Hard water

Water which does not produce lather with soap is called hard water.
Water which produces lather with soap is called soft water. Soft water contains less number of salts.
Soap is a sodium salt of higher fatty acid i.e., Sodium or Potassium salts of stearic or palmitic or oleic acid. Soap is highly soluble in soft water and forms lather immediately.

$$\underset{\text{Sod.stearate (soap)}}{C_{17}H_{35}COONa} + H_2O \longrightarrow \underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + NaOH$$

Soap forms insoluble salts with hard water and does not form lather.

$$\underset{\text{(Present in Hard water)}}{Ca^{2+}} + \underset{\text{Sodium stearate (Soap)}}{2C_{17}H_{35}COONa} \longrightarrow \underset{\text{Calciumstearate}}{(C_{17}H_{35}COO)_2Ca} + 2Na^{+}$$

$$\underset{\text{(Present in Hard water)}}{Mg^{2+}} + 2C_{17}H_{35}COONa \longrightarrow \underset{\text{Magnesiumstearate}}{(C_{17}H_{35}COO)_2Mg}$$

Types of hardness

1. **Temporary hardness**
2. **Permanent hardness**

Water Hardness

Temporary hardness

Reason:-

Presence of calcium or magnesium bicarbonate in the water

Solution:-

Boiling the water. The hydrocarbonates decompose, leaving insoluble calcium carbonate or magnesium carbonate – this is the scale found in kettles and boilers.

Equation:-

$Ca(HCO_3)_2 \rightarrow Ca\,CO_3 + CO_2 + H_2O$

Permanent hardness

Reason:-

Presence of calcium or magnesium sulphate/chlorides in the water.

Solution:-

Soften the water by adding sodium carbonate or by ion exchange.

Equation:-

$Na_2CO_3 + CaSO_4 \rightarrow Ca\,CO_3 + Na_2SO_4$

$$\text{Hardness of water} = \text{Weight of dissolved salt (mg/L)} \times \frac{\text{Equivalent wt of } CaCO_3}{\text{Equivalent wt of dissolved salt}}$$

Hard water

Units of hardness

It is expressed in terms of equivalents of $CaCO_3$.
Degree of hardness is expressed in ppm or degree clark (°cl) or degree French (°fr).

$$1 \text{ ppm} = 1\text{mg/l} = 0.1^{o}\text{fr} = 0.07^{o}\text{cl} = 0.07 \text{ gpg}$$

$$1^{o}\text{cl} = 14.3\text{mg/l} = 14.3 \text{ ppm} = 1.43^{o}\text{fr} = 1\text{gpg}$$

$$1^{o}\text{fr} = 10\text{mg/l} = 10\text{ppm} = 0.7^{o}\text{cl} = 0.7\text{gpg}$$

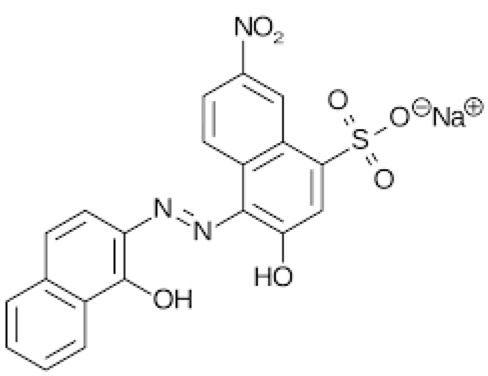
Hard water

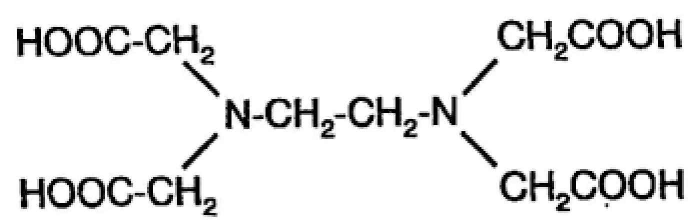
DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD

EDTA method is the most common and accurate method of determination of hardness of water. This method is called complexometric method

EDTA acts as complexing agent or chelating agent. ammonia – ammonium chloride solution acts as buffer

It forms complexes with various metal ions present in water. From the amount of the EDTA consumed during complex formation, the hardness of the water sample can be calculated.





$$Ca^{2+} + EBT \longrightarrow Ca\text{-}EBT$$
$$Mg^{2+} + EBT \longrightarrow Mg\text{-}EBT$$

$$Ca\text{-}EBT + EDTA \longrightarrow Ca\text{-}EDTA + EBT$$
$$Mg\text{-}EBT + EDTA \longrightarrow Mg\text{-}EDTA + EBT$$

Wine red   Colourless   Colourless   Blue colour

Hard water

$$\textbf{Hardness} = \frac{\text{Volume of EDTA} \times \text{Normality of EDTA} \times 50 \times 1000}{\text{Volume of water sample}}\ \textit{mg/L of } CaCO_3 \textit{ or ppm}$$

1. **50 ml of a sample water consumed 15 ml of N/20 EDTA before boiling and 5 ml of the same EDTA after boiling. Calculate the degree of total hardness and permanent hardness.**

Alkalinity of Water

Alkalinity of water is mainly due to the presence of anions like CO_3^{2-}, HCO_3^-, and OH^-
The estimation of alkalinity in water is done by titrating water sample against standard acid using phenolphthalein and methyl orange as indicators.
In this titration, two indicators are used as the different anions give end points at different pH values.

Possible combinations for alkalinity of water: 5 combinations possible
HCO_3^- and OH^- cannot be present together because H^+ ion of HCO_3^- neutralizes OH^-

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

$$H^+ + OH^- \rightarrow H_2O$$

$$H^+ + CO_3^{2-} \rightarrow HCO_3^-$$

Phenolphthalein End point (P)

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

methyl orange End point (M)

Alkalinity of Water

Phenolphthalein alkalinity in terms of $CaCO_3$ is calculated by using the formula

$$P = \frac{P1 \times \text{Normality of HCl} \times 50 \times 1000}{\text{Volume of water sample}} \; ppm$$

Methyl Orange alkalinity in terms of $CaCO_3$ is calculated by using the formula

$$M = \frac{M1 \times \text{Normality of HCl} \times 50 \times 1000}{\text{Volume of water sample}} \; ppm$$

Burette reading	**OH^- alkalinity**	**CO_3^- alkalinity**	**HCO_3^- alkalinity**
P = 0	-	-	M
P = M	P	-	-
P = ½ M	-	2P	-
P < ½ M	-	2P	M – 2P
P > ½ M	2P – M	2(M – P)	-

Alkalinity of Water

(b) A water sample is alkaline to both phenolphthalein and methyl orange. From this water sample 100 ml on titration with 1/50 N HCl required 12 ml of acid to reach phenolphthalein end point. When 4 drops of MO are added to the same solution and titration is further continued, the yellow color of the solution just turned pink after addition of another 4 ml of acid solution. Report the type of and extent of alkalinity present in the water sample. Also write the chemical reactions involved in the titration.

Burette reading	OH^- alkalinity	CO_3^- alkalinity	HCO_3^- alkalinity
P = 0	-	-	M
P = M	P	-	-
P = ½ M	-	2P	-
P < ½ M	-	2P	M – 2P
P > ½ M	2P – M	2(M – P)	-

Scale and Sludge

In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally, a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If precipitates formed are loose and slimy, these are known as "**sludges**"
while if the precipitate formed is hard and adhering on the inner walls, it is called as **"scale"**.

sludges	$MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$
scale	$CaCO_3$ $Mg(OH)_2$ $CaSO_4$

Chemical Methods: EDTA or N/50 HCl solutions

Prevention methods:

By using softened water

By blow down operation

SOFTENING OF WATER

INTERNAL TREATMENTS

1) Colloidal conditioning: In this method, colloidal agents like kerosene, tannin, agar- agar gel are added to boiler water.

2) Carbonate conditioning: Na_2CO_3 added to boiler water will react with the $CaSO_4$ present in dissolved state in boiler water

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$$

3) Calgon conditioning: Calgon is sodium hexa metaphosphate with the composition $Na_2[Na_4(PO_3)_6]$.

$$Na_2[Na_4(PO_3)_6] \rightleftharpoons 2\,Na^+ + [Na_4(PO_3)_6]^{2-}$$

$$\underset{\text{Scale forming ion}}{2\,Ca^{2+}} + [Na_4(PO_3)_6]^{2-} \rightarrow \underset{\text{Highly soluble complex}}{[Ca_2(PO_3)_6]^{2-}} + 4\,Na^+$$

4) Phosphate conditioning: converted into soft sludge by adding excess of soluble phosphates

$$2\,(PO_4)^{3-} + 3\,CaSO_4 \rightarrow \underset{\text{soft sludge}}{Ca_3(PO_4)_2} \downarrow + 3\,SO_4^{2-}$$

5) EDTA conditioning: using EDTA method

SOFTENING OF WATER

Water Softening Methods

- Clark’s Method (Lime-soda process)
- Zeolite (or Permutit) Process
- Ion exchange Process

Water Softening - Lime-soda process

Chemically converted all the soluble hardness causing impurities into insoluble Precipitates [such as $CaCO_3$, $Mg(OH)_2$, etc] which may be removed by settling and filtration.

For this purpose, a suspension of calculated amount of lime, $Ca(OH)_2$, and soda Na_2CO_3 are added.

For carbonate hardness

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O$$

$$Mg\ (HCO_3)_2 + 2\ Ca(OH)_2 = 2\ CaCO_3 + 2\ Mg(OH)_2 + 2H_2O$$

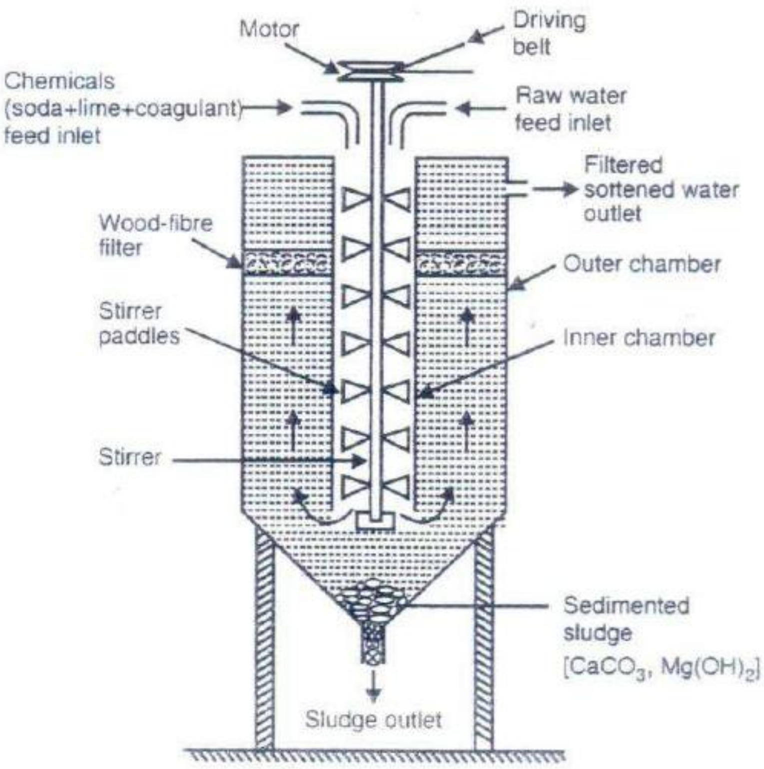
For permanent hardness

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$$

$$CaSO_4 + Na_2CO_3 = 2NaSO_4 + 2\ CaCO_3$$

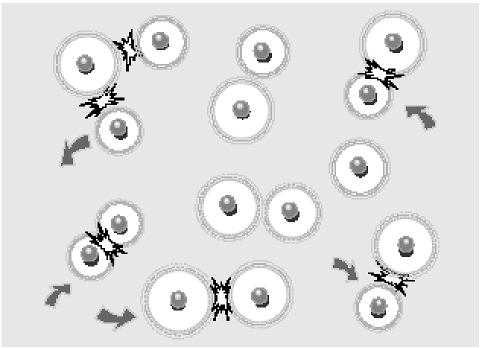
Water Softening - Lime-soda process

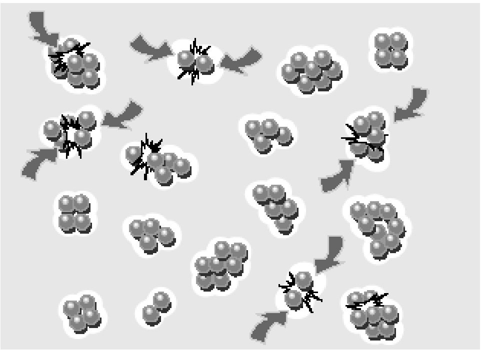
1. Cold Lime-soda process

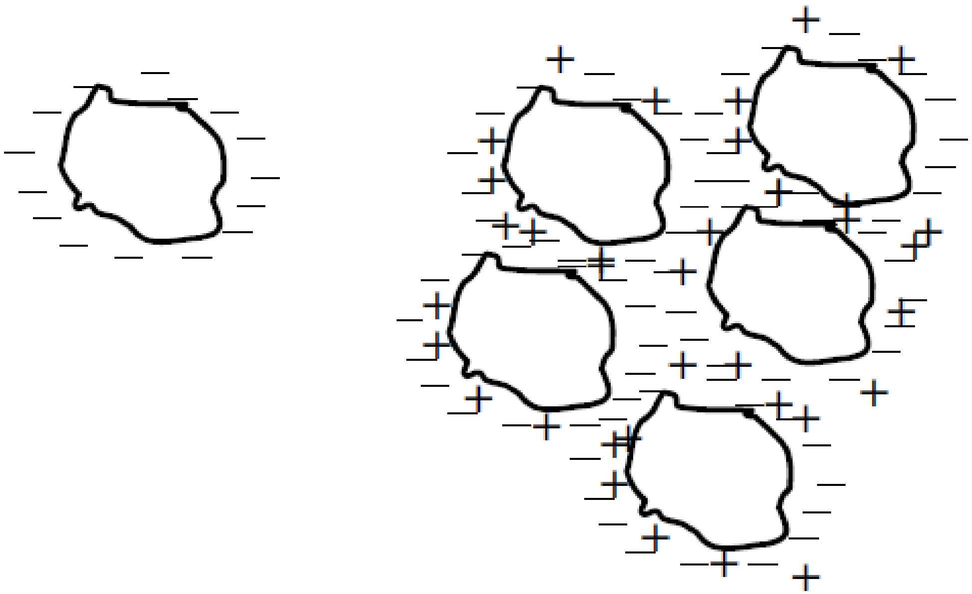


$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O$$

water treatment - Coagulation - Flocculation



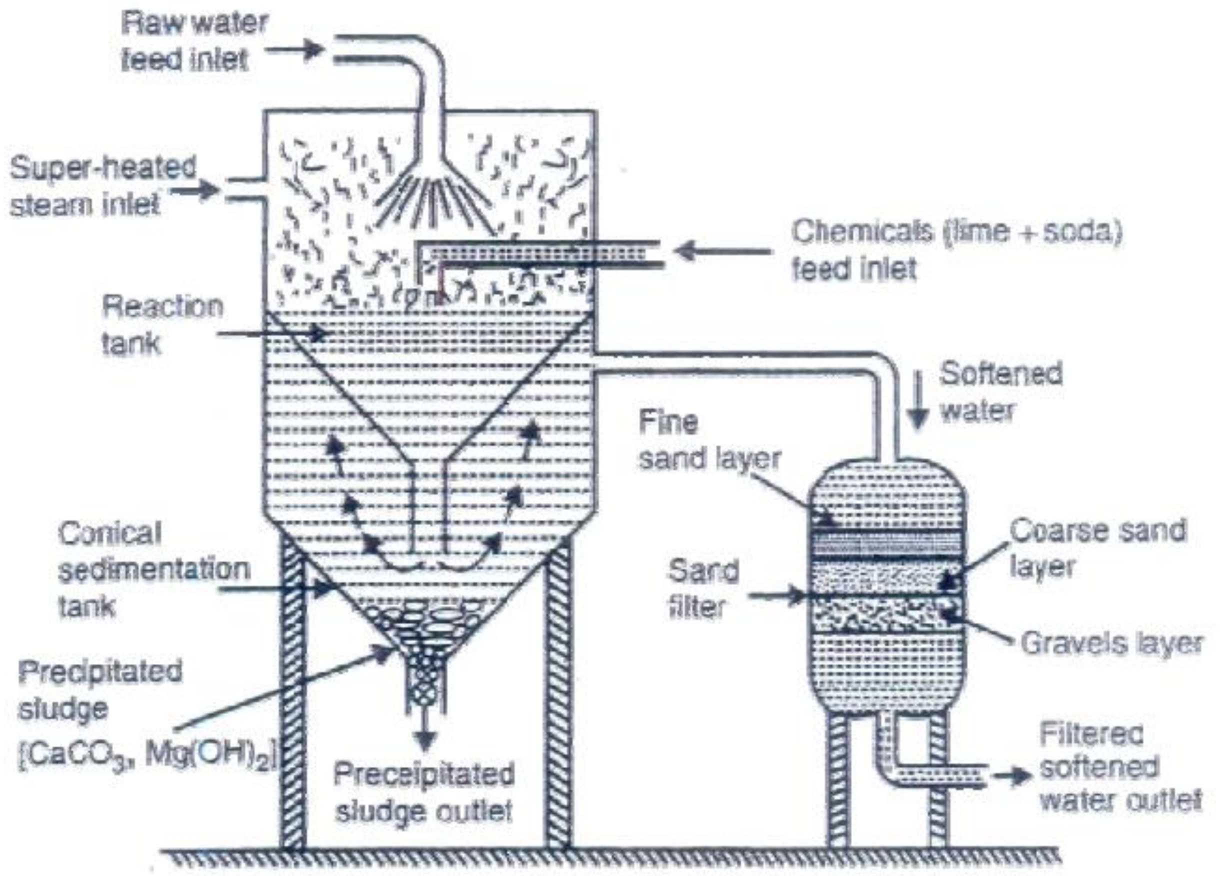




- $Al_2(SO_4)_3 \bullet nH_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + nH_2O$
- $FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$

Water Softening - Lime-soda process

2. Hot Lime-soda process

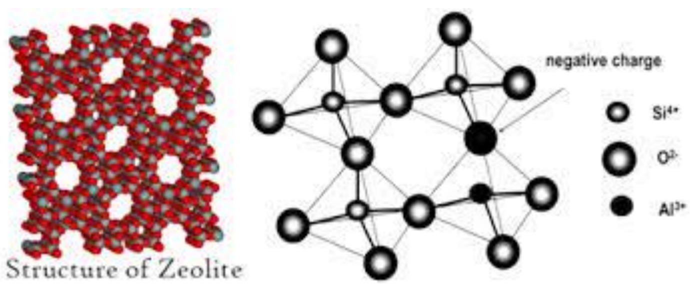


$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O$$

Calculate the quantity of lime and soda required to soften 10000 liters of water containing 219 ppm of $Mg(HCO_3)_2$ and 234 ppm of $Ca(HCO_3)_2$.

Water softening - Zeolite (or Permutit) Process

Zeolite is Hydrated sodium alumino Silicate, $Na_2O.\ Al_2O_3\ \mathbf{X}SiO_2\ \mathbf{Y}H_2O$ (X= 2-10, Y= 2-6)



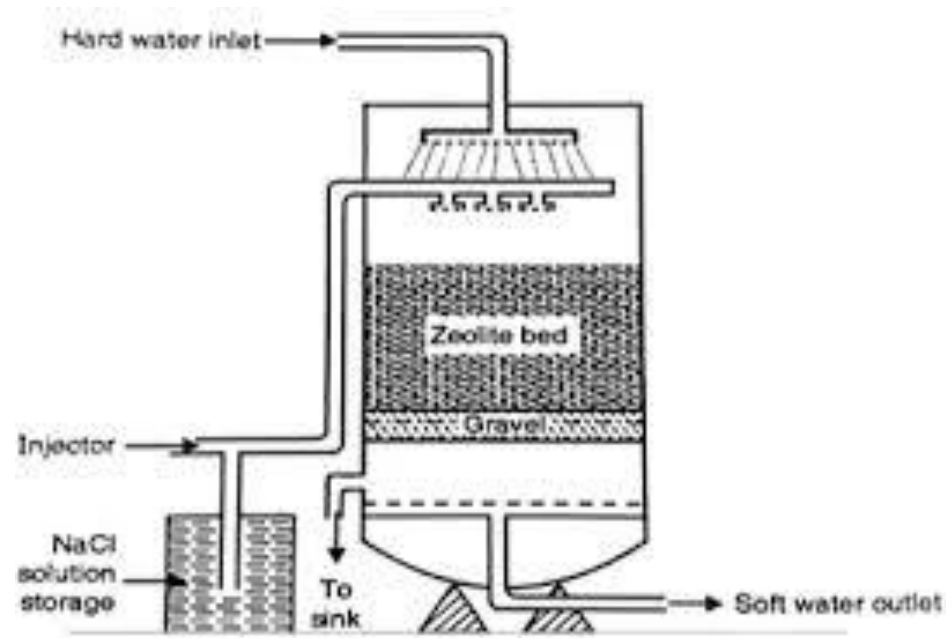
- **Chemical Reaction:**

$Ca(HCO_3)_2 + Na_2Ze \rightarrow CaZe + 2\ NaHCO_3$

$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$

$MgCl_2 + Na_2Ze \rightarrow MgZe + 2NaCl$

$Mg(NO_3)_2 + Na_2Ze \rightarrow MgZe + 2NaNO_3$



Regeneration:

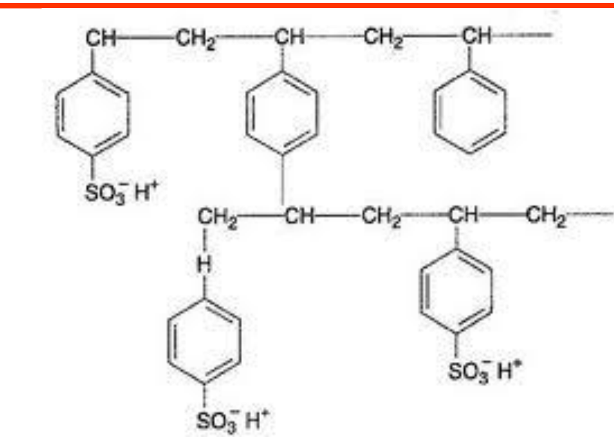
$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$

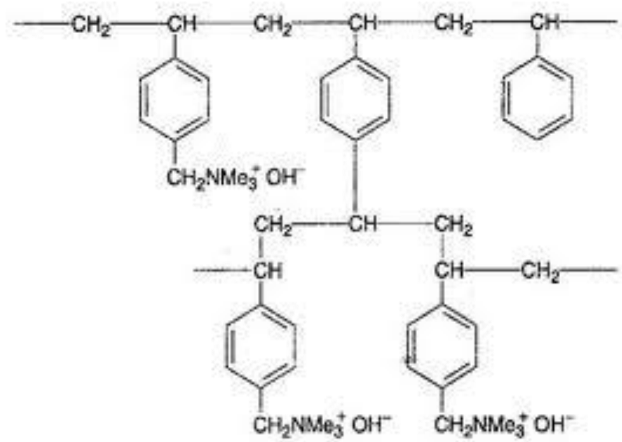
Water softening – Ion exchange Process

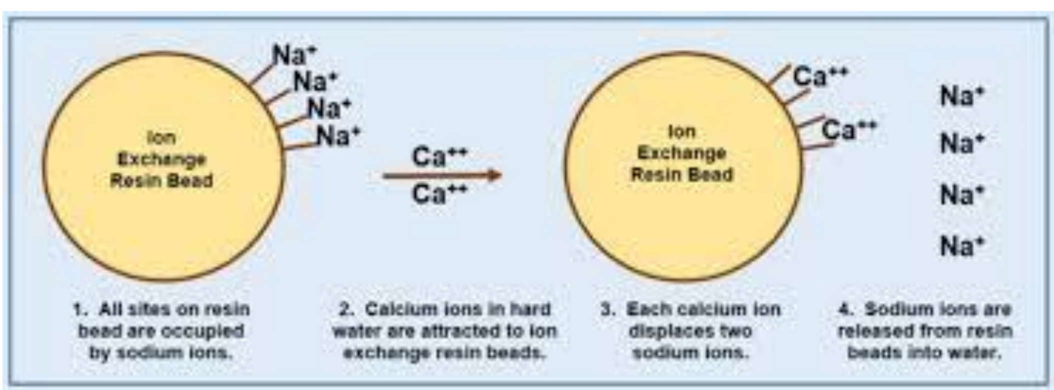
Resins are cross link polymers

Cation exchange resins: exchange cations present in hard water with H^{+}. They possess acidic groups such as –COOH, -SO_3H etc



Anion exchange resins: exchange anions present in hard water with OH^-. They possess basic groups such as OH^-, NH_2^- etc





Water softening – Ion exchange Process

Cation exchange resins

$$2\ RH^{+} + Mg^{2+} \rightarrow R_2Mg^{2+} + 2\ H^{+}$$

$$RH^{+} + Na^{+} \rightarrow RNa^{+} + H^{+}$$

$$3\ RH^{+} + Al^{3+} \rightarrow R_3Al^{3+} + 3\ H^{+}$$

Anion exchange resins

$$ROH^{-} + Cl^{-} \rightarrow RCl^{-} + OH^{-}$$

$$2\ ROH^{-} + SO_4^{2-} \rightarrow R_2SO_4^{2-} + 2\ OH^{-}$$

$$3\ ROH^{-} + PO_4^{3-} \rightarrow R_3PO_4^{3-} + 3\ OH^{-}$$

Regeneration:

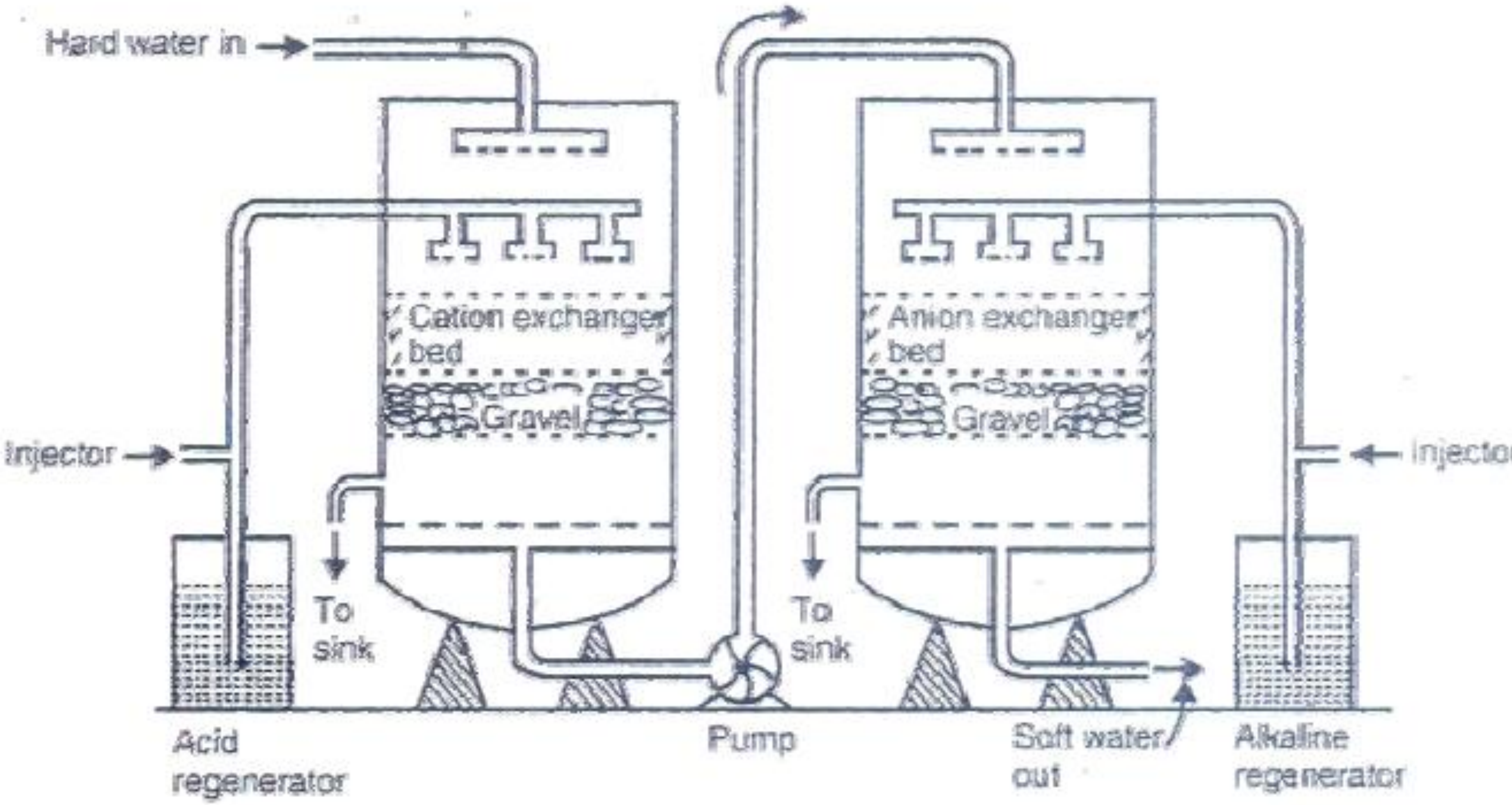
$$R_2Mg^{2+} + 2\ H^{+} \rightarrow 2\ RH^{+} + Mg^{2+}$$

$$R_3Al^{3+} + 3\ H^{+} \rightarrow 3\ RH^{+} + Al^{3+}$$

$$RCl^{-} + OH^{-} \rightarrow ROH^{-} + Cl^{-}$$

$$R_2SO_4^{2-} + 2\ OH^{-} \rightarrow 2\ ROH^{-} + SO_4^{2-}$$

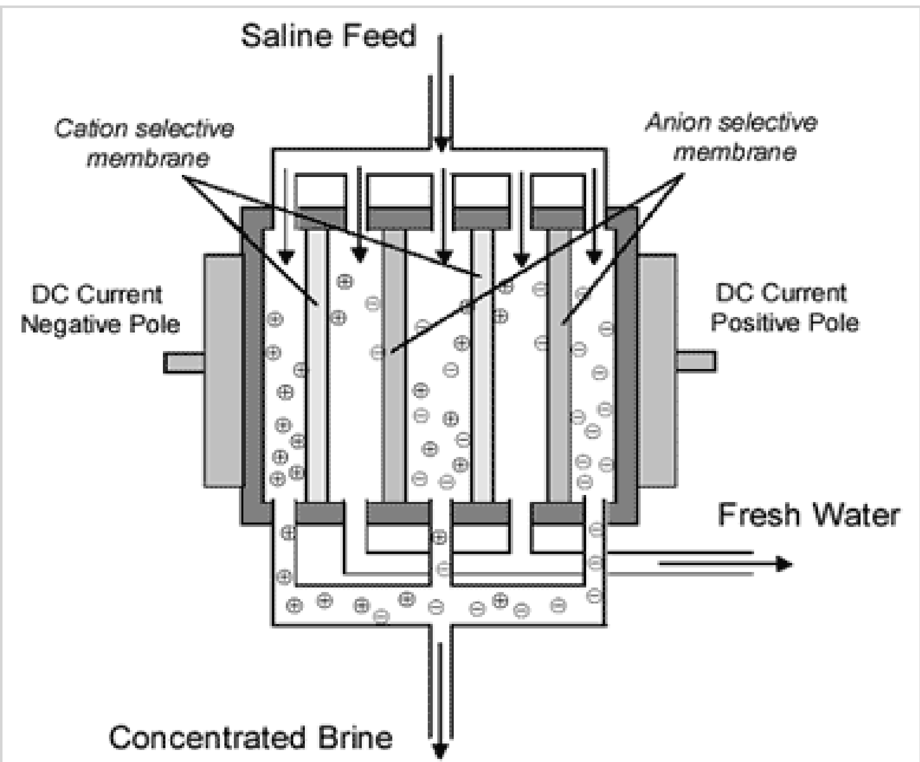
Water softening – Ion exchange Process



Desalination – Electrodialysis

Method of separation of ions from salt water by passing electric current. Semi permeable membranes are placed.

- As current applied Na^+ ions moves towards cathode and Cl^- moves towards anode
- As result brine concentration decreases in the middle compartment.
- Pure water is removed from the central compartment.
- Conc. Brines are replaced by fresh brine water.
- Much more effective separation Ion selective membranes are used

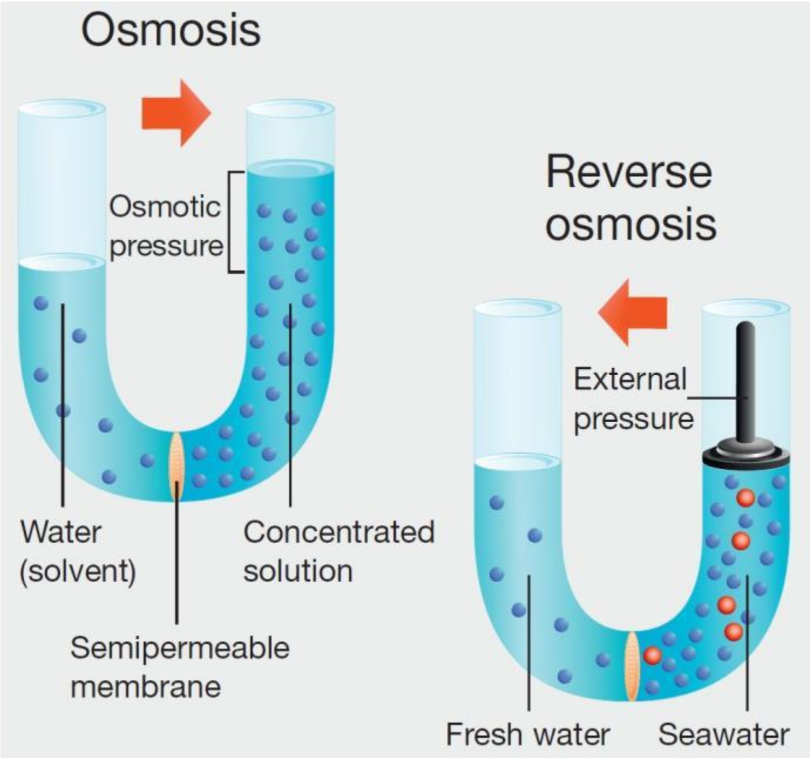


Disadvantages

- Organic matter, colloids and SiO_2 are not removed by ED system.
- Feedwater pre-treatment is necessary to prevent ED stacks fouling.
- Elaborate controls are required, and keeping them at optimum condition ca be difficult.
- Selection of materials of construction for membranes and stack is important to ensure compatibility with the feed stream.

Desalination - Reverse Osmosis

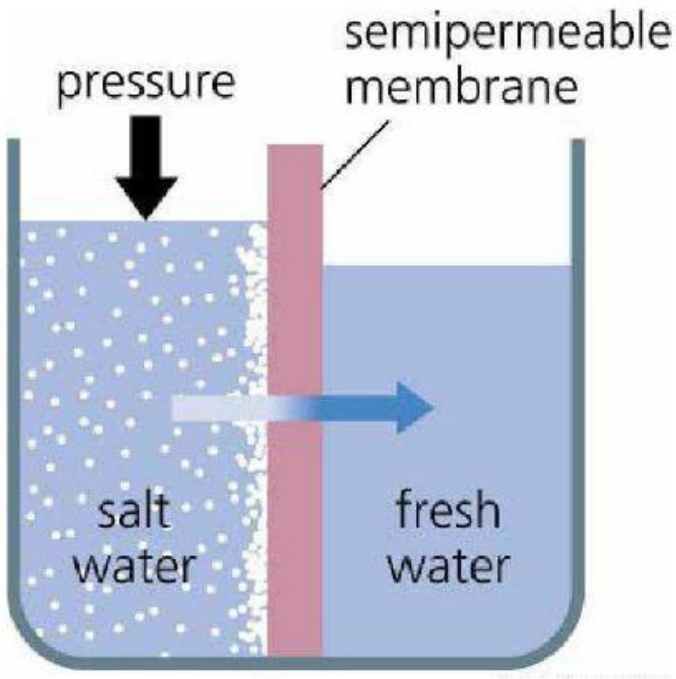
- Saltwater is forced through membrane sheets at high pressures (600 to 1200 psi)
- Membranes (Cellulose Acetate, Polyamide, Polymethylmethaacrylate) are designed to catch salt ions
- Process produces clean water and brine



Disadvantages

- It is a slow process and also wastes a large portion of the water that runs through the system
- High capital and operating cost Membranes are prone to fouling
- not applicable for concentrated solutions due to high pressure requirement
- High level of pretreatment is required in some cases
- RO removes minerals and ions that provide taste to the water and electrolytes important for human health

Sea Water Treatment – Reverse osmosis



The water present in sea water side is forced to pass through the membrane and enter into pure water side leaving behind all the impurities (like dissolved salts, organic impurities, etc.). Such a process of reversal of osmosis is called reverse osmosis.

Water Pollution

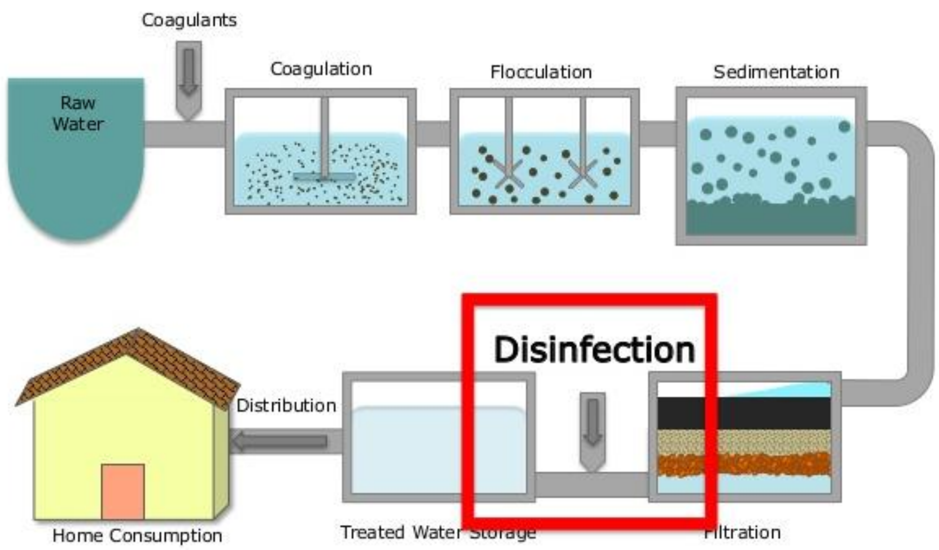
Categories of Contaminants

<u>Microbiological</u>
- Bacteria
- Virus
- Protozoa
- Helminths

<u>Physical</u>
- Turbidity
- Colour
- Odor
- Taste

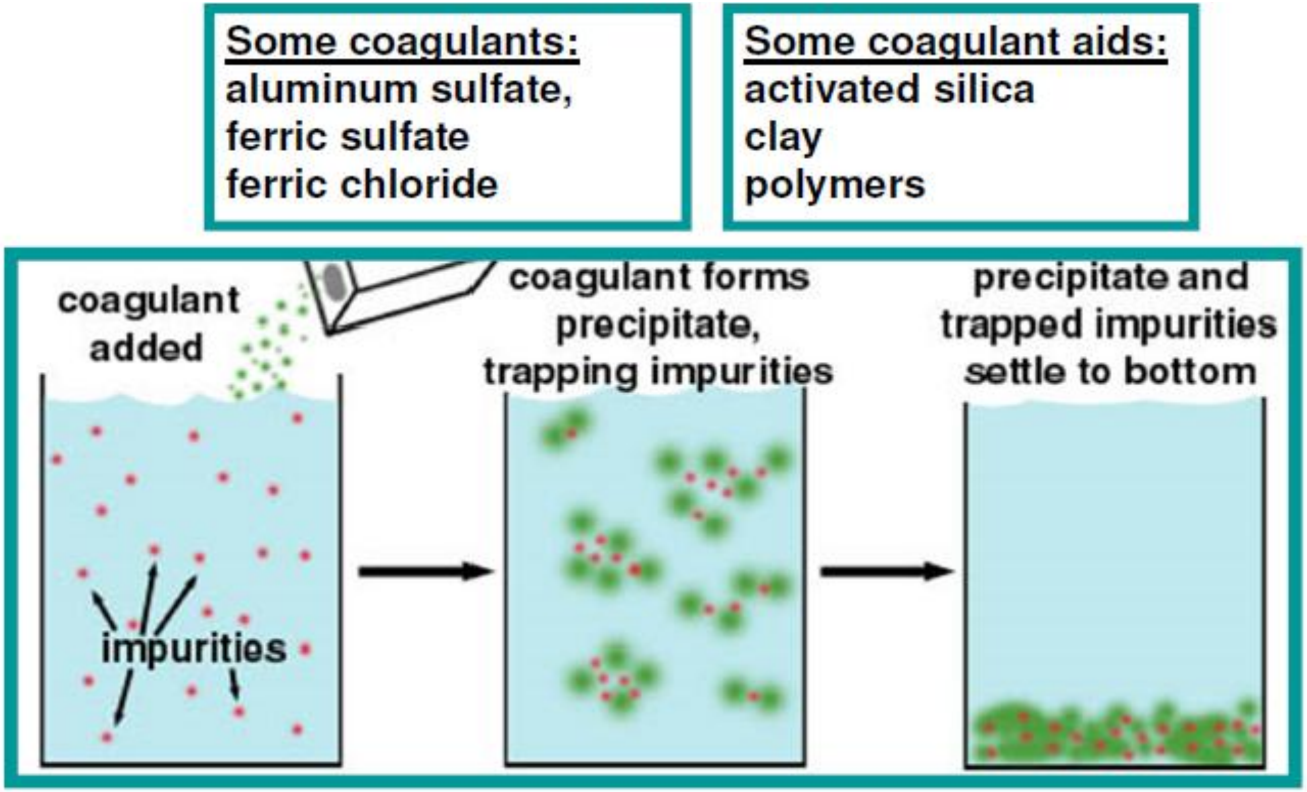
<u>Chemicals</u>
- Organic
- Inorganic
- pH

Conventional water treatment processes



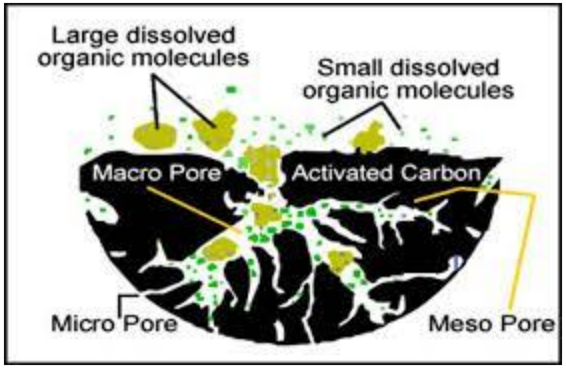
Process	Function
pre-sedimentation	solids removal
mixing, Coagulation, flocculation, settling	removal of ions, and solids using chemical addition
Filtration	removal of smaller particles
adsorption	removal of organic compounds and ions
disinfection	Inactivation or chemical killing of pathogens in water

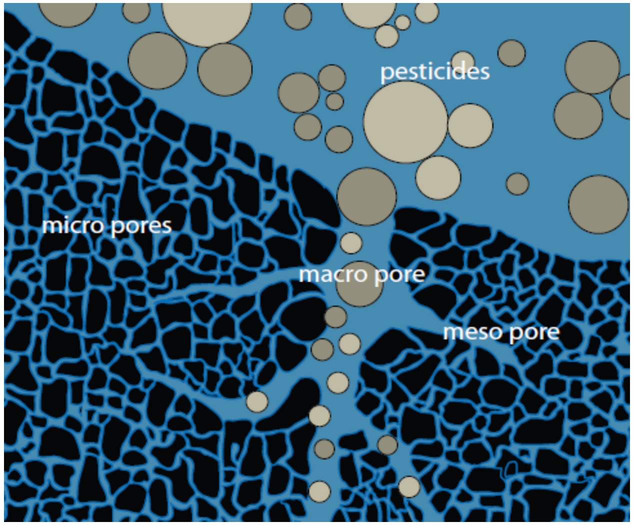
water treatment - Coagulation - Flocculation

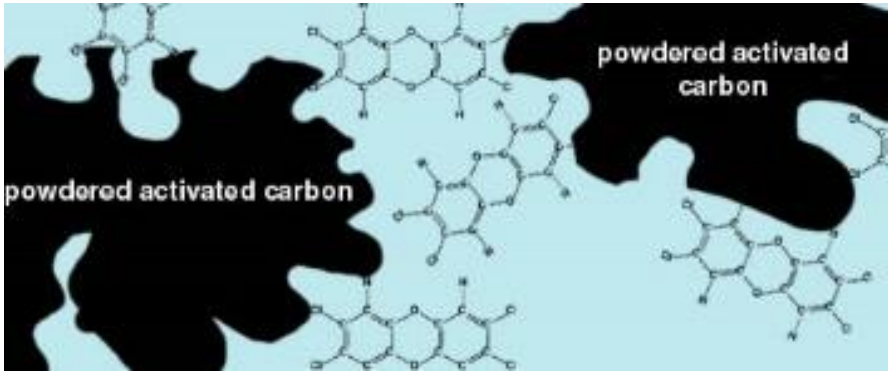


water treatment - Adsorption

A process called adsorption by which a variety of dissolved contaminants are attracted to and held (adsorbed) on the surface of the carbon particles. The characteristics of the carbon material (particle and pore size, surface area, surface chemistry, density, and hardness) influence the efficiency of adsorption.
Organic contaminants, unwanted coloring, and taste and- odor-causing compounds can stick to the surface of granular or powder activated carbon and are thus removed from the drinking water







Disinfection – Chlorination

Some common water-borne diseases prevented by disinfection

Bacterial - Typhoid fever, Para-typhoid, Bacterial diarrhea, Cholera etc

Virus – Hepatitis, Rotavirus diarrhea

Protozoan - Amoebiasis, Giardiasis, Crypto-sporidiasis

Physical agents: **heat, UV radiation**

Chemical agents: **chlorine, hypochlorites**, chloramine, chlorine dioxide, ozone, iodine, silver, salts of ammonium…

Chlorine Gas i.e. Cl_2 + Pure water

(a) <u>Hydrolysis</u> $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$

(b) <u>Ionisation</u> $HOCl \rightleftharpoons H^+ + OCl^-$

Hypochlorous acid — Hypochlorite Ion

$Cl_2 + NH_3$ (1 - 50 PPM)

$\downarrow$

NH_2Cl (Monochloramine)

$\downarrow$

$NHCl_2$ (Dichloramine)

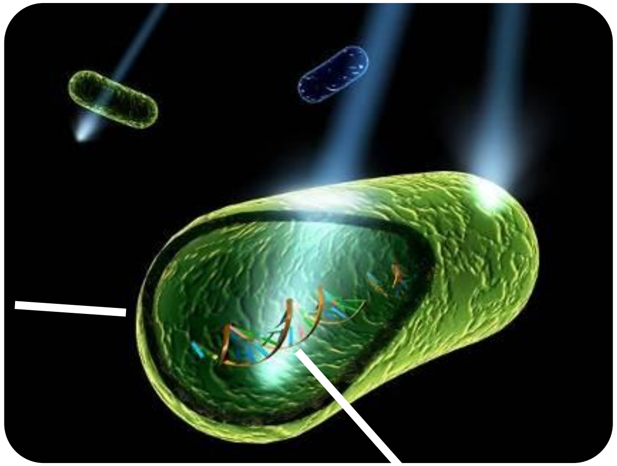
$\downarrow$

NCl_3 (Nitrogen trichloride)

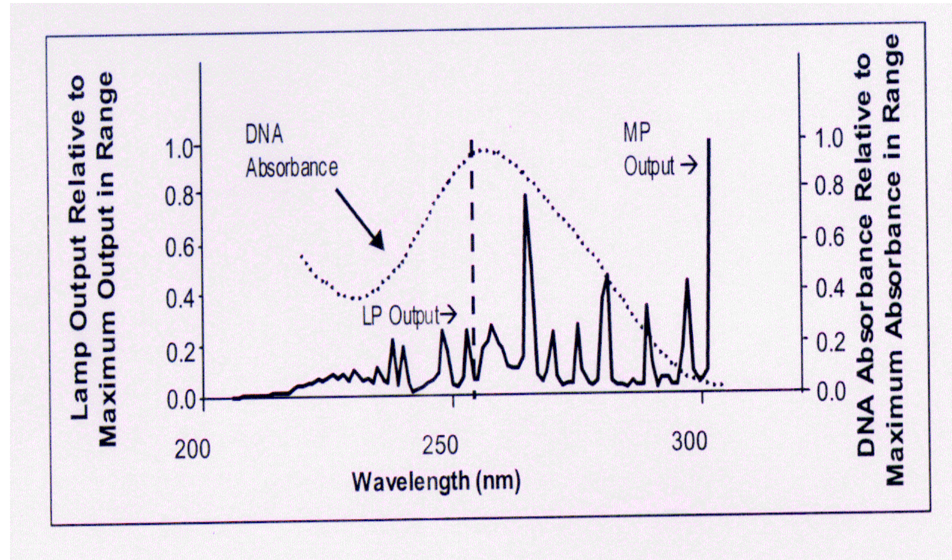
(Trichloramine)

Disinfection – UV light

Cell Wall



DNA Nucleic Acid



- UV light penetrates the cell wall
- The UV energy permanently alters the DNA structure of the microorganism
- The microorganism is “inactivated” and unable to reproduce or infect