

# **Chapter-I Types of Impurities in Water**

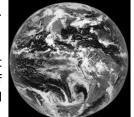
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Water is necessary for living beings (Humans, Animals & Plants.

Water is required in all human activities like domestic, agriculture and industries.

- ❖ Water covers 70% of the Earth i.e. 2/3<sup>rd</sup> part of the earth.
- ❖ 97% of the earth water is salt water and 3% is Fresh water; 2/3rd of fresh water is frozen in glaciers and polar ice caps.



Fresh water is renewable resource.

## **Sources of Water**

Surface Water

Frozen Water

**Underground Water** 

Rain Water

Sea Water

River Water

**Surface Water** 

Pond

and still water (Ponds, Lakes & Reservoirs).

Surface Water includes flowing water (Rivers & Streams)

Streams



Lake

Flowing Water

Still Water

Reservoir

#### **River Water**

River water contains dissolved minerals like chlorides. sulphates, bicarbonates of Sodium, Magnesium, Calcium and Iron.

River water contains suspended impurities of sand and rock and organic matter.

The composition of river water is not constant and depends on its contact with soil.

#### **Lake Water**

Lake water has high quantity of organic matter and lesser amount of dissolved minerals. Its chemical composition is also constant.

Rain water is the most purest form of water.

Rain water during its downward journey through the atmosphere it dissolves organic and inorganic suspended particles and gases like NO<sub>x</sub>, CO<sub>x</sub> and SO<sub>x</sub>.

#### Sea Water

Sea water is impure due to continuous evaporation increases dissolved impurity content and impurities thrown by the rivers as they join the sea.



Sea water is saline.

#### **Frozen Water**

Frozen Water includes Glaciers, Icebergs.

# **Underground Water**





well and springs. Free from organic

impurities, clear in appearance but contain large amount of dissolved salts.

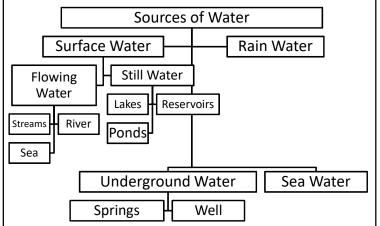
It includes Water from

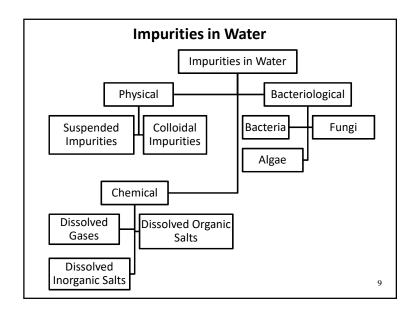


**Rain Water** 

Rain water is obtained as a result of evaporation from surface water.

**Sources of Water** 





# **Impurities in Water**

#### **Suspended Impurities:**

- > They impart turbidity, colour and odour to water.
- ➤ It may be Inorganic (Clay and Sand) or Organic (Oil, Vegetable and Animal matter) in nature.
- ➤ Suspended Impurities are Macroscopic . The size of suspended impurities ranges from 0 to 10-3 mm



## **Collodial Impurities:**

They impart turbidity, colour and odour to water.

It may be Inorganic (Clay and Sand) or Organic (Oil, Vegetable and Animal matter) in nature.

# **Dissolved Impurities:**

These impurities are due to the presence of dissolved salts like Carbonates, Bicarbonates, Chlorides and Sulphates of Calcium, Magnesium, Iron and Sodium.

Hardness is due the presence of these salts.

Dissolved gases like  $CO_2$ ,  $O_2$ , etc. also considered as dissolved impurities.

# Microorganisms:

They include bacteria, fungi and algae.

These impurities are introduced into water by animal or vegetable waste and through sewage flowing into the water body.

#### Hardness

Hardness is the characteristic of water which prevents the lathering of soap.

Hardness is the soap consuming capacity of water.

Hardness is due to the presence of certain salts of Ca and Mg and other Heavy Metals ions like Al<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup> dissolved in it.

$$\begin{array}{c} 2\mathsf{C}_{17}\mathsf{H}_{35}\mathsf{COONa} + \mathsf{CaCl}_2 & \longrightarrow & (\mathsf{C}_{17}\mathsf{H}_{35}\mathsf{COO})_2\mathsf{Ca} + 2\mathsf{NaCl} \\ \mathsf{Sodium\,Stearate} & \mathsf{Hardness} & \mathsf{Calcium\,Stearate} \end{array}$$

$$\begin{array}{c} 2\mathsf{C}_{17}\mathsf{H}_{35}\mathsf{COONa} + \mathsf{MgSO}_4 & \longrightarrow & (\mathsf{C}_{17}\mathsf{H}_{35}\mathsf{COO})_2\mathsf{Mg} + \mathsf{Na}_2\mathsf{SO}_4 \\ \mathsf{Sodium\,Stearate} & \mathsf{Hardness} & \mathsf{Magnesium\,Stearate} \end{array}$$

Cations which produces insoluble soap with soap solution will contribute to the hardness.

On the above basis Water is of Two Types; Hard Water and Soft Water

Hard Water	Soft Water
Water which do not produce lather with soap & form white curd/scum.	Water which produce lather with soap
Contain soluble Calcium & Magnesium salts	Do not contain dissolved Calcium & Magnesium salts
Cleansing quality is depressed	Cleansing quality is not depressed
Due to the dissolved salts boiling point of water is elevated	Less fuel and time are required for cooking of food.



# **Types of Hardness**

Hardness is of Two Types

❖ Temporary Hardness / Alkaline Hardness / Carbonate Hardness

The temporary hardness is due to the presence of carbonates and bicarbonates of Calcium & Magnesium. It can be removed by physical methods like boiling.

❖ Permanent Hardness / Non-Alkaline Hardness / Non-Carbonate Hardness

The permanent hardness is due to the presence of chlorides and sulphates of Calcium, Magnesium, Salts of heavy metals & Acids. It cann't be removed by physical methods like

Permanent hardness can not be removed by physical methods like boiling but it can be removed by Chemical Methods.

### **Units of Hardness**

- ☐ Parts per million (ppm): Parts of calcium carbonate equivalent hardness per 10<sup>6</sup> part of water.
- ☐ Milligrams per Litre (mg/L): Milligrams of calcium carbonate equivalent hardness per Litre of water.
- ☐ Degree Clark (°Cl): Parts of calcium carbonate equivalent hardness per 70,000 part of water.
- ☐ Degree French (°Fr): Parts of calcium carbonate equivalent hardness per 10<sup>5</sup> part of water.

# **Degree of Hardness**

- ☐ The hardness of water is expressed in terms of equivalent amount CaCO<sub>3</sub>.
- ☐ The reason for reporting hardness as equivalent amount of CaCO<sub>3</sub> is the ease in calculation as its Molecular weight CaCO<sub>3</sub> is 100 and equivalent weight is 50.

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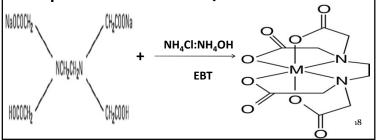
# Sodium 4-[(1-hydroxynaphthalen-2-yl-hydrazinylidene]-7-nitro-3-oxo-Y-naphthalene-1-sulfonate HO Na<sup>+</sup> SO<sub>3</sub> EBT Blue to wine red colour Scheme 1. Structure of EBT.

# **Relationship between the Units of Hardness**

1 ppm = 1 mg/L

1 ppm = 1 mg/L = 0.07 °Cl = 0.1 °Fr

Determination of Hardness by Complexometric Method / EDTA Method



- ☐ Ethylene Diammine Tetra Acetic Acid is tetraprotic acid, due to its limited solubility, it is not used directly.
- ☐ Disodium salt of Ethylene Diammine Tetra Acetic Acid is used (Molecular Weight 372.24)
- $\Box$  It combines with metal ions in 1:1 ratio in the presence of NH<sub>4</sub>Cl:NH<sub>4</sub>OH buffer solution and Eriochrome Black T is used as indicator.
- $\square$ NH<sub>4</sub>Cl:NH<sub>4</sub>OH buffer solution is used because the divalent metal are stable in slightly basic solution (pH=10).

☐ The colour of EBT is "Blue" and when it added to hard water it forms unstable complex of "Wine Red" colour.

☐ Metal-Indicator unstable complex when titrated with EDTA to form colourless Metal-EDTA complex.

Ca-EBT + EDTA 
$$\xrightarrow{\text{NH}_4\text{Cl:NH}_4\text{OH}}$$
 Ca-EDTA + EBT

$$pH = 10$$

$$\text{Metal-EDTA stable}$$

$$\text{complex}$$

$$\text{(Blue)}$$

☐ End point is achieved by the appearance of Blue Colour of Free EBT.

Calculation of Hardness of water: Unitary Method

Standardization of EDTA solution

Let the strength of Standard Hard Water (SHW) = S mg / L

1 Liter of SHW contain----- S mg of CaCO<sub>3</sub>

'V<sub>Std. SHW</sub>' mI of SHW contain----- (S x V<sub>Std. SHW</sub>) mg CaCO<sub>3</sub>

V<sub>Std. EDTA</sub> ml of EDTA ------ V<sub>Std. SHW</sub> ml of SHW

 $V_{\text{Std. EDTA}}$  ml of EDTA ----- S x  $V_{\text{Std. SHW}}$  ml of SHW

1 ml of EDTA contain-----  $\underline{S \times V_{Std. SHW}}_{Std. EDTA}$  mg CaCO<sub>3</sub>

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**Determination of Total Hardness of Unknown Hard Water** 

V<sub>TH UHW</sub> ml of UHW ------ V<sub>TH EDTA</sub> ml of EDTA

$$V_{\text{TH. UHW}}$$
 mI of UHW ------  $V_{\text{TH. EDTA}}$   $\left\{ \frac{S \times V_{\text{Std. SHW}}}{V_{\text{Std. EDTA}}} \right\}$  mg CaCO<sub>3</sub>

1 ml of UHW ----- 
$$\frac{V_{\text{TH. EDTA}}}{V_{\text{TH. UHW}}}$$
  $\frac{\text{S x V}_{\text{Std. SHW}}}{V_{\text{Std. EDTA}}}$  mg CaCO<sub>3</sub>

1000 ml of UHW ----- 1000 \* 
$$\frac{V_{\text{TH. EDTA}}}{V_{\text{TH. UHW}}}$$
  $\frac{\text{S x V}_{\text{Std. SHW}}}{V_{\text{Std. EDTA}}}$ 

 ${\rm mg\ CaCO_3}$ 

**Determination of Permanent Hardness of Unknown Hard Water**V<sub>PH. UHW</sub> ml of Boiled Water ------ V<sub>PH. EDTA</sub> ml of EDTA

$$V_{\text{PH. UHW}} \, \text{mI of UHW} ------ V_{\text{PH. EDTA}} - \frac{\text{S x V}_{\text{Std. SHW}}}{\text{V}_{\text{Std. EDTA}}} - \text{mg CaCO}_3$$

1000 ml of BHW ----- 1000 \* 
$$\frac{V_{PH. EDTA}}{V_{PH. UHW}}$$
  $\frac{S \times V_{Std. SHW}}{V_{Std. EDTA}}$ 

mg CaŒ⊕<sub>3</sub>

# Determination of Temporary Hardness of Unknown Hard Water

Temporary Hardness =

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# Calculation of Hardness of water: Molarity Method

**Calculation of Molarity of Standard Hard Water** 

Weight of CaCO<sub>3</sub> = W gm

Molecular weight of CaCO<sub>3</sub> = 100

Moles of CaCO<sub>3</sub> = Weight (W)
Molecular Weight

Volume of water = 'V' Litre

Morality of SHW (M1)= Weight (W)

Molecular Weight \* V

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## **EDTA solution Vs Standard Hard Water**

SHW EDTA

M1V1 = M2V2

 $M2 = \underbrace{M1V1}_{V2}$ 

# **EDTA solution Vs Sample Hard Water**

EDTA Sample Water

M2V2 = M3V3

 $M3 = \frac{M2V2}{V3}$ 

Total Hardness = M3 \* Molecular Mass of CaCO<sub>3</sub> \* 1000

ppm

**EDTA solution Vs Boiled Hard Water** 

EDTA Boiled Sample Water

M2V2 = M4V4

 $M4 = \frac{M2V2}{V4}$ 

Permanent Hardness = M4 \* Molecular Mass of CaCO<sub>3</sub> \* 1000

ppm

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Temporary Hardness =

Total Hardness - Permanent Hardness ppm

**Numerical on Hardness Estimation using EDTA Method** 

Annexure- 1

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# **Alkalinity**

Alkalinity is a measure of the ability of water to neutralize the acids.

Alkalinity of water means the total content of those substances which causes an increased hydroxide ion concentration upon dissociation or due to hydrolysis.

Alkalinity of water is due to the presence of

✓ HCO<sub>3</sub>- Temporary Hardness

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- ✓ OH- and CO<sub>3</sub><sup>2</sup>-
- ✓ HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>
- ✓ The possibility of OH<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> together is ruled out because they combine to form CO<sub>3</sub><sup>2-</sup>ions.

$$OH^-$$
 +  $HCO_3^ \longrightarrow$   $CO_3^{2-}$  +  $H_2O$ 

- ➤ Thus OH- and HCO<sub>3</sub>- ions can not exist together in water.
- $\succ$  Hence  $\mathrm{OH^{\text{-}}}$  ,  $\mathrm{CO_3^{2\text{-}}}$  and  $\mathrm{HCO_3^{\text{-}}}$  ions can not exist together in water.

# **Estimation of Alkalinity of water**

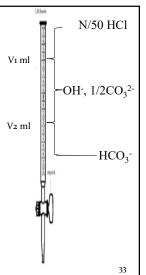
- > Fill the burette with N/50 HCl solution.
- ➤ Pipette out 20 ml of alkaline water sample in conical flask,

➤ Add a drop of Phenolphthalein, then the colour of solution becomes pink.

➤ Titrate against N/50 HCl till the solution becomes colourless. Note down the amount of acid used (V1 ml).

ightharpoonup Add a drop of Methyl Orange ; the  $^{V_2\,ml}$  solution become slightly orange. Continue the titration against N/50 HCl till the reappearance of light pink colour (V2 ml).

CO<sub>3</sub><sup>2-</sup> + H<sup>+</sup> 
$$\longrightarrow$$
 H<sub>2</sub>O  
 $CO_3^{2-}$  + H<sup>+</sup>  $\longrightarrow$  HCO<sub>3</sub><sup>-</sup>  
 $HCO_3^{-}$  + H<sup>+</sup>  $\longrightarrow$   $CO_2$  + H<sub>2</sub>O



Strength (M) = Normality (N3) x Equivalent weight of  $CaCO_3$  x 1000 ppm

# **Condition of Alkalinity**

S.No.	Results of Titration	Hydroxide	Carbonate	Bicarbonate
1	P = 0	NIL	NIL	M
2	P = M	P or M	NIL	NIL
3	$P = \frac{1}{2} M$	NIL	2P	NIL
4	P > ½ M	2P – M	2 (M – P)	NIL
5	P < ½ M	NIL	2P	M – 2P

**Numerical on Alkalinity** 

Annexure- 2

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# Calculation

ACID WATER

N1V1 = N2V2

 $N2 \text{ or Np} = \underbrace{N1V1}_{V2}$ 

Strength (P) = Normality (N2) x Equivalent weight of  $CaCO_3$  x 1000 ppm

For the same solution; V1 = V1+V2

For different solution; V1 = V2

ACID WATER

N1(V1+V2) = N3V3

N3 or N<sub>M</sub> =  $\frac{N1(V1+V2)}{V3}$ 

٧3

# **Boiler**

- ➤ Boiler is a closed vessel which is used to convert water into steam
- ➤ Boiler is made up of two parts

  Furnace: Provides heat by burning fuel.

**Boiler Proper:** Chamber where water is converted into steam.

> Water feed into boiler is known as "Boiler Feed Water".

➤ The Chemical Energy is converted into Heat Energy by combustion process which in turn is absorbed by water.



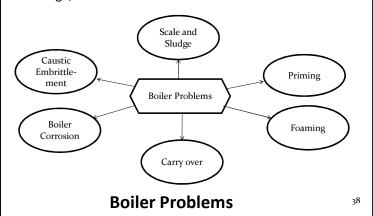
# **Boiler Problems**

> Essential requirement for boiler feed water:-

It should be free from
Turbidity, Oils, Dissolved Salts
Hardness and scale forming salts
Dissolved O<sub>2</sub> and CO<sub>2</sub>
Caustic Alkali

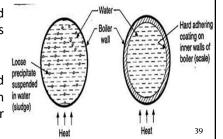
- > Proper treatment of boiler feed water is an important part of boiler operation and maintenance system.
- ➤ As the water is converted into steam, the concentration of dissolved solids increases and starts depositing inside the boiler thereby reduces boiler efficiency and leads to poor heat transfer.

➤ If the pre-treatment of boiler feed water is not done then it may lead to "Boiler Problems" like Priming, Foaming, Scale and Sludge, Boiler Corrosion and Caustic Embrittlement.



# Scale and Sludge

- ➤ In the boiler water is continuously evaporated to form steam. This increases the concentration of dissolved salts.
- ➤ A stage is reached when ionic product exceeds the solubility product (Ksp < Ip, supersaturated solution) and hence they are thrown out as precipitates.
- ➤ If the precipitate formed is soft loose and slimy is known as Sludge.
- If the precipitate formed suspend is hard and adhering on the inner wall of the boiler is known as Scale.



 $\checkmark$  If Solubility Product =  $K_{SP}$  and Ionic Product =  $[A^{y+}]^x[B^{x-}]^y$ 

 $ightharpoonup K_{SP} = [A^{y+}]^x[B^{x-}]^y == Solution is Saturated$ 

 $ightharpoonup K_{SP} > [A^{y+}]^x[B^{x-}]^y == Solution is Unsaturated$ 

 $ightharpoonup K_{SP} < [A^{y+}]^x[B^{x-}]^y == Precipitation will takes place$ 

# Sludge

❖ Sludge is soft, loose and slimy precipitate formed within the boiler.



❖ Sludge is formed by substance which have higher solubility in hot water than in cold water. For example MgCO<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub>.

❖ Sludge is formed at the comparatively colder part of the boiler and get collected at places where the flow rate is slow.

# **Disadvantages of Sludge**

- ✓ Sludge is bad conductor of Heat.
- ✓ Excessive Sludge formation affects the working of boiler and causes chocking of pipes.

# **Prevention of Sludge Formation**

- ✓ Use of Soft Water.
- ✓ By frequently "Blow Down Operation" i.e removal of concentrated water through tap at the bottom of the boiler when extent of hardness becomes high.

# ✓ Decomposition of Calcium Sulphate

The solubility of  $CaSO_4$  in water decreases with the increase in temperature.  $CaSO_4$  is soluble in cold water but completely insoluble in super heated water.

Low solubility of  $CaSO_4$  is due to the increased ionization at high temperature and less availability of water molecules for solvation at high temperature.

 ${\rm CaSO_4}$  precipitates as hard scale on hotter parts of boiler and high pressure boilers.

# √ Hydrolysis of Magnesium Salts

Dissolved salts of Magnesium hydrolyze at high temperature to form a soft  $Mg(OH)_2$  scale.

#### Scale

❖ Scale are hard deposits firmly sticking to the inner wall of the boiler.



#### Scale is formed due to the following reasons

✓ Decomposition of Calcium Bicarbonate

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2 \uparrow$$

Scale composed of CaCO<sub>3</sub> is soft and main cause of scale formation in the low pressure boilers.

In High pressure boiler  $CaCO_3$  is soluble due to the formation of  $Ca(OH)_2$ .

$$CaCO_3 \longrightarrow Ca(OH)_2 + CO_2 \uparrow$$

$$MgCl_2 \longrightarrow Mg(OH)_2 + 2 HCl$$

#### ✓ Presence of Silica

Even if small quantity of  $SiO_2$  is present then it may deposit as calcium silicate ( $CaSiO_2$ ) and Magnesium Silicate ( $MgSiO_2$ ). These deposit adhere to the inner surface of boiler very firmly. The main source of silica is the Sand Filter.

# **Disadvantages of Scale**

- Wastage of Fuel
- Lowering of Boiler Safety
- Decrease of Boiler Efficiency
- Danger of Boiler Explosion

### **Removal of Scale Formation**

- Removal by Mechanical Methods- Scrapping
- If scale is brittle, it can be removed by Thermal shocks
- If the scale is loosely adhering then it can be removed by "Blow Down Operation" (i.e. Heating the boiler & then sudden cooling.
- If the scale is adherent and hard then can be removed by dissolving them in chemicals;
- **▶** CaCO₃ scale can be removed by adding 5-10% HCl
- ➤ CaSO<sub>4</sub> scale can be removed by adding EDTA

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# ✓ Priming can be avoided by

- > Controlling the rapid change in steaming velocities.
- Proper design of the Boiler.
- Ensuring sufficient softening.
- > By blowing off the sludge and scale from time to time.
- > Filtration of Boiler Feed Water

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# **Priming**

❖ When steam is produced rapidly in the boiler, some droplets of the liquid water are carried along with the steam. This process of "Wet Steam" formation is called Priming.

# ✓ Priming is caused by

- Presence of Dissolved impurities and Suspended impurities.
- > Steam Velocities high enough to carry droplets of water into the steam pipe.
- Sudden Boiling
- > Faulty design of Boiler

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# **Foaming**

- ❖ Foaming is the formation of persistent foam or bubbles at the water surface in the boiler which do not break easily.
- ❖ Foaming is caused due to the presence of Oil and Alkalis in the boiler feed water.



❖ Oil and Alkalis reacts to form soaps which greatly reduces the surface tension of water & increases the foaming tendency of the water.

- √ Foaming can be avoided by
- Addition of Anti-foaming agent which reduces the surface tension (Like Castor oil).
- > Removal of foaming agent oil from Boiler feed water.

# **Carry Over**

The phenomenon of carrying of water along with impurities by steam is called carry over.

Carry Over is due to Priming & Foaming.

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Carry Over and Priming & Foaming occurs together and they are objectionable.

Dissolved Solids or Suspended Solids in boiler water are carried by the wet steam to super heater or steam turbine blades where they get deposit as water evaporates.

Dissolved Solids may enter the part of other machinery, thereby decreasing their life

The maintenance of the boiler pressure become difficult because of improper judgement of actual height of water column.

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#### **Boiler Corrosion**

- ❖ Boiler corrosion is the decay or disintegration of the boiler material either due to chemical or electrochemical reaction with its environment.
- ✓ Boiler Corrosion is caused due to following reasons-

# **Dissolved Oxygen:**

This is the most common reason of Boiler Corrosion. In boiler the oxygen is introduced through the raw water supply. Water usually contain 8 ppm of Oxygen at room temperature. As the water is heated this dissolved oxygen is set free and boiler starts corroding.



Dissolved oxygen reacts with Iron (Fe) in the presence of water to form Ferric Oxide (Rust).

4 Fe + 
$$2H_2O$$
 +  $O_2$   $\longrightarrow$  4Fe(OH)<sub>2</sub>  
4Fe(OH)<sub>2</sub> +  $O_2$   $\longrightarrow$  2[Fe<sub>2</sub>O<sub>3</sub> . 2H<sub>2</sub>O]

# **Removal of Dissolved Oxygen**

✓ By adding Hydrazine or Sodium Sulphite or Sodium Sulphide

➤ Hydrazine (N<sub>2</sub>H<sub>4</sub>) is the ideal chemical for the removal of disolved oxygen. It reacts with oxygen to form Nitrogen and water. Nitrogen is harmless. Hydrazine removes oxygen without increasing the concentration of dissolved solids.

➤ Excess amount of Hydrazine (N<sub>2</sub>H<sub>4</sub>) must not be taken because it decomposes to give Ammonia which may cause corrosion of some alloys like Brass used in condenser tubes.

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

➤If Sodium Sulphite or Sodium Sulphide is used for the removal of dissolved oxygen then Sodium Sulphate is formed which decomposes in high pressure boilers to form SO<sub>2</sub>. The SO<sub>2</sub> enters into the steam pipes and forms Sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) in steam condensate.

## **Removal of Carbon Dioxide**

#### √ By Mechanical Deaeration

➤This process consist of spraying of water over preheated perforated plates stacked in a degasifier. Removal of dissolved carbon dioxide is ensured by applying high temperature and vacuum.

√ By Filtering water through Lime Stone

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

> This method increases hardness.

√ By adding Ammonium Hydroxide

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

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#### ✓ By Mechanical Deaeration

This process consist of spraying of water over preheated perforated plates stacked in a degasifier. Removal of dissolved oxygen is ensured by applying high temperature and vacuum.

#### **Dissolved Carbon Dioxide:**

Main source of CO<sub>2</sub> in boiler water are dissolved CO<sub>2</sub> in raw water and decomposition of Bicarbonates in water.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + CO_2 + H_2O$$

CO<sub>2</sub> in the presence of water forms Carbonic acid (H<sub>2</sub>CO<sub>3</sub>) which has corrosive effect on boiler material.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

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#### **Boiler Corrosion due to Mineral Acids:**

Magnesium Chloride if present in boiler feed water undergoes hydrolysis producing HCl.

$$MgCl_2 + H_2O \longrightarrow Mg(OH)_2 + 2HCI$$

Liberated HCl reacts with Iron (Fe) to form Ferrous Hydroxide which in turn is converted into Rust.

Small amount of HCl causes corrosion to larger extent since HCl is produced in chain like manner. Hence small amount of  ${\rm MgCl_2}$  causes corrosion of Iron to larger extent.

#### **Caustic Embrittlement**

Caustic Embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by Lime-Soda Process, it is likely that some residual Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>) may be present in the soft water.

In high pressure boilers Na<sub>2</sub>CO<sub>3</sub> decomposes to give Sodium Hydroxide (NaOH) and CO<sub>2</sub> thus makes water "Caustic".

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

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This caustic water flow into the minute hair cracks, present in the inner side of boiler by capillary action.

On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, thereby dissolving Iron of boiler as Sodium Ferroate ( $Na_2FeO_2$ ).

$$Na_2FeO_2 + 4H_2O \longrightarrow 6NaOH + Fe_3O_4 + H_2$$

The Iron surrounded by dil. NaOH acting as Cathode, while the Iron surrounded by concentrated NaOH act as Anode.

The Iron in the anodic parts gets corroded.

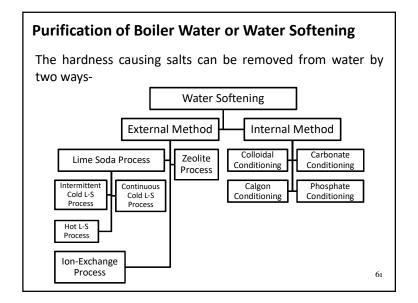
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# **Prevention of Caustic Embrittlement**

➤ By adding Sodium Phosphate as softening reagent, instead of Sodium Carbonate in external treatment of boiler water.

➤ By adding Sodium Sulphate to boiler which blocks the hair cracks and prevents the infiltration of caustic soda solution into these areas.

➤ By adding tannin or lignin to boiler which blocks the hair cracks and prevents the infiltration of caustic soda solution into these areas.



 $\succ$  If small amount of coagulants like Alum K₂SO₄.Al₂SO₄.24H₂O; Aluminium Sulphate [Al₂(SO₄)₃] or Sodium Aluminate [NaAlO₂] are added, they hydrolyze to Al(OH)₃ which entraps the fine precipitate of CaCO₃ & Mg(OH)₂.

$$NaAlO_2$$
 +  $2 H_2O$   $\longrightarrow$   $NaOH$  +  $Al(OH)_3$  Sodium Aluminate

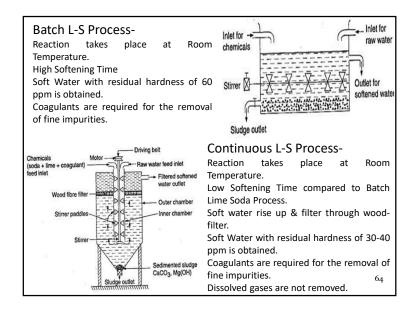
$$Al_2(SO_4)_3 + 3 Ca(HCO_3)_2 \longrightarrow 2 Al(OH)_3 + 3CaSO_4 + 6 CO_2$$

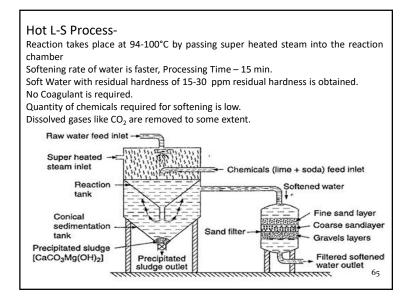
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#### **External Method**

#### **Lime Soda Process**

- ➤ The basic principle of Lime Soda Process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling or filtration.
- $\triangleright$  Calculated quantity of milk of lime [Ca(OH)<sub>2</sub>] and Sodium Carbonate [Na<sub>2</sub>CO<sub>3</sub>] is added.
- At Room Temperature the precipitate formed is very fine & do not settle down easily and causes difficulty in filtration.
- ➤ Fine precipitate of CaCO<sub>3</sub> and Mg(OH)<sub>2</sub> result in "after deposition", later in pipes, boiler tubes producing scales.





Constituent		Reactions		Need
Ca(HCO <sub>3</sub> ) <sub>2</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub>	+ Ca(OH) <sub>2</sub> →	$2CaCO_3 + H_2O$	L
CO <sub>2</sub>	CO <sub>2</sub>	+ Ca(OH) <sub>2</sub> →	CaCO <sub>3</sub> + H <sub>2</sub> O	L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	Mg(HCO <sub>3</sub> ) <sub>2</sub>	+ 2Ca(OH) <sub>2</sub> > 2C	$CaCO_3 + Mg(OH)_2 + H_2O$	2L
CaCl <sub>2</sub> CaSO <sub>4</sub>	CaCl <sub>2</sub> CaSO <sub>4</sub>	$\begin{array}{cccc} + & Na_2CO_3 & \longrightarrow \\ + & Na_2CO_3 & \longrightarrow \end{array}$	CaCO <sub>3</sub> + NaCl CaCO <sub>3</sub> + Na <sub>2</sub> SO <sub>4</sub>	S
MgCl <sub>2</sub>	MgCl <sub>2</sub> CaCl <sub>2</sub>	` /=	Mg(OH) <sub>2</sub> + CaCl <sub>2</sub> CaCO <sub>3</sub> + NaCl	L+S
${\rm MgSO_4}$	MgSO <sub>4</sub> CaSO <sub>4</sub>	$\begin{array}{ccc} + & \text{Ca(OH)}_2 & \longrightarrow \\ + & \text{Na}_2\text{CO}_3 & \longrightarrow \end{array}$	$Mg(OH)_2 + CaSO_4$ $CaCO_3 + Na_2SO_4$	
NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	+ Ca(OH) <sub>2</sub> → Ca	$aCO_3 + H_2O + Na_2CO_3$	L-S
Free Acids (HCl)	HCl CaCl <sub>2</sub>	$\begin{array}{cccc} + & \text{Ca(OH)}_2 & \longrightarrow \\ + & \text{Na}_2\text{CO}_3 & \longrightarrow \end{array}$	4 4	L+S
FeSO <sub>4</sub>	FeSO <sub>4</sub> CaSO <sub>4</sub>	$+ Ca(OH)_2 \longrightarrow + Na_2CO_3 \longrightarrow$		L+S

# **Limitation of Lime Soda Process**

- ➤ Its not possible to remove all the hardness from water. In actual practice about 50-60 ppm will remain as residual hardness.
- ➤ Soft water contain appreciable concentration of soluble salts such as calcium sulphate and can not be used in high pressure boilers.
- ➤ We normally tolerate final total hardness on the order of 75-120 ppm as CaCO<sub>3</sub> but the Magnesium content should not exceeds 40 ppm as CaCO<sub>3</sub>.

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# **Calculation of Lime & Soda Requirement**

- $\triangleright$  Ignore all those impurities like NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ash which do not causes hardness.
- ➤ Convert all the hardness causing impurities into their CaCO<sub>3</sub> equivalent.

Equivalent of  $CaCO_3$  = w x Molecular weight of  $CaCO_3$ 2 x Equivalent weight of Hardness producing substance

➤ Lime Requirement-

➤ Soda Requirement-

106 [ Per Ca<sup>2+</sup> + Per Mg<sup>2+</sup> + Fe<sup>2+</sup> + Al<sup>3+</sup> + H<sup>+</sup> - HCO<sub>3</sub><sup>-</sup> ] Volume of Water x Purity

ightharpoonup If 'x' is the purity of lime & 'y' is the purity of soda then Purity of Lime = 100 / x & Purity of Soda = 100 / y

#### **Numerical on Lime Soda Process**

#### Annexure-3

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#### > Synthetic Zeolite

Porous and posses gel like structure.

They are prepared by heating together sodium carbonate  $(Na_2CO_3)$ , alumina  $(Al_2O_3)$ , silica  $(SiO_2)$ .

Synthetic Zeolite posses higher exchange capacity per unit weight compared to natural zeolite.

#### **▶** Process:

Hard water is percolated at specified rate through bed of zeolite.

The hardness causing ions Ca<sup>2+</sup>, Mg<sup>2+</sup> etc. are retained by zeolite as CaZe & MgZe respectively and outgoing water contain Sodium Salts.

The water becomes free from hardness causing cations i.e.  $Ca^{2+}$ ,  $Mg^{2+}$ .

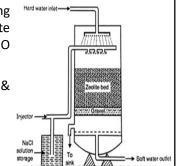
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#### **Zeolite Process or Permutit Process**

 $\triangleright$  Zeolites are naturally occuring hydrated sodium alumino silicate (like Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>. x SiO<sub>2</sub>.y H<sub>2</sub>O where x = 2-10, y = 2-6).

➤ Zeolites are porous in nature & also known as Permutit.

Zeolites are of two types-Natural Zeolite Synthetic Zeolite



➤ Natural Zeolite: Non porous, Amorphous & Durable.

**For e.g.:** Natrolite [Na $_2$ O.Al $_2$ O $_3$ . 4 SiO $_2$ .2 H $_2$ O], Laumonite [CaO. Al $_2$ O $_3$ . 4 SiO $_2$ .4 H $_2$ O], Harmotome [ BaO.K $_2$ O Al $_2$ O $_3$ . 5 SiO $_2$ .5 H $_2$ O],

# > Regeneration:

After some time the zeolite is completely converted into CaZe & MgZe. The zeolite bed ceases to soften water i.e. it gets exhausted.

The zeolite bed is regenrated by passing concentrated Sodium Chloride (Brine) solution

Instead of NaCl, NaNO<sub>3</sub>, KCl, KNO<sub>3</sub> can also be used for regeneration but NaCl is used due to its low cost & products of regeneration (CaCl<sub>2</sub> & MgCl<sub>2</sub>) are highly soluble in water.

After regeneration the zeolite bed is rinsed with soft water to remove excess amount of NaCl, CaCl<sub>2</sub> & MgCl<sub>2</sub>.

#### **Limitation of Zeolite Process**

- ✓ If the supplied water is turbid then suspended impurities should be removed first otherwise it will clog the pores of zeolte bed.
- $\checkmark$  If the supplied water contain large quantity of Mn<sup>2+</sup> or Fe<sup>2+</sup> then they must be removed first because these ions produce MnZe & FeZe, which are very difficult to regenerate.
- $\checkmark$  If mineral acids are present in the supplied water then they will destroy zeolite bed. So, supplied water must be neutralised with soda in advance.

✓ Anions are not removed by this process. The Bicarbonate present in hard water get converted to NaHCO $_3$  which goes into the soft water. If it is used in high pressure boilers then it dissociates into NaOH & CO $_2$ .

NaHCO<sub>3</sub> — NaOH + CO

 $\checkmark$  NaOH & CO $_2$  are responsible for Caustic Embrittlement & Boiler Corrosion respectively.

# **Advantages of Zeolite Process**

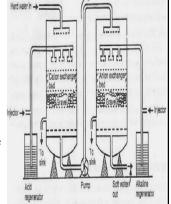
- ✓ The hardness is nearly completely removed.
- ✓ Water of about 10 ppm residual hardness is produced.
- ✓ The impurities are not precipitated, so there is no danger of sludge formation.
- $\checkmark$  The process automatically adjust itself to water of different hardness.

# ✓ Ion-Exchange Process

Removal of all the ions present in water is called Demineralization. The demineralization is done by Ion exchange resins.

- ❖ Ion exchange resin are insoluble, cross linked, high molecular weight, long chain organic polymer with microporous structure.
- ❖ The functional groups attached to the chains are may= responsible for ion exchange.
- ❖ Ion Exchange resins are of two types-

Cation Exchange Resin (R-H+) Anion Exchange Resin (R+OH-

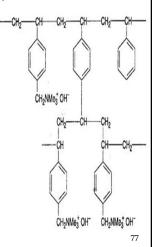


# Cation Exchange Resins (RH+)

- They are styrene —divinyl benzene copolymer which on sulphonation or carboxylation becomes capable to exchange their hydrogen ions with cations in water.
- They have acidic functional group like –SO<sub>3</sub>H, -COOH or –OH, capable of exchanging the cationic portion of minerals with their hydrogen ions.

# Anion Exchange Resins (R'OH-)

- These after treatment with dil NaOH becomes capable to exchange their –OH anions with the anions of water.



# Process Cation F

#### **Cation Exchange**

• The hard water is first passed through the cation exchang column which removes all the cations present in water then equivalent amount of H<sup>+</sup> ions are released from this column into water.

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$
  
 $2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$ 

#### Anion Exchange

 After cation exchange column the water is passed through anion exchange column which removes all the anions present in water then equivalent amount of OHions are released from this column into water.

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#### 

• The H+ and OH- ions released from both the column combine to produce water.

$$H^+$$
 +  $OH^ \longrightarrow$   $H_2O$ 

 Thus water coming out of exchanger is free from cations as well as anions. Ion free water is known as Deionised or Demineralised water.

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# Regeneration

- When capacities of cation and anion exchanger to exchange H<sup>+</sup> and OH<sup>-</sup> ions respectively are lost they are said to be exhausted.
- The exhausted cation exchange column is regenerated by passing dil HCl or dil H<sub>2</sub>SO<sub>4</sub>.

• The exhausted anion exchange column is regenerated by passing dil NaOH.

# **Advantages of Ions Exchange Process**

- √ The process can be used to soften highly acidic or alkaline water.
- ✓ It produces water of very low hardness (~2ppm).

# **Disadvantages of Ions Exchange Process**

- ✓ Turbidity in water reduces the efficiency of the process.
- ✓ Installation cost and operating cost is high.

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# **❖** Colloidal Conditioning

 Scale formation can be avoided in low pressure boilers by adding substances like Kerosene, tannin, agar-agar etc. which get adsorbed over the scale formation precipitate, thereby resulting in non-sticky and loose deposits which can be removed easily by blow down operation.

# Carbonate Conditioning

- Its used in low pressure boilers.
- For a salt to precipitate the ionic concentration should exceeds the solubility product [Ksp < Ip].
- $\bullet$  Scale formation can be avoided by adding  $\mathrm{Na_2CO_3}$  to the boiler feed water.  $$_{8_3}$$

**Internal Treatment** 

- ✓ It means treating raw water inside the boiler. Its also known as sequestration.
- ✓ In this process an ion is prohibited to exhibit its original character by complexing or converting into more soluble salt by adding appropriate reagent.
- > Internal treatment methods are-
- Colloidal Conditioning
- Carbonate Conditioning
- Calgon Conditioning
- Phosphate conditioning

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 Scale forming salts like CaSO<sub>4</sub> is converted into CaCO<sub>3</sub>, which can be removed easily.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

# **❖** Calgon Conditioning

- Calgon is **Sodium hexa meta phosphate** i.e. Na<sub>2</sub>[Na<sub>4</sub>(PO<sub>3</sub>)<sub>6</sub>].
- Calgon converts the scale forming impurity like CaSO<sub>4</sub> into soluble compound, which are harmless to boiler.

$$Na_{2}[Na_{4}(PO_{3})_{6}] \longrightarrow 2 Na + [Na_{4}(PO_{3})_{6}]^{2}$$

$$[Na_4(PO_3)_6]^{2-} + CaSO_4 \longrightarrow 2 Na_2SO_4 + [Ca_2(PO_3)_6]^{2-}$$
Soluble Complex<sub>4</sub>

- At low temperature and pressure, it forms stable and soluble complex with calcium salt.
- At high temperature and pressure, its converted into Sodium orthophosphate which reacts with calcium salts to form calcium orthophosphate.

# **❖**Phosphate Conditioning

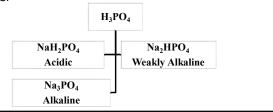
• It is applicable to high pressure boilers.

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• Scale formation is avoided by adding Sodium Phosphate which reacts with Ca<sup>2+</sup> & Mg<sup>2+</sup> salts to form non adherent and easily removable soft sludge of Calcium and Magnesium Phosphate.

$$CaCl_2 + Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6 NaCl$$
  
 $CaSO_4 + Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6 Na_2SO_4$ 

 Choice of Phosphate salt depends upon alkalinity of boiler feed water-



# Specification for potable water

Water is colourless, odourless, tasteless and universal solvent and usually contains several impurities (Gases, Solids and Colour)

# Specification for potable water as per Bureau of Indian Standards

S.No.	Characteristics	Desirable Limit (mg/L)
1	1 Colour, Odour, Taste Colourless, Odourless and Tas	
2	Turbidity	< 10 ppm
3	Alkalinity	pH = 7-7.5
4	рН	6.9
5	Dissolved Oxygen	
6	Chloride	250
7	Total Hardness (as CaCO3) mg/L	< 500

S.No.	Characteristics	Desirable Limit (mg/L)
8	Sulphate	400
9	Nitrate	45
10	Cyannide	0.2
11	Fluoride	1.5
12	Chromium	0.05
13	Lead	0.05
14	Arsenic	0.05

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# > Drinking Water Treatment

- Rivers, Lakes, Well are the most common source of water and do not confirm the specification of drinking water.
- Actual treatment method to be adopted depends upon the nature of impurities.

S.No.	Impurity	Treatment Process
1	Floating matter such as leaves, wood pieces etc.	Screening
2	Suspended Impurities such as sand, clay etc.	Sedimentation
3	Fine suspended inorganic matter	Sedimentation with Coagulation
4	Microorganisms and Colloidal impurities	Filtration
5	Pathogenic Bacteria	Disinfection

# **Screening**

- It is the process of removing floating material like wood pieces, leaves, etc. from water.
- Raw water is passed through screens having holes, when floating matter is retained by them and water is allowed to pass.

#### Sedimentation

- It is the process of removing suspended impurities by allowing the water to stand undisturbed in big tank for 2-8 hrs.
- Most of the particles settle down at the bottom of the tank due to gravitational force.





# Sedimentation with coagulation

- Finely divided silica , clay and organic matter do not settle down easily and can not be removed by only by sedimentation.
- If coagulants (Alum [K<sub>2</sub>SO<sub>4</sub>.Al<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.24 H<sub>2</sub>O], Sodium Aluminate NaAlO<sub>2</sub>) are added to water which hydrolyse to form gelatinous precipitate of Al(OH)<sub>3</sub>.
- Colloidal impurities carry negative charge and coagulants give Al3+ ions which neutralize the colloidal particles and form flocculate. Due to force of gravity these bigger particles settle down.

Chemical Coagulants	Ideal pH range of use
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	6.5-8.5
NaAlO <sub>2</sub>	5.5-8.0
FeSO <sub>4</sub>	>8.5
	01

#### **Filtration**

- A water filter removes the impurities by minimizing contamination of water using fine physical barrier, a chemical process or a biological process.
- Activated Charcoal is used as decolourising agent.

#### Disinfection

- The process of destroying/killing the pathogenic bacteria in water is known as disinfection.
- The process of complete destruction of all living organisms is known as sterilisation (Like Boiling). Sterilisation kills the bacteria for some time and does not provide any protection against future contamination.

#### Methods of Disinfection

(a) By Bleaching powder

(b) By Chlorination

(c) By Chloramine

(d) By Ozone

(e) By Ultraviolet radiation

(f) By KMnO<sub>4</sub>

#### > Disinfection by bleaching powder

Disinfection can be done by adding Bleaching powder ( $CaOCl_2$ ) to the water

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2$$
 +  $H_2O \longrightarrow HCI$  + HOCI (Hypochlorous Acid)

#### Drawbacks-

- Excess of bleaching powder imparts bad taste & smell to water.
- Bleaching powder is not stable so it deteriorates.
- It introduces Calcium in water and thus increases hardness.
- The disinfection properties of chlorine in water are based on the oxidising power of oxygen atom & on chlorine substitution reactions.
- Hypochlorous acid (HOCl) is electrically neutral while Hypochlorite ion (OCl<sup>-</sup>) is electrically negative.
- Hypochlorous acid (HOCI) is strong disinfectant than OCI<sup>-</sup>. HOCI breaks into HCI and atomic oxygen (O), which is strong disinfectant.
- By nature the cell wall of pathogenic microorganism is negatively charged. Hypochlorous acid penetrates cell wall & kills the microorganisms or suffers reproductive failure.

S.No.	pН	HOCI	OCI-
1	6	80%	20%
2	7.5	50%	50%
3	8	20%	80%

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## > By Chlorination

Chlorine is used as disinfectant in water treatment. It can be used directly as gas or in form of concentrated solution in water.

It produces hypochlorous acid which is germicide.

$$Cl_2$$
 +  $H_2O$   $\longrightarrow$  HOCl +  $H^+$  +  $Cl^-$ 

**Hypochlorous Acid** 

Depending on pH value, hypochlorous acid gets convert into hypochlorite ion

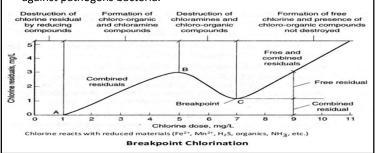
$$Cl_2$$
 +  $2H_2O \longrightarrow HOCI + H_3O^+ + CI^-$ 

$$HOCI + H_2O \longrightarrow H_3O^+ + OCI^-$$

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# > Break Point Chlorination / Free Residual Chlorination

- It means chlorination of water to such an extent that living organism as well as other organic impurities in water are destroyed.
- It involves addition of sufficient amount of chlorine to oxidise organic matter, reducing substances and free ammonia in raw water, leaving behind free chorine which possesses disinfection action against pathogens bacteria.



- Stage-I: Initially for lower chlorine doses of Chlorine, there is no free chlorine since all the added chlorine gets consumed in the oxidation of reducing substances present in water.
- Stage-II: As the amount of chlorine dosage is increased, amount of residual chlorine also steady increases. In this stage formation of chloro-organic takes place without oxidising them.
- Stage-III: At higher dose of applied chlorine, oxidation of organic compounds and microorganisms takes place & the amount of chlorine free chlorine also decreases. When oxidative destruction is complete it reaches a minima.
- Stage-IV: After minima, the added chlorine is not used in any reaction. Thus the residual chlorine keeps increasing in direct proportion to added chlorine.

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# > Disinfection by UV Radiation

- Water is passed in thin layer around the lamp because the germicidal action of UV radiation depends on the intensity of the light, depth of exposure and contact time.
- Turbidity & minor traces of Iron reduces the light transmission.

#### > Sea Water Treatment

- Water containing high concentration of dissolved solids with peculiar salty or brackish taste is called brackish water. For e.g. Sea Water containing 3.5% of dissolved salts.
- The removal of dissolved solids (NaCl) from water is known as desalination process.

#### > Methods of Desalination

(a) Reverse Osmosis

(b) Distillation

(c) Electrodialysis

(d) Freezing

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# > Disinfection by Chloramine

 Chloramine has better bactericidal action than chlorine. Its more stable and does not produce any odour.

## > Disinfection by Ozone

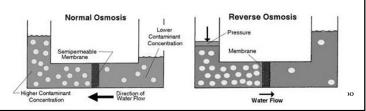
 Ozone is made by passing oxygen through ultraviolet light or an electrical discharge. Ozone is highly unstable breaks into oxygen and nasent oxygen.

$$O_3 \longrightarrow O_2 + [O]$$

 $\bullet$  Nasent oxygen is powerful oxidising agent and oxidises organic matter and also kills bacteria. The main advantage of ozonation is lack of taste & odour.  $$_{98}$$ 

# Reverse Osmosis / Super or Hyper Filtration

- Osmosis is the phenomenon by virtue of which flow of water takes place from a region of low concentration to high concentration, when two solutions of different concentration are separated by semi-permeable membrane. Semi-permeable membrane do not allow the passage of solute but allows the passage of solvent only.
- The flow of solvent continues till the concentration is equal on both
  the sides of semi-permeable membrane. The driving force for
  osmosis is known as Osmotic Pressure.



- If the hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reversed; it is forced to move from concentrated side to dilute side across the membrane.
- Since semi-permeable membrane do not allow the passage of solute but allows the passage of solvent only. The concentrated solution becomes more concentrated.
- There are 03 types of R.O. membrane
- (a) Cellulosic
- (b) Fully aromatic polyamide
- (c) Thin Film Composite
- The pore size of R.O. membrane is around 0.0001 micron. A pressure of about 15-40 Kg/cm<sup>2</sup> is applied for separating water from contaminants.

