

# Unit-1: Water Chemistry

## Sources of water:

**Natural sources of water:** Rainwater, oceans, rivers, lakes, streams, ponds and springs

**Man-made sources** : Dams, wells, tube wells, hand-pumps, canals, etc.

Water is required for agricultural, municipal and industrial purposes. For industrial purposes, natural waters are broadly divided into:

### 1. Surface waters:

i) Flowing waters e.g., streams and rivers (Moorland surface drainage)

ii) Still waters e.g., ponds, lakes and reservoirs (Low land surface drainage)

### 2. Underground supplies:

i) Deep well waters & springs:

ii) Water from shallow wells

### 3. Rain Water

### 4. Estuarine and Sea water

The three major sources of water for industrial use are:

a) Moorland surface drainage

b) Low land surface drainage

c) Deep well waters

## IMPURITIES OF WATER:

Type of Impurity	Examples
1) Dissolved impurities: a) Inorganic salts i) Cations:  ii) anions:  b) Gases  c) Organic salts	$\text{Ca}^{+2}, \text{Mg}^{+2}, \text{Na}^+, \text{K}^+, \text{Fe}^{+2}, \text{Al}^{+3}$ traces of $\text{Zn}^{+2}$ and $\text{Cu}^{+2}$ $\text{Cl}^-, \text{SO}_4^{2-}, \text{NO}_3^-, \text{HCO}_3^-$ & sometimes $\text{F}^-$ & $\text{NO}_2^-$ $\text{CO}_2, \text{O}_2, \text{N}_2$ oxides of $\text{N}_2$ & sometimes $\text{NH}_3, \text{H}_2\text{S}$
2) Suspended impurities a) Inorganic b) Organic	Clay and sand Oil globules, Vegetable and Animal matter
3) Colloidal impurities	Finely divided Clay & Silica, Products from organic waste colouring matter, amino acids etc.
3) Bacterial impurities	Bacteria, other microorganisms and other forms of animal & vegetable life

## **Impurities in various sources of water:**

### **River water:**

contains dissolved minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron.

It also contains suspended impurities of sand, rocks and organic matter. The composition of river water is not constant.

### **Lake water:**

has high quantity of organic matter present in it but lesser amount of dissolved minerals.

Its chemical composition is also constant.

### **Rain water:**

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

Probably it is the purest form of natural water. But during its downward journey through the atmosphere it dissolves organic and inorganic suspended particles and considerable amount of industrial gases like (CO<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub> etc.).

Rain water is expensive to collect and is irregular in supply.

### **Underground water:**

is free from organic impurities and is clearer in appearance due to the filtering action of the soil. it contains large amount of dissolved salts.

**Sea water:** is very impure due to two reasons:

1. Continuous evaporation increases the dissolved impurities content, which is further increased by the impurities thrown by rivers as they join sea.
2. It is too saline for most industrial uses except cooling.

## **Effect of Water on Rocks and Minerals.**

### **1. Dissolution:**

Mineral rocks such as NaCl and CaSO<sub>4</sub>.2H<sub>2</sub>O get readily dissolved in water

### **2. Hydration:**

Disintegration of rocks due to hydration of some minerals

Example:

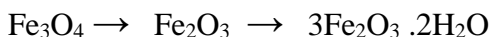


Anhydrite      gypsum



Olivine              Serpentine

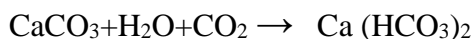
### **3. Effect of dissolved oxygen :** leads to oxidation & hydration



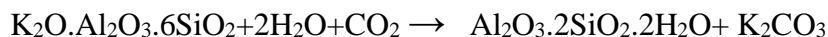
Magnetite      haematite      Limonite

### **4. Effect of dissolved CO<sub>2</sub>:**

Dissolved CO<sub>2</sub> converts the insoluble carbonates of Ca, Mg and Fe into their relatively soluble bicarbonates.



Rock forming minerals like silicates and aluminosilicates of Na, K, Ca and Fe are attacked by  $\text{CO}_2$  and produce soluble  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and silica.

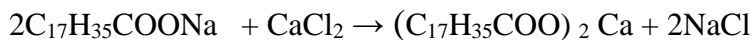


### Effect of impurities on properties of water:

Properties	Impurities	Removed by
<u>Colour</u>  Yellowish tinge Yellowish red Red-Brown	dissolved or colloiddally dispersed organic matter (metals & metallic salts of iron ,manganese, peat ,algae)  Indicate the presence of chromium and appreciable amount of organic matter.  Presence of Iron  Peaty matter	Coagulation, settling, absorption, filtration & sometimes chlorination.
<u>Turbidity</u>	Finely divided insoluble impurities: Inorganic: clay, slit. silica, etc or Organic: finely divided vegetable or animal matter, oils, fats, microorganisms etc	Sedimentation followed by coagulation and filtration/ coagulation & settling/ coagulation, settling and filtration
<u>Taste</u>  Bitter Soapy taste Brackish Palatable	Dissolved minerals  Fe, Al, Mn, $\text{SO}_4^{2-}$ or excess of lime Sodium bicarbonate Unusual amounts of salts Dissolved gases( $\text{CO}_2$ ) and minerals(nitrates)	
Properties	Impurities	Removed by
Odour  Grassy Offensive Peaty Earthy	Living organisms, decaying vegetation(including algae, fungi, weeds),sewage/industrial effluent Presence of Algae(liberation of traces of oil) Iron & Sulphur bacteria Colloidal vegetable matter Finely divided clay & sand	Organic tastes & odours are removed by activated carbon, aeration, aeration followed by activated carbon
Hardness	Dissolved mineral matter such as $\text{Ca}^{+2}$ , $\text{Mg}^{+2}$ , $\text{HCO}_3^-$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ etc	
Alkalinity	$\text{HCO}_3^-$ , $\text{SiO}_3^{2-}$ , $\text{HSiO}_3^-$ , some times $\text{CO}_3^{2-}$	

## Hardness

- It is the characteristic property of water that prevents the lathering of soap.
- It is also defined as soap (sodium salts of long chain fatty acids such as oleic acid, palmitic acid, stearic acid) consuming capacity of water or the capacity of precipitation of soap.
- It is mainly due to the presence of calcium and magnesium ions, which react with sodium salts of long chain fatty acids present in the soap to form insoluble scums of calcium and magnesium soaps (don't have detergent value)



Sodium stearate

calcium stearate

Soap (soluble)

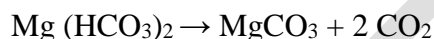
calcium soap (insoluble)

### Two types of hardness:

#### 1) **Temporary hardness or carbonate hardness :**

Due to presence of dissolved bicarbonates of  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$

It is removed by mere boiling of water.



#### 2) **Permanent hardness or non carbonate hardness**

Due to presence of dissolved chlorides and sulphates ( $\text{Cl}^-$  &  $\text{SO}_4^{2-}$ ) of  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$

It cannot be destroyed by boiling.

**Total Hardness** = Temporary hardness + Permanent hardness

### Expression of hardness as Equivalents of Calcium Carbonate

Generally the concentration of hardness of water is usually expressed in terms of equivalents of  $\text{CaCO}_3$ .

Reason for choosing  $\text{CaCO}_3$ : it is most insoluble salt that can be precipitated in water treatment

Its molecular weight is 100 (equivalent mass = 50)

**Equivalents of  $\text{CaCO}_3$  =**  $\frac{\text{Mass of hardness causing substance}}{\text{Chemical equivalent of } \text{CaCO}_3}$

**Chemical equivalent of hardness causing substance**

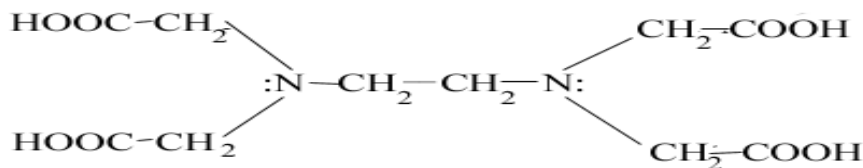
### **Units of hardness & their inter relationship:**

Unit	No. of parts of $\text{CaCO}_3$ equivalent hardness per	Abbreviation
Parts per million	$10^6$ parts of water	ppm
Milligrams per litre	One litre of water	mg/L
Degree Clarke	70,000 parts of water	$^\circ\text{Cl}$
Degree French	$10^5$ parts of water	$^\circ\text{Fr}$

**Estimation of hardness by EDTA method:**

Gives more accurate results.

Ethylene Diamine Tetra Acetic acid (**EDTA**) is a polydentate ligand. EDTA forms complexes with hardness causing ions such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$



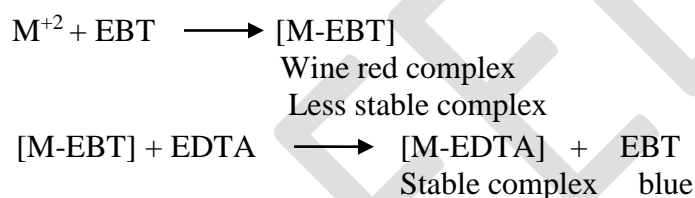
structure of EDTA

Estimation of hardness of water with EDTA is a complexometric type of titration.

Titration is carried out by adding basic buffer solution (to maintain pH around 10) to a water sample in presence of EBT (eriochrome black-T) indicator.

Indicator forms unstable wine red complex with hardness causing ions.

On titrating this solution with EDTA, a stable metal-EDTA complex is formed and free indicator ions are liberated into the solution. Colour of the solution turns from wine red to blue.

**Procedure:****Preparation of standard hard water:**

1.0 g of pure, dry  $\text{CaCO}_3$  is dissolved in minimum quantity of dil HCl & then evaporates it to dryness on water bath. Residue is dissolved in distilled water and makes it up to 1L solution.

1ml of this solution = 1mg of  $\text{CaCO}_3$  equivalent hardness.

**Standardization of EDTA solution:**

50ml of standard hard water + 10ml of Basic buffer  $\xrightarrow{\text{EDTA}}$  Blue  
+ 2-3 drops indicator End point

Let the Volume of EDTA consumed be =  $V_1$  ml

**Determination of total hardness:**

50ml of unknown water sample + 10ml of Basic buffer  $\xrightarrow{\text{EDTA}}$  Blue  
+ 2-3 drops indicator End point

Let the Volume of EDTA consumed be =  $V_2$  ml

**Determination of permanent hardness:**

250 ml of water sample  $\xrightarrow{\text{boiled it till the volume reduced to 50ml}}$  Filter & wash & Make up to 250ml

50ml of boiled water sample + 10ml of Basic buffer  $\xrightarrow{\text{EDTA}}$  Blue  
+ 2-3 drops indicator End point

Let the Volume of EDTA consumed be =  $V_3$  ml

## Calculations:

### Determination of total hardness:

$$\text{Total hardness} = \boxed{1000 \times V_2/V_1 \text{mg/L}}$$

### Determination of permanent hardness:

$$\text{Permanent hardness} = \boxed{1000 \times V_3/V_1 \text{mg/L}}$$

$$\begin{aligned}\text{Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ &= 1000 (V_2 - V_3)/V_1\end{aligned}$$

### Significance of determination of hardness:

- to measure of the quality of water .
- Important to industry as the  $\text{CaCO}_3$  gets precipitated on heating water, it clogs boilers & pipes.

### Disadvantages of hard water:

#### ➤ In domestic use:

- Washing:** causes wastage of soap as it doesn't give lather until the hardness causing ions gets precipitated. Quality of the cloth gets spoiled.
- Bathing:** cleansing quality of soap is lowered so wastage of soap.

**Steam generation in boilers:** causes troubles such as scale & sludge formation, corrosion, Priming & foaming and caustic embrittlement

Major boiler troubles caused by the use of unsuitable water are:

- Carry over: Priming & Foaming
- Sludge & Scale formation
- corrosion
- Caustic embrittlement

### Sludge:

Soft, loose and slimy precipitate formed within the boiler.

Formed at colder portions of the boiler and are collected at the bends.

Formed by substances which have greater solubilities in hot water than in cold water, *e.g.*,

$\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , *etc*

Easily removed with wire brush

### Disadvantages of sludge formation

Sludges are poor conductors of heat, so they tend to waste a portion of heat generated.

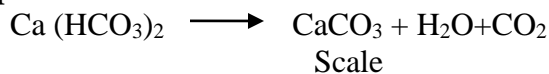
- Excessive sludge formation disturbs the working of the boiler.
- By using well softened water 2) by blow down operation i.e. drawing off apportion of the concentrated water.

**Scale:**

Hard deposits firmly sticking to the inner walls of the boiler.

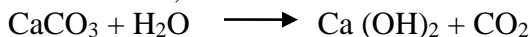
Difficult to remove, even with the help of hammer & Chisel.

Formed due to:

**i) Decomposition of Calcium bicarbonate:**

(Soft, formed mainly in low pressure boilers)

In high pressure boilers,  $\text{CaCO}_3$  is soluble due to formation of  $\text{Ca (OH)}_2$

**ii) Deposition of  $\text{CaSO}_4$ :**

Solubility of  $\text{CaSO}_4$  decreases with increase in temperature.

Completely insoluble in super heated water.

Hard scale formation in high pressure boilers

**iii) Hydrolysis of Magnesium salts:**

Soft scale formation due to hydrolysis of Mg salts in high pressure boiler.

**iv) Presence of silica:**

Deposits of Ca/Mg silicates, which adheres firmly to the inner boiler walls. It is difficult to remove.

**Prevention of scales formation: Internal treatment (Sequestration):** involves either to precipitate the scale forming impurities in the form of sludge or to convert them into compounds, by adding chemicals. It is followed by blow down operation

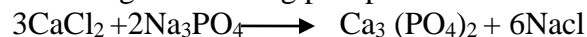
**Important internal conditioning/treatment methods:****Colloidal conditioning:**

In low pressure boilers, scales can be avoided by adding organic substances like kerosene, tannin, agar-agar, which forms slime loose precipitates. easily removed by blow down operation.

**Phosphate conditioning:**

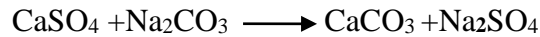
In high pressure boilers scale formation can be avoided by adding sodium phosphate

React with hardness of water forms non adherent, easily removable soft sludge of Ca / Mg phosphates.



### Carbonate conditioning:

In low pressure boilers scale formation can be avoided by adding sodium carbonate to boiler water, when  $\text{CaSO}_4$  is converted into calcium carbonate in



Consequently deposition of  $\text{CaSO}_4$  as scale doesn't take place and calcium is precipitated as loose sludge of  $\text{CaCO}_3$  which can be removed by blow down operation.

### Calgon conditioning:

The process involves the addition of calgon to boiler water. It prevents scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .

Calgon = sodium hexa meta phosphate



### Caustic embrittlement:

The formation of brittle and in crystalline cracks in the boiler shell is called caustic embrittlement.

It is a type of boiler corrosion, caused by highly alkaline water in the boiler.

In lime-soda process, it is likely that, some residual  $\text{Na}_2\text{CO}_3$  is still present in the softened water

This  $\text{Na}_2\text{CO}_3$  decomposes to give  $\text{NaOH}$  and  $\text{CO}_2$  due to which the boiler water becomes "Caustic".



This caustic water flows inside the boiler and causes some minute hair cracks, by capillary action. On evaporation of water, the dissolved caustic soda increases its concentration which attacks the surrounding area, thereby dissolving iron of boiler as sodium ferrate which causes embrittlement of boiler parts such as bends joints, reverts etc, due to which the boiler gets fail.

Joints & bends | High conc of  $\text{NaOH}$  | low conc. (dil)  $\text{NaOH}$  | Plane surface

Anodic site + |

| Cathodic site -

### Prevention methods:

By using sodium phosphate as softening reagent in the external treatment of boiler water.

By maintaining pH value of water and neutralization of alkali.

By adding Tannin or lignin or sodium sulphate to block the hair cracks thereby preventing the infiltration of caustic soda solution



## Water Softening

The concentration of dissolved impurities mostly determines the hardness of water. The process of removing hardness causing salts from water is called water softening.

In industry, main three methods employed for softening of water are:

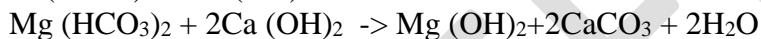
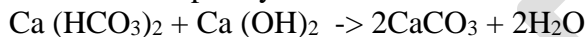
- 1) Lime-soda process
- 2) Zeolite or Permutit process
- 3) Ion exchange process

### 1) Lime soda process:

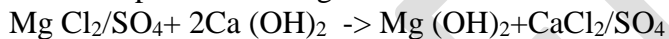
- Chemical precipitation is one of the more common methods used to soften water.
- In this process soluble salts of calcium and magnesium are converted into insoluble salts.
- Chemicals used are:
  - Lime (calcium hydroxide,  $\text{Ca}(\text{OH})_2$  and
  - Soda ash (sodium carbonate,  $\text{Na}_2\text{CO}_3$ )
- Generally about 10% excess chemicals are added for quick completion of the reactions
- The reactions taking place are summarized as follows:

#### Lime reactions:

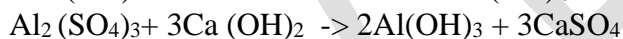
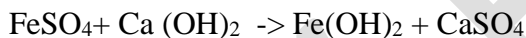
Removal of temporary hardness:



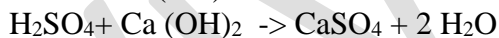
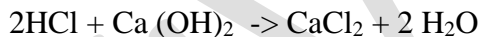
Removal of permanent magnesium hardness:



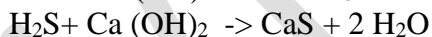
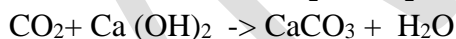
Removal of dissolved iron and aluminium salts:



Removal of free mineral acids:



Removal of dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$ :



#### Soda reactions:

Removal of all the soluble calcium permanent hardness (which is originally present & introduced during the removal of  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  etc., by lime)



Lime removes temporary hardness efficiently without introducing any soluble salts.

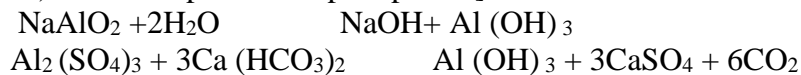
#### Lime soda process is of two types:

- i) Cold lime soda process
- ii) Hot lime soda process

#### Cold lime soda process:

- The process is carried out at room temperature.
- The precipitates so formed are finely divided and can't be settled or filtered easily.

- Hence small amounts of coagulants (like alum, sodium aluminate, aluminium sulphate, etc.), are added to settle down the fine precipitates. [hydrolyse to flocculent, gelatinous precipitate of  $\text{Al}(\text{OH})_3$  and entraps the fine precipitates]



#### Method:

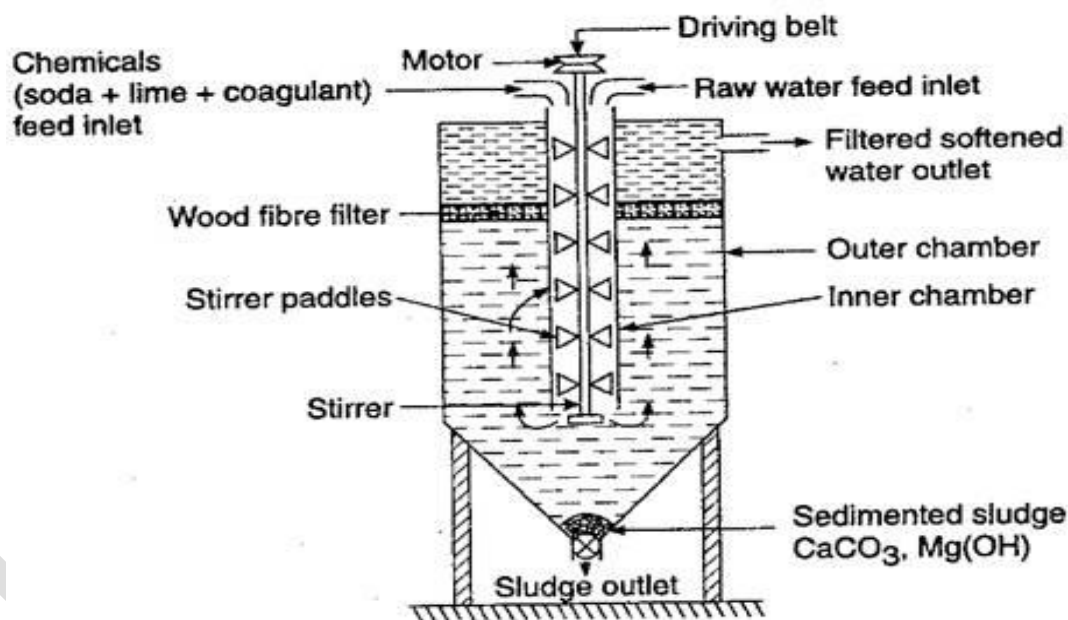
Raw water and calculated quantities of chemicals (lime + soda + coagulant) are fed from the top into the inner vertical circular chamber, which is provided with a paddle stirrer.

Vigorous stirring and continuous mixing is carried out to facilitate thorough mixing of raw water and chemicals.

The soft water that comes out into the outer co-axial chamber rises up and passes through fiber filter where traces of sludge are removed and filtered soft water passes through the outlet provided.

Sludge that is formed settles down to the bottom of the outer chamber and can be frequently removed through the sludge outlet.

Residual hardness of soft water is about 50-60 ppm.



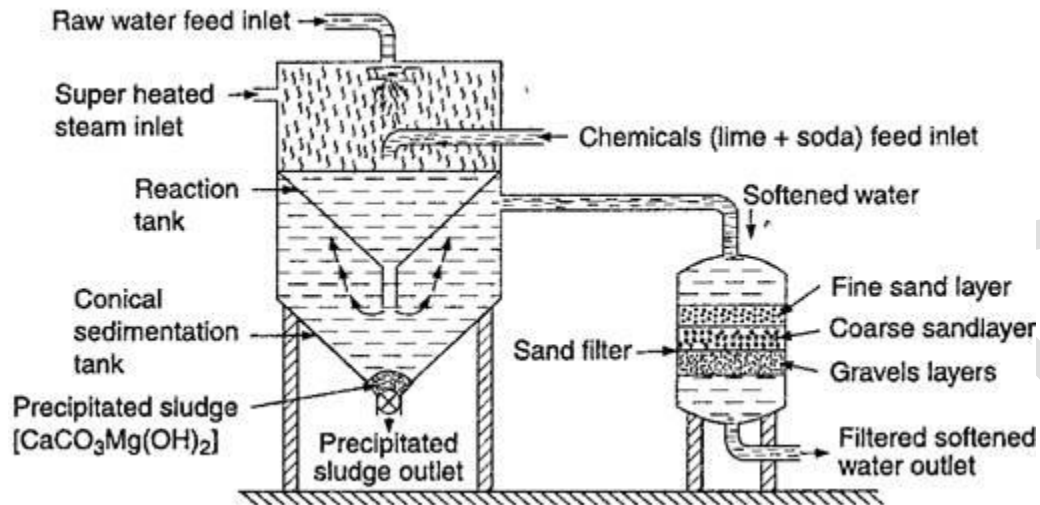
Continuous cold lime-soda softener

#### Hot lime soda process:

- The process is carried out at a temperature of  $94^{\circ}\text{C}$ - $100^{\circ}\text{C}$ .
- Reaction proceeds faster
- Elevated temperatures reduce the viscosity of water and increase the rate of aggregation of the particles.
- Hence both the settling and filtering rates are increased.
- So no need of adding any coagulant as the sludge settles down very easily.
- Dissolved gases are driven out of the solution to some extent at the higher temperature.
- A smaller excess of chemicals is needed than with the cold process.
- Softening capacity of this process is several times greater than cold process.

- Residual hardness of soft water is about 17-34 ppm.

A typical hot lime-soda softener consists of three parts:



Continuous hot lime-soda softener

- Reaction tank:**  
has three separate inlets for Raw water, chemicals and super heated steam, in which the Raw water, chemicals and super heated steam are thoroughly mixed.
- Conical sedimentation vessel:**  
in which sludge settles down.
- Sand filter:**  
it ensures complete removal of sludge from the softened water.

Advantages of L.S.Process:

- i) the process increases the pH value of the treated water, there by corrosion of the distributed pipes is reduced.
- ii) quantity of minerals in the water are also reduced
- iii) Iron & manganese are also removed to some extent
- iv) Amount of pathogenic bacteria is also considerably reduced due to alkaline nature of treated water.
- v) Very economical

Disadvantages of L.S.Process:

- i) Careful operation and skilled supervision is required
- ii) Disposal of large amounts of sludge is a big problem
- iii) do not produce water of zero hardness, not good for boilers.(possess appreciable amounts of sodium sulphate and can't be used in high pressure boilers)

### Conclusions from L-S process:

- |   |  |
|---|--|
| 1 equivalent of Calcium temporary hardness requires   | 1 equivalent of lime                           |
| 1 equivalent of magnesium temporary hardness requires | 2 equivalent of lime                           |
| 1 equivalent of magnesium permanent hardness requires | 1 equivalent of lime &<br>1 equivalent of soda |
| 1 equivalent of calcium permanent hardness requires   | 1 equivalent of soda                           |
- The permanent hardness introduced during the removal of  $Mg^{+2}$ ,  $Fe^{+2}$ ,  $Al^{+3}$ ,  $HCl$ ,  $H_2SO_4$  etc., by lime is taken into consideration while calculating soda requirement.

### Steps for calculating Lime-soda requirement:

Note the units

Ignored the substances which don't contribute towards hardness ( $KCl$ ,  $NaCl$ ,  $SiO_2$ ,  $Na_2SO_4$ ,  $Fe_2O_3$  etc.,)

Convert hardness causing substances into equivalents of  $CaCO_3$

Lime required for softening =  $74/100$  [Temp. 'Ca' hardness + 2\* Temp Mg hardness + Per. Mg hardness]

Soda required for softening =  $106/100$  [Per. Ca hardness + Ca permanent hardness introduced during lime reactions]

Note: i) For every 1 equivalent of  $HCO_3^-$  the corresponding reduction in the dose of soda should be taking into consideration while calculating soda requirement.



ii) if impurities are given as  $CaCO_3$  or  $MgCO_3$  – considered to be due to  $Ca(HCO_3)_2$  or  $Mg(HCO_3)_2$  respectively and are expressed in terms of  $CaCO_3$  or  $Mg$

iii) if analytical report shows the quantities of  $Ca^{+2}$  &  $Mg^{+2}$  then

1 equivalent of soda required for  $Ca^{+2}$

1 equivalent of lime and soda required for  $Mg^{+2}$

iv) if the purity of lime & soda is given, the actual requirement of lime and soda are calculated accordingly.

Eg: if lime is 90% purity – above formula is multiplied by  $100/90$

## Ion exchange or deionization or demineralization process

Ion-exchange water softening is an extremely popular method of water softening.

A reversible exchange of ions takes place between the stationary ion exchange phase and the external liquid mobile phase.

Ion exchange resins are insoluble, cross linked, high mol.wt., organic polymers and the functional groups attached to the chains are responsible for the ion exchange properties.

These are of two types

- Cation exchange resins
- Anion exchange resins

### Cation exchange resins ( $\text{RH}^+$ ):

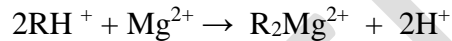
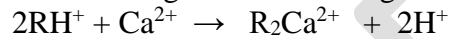
These are capable of exchanging  $\text{H}^+$  ions with the cations.

### Anion exchange resin ( $\text{ROH}^-$ )

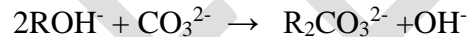
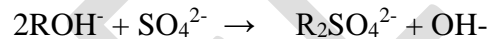
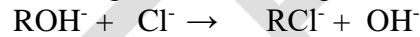
These are capable of exchanging  $\text{OH}^-$  ions with the anions.

#### Process:

The hard water is passed first through cation exchange column, reactions are



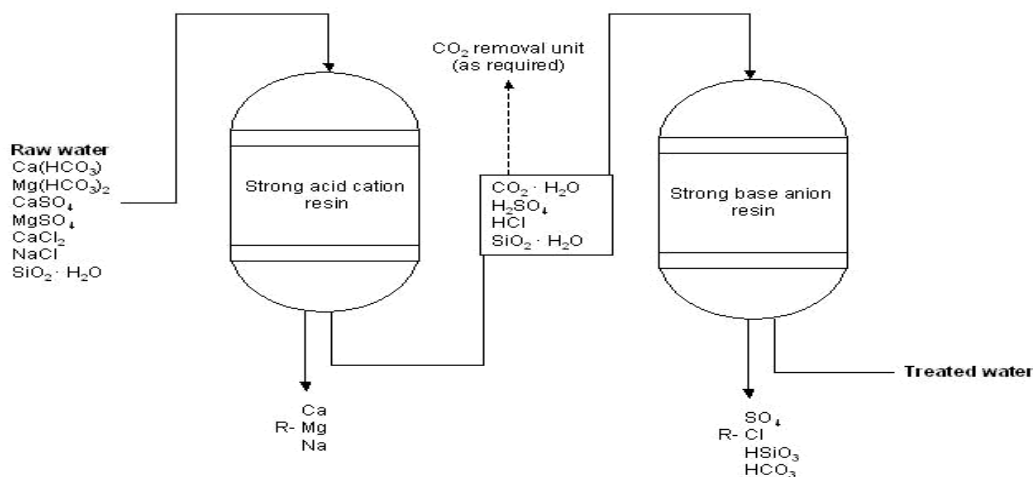
The hard water is now passed through anion exchange column, reactions are



$\text{H}^+$  and  $\text{OH}^-$  ions are released from the cation exchange and anion exchange columns respectively get combined to produce water molecule.



Water coming out from the exchanger is free from cations and anions and is known as deionized or demineralised water

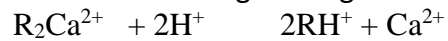


Demineralization of water

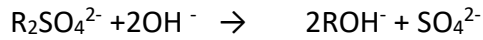
**Regeneration of exhausted bed:**

When the beds are getting exhausted then they are regenerated .

The exhausted cationic exchanger is regenerated by washing with acids like HCl, H<sub>2</sub>SO<sub>4</sub> etc



The exhausted anion exchanger is regenerated by washing with bases like NaOH



The columns are washed with deionized water and washings are passed to sink or drain.

Now they are ready for softening process.

**Advantages**

- Produce water of very low hardness (2ppm )
- The process can be used to soften highly acidic or highly alkaline waters.
- Water produced by this process water can be used in high pressure boilers

**Disadvantages**

- High capital cost and chemicals & equipment are costly
- If water contains turbidity efficiency of the process decreases.

### Zeolite (boiling stone) or Permutit process:

Zeolite is nothing but hydrated sodium aluminum silicates

It has capability to exchange reversibly its sodium ions with hardness producing ions

Zeolites are also known as permutits.

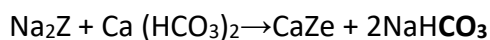
It is also referred as Base exchanger as it has capability to exchange basic radicals.

### Procedure:

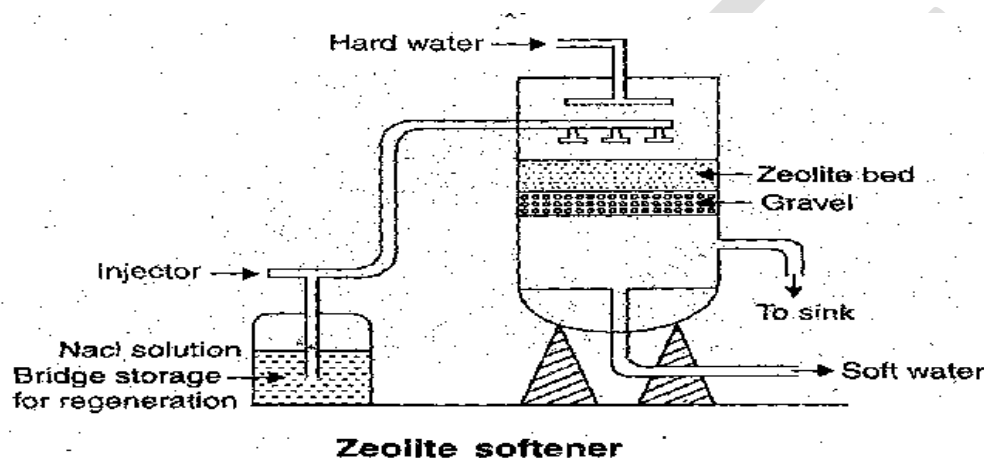
In this process hard water is allowed to move through a bed of zeolite.

The hardness causing ions ( $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$ ) in the water sample are taken up by zeolite and simultaneously release the equivalent sodium ions.

Reactions:



### Diagram:



### Regeneration:

After some time zeolite bed is exhausted (stops to function) and it can be regenerated and reused.

Brine is widely used to regenerate the bed



### Limitations:

1. Suspended matter must be removed as it clogs the pores of zeolite bed.
2. Hot water shouldn't be used as it is dissolved in it.
3. Acid radicals can't be removed.
4. pH of the treated water should be around 7.0

### Advantages:

1. Hardness of water is removed up to 10ppm.
2. It occupies small space and no sludge is formed.

### Disadvantages:

1. The treated water contains more sodium salts than in lime soda process.
2. It only replaces  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$  ions by  $\text{Na}^{+}$  ions leaving acidic ions like  $\text{HCO}_3^{-}$  and  $\text{CO}_3^{2-}$  in softened water.

## Desalination

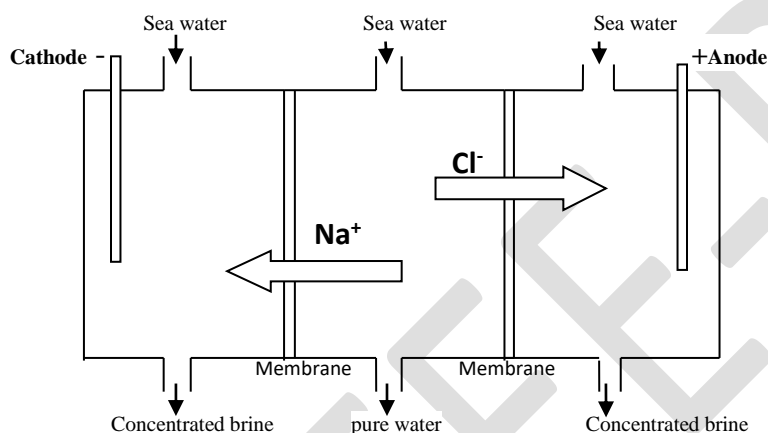
The process of removing common salt (sodium chloride) from the water is known as desalination.

Commonly employed methods for desalination of brackish water are:

- i) Electro dialysis
- ii) Reverse osmosis

### i) Electrodialysis:

It is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential.



Line diagram of electro dialysis

When direct electric current is passed through saline water, the Na<sup>+</sup> ions moves towards cathode (-ve pole) and the chloride ions moves towards anode (+ve pole) through membrane.

The concentration of brine decreases in the central compartment, where as the concentration in outer compartments increases.

Desalinated brine (pure water) is removed from time to time, while concentrated one is replaced by fresh brine.

Ion selective membranes are employed for more efficient separation, which has permeability for one kind of ions.

Cation selective membrane (possess functional groups such as  $\text{RSO}_3^-$ ) is permeable to cations only

Anion selective membrane (possess functional groups such as  $\text{R}_4\text{N}^+\text{Cl}^-$ ) is permeable to anions only

### Electrodialysis cell:

It consists of a large number of paired sets of rigid plastic membrane.

Saline water is passed at a pressure of  $5\text{--}6 \text{ kg m}^{-2}$  between membrane pairs.

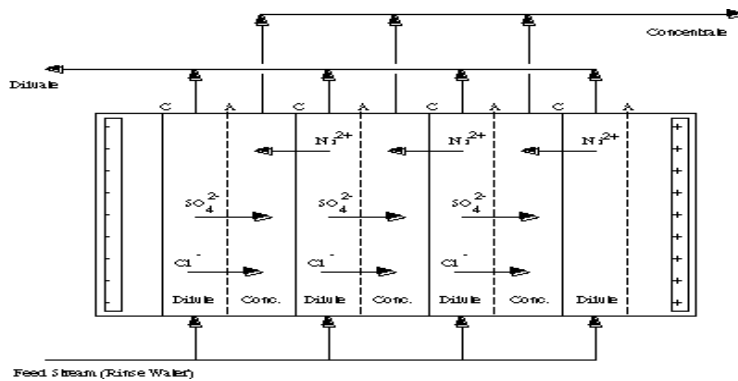
Electric field is applied  $\perp$  to the direction of water flow

Fixed +ve charges inside the membrane repel +ve charge ions ( $\text{Na}^+$ ) and permits -vely charged ions.

Fixed -ve charges inside the membrane repel -ve charge ions ( $\text{Cl}^-$ ) and permits +vely charged ions.

Alternative streams of pure water and brine water are obtained.





### Advantages of desalination:

- It is a compact unit
- It is economical.
- Best suited if electricity is easily available.

### Reverse osmosis. (R.O)

Reverse osmosis is one of the membrane filtration processes. The process is used to remove salts and organic micro pollutants from water.

In this process

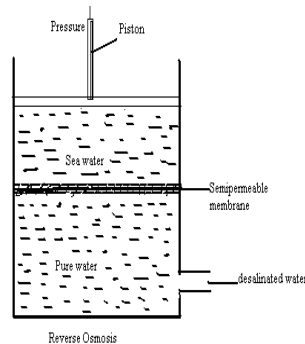
When it is subjected to a hydrostatic pressure greater than the osmotic pressure on the concentrated side solvent passes through a semi permeable membrane in a reverse direction. This phenomenon is called reverse osmosis.

In this process pure solvent (water) is separated from its contaminants, rather than removing contaminants from water. Sometimes it is also called super/hyper filtration.

### Method:

Pressure (of the order  $15\text{--}40 \text{ kg cm}^{-2}$ ) is applied to the sea water/impure water.

The membrane consists of very thin films of cellulose acetate/ superior membrane made of polymethacrylate and polyamide polymers, affixed to either side of the perforated tube.



### Advantages:

- Removes ionic and non-ionic colloidal particles and high molecular weight organic matter.
- It removes colloidal silica
- The life time of semi permeable membrane is high.
- Membrane can be replaced within few minutes.
- Low capital and operating cost & high reliability

## Municipal water treatment

Potable water: means safe to drink

Essential requirements:

- clear
- Colorless and Odorless
- Pleasant in taste
- It should not have turbidity (not exceed 10 ppm)
- pH should be in the range of 7.0-8.5
- Free from gases like  $H_2S$  & minerals like Pb, As, Cr & Mn salts
- Total hardness should be less than 500 ppm
- Free from disease producing bacteria

Sources for municipal water supply: Rivers, Wells, Lakes

Various steps involved in the treatment of municipal water:

Type of impurity	Process to be employed
Floating matter( leaves, wood pieces)	Screening
Suspended (Clay, Sand)	Plain sedimentation
Fine suspended inorganic matter	Sedimentation with coagulation
Micro organisms & colloidal impurities	Filtration
Pathogenic bacteria	Disinfection

### Screening:

The raw water is passed through screens & floating matter is retained.

### Sedimentation:

Suspended impurities are removed by allowing the water to stand undisturbed for few hours (about 2-8 hr) in big tanks (5m deep).

Due to force of gravity most of the particles settles down at the bottom of the tank. about 70-75% of the suspended matter can be removed.

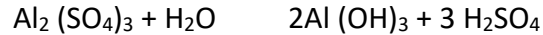
### Sedimentation with coagulation:

- Plain sedimentation can't remove finely divided silica, clay and organic matter.
- Sedimentation with coagulation is a process of removing fine particles by addition of chemicals (coagulants) before sedimentation.
- These impurities are in colloidal form, may carry -ve charge and don't coalesce (come together) due to mutual repulsion.
- Commonly used coagulants are Alum ( $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ), Sodium aluminate ( $NaAlO_2$ ) etc.
- Due to neutralization of charge on the particles/ mechanical entrainment by coagulants, the colloidal particles become closure, forms bigger particles and coalesce together. This process is called coagulation.

- Coagulation process permits the particles to aggregate together until denser particles are formed, which falls through still water at a reasonable rate and is called flocculation.

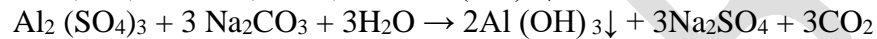
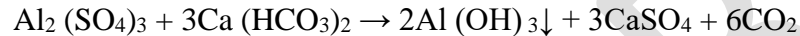
- Explanation with example:

Aluminium (most common coagulant) gets hydrolysed to form aluminium hydroxide and sulphuric acid.



$\text{Al}(\text{OH})_3$  acts as flocculent (enormous surface area) and removes the impurities either by neutralizing the charge or by adsorption and mechanical entrainment.

In alkaline water (lime/ $\text{Na}_2\text{CO}_3$  is added if it is not sufficiently alkaline) the reaction is



[Acidic waters are treated with sodium aluminate or in conjugation with  $\text{Al}_2(\text{SO}_4)_3$



- Coagulant aids (lime, fuller's earth, poly electrolytes) are added to increase the efficiency of the process.
- Generally coagulants are added in solution form with the help of mechanical flocculators, for thorough agitation.
- Substantial reduction of bacteria also takes place during this process. ( $\text{O}_2$  i.e. released by some coagulants destroys some bacteria, breaks up some organic compounds, partial removal of color & taste producing organisms.)

### Filtration:

- It is the process of clarification of water by passing the water through a porous material, which is capable of retaining coarse impurities on its surface & in the pores. [Porous material used – filtering media, equipment used – filter]
- Common materials used as filtering media: quartz sand(0.5-1.0mm), crushed anthracite(0.8-1.5mm), porous clay
- Slow sand filtration (2gal/Sqft/hr) is generally employed in municipal water treatment.
- Process:

A typical sand filter consists of a tank with a bed containing fine sand (top layer), coarse sand, coarse gravel (bottom layer).

It is provided with inlet for sedimented water and under drain channel at the bottom for exit of filtered water

Sedimented water is distributed uniformly over the bed and flows slowly through various layers.

Rate of filtration slowly decreases due to retention of impurities in the pores.

Top layer is scrapped and replaced with clean sand to increase the efficiency of process.

## FILTER AND THEIR CLASSIFICATION

### 1. Slow sand filter (SSF)

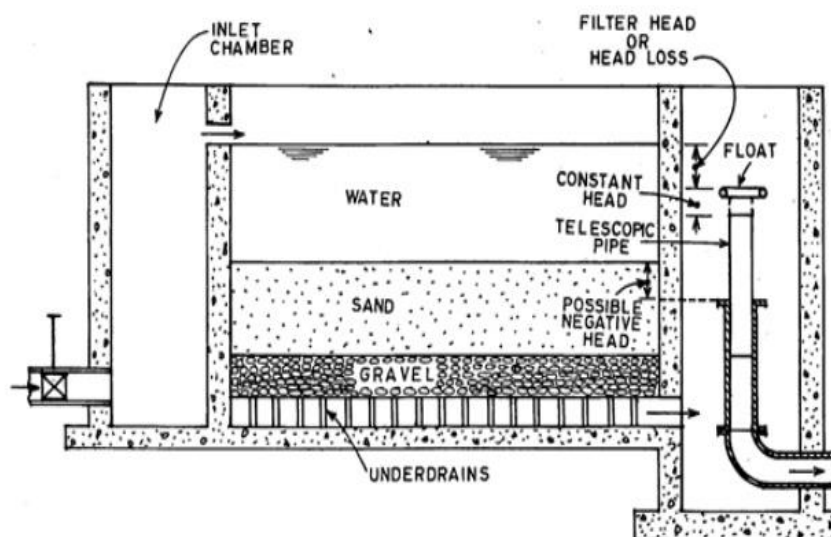


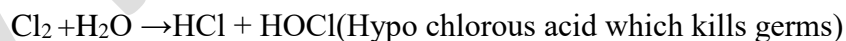
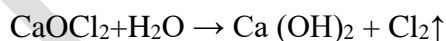
Fig 6.19 Section of slow sand filter (Source: Modi, 1998)

#### Removal of microorganisms:

Removal of pathogenic (Disease causing microorganism) is known as disinfection. Chemicals or substances added to water for killing bacteria are known as disinfectants.

#### Bleaching powder(CaOCl<sub>2</sub>):

About 1 kg of bleaching powder is added to 1000 Kiloliters of water and allowed to stand for several hours. Hypochlorous acid that is produced is a powerful germicide.



Disinfecting action of bleaching powder is due to available chlorine in it.

#### Limitations:

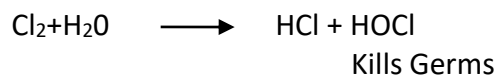
It is unstable, difficult to store

It introduces calcium in water which increases hardness of water.

Excess of it gives bad taste.

#### Addition of chlorine – (Chlorination)

Addition of liquid chlorine or gaseous chlorine to water produces hypochlorous acid, which kills microorganisms.



Chlorine is good disinfectant at a pH of 6.5 (lower pH). HOCl is about 80 times more destructive to bacteria than  $\text{OCl}^-$  (hypochlorite ion can not inactivate the enzyme action).

### **Factors effecting efficiency of chlorine:**

#### **Time of contact**

Number of Micro-organisms destroyed by chlorine per unit time is proportional to number of microorganisms remaining alive. So death is maximum at starting and decreases with time.

#### **Temperature of water**

Higher the temperature, the rate of reaction with enzymes is faster. Destroy of microorganisms increase with rise of temperature. .

#### **PH value of water**

Lower the PH value, the reaction is faster & a small contact period is required to kill same % of microorganisms.

#### **Advantages:**

- Effective & economical
- It requires very little space.

#### **Disadvantages:**

- Excess of chlorine produces unpleasant odour&taste.
- Free chlorine should not exceed 0.1-0.2ppm
- It is more effective below 6.5 & less effective at higher PH values.

### **Break point chlorination or Dip point (Free residual chlorine):**

It involves addition of sufficient amount chlorine to oxidize:

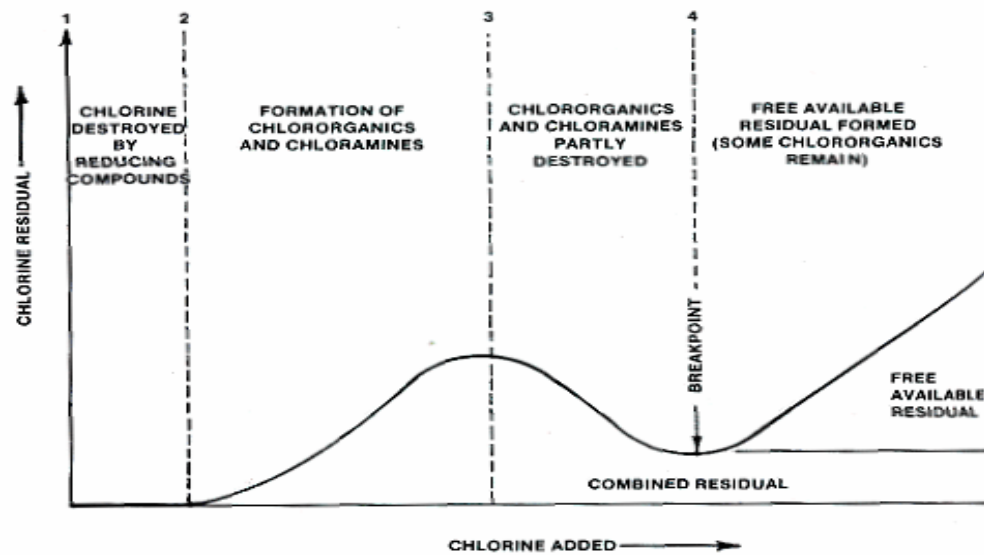
Organic matter, reducing substances, free ammonia, leaving behind free chlorine which possess disinfecting action against pathogenic bacteria.

The addition of chlorine at the dip or break is called as Breakpoint chlorination. At the dip or break point chlorination, free residual chlorine is present which removes pathogenic bacteria.

**A graph between dosage of applied chlorine and residual chlorine is as shown in the Fig. From this fig it is shown that:**

- i) At lower dosages of  $\text{Cl}_2$  (initially) all the chlorine added is consumed for complete oxidation of reducing substances like  $\text{H}_2\text{S}$ . No residual chlorine.
- ii) With the increase of amount of chlorine dosage, a steady increase in amount of residual chlorine is observed. It is due to formation of chloro organic compounds without oxidising them.
- iii) when the dosage of chlorine is further increased, oxidation of chloroorganic compounds takes place and the free residual chlorine decreases and reaches a dip where oxidative destruction is complete.
- iv) Here after any addition of chlorine is not used in any reaction and the residual chlorine is increased. It acts as disinfectant and removes pathogenic bacteria.

Sufficient chlorine i.e added at dip is known as break point chlorination or Free residual chlorination. It ensures complete destructio of organic compounds which gives bad taste and colour.



#### Advantages:

- It oxidizes completely organic compounds, ammonia and other reducing compounds.
- Removes colour in water, due to presence of organic matter.
- Destroy disease producing (100%) bacteria.
- Removes bad taste and odour
- Prevents growth of any weed.