WATER CHEMISTRY

Water is one of the essential requirements for the survival of all living beings. Water is used for domestic, agricultural, industrial purposes. However water used for human activities should be free from impurities.

Water contains suspended impurities like clay, sand, vegetable and animal matter which impart colour, odour& turbidity. It also contains colloidal impurities, dissolved impurities &Microorganism.

HARDNESS OF WATER: 'Hardness' in water is that characteristic, which 'prevents the lathering of soap'. This is due to the presence of certain salts of Ca, Mg and other heavy metal ions like Al^{+3}, Fe^{+3}& Mn^{+2} dissolved in water. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acids like oleic, palmitic or stearic) does not produce lather, but forms a white scum or precipitate. This is formed due to the formation of insoluble soaps of calcium and magnesium.

$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2\ NaCl$
(Sodium stearate)   (Calcium stearate)
$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2\ Mg \downarrow + Na_2SO_4$
                                                                (Magnesium stearate)

Hard Water: The water which does not produce lather with soap solution readily, but forms a white curd, is called 'hard water'.
Soft water: The water which produces lather easily on shaking with soap solution is called 'soft water'.

*Hardness Types:*Hardness of water is of two types:
i)**Temporary Hardness:** Temporary Hardness is caused by the presence of dissolved bicarbonates of Ca, Mg and other heavy metals and the carbonate of iron.
The salts responsible for the temporary hardness are $Ca(HCO_3)_2$& $Mg(HCO_3)_2$.The temporary hardness can be removed by boiling of water. On boiling bicarbonates decompose to insoluble carbonates or hydroxides.
$Ca\ (HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$
$Mg\ (HCO_3)_2 \longrightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$
ii)**Permanent Hardness:** It is due to the presence of dissolved chlorides and sulphates of Ca, Mg, Fe and other heavy metals. The salts responsible for permanent hardness are:
$CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$ etc.

Permanent Hardness is also known as non-carbonate hardness or non-alkaline hardness. This cannot be removed by boiling. Total Hardness of water is the sum of temporary hardness and permanent hardness of water.

Units of Hardness:
1.**Parts per million (ppm)**: It is the number of parts of $CaCO_3$ equivalents of hardness producing salt by weight present in one million parts of water.

> 1ppm = 1part of $CaCO_3$ equivalent hardness in 10^6 parts of H_2O

2.**Milligrams Per Litre (mg/lt):** It is the number of mg of $CaCO_3$ equivalents of hardness producing salt in one litre of water.

> 1mg/lt = 1 mg. of $CaCO_3$ equivalent hardness per one litre.

3.**Clarke's Degree (or) Degree clarke (^{0}Cl):** It is the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water. It is denoted by '^{0}Cl'.

> 1^0Cl = 1 part of $CaCO_3$ equivalent hardness per 70,000 parts of water.

4.**Degree French (^{0}Fr):** It is the number of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

> 1^0Fr = 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.

So,
1 ppm = 1 mg/lt = 0.07 ^{0}Cl = 0.1 ^{0}Fr
Degree of Hardness: Hardness of water is expressed in terms of equivalents of $CaCO_3$ is called 'degree of Hardness'.

$$\text{Equivalents of } CaCO_3 \text{ (or) } CaCO_3 \text{ equivalents} = \frac{\text{Mass of Hardness producing Substance in mg/lt}}{\text{Chemical equivalent of hardness Producing substance}} \times \text{Chemical equivalent of } CaCO_3$$

$$\text{Equivalents of } CaCO_3 \text{ (or) } CaCO_3 \text{ equivalents} = \frac{\text{Mass of Hardness producing Substance in mg/lt}}{\text{Chemical equivalent of hardness Producing substance}} \times \frac{100}{2}$$

Since chemical equivalent of $CaCO_3 = \dfrac{Mol.wt}{2} = \dfrac{100}{2} = 50$.

Eg:	Mol.wt	Chemical eqvt	Multiplication factor
1) $Ca(HCO_3)_2$ –	162	81	100/162
2) $Mg\,CO_3$ –	84	42	100/84
3) HCO_3^- –	61	61	100/122

DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD:

Principle: Ethylene diamine tetra acetic acid (EDTA) in the form of its sodium salt yield the anion which forms stable complex ions with Ca^{+2} & Mg^{+2}.

NaOOC.H₂C   CH₂.COONa   ⁻OOC.H₂C   CH₂.COO⁻

N-CH₂-CH₂-N   ⇒   N-CH₂-CH₂-N

HOOC.H₂C   CH₂.COOH   ⁻OOC.H₂C   CH₂.COO⁻

Di SodiumEDTA   *EDTA ion*

EDTA ion $+$ M^{+2} (Ca^{+2} or Mg^{+2})   ⇒

CH₂.COO———M———OOC.H₂C

N ———— CH₂—CH₂ ———— N

CH₂.COO⁻   ⁻OOC.H₂C

EDTA –Metal complex

In order to determine the equivalent point, Eriochrome black–T (EBT) indicator is used. When EBT is added to hard water at a p^H = 10, using ammonia – ammonium chloride buffer (NH_4OH – NH_4Cl), EBT forms a wine red unstable complex with Ca^{+2} or Mg^{+2} ions. When this solution is titrated with EDTA, EDTA forms a stable complex with Ca^{+2} or Mg^{+2} and the end point changes from wine red to deep blue colour.

M^{+2} + EBT ⟶ M – EBT
(Unstable wine red complex)

M−EBT + EDTA ⟶ M – EDTA + EBT
(stable complex)   (Blue)

EXPERIMENT – Preparation of Reagents

1.**Preparation of standard hard water:** Dissolve 1g of pure $CaCO_3$ in minimum quantity of dil.HCl and evaporate it to dryness on a water bath, and make up to 1 lt with distilled water (1mg/ml of $CaCO_3$)

2.**Preparation of EDTA Solution:** Dissolve 4gm of EDTA and add 0.1g of $MgCl_2$ to it. Make up to 1lt using distilled water.

3.**Preparation of Indicator :** Dissolve 0.5gm of Eriochrome black – T in 100ml alcohol.

4.**Preparation of Buffer (NH_4OH – NH_4Cl) solution :** Add 67.5g of NH_4Cl to 570 ml of conc. NH_3 & dilute with distilled water to 1 litre.

Procedure:

1.**Standardisation of EDTA solution :** Rinse and fill the burette with EDTA solution. Pipette out 50ml of standard hard water in a conical flask, add 10ml of NH_4OH-NH_4Cl buffer and 3 or 4 drops of EBT indicator. Titrate it against EDTA solution till the colour changes from wine red to blue. Let the vol.of EDTA consumed be **V_1 ml**.

2.**Determination of Total Hardness of water :** Pipette out 50 ml of unknown water sample in a conical flask, add 10 ml of NH_4OH – NH_4Cl buffer and 3 or 4 drops of indicator (EBT) . Again titrate it against EDTA solution till the colour changes from wine red to blue. Let the vol. of EDTA consumed be **V_2 ml.**

3. **Determination of PERMANENT HARDNESS of Water :** Take 250ml of water sample in a beaker & boil till its volume is reduced to about 50 ml (all the bicarbonates convert into insoluble carbonates, $CaCO_3$ and hydroxides, $Mg(OH)_2$). Filter, wash the precipitate with distilled water, and collect the filtrate & washings in a 250ml volumetric flask and make up the volume using distilled water. Then take 50ml of this water, add 10ml of NH_4OH-NH_4Cl buffer and 3 or 4 drops of EBT indicator & titrate against EDTA . Let the vol.of EDTA consumed be **V_3 ml.**

Calculations:

i) **Standardisation of EDTA solution:**

V_1 ml of EDTA = 50ml of standard hard water

Since each 1ml of std hard water contains 1mg of $CaCO_3$,

Hence V_1 ml of EDTA = 50mg of $CaCO_3$

$\Rightarrow$ 1ml of EDTA = $\dfrac{50}{V_1}$ mg of $CaCO_3$ eqvt hardness

ii)**Determination of Total hardness of water:**

50ml of unknown hard water sample $= V_2$ ml of EDTA

$$= V_2 \times \frac{50}{V_1} \text{ mg of } CaCO_3 \text{eqvt}$$

∴ 1000ml (or 1lt) of unknown hard water sample

$$= V_2 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000 = 1000\frac{V_2}{V_1} \text{mg of } CaCO_3 \text{eqvt hardness}$$

Hence total hardness of water $= 1000\frac{V_2}{V_1}$ mg/lt

or

$$\boxed{\textbf{Total Hardness of water} = 1000\ \frac{V_2}{V_1}\ \textbf{ppm}}$$

iii)**Determination of Permanent Hardness of water:**

As, 50ml of boiled water $= V_3$ ml of EDTA

$$= V_3 \times \frac{50}{V_1} \text{ mg of } CaCO_3 \text{eqvt hardness}$$

∴ 1000ml boiled water $= V_3 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000 = 1000\frac{V_3}{V_1}$ mg/lt

or

$$\boxed{\textbf{Permanent Hardness of water} = 1000\ \frac{V_3}{V_1}\ \textbf{ppm}}$$

iv**)Determination of Temporaty Hardness of Water:**

Temporary Hardness = Total Hardness – Permanent Hardness

$$= 1000\ \frac{V_2}{V_1} - 1000\frac{V_3}{V_1}\ \text{ppm}$$

or

$$\boxed{\textbf{Temporary Hardness} = \frac{\textbf{1000 (V}_2 - \textbf{V}_3\textbf{)}}{\textbf{V}_1}\quad \textbf{ppm}}$$

Numericals:

1) A Standard hard water contains 15gms of $CaCO_3$ per litre. 20ml of this required 25ml of EDTA Solution,100ml of sample water required 18ml of EDTA solution. The sample after boiling required 12ml of EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm.

Sol. (i) **Standardisation of EDTA Solution**:

Given 1 lit of standard hard water contains 15gms of $CaCO_3$

∴ 1ml of standard hard water contains 15mg of $CaCO_3$

Now 25ml of EDTA　= 20ml of standard hard water

= 20x15 = 300mg of $CaCO_3$

$\Rightarrow$ 1ml of EDTA = $\dfrac{300}{25}$ = 12mg of $CaCO_3$eqvt hardness

ii)**Determination of total hardness of water:**

100ml of sample water =　18ml of EDTA

= 18x12 = 216 mg of $CaCO_3$eqvt hardness

∴1lit of sample water　= 2160mg of $CaCO_3$eqvt hardness

Hence total hardness of water = **2160 ppm.**

iii)**Determination of Permanent hardness of water:**

100ml of boiled water = 12 ml of EDTA

= 12x12 = 144 mg of $CaCO_3$eqvt hardness

∴1lit of boiled water　= 1440 mg of $CaCO_3$eqvt hardness

Hence permanent hardness of water = **1440 ppm**.

iv)**Determination of temporary hardness of water:**

Temporary hardness = Total hardness – permanent hardness

= 2160 – 1440 = 720ppm

∴ Temporary hardness = **720 ppm**

2) Calculate the temporary hardness, permanent hardness of sample water containing the following:

$Ca(HCO_3)_2$ = 4.86 mg/lt ;　$Mg(HCO_3)_2$ = 5.84 mg/lt

$CaSO_4$　= 6.80 mg/lt&$MgSO_4$ = 8.40 mg/lt

(Atomic weights: Ca = 40, Mg = 24, C = 12, S = 32, O = 16, H = 1)

Sol: Mol wt. of $Mg(HCO_3)_2$ = 146 ;　$CaSO_4$　= 136

$Ca(HCO_3)_2$ = 162 ;　$MgSO_4$　= 120

Conversion into $CaCO_3$ equivalents

ConstituentMultiplication factorCaCO$_3$ equivalent

Constituent	Multiplication factor	CaCO$_3$ equivalent
$Ca(HCO_3)_2$ = 4.86mg/lt	100/162	4.86 x $\dfrac{100}{162}$ = 3.0mg/lt
$Mg(HCO_3)_2$ = 5.84mg/lt	100/146	5.84 x $\dfrac{100}{146}$= 4.0mg/lt
$CaSO_4$　= 6.80mg/lt	100/136	6.80 x $\dfrac{100}{136}$ = 5.0mg/lt
$MgSO_4$　= 8.40mg/lt	100/120	8.40 x $\dfrac{100}{120}$ = 7.0mg/lt

Temporary Hardness is due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$

$$= (3+4) \text{ mg/lt} = 7\text{mg /lt} = \textbf{7ppm}$$

Permanent Hardness is due to $CaSO_4$ and $MgSO_4$

$$= (5+7) \text{ mg/lt} = 12\text{mg /lt} = \textbf{12ppm}$$

ALKALINITY OF WATER: The acid neutralization capacity of water is termed as 'alkalinity of water'. The alkalinity of water is due to the presence of i) Caustic alkalinity (due to OH^- & CO_3^{2-} ions) and ii) Temporary Hardness (due to HCO_3^- ions)

These can be estimated separately by the titration against standard acid using phenolphthalein & Methyl orange indicators. The determination is based on the following reactions:

i) $(OH^-) + (H^+) \longrightarrow H_2O$

ii) $(CO_3^{2-}) + (H^+) \longrightarrow HCO_3^-$ **P**   **M**

iii) $(HCO_3^-) + (H^+) \longrightarrow H_2O + CO_2$
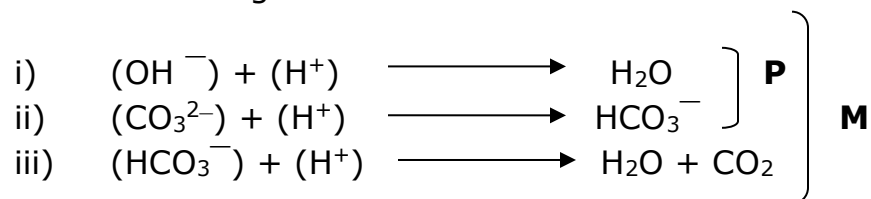
The titration of the water sample against a standard acid up to phenolphthalein end – point marks the completion of reactions (i) & (ii) (hydroxide plus one – half of the normal carbonate present). And the titration of the water sample against a standard acid to methyl orange end-point marks the completion of reactions (i), (ii) & (iii) (Total alkalinity due to hydroxide, carbonate & bicarbonate ions). The amount of acid used after phenolphthalein end point corresponds to one-half of normal carbonate plus all the bicarbonates.

The possible combinations of ions causing alkalinity in water are:

i) OH^- only   or

ii) CO_3^{2-} only   or

iii) HCO_3^- only   or

iv) OH^- and CO_3^{2-} together   or

v) CO_3^{2-} and HCO_3^- together.

The possibility of OH^- and HCO_3^- ions together is ruled out, because they combine instantaneously to form CO_3^{2-} ions.

$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$$
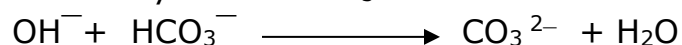
So, all the three (OH^-, CO_3^{2-} and HCO_3^-) cannot exist together.

Procedure: Pipette out 100 ml of water sample in a clean comical flask. To it, add 2 or 3 drops of phenolphthalein indicator. Titrate the solution with N/50 H_2SO_4 till the pink colour is just discharged. Then to the same solution, add 2 or

3 drops of methyl orange indicator and continue the titration, till the pink colour reappears.

Calculations:

Let the vol. of acid used to phenolphthalein end point $= V_1$ ml

Extra vol.of acid used to methyl orange end point $= V_2$ ml

100ml of water sample up to phenolphthalein end point $= V_1$ ml of N/50 H_2SO_4

$\therefore$ 100ml x N_P = V_1 x N/50

Or Normality, $N_P = \dfrac{V_1}{100} \times \dfrac{1}{50}$ N $= \dfrac{V_1}{5000}$N

Strength of alkalinity up to phenolphthalein end point in terms of

$CaCO_3$eqvt$= \dfrac{V_1}{5000}$x 50 g/l x 1000 $\dfrac{mg}{g}$ ($\therefore$Eqvt. wt of $CaCO_3 = \dfrac{mol.wt}{2} = \dfrac{100}{2} = 50$)

$$\boxed{P = 10V_1 \text{ mg/l} = 10V_1 \text{ ppm}}$$

Now 100 ml of water up to methyl orange end point$\simeq$ (V_1+V_2) ml of N/50 H_2SO_4

$\therefore$ 100 ml x N_M= (V_1+V_2) ml x $\dfrac{N}{50}$

Or normality, $N_M = \left(\dfrac{V_1+V_2}{100}\right)\dfrac{ml}{ml} \times \dfrac{N}{50} = \left(\dfrac{V_1+V_2}{5000}\right)$ N

$\therefore$Strength of total alkalinity in terms of $CaCO_3$eqvt $= \left(\dfrac{V_1+V_2}{5000}\right)$x 50 g/l x 1000 $\dfrac{mg}{g}$

$$\boxed{M = 10(V_1+V_2) \text{ mg/l} = 10(V_1+V_2) \text{ ppm}}$$

1. When P = 0, both OH^-& CO_3^{2-} are absent and alkalinity is due to HCO_3^- only

2. When P = M, both CO_3^{2-}& $HCO_3^-$are absent and alkalinity is due to OH^- only

3.When P = 1/2 M or $V_1=V_2$ only CO_3^{2-} is present, since half of carbonate neutralization (i.e,$CO_3^{2-} + H^+\rightarrow HCO_3^-$) takes place with phenolphthalein, while complete carbonate neutralization(i.e, $CO_3^{2-} + H^+\rightarrow HCO_3^-$, $HCO_3^- + H^+\rightarrow H_2O + CO_2$) occurs when methyl orange is used.

   Thus, alkalinity due to $CO_3^{2-}= 2P$

4. When P > 1/2 M or $V_1>V_2$; both CO_3^{2-}& OH^-ions are present.Now half of CO_3^{2-} (i.e, $HCO_3^- + H^+\rightarrow CO_2 + H_2O$) equal to (M−P)

   So, alkalinity due to complete $CO_3^{2-}= 2$ (M−P)

   Alkalinity due to $OH^- = M - 2(M-P) = (2P-M)$

5. When P < 1/2M or $V_1<V_2$; both CO_3^{2-}& HCO_3^- ions are present.

   Now alkalinity due to $CO_3^{2-} = 2P$

alkalinity due to HCO_3^- $= (M-2P)$

S.No	Results of Titrations	Alkalinity due to		
		Hydroxide (OH^-)	Carbonate (CO_3^{2-})	Bicarbonate (HCO_3^-)
1	P = 0	0	0	M
2	P = M	P = M	0	0
3	P = 1/2M	0	2P	0
4	P > 1/2M	2P−M	2(M−P)	0
5	P < 1/2M	0	2P	M−2P

Problems:

1) 500ml of a water sample , on titration with N/50 H_2SO_4 gave a titre value of 29 ml to phenolphthalein end point and another 500 ml sample on titration with the same acid gave a titre value of 58 ml to methyl orange end point. Calculate the alkalinity of the water sample in terms of $CaCO_3$ and comment on the type of alkalinity present.

Sol. 500ml of water up to phenolphthalein end point ≃ 29ml of N/50 H_2SO_4

∴ 500ml x N_P = 29ml x N/50

or Normality, $N_P = \dfrac{29}{500}$ x $\dfrac{1}{50}$ N

Strength of alkalinity up to phenolphthalein end – point in terms of
 $CaCO_3$eqvt = N_P x 50 x 1000 ppm

$= \dfrac{29}{500}$ x $\dfrac{1}{50}$ x 50 x 1000   ⇒**P = 58 ppm**

Given, 500ml of water up to methyl orange end point ≃ 58ml of N/50 H_2SO_4

∴ 500ml x N_M = 58ml x N/50

⇒ Normality, $N_M = \dfrac{58}{500}$ x $\dfrac{1}{50}$ N

   Strength in terms of $CaCO_3$eqvt = M = N_M x 50 x 1000 ppm

      M $= \dfrac{58}{500}$ x $\dfrac{1}{50}$ x 50x 1000   ⇒**M = 116 ppm**

From P & M values,   P = 1/2M

Hence only CO_3^{2-} ions are present

Alkalinity of water due to **CO_3^{2-} = 2P = M = 116 ppm**

2) A Sample of water was alkaline to both phenolphthalein & methyl orange 100ml of this water sample required 30ml of N/50 H_2SO_4 for phenolphthalein end point and another 20ml for complete neutralization. Determine the types and extent of alkalinity present.

Sol. 100ml of water up to phenolphthalein end point = 30ml of N/50 H_2SO_4

∴ 100ml x N_P = 30ml x N/50

Or Normality, $N_P = \dfrac{30}{100} \times \dfrac{1}{50}$ N

Strength of alkalinity up to phenolphthalein end point in terms of CaCO₃eqvt = N_P x 50 x 1000 ppm

$P = \dfrac{30}{100} \times \dfrac{1}{50} \times 50 \times 1000 = 300$ ppm ⇒ **P = 300 ppm**

As, 100ml of water up to methyl orange end point = 30+20 = 50ml of N/50 H_2SO_4

∴ 100ml x N_M = 50ml x N/50

⇒ Normality, $N_M = \dfrac{50}{100} \times \dfrac{1}{50}$ N

Strength (in terms of CaCO₃eqvt) = M = N_M x 50 x 1000 ppm

⇒M = $\dfrac{50}{100} \times \dfrac{1}{50} \times 50 \times 1000 = 500$ppm ⇒**M = 500 ppm**

Since P>1/2M. Hence OH^- and $CO_3{}^{2-}$ ions are present

Alkalinity due to **OH⁻ = 2P−M** = 2x300-500 **= 100 ppm**

& Alkalinity due to **CO₃²⁻ = 2 (M−P) =** 2 (500-300) **= 400 ppm**

Hence the given water sample contains:

OH⁻ alkalinity = 100ppm & $CO_3{}^{2-}$ alkalinity = 400ppm

3) 200ml of water sample, on titration with N/50 H_2SO_4 using phenolphthalein as indicator, gave the end point when 10 ml of acid were rundown. Another lot of 200 ml of the sample also required 10 ml of the acid to obtain methyl orange end point. What type of alkalinity is present in the sample and what is its magnitude?

Sol. 200 ml of water up to phenolphthalein end point = 10 ml of N/50 H_2SO_4

∴ 200ml x N_P= 10ml x N/50

or Normality, $N_P = 10 \times \dfrac{1}{50} \times \dfrac{1}{200}$ N $= \dfrac{1}{1000}$ N

Hence P = N_p x 50 x 1000 ppm

⇒P = $\dfrac{1}{1000} \times 50 \times 1000 = 50$ ppm ⇒ **P = 50 ppm**

Again, 200ml of water up to methyl orange end point = 10ml of N/50 H_2SO_4

∴ 200 ml x N_M = 10 ml x N/50

⇒ Normality, $N_M = 10 \times \dfrac{1}{50} \times \dfrac{1}{200}$ N $= \dfrac{1}{1000}$ N

Hence M = N_M x 50 x 1000 ppm

⇒ M = $\dfrac{1}{1000} \times 50 \times 1000 = 50$ ppm ⇒**M = 50 ppm**

From values of P &M,P = M

Hence, only OH⁻ ions are present and the alkalinity due to **OH⁻ = 50ppm**.

WATER SOFTENING: The process of removing of hardness producing salts from water is known as water softening.

Ion Exchange Method: This method is also called as deionization or demineralization process. In this method, ion-exchange resins play an important role. Ion exchange resins are insoluble, long chain, cross – linked organic polymers. These have micro porous structure and have functional groups at its ends which are responsible for the ion – exchanging properties. These ions can be exchanged with the ions of hardness producing salts.

Ion – exchange resins are of two types namely

    a) Cation exchange resins   b) Anion exchange resin

i)**Cation exchange resins (or) Acidic resins (R⁻H⁺):** These are mainly styrene – divinyl benzene copolymers, containing acidic functional groups like $-SO_3H$, $-COOH$, $-OH$ (phenolic) etc act as cation exchange resins. These can exchange their H^+ ions with the cations in the water.

ii)**Anion exchange resins (or) Basic resins (R⁺OH⁻):** These are styrene-divinyl benzene or amine-formaldehyde copolymers, which contain basic functional groups like amino, or quaternary ammonium $(-N^+R_3)$ or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil.NaOH solution become capable of exchanging their OH⁻ ions with anions in water.

Process: The Hard water is first passed through cation exchanger. All cations like Ca^{+2}, Mg^{+2} etc in water are exchanged with equivalent amounts of H^+ ions resin. Thus H^+ ions are released from resin to water.

$$2R^-H^+ + Ca^{+2} \longrightarrow R_2Ca + 2H^+$$
$$2R^-H^+ + Mg^{+2} \longrightarrow R_2Mg + 2H^+$$
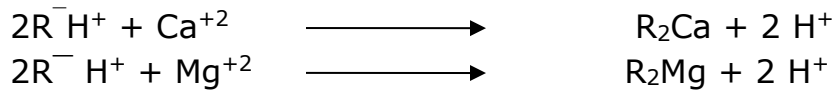
Water from cation exchanger column is then passed through anion exchanger. In this column all anions like Cl^-, SO_4^{2-} etc are exchanged with equivalent amounts of OH^- ions of resin. Thus OH^{--} ions are released from resin to water.

$$R^+OH^- + Cl^- \longrightarrow RCl + OH^-$$
$$2R^+OH^- + SO_4^{2--} \longrightarrow R_2SO_4 + 2OH^-$$
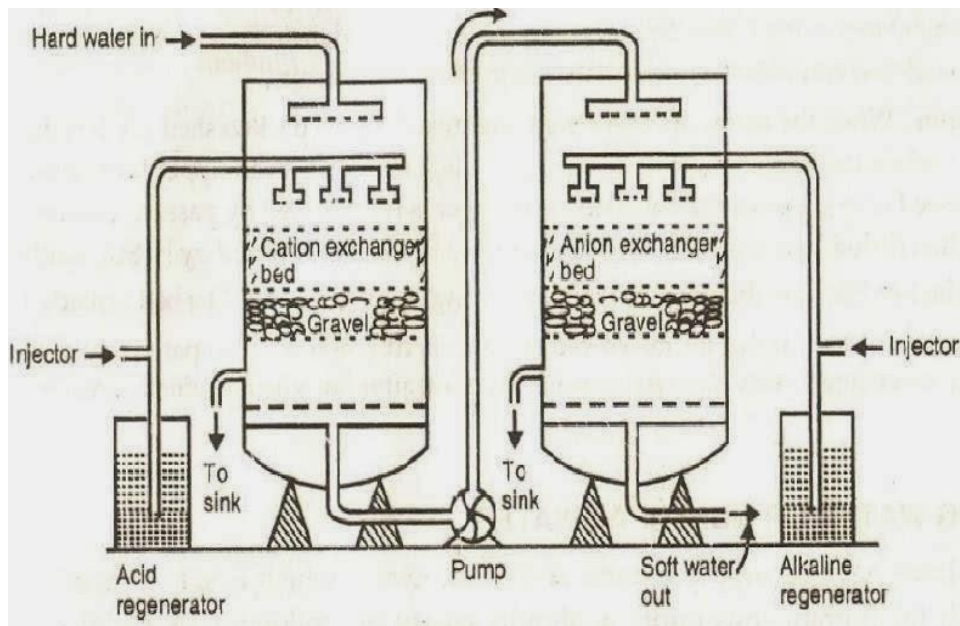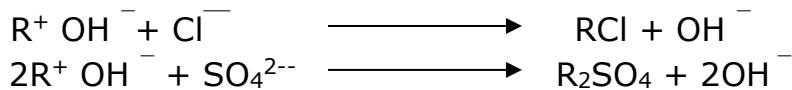
The H^+ & OH^{--} ions released from cation & anion exchangers respectively combines to give H_2O molecule.

$$H^+ + OH^- \longrightarrow H_2O$$
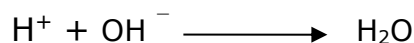
Therefore water coming out from the exchanger is free from cations as well as anions and hence called de-mineralised or de-ionised water . It is also free from acidity or alkalinity and hence is as pure as distilled water.

Regeneration : The ion exchangers may lose their exchanging ability after a long run. They are said to be exhausted. Hence they should be regenerated from time to time. The exhausted cation exchanger column is regenerated by passing either dil.HCl or dil.H_2SO_4.

$$R_2Ca + 2H^+ \longrightarrow 2RH + Ca^{+2} \text{ (washing)}$$
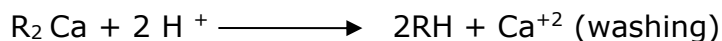
The column is washed with de-ionized water & washing is passed to sink or drain.
The exhausted anion exchanger column is regenerated by passing by dil. NaOH solution.

$$R_2SO_4 + 2\ OH^- \longrightarrow 2ROH + SO_4^{2-}\ \text{(washing)}$$

The column is washed with de-ionized water & washing is passed to sink or drain.

Advantages:i)   Produces water of very low hardness (2 ppm)

ii) Used to soften highly acidic or alkaline water

Disadvantages:i) The equipment is costly & more expensive chemicals are needed **(ii)** If the turbidity of the water is more than 10 ppm, then the output of the process is reduced.

REVERSE OSMOSIS: When two solutions of unequal concentrations are separated by a semi- permeable membrane which does not permit the passage of dissolved solute particles, (i.e, molecules and ions) flow of solvent takes place from the diluted solution to concentrated solution. This is called 'Osmosis'.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side , the solvent is forced to move from higher concentration to lower concentrated side across. Thus the solvent flow is reversed & hence this method is called 'reverse osmosis'.

Thus in reverse osmosis, pure water is separated from contaminated water. This membrane filtration is also called 'super filtration or hyper filtration..

Process: In this method, a pressure of 15 to 40 kgs/cm^2 is applied to sea water/Impure water. Pure water is forced
out through the semi permeable membrane leaving behind the dissolved salts. The membrane is made up of a very thin film of cellulose acetate affixed on either sides
 of a perforated tube. More superior membranes are made up of poly methyl-methacrylate, polyamides etc.
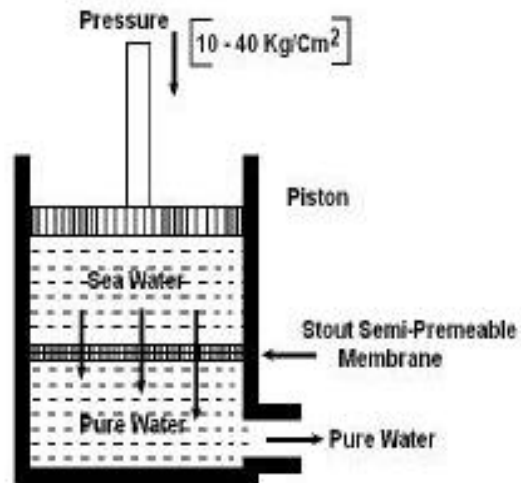
Advantages :

i)Both ionic & non-ionic, colloidal and high molecular weight organic matter is removed from water sample by this method.

ii)The cost of purification of water& the maintenance cost is less.

iii)Replacement of semi permeable membrane is easy and its life time is quite high (about 2 years)

iv)The water produced by this method can be used for high pressure boilers.

SPECIFICATIONS OF POTABLE WATER   (DRINKING WATER):

The water which is safe to drink & is fit for human consumption is called as 'Drinking or potable water.'

The specifications which are recommended for a drinking water are:
1) It should be colourless & odourless
2) It should be pleasant in taste
3) It should be perfectly cool
4) Its turbidity should be less than 10 ppm
5) It should be free from objectionable dissolved gases like H_2S (<0.05 ppm)
6) It should be free from lead, arsenic, chromium & Manganese salts(<0.05 ppm).
7) Its alkalinity should not be high. p^H should be in the range of 6.5 – 8.5.
8) It should be reasonably soft, total hardness should be less than 500 ppm.
9) It should be free from disease – producing micro organisms.
10) Chloride, Fluoride & Sulphate contents should be less than 250ppm, 1.5ppm and 250 ppm respectively.

DISINFECTION OF DRINKING WATER BY CHLORINATION:

The process of destroying/killing the disease producing bacteria, micro organisms, etc from the water and making it safe for use is called **'disinfection'** and the chemicals or substances, which are added to water for killing the bacteria, etc are known as **'disinfectants'**.

Chlorine can be employed directly as a gas or in the form of concentrated solution in water. It produces hypo chlorous acid, which is a powerful germicide.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
$$HOCl + Bacteria \longrightarrow Bacteria \text{ are killed}$$
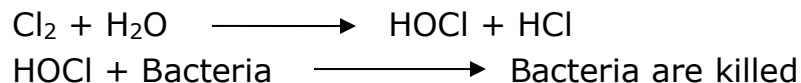
Apparatus used for disinfection by chlorine is called as **chlorinator**. It is a large tower which contains number of baffle plates. Water and proper quantity of concentrated chlorine solution are introduced from its top. During their passage through the tower, they get thoroughly mixed. For filtered water, about 0.3 to 0.5 ppm of Cl_2 is sufficient. The treated water is taken out from the bottom. Time of contact, temperature of water & p^H value of H_2O are the factors which affect the efficiency of chlorine.

Advantages of chlorine:
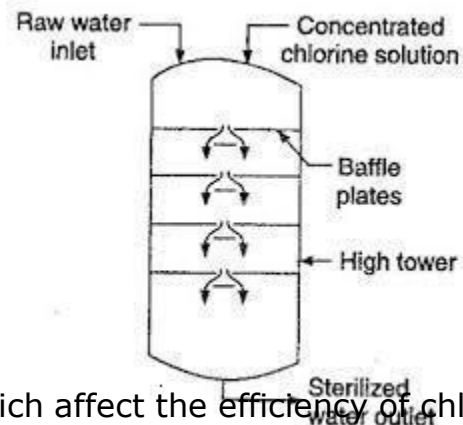
i) The use of chlorine is effective and economical

ii) It is stable and does not deteriorate on keeping

iii) It can be used at low as well as high temperatures

iv) It does not introduce any salt impurities in the treated water

Disadvantages:

i) If excess of chlorine is added, it produces an unpleasant taste &odour.

ii) Excess chlorine produces irritation on mucous membrane

iii) It is not effective at higher p^H values

BREAK–POINT CHLORINATION   (FREE-RESIDUAL CHLORINATION):

The break-point chlorination means the chlorination of water to such an extent that living organisms as well as other organic impurities in water are destroyed.

It involves in addition of sufficient amount of chlorine to oxidize organic matter, reducing substances and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfecting action against pathogenic bacteria.
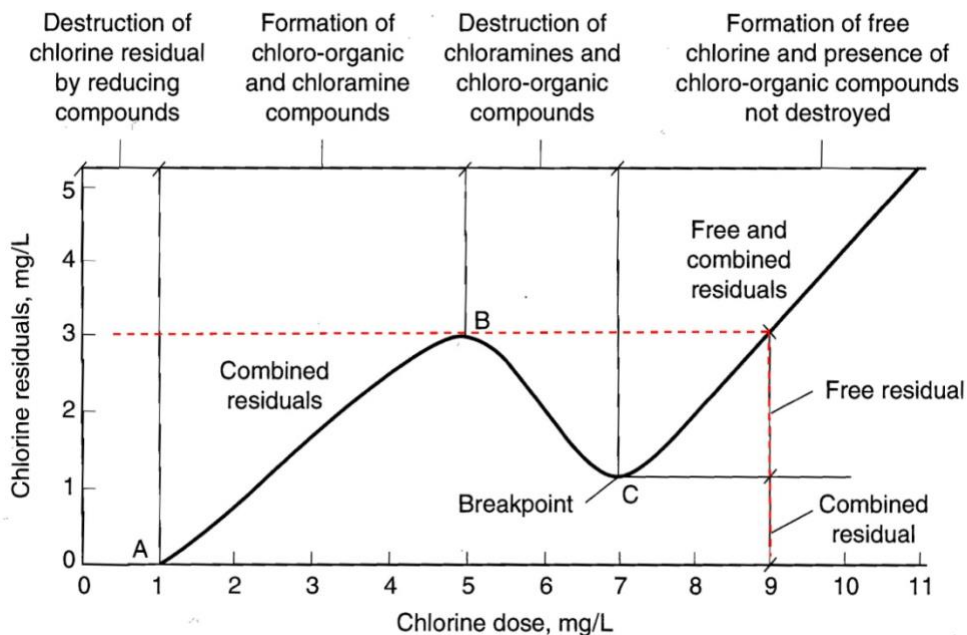
Initially for lower doses of Cl_2, the complete oxidation of reducing substances present in water takes place. As the amount of chlorine dosage is increased, an amount of residual chlorine also shows steady increase. At this stage, the formation of chloro organic compounds without oxidizing them takes place. At still higher dose, the oxidation of organic compounds and micro organisms sets in consequently the amount of free residual chlorine also decreases. When the oxidative destruction is complete it reaches a minima. After minima, the added

chlorine keeps the residual chlorine increasing. Hence, sufficient chlorine (corresponding to minima in the curve) has to be added for effective killing of the micro organisms. Addition of chlorine in such dosages is known as break point or free residual chlorination.

Advantages:

1) It oxidizes completely organic compounds, ammonia and other reducing compounds.
2) It removes colour in water, due to the presence of organic matters
3) It destroys completely (100%) all the disease producing bacteria
4) It removes the odour and taste from the water
5) It prevents the growth of any weeds in water.

CORROSION

CORROSION: The gradual deterioration of metal from its surface due to chemical or electrochemical interactions with its environment is called 'CORROSION'.

Eg: Fe forms a reddish scale of hydrated ferric oxide ($Fe_2O_3.3H_2O$) on its surface due to the interaction of iron with oxygen in atmosphere.

Causes of Corrosion: Metals exist in the form of oxides, sulphides, carbonates, sulphates etc in the earth crust. Metals are stable in their combined state. Pure metals extracted from their ore are thermodynamically unstable and tend to go back to their original combined state. Hence metals show a greater tendency to interact with its environment either chemically or electro chemically.

Ore of a metal $\xrightarrow{\text{Metallurgical Operations}}$ **Pure Metal** $\xrightarrow{\text{Environment}}$ **Corroded Metal**
(Thermodynamically stable) (Thermodynamically unstable)

However there are some metals which are excellent corrosion resistant in their pure form even in natural environment.

Effects of Corrosion: Corrosion causes the following effects:
1) Loss in useful properties of metals and thus loss in efficiency.
2) Decreases the production rate as the corroded equipment consumes much time.
3) Increases the maintenance and production cost as the corroded equipment requires painting etc.
4) Contamination of products may occur in the corroded equipment.

TYPES OF CORROSION: There are two types of corrosion namely
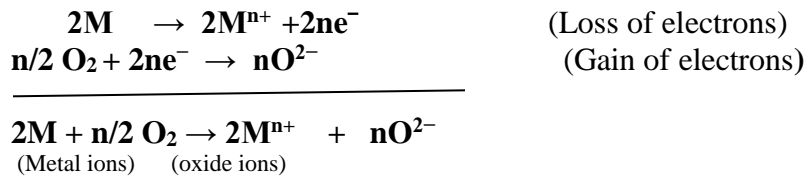
1)   Dry Corrosion (or) Chemical Corrosion
2)   Wet corrosion (or) Electro Chemical Corrosion

1. DRY CORROSION (or) CHEMICAL CORROSION:

Dry corrosion occur by the direct chemical action of environment or atmospheric gases like oxygen chlorine, hydrogen sulphide, nitrogen, sulphur dioxide etc in immediate proximity. Dry corrosion is of 3 types:

(a) Oxidation Corrosion: Oxidation corrosion takes place by the direct action of oxygen on metals in the absence of moisture.

$$2M \rightarrow 2M^{n+} + 2ne^- \qquad \text{(Loss of electrons)}$$
$$n/2\ O_2 + 2ne^- \rightarrow nO^{2-} \qquad \text{(Gain of electrons)}$$
$$\overline{2M + n/2\ O_2 \rightarrow 2M^{n+} + nO^{2-}}$$
$$\text{(Metal ions)} \quad \text{(oxide ions)}$$

Alkali metals (Li, Na, K, Rbetc) and alkaline earths (Be, Ca, Sretc) under go oxidation corrosion at low temperature, while the other metals (except Au, Ag &Pt) of high temperatures.

Mechanism: Oxidation occurs first at the surface of the metal & the resulting metal oxide forms a barrier that restricts further oxidation. For further oxidation either metal atoms has to diffuse outwards through the scale or oxygen has to diffuse inwards through the scale to metal.Since metal ion is smaller than that of the oxygen, it has higher mobility. Nature of the oxide layer plays an important role in oxidation corrosion.
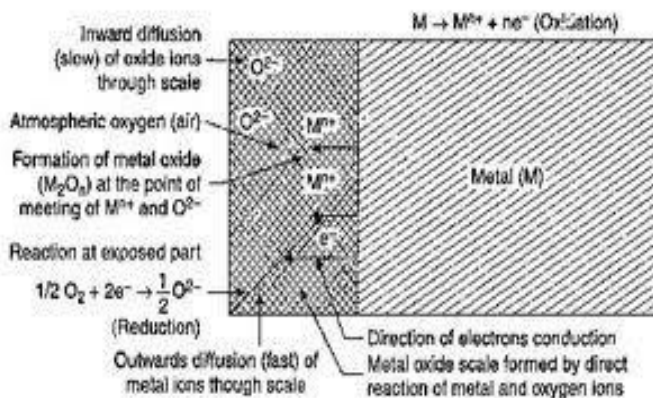
i)Stable: A Stable layer is fine – grained in structure and is impervious, stable and tightly adhered, then it act as protective coating and prevents further corrosion of metal.
Eg: The oxide layers of Al, Pb, Cu, Pt etc protects the metals from further corrosion.

ii)Unstable: If the oxide layer is unstable, it decomposes back into the metal and oxygen. In such case oxidation corrosion is not possible

$$\text{Metal oxide} \leftrightharpoons \text{Metal} + O_2$$
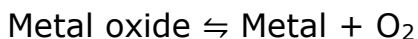
Eg: Ag, Au &Pt do not undergo oxidation corrosion.

iii) Volatile: If the oxide layer is volatile i.e, Volatilizes as soon as it is formed, then the metal surface remains exposed for further attack. This causes rapid & continuous corrosion, leading to excessive corrosion.

Eg: Molybdenum oxide (MoO_3) is volatile

iv)Porous: If the oxide layer is porous i.e, having pores or cracks, then the atmospheric oxygen have access to the underlying surface of metal, there by the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

Pilling –Bedworth rule: According to it "an oxide is protective or non porous, if the volume of the oxide is at-least as great as the volume of the metal from which it is formed" and "if the volume of the oxide is less than the volume of metal, the oxide layer is porous (or non-continuous) and hence non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below."

Alkali and alkaline – earth metals (like Li,K,Na,Mg) form oxides of volume less than the volume of metals, where as the metals like Al forms oxide, whose volume is greater than that of the metal (Al).

(b)   Corrosion by other gases like SO_2, CO_2 , Cl_2, H_2S, F_2 etc.

Some gases like Cl_2 causes corrosive effects on metals depending upon the chemical affinity & formation of protective or non-protective layers on the metal.

Eg: (1) Silver metal on exposure to Cl_2 gas, forms a protective, non-porous chloride layer which prevents further corrosion with chlorine.

2Ag + Cl_2→ 2AgCl
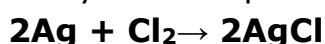
(2) Tin (Sn) on exposure to Cl_2 gas, forms a porous, non-protective chloride layer and hence tin metal undergo excessive corrosion.

Sn + 2Cl_2→ $SnCl_4$(Volatile)

(c) Liquid Metal Corrosion: This type of corrosion occurs when liquid metal is allowed to flow over a solid metal at high temperature which leads to weakening of solid metal. This happens due to the dissolution of solid metal in the liquid metal or penetration of liquid metal into the solid metal. This type of corrosion occurs mostly in nuclear reactions.

eg: The coolant (liquid sodium metal) corrodes Cadmium rods in nuclear reactor.

2.WET CORROSION (or) ELECTROCHEMICAL CORROSION:

When corrosion takes place by the transfer of electrons from anodic parts of metal to cathodic part through a conductive solution, it is called 'electrochemical corrosion'.

This type of corrosion occurs (i) where a conducting liquid is in contact with metal or (ii) when two dissimilar metals or alloys are either immersed or dipped partially in a solution.

Mechanism of Wet corrosion: This type of corrosion involves the flow of electron – current between the anodic and cathodic regions. This takes place in the following steps:

(a) Formation of anodic and cathodic regions on the surface of metal .
(b) At anodic region metal atoms undergo oxidation to give metal ions . Hence corrosion takes place at anodic area.

$\qquad$ At anode: $\qquad$ $M \rightarrow M^{n+} + ne^-$ $\qquad$ (oxidation)

(c) At cathodic region reduction of non-metallic species existing in conducting medium takes place.
(d) Diffusion of metallic and non-metallic ions towards each other forming corrosion product somewhere in between cathode and Anode.

Depending upon the nature of corrosive environment, cathodic reactions consume electrons either by (i) Evolution of hydrogen or (ii) By the absorption of oxygen.

(i) Evolution of hydrogen-type wet corrosion:

If the conducting medium is in acidic and is free from dissolved oxygen, then H_2 gas is liberated at cathode. In this type anode is very large and cathode is small.

Mechanism of wet corrosion by hydrogen evolution
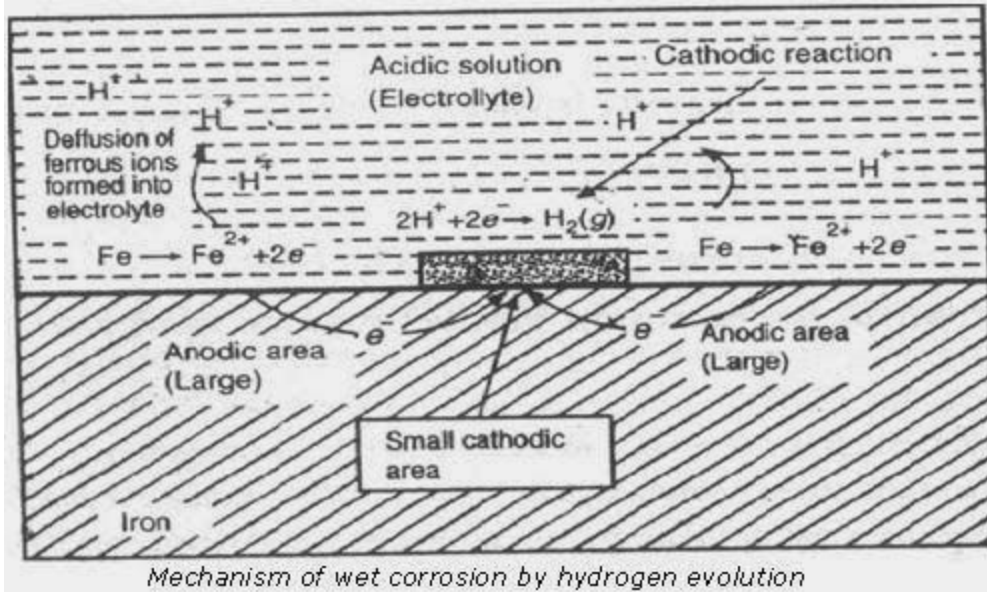
Eg: 'Fe' undergoes this type of wet corrosion in acidic environment. When 'Fe' metal is not of uniform thickness, then the area of more thickness act as cathode & the remaining area act as anode.
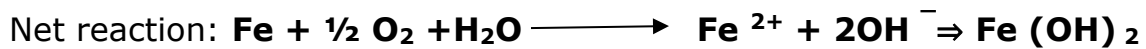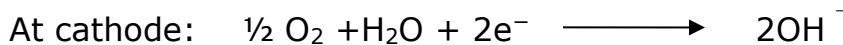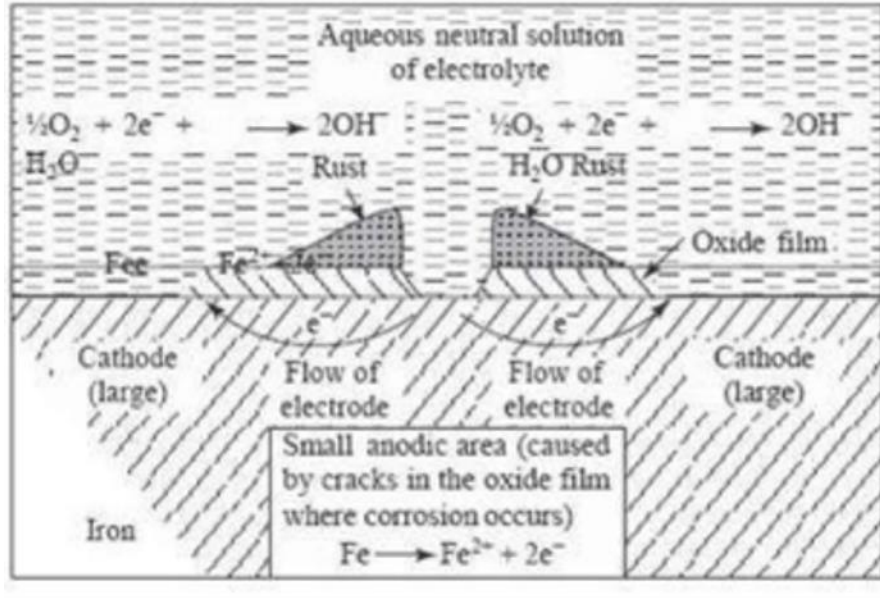
At anode:	$Fe \rightarrow Fe^{2+} + 2e^-$
At cathode:	$2H^+ + 2e^- \rightarrow H_2 \, (g)$
Net reaction:	$Fe + 2H^+ \rightarrow Fe^{+2} + H_2$
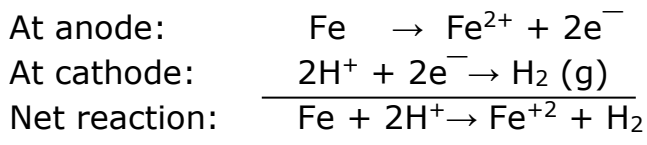
(ii) **Absorption of oxygen-type wet corrosion**:
If the conducting medium is in neutral or weakly alkaline medium and contains dissolved oxygen, then the oxygen gas is absorbed at cathode. In this type, cathode is very large & anode is small.

Eg: Rusting of iron in neutral aqueous solution of electrolytes (like NaCl sol.) in the presence of atmospheric oxygen.

When the surface of iron coated with a thin film of iron oxide develops cracks, and then anodic area is formed at the crack, while the well metal parts act as cathode (large area).

At anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

At cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Net reaction: **$Fe + \frac{1}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \Rightarrow Fe(OH)_2$**

Fe^{+2} ions from anode & OH^- ions from cathode diffuse towards each other and forms $Fe(OH)_2$, which further oxidizes to ferric oxide if sufficient O_2 is present.
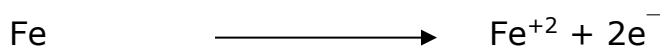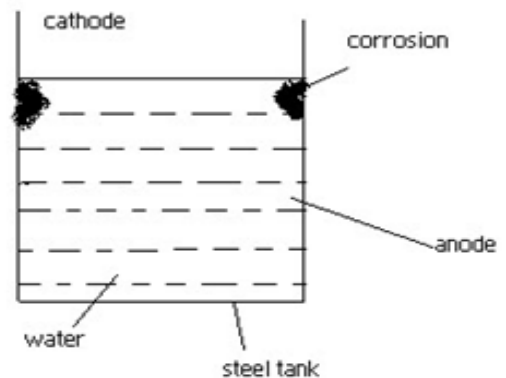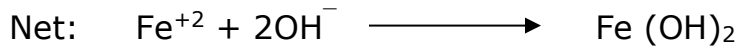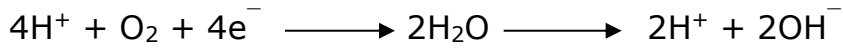
   $Fe^{2+} + 2OH^- \Rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 + 2H_2O \Rightarrow 4Fe(OH)_3$ or $Fe_2O_3.H_2O$ (yellow rust)
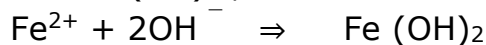
If the supply of O_2 is limited, then black anhydrous magnetite (Fe_3O_4) is formed.

WATER LINE CORROSION:

It is also an example of oxygen – concentration cell corrosion. This type of corrosion is common in ships, Iron tanks used for storing water etc.

When water is stored in a steel tank, then corrosion takes place along the line just beneath the level of water meniscus. The area above water line is highly oxygenated and acts as cathode. The area just beneath the water meniscus is poorly oxygenated and acts as anode and hence gets corroded.

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

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

Net: $Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2$

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In case of ships, this kind of corrosion is often accelerated by marine plants attaching themselves to the sides of ships. The use of special antifouling paints restricts this to some extent.

Note: The concentration of dissolved oxygen in water is greater at the surface than deeper down.

PITTING CORROSION:

Pitting corrosion is a localized accelerated attack, resulting in the formation of cavities around which the metal is relatively unattached.

Generally, cavities, pinholes, pits & cracking of protective film developed on the metal surface, creates the formation of small anodic areas in the less oxygenated parts and large cathodic areas in more oxygenated parts.
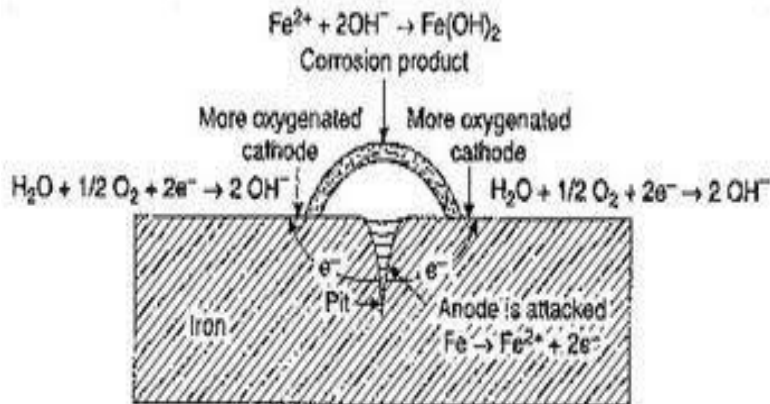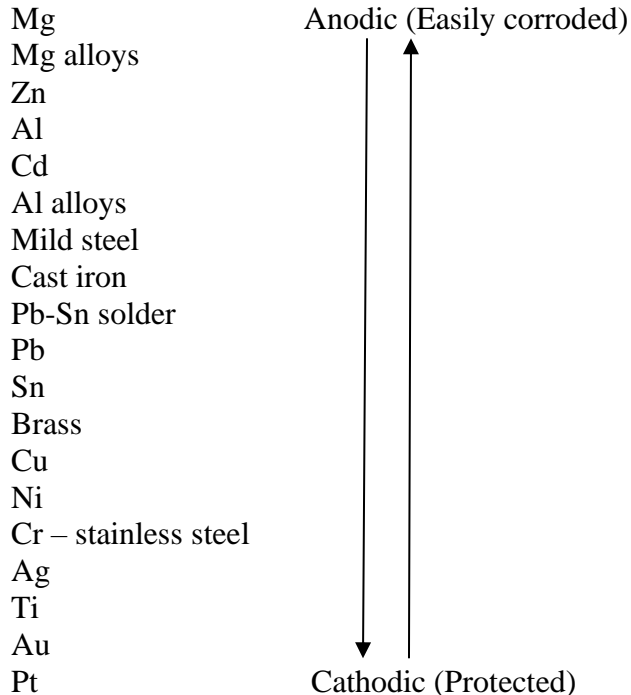

When the surface area of cathode is greater, greater will be its demand for electrons and hence rate of corrosion at anode increases . Metals owing their corrosion resistance to their passive state, show a marked pitting under all conditions, which lead to the destruction of their passivity. For eg: stainless steel and aluminum show a characteristic pitting in chloride solution.

The presence of the extraneous impurities (like sand, dust, scale etc) embedded on the surfaces of metals also lead to pitting.

GALVANIC SERIES:

The galvanic series is prepared which give real & useful information regarding the corrosion behavior of metals and alloys in the given environment.

Galvanic series

Mg   Anodic (Easily corroded)
Mg alloys
Zn
Al
Cd
Al alloys
Mild steel
Cast iron
Pb-Sn solder
Pb
Sn
Brass
Cu
Ni
Cr – stainless steel
Ag
Ti
Au
Pt   Cathodic (Protected)

FACTORS AFFECTING THE RATE OF CORROSION:

The rate or extent of corrosion mainly depends upon the following.

(a) Nature of Metal :

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

(**ii) Relative areas of 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 areas of the cathodic part & the anodic part.

      Corrosion is more rapid and severe, and highly localized, if the anodic area is small (e.g.: a small steel pipe fitted in a large copper tank), because the current density at a small anodic area is much greater, and the demand for electrons (by the large cathodic areas) can be met by the small anodic areas only by undergoing 'corrosion more briskly'.

(iii) Nature of the corrosion product:

(a) If the corrosion product is insoluble, further corrosion of metal is suppressed, but if the corrosion product is soluble in corroding medium then corrosion of metal will be faster.

eg : 'Pb' in H_2SO_4 forms an insoluble $PbSO_4$ in H_2SO_4 and hence reduces the corrosion rate.

(b) If the corrosion product is volatile, then the underlying metal surface undergo further attack and hence corrosion rate is more.

(iv) Purity of metal : Impurity present in a metal cause heterogeneity and thus tiny electrochemical cells are set up at the exposed part of the impurity and corrosion takes place around the impurity. For example, Zn metal containing Pb or Fe as impurity undergoes corrosion. Hence greater the impurity, greater is the corrosion rate or lesser the purity of metal, greater is the corrosion rate.

(v) Nature of surface oxide film : The ratio of volumes of metal oxide to the metal, is known as 'specific volume ratio'. Smaller the specific volume ratio, greater is the oxidation corrosion, because oxide film formed will be porous, through which oxygen can diffuse and bring about further corrosion.

Eg: The specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. So, the rate of corrosion of W is least, even at higher temperatures.

(b) Nature of Environment :

(i) Effect of Temperature: Increase in temperature of the corroding environment increases reaction rate. Hence rate of corrosion also increase. In case of differential aeration, increase in temperature increases the rate of diffusion of O_2, therefore the rate of corrosion (differential aeration) decreases.

(ii) Effect of Humidity: Greater the humidity in the environment, greater is the corrosion rate. This is due to the fact that moisture act as solvent for gases like O_2, H_2S, SO_2 etc.

Eg : Atmospheric corrosion of Iron is slow in dry air compared to moist air.

(iii)Effect of p^H : Lesser the p^H of the corroding medium, greater will be the corrosion rate. Since the corrosion of metals will be more in acidic medium. However amphoteric metals (like Al, Pbetc) dissolve in alkaline solutions as complex ions.

Eg: Corrosion of 'Zn' can be minimized by increasing p^H of the corroding medium to 11. Generally metals corrode more in acidic media than alkaline or neutral media.

CORROSION CONTROL METHODS:

CATHODIC PROTECTION: It is also called as '**electro chemical protection'**. We know that metal under goes corrosion by oxidation.

$$M \longrightarrow M^{n+} + ne^{-}$$
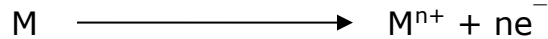
The dissolution of a metal can be prevented by forcing the metal to behave like a cathode. This is the principle of cathodic protection. Due to the absence of anodic area on the metal, corrosion will not occur.
Cathodic protection is of two types:
(i) Sacrificial anodic protection   (ii) Impressed current cathodic protection.

i) Sacrificial anodic protection: In this method, the metal can be saved from corrosion by connecting it with more active metal through a wire, so that the parent metal becomes cathodic, while the active metal becomes
anodic. The active metal is sacrificed in the process of saving the metal from corrosion hence called 'Sacrificial anode".
Eg: Metals commonly used as sacrificial anodes are Zn, Mg, Al and their alloys. 'Zn' is used in soil etc.
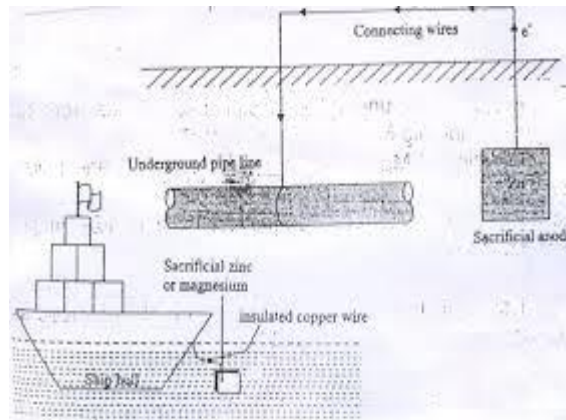
Applications: This method is applicable for
(1) The protection of underground cables, pipelines from soil corrosion
(2) Protection of ships & boat hulls from marine corrosion (by hanging Mg or Zn sheets around the hull through wire)
(3) Domestic water boilers and tanks are protected from rust formation by hanging Mg rod or sheet into the tank.

ii) Impressed current cathodic protection: In this method, the current from external source (impressed current) is applied in opposite direction to nullify the corrosion current. This is done to convert the corroding metal from anode to
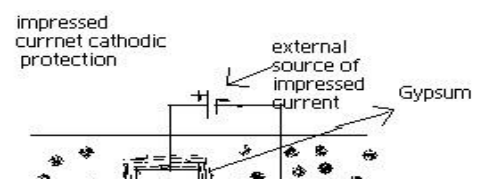
cathode. An insoluble anode like graphite, carbon, stainless steel etc is used in this method.

The insoluble anode and the parent metal (cathode) are connected to the source of direct current through an insulated wire. The anode is buried in back fill (gypsum) to increase theelectrical contact with the surrounding soil.

Applications: This method is applicable for

1) The protection of large structures for long term operations like buried pipelines, tanks, marine piers, transmission line towers etc.

SURFACE COATINGS

Metals can be protected from corrosion by applying metallic or non-metallic coatings.

Methods of Application of Metallic Coatings :

Hot Dipping : The process of coating of a base metal (like iron, steel and copper) by immersing it in the molten coat metal (like Zn or Sn etc) is called ' hot dipping '.

In this a well cleaned base metal is immersed in a bath of molten coating metal and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Eg: Galvanizing & Tinning etc.

Galvanizing : Galvanizing is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting.

Galvanizing of sheet steel.
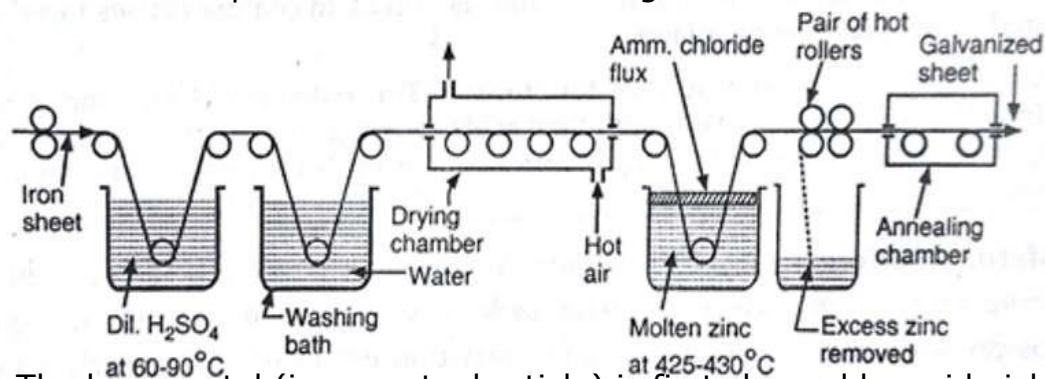
The base metal (iron or steel article) is first cleaned by acid pickling using dil.H_2SO_4 solution at 60-90°C for 15-20 minutes. It is then treated with 5% HF to dissolve the sand particles and then cleaned with 5-20% solution of zinc

ammonium chloride to remove superficial oxides, if present. It is then dipped in molten zinc at 425-430˚C.The surface of the bath is covered by NH$_4$Cl 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 and finally it is annealed at 650˚C and cooled slowly.

Applications: It is used to protect iron used for roofing sheets, wires, pipes, nails, bolts, screws etc.

Galvanized utensils cannot be used for preparing and storing food stuffs because Zn dissolves to form highly toxic or poisonous compounds.