

CORROSION

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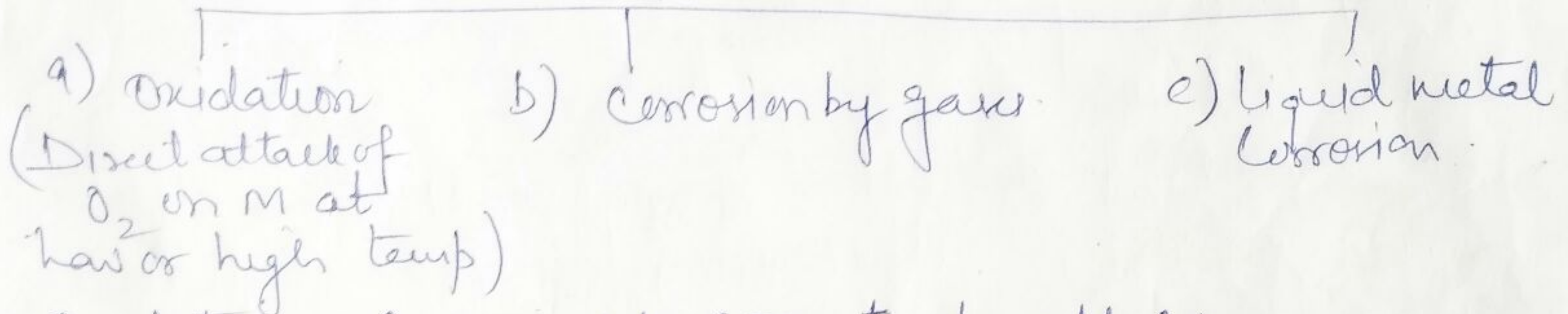
Corrosion: degradation or deterioration of metal by chemical or electrochemical action of environment.

* There are two types of Corrosion.

A) Direct Chemical Corrosion or dry corrosion.

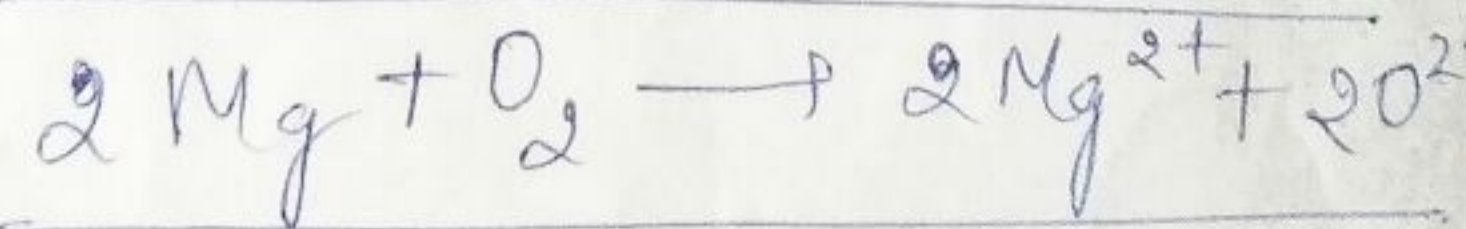
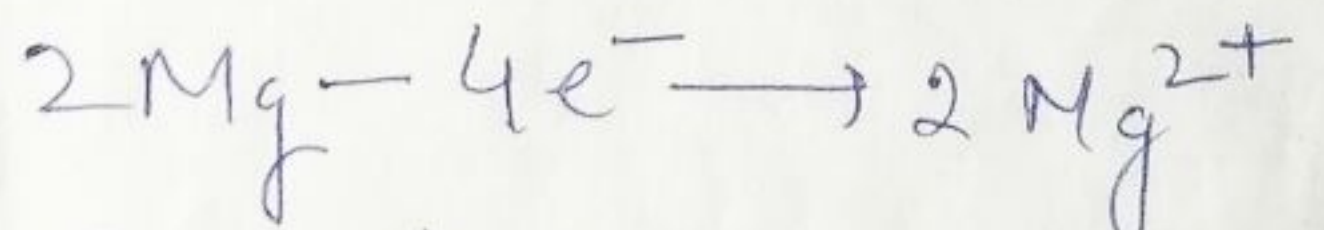
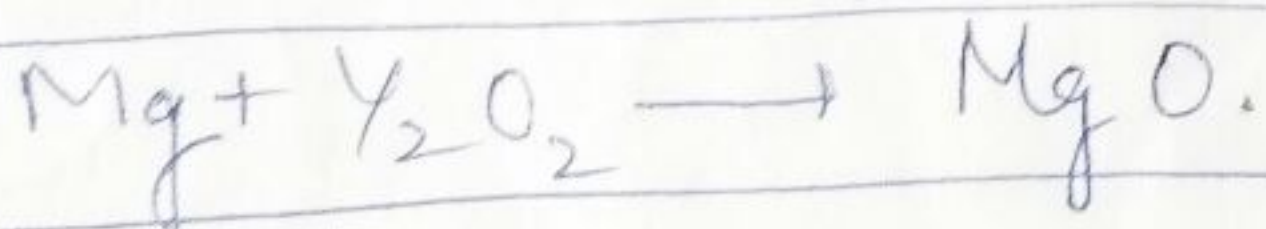
Corrosion takes place by direct chemical action of atmosphere or environmental gases (O_2 , SO_2 , H_2S , halogens etc) or anhydrous liquid on Metal Surface.

Dry



In Oxidation, Corrosion at room temp all M are slightly oxidised but at high " all M are oxidised but at low temperature, alkali & alkaline (Na, K, Rb) earth metals are oxidised.

Mechanism:



Oxidation Occurs at surface of M. Metal & Oxygen combine to form MO (thin film) whose thickness is less than 300 Å. this film protects further oxidation. But Oxⁿ occurs via outward diffusion of Metal ions or inward diffusion of O. Outward diffusion of " " is much more easier because Mⁿ⁺ are smaller than O²⁻ and highly mobile.

* Film formed may be: a) Stable: Here layer forms a shield for Metal surface. Layer consist of fine grain particles which tightly stick to Metal surface and doesnot allow O₂ to diffuse into surf. This prevent Metal from Corrosion ex Al, Pb, Cu

(2)
Unstable film :- Layer so formed decomposes into metal and Oxygen again and so corrosion is not possible eg Ag , Au .

Porous: formed in alkaline earth metals and alkali metals in which $V_{\text{oxide}} < V_{\text{metal}}$ and thus corrosion continues until whole of the M is oxidised. But in case of Al oxide of higher Vol is formed so protective in nature.

Pilling Bedsworth Rule :- Protective and non protective nature of oxide layer depends mainly on this rule. Oxide layer is protective if V_{oxide} is as great as V_M from which it is formed.

Porous layer if $V_{\text{oxide}} < V_M$ as smaller the area covered by layer more easily Oxygen can diffuse and cause corrosion.

4. Volatile: Layer rapidly evaporates after formation at higher temperature. As they " they leave next layer of Metal surface for further corrosion and process occurs rapidly. eg oxides of Mo & W.

b) Corrosion by other gases :- like SO_2 , Cl_2 , CO_2 , H_2S , F_2 etc. This depends on affinity of Metals with these gases. Degree of attack depends on the formation of protective or non protective film on the surface.

(1) If film formed is protective (non porous), then intensity of attack decreases eg AgCl .

(2) If film formed is non protective (porous) the metal is destroyed rapidly eg when Cl_2 attack Sn forms SnCl_2 (volatile) evaporates rapidly and fresh Metal surface is exposed to corrosion.

(c) Liquid Metal Corrosion :- Occurs in Nuclear reactors. This happens when liquid flows over solid Metal at higher temp. 2 of the possibilities of corrosion a) Either liquid flows

Set or Electrochemical Corrosion (Fundamental)

Wet Chemical
(Rxⁿ b/w M & Liquid)

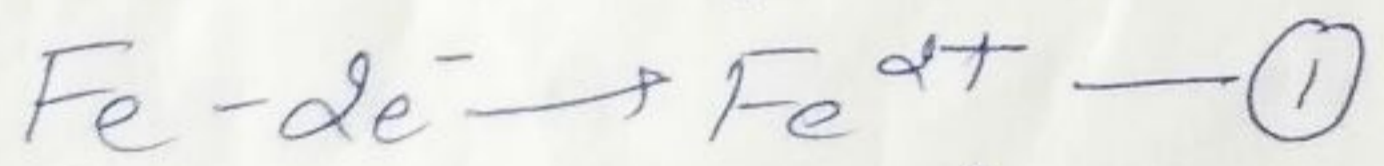
Under Water
(Water is sufficient but air is limited)

Soil Corrosion
(Underground Corrosion takes place in pipes & Fe²⁺ material in concrete)

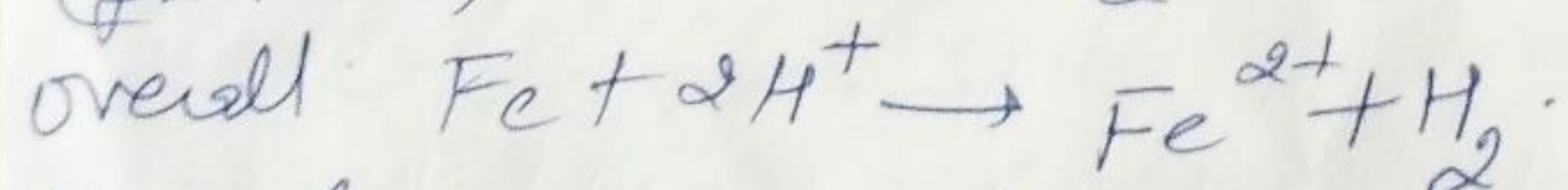
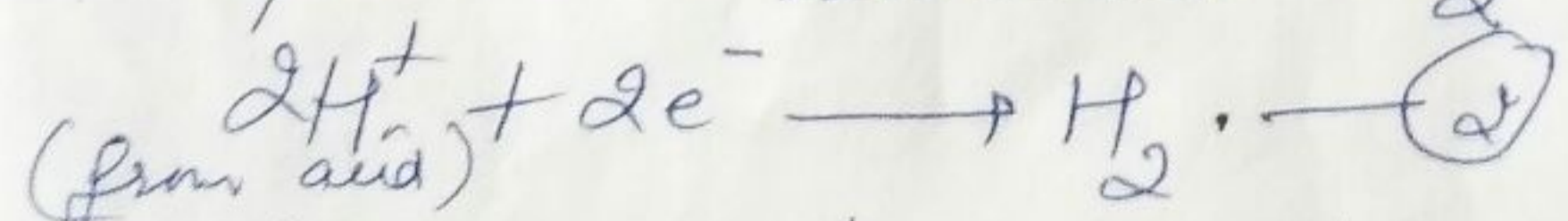
Electrochemical theory:-

All M have tendency to pass into solⁿ, which is measured in terms of electrode potential (E). If more reactive metal (having low E) is in contact with less reactive (having high E), a galvanic cell is set up. The metal having (low E) act as anode and get dissolved as corresponding M²⁺ with liberation of electrons to other metal (less reactive, High E) will act as cathode and gets protected in process. Depending on nature of corrosive environment mechanism of electrochemical corrosion can be explained in terms of

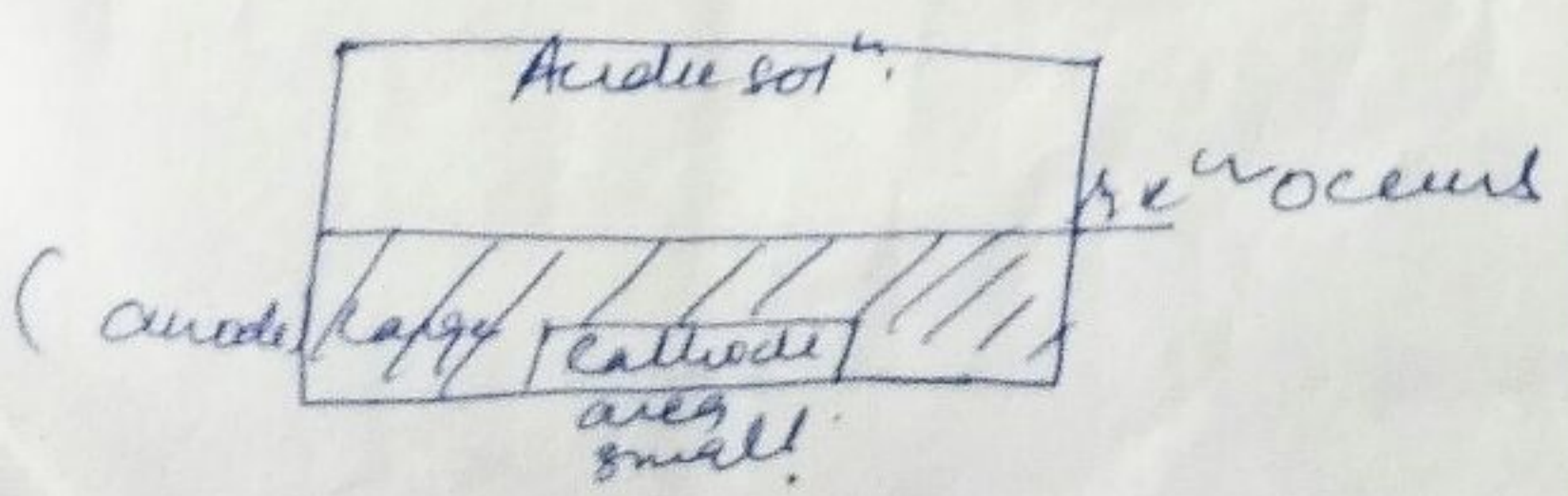
(I) Evolution of H₂
(Occurs in acidic environment)
On Anode M, oxidation occurs and thus loses e⁻ to the environment and pass into the solⁿ in the form of free ions.



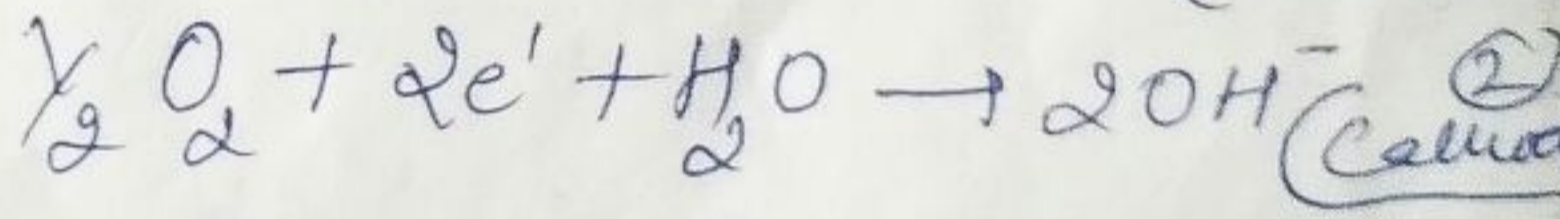
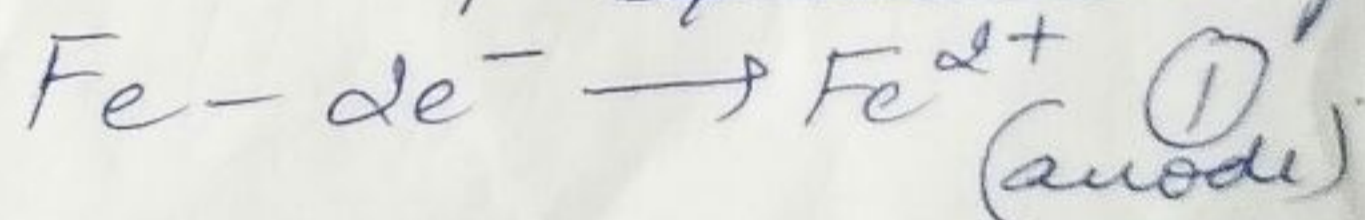
The e⁻ flows via M from anode to cathode where H⁺ accepts and reduced to H₂



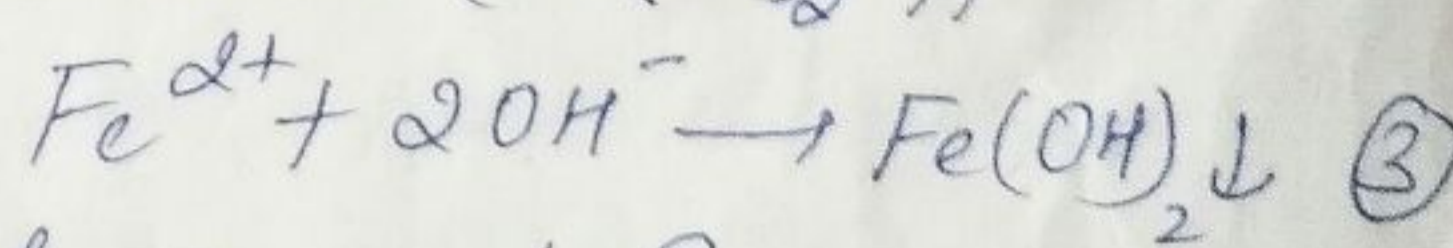
Here large area act as anode.



(II) Absorption of O₂
(Occurs in Fe in presence of aqueous solⁿ)



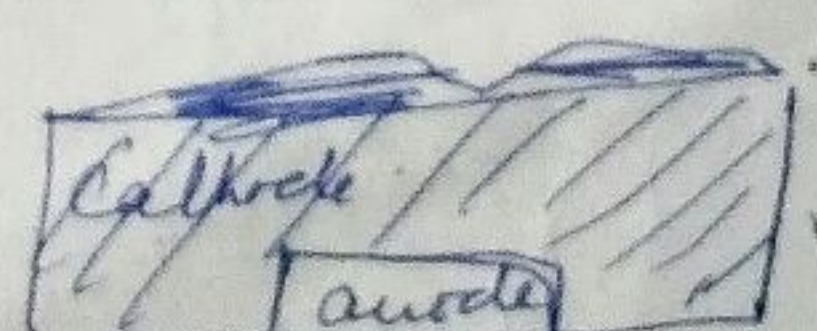
Fe²⁺ and OH⁻ diffuse and combine (Fe(OH)₂) ppted



If enough Oxygen then
4Fe(OH)₂ + O₂ + 2H₂O → 4Fe(OH)₃

This product corresponds to Fe₂O₃ · xH₂O (yellow rust)

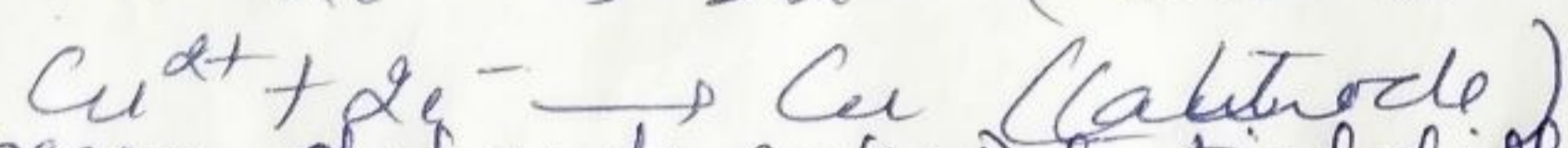
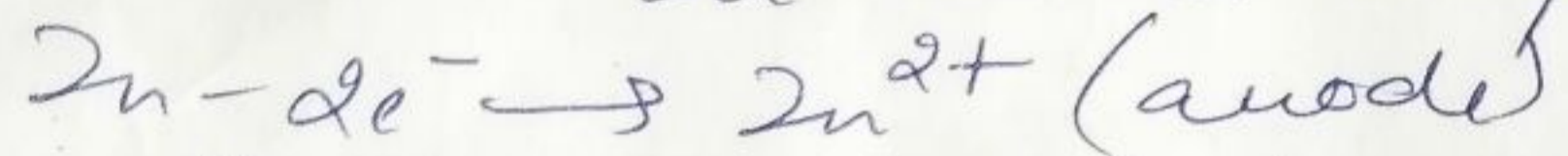
Here large area is cathode and small area is anode.



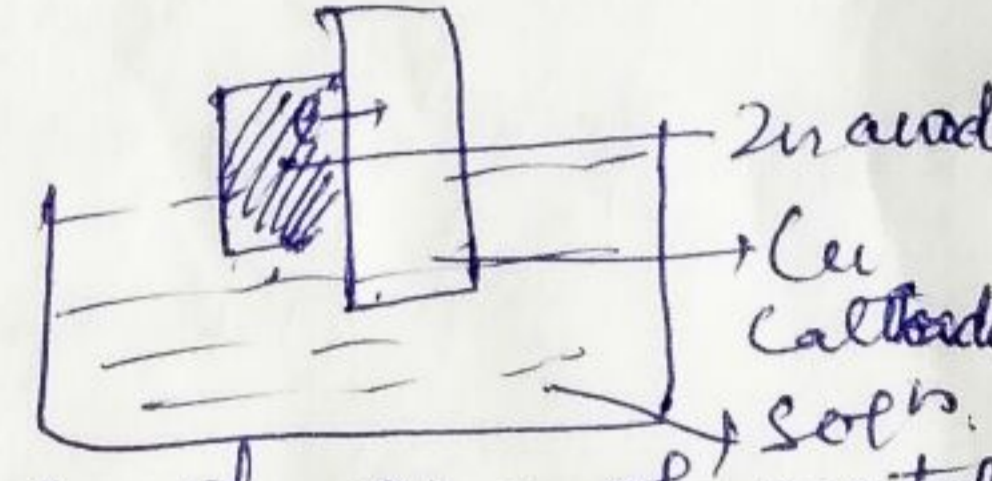
Bi metallic

Galvanic Cell ~~and~~ Corrosion: - Cell is formed if two different Metals (eg Zn & Cu) are directly or electrically connected and exposed to an electrolyte. M (higher in electrochemical series) → Anode is corroded. M (lower in electrochemical series) → Cathode is protected.

In Zn Cu Couple.



Corrosion depends on (i) Potential diff b/w metals and area of metal



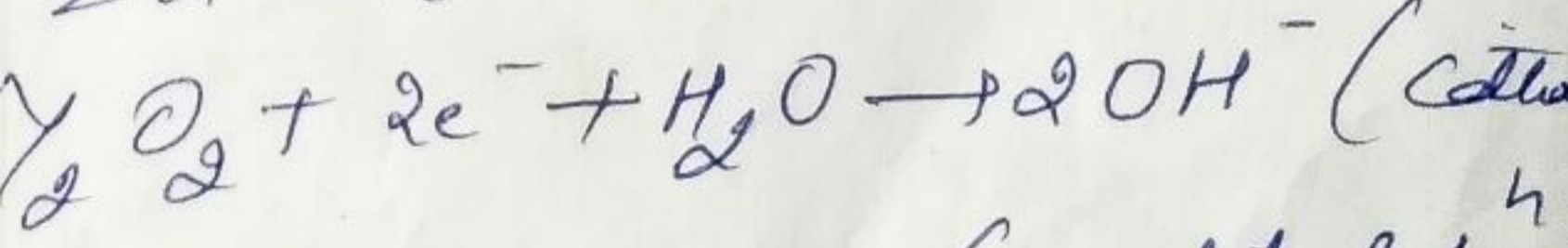
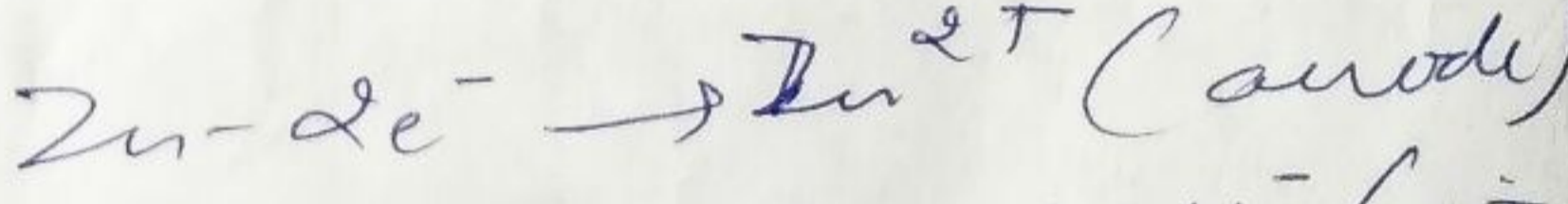
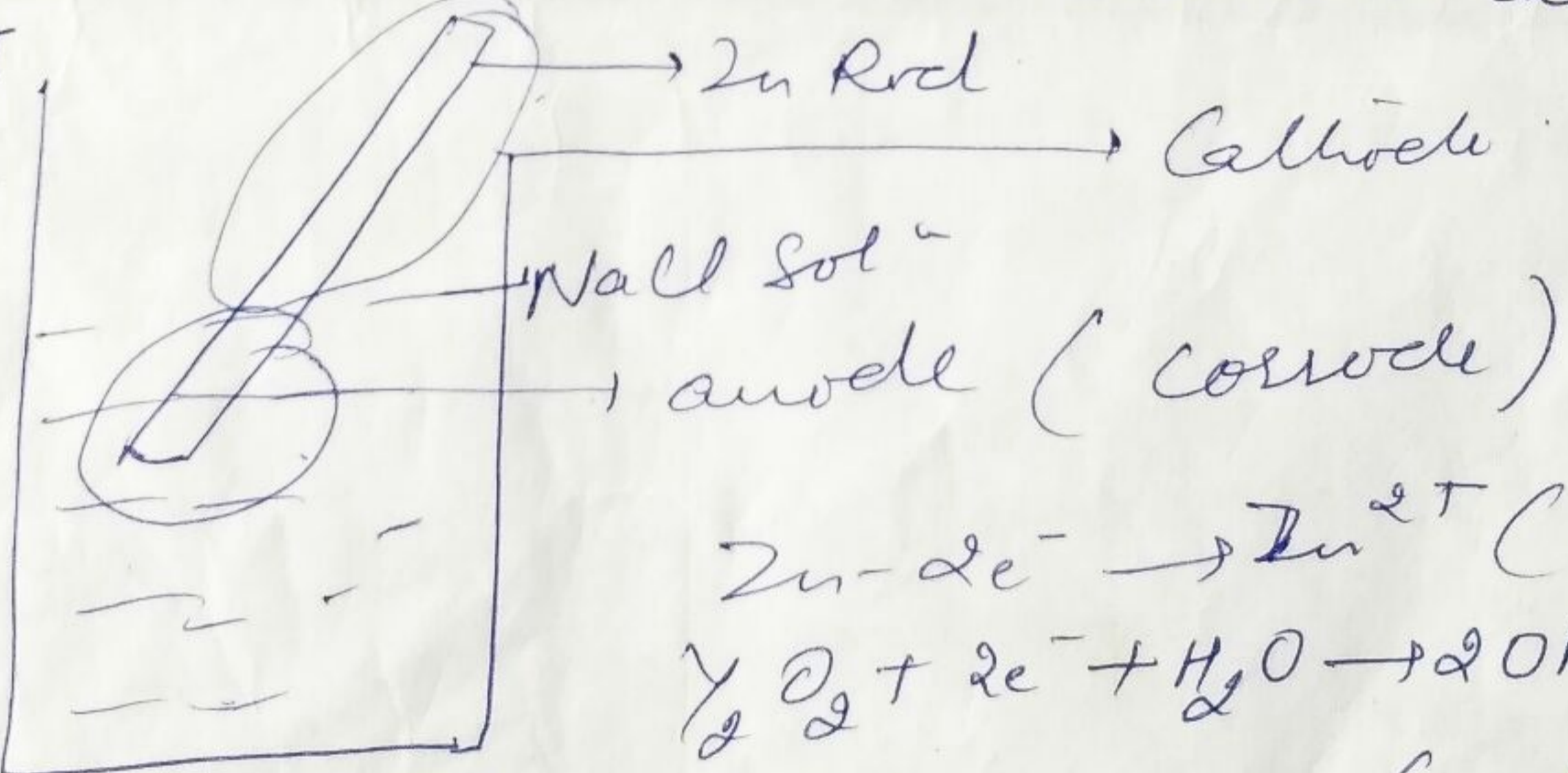
Concentration Cell (Differential aeration Corrosion)

Electrode potential: Potential diff. ^(Pd) b/w conc. of M^{2+} and -vely charged metal surface (Pd b/w electrode and electrolyte).

This type of cell is formed when M is kept at diff air concentration. Less Oxygenated (anode) Highly Oxygenated (Cathode). This develops electrode potential and metal corrodes due to flow of current.

called differential current which corrodes anodic part.

* This corrosion is increased by dirt, scales etc.



So Iron Corrodes under drop of water (salt solⁿ)

Underground or Soil Corrosion: In soil,

presence of moisture, bacteria, microorganisms and electrolyte are responsible for it. When amount of Free O_2 is less - say in water logged soil, microbiological corrosion takes place because bacteria and microorganisms can grow in the environment.

Stress Corrosion or stress cracking

Corrosion takes place due to tensile stress and corrosive environment. It can lead to cracking of metal also called stress cracking.

- Tensile stress may be due to welding, heavy working, thermal treatment etc. So metal under stress becomes more anodic
- Corrosive Environment such as presence of caustic alkalis and nitrate solⁿ causes corrosion of steel. Cl⁻ solⁿ causes corrosion of stainless steel. NH₃ " " " " Brass.
- Common Corrosion in alloys and its extension depends on its metallurgical conditions.

Mechanism: It occurs by electrochemical phenomenon. Stress in particular zone — causes act as anode. w. o. t. more cathodic areas at metal surface.

Types :-

(A) Season cracking :- Stress corrosion of Copper alloys, i.e. Brass (Cu + Zn) particularly. So when cold drawn brass articles such as cartridges are exposed to NH₃. they develop cracks due to stress corrosion. this is called season cracking.

Prevention :- Subjecting alloy to low temp annealing which will remove internal stress.

- (B) Caustic embrittlement :-
- (C) Corrosion fatigue :- due to repeated cyclic stresses caused by vibration, shaking, flexing in presence of corrosive environment. These make the specific regions of m less elastic which in turn become a crack

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Protection against Corrosion

1. Using Pure Metal

Pure metals are resistant to corrosion in comparison to impure one. But corrosion resistance of metal depends on the nature of corrosive environment. For example, when Al is highly pure forms an oxide film which is protective in nature but when Al is impure this oxide film helps in corrosion.

2. Proper Designing

The design of the material should be such that if corrosion occurs it should be uniform and not localised (because localised corrosion is more harmful some important points of design are given below)

- (i) The contact of dissimilar metals in presence of corroding solution should be avoided.
- (ii) If two metals are to be used together they should be close to each other in electro chemical series.
- (iii) When anodic and cathodic material are used together then the area of anodic material should be large.
- (iv) The anodic material should not be coated or painted because any damage in coating would cause rapid localized corrosion.
- (v) The material should not have sharp corners and crevices because they help in accumulation of impurities.

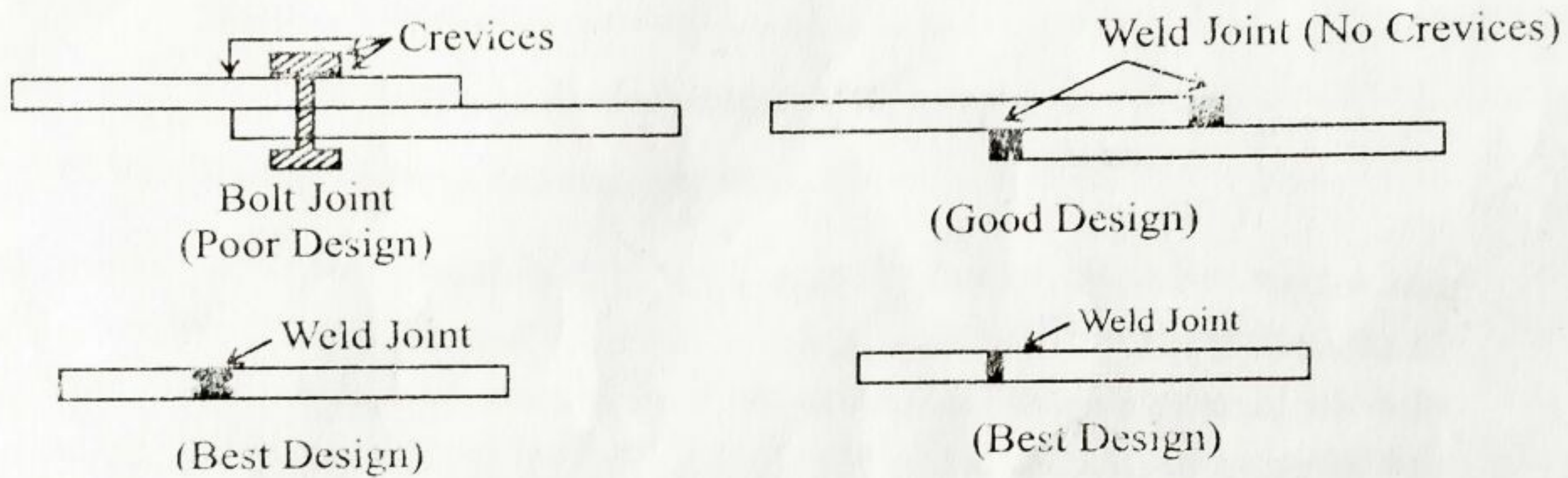


Fig. 5.10: Different types of Joints

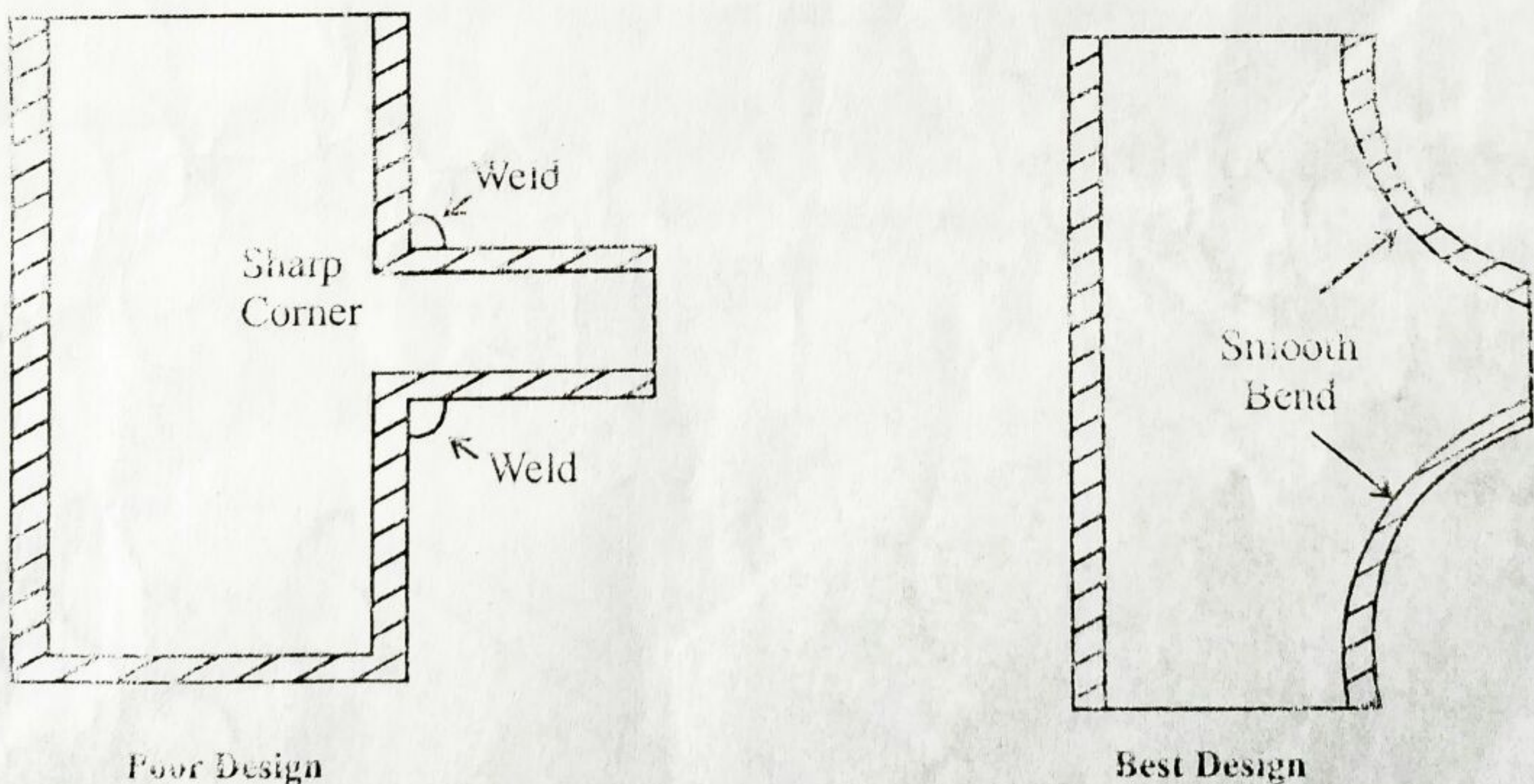


Fig. 5.11: Prevention of corrosion by design

Cathodic Protection

In this method the metal to be protected is forced to behave like a cathode, so that corrosion does not occur. Cathodic protection is carried out by two methods.

(i) Impressed Current Cathodic Protection

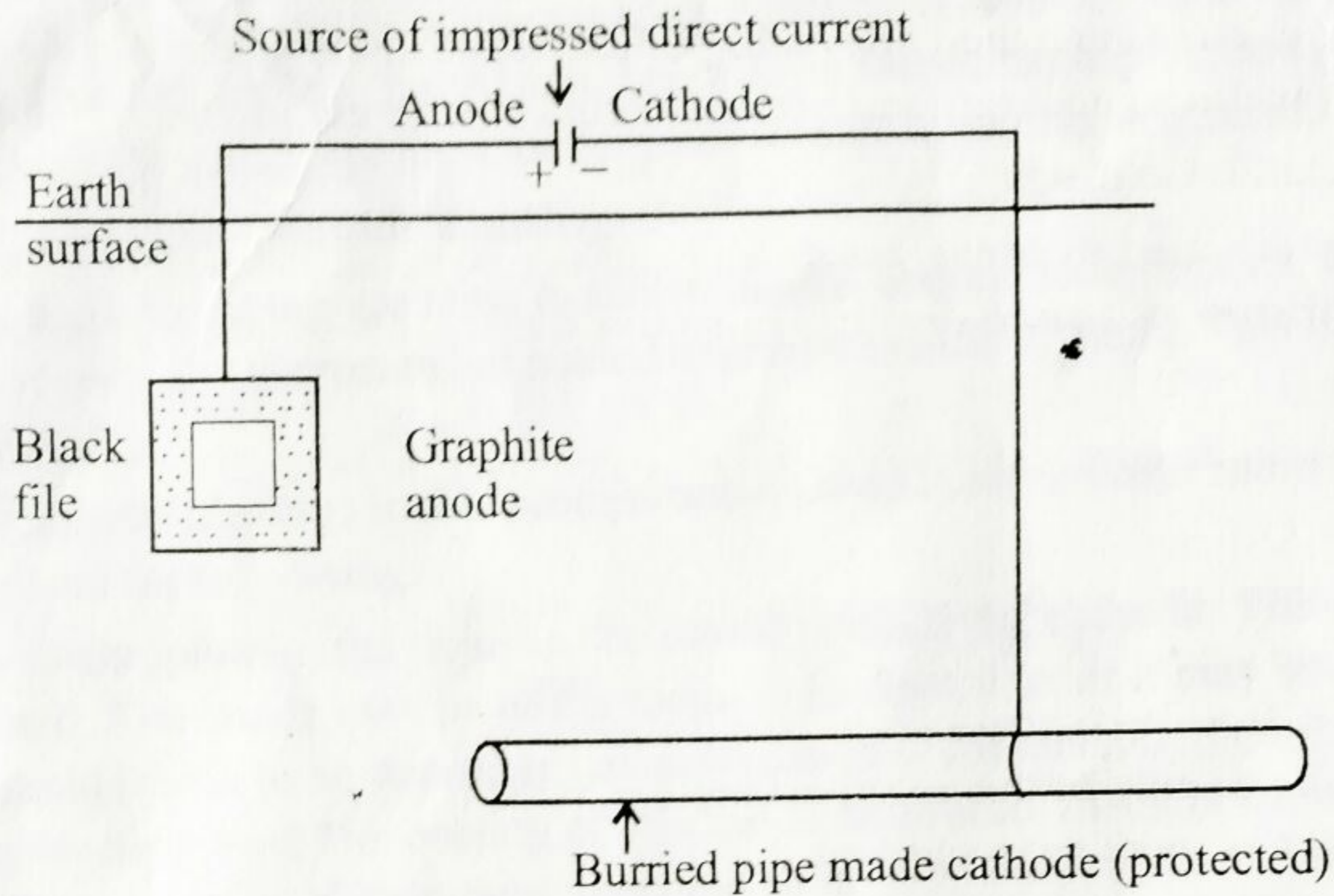


Fig. 5.12 : Impressed current cathodic protection

In this method, current from an external source is applied in the opposite direction to neutralize the corrosion current. This is done to convert corroding metal from anode to cathode. Once the metal becomes cathodic, it is protected from corrosion. The anode may be either an inert material or one which deteriorates and will have to be replaced periodically. The commonly used anodes materials are graphite, carbon, stainless steel, scrap iron, high silicon iron and platinum. The anode is buried in back fill such as gypsum to increase the electrical contact between itself and the surrounding soil. This protection technique is employed in the case of buried structures such as pipe lines, tanks, transmission line towers, etc.

(ii) Sacrificial Anodic Protection

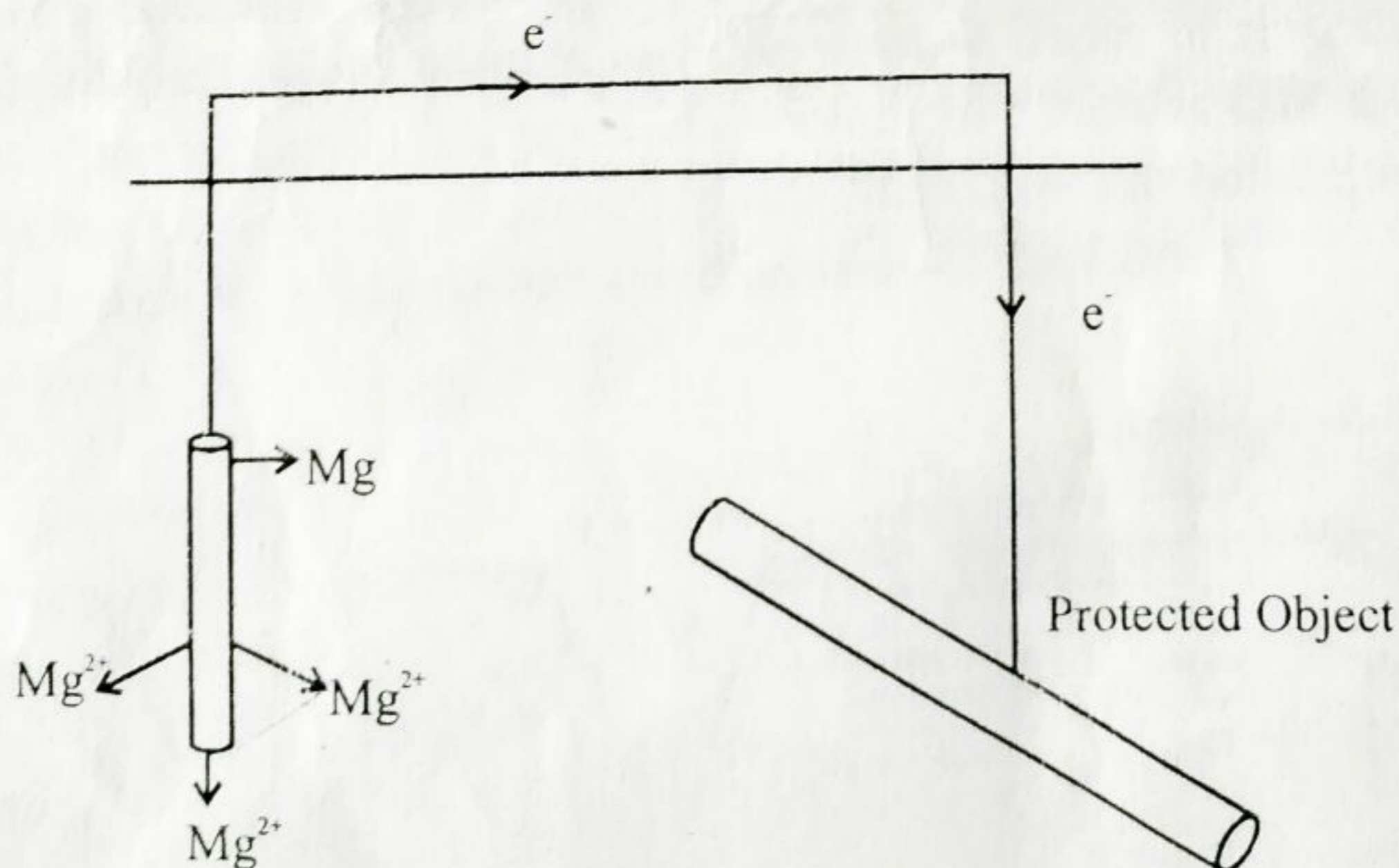


Fig. 5.13: Sacrificial anodic protection



In this method an anode of a more strongly reducing metal is sacrificed to protect the object.

The metal structure can be saved from corrosion by connecting it with wire to a more active metal (i.e., more anodic) so that all the corrosion is concentrated at the more active metal. The more active metal gets corroded and hence the objects to be saved are protected. The active metal employed is called sacrificial anode. This anode when it is consumed completely is replaced by fresh one. Metals commonly employed in sacrificial anode are Mg, Zn, Al and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, and water tanks etc.

4. Protective Metallic Coatings

Protective coating are used to isolate anode and cathode regions. In metallic coatings noble metals or metals resistant to corrosion are coated over more reactive metal. This is done by electroplating, hot dipping, vaporising etc.

(i) **Electroplating:** In this process noble metal is coated over more reactive metal. Most common are tin plating and nickel plating.

In electroplating, the object to be plated is made the cathode. The electrolyte is a salt of the metal to be deposited. The anode may be of the metal to be deposited or it may be an inert electrode (such as graphite). The anode (metal to be deposited) dissolves to coat the metal in the solution Au, Ag, Cu, Ni, Cu, Zn, Sn etc. can be electroplated. The coating of this metal on another metal is known as tinning Tin being less reducing protects the metal which is more reducing to it.

(ii) **Vapourising:** In this process vapours of some of the metal are allowed to strike metallic surface with which they form the alloy. Zn and Al are used for this purpose. Coating of Zinc to metals is known as galvanizing. The Zn Metal projects the underlying metal sacrificially if the underlying metal is less reducing than zinc. In case of zinc, zinc dust is heated strongly. The vapours thus formed are then condensed on iron thus a thin layer of zinc is formed on iron surface. This process is called sheradizing.

(1) Methods of Application of Metal Coatings

If the alloy or metal to be used has low melting point then dipping is a very convenient method. The metal to be coated is passed through a bath of the molten coating metal and the thickness of the coating is adjusted by squeezing of the excess of the coating metal with rollers. Coating of zinc on iron by this process is called galvanizing and coating of tin on iron is known as tinning.

(a) **Galvanising:** The process of coating a layer of zinc on steel is called galvanising. The steel article is first pickled with dilute sulphuric acid to remove traces of rust, dust, etc. at 60–90° C for about 15 to 20 minutes. Then the metal is dipped in a molten zinc bath at 430° C. The surface of the bath is covered with ammonium chloride flux to prevent oxide formation on the surface of molten zinc. The coated base metal is then passed through rollers to correct the thickness of the film.

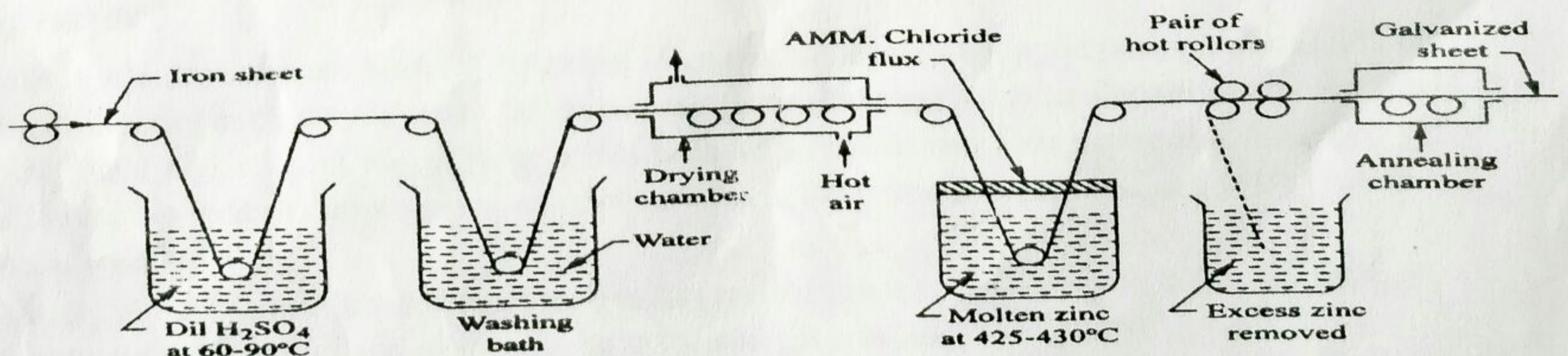
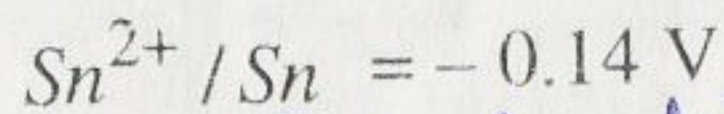
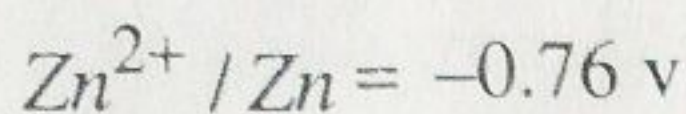
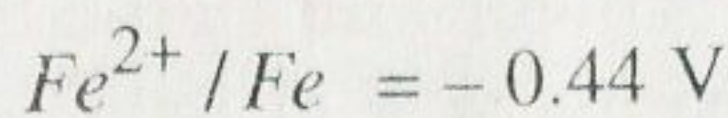
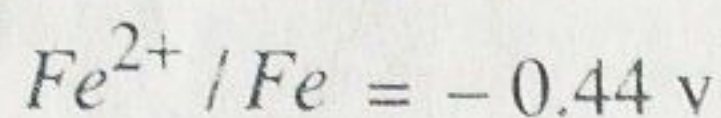


Fig. 5.14: Galvanisation of steel sheet

(b) **Tinning:** The coating of tin on iron is called tin plating or tinning. In tinning, the base metal is first pickled with dilute sulphuric acid to remove surface impurities. Then it is passed through molten tin covered with zinc chloride flux. Then tin coated article is passed through a series of rollers immersed in a palm oil bath to remove the excess tin. Tin-coated utensils are used for storing foodstuffs, pickles, oils, etc.

But the process of galvanization is far better than tinning.



(less reactive)

Galvanising is preferred over tinning because tin is cathodic to iron whereas zinc is anodic to iron. So, if the protective layer of the tin coating has any cracks, iron will corrode. If the protective layer of the zinc coating has any cracks, iron being cathodic does not get corroded. The corrosion products fill up the cracks, thus prevents corrosion.

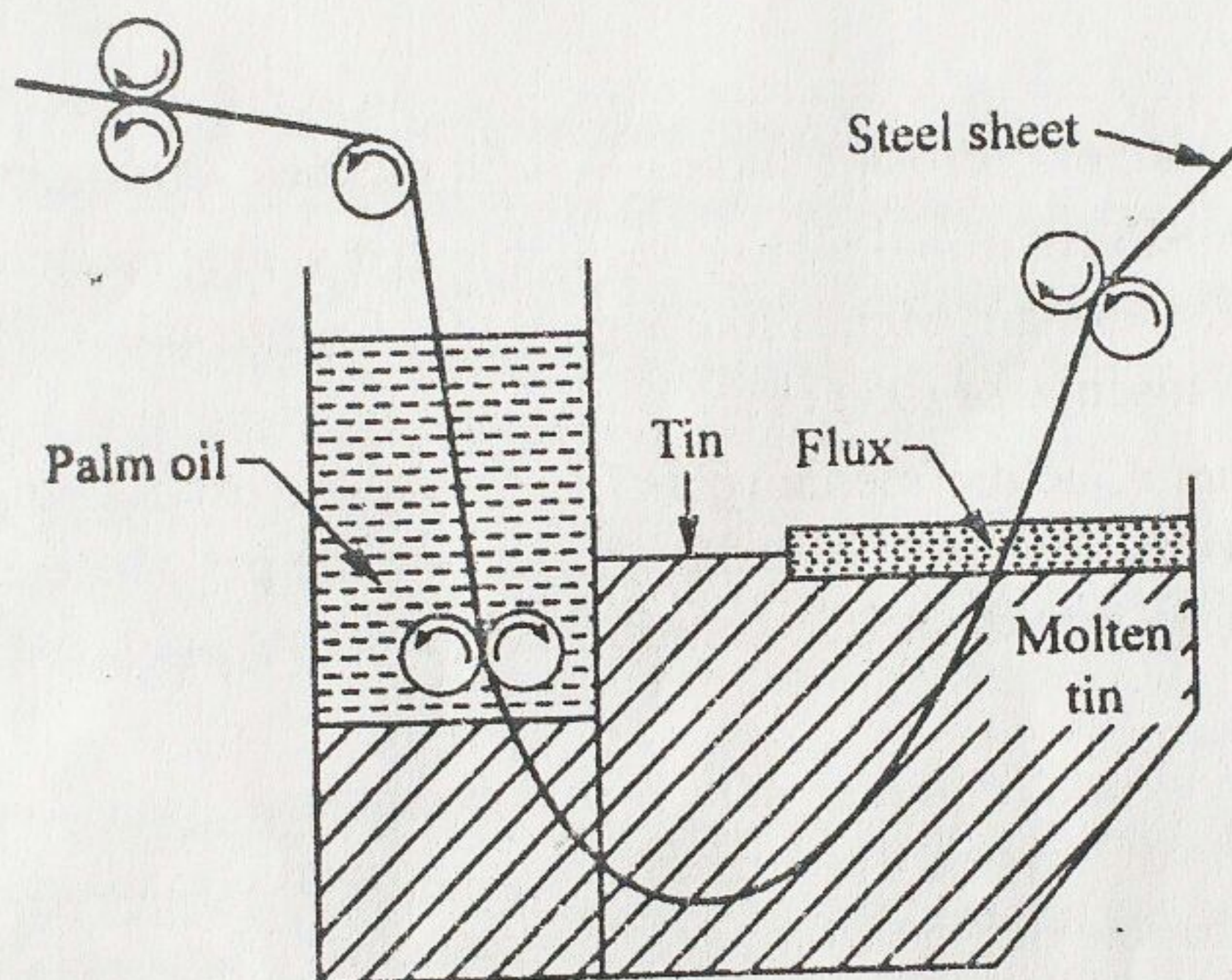


Fig. 5.15: In the tinning of steel sheets, the steel passes through a layer of flux into the molten tin and then emerges between pairs of rollers from a layer of palm oil.

Factors Influencing Corrosion

The rate and extent of corrosion depend mainly on-

- (1) The nature of the metal or metallic factor.
- (2) The nature of the environment or environmental factor.

Metallic factor

(i) **Position in Electrochemical Series:** The extent of corrosion depends upon the position of metal in the electrochemical series and galvanic series. When two metals or alloys are put in an electrolyte and electrical contact, the metal higher up in the galvanic series behaves as anode and being corroded. Similarly, the greater difference in their oxidations potential of two metals in the galvanic series the faster is the corrosion of the anodic metal of alloy.

(ii) **Purity of the Metal:** The impurities present in a metal form tiny galvanic cells at the exposed parts under appropriate environment and the anodic parts formed get corroded. It increases with the increase in the impurities that a pure metal is immune to corrosion.

(iii) **Physical State of the Metal:** The physical state of the metal such as orientation of grains, grain structures, localized stresses, scratches etc., highly influence the rate of corrosion. For example grain boundaries are attacked more rapidly than the grain faces when exposed to a corrosive. Similarly, smaller the grain-size of the metal or alloy, greater will be its solubility as compared to the macroscopic crystal and hence, greater will be its corrosion.

$$\text{Size} \propto \frac{1}{\text{Corrosion}}$$

(iv) **Relative Areas of the Anodic and Cathodic Parts:** When two dissimilar metals or alloys are in contact, the rate and extent of corrosion is directly proportional to the areas of cathodic part and inversely proportional to the areas of anodic part, i.e. if the anodic area is small, corrosion is more rapid, severe and highly localized.

$$\frac{\text{anodic}}{\text{Cathodic}} \propto \frac{1}{\text{corrosion}}$$

(v) **Volatility of Corrodants:** Itcorrosive products are volatile in **nature**, they volatile as soon as they are formed. Hence, the underlying metal surface is exposed for further attack, resulting rapid and continuous corrosion.

Environmental Factors

- ∝ (i) **Temperature-** With increase of temperature the rate of chemical reaction and diffusion increases. Thus, in general the rate of corrosion increases with increase in temperature.
- ∝ (ii) **Moisture of air-** Corrosion of iron is almost negligible in dry air at room temperature. But it increases with increase in moisture of air. Metals like Mg, Al, Zn, Cr, Mn and Fe may be corroded in presence of water even in the absence of oxygen.
- ∝ $\frac{1}{\text{pH}}$ (iii) **Effect of pH-** in general, acidic media (pH < 7) is more corrosive than alkaline or neutral media. Thus, corrosion of metals can be reduced by increasing the pH of the environment, e.g. Zn shows rapid corrosion even in weakly acidic solution like carbonic acid, suffers minimum corrosion at pH = 11.
- ∝ (iv) **Concentration of oxygen and formation of oxygen concentration cells-** The rate of corrosion increases with increasing supply of oxygen. The region where oxygen concentration is lesser becomes anodic and oxygen concentration rich portion becomes cathodic. The anodic portion suffers corrosion. The mechanism has been already discussed under electrochemical theory of corrosion.
- (v) **The concentration and nature of other ions present in the medium-** Some, ions like chloride ions destroy the passive film and corrode many metals and alloys. On the other hand, some anion like silicate inhibit corrosion by forming an insoluble reaction product (silica gel).

EXAMINATION QUESTIONS

Assignment 6.

- Q.1. What is corrosion ? Explain various factors that affect corrosion with suitable examples.
- Q.2. Write short notes on the following.
- (i) Special methods of corrosion protection.
 - (ii) Stress corrosion cracking.
- Q.3. (a) Discuss the rusting by electrochemical theory of corrosion.
 (b) Write any four factors influencing corrosion and discuss briefly.
 (c) How corrosion can be controlled by sacrificial anode?
- Q.4 (a) What is corrosion ? Discuss the mechanism of electrochemical corrosion.
 (b) Explain cathodic protection methods to minimize corrosion.