CORROSION FORM

we have mainly (more or less implicitly) assumed that:

1) electrochemical corrosion is the only deterioration mechanism;

2) anodic and cathodic reactions take place all over the electrode surface, but not simultaneously at the same place, i.e. the anodic and cathodic reactions exchange places, constantly or frequently. Closely related to this dynamic behavior it is assumed that:

3) there are no significant macroscopic concentration differences in the electrolyte along the metal surface, and the metal is fairly homogeneous.
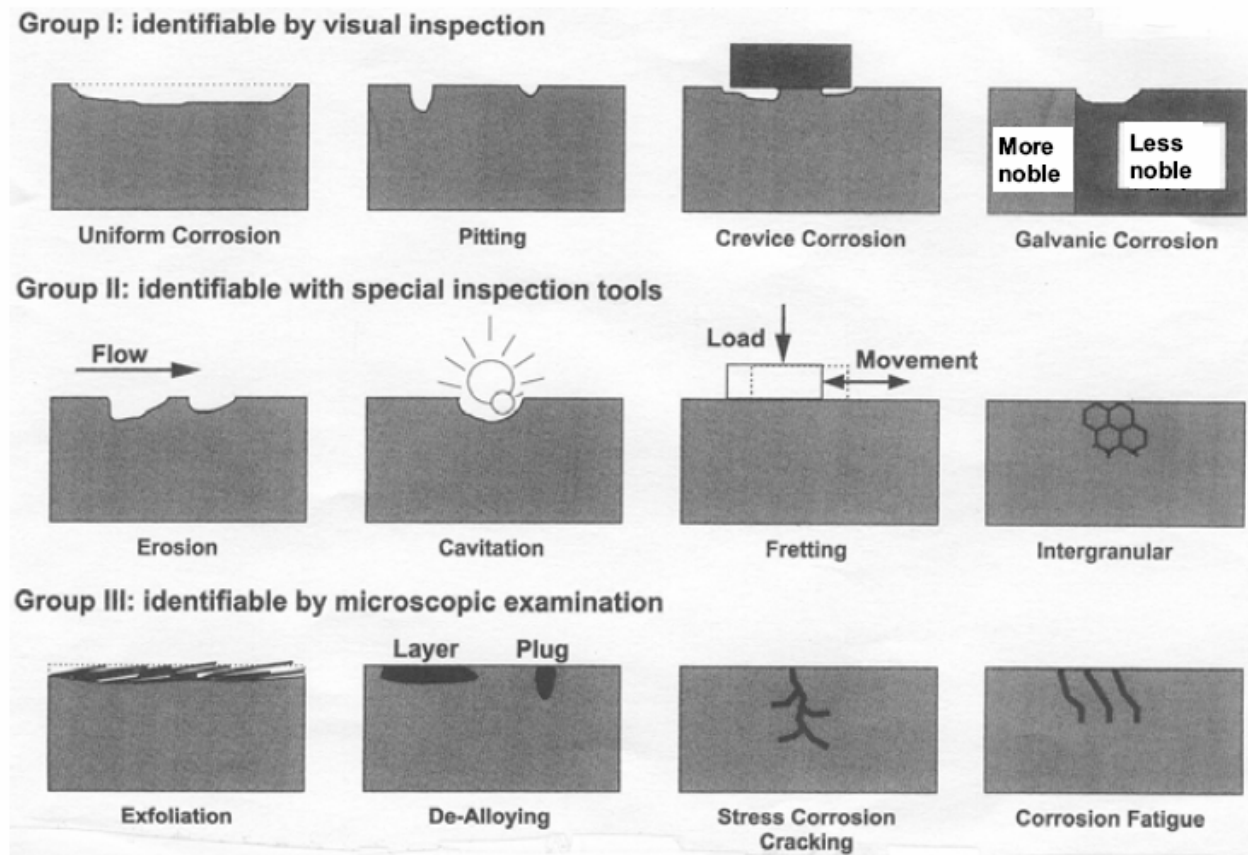
These three assumptions lead to *uniform (general)* corrosion. But this is only one of several corrosion forms that occur under different conditions. The other forms of corrosion depend on the deviations from the mentioned assumptions. Such deviations may be due to:

      a) the design (the macro–geometry of the metal surfaces)

      b) the combination of metal and environment

      c) the state of the surface (particularly cleanliness and roughness)

      d) other deterioration mechanisms

On this basis, the following corrosion forms can be defined:

1. Uniform (general) corrosion
2. Galvanic (two–metal) corrosion
3. Thermogalvanic corrosion
4. Crevice corrosion (including deposit corrosion)
5. Pitting, pitting corrosion
6. Selective attack, selective leaching (de–alloying)
7. Intergranular corrosion (including exfoliation)
8. Erosion corrosion
9. Cavitation corrosion
10. Fretting corrosion
11. Stress corrosion cracking
12. Corrosion fatigue

A simple illustration of the various forms of corrosion is shown in below Figure

Group I: identifiable by visual inspection

Uniform Corrosion Pitting Crevice Corrosion Galvanic Corrosion

More noble Less noble

Group II: identifiable with special inspection tools

Flow

Load Movement

Erosion Cavitation Fretting Intergranular

Group III: identifiable by microscopic examination

Layer Plug

Exfoliation De-Alloying Stress Corrosion Cracking Corrosion Fatigue
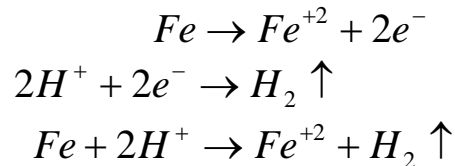
1- UNIFORM CORROSION

This is a uniform and general attack, in which the entire metal surface area exposed to the corrosive environment is converted into its oxide form, It is the uniform thinning of a metal without any localized attack, corrosion does not penetrate very deep inside, and the most familiar example is the rusting of steel in air.

Uniform corrosion is assumed to be most common form of corrosion and particularly responsible for most the materials loss. Traditionally, however it is not recognized as dangerous form of corrosion, because:
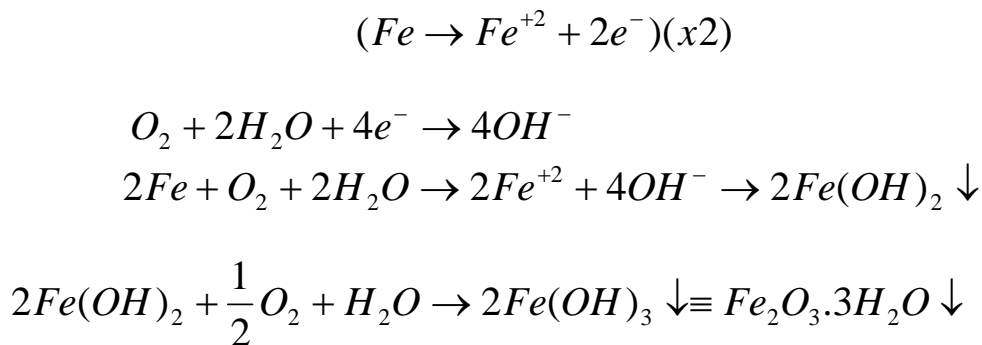
1. Prediction of thickness reduction rate can by means of simple tests .corresponding corrosion allowance can be added taking into account strength requiring and lifetime.

2. Available protection methods are usually so efficient that the corrosion rate is reduced to an acceptable level. Actual methods are application of coatings, cathodic protection or possibly change of environment or material.

Aqueous corrosion of iron (Fe) in H_2SO_4 solution is examples of uniform attack since Fe can dissolved (oxidize) at a uniform rate according to the following anodic and cathodic reactions, respectively.

$$Fe \rightarrow Fe^{+2} + 2e^-$$
$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$
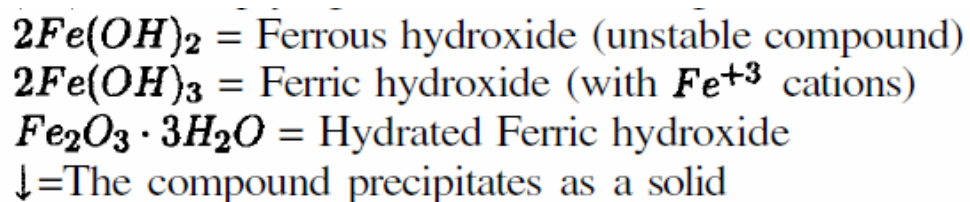$$Fe + 2H^+ \rightarrow Fe^{+2} + H_2 \uparrow$$

Atmospheric corrosion of a steel structure is also a common example of uniform corrosion, which is manifested as a brown-color corrosion layer on the exposed steel surface. This layer is a ferric hydroxide compound known as **Rust**. The formation of Brown Rust is as follows
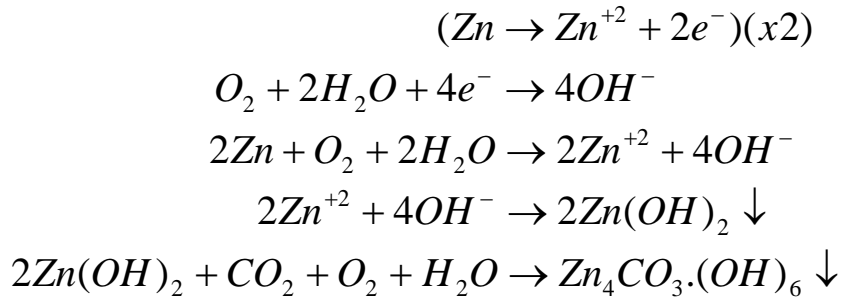
$$(Fe \rightarrow Fe^{+2} + 2e^-)(x2)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{+2} + 4OH^- \rightarrow 2Fe(OH)_2 \downarrow$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 \downarrow \equiv Fe_2O_3.3H_2O \downarrow$$

Where
(x2)= Multiplying factor for balancing the number of electron

$2Fe(OH)_2$ = Ferrous hydroxide (unstable compound)
$2Fe(OH)_3$ = Ferric hydroxide (with Fe^{+3} cations)
$Fe_2O_3 \cdot 3H_2O$ = Hydrated Ferric hydroxide
$\downarrow$ =The compound precipitates as a solid

In addition, Zinc can uniformly corrode forming a White Rust according to the following reactions

$$(Zn \rightarrow Zn^{+2} + 2e^-)(x2)$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$2Zn + O_2 + 2H_2O \rightarrow 2Zn^{+2} + 4OH^-$$
$$2Zn^{+2} + 4OH^- \rightarrow 2Zn(OH)_2 \downarrow$$
$$2Zn(OH)_2 + CO_2 + O_2 + H_2O \rightarrow Zn_4CO_3.(OH)_6 \downarrow$$

In fact, the compound or is **$Zn_4CO_3.(OH)_6$** or **$ZnCO_3.Zn(OH)_2$** is zinc carbonate or **white rust** or wet-storage stain (porous).
Atmospheric corrosion of aluminum is due to a passive oxide film formation instead of a porous layer. The gray/black-color film may form as follows

$$(Al \rightarrow Al^{+3} + 3e^-)x2$$

$$\frac{3}{2}O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$$

$$2Al + \frac{3}{2}O_2 + 3H_2O \rightarrow 2Al^{+3} + 6OH^- \rightarrow Al_2O_3.3H_2O \downarrow$$
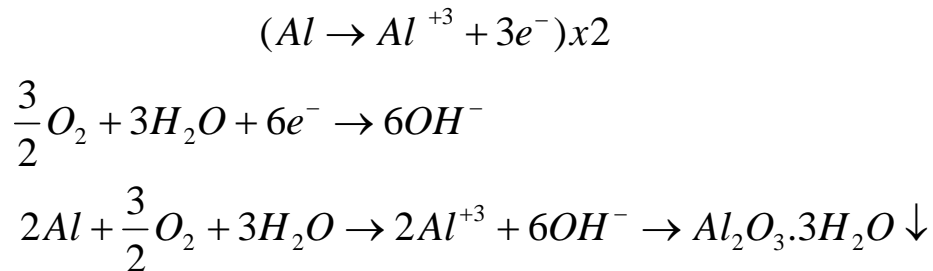
Some factor effect on uniform corrosion

1. Effect of pollutants: corrosion can proceed in a dry environment without any moisture if trace of sulfur components or H_2S or other pollutants are present in the air. i.e. tarnishing of silver in dry air .the arte of corrosion in presence of SO_2 increase in the presence of moisture

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad \text{(Sulfuric acid)}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad \text{(Sulfurous acid)}$$

$$SO_2 + 2Fe_2O_3 \rightarrow FeSO_4 + Fe_3O_4$$
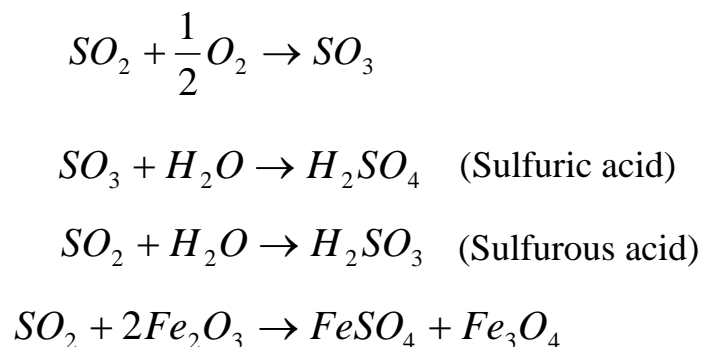
The $FeSO_4$ formed accelerate corrosion, once rusting has started, corrosion can not be stopped even after SO_2 is removed from air.

2. Effect of humidity: Corrosion can be caused in the atmosphere when about 70% of the humidity is present, as this is the value in equilibrium with saturated NaCl solution and NaCl is commonly present on surfaces. In the presence of such humidity, an invisible thin film of moisture is formed on the surface of a metal. The thin film of moisture acts as an electrolyte for the passage of current Structures which are exposed to open air, are affected by damp environments. Beyond 80% relative humidity, a sharp increase in the rate of corrosion is observed.

3. Water layer: If visible water layers are formed on the metal surface, corrosion initiates. Splashing of seawater, rain and drops of dew provide the wet environment. The water layer on the metal surface acts as an electrolyte and provides a passage for the flow of current, similar to the situation in a corrosion cell.

4. Dew formation: If the dew becomes acidic, due to the presence of SO2, it increases the rate of corrosion .Automobiles left open in the air may be subject to corrosion through acidic dew formation

5. Corrosion products: If the corrosion product on the metal surface is microporous, it can condense the moisture, below the critical value. Corrosion proceeds rapidly in such a case, even if the moisture content is below the critical limit

Mechanism of uniform corrosion

Corrosion mechanism in aqueous solution has been amply demonstrated. A very thin layer of electrolyte is present. It is probably best demonstrated by putting a small drop of seawater on a piece of steel. On a metal surface exposed to atmosphere, only a limited quantity of water and dissolved ions are present, whereas the access to oxygen present in the air is unlimited. Corrosion products are formed close to the metal surface, unlike the case in aqueous corrosion, and they may prevent further corrosion by acting as a physical barrier between the metal surface and environment, particularly if they are insoluble as in the case of copper or lead. The following is a simplified mechanism of aqueous corrosion of iron
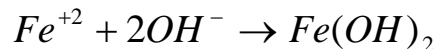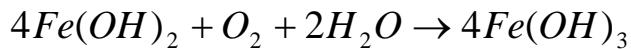At anodic areas, anodic reaction takes place:

$$Fe \rightarrow Fe^{+2} + 2e^-$$
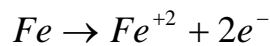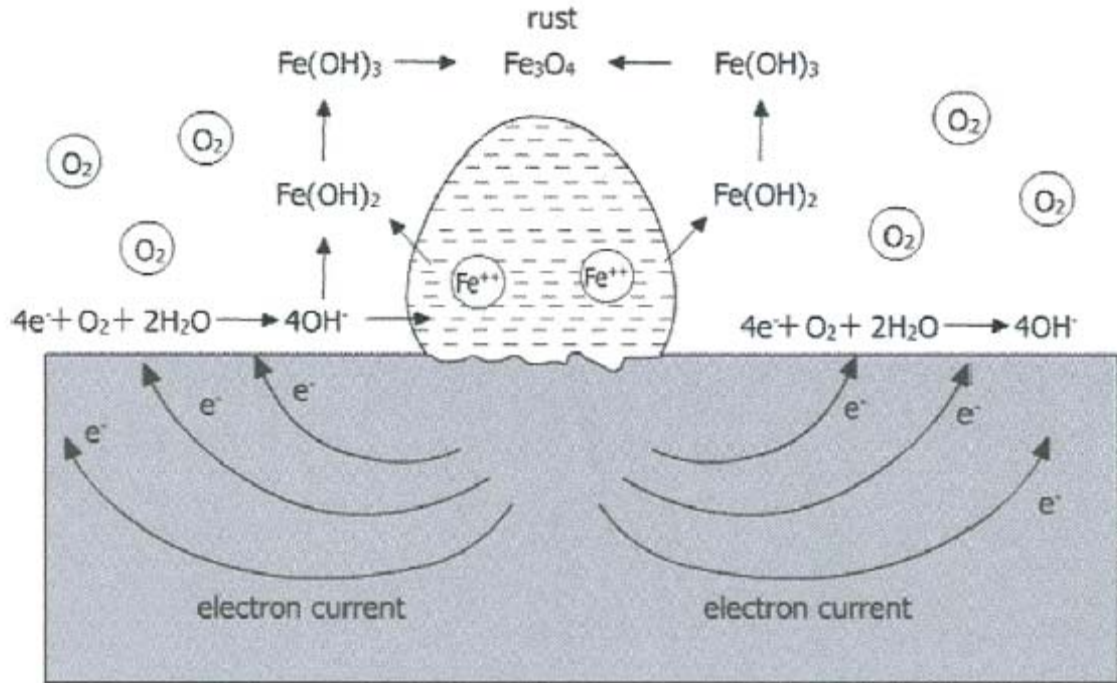
At cathodic areas reduction of Oxygen takes place

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
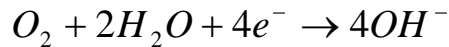
The OH ions react with iron ions , produced at the anode

$$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$$

With more access to Oxygen in the air , $Fe(OH)_2$ oxidizes to $Fe(OH)_3$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

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

$$4Fe(OH)_3 + O_2 \rightarrow 2Fe_2O_3.3H_2O + 2H_2O$$
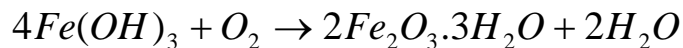
Rust ($Fe_2O_3.3H_2O$) is formed halfway between the drop center and the periphery .the electrons flow from the anode (drop center) to cathode (periphery) in the metallic circuit. The current flow is shown in above figure. The ferrous ions on the surface of iron are soluble whereas those in solution are oxidized by oxygen to insoluble hydrated oxides of ferric called rust. The rust is formed away from the corroding site.

The corrosion rate is very high if the ferrous ion is oxidized to ferric oxide rapidly. $Fe(OH)_3$ is insoluble and if it forms away from a metal surface, the corrosion reaction speeds up as equilibrium is to be maintained by supplying more ferrous ions (Fe^{+2}) from the surface. If, however, $Fe(OH)_3$ is formed on the surface of a metal very rapidly, the corrosion is prevented (a passive film).

Example of uniform corrosion
(1) Tarnishing of silver ware.
(2) Tarnishing of electrical contacts.
(3) Rusting of steels in open air.
(4) Corrosion of offshore drilling platforms.
(5) Corrosion of galvanized steel stairways.
(6) Failure of distillation columns.
(7) Corrosion of electronic components.
(8) Corrosion of underground pipes (composite asphalt coated).
(9) Corrosion of automobile bodies.
(10) Corrosion of heat exchanger tubes.
(11) Corrosion of structural steels.

Corrosion allowance. A popular remedy is to make a corrosion allowance. After calculating the rate of corrosion penetration and knowing how much thickness of the metal would be reduced after a specified period, an equivalent amount of thickness maybe added to prevent the loss of designed thickness. A corrosion allowance is, therefore, made at the design stage to prevent the loss of thickness by general corrosion. For instance, if the predicted rate of corrosion for a new carbon-steel product cooler is 4 mpy, as the unit is designed for 15 years, the required corrosion allowance is 4 mpy x 15 years = 60 mils (0.060 in). The general practice is to allow 1/8 in, or 3.2 mm minimum corrosion allowance.

$$\text{Estimation of remaining life (years)} = \frac{\text{Remaining corrosion allowance (mils)}}{\text{Present corrosion rate (mpy)}}$$

For example, consider a crude oil tower overhead pipeline. Due to some accident, the crude tower was shutdown. The general wall thickness measured was 0.14 in on a 35 in diam. carbon steel overhead line. The minimum thickness required is 0.15 in. The current corrosion rate is 40 mils/year. Another shutdown for inspection is scheduled to take place after two years. Use the above equation to estimate the remaining life

$$2\,years = \frac{\text{Corrosion allowance remaining}}{40mpy}$$

So corrosion allowance remaining = 80 mils (0.080 in)

The required remaining thickness = 0.15 in + 0.080 in = 0.23 in.
The best solution, therefore, would be to install reinforcing plates of above 0.20 inch in thickness. Use a magnesium anode rod inside the tank containing brackish water or the high conductivity water.
(2) Reduce operating temperatures.
(3) Coat the steel surface with epoxy-phenolic coating.
(4) Do not allow the insulation to become wet.
(5) Inspect the insulation periodically.
(6) Avoid exposure to dust storm. During the Gulf war, helicopter rotor blades were subjected to severe corrosion by dust storm. The general corrosion was of such a high magnitude that the thickness of some rotor blades was reduced to 5 mm.

2-GALVANIC CORROSION
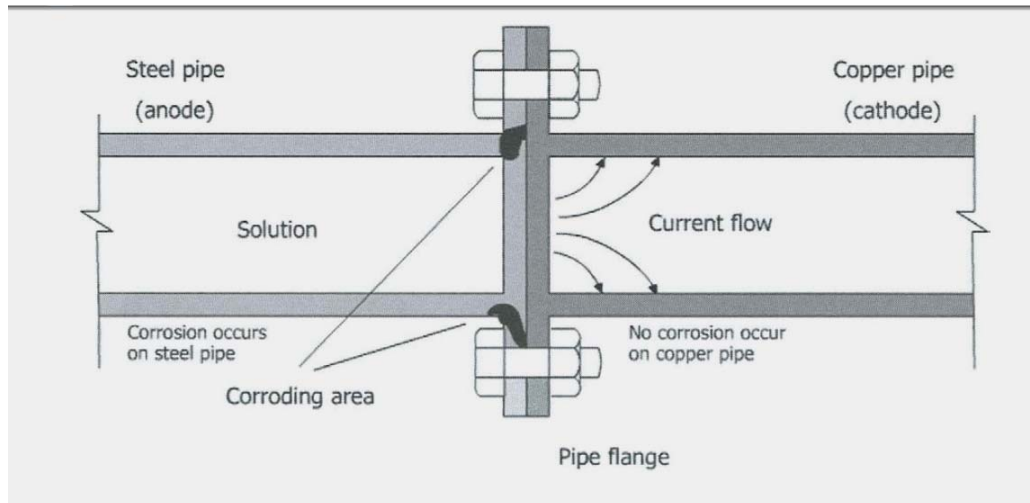
Galvanic corrosion occurs when two metals with different electrochemical potentials or with different tendencies to corrode are in metal-to-metal contact in a corrosive electrolyte.
When two metals with different potentials are joined, such as copper (+0.334 V) and iron (-0.440 V), a galvanic cell is formed. A cell in which the chemical change is the source of energy, is called a galvanic cell The corrosion which is caused due to the formation of the galvanic cell is, therefore, called galvanic corrosion. The driving force for corrosion is a potential difference between different materials. This force was described by Luigi Galvani, late in the eighteenth century. Between the two different materials connected through an electrolyte, the less noble will become the anode and tend to corrode.
Mechanism of galvanic corrosion
For the formation of a galvanic cell, the following components are required:
(1) A cathode.
(2) An anode.
(3) An electrolyte.
(4) A metallic path for the electron current

Steel pipe (anode) | Copper pipe (cathode)

Solution

Current flow

Corrosion occurs on steel pipe

No corrosion occur on copper pipe

Corroding area

Pipe flange

In the case of copper and steel, copper has a more positive potential according to the e.m.f. series, hence, it acts as a cathode. On the other hand, iron has a negative potential in the e.m.f series (—0.440 V), hence, it is the anode. As a matter of principle, in a galvanic cell, the more noble metal always becomes the cathode and the less noble always the anode. Moisture acts as an electrolyte and the metal surface provides a metallic path for the electron current to travel.

Factors effect on galvanic corrosion
The following factors significantly affect the magnitude of galvanic corrosion:
A. Position of metals in the galvanic series.
B. The nature of the environment.
For instance, water containing copper ions, like seawater, are likely to form galvanic cells on a steel surface of the tank. If the water in contact with steel is either acidic or contains salt, the galvanic reaction is accelerated because of the increased ionization of the electrolyte. In marine environments, galvanic corrosion may be accelerated due to increased conductivity of the electrolyte. In cold climates, galvanic corrosion of buried material is reduced because of the increased resistivity of soil. In warm climates, on the other hand, it is the reverse because of the decreased resistivity of the soil.
C. Area, distance and geometric effects
Effect of Area
The anode to cathode area ratio is extremely important as the magnitude of galvanic corrosion is seriously affected by it. The area ratio can be unfavorable as well as favorable. The area ratio of the anode to cathode plays a dominant role in galvanic corrosion. As a given amount of current flows in a galvanic couple, the current density at the anode or cathode controls the rate of corrosion. For a given amount of current,

the metal with the smallest area has the largest current density and, hence, is more damaged if corrosion occurs at it.

Effect of Distance

It is a known principle that the solution conductivity varies inversely with the length of the conduction path. Most corrosion damage is caused by current which cover short paths. Hence, the greatest galvanic damage is likely to be encountered near the junction of the two metals and the severity would be decreased with increased length. If two different metals are far away from each other, there would be no risk of galvanic corrosion, because of very little current flow.

Effect of Geometry

Geometry of components and their design also influence galvanic corrosion. As current does not flow around the corners

METHODS OF P R E V E N T I O N OF GALVANIC C O R R O S I ON

(1) Select metals, close together, as far as possible, in the galvanic series.

(2) Do not have the area of the more active metal smaller than the area of the less active metal.

(3) If dissimilar metals are to be used, insulate them.

(4) Use inhibitors in aqueous systems whenever applicable and eliminate cathodic depolarizers.

(5) Apply coatings with judgment. Do not coat the anodic member of the couple as it would reduce the anodic area and severe attack would occur at the inevitable defect points in the coating. Therefore, if coating is to be done, coat the more noble of the two metals in the couple which prevents electrons being consumed in a cathodic reaction such as

$$2H^+ + 2e^- \rightarrow H_2$$
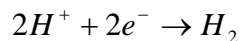
which is likely to be corrosion rate controlling.

(6) Avoid joining materials by threaded joints.

(7) Use a third metal active to both the metals in the couple.

(8) Sacrificial material, such as zinc or magnesium, may be introduced into this assembly. For instance, zinc anodes are used in cast iron water boxes of copper alloy water-cooled heat exchangers.

(9) In designing the components, use replaceable parts so that only the corroded parts could be replaced instead of the whole assembly.