1.   DEFINITION OF CORROSION:

Corrosion is the deterioration of the metal due to its interaction with the surrounding environment.

- Corrosion is the process by which the surface of metal is destroyed by a chemical or electrochemical reaction between the metal and its environment, leaving the surface pitted.
- Deterioration by physical causes such as erosion is not included in corrosion. But in many cases chemical attack accompanies physical deterioration, as described by terms as corrosion-erosion.

1.1   FORMS OF CORROSION:
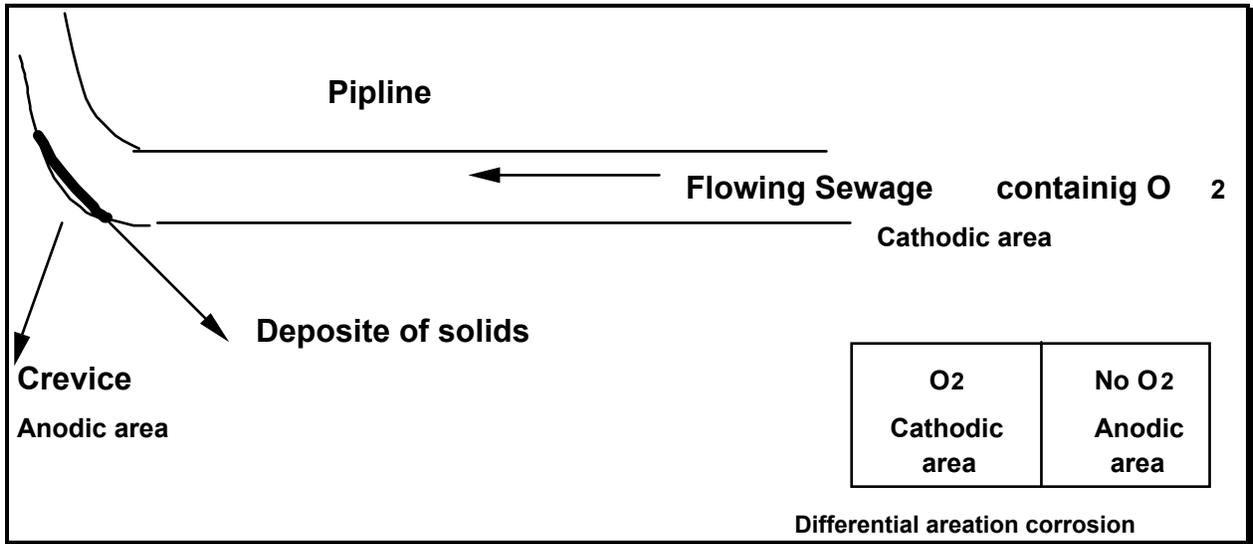
i.   GALVANIC CORROSION.
Macroscopic corrosion is intense at seaside "salt-spray"

"Area Effect"
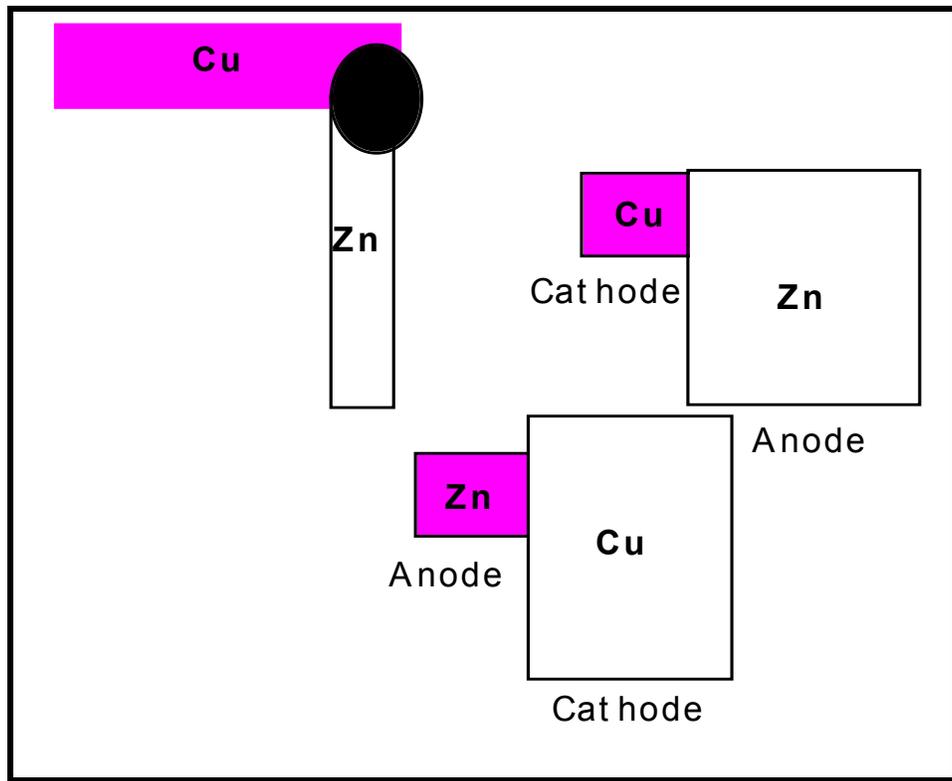
The large area of anode lead to small anodic current density , and small area of cathode lead to large cathodic current density and this lead to low corrosion rate and visa virsa for large area of cathode and small area of anode.
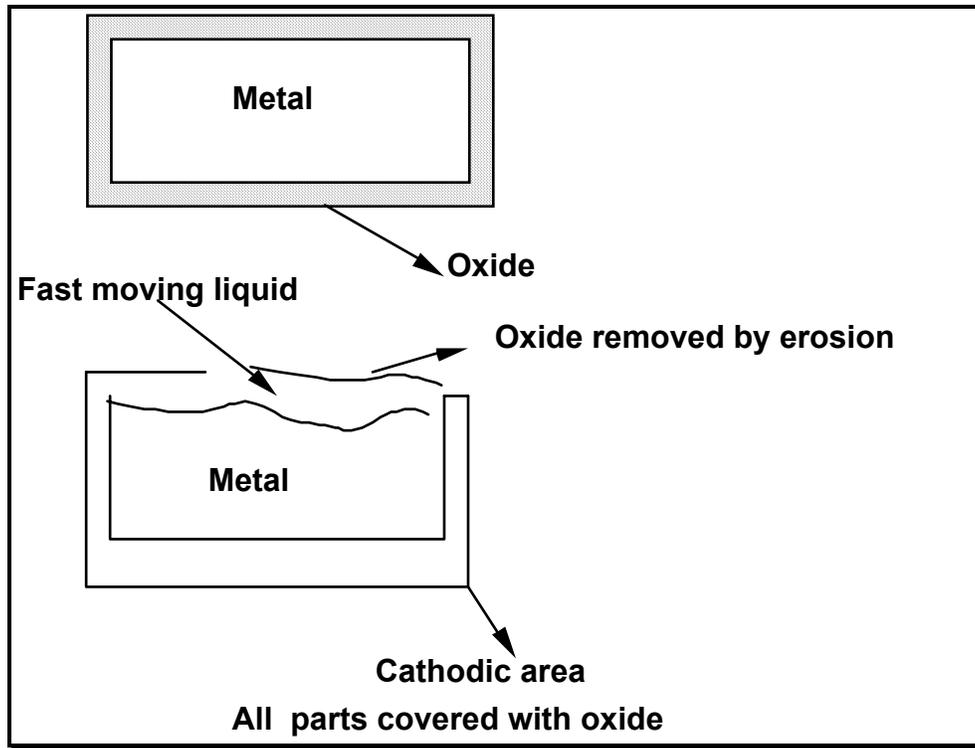
ii.   CREVICE CORROSION:

Pipline

Flowing Sewage   containig O 2

Cathodic area

Deposite of solids

Crevice

Anodic area

O2	No O 2
Cathodic area	Anodic area

Differential areation corrosion

   Take for example the case of sewage pipeline. Thin layers of stagnant liquid is present, the O_2 in these thin layers is consumed. The flowing liquid is rich in O_2 and O_2 diffusion to crevice is very slow.

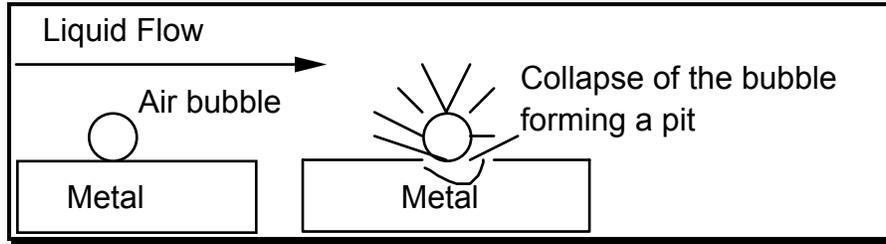## iii. EROSION CORROSION "MECHANICAL AND ELECTROCHEMICAL":

A liquid containing solid particles is moving fast over the surface of a metal covered with an air-formed oxide film.
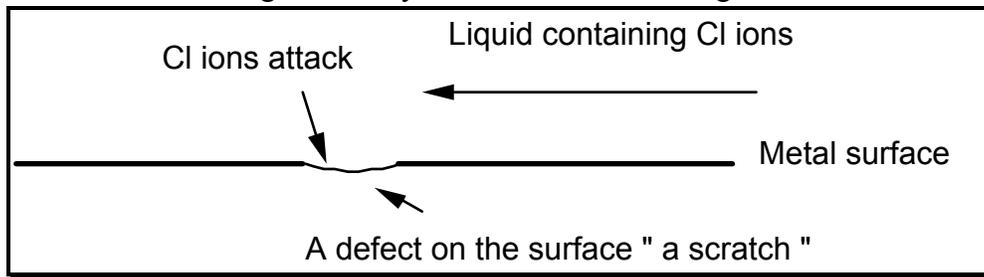
Metal

Oxide

Fast moving liquid

Oxide removed by erosion

Metal

Cathodic area

All parts covered with oxide

a)   CAVITATIONAL DAMAGE "A FORM OF EROSION": This results from the

formation and collapse of bubbles of vapor in a liquid near the metal surface causes pits, and this occurs frequently when we have a metal moving in a liquid. At prolonged times the metal is perforated
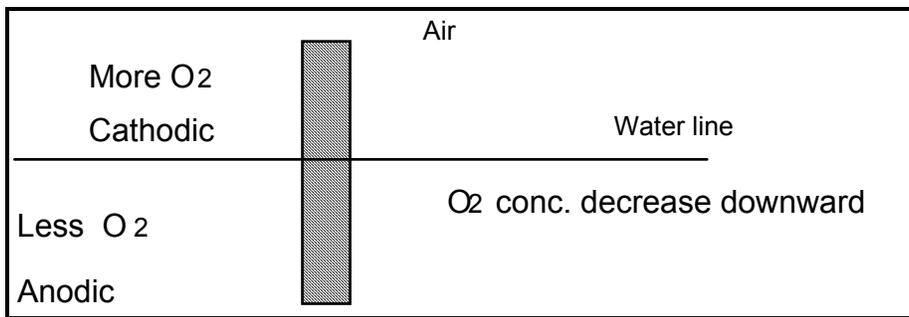
```
Liquid Flow
     ──────────▶
           Air bubble        Collapse of the bubble
              ○                forming a pit
     ┌──────────────┐      ┌──────────────┐
     │    Metal     │      │    Metal     │
     └──────────────┘      └──────────────┘
```

b)   **FRETTING CORROSION:** When two metals are in contact under load, they are welded together forming what is known as cold-welds. When the two metals are parts of an engine, the vibration of the engine destroy the cold-welds resulting in metallic debris.

```
                    Liquid containing Cl ions
      Cl ions attack        ◀─────────────────
              ↘
      ──────────────╲╱──────────────    Metal surface
                    ↙
          A defect on the surface " a scratch "
```

iv. PITTING CORROSION: Soluble metal chloride is formed at the defects, that leads to the loss of metal and the formation of a pit . The pit becomes deeper with further attack by Cl ions until it perforates the metal

v.   DIFFERENTIAL OXYGENATION CORROSION:
   Piers at sea-side are supported by heavy steel pillars as schematically shown and the difference in O_2 concentration will cause corrosion.

```
                         Air
      More O₂        ▓
      Cathodic       ▓          Water line
     ─────────────   ▓   ─────────────────────
                     ▓     O₂ conc. decrease downward
      Less  O₂       ▓
      Anodic         ▓
```

vi.   HYDROGEN DAMAGE:
"a" BLISTERING: Hydrogen atoms produced by the cathodic reaction diffuse into Fe-metal . Hydrogen atoms combine to form H_2 causing a pressure inside and results in a blister. The blister bursts and damages the metal .
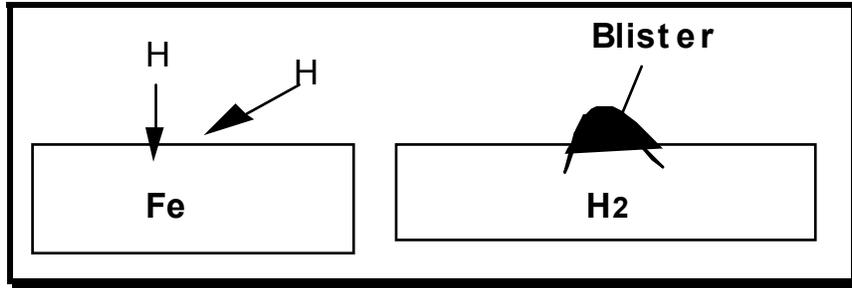
"b" EMBRITTLEMENT:

Some diffusion of Hydrogen atoms inside a metal, here the active Hydrogen atoms combine with the metal to form mtal hydride which is usually brittle the metal hydride falls a part and the metal becomes a powder.

1.2   ELECTROCHEMICAL PROTECTION PROCESSES

In electrochemical protection the metal surface is held at a potential where the corrosion rate is for all kinds of corrosion negligible. If several types of corrosion exist in the system there is in general a potential for every type of corrosion where the corrosion rate is negligibly "small" the boundary potential of these regions is called the protection potential. Potential control is achieved by polarization with direct current[either cathodic or anodic protection]. The current which flows as a result is termed the protection current. Corrosion can be reduced by "Forced draining" or draining of the stray current, by means of an imposed potential. In these methods the potential is reduced and hence the principle cathodic protection.

1.3- CATHODIC PROTECTION:

Principle

The potential of the metal to be protected is shifted in a negative direction to produce a cathodic protective action.

TWO METHODS ARE AVAILABLE FOR CATHODIC PROTECTION:

a)   The metal to be protected is electrically connected to a second less Noble metal in the same media. A corrosion cell is formed in which the less noble metal goes into solution through anodic dissolution, and hence the more noble metal is cathodically protected.[Galvanic coupling]
b)   The metal to be protected is connected to negative pole of an external battery while a second metal is connected to the positive as anode.[Impressed current]

Experiment

Practically in the cathodic protection there are some encountered problems due to the resistive component of the voltage drop. These can be eliminated by using what so called the technique of instantaneous off measurements. The electrochemical processes occurring in cathodic protection are strongly dependent on time owing to the polarization effects of the cathodically formed surface films. This time dependence is investigated by two Experiments.

(a) CATHODIC PROTECTION WITH GALVANIC ANODES:

GENERAL

In this case we investigate for example the cathodic protection of carbon steel by zinc or magnesium. Protective current and potentials are determined. The potential distribution along a half galvanized rod is measured in two conducting electrolytes .

METHOD:

Cathodic protection is produced by connecting the steel specimen to the Zinc or magnesium anode as shown in fig.( ). The current is measured by the voltage drop across a resistor. The potential is measured against a reference electrode. The point where the protective potential of steel is just reached is of. particular interest The experiment is carried out with a low conductivity electrolyte (10000 Ω cm) and a more conductive electrolyte (100 Ω cm). The principle of the potential distribution measurement is shown in fig ().

(b) CATHODIC PROTECTION BY IMPRESSED CURRENT:

Cathodic protection of carbon steel by impressed current is investigated under condition of soil corrosion.

METHOD:

 Cathodic protection with a circuit consisting of the specimen to be protected, an inert anode, the elecirolyte and the current source .For the measurement two methods are carried out:

1.   Potential-time measurement and instantaneous off mesurement to eleminate the ohmic potential drop in the electrolyte under galvanostatic condition.
2.   Current-time measurements under potentiostatic condition.

1 POTENTIAL-TIME CURVES AND INSTANEOUS OFF MEASUREMENT:

The metal to be protected "carbon steel" is immersed in the solution with specific resistance of (1000 Ω cm) and a reference capillary electrode is placed at the near and the far ends of the metal to be protected as in fig (), to eliminate the ohmic potential drop in the electrolyte at the far end of the steel specimen, the current is quickly interrupted and simultaneously the potential time curve is obtained with a rapid recorder the current is always interrupted for a very short time to alter the polarization state of the electrode as little as possible care must be taken not to disturb the electrolyte.

2 CURRENT-TIME CURVES:

The metal to be protected "carbon steel" is immersed in the solution with specific resistance (1000 Ω cm) and potentiostatic circuit as shown in fig ( ). The current is measured at intervals of 1 min. over a period of 10 min. the potential at the end of the specimen nearest to the anode is measured with a second reference electrode. Finally the effect of stirring on the protective

current is investigated.

1.4 ANODIC PROTECTION:

Some metal e.g. "Iron and Stainless Steel" can be protected effectively by making them anods, and shifting their potential into the passive region of the anodic polarization curve. The passive potential is electronically maintained constant by a potentiostate.

ANODIC PROTECTION:

EXPERIMENT :

The anodic protection of an unalloyed steel in a solution is investigated by weight loss measurement. Current density - potential curves are obtained to determine the protective potential region the fall in the protective current with time at previously determined working potential in the protective region is measured. To get an efficient anodic protection, the potential should be kept   at point (x) cf fig (1) .

METHOD:

The weight loss rate of a potentiostatically anodically protected and an unprotected steel specimen is measured by weighing, using the apparatus shown in fig ( ). We choose the working potential in the middle of the passive region and the protective current measured as a function of time.

- **EXPERIMENTAL-PROCEDURE**:
A cylindrical working electrode is polished and degreased to determinethe current density-potential curve. The potentiostatic circuit is connected and the free corrosion potential is measured by changing the potential (in steps of 100 mv from the free corrosion over the active and passive regions up to the transpassive region. The measurement are discontinued at a transpassive current density of 0.50 mA. The working potential for anodic potential is determined from the current-potential curve.

To investigate the action of anodic protection two specimens are given the same pre-treatment and weight one specimen is held at the working potential determined above and the other is allowed to corrode freely. At time " t = 0" the electrode is placed in the electrolyte and the protective current is measured over a period of 45 min. It is important to record the current accurately in the first few minutes. Finally the electrode is taken out of the electrolyte washed with distilled water, dried and weighted.

STRAY CURRENT CORROSION AND STRAY CURRENT PROTECTION:

If a metallic conductor is situated in an electrolyte through which a direct current is flowing a current flows in the conductor which corresponds approximately to the current flow in the displaced volume of electrolyte, as a simple approximation, assuming a rod shaped conductor and neglecting polarization effects ohm's law gives

. The interposed conductor current is proportional to the potential to the potential difference " Δu" between the ends of the conductor for a given specific conductivity. The following figure show the correlation in simplified form fig (1.8). A direct current flows through the filled with electrolyte between the cathode and anode of the external current circuit, producing a potential drop in the solution. The interposed conductor leads to short-circuit between points "A" and "D" so that the whole of its surface becomes an equipotential surface. The potential of the interposed conductor is therefore more positive in the region "A" by u2 in the region "D" more negative by the same amount than the free corrosion potential of the interposed conductor in the electrolyte solution the region "A" therefore become an anode and region "D" become a cathode. As a consequence of the interposed conductor effect, stray current corrosion occurs at "A" provided that the potential difference " u" is sufficient for the electrode reaction to take place "initial condition of the interposed conductor in fig (1.9). For stray current protection by drainage the interposed conductor in connected in series with an external resistor to the cathode of the stray current producing circuit "principle of cathodic protection" this means that the potential has to be lowered at least to the free corrosion potential "corresponding to the position of the stray current drain in the above fig (1.8 & 1.9). The explanation given here is a highly simplified representation. In practice the relationships are much more complicated, particularly if the stray current are to be calculated

2. INHIBITION.

Inhibitors are substances which when added to a medium reduce the corrosion rate. The inhibitors are classified into:

I INORGANIC INHIBITORS:

This type of chemicals generally stimulates the passivation of metal by substantial increase of corrosion potential towards noble value inorganic inhibitors belongs the species with noble redox potential and able to be easily reduced.

I.a- ANODIC INHIBITORS:

Oxidising Inhibitors they are anions ~f weak acids as "nitrile, chromate, phosphates carbonites" which form a protective film of oxide or hydroxide on the metal surface and this substance increases anodic polarization.

From anodic inhibitor polarization curve we have the following result inhibitor decrease "Icorr" and shifts "Ecorr" in the positive direction.

Inhibitor may change the slope of the anodic part and make shift Ecorr to more + ve and this lead to decrease Icorr and corrosion rate. Or may cause paralel shif

anodic curve and this lead to shift of "Ecorr" to more +ve and decrease the Icorr and corrosion rate.

I.b- CATHODIC INHIBITORS:

They include cations, which form in neutral solution protective surface films of insoluble salts bY reaction

or by precipition salt of, mg, Zn, Mn Ni from insoluble hydroxides especially at the cathodic areas which are more alkaline due to the hydroxyl ions produced by reduction of oxygen . Salt of (Ca) can precipitate as calcium carbonate in water containing CO_2 at the cathodic area wher the pH is high enough to give sufficient carbonate ion concentration. The salt films are often quite thick and may be visible, particularly of oxygen on the metal surface. From the curve of Tafel line note that :

In figure (2.3) Inhibitor decrease Icorr and shift "Ecorr" to more negative value by changing the slope of Tafel line. In fig.(2.4) Inhibitor cause paralel shift of Tafel

The concentration of the inhibitor needed to give protection will depend on:

1-   Composition of the environment 2- Temperature 3- Velocity of the liquid environment past the Metal 4- The presence or absence of internally or externally applied stresses.

FACTORS EFFECT ON INHIBITION EFFICIENCY:

1-   The surface plays a very importent rol, a clear smooth metal surface usually regquires a lower concentration of inhibitor than rouoh or dirtv surface
3-   The kind of media. 4- pH value must be known with accuracy Thls because Nitrites "a) Example" lose their effectiveness below pH of 5.6-6 and for pdy phosphate and chromate, the critical pH value are 5.6 to 7.5 respectively. Temperature when increase higher concentr'ation of inhibitor are usually necessary. Sometimes chemicals lose their efficiency as in case of pdy phosphate which becomes ortho phosphat which are ineffective at initial concentration if temperature higher than 40 °C.

II.   ORGANIC INHIBITORS:
Inhibitor are adsorped on the surface, the mode of adsorption are depended upon.

1-   Chemical structure of the molecule and nature of metal surface. 2- Electrochemical potential at the metal solution interface and chemical composition of the solution. Adsorption of organic inhibitor is considered as chemisorption by chairing electron's between inhibitor and metal covalent bond or electron transfere or donation from adsorbed molecules. The protective action "Z" of an inhibitors in percent is defined as:
The inhibitive action of a substance is mostly a function

Correct design of the component for corrosion protection Correct planning of the total corrosion protection system Careful preparation and testing of the surface Correct choise of coating material and protective system Careful operation and supervision of the corrosion protection.

of the electrode potential, for this reason many inhibitors are effective only in limited potential regions, this potential depended protective action can be duo to potential dependent adsorption or desorption processes or oxidation or reduction changes of the inhibitor on the metal surface .

Inhibitor can also pervent hydrogen diffusion into the metal, this occure in the inhibition of hydrogen permeation through a carbon steel is determined by electrochemical oxidation of the hydrogen.

ORGANIC COATINGS: Organic coatings have similar propertes to plastics since binder materials and plastics both have polymeric structures, for corrosion protection it is therefore significant organic coating are able to absorb organic solvent and allow them to permeate conductivity of the coating. These substance can reach the base material coating interface by permetion "diffusion and phase boundary reaction" and migration in presence of an electric field due to potential difference they miliate electrolytic reaction on the basis metal anodic "Pitting, corrosion, anodic bubbles".Carbon and alloy steels are the mean materials protected by organic coatings, to achieve long term protection several factors must be observed, of which the most importent

Indepedent of type of coating material a distinction is made between:

"a" Thin Coating
"b" Thick coating.

"a" THIN COATING:

Thin coating consists mainly of multilayer system or reactive resins with a total film thickness of under about 0.8 mm coatings of greater thickness are termed thick coatings they consist mainly of bituminous materials or thermoplastic polymers, and in a few cases, thermosetting plastics, they are used for example as the outer protection for pipes buried in the ground, usually in combination with cathodic protection, corrosive action can be multifarious corrosive media against which the coating itself must be corrosion resistant include:atomsphere water

s o i l chemicals.

The following can also be present in addition to the effect of the medium:cathodic effect anodic effect temperature gradient effects

CATHODIC EFFECT AT THE SURFACE OF THE COATED MATERIAL CAN BE CAUSED BY:

Corrosion of the basis material at gaps in coated "pores" Contact with an inert anode "under uncoated parts of the material" Cathodic corrosion protection 4- Stray currents entering the material "from electrochemical protection measures". 5- Passive base material at gabs in the coating in the neighbourhood of pores or defects 6- Contact with an impressed current cathode 7- Stray current leaving the material .

• In some few cases corrosion of the coating system is occure this is due to :a- Reduction or loss of adhesion in coatings free of pores b- Pitting corrosion of the base material in the neigbourhood of pores or defects in the coating.
c- Cathodic "Alkaline" disbonding. d- Formation of blisters.

BLISTER:

The following mechanism of blister formation can be identified:

1-   Osmotic blisters
2-   Blister arising from temperature gradient
3-   Cathodic blisters
4-   Anodic blisters

1-   OSMOTIC BLISTER:

If the surface hase salt particles or other hydrophilic substance are exposed before coating to the action of water an osmotic pressure exists between salt solution and pure water, migration of water to the salt particles occures, the magnitude uf the osmotic pressure increase with increasing difference in the salt concentration in two solution. The content of the blister is a salt solution whose pH depends on type of salt "hydrolysis".

2-BLISTER ARISING FROM, TEMPERATURE GRADIENTS:

Occure on clean surface only when the material of the surface is colder than the medium. Since the vapour pressure of water increase with temperature and condensation of water vapour occures on the colder part of the surface. The content of the blisters in neutral water, Blister formation in organic coatings or carbon steel as

a result of a temperature difference between the base metal and the medium is investigated. The double-side coated specimens are exposed to adrop in temperature between material and medium to achieve this they are clamped as the dividing wall between two cells through which water at different temperatures flows. Heat transfer occures from one cell to the other one surface of the coated specimen is thus cooled while the other is heated. Tap water is passed through one cell and held at constant temperature by a heater and thermostate, the other half of the double cell contains flowing water held at a different temperature controlled by the second thermostate and heater. So that temperature difference of 1°, 7° and 20 °C can be obtained, the experiment is ended after "24 h" the specimen is examined on both sides for blisters.

of blisters is alkaline, coatings can be considered as resistance to cathodic blisters if the specific resistance of the coating is at least 106 to 108 cm, according to the level of the cathodic potential.

3.   CATHODIC BLISTERS:

Cathodic blister containing alkali occure when the coated is a cathode since oxygen and water vapour can permeate through most coating they can be cathodically reduced at the material surface with the formation of oH ions, for the continuation of this reaction the presence of cation is necessary, therefore cations (Na+) must also diffuse through the coating at the same time because the content

4-   ANODIC BLISTERS:

Anodic blisters are the result of the surface becoming anodic, Hydrogen ions are formed as a result of anodic dissolution of the metal and the hydrolysis of the corrosion products, the

electrochemical reaction can occure only if migration of anions as "Cl , SO_4 , NO_3" occure.