CLASSIFICATION OF CORROSION
CHAPTER 2

LECTURER
SAHEB M. MAHDI

Classification of corrosion :

Corrosion has been classified in many different ways . One method divides corrosion in to low - temperature and high – temperature corrosion . Another separates corrosion in to direct combination (or oxidation) and electro – chemical corrosion . The preferred classification here is (1) Wet corrosion . and (2) Dry corrosion .

► **Wet corrosion :-** Occurs when a liquid is present . This is usually involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion by far .

Wet Corrosion : chemical reaction of a metal with the atmosphere in presence

water like

$Fe + H_2O \longrightarrow$ No Corrosion

$Fe + H_2O + Oxygen \longrightarrow Fe(OH)_2$ Or $Fe(OH)_3$

Chlorides may be wet Cl_2 [$H_2O + Cl_2 \longrightarrow HCl + HOCl$]

Salts like NaCl , MgCl , $CaCl_2$, ….. etc

$NaCl + H_2O \longrightarrow NaOH + HCl$

corrosion by $H_2O + O_2$ at room temp. is about 1/20 th to that of H_2O + chlorides

- **Dray Corrosion :** Occurs in absence of a liquid phase or a above the dew point of the environment . Vapors and gases are usually the corrodents . Dry corrosion is most often associated with high temperatures . like Oxidation of metals

$$Fe + O_2 \longrightarrow Fe_2O_3 \ , Fe_3O_4 \ , FeO$$

Dry chlorine is practically non-corrosive to ordinary steel , but moist chlorine dissolved in water , is extremely corrosive and attacks most of common metals and alloys. The reverse is true for Titanium – dry chlorine gas is more corrosive than wet chlorine .

Sulfides H_2S it is very highly corrosive substance.

H_2S → Dry – forms Iron sulfide

H_2S → Wet – forms Oxy – sulfides

(H_2S + H_2O) + hydrogen embrittlements

SO_2 : has no corrosion effect but in presence of moisture and oxygen at forms sulfides.

Electro – Chemical Process :

There are two reactions taking place at the same time,

a) Anodic reaction (Oxidation).

b) Cathodic reaction (Reduction).

$$Fe \longrightarrow Fe^{+2} + 2e \quad \text{(anodic reaction)}$$

$$1/2O_2 + H_2O + 2e \longrightarrow 2(OH)^- \quad \text{(Cathodic reaction)}$$

$$2Fe + 3/2O_2 + 3H_2O \longrightarrow 2Fe(OH)_3 \quad \text{[Rust]}$$

Anodic and Cathodic reaction have to take place at the same rate other wise the rate of corrosion would became slow .

Normally the Cathodic reaction is the rate controlling process .There are various types of Cathodic reactions possible under different conditions :

$$M \longrightarrow M^{+2} + 2e \quad \text{anodic}$$

Cathodic reactions:

1) Hydrogen evolution $2H^+ + 2e \longrightarrow H_2$ (gas)

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Or

$$Zn \longrightarrow Zn^{+2} + 2e \quad \text{(anodic)}$$

$$2H_+ + 2e \longrightarrow H_2 \quad \text{(Cathodic)}$$

2) Oxygen reduction

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

[in acidic medium with oxygen]

3) Oxygen reduction $O_2 + H_2O + 4e \longrightarrow 4(OH)$

[in neutral or basic medium] This is the most kind reaction happens

4) Metal Ion reactions

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$

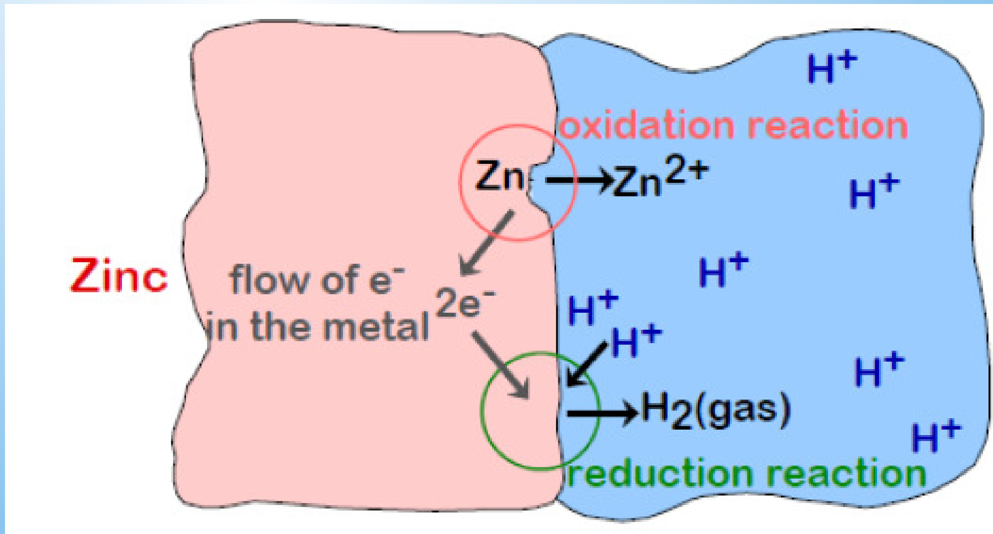
$$M^{+3} + e \longrightarrow M^{+2}$$

5) Metal deposition

$$M^{+} + e \longrightarrow M\downarrow$$

An overall electrochemical reaction must consist of at least one oxidation and one reduction reaction, and will be the sum of them; often the individual oxidation and reduction reactions are termed half-reactions. There can be no net electrical charge accumulation from the electrons and ions; that is, the total rate of oxidation must equal the total rate of reduction, or all electrons generated through oxidation must be consumed by reduction.

Example 1: Zinc metal immersed in an acid solution containing H^+



Adapted from Fig. 17.1, *Callister 6e.* (Fig. 17.1 is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- zinc will experience oxidation or corrosion according to,

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

- H^+ ions are reduced according to,

$$2H^+ + 2e^- \longrightarrow H_2\,(gas)$$

- The total electrochemical reaction

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2\,(gas)$$

Example 2: **Oxidation or rusting of iron in water, which contains dissolved oxygen, This process occurs in two steps:**

- **Fe is oxidized to Fe^{2+} [as $Fe(OH)_2$]**

$$Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

- **Fe^{2+} to Fe^{3+} [as $Fe(OH)_3$]**

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \longrightarrow 2Fe(OH)_3$$

Rate of corrosion :-

The most common methods used are

1 – Weight loss in mg or gram.

2 - % weight change.

Poor – sample shape and exposure Time influence results.

3 – Milligram / sq. decimeter / day . (mdd).

4 – Grams / sq. decimeter / day .

5 - Grams / sq. centimeter / hour

6 - Grams / sq. meter / hour .

7 - Grams / sq. inch / hour .

8 - Moles / sq. centimeter / hour .

Good – but expressions do not give penetration rates .

9 - Inch / year .

10 - Inch / month .

11 – mm / year most common method .

Better – expressions give penetration rates.

12 – Mils per Year (MPY) . mil = 1/ 1000 .

Best – expresses penetration Without decimals or large numbers.

$$MPY = \frac{534\,W}{DAT}$$

Where

W = weight loss in mg .

D = density of metal in g / cm^3 .

A = area of specimen I sq in .

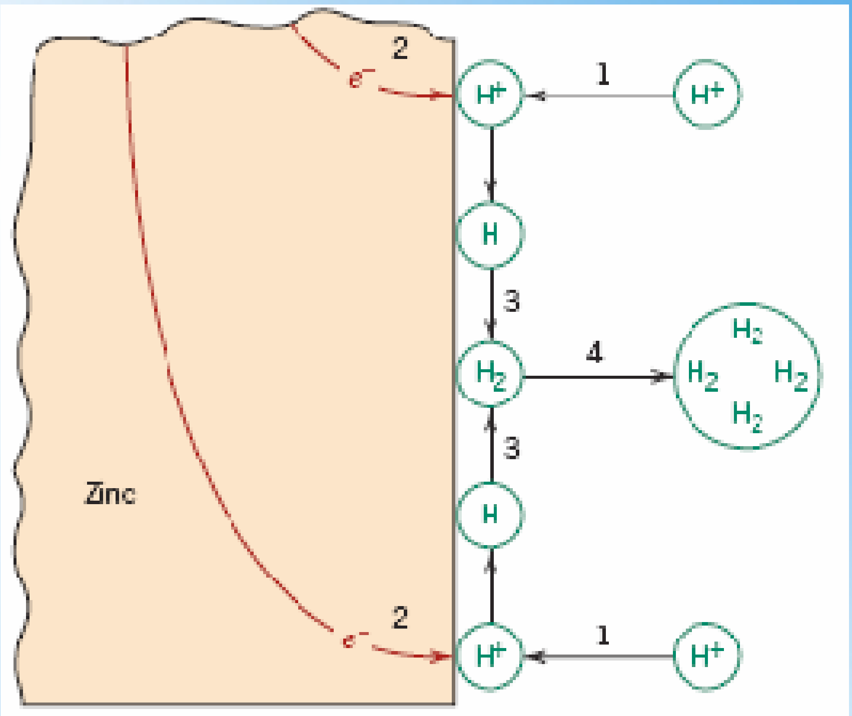
T = exposure time , hr.

Polarization :-

The rate of an electro-chemical reaction is limited by various physical and chemical factors. Hence an electro-chemical reaction is said to be polarized or retarded by these environmental factors.
Polarization can be divided in to two different types :

1)Activation Polarization : It is controlled by the reaction sequence at metal – electrolyte interface. This is like the hydrogen evolution reaction on zinc during corrosion in acid solution .

Step 1: adsorb or attracted H^+ to the surface .
Step 2: electron transfer to H^+ .
Step 3: reduce the H^+ to H_2 .
Step 4: hydrogen molecules combine to form a bubble of hydrogen gas .



The speed of reduction of hydrogen ions will be controlled by the slowest of these steps.

2)Concentration Polarization : It is controlled by the diffusion in the electrolyte . For the case of hydrogen evolution , the number of H^{+} in the solution is quite small, and the reduction rate is controlled by the diffusion of hydrogen ions to the metal surface . Reduction rate controlled by bulk solution rather than at the metal surface.

Activation polarization usually is controlling factor during corrosion in media containing a high concentration of active aspects .(concentrated acids). **Concentration polarization** generally predominates in the dilute acids , aerated salt solutions .

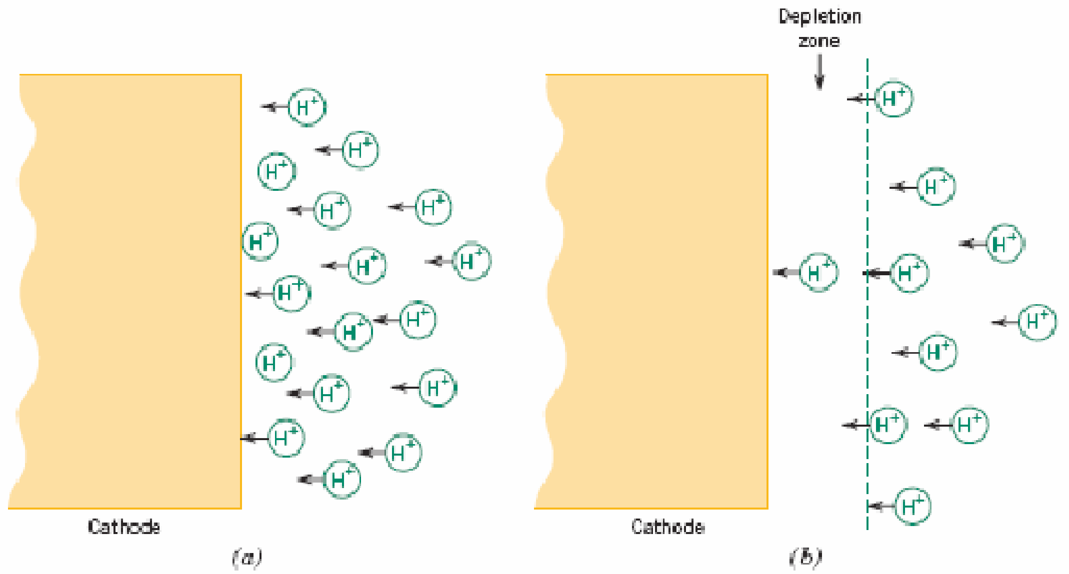


Figure 17.8 For hydrogen reduction, schematic representations of the H^{+} distribution in the vicinity of the cathode for (*a*) low reaction rates and/or high concentrations, and (*b*) high reaction rates and/or low concentrations wherein a depletion zone is formed that gives rise to concentration polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd

Passivity :-

The phenomenon is rather difficult to define because of its complex nature and specific conditions under which it occurs.

Passivity refers to the loss chemical reactivity experienced by certain metals and alloys under particular environmental conditions.

Fe ,Ni , Si , Cr , Ti , Al , and their alloys can be passive in certain conditions.

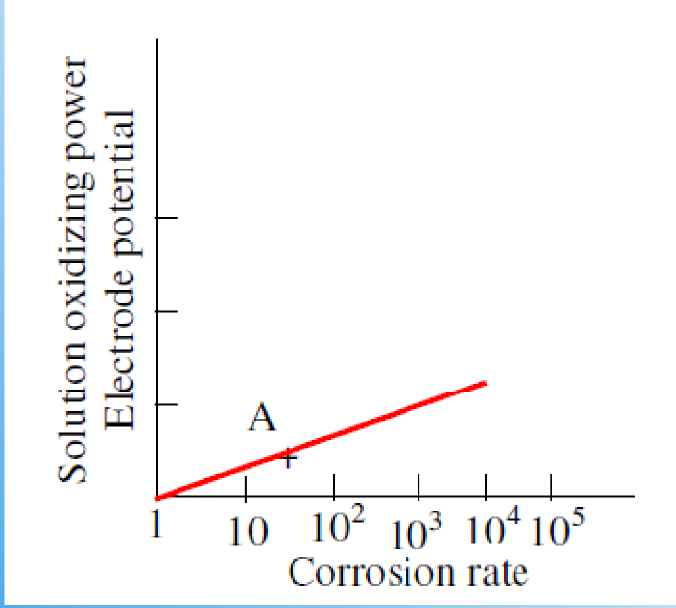


Fig. (1) Corrosion rate of the a metal as a Function of solution oxidizing power (electrode potential) active metal (non-passive)

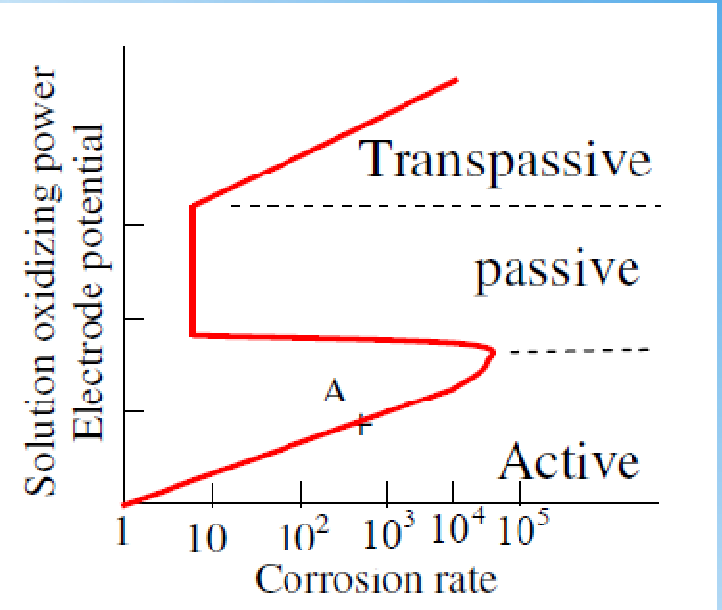
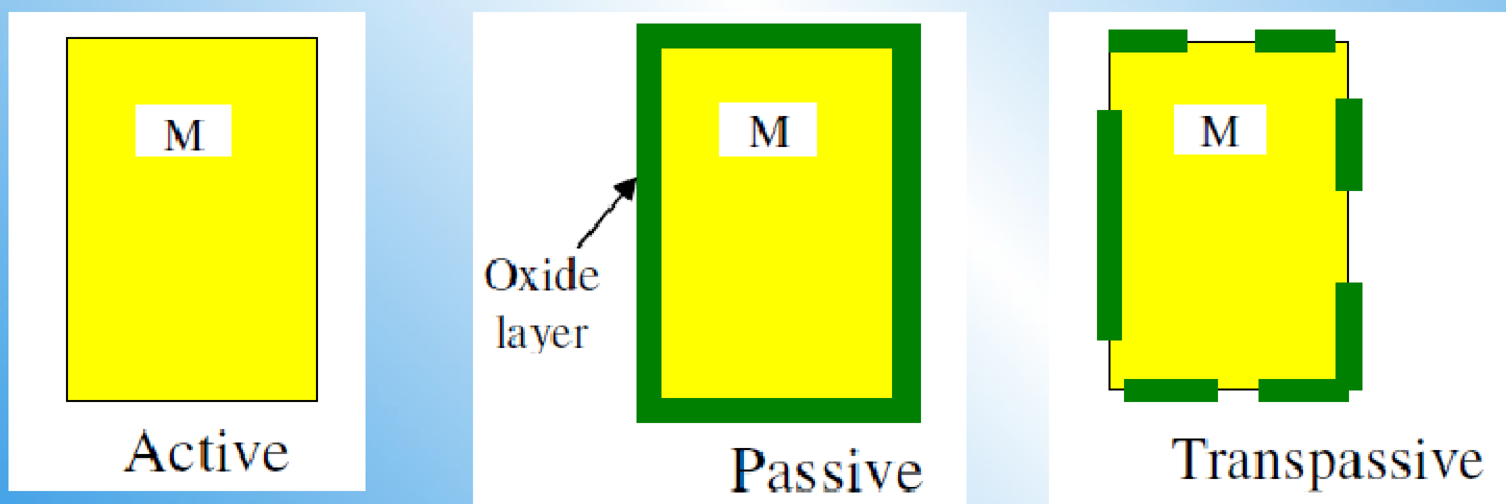


Fig. (2) Corrosion characteristics of an active-passive metal as function of solution oxidizing power

Fig.(1) refer to active metal in air-free acid solution it is corrode and corrosion rate increase by adding oxygen or ferric ions.
Fig.(2) illustrates the typical behavior of a metal of which demonstrates passive effects .

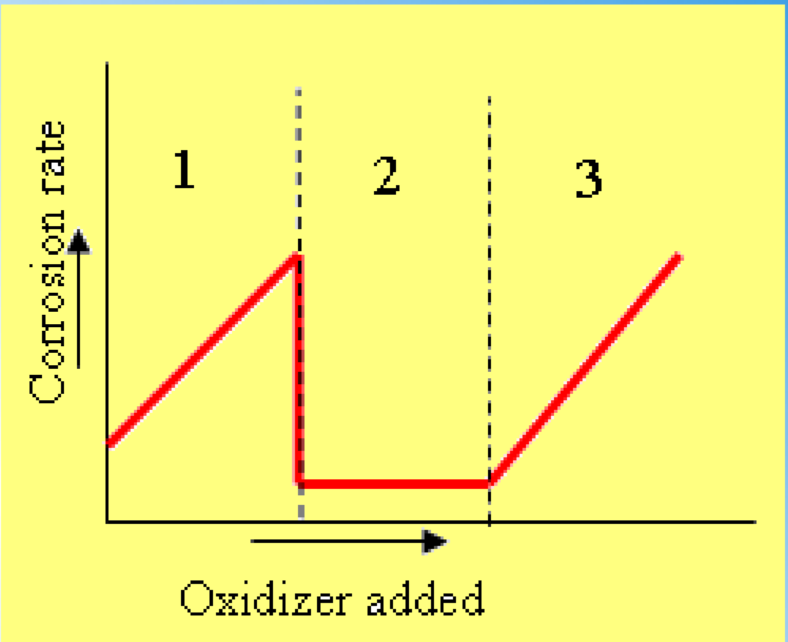
There are three regions, Active , Passive & Transpassive.
Active region : **the behavior of a normal metal.**
Passive region: **If more oxidizing agent is added the corrosion rate suddenly decrease, this mean that this region begin.**
Transpassive region: **with further increase in oxidizing agents the corrosion rate again increase with increasing oxidizer power.**



Factors effecting on corrosion rates :

1) Environments effects: It is desirable to change process variables.

(i) Effect of Oxygen and Oxidizers : The effect of oxidizers on corrosion Rate can be represented by the graph Shown here .



Examples

Region 1

Corrosion rate Oxidizer

Monel alloy in HCl + O_2 (Ni + Cu alloys)

Cu in $H_2SO_4 + O_2$

Fe in $H_2O + O_2$

Regions 1 – 2

18Cr-8Ni in $H_2SO_4 + Fe^{+3}$

Ti in HCl + Cu^{+2}

Region 2

18Cr-8Ni in HNO_3

Hastelloy C in $FeCl_3$ (Ni alloy with alloying elements)

Region 2 – 3

18Cr-8Ni in $HNO_3 + Cr_2O_3$

Region 1 – 2 – 3

18Cr-8Ni in concentrated $H_2SO_4 + HNO_3$ mixtures at elevated temperatures.

(ii) Effects of Velocity : **Mean the velocity of medium .**

The effects of velocity on corrosion rate are, like the effect of oxidizer additions, complex and depend on the characteristics of the metal and the environment to which it is exposed. If rate of corrosion is controlled by Activation polarization then there is no effect of velocity. If the process is diffusion controlled (concentration polarization). Then the corrosion rate increase with increasing velocity.

Examples

Curve A

Corrosion rate velocity

1: Fe in $H_2O + O_2$

Cu in $H_2O + O_2$

1 – 2 : 18Cr-8Ni in $H_2SO_4 + Fe^{+3}$

Ti in HCl + Cu^{+2}

Curve B :

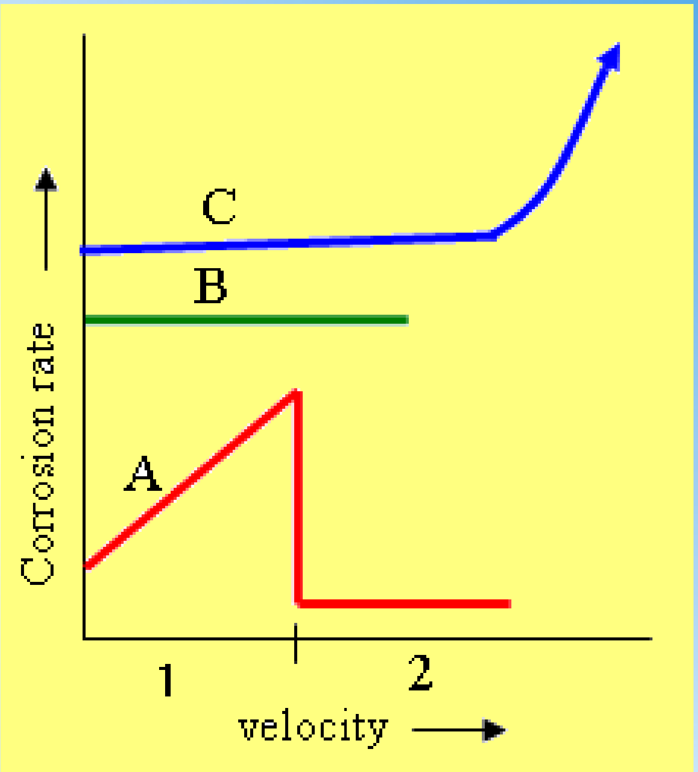
Fe in dilute HCl

18Cr-8Ni in H_2SO_4

Curve C :

Pb in dilute H_2SO_4

Fe in concentrated H_2SO_4



(iii) Effect of Temperature: **Temp. increases the rate of almost all chemical reactions. By increasing Temp. the conductivity of the metal and the medium increases and also the diffusion rate in the medium increase. Therefore the corrosion rate also increases .**

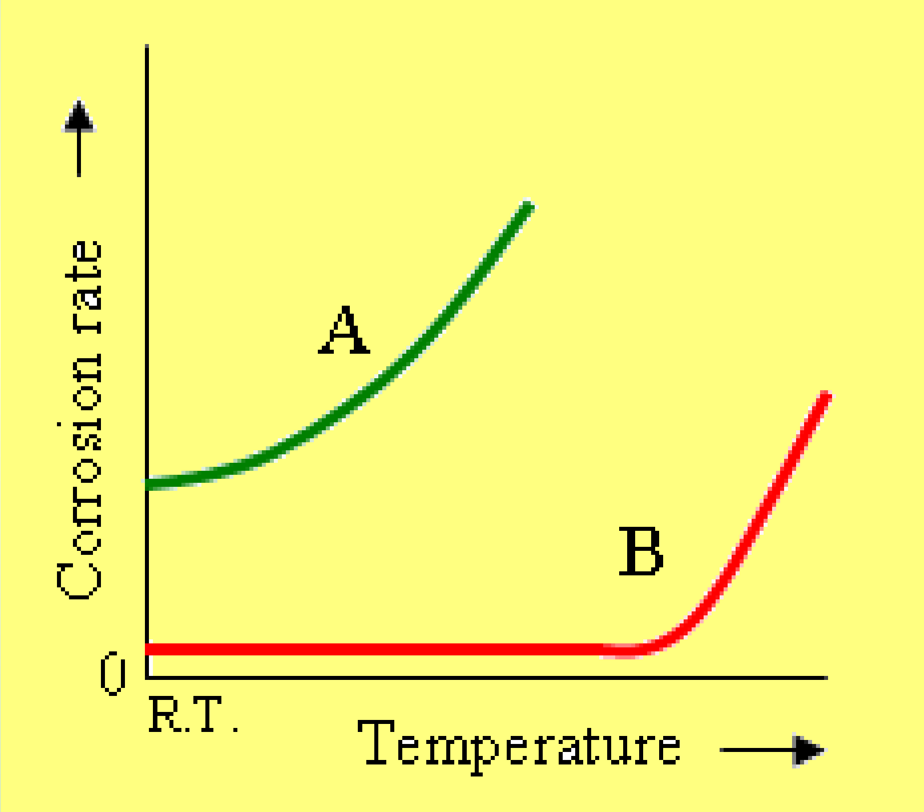
Examples

Curve A :

- 18Cr-8Ni in H_2SO_4
- Ni in HCl
- Fe in HF

Curve B :

- 18Cr-8Ni in HNO_3
- Monel in HF
- Ni in NaOH



(iV) Effects of Corrosion Concentration : **(concentration of corrosive medium). Many materials which exhibit passivity effects are only negligible affected by wide changes in corrosive concentration (curve A) . The reduction in rate after a Maximum is due to the difficulty in ionization with the increase in concentration of corrosive medium (curve B).**

Examples

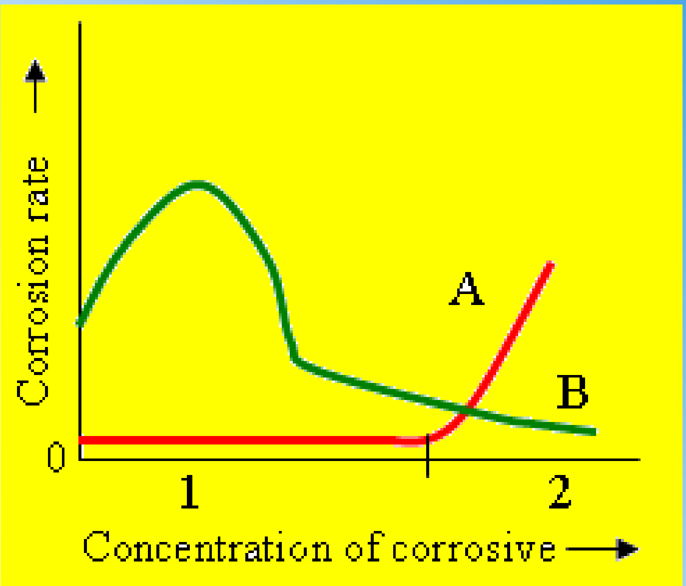
Curve A :

1 : Ni in NaOH
18Cr-8Ni in HNO3
Hastelloy B in HCl
Ta in HCl

1 – 2 : Monel in HCl
Pb in H_2SO_4

Curve B :

Al in acetic acid and HNO_3
18Cr-8Ni in H_2SO_4 , & Fe in H_2SO_4

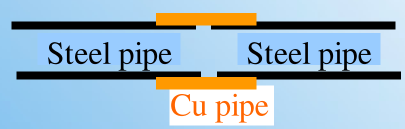


(V) Effects of Galvanic Coupling : By this we mean , when two dissimilar metals are in contact each other . Under this condition the corrosion rate of one metals stops and the corrosion rate of the other metal becomes faster . This depends on the Electro-Potential of the two metals.

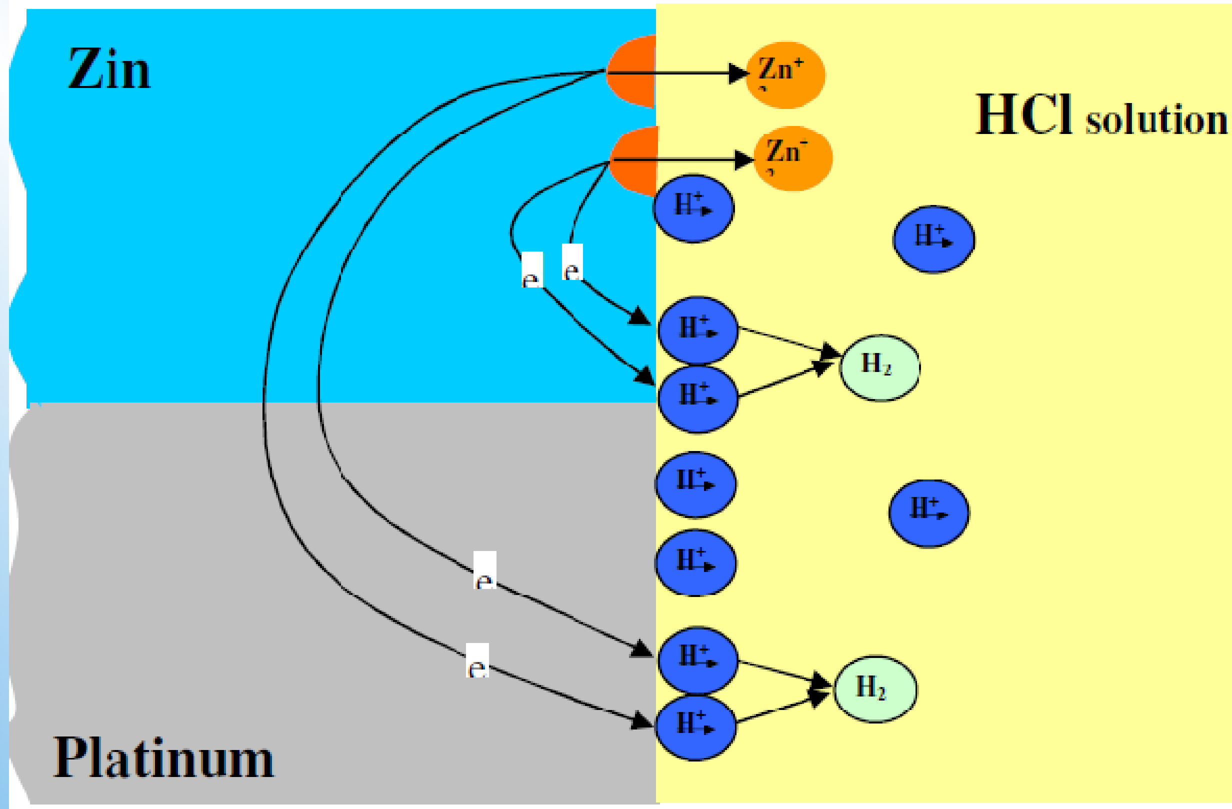
$$Fe \rightarrow Fe^{+2} + 2e$$

Case 1

Case 2



corrosion rate of iron will be faster



2) Metallurgical Aspects:

Polycrystalline Would corrode much faster than single crystal. And is due to the presence of grain – Boundaries in Polycrystalline grain boundaries are the regions of high Energy their for their Chemical reactivity is higher than the rest of materials.

1- Effect of Grain boundary.

2- Metal purity.

2-Effect of various phases in the alloys presence of phases alloys have the same effect as Galvanic – coupling in .

3- Different metals.

4- Residual stresses.

5- The strain hardening deformation.