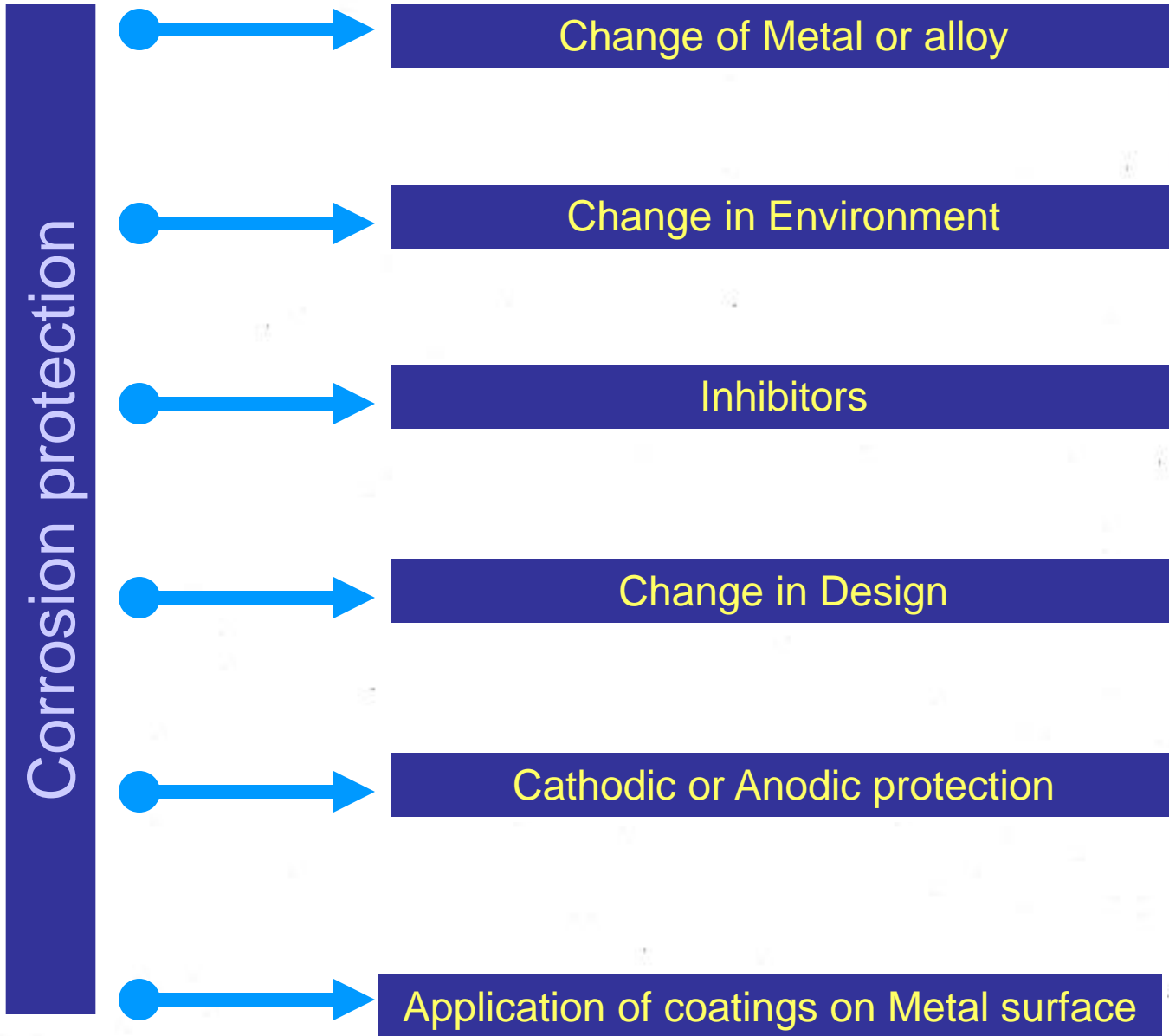




**CHAPTER 5**  
**CORROSION PROTECTION**  
**AND CORROSION TEST**

**LECTURER**  
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# 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, ( St. 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 , ( Ti ).
- 9) For all conditions except for HF , ( Ta ).
- 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.



## **Nonmetallics:-**

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 oxidizing acids ( e.g. nitric acid ) , less resistance to solvents , low temp. limitations.

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

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

**Wood** is attacked by aggressive environments.

## 2) Alteration of environment



### ***changing mediums :-***

- 1- lowering temperature :In most cases the corrosion rate will be less or stop. But in some cases by reducing the Temp. the corrosive will be faster ,e.g. fresh water or seawater are less corrosive at high temp. because oxygen is removed from the water.
- 2- Decreasing velocity : Excepts for pitting and erosion corrosion all the other types of corrosion rate is reduced by reducing in velocity .SCC stop with increasing medium velocity because pitting is stopped.
- 3- Removing oxygen or oxidizer from the system :- For most metals except for St.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 conc. 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 classify 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 a 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 SCC 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

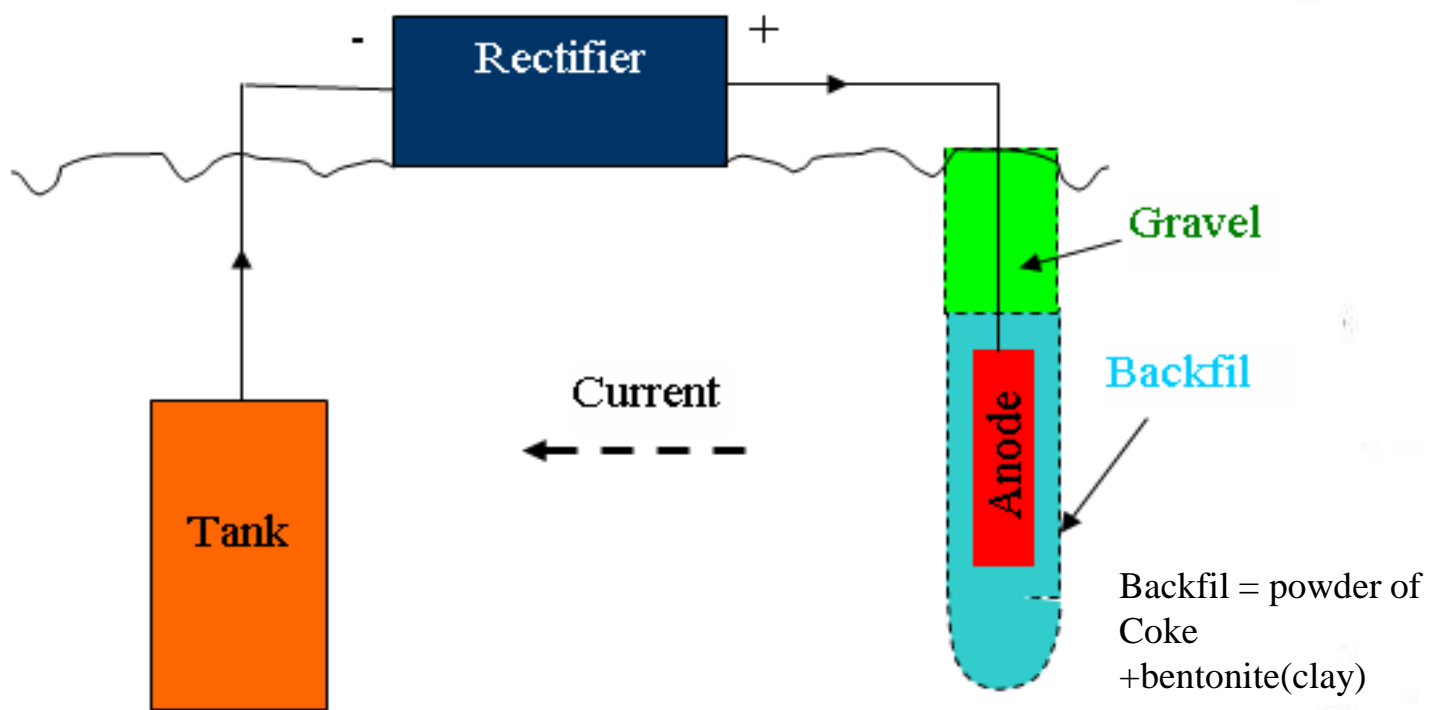


**(I) Cathodic protection :** The principles of Cathodic protection may be explained by considering the corrosion of a typical metal M in an acid environment.

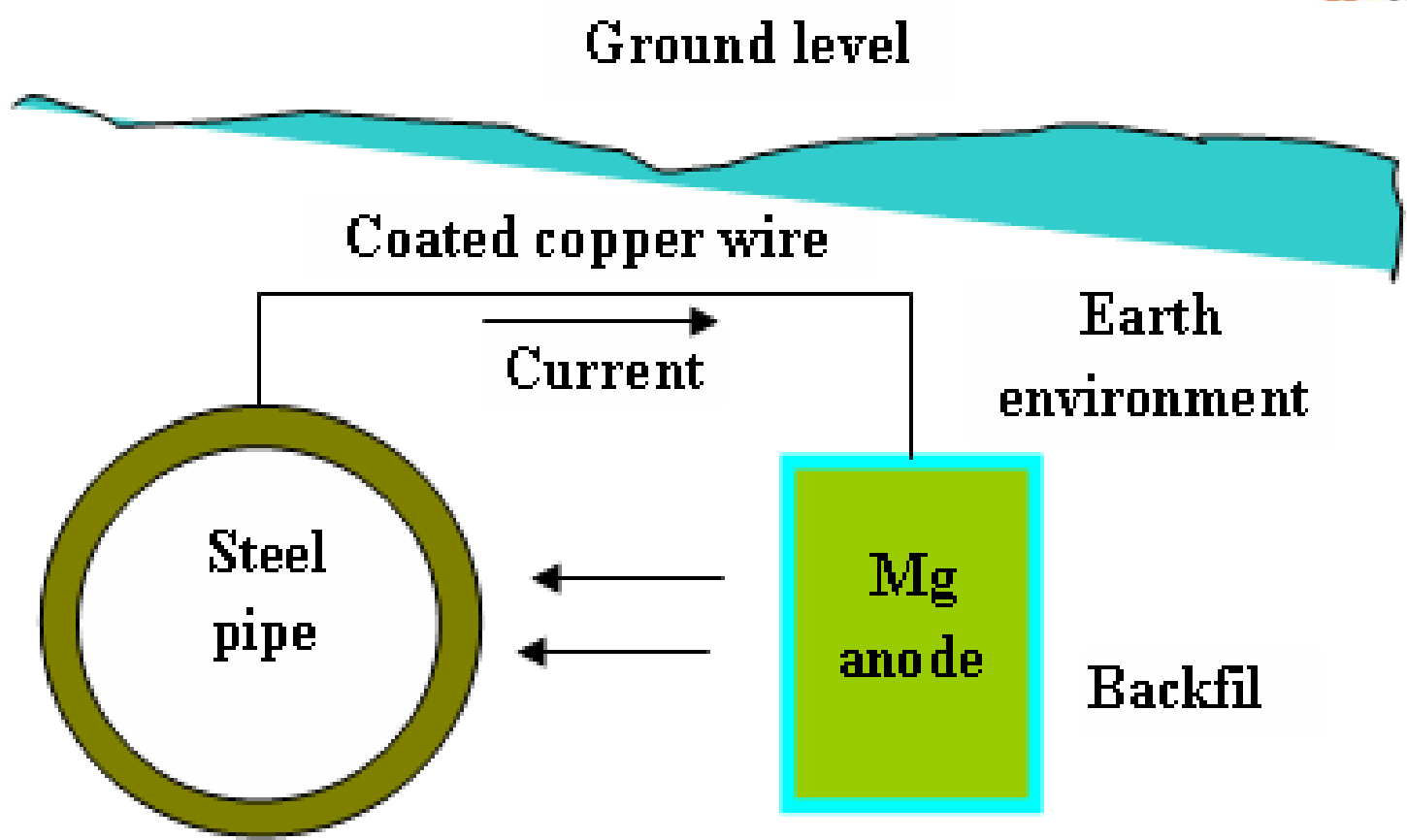


Cathodic protection is achieved by supplying electrons to the metal structure to be protected. If current is considered to flow from (+) to (-) , as in conventional electrical theory , then a structure is protected if current enters it from the electrolyte. Conversely , accelerated corrosion occurs if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



**Fig.(1)Cathodic protection of an underground tank using impressed current**



**Fig.(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.

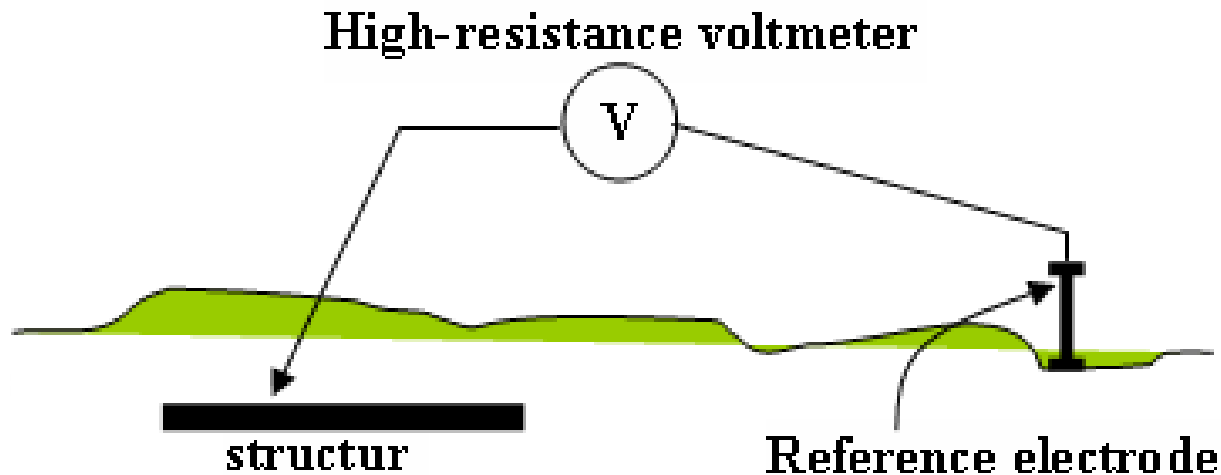


Fig.(3) Pipe potential measurements with a reference electrode



**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	Aluminum-Tin
Theoretical consumption ,Lb/amp-year	9	23	6.5
Actual consumption, Lb/amp-year	18	25	16-20
Potential vs. Cu / CuSO <sub>4</sub>	-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.

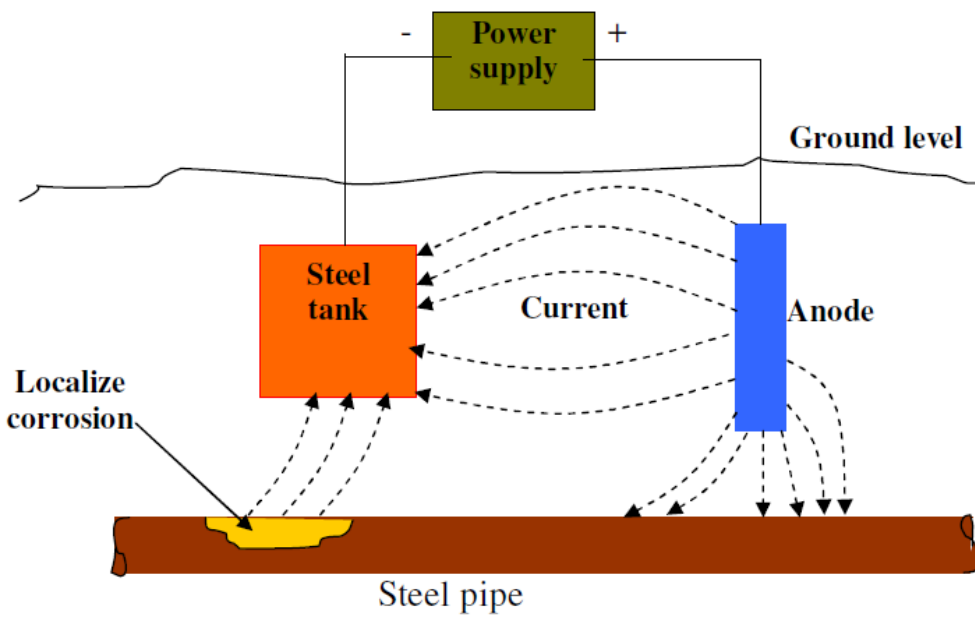


Fig.(4) illustrates stray currents resulting from a Cathodic-protection system. The buried tank cathodically protected, the pipe line nearby will fail rapidly due to the stray-current filed. It is possible to apply Cathodic protection to prevent stray current attack, but it will produce stray current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

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

Fig (4) Stray current resulting from Cathodic protection.

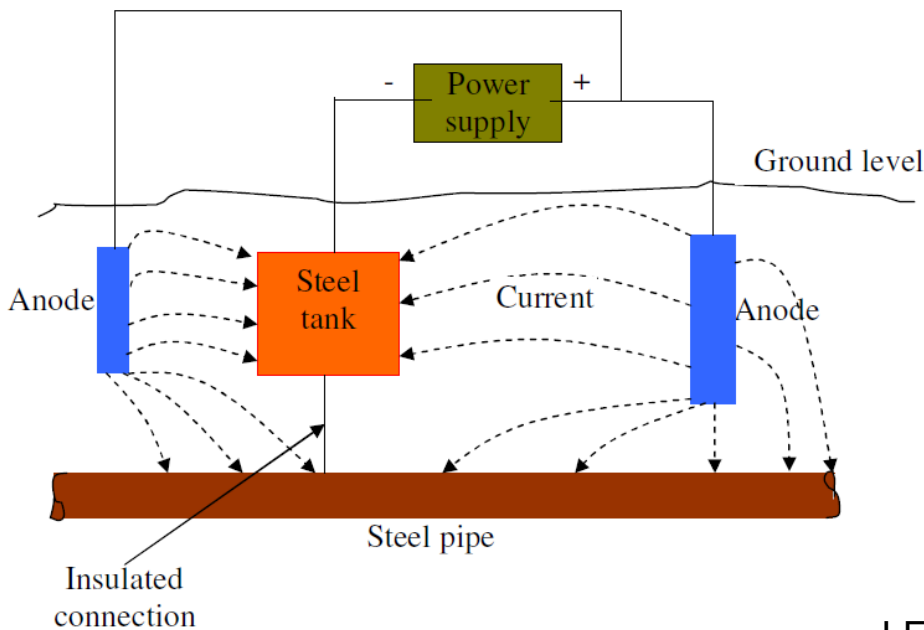


Fig.(5) Prevention of stray-current corrosion by proper design.

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**(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.

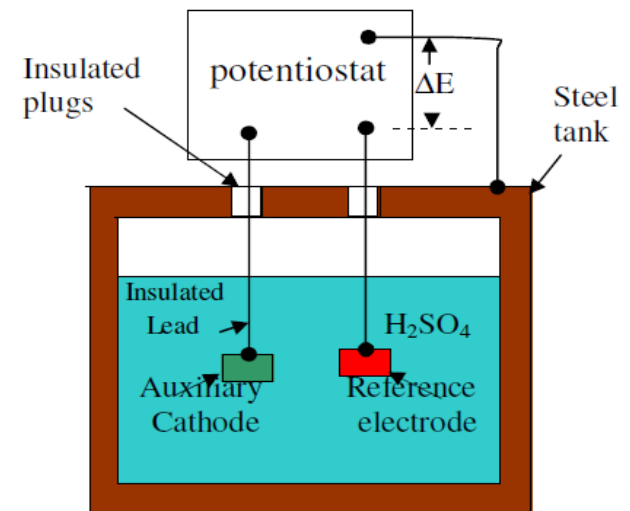
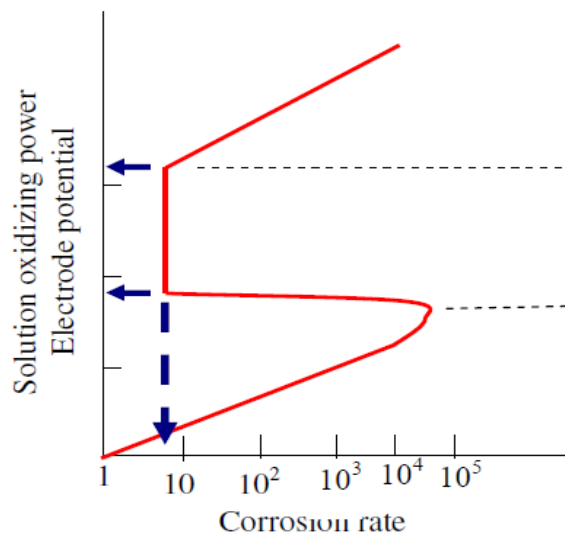


Fig. (6) Anodic protection of a steel storage tank containing H<sub>2</sub>SO<sub>4</sub>.



Table (2) Anodic protection of Austenitic Stainless Steel at 30°C. ( protected at 0.5 volts vs. Saturated Calomel Electrode )

Alloy type	Environment (air exposed)	Corrosion rate, mpy	
		Unprotected	Anodically protected
304 (19Cr-9Ni)	N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-5</sup> M NaCl	14	0.025
	N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-3</sup> M NaCl	2.9	0.045
	N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-1</sup> M NaCl	3.2	0.20
	10N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-5</sup> M NaCl	1930	0.016
	10N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-3</sup> M NaCl	1125	0.04
	10N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-1</sup> 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	Weak to aggressive	Weak to moderate
Relative cost		
Installation	High	Low
Operation	Very low	Medium to high
Throwing power	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  $\text{Cl}^-$  and for  $\text{H}_2\text{O}$ .

### *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 accelerated localized attack . Examples of metal – coated galvanized steel, glassed steel tanks represents ceramic coating , also anodized aluminum and chromized steel .





**1-Electro-deposition :-** This process also called electroplating , 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 are 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.



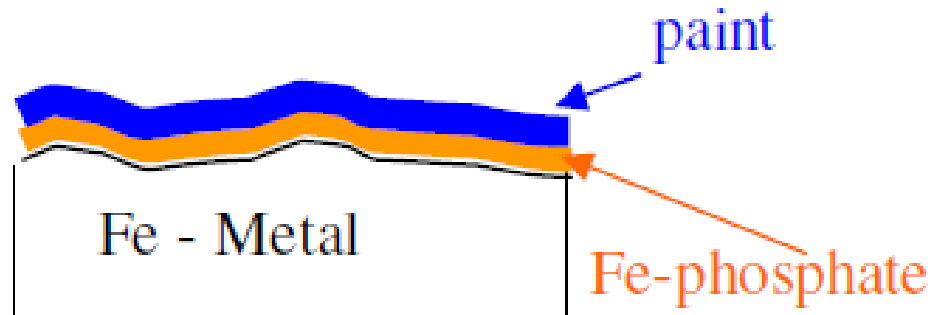
**II) Organic Coatings :-** These involve a relatively thin barrier between substrate material and the environment. Paints , Varnishes , Lacquers , and similar coatings doubtless protect more metal on a tonnage basis than any other method for combating corrosion. There are three main factors to consider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

**Surface preparation** involves surface roughening to obtain mechanical bonding as well as removal of dirt , rust , mill scale , oil , grease , welding flux . cravon 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 ).

} 6 months

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 temp.**

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

**4-Effect of surface area measurement.**



$$W = \frac{I t M}{n f}$$

## Weight change measurements :-

These are cyclic tests in a given environment and the gain or loss in wt. is measured at regular intervals . e.g. every 50 hrs, of testing.

2000/mpy = no. of hrs. e.g. 2000/5 mpy = 400hrs.

Aeration ( presence of oxygen ).

In the corrosion system in most- cases corrosion rate increase with the presence of O<sub>2</sub> except that of Al – where it forms a protective oxide layer .

Wt. Loss or gain / cm<sup>2</sup> → mpy

mpy X sp. Gravity of metals = 1.44 mdd

( rate of corrosion )

$$W = \frac{I t M}{n f}$$

Where I = current in amp.

t = time in sec.

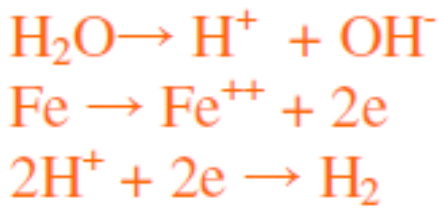
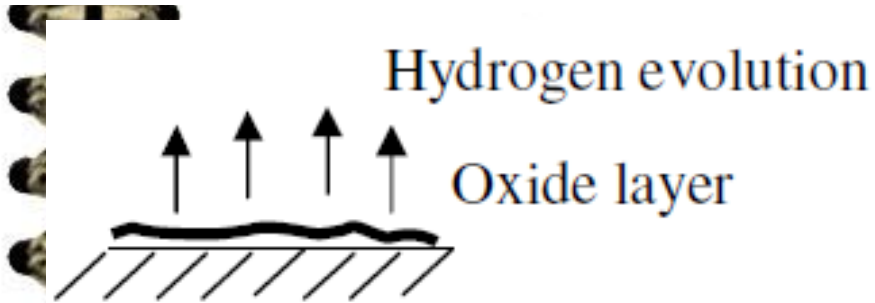
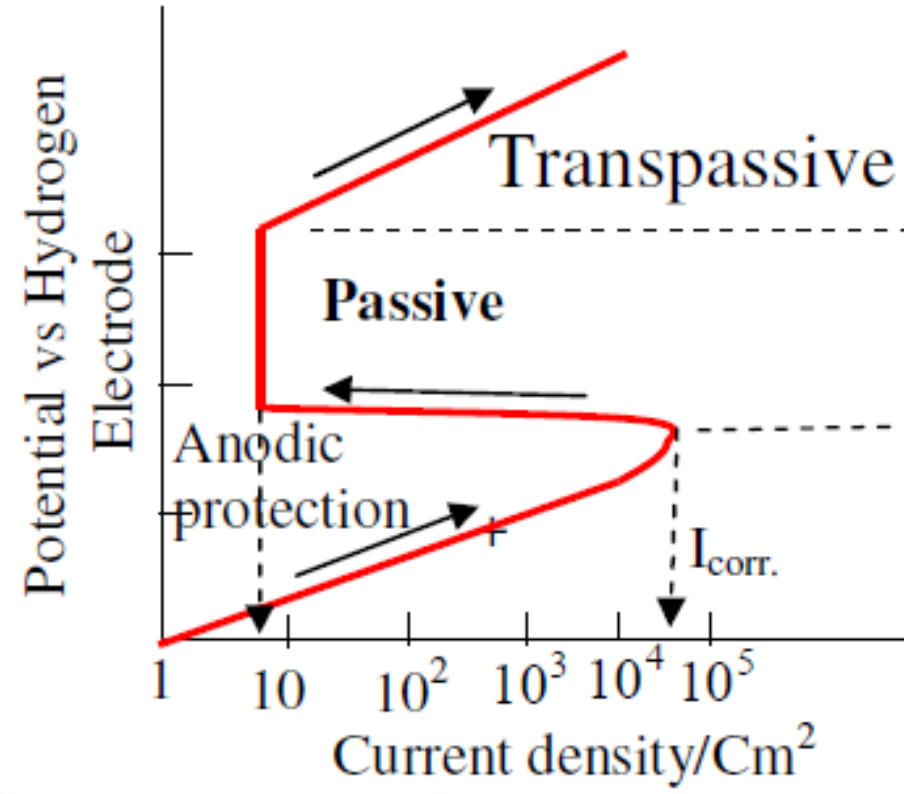
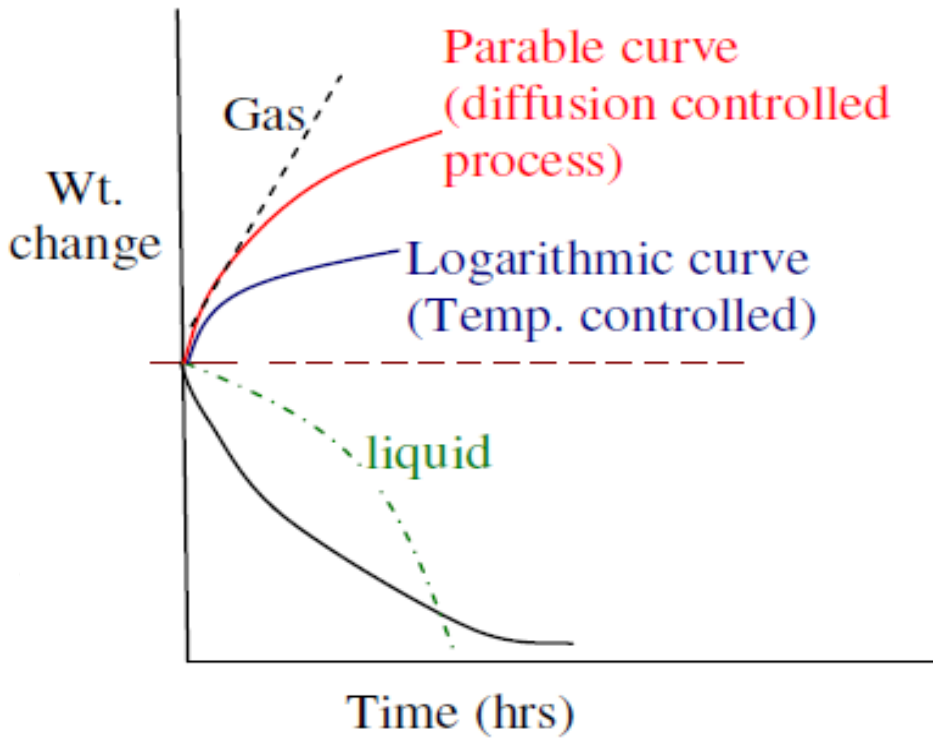
M = mole wt. atomic weight of metal.

n = valence of metal.

f = faraday = 96500 coulombs.

1 faraday = deposits or dissolves 1 equivalent weight of metal  
= 96500 coulombs.

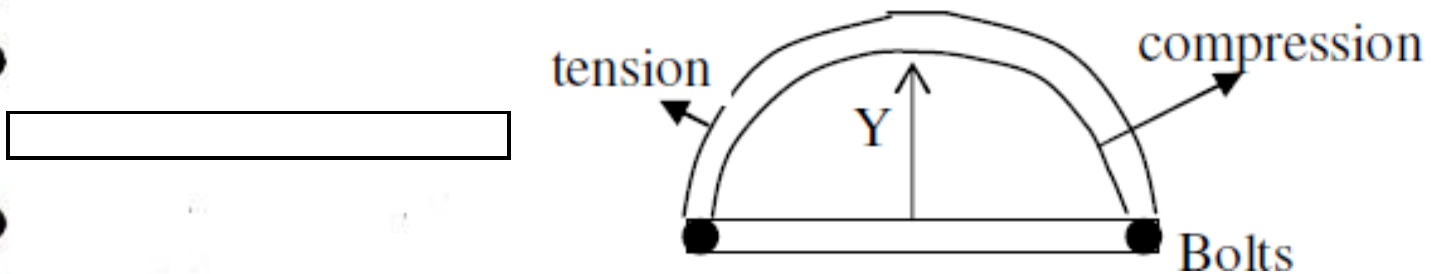
$$Eq.Wt. = \frac{Atomic\ wt.}{valency}$$



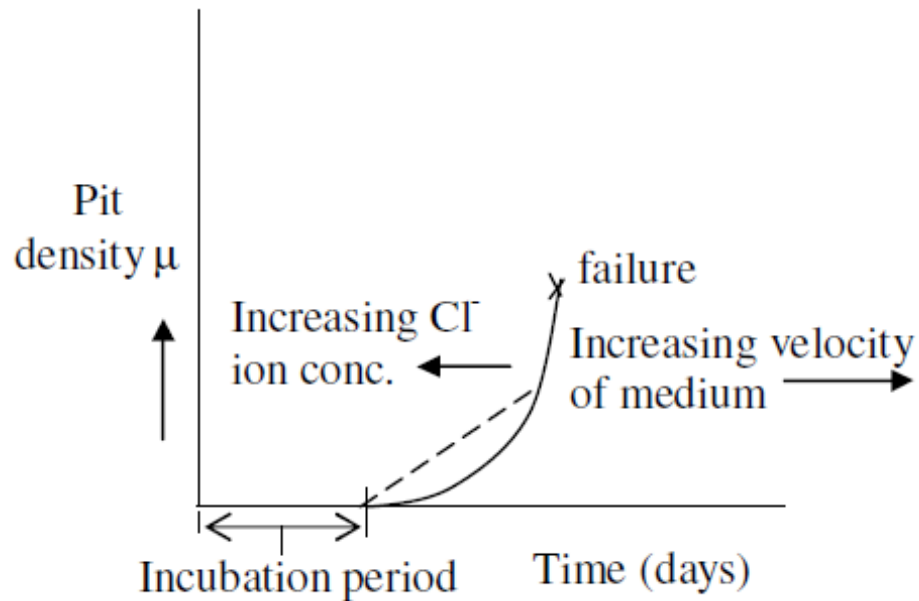


## Stress-corrosion tests:

Time for cracking is measured at various stress levels and / or various corrosive concentrations.



Pitting happens only on chloride lands .and they are increased with increasing velocity of medium.





Increases in velocity generally result in increased attack, particularly if substantial rates of flow are involved. The effect may be nil or increase slowly until a critical velocity is reached, and then the attack may increase at a rapid rate.

*Table 3-6 Corrosion of Metals by Seawater Moving at Different Velocities*

<i>Material</i>	<i>Typical corrosion rates, mdd</i>		
	<i>1 ft/sec*</i>	<i>4 ft/sec†</i>	<i>27 ft/sec‡</i>
Carbon steel	34	72	254
Cast iron	45	—	270
Silicon bronze	1	2	343
Admiralty brass	2	20	170
Hydraulic bronze	4	1	339
G bronze	7	2	280
Al bronze (10% Al)	5	—	236
Aluminum brass	2	—	105
90-10 Cu Ni (0.8% Fe)	5	—	99
70-30 Cu Ni (0.05% Fe)	2	—	199
70-30 Cu Ni (0.5% Fe)	<1	<1	39
Monel	<1	<1	4
Stainless steel type 316	1	0	<1
Hastelloy C	<1	—	3
Titanium	0	—	0

\* Immersed in tidal current.

† Immersed in seawater flume.

‡ Attached to immersed rotating disk.

SOURCE: International Nickel Co.



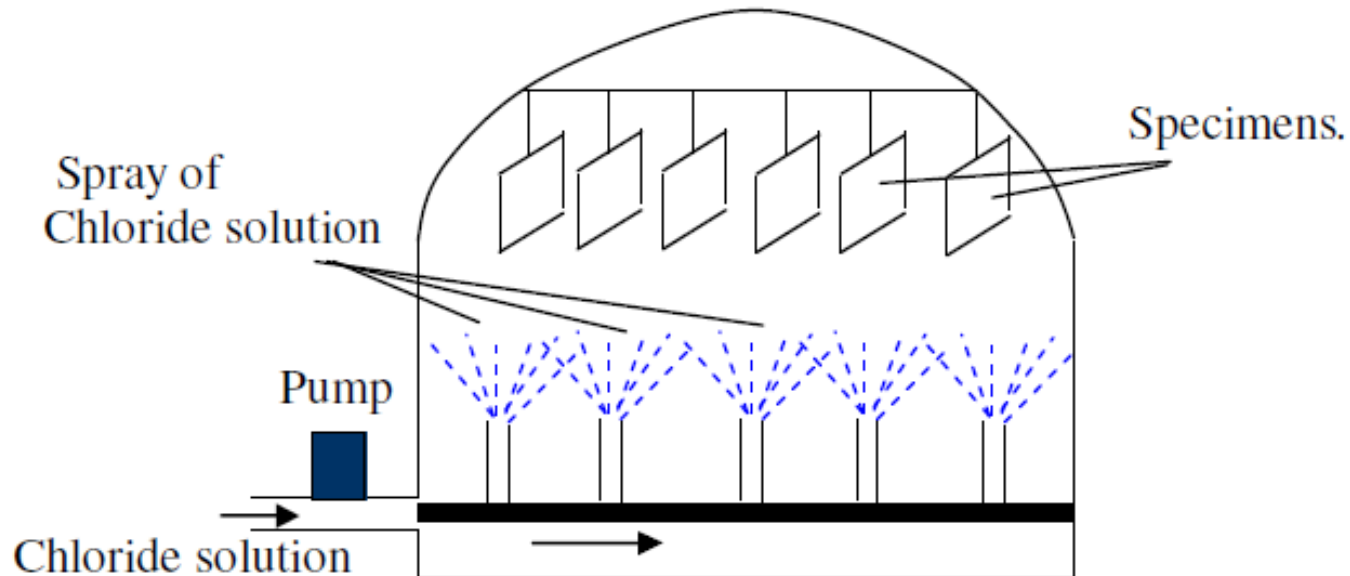
## Fatigue Test :-

This is a normal test except the corrosive environment is used for most metals , fatigue strength reduces in presence of corrosives , and their concentration .

## Salt – spray test :-

This test is carried out for painted surfaces of 2000hrs metals and for electro – deposited metals e.g. chromium plates , Ni or Au plates etc.

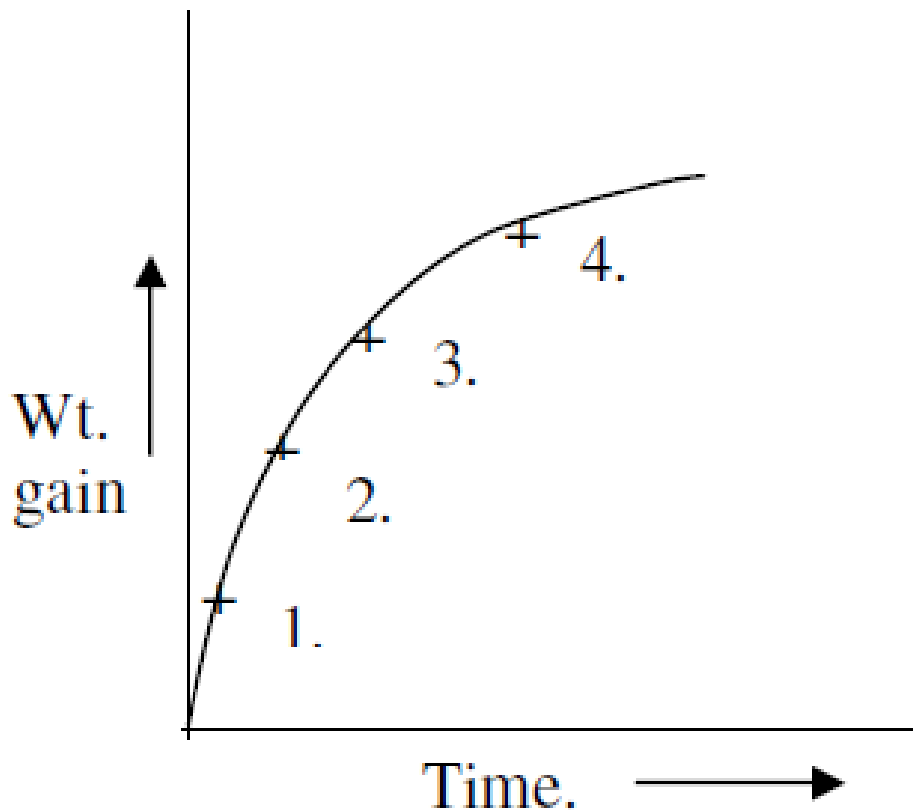
Acidified chloride solution is used in this case Time for start of corrosion is tested ( 10% NaCl solution ) used for all tests but for Cr we added 2- 10% acid.





## High temp. , Gas – metal reaction tests :-

In this test the change in weight of specimen is measured at various time intervals. The rate plot is made in between wt. gain and time.



Gas-metal reaction tests in which gain in weight is measured at various intervals of time are only valid if the oxide layer or corrosion produce is strongly bonded to the metal substrate, if the oxides fall-off during the reaction or during cooling, then the test has no quantitative value.

