Corrosion

Introduction :

Corrosion is a process of gradual deterioration or eating away of a metal from its surface due to the unwanted chemical or electrochemical reaction of metal with its environment.

For example, formation of a layer of reddish scale or hydrated ferric oxide (Fe_3O_4) on the surface of iron, also known as "rusting of iron".

Another example is formation of green film of basic carbonate [$CuCO_3 + Cu(OH)_2$] on the surface of copper, when exposed to moist air containing carbon dioxide.

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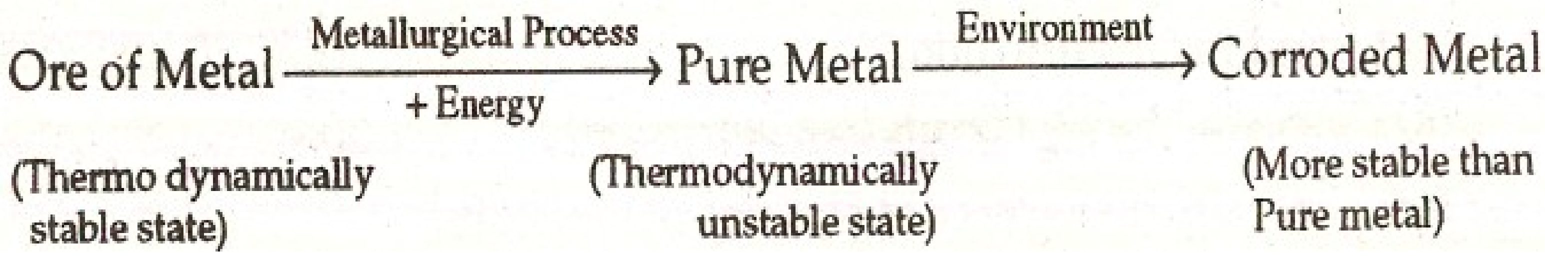
Cause of corrosion :

Metals exist in nature in the form of carbonates, sulphides and sulphates.

These chemically combined states of metal "known as ore" has a low energy and is thus thermodynamically stable state of metal. A considerable amount of energy is required during metallurgy. The extracted metal has higher energy and thus it is thermodynamically unstable state. Metals do this interacting chemically or electro-chemically with its environment to form compound at the surface and thus metal undergo corrosion.



$$\text{Ore of Metal} \xrightarrow[\text{+ Energy}]{\text{Metallurgical Process}} \text{Pure Metal} \xrightarrow{\text{Environment}} \text{Corroded Metal}$$

(Thermo dynamically stable state)

(Thermodynamically unstable state)

(More stable than Pure metal)

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Corroded metal is thermodynamically more stable than pure metal but due to corrosion useful properties of a metal such a malleability, ductility and electrical conductivity are lost.

Effects of corrosion :

Effects of corrosion are given below:

(i) Loss of useful properties of metal and thus loss of efficiency.

(ii) Decrease in production rate, because efficiency is less and replacement of corroded equipment or machinery is time consuming.

(iii) Increase in maintenance and production cost.

(iv) Contamination of product.

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Theories of Corrosion :

Different theories of corrosion are:

(1) Acid theory

(2) Direct chemical attack or dry corrosion theory

(3) Electrochemical or wet corrosion theory.

(1) Acid Theory :

This theory is particularly applicable to rusting of iron in the atmosphere.

According to this theory, rusting of iron is due to the continued action of oxygen, carbon dioxide and moisture, converting the metal into a soluble ferrous bicarbonate which is further oxidised to the basic ferric carbonate and finally converted to hydrated ferric oxide. Chemical reactions are:

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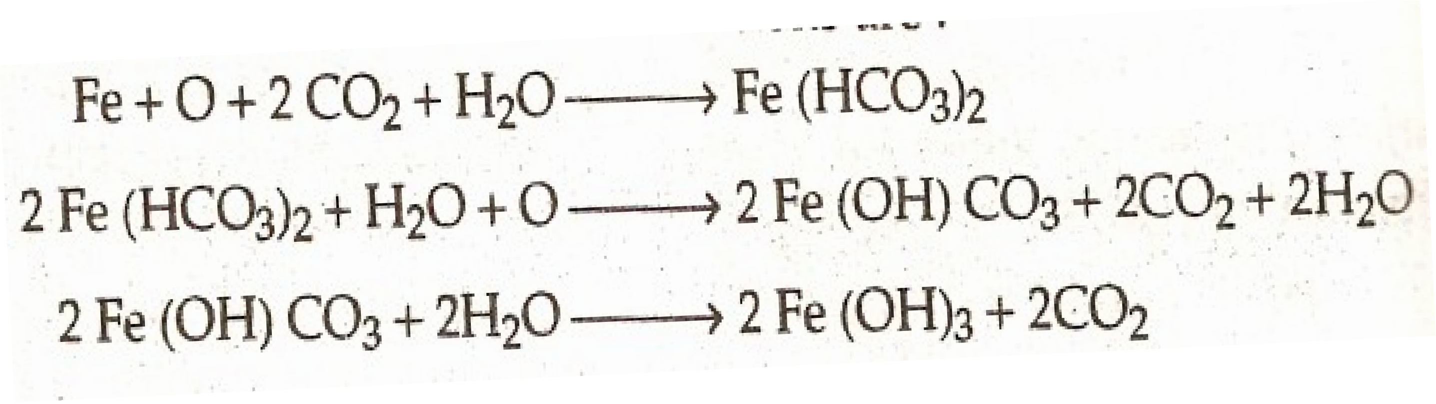

$$Fe + O + 2\,CO_2 + H_2O \longrightarrow Fe\,(HCO_3)_2$$

$$2\,Fe\,(HCO_3)_2 + H_2O + O \longrightarrow 2\,Fe\,(OH)\,CO_3 + 2CO_2 + 2H_2O$$

$$2\,Fe\,(OH)\,CO_3 + 2H_2O \longrightarrow 2\,Fe\,(OH)_3 + 2CO_2$$

This theory is supported by the following facts:

(i) Rust analysis shows the presence of ferrous· and ferric carbonates alongwith hydrated ferric oxide.

(ii) Retardation of rusting in presence of added lime or NaOH to the water in which iron is immersed.

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Electrochemical or Wet corrosion theory :

It takes place under moist or wet conditions through the formation of short circuited galvanic cells. Electrochernical or wet corrosion is more common than dry corrosion. Electrochemical corrosion involves:

(i) Separate 'anodic' and 'cathodic' areas between which current through the conducting medium.

(ii) Occurrance of oxidation (corrosion) at anodic areas which generates metallic ions,

(iii) Non-metallic ions like OH^- or O^{2-} are formed at cathodic areas, and

(iv) Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.

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For example:

Rusting of iron in neutral aqueous solution of electrolyte in the presence of oxygen or in acidic environment with evolution of hydrogen.

Fe^{2+} ion originates at anode and OH^- ions originate from cathode. Smaller Fe^{2+} ions diffuse more rapidly than the larger OH^- ions, so corrosion occurs at the anode, but corrosion product rust deposited near cathode.

The electrons released at anode are conducted to the cathode and are responsible for various cathodic reactions like

(i) Hydrogen evolution: In absence of O_2

(a) In acidic medium: $2H^+ + 2e^- \longrightarrow H_2$

(b) In neutral or alkaline medium:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

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(ii) Oxygen absorption: In presence of dissolved oxygen

(a) In acidic medium:

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$$

(b) In neutral or weakly alkaline medium:

$$2H_2O + O_2 + 4e^- \longrightarrow 4\,OH^-$$

(iii) Electroplating : At cathode, metal ions collect the electrons and get deposited on the surface of cathode.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

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Types of Corrosion:

1. **Galvanic corrosion :**

   It takes place when different metals are jointly exposed to corrosive atmosphere. The metal which is higher up in electrochemical series, with more negative electrode potential will act as anode and undergo corrosion. example, Zn and Cu; Fe and Cu; Zn and Ag. In the Zn-Cu galvanic cell, Zn act as anode where oxidation and corrosion occurs and Cu act as cathode and is protected.

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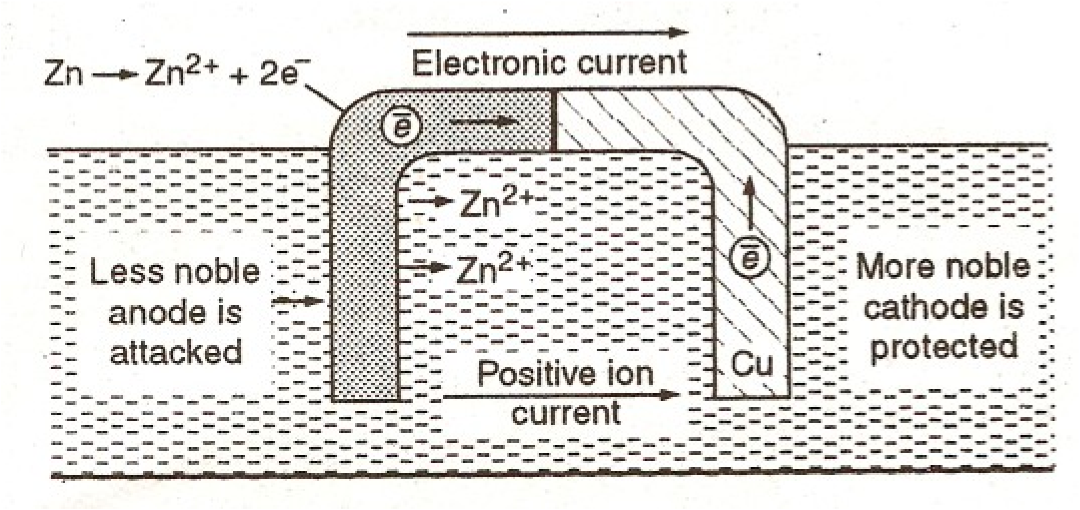

Galvanic corrosion can be minimised by

(i) Avoiding galvanic couple.

(ii) Providing insulating material between the two metals.

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Pitting corrosion :

Pitting corrosion is a localized accelerated attack resulting in the formation of cavities around which the metal is relatively unattacked, therefore, pitting corrosion results in the formation of pinholes, pits and cavities in the metal. Pitting is, usually, the result of the breakdown or cracking of the protective film on the metal at specific points. This gives rise to the formation of small anodic and large cathodic areas.

The presence of extraneous impurities (like sand, dust, scale etc.) embedded on the surface of metals also leads to the pitting. Owing to the differential amount of oxygen in contact with metal, the small part (Underneath the impurity) become the anodic areas and surrounding large parts become the cathodic areas.

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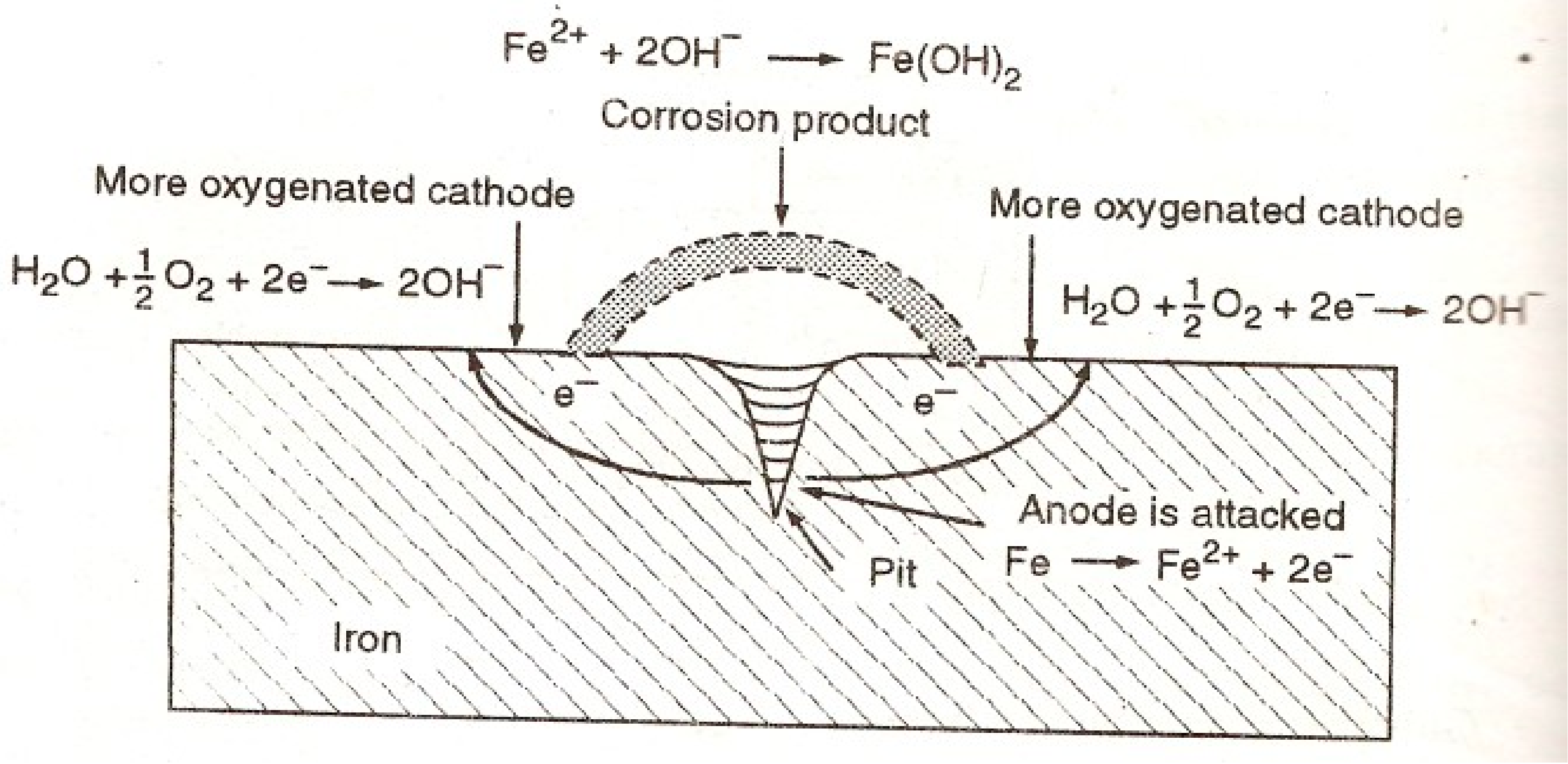
Intense corrosion thus start just undemea impurity. Once a small pit is formed the rate of corrosion will be increased.



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Stress corrosion: Stress corrosion is the combined effect of static tensile stresses and the corrosive environment on the metal stresses that cause cracking result from residual cold working and quenching, welding, thermal treatment or due to applied loads during service. In such cases, the metal under stress becomes more anodic and tend to increase the rate of corrosion.

For stress corrosion to occur presence of tensile stress and specific corrosive environment is necessary. The corrosive agents are highly specific and selective like:

(i) Caustic alkalis and strong nitrate solution for mild steel. (ii) Traces of ammonia for brass.

(iii) Acid chloride solution for stainless steel.

This type of corrosion involves in a localized electrochemical corrosion occurring along narrow paths, forming anodic areas with respect to the more cathodic areas at the metal surface. Presence of stress produces strains which result in localized zones of higher electrode potential.

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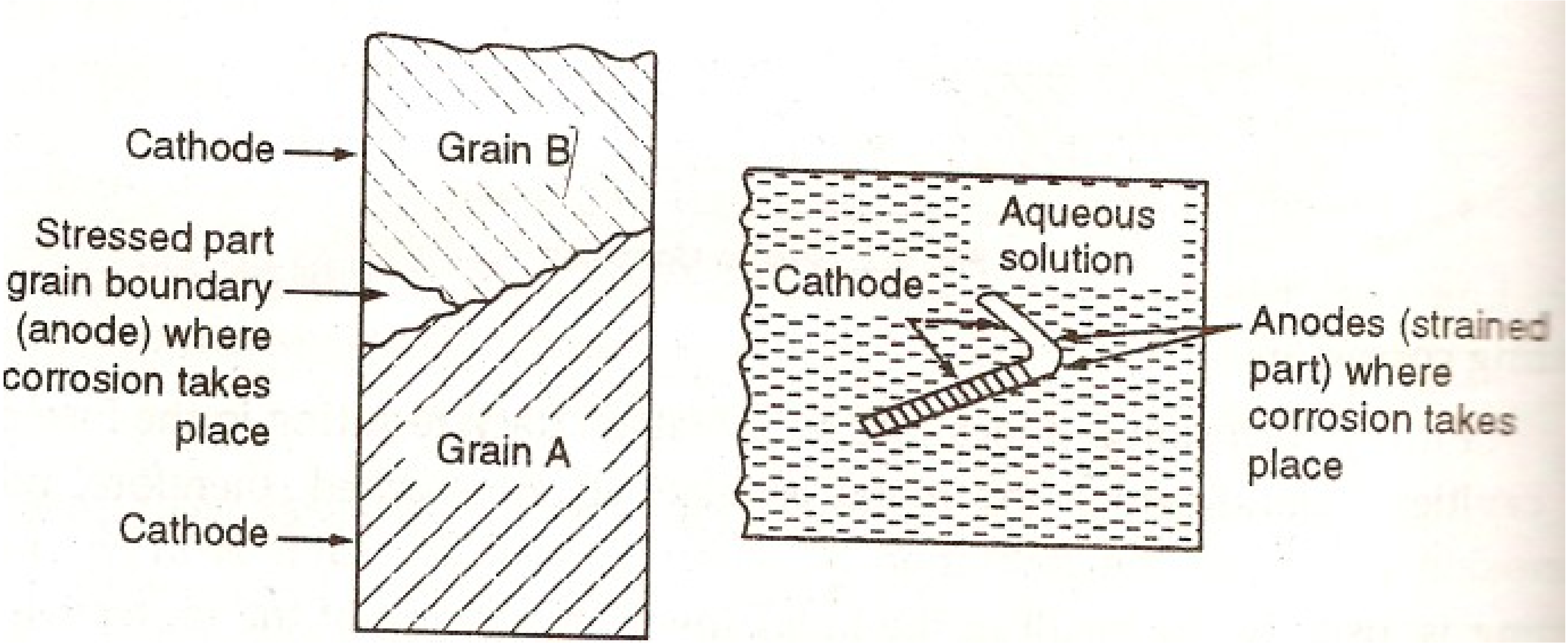
These become so chemically active that they are attacked, even by a mild corrosive environment, which result in the formation of a crack, which grows and propagates in a plant, until failure occurs or it may stop, after progressing a finite distance.



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Concentration cell corrosion or Differential aeration corrosion :

It occurs when metallic surface is partially immersed in an electrolyte and partially exposed to air.

Poor oxygenated metallic part becomes anodic and undergoes oxidation.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

Oxygen rich metallic part becomes cathodic. At the cathode, O2 takes up electrons to form OH^- ions.

$$1/2O_2+H_2O+2e^- \longrightarrow 2OH^-$$

The Zn^{2+} and OH^- ions interact to give $Zn\,(OH)_2$ Therefore, corrosion occurs at anode.

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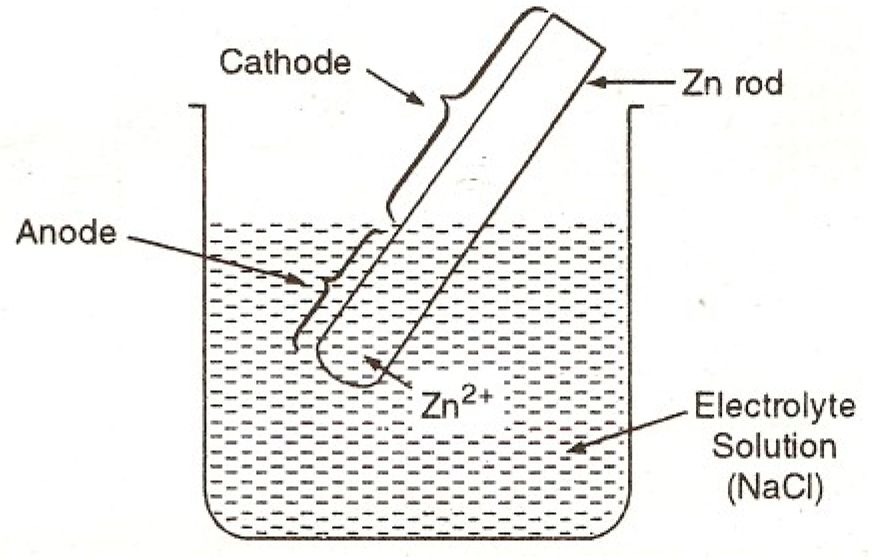

Water-line Corrosion :

When water is stagnant in a steel tank, the concentration of Oxygen above the water surface is greater than that under the surface. This generates an oxygen concentration cell. In this cell the metal just above the water level is cathodic w.r.t. the metal below the water level.

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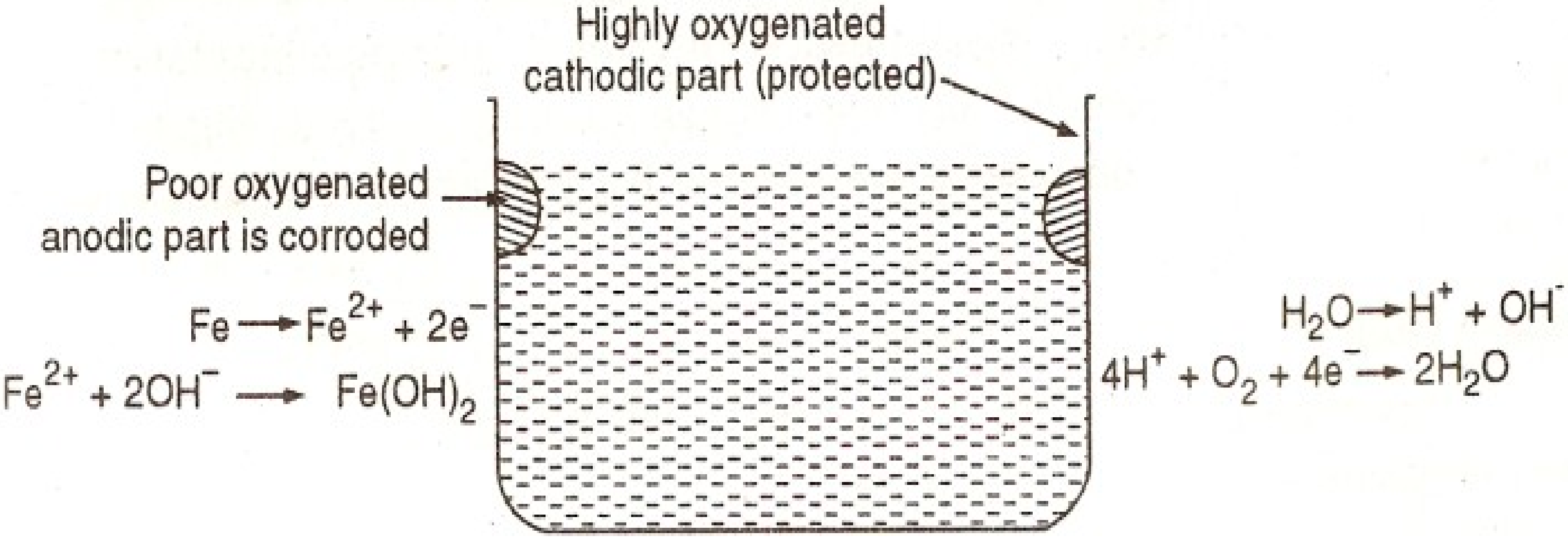
Corrosion occurs at the anodic part, the metal just below the water level.

The cathodic area completely unaffected by corrosion.



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Passivity : Passivity means the lack of activity under conditions where a metal would be expected to react readily. There are certain metals which are passive to certain corroding agents. For example; iron is passive to conc. HNO_3. Aluminium has no action with conc. HNO_3 in absence of chlorides etc.

Metals which are susceptible to corrosion are made passive by alloying with one or more of metals which are passive or resist corrosion. For example; Iron is rendered passive by alloying it with any of the transition metals such as chromium, nickel and molybdenum.

The quantity of passive metal to be added depends upon the environments. For example; Iron-chromium alloy, when the quantity of chrome added is from 12 to 20%, the alloy is passive to neutral salt solution but no concentration of chromium in iron makes the alloy passive to hydrochloric acid.

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FACTORS INFLUENCING CORROSION : The rate and extent of corrosion, depends on the following factors :

1. Nature of the metal:

(i) Position in the galvanic series: The greater the oxidation potential, when the metal is higher up in the galvanic series, greater is its tendency to become anodic and hence greater is the rate of corrosion.

(ii) Purity of metal: Lesser is the percentage purity of a metal, faster is the rate of corrosion. The impurities present in a metal cause heterogeneity and thus tiny electrochemical cells are set up at the exposed part of the impurity and corrosion of metal around the impurity takes place due to local action.

(iii) Physical state of the metal: The rate of corrosion is influenced by physical state of metal. The smaller the grain size of the metal or alloy, the greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

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(iv) Nature of the oxide film: The ratio of the volumes of the metal oxide to the metal, is known as "specific volume ratio". Greater the specific volume ratio, lesser is the oxidation corrosion rate.

(v) Relative areas of the anode and cathode: When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of the cathodic part and the anodic part. When cathodic area is smaller, the demand for electrons will be less and this result in the decreased rate of disolution of metal at anodic regions.

(vi) Solubility of corrosion products: In the electochemical corrosion, if the corrosion product is soluble in corroding medium, then corrosion proceeds at a faster rate. For example, Pb in H_2SO_4 medium forms $PbSO_4$ which is insoluble in the corroding medium, hence corrosion proceeds at a smaller rate.

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(vii) Volatility of corrosion products: Rapid and continuous corrosion of metal take place if corrosion product is volatile. This is due to the fact that as soon as corrosion product is formed, it volatilize, thereby leaving the underlying metal surface for further attack.

2. Nature of the corroding environment:

(i) Temperature: With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.

(ii) Humidity of air : The greater is humidity, the greater is the rate and extent of corrosion. This is due to the fact that moisture acts as a solvent for O_2, H_2S, SO_2 and NaCl etc. to furnish the electrolyte essential for setting up a corrosion cell.

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(iii) Effect of pH: Corrosions of those metal which are readily attacked by acids can be reduced by increasing the pH of the attacking environment.

(iv) Presence of impurities in atmosphere: Corrosion of metals is more in areas near to the industry and sea. This is due to the fact that corrosive gases like H_2S, SO_2, CO_2 and fumes of H_2SO_4 and HCl in the industrial areas and NaCl of sea water leads to increased conductivity of the liquid layer in contact with the metal surface, thereby increase the corrosion rate.

(v) Presence of suspended particles in atmosphere: In case of atmospheric corrosion; (a) if the suspended particles are chemically active in nature [like NaCl, $(NH_4)_2SO_4$], they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion;

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(b) if the suspended particles are chemically inactive in nature *(e.g.,* charcoal), they absorb both sulphur gases, and moisture and slowly enhance corrosion rate.

CORROSION CONTROL:

Following are the methods for control of corrosion :

(i) Suitable designing: The design of the material should be such that corrosion if occurs is uniform and not localized. Following precautions must be taken :

(a) The contact of dissimilar metals in presence of corroding solution is to be avoided.

(b) The anodic material should have as large area as possible when two dissimilar metals are in contact.

(c) When two dissimilar metals in contact have to be used, they should be as close as possible in electrochemical series.

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(d) An insulating filling may be used to avoid direct metal-metal electrical contact.

(e) The anodic metal should not be painted or coated because any break in coating would cause rapid localized corrosion.

(f) A suitable design should avoid presence of cracks between adjacent parts of the structure.

(g) Sharp comers are the poor design and should be avoided because they favour accumulation of solids.

(h) The equipment should be supported on legs for free circulation of air.

(i) Uniform flow of corrosive liquid is desirable.

(j) A suitable design should prevent condition subjecting some areas of structure to stress.

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(ii) Using pure metal: Impurities in a metal cause heterogeneous state thereby accelerating corrosion rate. Corrosion resistance of a metal may be improved by increasing its purity. Corrosion resistance of a purified metal also depends on the nature of corroding environment.

(iii) Using metal alloys: Corrosion resistance of most metals is increased by alloying them with suitable elements. *e.g.,* Cr is the best suitable alloying metal for iron. Steel containing 13% Cr are used in surgical equipments.

(iv) Cathodic protection: The principle is to force the metal to behave like cathode so that corrosion does not occur. Two types of cathodic protections are possible.

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(a) Sacrifical protection: In this method the metal to be protected is connected by a wire to a more anodic metal. The more active metal losses electrons and gets corroded slowly thereby protecting the parent cathodic metal. *e.g.,* Galvanisation process where iron is protected by covering with zinc. Some sacrificial anodes commonly employed are Mg, Zn, Al etc. Applications of this method include underground cables, water tanks etc.

(b) Electrical cathodic protection: In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The current is derived from direct sources like battery of rectifier on A.C. line with an insoluble anode (graphite, platinum).

This technique is used for long term operations.

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(v) Modifying the environment: The rate of corrosion also depends on corroding environment. The corrosive nature of environment can be reduced by,

(a) Deaeration: Driving out dissolved oxygen by adjustment of temperature with mechanical agitation.

(b) Deactivation: This involves addition of chemicals capable of combining with oxygen in aqueous solution.

e.g.,

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2\uparrow + 2H_2O$$

(c) Dehumidification: Reduction of moisture content of air belongs to this step. *e.g.,* alumina or silica gel can absorb moisture which are used in air-conditioning shop.