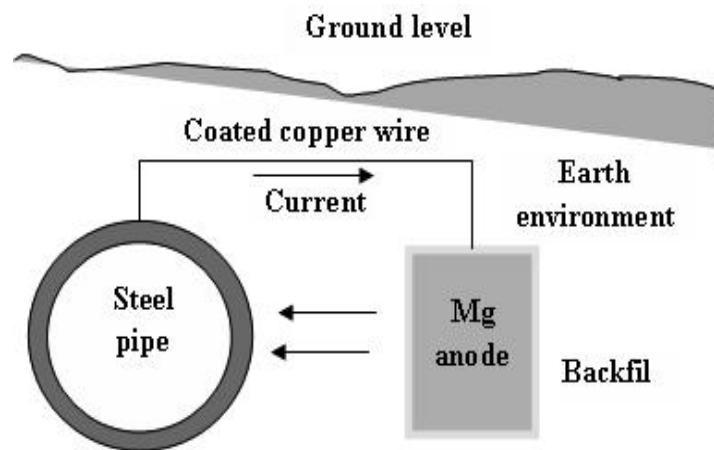Figure (1) Cathodic protection of an underground tank using impressed

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.
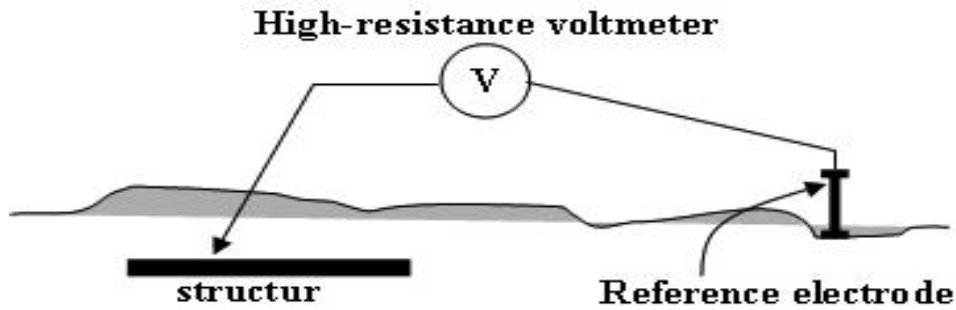
Figure(3) Pipe potential measurements with a reference electrode

Anode selection for Cathodic protection is based on engineering and economic considerations. Table 1 compares several types of sacrificial and impressed-current anodes.

Table 1: comparisons of sacrificial and impressed - current anodes for cathodic protection.

	Sacrificial anodes		
	Magnesium	Zinc	Alumnum-Tin
Theoretical consumption lb/amp.year	9	23	6.5
Actual consumption lb/amp.year	18	25	16-20
Potential vs. Cu/CuSO$_4$	-1.7	-1.15	-1.3

Stray – current effects are often encountered in Cathodic-protection systems. Stray current means extra current which is present in the soil near the industrial area, power a metallic object is placed in a strong current field, a potential difference develops across it and accelerated corrosion occurs at points where current leaves the object and enters the soil.
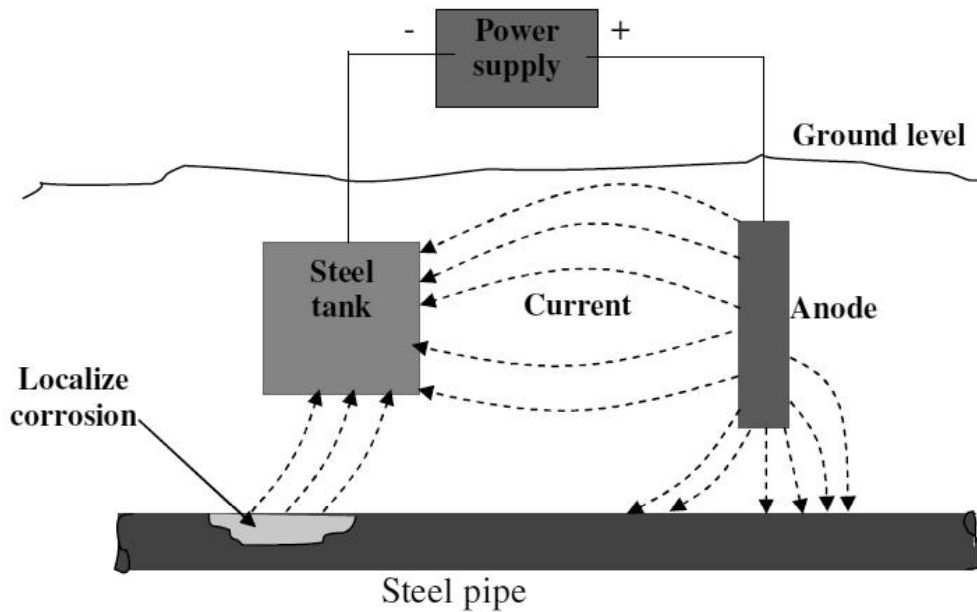
Fig (4)Stray current resulting from Cathodic protection.

Figure (4) illustrates stray currents resulting from a Cathodic-protection system. The buried tank catholically protected the pipe line nearby will failed rapidly due to the stray-current filed. It is possible to apply cathodic protection to prevent stray current attack, but it will produce stray current attack of the buried tank.
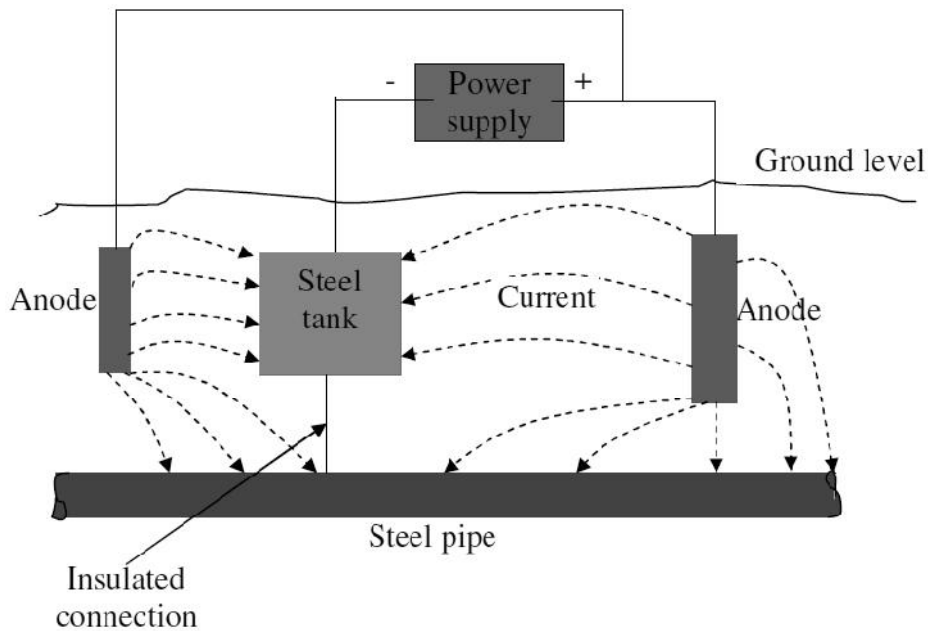

Fig.(5)Prevention of stray-current corrosion by proper design.

The solution to this problem is by electrically connecting the tank and pipe by a buss connector and rearranging anodes as shown in figure (5). In this system of protection a constant current is maintained or applied in order to maintain a constant potential difference.

(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 indicted 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.
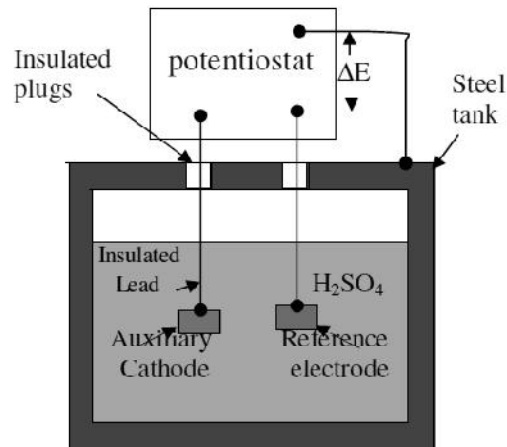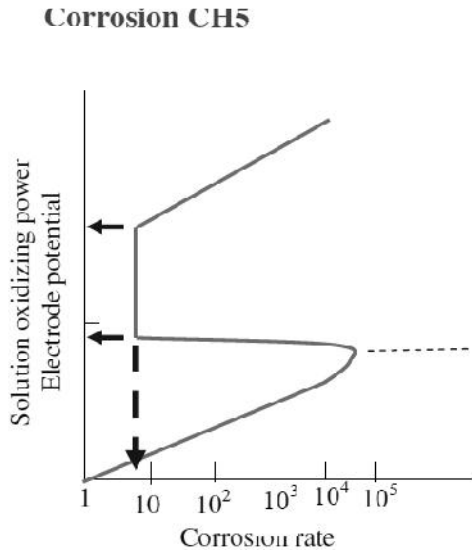

Fig. (6) Anodic protection of a steel storage tank containing H_2SO_4 .

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

		Corrosion rate, mpy	
Alloy type	Environment (air exposed)	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.

I) 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 0.25mm 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 dichromates), 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. And
   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.
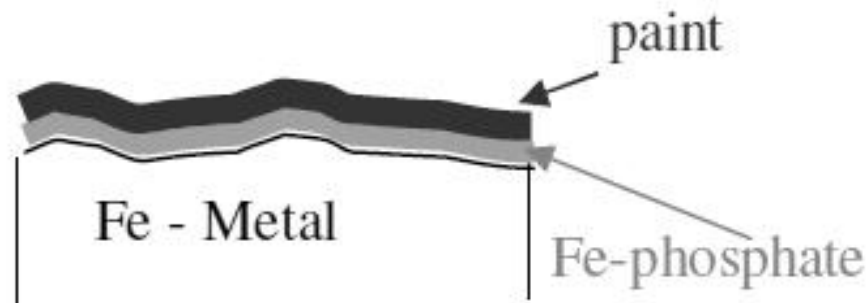
Corrosion Test
Methods used for corrosion testing.
1) Wt. increase or decrease during corrosion. (Measure the change in weight with time).
2) Electro-chemical method.
   ➢ Measure current flow with time.
   ➢ Measure change in potential with time.
3) Electrical resistance measurements with time.
Purpose 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. Filed 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