Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

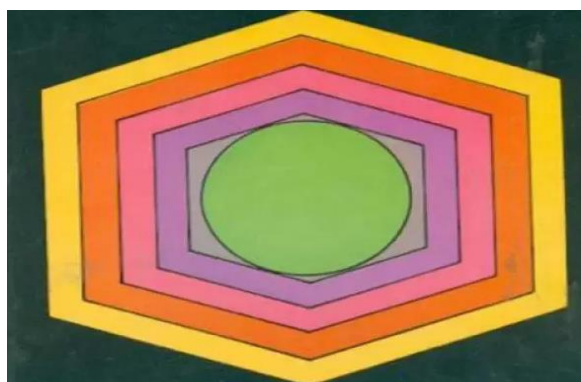# ENGINEERING CHEMISTRY –Simplified Approach
[MODULE 1 and 2]
Department of Chemistry
School of Advanced Science
Vellore Institute of Technology,Vellore

By
Dr.S.Karthikeyan
Dr.D.Raja Gopal
Dr.A.Siva Kumar

Authors : Dr.S.Karthikeyan ,Dr.D.Raja Gopal, Dr.A.Siva Kumar

Department of Chemistry,SAS

CHY1701 Engineering Chemistry   **Module 1 and 2**

WATER TECHNOLOGY & WATER TREATMENT

Introduction:

Water is nature's most wonderful, abundant, useful compound and is an essential without it one cannot survive.

It occupies a unique position in industries. Its most important use is as an engineering material in the *steam generation.*

Water is also used as c*oolant* in power and chemical plants.

It is also used in other fields such as production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, etc.

Occurrence:

Water is widely distributed in nature. It has been estimated that about 75% matter on earth's surface consists of water. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90-95% of water.

Sources of Water:

Different sources of water are:

1. Surface Waters: Rain water (purest form of natural water), River water, Lake Water, Sea water (most impure form of natural water).

2. Underground Waters: Spring and Well water. Underground waters have high organic impurity.
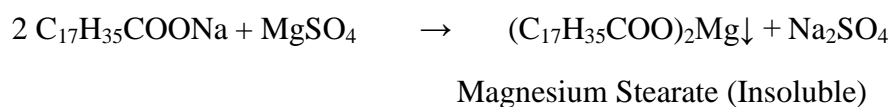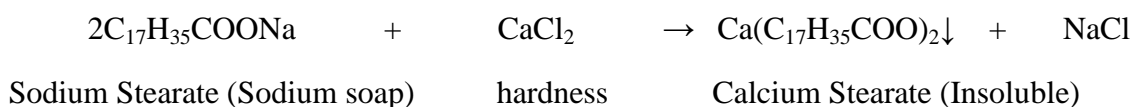
What is hardness of water ?

Hardness:-

Hardness of water is a characteristic property by which water "*prevents lathering of soap".* It is defined as the soap consuming capacity of water.

Causes:

- The hardness of water is due to presence of certain salts (mainly bicarbonates, sulphates and Chlorides) of Ca, Mg and few other heavy metal salts dissolved in water.

- A sample of hard water when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) do not produce lather with soap, but on the other hand forms a white scum or precipitate.

- The precipitate is formed due to insoluble soaps of Ca and Mg.

Reactions:-

$$2C_{17}H_{35}COONa \quad + \quad CaCl_2 \quad \rightarrow \quad Ca(C_{17}H_{35}COO)_2\downarrow \quad + \quad NaCl$$

Sodium Stearate (Sodium soap)   hardness   Calcium Stearate (Insoluble)

$$2\ C_{17}H_{35}COONa + MgSO_4 \quad \rightarrow \quad (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$$

Magnesium Stearate (Insoluble)

Thus the water which does not produce lather with soap solution readily is called **HARD WATER** and water which lathers easily on shaking with soap solution is called **SOFT WATER**.
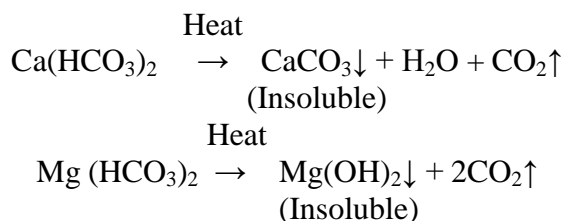
Carbonate and non-carbonate hardness of water

Types of hardness:

1. **Temporary** or **carbonate hardness**:-

   - It is caused by the presence of dissolved bicarbonates of Ca, Mg and other heavy metals and carbonate of Iron.

   - Temporary hardness is mostly destroyed by mere boiling of water i.e., when bicarbonates are decomposed, they yield insoluble carbonates or hydroxides, which are deposited as *'crust'* at the bottom of the vessel.

Reactions:-

$$Ca(HCO_3)_2 \quad \xrightarrow{Heat} \quad CaCO_3\downarrow + H_2O + CO_2\uparrow$$
(Insoluble)

$$Mg\ (HCO_3)_2 \quad \xrightarrow{Heat} \quad Mg(OH)_2\downarrow + 2CO_2\uparrow$$
(Insoluble)

2. PERMANENT or NONCARBONATE HARDNESS:-

- It is due to presence of chlorides and sulphates of Ca, Mg, Fe and other heavy metals.

- It is not destroyed upon boiling.

- It can be eliminated by different techniques like, Lime Soda process, Ion exchange process, Zeolite process, etc.

Total Hardness= Temporary Hardness + Permanent Hardness.
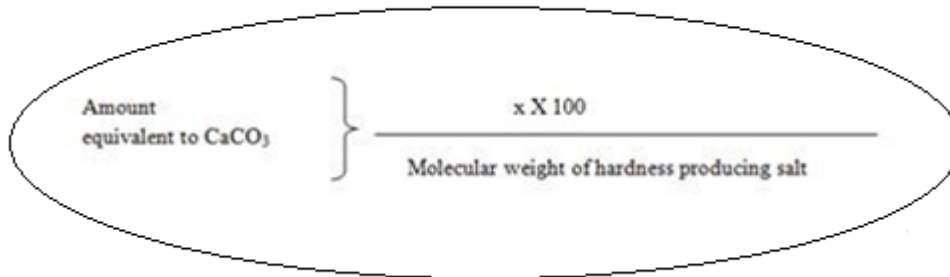
Expression of hardness of water

Equivalents of $CaCO_3$:-

- The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of $CaCO_3$.

   $CaCO_3$ is chosen as a standard because,

 i) Its molecular weight (100) and ii) equivalent weight (50) is a whole

number, so the Calculations in water analysis can be simplified.

$$\text{Amount equivalent to } CaCO_3 = \frac{x \times 100}{\text{Molecular weight of hardness producing salt}}$$

Where x $\longrightarrow$ Mass of hardness producing salt

Calculation of equivalents of CaCO₃:

Salt/ion	Molar mass	Chemical Equivalent Or Equivalent Weight	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	100/120
$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Ca(NO_3)_2$	164	82	100/164
$Mg(NO_3)_2$	148	74	100/148
HCO_3^-	61	61	100/122
OH^-	17	17	100/34
CO_3^{2-}	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al_2(SO_4)_3$	342	57	100/114
$FeSO_4.7H_2O$	278	139	100/278
H+	1	1	100/2
HCl	36.5	1	100/73

Units of hardness:-

1. Parts Per Million (ppm):- is the parts of $CaCO_3$ equivalent hardness per 10^6 parts of water i.e., 1ppm= 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

2. Milligrams Per Litre (mg/L):- number of milligrams of $CaCO_3$ equivalent hardness present per liter of water.

    1mg/L=1mg of $CaCO_3$ equivalent hardness of 1L of water= 1kg=1000g=10^6mg.

    ∴1mg/L=1mg of $CaCO_3$ eq per 10^6 mg of water=1ppm.

3. Clarke's degree (^{0}Cl):- the no. of grains (1/7000lb) of $CaCO_3$ equivalent hardness per gallon (10lb) of water or it is parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

    ∴1 ^{0}Cl= 1 grain of $CaCO_3$ eq hardness per gallon of water

    = 1 part of $CaCO_3$ hardness eq per 10^5 parts of water.

4. Degree French (^{o}Fr):- parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

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

5. Milli-equivalent per liter (meq/L):- is the number of milli-equivalents of hardness present per liter.

    1meq/L= 1meq of $CaCO_3$ per liter of water

    = 10^{-3}x 50 g of $CaCO_3$ eq. per liter

    = 50 mg of $CaCO_3$ eq. per liter = 50 mg/L of $CaCO_3$ eq. = 50ppm.

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1° Fr = 0.07 ^{o}Cl = 0.02 meq/L

1 mg/L = 1 ppm = 0.1 ^{o}Fr = 0.07 ^{o}Cl = 0.02 meq/L

1 ^{o}Cl = 1.433 ^{o}Fr = 14.3 ppm = 14.3 mg/L = 0.0286meq/L

1 ^{o}Fr = 10 ppm = 10 mg/L = 0.7 ^{o}Cl = 0.2 meq/L

1 meq/L = 50 mg/L = 50 ppm = 5 ^{o}Fr = 0.35 ^{o}Cl

Estimation of hardness of water by complexometric method.

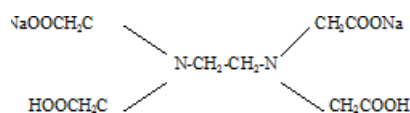*Estimation of temporary and permanent hardness:-*

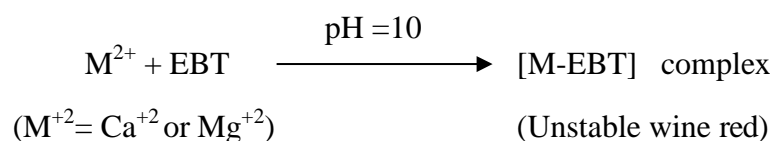a) *EDTA(Ethylene Di amine Tetra Acetic acid) Method:-*
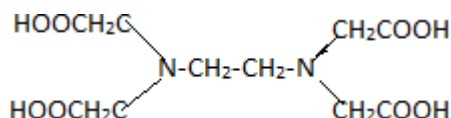
Principle:

This is a complexometric method. It is in the form of its sodium salt which yields the anion and this forms complex with Ca^{+2} and Mg^{+2} ions.

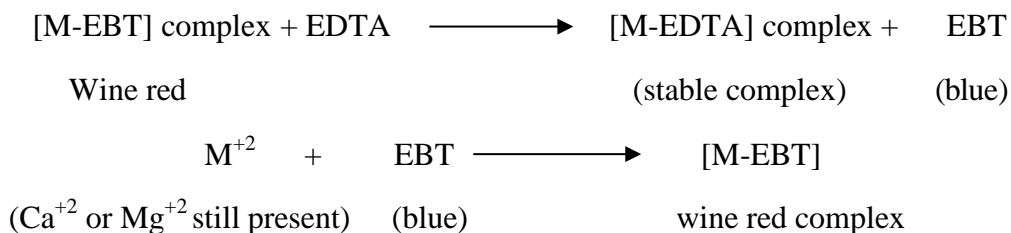(Molecular Wt. - 372.24, Equivalent Wt. - 186.14 i.e., M=2N)

In order to determine the equivalence point (i.e., just completion of metal-EDTA complex formation) indicator **Eriochrome Black-T** (**EBT)** an alcoholic solution of blue dye is employed which forms an unstable *wine red* complex with Ca^{+2} and Mg^{+2} ions. The indicator is effective at about pH 10.

When EBT is added to hard water, buffered to a pH of about 10 (employing NH_4OH-NH_4Cl buffer), a wine red unstable complex is formed. Thus,

$$M^{2+} + EBT \xrightarrow{\text{pH} =10} \text{[M-EBT]} \quad \text{complex}$$

$$(M^{+2}= Ca^{+2} \text{ or } Mg^{+2}) \qquad\qquad \text{(Unstable wine red)}$$

During the course of titration against EDTA solution, EDTA combines with M^{+2} (or Ca^{+2} or Mg^{+2}) ions from stable complex M-EDTA and releasing free EBT, which instantaneously combines with M^{+2} ions still present in the solution, thereby wine red color is retained. Thus, titration

$$\text{[M-EBT] complex} + EDTA \longrightarrow \text{[M-EDTA] complex} + \quad EBT$$

Wine red   (stable complex)   (blue)

$$M^{+2} \quad + \quad EBT \longrightarrow \text{[M-EBT]}$$

$(Ca^{+2}$ or Mg^{+2} still present)   (blue)   wine red complex

When nearly all M^{+2} (Ca^{+2} or Mg^{+2}) ions have formed [M-EDTA] complex, then next drop of EDTA added drop wise displace the EBT indicator from [M-EBT] complex and <u>wine red</u> color changes to <u>blue</u> color (due to EBT).

Thus at equivalence point,

[M-EBT] complex + EDTA $\longrightarrow$ [M-EDTA] complex + EBT
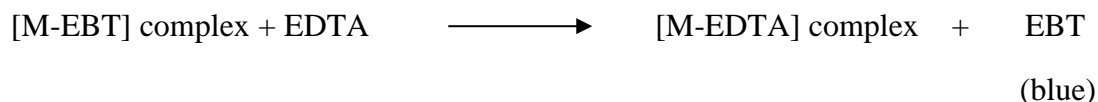
(blue)

Thus, change of **wine red** to **blue** color marks the **end point** of titration.

Steps involved:

1. *Preparation of Standard Hard Water*: Dissolve 1gm of pure dry $CaCO_3$ in minimum quantity of dil. HCl and then evaporate the solution to dryness on water bath. Dissolve the residue n distilled water to make 1L solution. Each 1ml of this solution contains 1mg of $CaCO_3$ hardness.

2. *Standardization of EDTA solution*: Rinse and fill the burette with EDTA solution. Pipette out 50ml of standard hard water in a conical flask. Add 10-15ml of buffer solution and 4 drops of indicator. Titrate with EDTA solution till wine red color changes to clear blue. Let the volume used be V_1ml.

3. *Titration of Unknown Hard Water*: Titrate 50ml of water sample just in step5. Let the volume used be V_2ml.

4. *Titration of Permanent Hardness*: Take 250ml of water sample in a large beaker. Boil till the volume is reduced to about 50ml (all the bicarbonates are decomposed into insoluble $CaCO_3+Mg(OH)_2$). Filter, wash the precipitate with distilled water collecting filtrate and washings in a 250 ml measuring flask. Finally make up the volume to 250ml with distilled water. Then titrate 50ml of boiled water sample just as in step 5. Let the volume used be V_3ml.

Calculations:

50 ml of standard hard water = V_1 ml of EDTA.

$\therefore$ 50 x 1mg of $CaCO_3$ = V_1 ml of EDTA

$\therefore$ 1ml of EDTA = $50/V_1$ mg of $CaCO_3$ eq.

50 ml of given hard water = V_2 ml of EDTA.

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

$\therefore$1L (1000ml) of given hard water = $\frac{V_2 \times 1000}{V_1}$mg of $CaCO_3$ eq.

Total Hardness of water = 1000 V_2/V_1 mg/l

$\qquad\qquad$ = 1000 V_2/V_1 ppm.

Now 50ml of boiled water = V_3 ml of EDTA.

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$$= \frac{V_3 \times 1000}{V_1} \text{ mg of } CaCO_3 \text{ eq.}$$

∴1L(1000ml) of boiled water = $1000V_3/V_1$ mg of $CaCO_3$ eq

∴ Permanent hardness = $1000V_3/V_1$ ppm.

Temporary Hardness= total hardness- permanent hardness

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

Advantages of EDTA method:

This method is preferable because of 1) greater accuracy,

2) Convenience,

3) More rapid procedure.

Numerical Problems based on hardness of water:-

1. Calculate the temporary and permanent hardness of water sample containing $Mg(HCO_3)_2$= 7.3mg/L, $Ca(HCO_3)_2$= 16.2mg/L, $MgCl_2$= 9.5mg/L, $CaSO_4$=13.6mg/L).

Solution: conversion into $CaCO_3$ equivalents:

Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 7.3mg/L	100/146	7.3X100/146= 5mg/L
$Ca(HCO_3)_2$= 16.2mg/L	100/162	16.2X100/162=10mg/L
$MgCl_2$= 9.5mg/L	100/95	9.5X100/95= 10mg/L
$CaSO_4$=13.6mg/L	100/136	13.6X100/136= 10mg/L

∴ Temporary hardness of water due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ =

=5+10=15mg/L or 15ppm.

Permanent hardness due to $MgCl_2$ and $CaSO_4$ = 10+10=20mg/L or 20ppm.

2. Calculate the temporary and total hardness of a water sample containing $Mg(HCO_3)_2$= 73mg/L, $Ca(HCO_3)_2$= 162mg/L, $MgCl_2$= 95mg/L, $CaSO_4$=136mg/L.

Solution: calculation of $CaCO_3$ equivalents:

Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 73mg/L	100/146	73X100/146= 50mg/L
$Ca(HCO_3)_2$= 162mg/L	100/162	162X100/162=100mg/L

MgCl$_2$= 95mg/L	100/95	95X100/95= 100mg/L
CaSO$_4$=136mg/L	100/136	136X100/136= 100mg/L

∴ Temporary hardness of water due to Mg(HCO$_3$)$_2$ and Ca(HCO$_3$)$_2$ =

=100 + 50=150mg/L or ppm.

Total hardness of water= 50+100+100+100=350 mg/L or ppm.

3. 50ml of a sample water consumed 15ml of 0.01 EDTA before boiling and 5ml of the same EDTA after boiling. Calculate the degree of hardness, permanent hardness and temporary hardness.

Solution: 50ml of water sample = 15ml of 0.01M EDTA

$= \underline{15x100}$ ml of 0.01EDTA=300ml of 0.01M EDTA
     50

  = 2x300ml of 0.01 N EDTA (Molarity of EDTA=2xNormality of EDTA)

  = 600 ml or 0.6 L of 0.01 eq. of CaCO$_3$.

  = 0.6x0.01x50 gCaCO$_3$ eq.

Hence total hardness= 0.30g or 300mg of CaCO$_3$ eq= 300mg/L or ppm.

Now 50ml of boiled water = 5ml of 0.01M EDTA

∴1000ml of boiled water= $\underline{5x1000}$ ml of 0.01M EDTA
                              50

                = 100mL of 0.01M EDTA

                = 200mLor 0.2 L of 0.01N EDTA

                = 0.2x0.01x50g of CaCO$_3$ eq

                = 0.1g or 100mg of CaCO$_3$ eq

Hence permanent hardness = 100mg/L or ppm

∴Temporary hardness= 300-100=200ppm.

4. 0.5g of CaCO$_3$ was dissolved in HCl and the solution made up to 500ml with distilled water. 50ml of the solution required 48ml of EDTA solution for titration. 50ml of hard water sample required 15ml of EDTA and after boiling and filtering required 10ml of EDTA solution. Calculate the hardness.

Solution: 500ml of SHW = 0.5g or 500mg CaCO$_3$ eq

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∴1ml SHW= 1mg $CaCO_3$ eq

Now 48ml of EDTA solution = 50/48 mg $CaCO_3$ eq

∴1ml of EDTA solution= 50/48 mg $CaCO_3$ eq

Calculation of the total hardness of water:

50ml hard water = 15ml EDTA = 15x50/48 mg of $CaCO_3$ eq

∴1000ml of hard water= $\underline{15.625 \times 1000}$ = 312.5 mg $CaCO_3$ eq

$$50$$

Hence total hardness= 312.5mg/L or 312.5 ppm.

Why is hard water harmful to boilers?

Boiler feed water:

- A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat.

- Water is mainly used in boilers for the generation of steam(for industries and power houses).   A boiler feed water should correspond to the following composition:

1. Its hardness should be below 0.2 ppm.

2. Its caustic alkalinity (due to OH^-) should lie in between 0.15ppm to 0.45ppm.

3. Its soda alkalinity (due to Na_2CO_3) should lie in between 0.45ppm to 1ppm.

Essential requirements of boiler feed water:

1. Hardness causing and scale forming constituents like salts of calcium and magnesium. This is because scale formation would result in wastage of fuel, lowering of boiler safety, decrease in efficiency and danger of explosion.

2. Caustic alkali to avoid caustic embrittlement.

3. Dissolved gases like oxygen, carbon dioxide etc. in order to prevent boiler corrosion.

4. Turbidity, oil etc. to reduce the tendency for priming and foaming.

Hence water must be softened before use in boilers.

BOILER TROUBLES:

Scale and sludge formation:

- In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively.

- When the dissolved salts concentration increases and reaches saturation point, they are thrown out of water in the form of precipitates on the inner wall of the boiler.

- If the precipitation takes place in the form of loose and slimy precipitate it is called *sludge*.

- If the precipitated matter forms a hard adhering crust or coating on the inner walls of the boiler, it is called *scale*.

SLUDGE: It is a soft, loose and slimy precipitate formed within the boiler.

Reasons:

- It is formed at comparatively <u>colder portions</u> of the boiler and collects where the flow of water rate is slow or at bends.

- Sludge's are formed by substances which have greater solubility's in hot water than in cold water. Eg; $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

Disadvantages:

- Sludge's are poor conductor of heat which tends to waste a portion of heat generated.

- If sludge's are formed along with scales, then sludge gets entrapped in the latter and both get deposited as scales.

- Sludge formation disturbs the working of the boiler as it settles in the region of poor water circulation such as pipe connection; plug opening, guage-glass connection thereby causing even choking of the pipes.
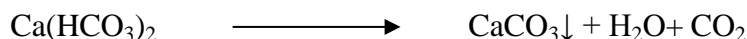
Prevention:

- ✓ By using well softened water

- ✓ By frequent **"Blow Down" operation** i.e., drawing off a portion of the concentrated water.

Sludge   Scale

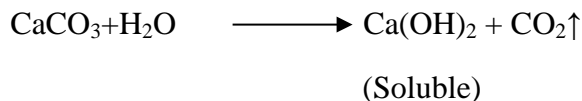Heat   Heat
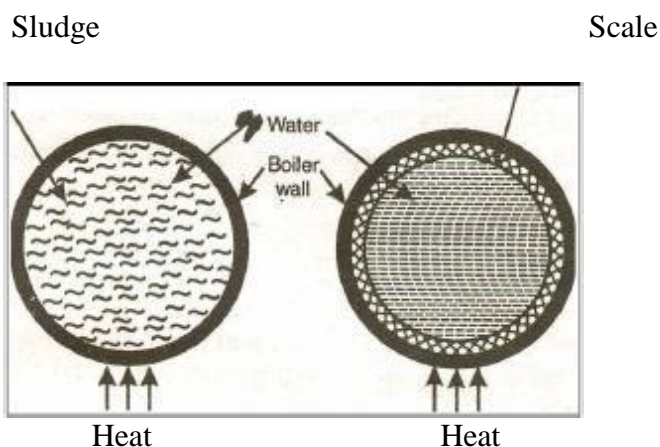
SCALES: These are hard deposits which stick firmly to the inner surfaces of the boiler. These are difficult to remove.

Formation of Scales:

1. *Decomposition of $Ca(HCO_3)_2$:-*

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

The formation of $CaCO_3$ scale is soft and is the main cause of scale formation in low pressure boiler. In high pressure boilers, $CaCO_3$ is soluble.

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

(Soluble)

2. *Deposition of $CaSO_4$:-*

The solubility of $CaSO_4$ in water decreases with rise in temperature i.e., $CaSO_4$ is soluble in cold water but completely insoluble in super-heated water. $CaSO_4$ gets precipitated as hard scale on the heated portions of the boiler. This is the main cause of scales in high pressure boilers.

3. *Hydrolysis of Magnesium Salts:-*

The Mg salts dissolved undergo hydrolysis at high temperature forming $Mg(OH)_2$ precipitate which forms a soft type of scale.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2HCl\uparrow$$

(scale)

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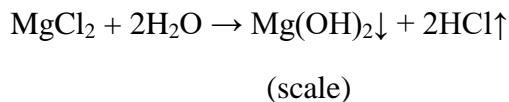
4 *Presence of Silica:-*

Silica present in small quantities deposits as calcium silicate ($CaSiO_3$) or $MgSiO_3$. These deposits stick very firmly and are very difficult to remove. Important source of silica in water is the sand filter.

Disadvantages:

1. Wastage of fuel: Scales have a low thermal conductivity so rate of heat transfer from boiler to inside water is greatly decreased due to which excessive or over heating is done and this causes increase in fuel consumption.

The wastage of fuel depends upon the thickness and nature of scale as:

Thickness (mm)) 0.325 0.625 1.25 2.5 12

Wastage of fuel 10% 15% 50% 80% 150%

2. Lowering of boiler safety: the overheating of boiler tube makes boiler softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of steam especially in high pressure boilers.

3. Decrease in Efficiency: scales may deposit in the valves and condensers of the boilers and choke them partially. This results in decrease in efficiency of the boiler.

4. Danger of explosion: the thick scales formed if cracked due to uneven expansion the water comes suddenly in contact with overheated iron plates. This causes infiltration of a large amount of steam suddenly, so sudden high pressure is developed which causes explosion of boiler.

Removal of Scales:-

- ✓ If scales are loosely adhering they can be removed with the help of scrapper or wire brush or piece of wood.

- ✓ By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water) if they are brittle.

- ✓ If the scales are hard and adhering, then dissolving them and by adding chemicals. For Eg. $CaCO_3$ scales are dissolved by using 5-10% of HCl and $CaSO_4$ scales can be dissolved by adding EDTA with which they form soluble complexes.

- ✓ By frequent blow-down operation if scales are loosely adhering.

Prevention of scales:

1) External Treatment: includes efficient 'softening of water' (i.e. removing hardness producing constituents of water) which is discussed separately.

2) Internal Treatment: includes softening of water by adding a proper chemical to the boiler water. It is discussed in softening methods.

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Distinguish between scales and sludges

S.No	Sludge	Scale
1.	They are soft, loose and slimy precipitate.	They form hard deposits.
2.	They form non-adherent deposits and can be easily removed.	They stick firmly to the inner surface of the boiler and are very difficult to remove.
3.	They are formed by substances like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$, etc.	They are formed by substances like $CaSO_4$, $Mg(OH)_2$, etc.
4.	They are formed at comparatively colder portions of the boiler.	They are formed at heated portions of the boiler.
5.	They decrease efficiency of boiler but are less dangerous.	They decrease efficiency of boiler and chances of explosion are also there.
6.	They can be removed by blow down operation.	They can't be removed by blow down operation.

Caustic embrittlement:-

- The phenomenon in which the boiler materials becomes brittle due to the accumulation of caustic substances is known as "Caustic Embrittlement"

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

- During softening process by Lime-Soda process, free Na_2CO_3 is usually present in small proportion.

- In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2 and this makes the boiler water '*caustic*'.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$
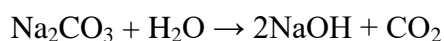
- The NaOH containing water flows into minute hair cracks always present in inner side of boiler by capillary action.

- Here water evaporates and the dissolved caustic soda concentration increases progressively.

- This caustic soda attacks the surrounding area, thereby dissolving iron of the boiler as sodium ferroate. This causes embrittlement of boiler parts (like bends, joints, etc.,) causing even failure of the boiler.

- Caustic cracking can be explained by considering the following concentration cell:

    -

Iron at rivets, bends, joints, etc.	concentrated NaOH solution	Dilute NaOH solution	Iron at plane surfaces

- The iron surrounded by dil. NaOH becomes the cathodic side; while the iron in contact with con. NaOH becomes anodic part; which is consequently dissolved or corroded.

Prevention of caustic embrittlement:

Caustic embrittlement can be avoided:

✓ By using Na_3PO_4 as softening reagent instead of Na_2CO_3.

✓ By adding tannin or lignin to boiler water since these block the hair cracks there by preventing infiltration of caustic soda solution in these.

✓ By adding Na_2SO_4 to boiler water. Na_2SO_4 is added to boiler water so that the ratio $\dfrac{Na_2\,SO_4\ Concentration}{NaOH\ Concentration}$ is kept as 1:1:2:1 and 3:1 in boilers working respectively at pressures up to 10, 20 and 30 atmospheres.

Disadvantages of caustic embrittlement:

The cracking or weakening of the boiler metal causes failure of the boiler.

Priming and foaming:

Priming:

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along with the steam. This process of *'wet steam'* formation is known as **'Priming'**.

Causes:

Priming is caused by:

1. The presence of large amount of dissolved salts

2. High steam velocities

3. Sudden boiling
4. Improper boiler design

5. Sudden increase in steam production rate.

Prevention:

✓ By fitting mechanical purifiers

✓ Avoiding rapid change in steam rate

✓ Maintaining low water levels in boilers

✓ Effective softening and filtration of boiler feed water

✓ Blow down of the boiler.

Foaming:

The phenomenon of formation of *persistent foam or bubbles* on the surface of water inside the boiler, which do not break easily is called as foaming.

Causes:

1. Pure water has very little foaming whereas the water containing dissolved impurities and suspended matter has a greater tendency to produce foam.

2. The presence of large quantity of suspended impurities and oils lowers the surface tension producing foam.

Prevention:

✓ Adding antifoaming chemicals like castor oil.

✓ Besides castor oil, Gallic acid and tannic acids, corn oil, cotton seed oil, sperm oil, bees wax, etc., are also used as antifoaming agents.

✓ Blow down operation of the boiler can prevent foaming.

✓ Removing oil form boiler water by adding compounds like sodium aluminate.

Disadvantages of Priming and Foaming:

Priming and Foaming usually occur together. They are objectionable because:-

1. The dissolved salts in boiler water are carried by the wet steam to super heater and turbine blades where they get deposited and reduce the efficiency.

2. The dissolved salts enter the parts of other machinery where steam is used thereby decreasing the life of machinery.

3. The actual height of the water column cannot be judged thereby making the maintenance of boiler pressure becomes difficult.
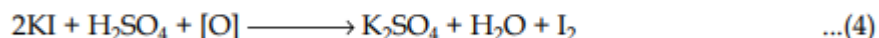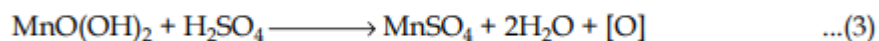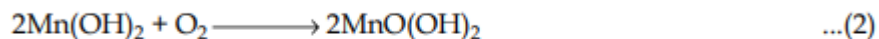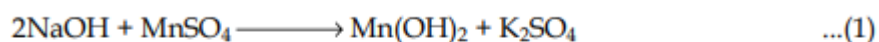
Measurement of Dissolved oxygen by Winkler's method

Dissolved oxygen (DO) determination measures the amount of dissolved (or free) oxygen present in water or wastewater. Aerobic bacteria and aquatic life such as fish need dissolved oxygen to survive. If the amount of free or DO present in the wastewater process is too low   (< 3 ppm) , the aerobic bacteria that normally treat the sewage will die. If DO content is above 8 ppm, it leads to corrosion in high pressure boilers.

 DO is determined by the Iodometric titration   developed by Winkler.

1. Dissolved molecular oxygen in water is not capable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used. Mn(OH)2 is produced by the action of KOH on MnSO4.

2. Mn(OH)2 so obtained reacts with dissolved molecular oxygen to form a brown precipitate of basic manganic oxide, MnO(OH)2.

3. MnO(OH)2 then reacts with concentrated sulphuric acid to liberate nascent oxygen.

4. Nascent oxygen results in oxidation of KI to I2.

5. This liberated iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator.

6. Thiosulphate reduces iodine to iodide ions and itself gets oxidized to tetrathionate ion. (Refer the reactions below.)

Reactions

$$2NaOH + MnSO_4 \longrightarrow Mn(OH)_2 + K_2SO_4 \qquad ...(1)$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2 \qquad ...(2)$$

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O] \qquad ...(3)$$

$$2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + H_2O + I_2 \qquad ...(4)$$

$$I_2 + I^- \longrightarrow I_3^- \qquad ...(5)$$

$$2S_2O_3^{2-} + I_3^- \longrightarrow 3I^- + S_4O_6^{2-} \qquad ...(6)$$

Boiler corrosion:

- The decay of boiler material by chemical or electrochemical attack by its environment is known as "**Boiler corrosion**".

- The main reasons for boiler corrosion are:-

Dissolved Oxygen: water contains usually about 8ml of dissolved oxygen per liter at room temperature.
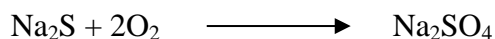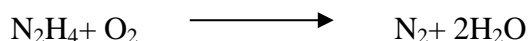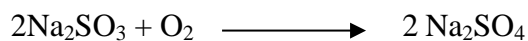
Disadvantages of dissolved oxygen:

In presence of prevailing high temperature, the dissolved Oxygen attacks boiler material as follows:

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2\downarrow$$

$$4Fe(OH)_2\downarrow + O_2 \longrightarrow 2[Fe_2O_3.2H_2O]\downarrow \text{ (rust)}$$
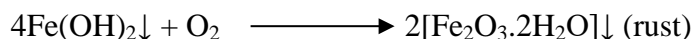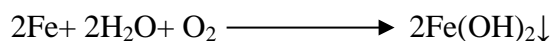
Removal of dissolved Oxygen:

1) By adding calculated quantity of Sodium sulphite (Na_2SO_3) or hydrazine(N_2H_4) or sodium sulphide (Na_2S).

$$2Na_2SO_3 + O_2 \longrightarrow 2\ Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

Hydrazine is an ideal internal treatment chemical for the removal of dissolved oxygen.

Azamina 8001-RD (a polyvalent organic compound) has been employed for degassing water in minimum time.

2) By Mechanical de-aeration i.e., spraying water through a perforated plate fitted in degasification tower, heated from sides and connected to a vacuum pump as shown in the figure.
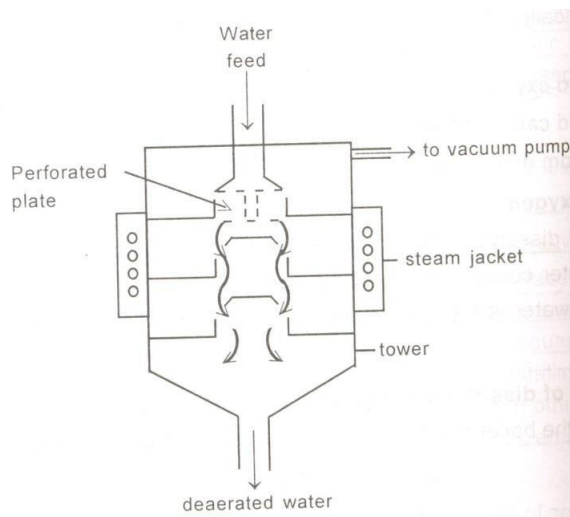
High temperature, low pressure and large exposed surface (provided by perforated plates) reduce the dissolved oxygen in water.

3) Dissolved Carbon dioxide: has a slow corrosive effect on the materials of boiler plate.

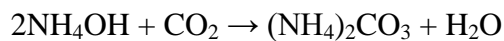Under the high temperature and pressure the bicarbonates decompose to produce CO2.

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2\uparrow$$
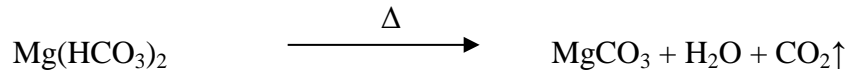
Disadvantages of CO$_2$:

It has slow corrosive effect on boiler plates by producing the carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Removal of CO$_2$:

By adding calculated amount of ammonia.

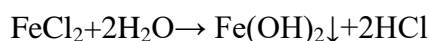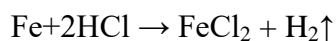$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

By mechanical deaeration process along with oxygen.

Acids from dissolved salts: *water* containing dissolved Mg salts liberate acids on hydrolysis.

Ex: $MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 \downarrow + 2HCl$
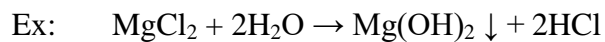
Disadvantages of acids:

The acids react with the iron of boiler plate in a chain reaction producing HCl again and again.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2\downarrow + 2HCl$$

Presence of even a small amount of $MgCl_2$ will have corrosion of iron to a large extent.

Prevention of acid corrosion:

✓ By softening of boiler water to remove $MgCl_2$ from the water.

✓ By frequent blow down operation.

✓ Addition of inhibitors to form a thin film on the surface of the boiler protecting the metal from attack. Sodium silicates, sodium phosphates and sodium chromate acts as good corrosion inhibitors.

Softening   methods:

The process of removing hardness-producing salts from water is known as softening of water.

> **1)**   **Internal treatment**
>
> **2)**   **External treatment**

Water used for industrial purposes should be sufficiently pure. It should therefore be freed from hardness producing salts before use.

The process of removing hardness producing salts from water is known as *'Softening'* of water.

1) *Internal treatment: (sequestration)*

- In this process, an ion is prohibited to exhibit its original character by *complexing* or converting into other more soluble salt by adding appropriate agent.

- An internal treatment is accomplished by adding a proper chemical to the boiler water either:

   i) To precipitate the scale forming impurities in the form of sludges which can be removed by blow-down operation   or

   ii) To convert them into compounds which will stay in the dissolved form in water, and thus do not cause harm.

The important internal conditioning /treatment methods are:

1) Phosphate Conditioning:

In high pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water, forming non-adherent and easily removable, soft sludge of Ca and Mg phosphates which can be removed by blow-down operation.

$$Eg.\ 3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$$
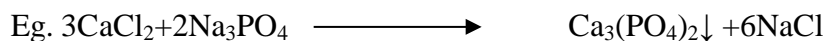
The main phosphates employed are

1. NaH_2PO_4: sodium dihydrogen phosphate(acidic)

2. Na_2HPO_4: disodium hydrogen phosphate(weakly alkaline)

3. Na_3PO_4: trisodium phosphate(alkaline)

The choice of salt depends upon the alkalinity of boiler feed water.
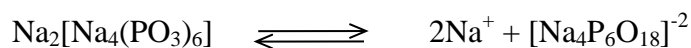
2) Carbonate Conditioning:

In low pressure boilers, scale formation can be avoided by adding Sodium carbonate to boiler water, when $CaSO_4$ is converted to $CaCO_3$ in equilibrium.

21

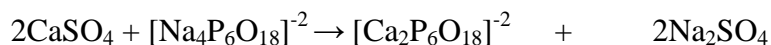$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$$
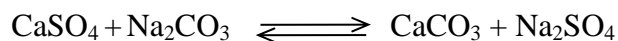
3) Calgon Conditioning:

Involves adding calgon (sodium hexa meta phosphate $(NaPO_3)_6$) to boiler water.

It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

$$Na_2[Na_4(PO_3)_6] \rightleftharpoons 2Na^+ + [Na_4P_6O_{18}]^{-2}$$

(Sodium hexa meta phosphate)

$$2CaSO_4 + [Na_4P_6O_{18}]^{-2} \rightarrow [Ca_2P_6O_{18}]^{-2} + 2Na_2SO_4$$

(Soluble complex ion)

2) External treatment:

Involves Lime-Soda, Zeolite, Ion-exchange process.

a) Lime-Soda process:

In this process, **lime** [$(Ca(OH)_2)$] and **soda** [Na_2CO_3] are the reagents used to precipitate the dissolved salts of Ca^{+2} and Mg^{+2} as $CaCO_3$ and $Mg(OH)_2$ which are later on filtered off.

Lime reacts with temporary hardness causing salts, Mg permanent hardness, CO_2, acids, bicarbonates and alums.

Lime cannot remove permanent hardness which should be removed by soda.

Precautions to be followed during process:

Only calculated amounts of lime and soda must be added. Excess of lime-soda causes boiler troubles like corrosion and caustic embrittlement.

The chemical reactions of lime and soda are slow and the precipitates $CaCO_3$ and $Mg(OH)_2$ are very fine.

Proper time must be given for the reactions of softening process to complete, because all the reactions of the process are slow.
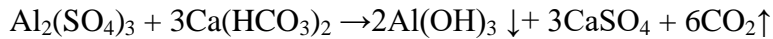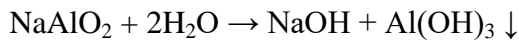
Cold lime soda process:

Calculated amounts of lime and soda are mixed with water at room temperature.

The precipitates formed are finely divided which do not settle down and can"t be filtered easily.

So, it is essential to add small amounts of coagulants (like alum, aluminium sulphate, sodium aluminate) which hydrolyse to flocculent, gelatinous precipitate of $Al(OH)_3$ and entraps the precipitate.

Use of sodium aluminate as **Coagulant** also helps in the removal of silica as well as oil present in the water.

Cold lime soda process provides water containing residual hardness of 50-60 ppm.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$$

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

Method:

Raw water and calculated quantities of chemicals (lime+soda+coagulant) are fed from the top into inner vertical circular chamber fitted with a vertical rotating shaft carrying a number of paddles.

As the raw water and chemicals flow down, there is vigorous stirring and continuous mixing whereby softening of water takes place.

The heavy sludge settles down in the outer chamber by the time softened water reaches up.

The softened water then passes through a filtering media (made of wood fibres) to ensure complete removal of sludge.

Filtered soft water finally flows out continuously through the outlet at the top and sludge settling at the bottom of the outer chamber is drawn off occasionally.

Hot Lime Soda Process:

It involves treating water with softening chemicals at a temperature of 80^0-150^0 C. Since hot process is operated at a temperature close to the boiling point of the solution,
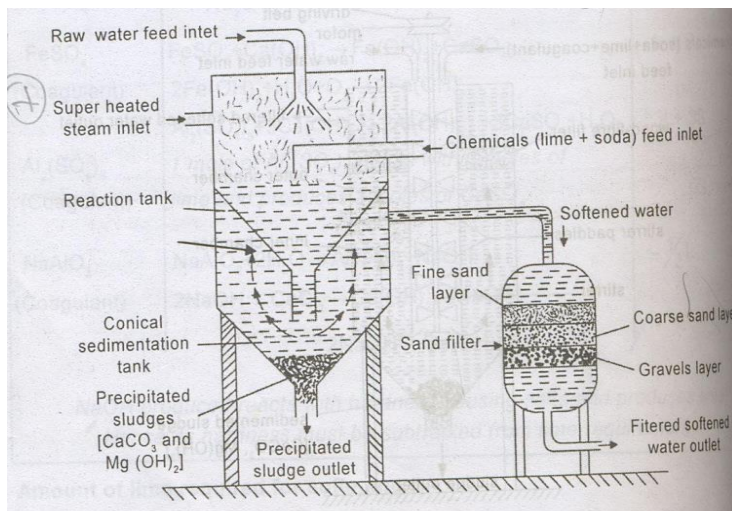
a) The reaction proceeds faster,

b) Softening capacity of hot process is increased,

c) The precipitate and sludge formed settle down rapidly and hence no coagulants are needed,

d) Much of the dissolved gases (CO2) are driven out,

e) Viscosity of softened water is lower so filtration of water becomes much easier.

Hot lime soda process produces water of residual hardness of 15-30ppm.

Process:

It contains essentially three parts

1) A *reaction tank* in which water, chemical and steam are thoroughly mixed.

2) A *conical sedimentation vessel* in which sludge settle down.

3) A *sand filter* which ensures complete removal of sludge from the softened water.

Advantages of Lime-Soda process:

1) It is very economical.

2) The process increases the pH value of treated water thereby corrosion of distribution pipes is reduced.

3) Besides removal of hardness causing salts, minerals, iron and manganese present in water is removed.

4) Due to alkaline nature, amount of pathogenic bacteria in water is considerably reduced.
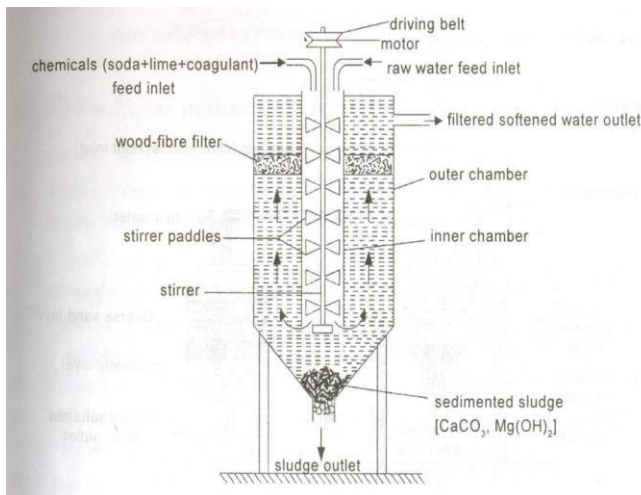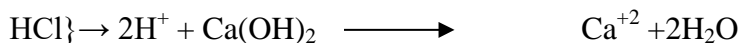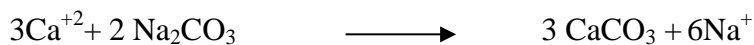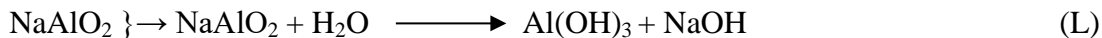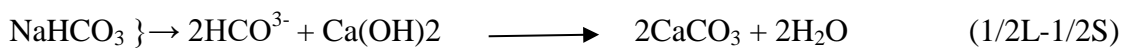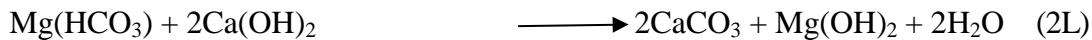
Disadvantages Of Lime-Soda Process:

1) Skilled supervision is required for efficient and economical softening.

2) Disposal of large amounts of sludge poses a problem.

3) This can remove hardness only up to 15ppm, which is not good for boilers.

Differences between cold and hot lime soda process.

S.No	Cold Lime Soda Process	Hot Lime Soda Process
1.	It is done at room temperature.	It is done at elevated temperatures (84-100 ^{0}C).
2.	It is slow process.	It is rapid process.
3.	Use of coagulants is must.	Coagulants are not needed.
4.	Filtration is not easy.	Filtration is easy as viscosity of water becomes low at elevated temperatures.
5.	Softened water has residual hardness around 60 ppm.	Softened water has residual hardness around 15-30 ppm.
6.	Dissolved gases are not removed.	Dissolved gases such as CO_2 are removed to some extent.
7.	It has low softening capacity.	It has high softening capacity.

Points to be followed while solving problems in lime soda problems:

1) To convert the hardness of the hardness causing salts in terms of $CaCO_3$ equivalents.

2) If $CaCO_3$ is given as hardness causing salt, it should also be considered as temporary hardness expressed in terms of $CaCO_3$.

3) $MgCO_3$, $Mg(HCO_3)_2$, should be converted to $CaCO_3$ equivalents.

4) Some salts like NaCl, KCl, Silica, K_2SO_4, Fe_2O_3 neither cause hardness nor react with lime and soda. Hence they must not be considered for calculation of lime and soda required.

5) The hardness of $Al_2(SO_4)_3$ must be multiplied by 3 for both lime and soda, HCl hardness must be multiplied by 0.5, $Mg(HCO_3)_2$ hardness must be multiplied by 2, $NaHCO_3$, $KHCO_3$, $NaAlO_2$ hardness must be multiplied by 0.5 and should be subtracted for calculation of amount of lime and soda required respectively.
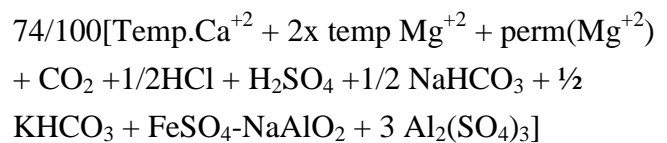
$Mg(HCO_3) + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$ (2L)

$NaHCO_3 \} \rightarrow 2HCO^{3-} + Ca(OH)2 \longrightarrow 2CaCO_3 + 2H_2O$ (1/2L-1/2S)

$KHCO_3 \} \rightarrow$

$NaAlO_2 \} \rightarrow NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$ (L)

$Al_2(SO_4)_3 \; 2Al^{+3} + 3Ca(OH)_2 \longrightarrow 2\; Al(OH)_3 + 3Ca^{+2}$ (3L+3S)

$3Ca^{+2} + 2\; Na_2CO_3 \longrightarrow 3\; CaCO_3 + 6Na^+$

$HCl\} \rightarrow 2H^+ + Ca(OH)_2 \longrightarrow Ca^{+2} + 2H_2O$

$Ca^{+2} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$ (L+S)

6) Soda (Na_2CO_3) reacts only with permanent hardness causing Ca^{+2} salts.

Now 100 parts by mass of $CaCO_3$ are equivalent to:

74 parts of $Ca(OH)_2$ and 106 parts of Na_2CO_3.

∴ Lime requirement for softening=

$74/100[Temp.Ca^{+2} + 2x\; temp\; Mg^{+2} + perm(Mg^{+2}) + CO_2 + 1/2HCl + H_2SO_4 + 1/2\; NaHCO_3 + ½ \; KHCO_3 + FeSO_4 - NaAlO_2 + 3\; Al_2(SO_4)_3]$

all in terms of $CaCO_3$ equivalents.

∴Soda requirement for softening =

106/100 [permanent (Ca^{+2} + Mg^{+2} + Fe^{+2}) + 1/2HCl + H_2SO_4 -1/2$NaHCO_3$-1/2$KHCO_3$+3$Al_2(SO_4)_3$]

all in terms of $CaCO_3$ equivalents.

Numerical Problems based on Lime-Soda Process:

1. Calculate the amount of lime and soda required for the treatment of 10,000l of water containing the following salts dissolved per litre. $CaCO_3$=50 mg, $CaCl_2$=11.1 mg, $MgSO_4$=12 mg, $NaHCO_3$=7.25 mg, silica=10 mg.

Solution: conversion of the hardness in terms of $CaCO_3$ equivalents:

Constituent Multiplication factor $CaCO_3$ equivalent

$CaCO_3$=50 mg 100/100 50x100/100=50 mg/L
$CaCl_2$=11.1 mg 100/111 11.1x100/111=10 mg/L

$MgSO_4$=12 mg 100/120 12x100/120=10 mg/L

$NaHCO_3$=7.25 mg 100/84 7.25x100/84=8.63 mg/L

Amount of lime required= 74 [$CaCO_3$+1/2 $NaHCO_3$+$MgSO_4$]

100

= 74 [50+4.3+10]

100

= 47.58 mg/L

Amount of lime required for 10,000L of water= 47.58x10,000

= 4,75,800 mg/10,000L

= 0.4758 Kg/10,000L.

Amount of Soda required=106 [$CaCl_2$+$MgSO_4$-1/2 $NaHCO_3$]/100

= 106 [10+10-4.3] /100

= 16.64mg/L

Soda required for 10,000L of water= 16.64x10,000

= 166400 mg/10,000L

= 0.1664 Kg/10,000L.

2. Explain with chemical equations and calculate the amount of lime and soda required for softening of 1,00,000l of water containing the following:

HCl=7.3 mg/L, $Al_2(SO_4)_3$=34.2mg/L, $MgCl_2$=9.5mg/L, NaCl=29.25mg/L.

Purity of lime is 90% and that of soda is 98%. 10% of chemicals are to be used in excess in order to complete the reaction quickly.

Solution: conversion into $CaCO_3$ equivalents:

Constituent Multiplication factor $CaCO_3$ equivalent

HCl=7.3 mg/L 100/73 7.3x100/73=10 mg/L

$Al_2(SO_4)_3$=34.2 mg/L 100/114 34.2x100/114=30 mg/L

$MgCl_2$=9.5 mg/L 100/95 9.5x100/95=10 mg/L

Lime requirement= 74/100[HCl+ $3Al_2(SO_4)_3$+ $MgCl_2$]x volume of water x100/%purity

= 74/100(10+90+10) x 1,00,000 x 100/90

= 9.04 Kg
∴Lime required (using 10% excess) = 9.04x110/100= 9.944 Kg

Soda requirement=106/100[HCl + $Al_2(SO_4)_3$+ $MgCl_2$]x volume of water x100/%purity

= 106/100(10+90+10) x1,00,000 x 100/98

= 11.8 Kg

∴Soda required (using 10% excess) = 11.8x 110/100= 12.98 Kg.

Ion exchange/deionization/demineralization:-

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure and the functional groups attached to the chains are responsible for ion exchanging properties.

Resins containing acidic functional groups (-COOH, $-SO_3H$) are capable of exchanging their cations; those containing basic functional groups ($-NH_2$=NH-) as HCl are capable of exchanging their anions with other anions, which comes in their contact.

The ion exchange resins may be classified as :-

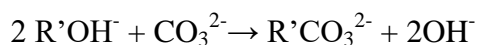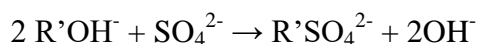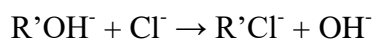1) **Cation Exchange Resins (RH$^+$):-** are mainly styrene-divinyl benzene co-polymers which on sulphonation or carboxylation become capable to exchange their H$^+$ ions with cations in the water.

2) **Anion Exchange Resins (R'OH$^-$):-** are styrene-divinyl benzene and amine formaldehyde copolymers which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of resin matrix. These, after treatment with dil NaOH solution, become capable to exchange their OH$^-$ anions with anions in water.

Process:-

Raw water is first passed through cation exchanger and the removal of cations take place like Ca^{+2}, Mg^{+2} etc takes place and equivalent amount of H$^+$ ions are released from this column to water. Thus,

$$2RH^+ + Ca^{+2} \rightarrow R_2Ca^{+2} + 2H^+$$

$$2RH^+ + Mg^{+2} \rightarrow R_2Mg^{+2} + 2H^+$$
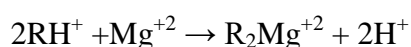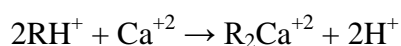
After cation exchange column the hard water is passed through anion exchange column, which removes all the anions like SO$_4^{2-}$, Cl$^-$ etc present in the water and equivalent amount of OH$^-$ ions are released from this column to water.

$$R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-$$

$$2 R'OH^- + SO_4^{2-} \rightarrow R'SO_4^{2-} + 2OH^-$$

$$2 R'OH^- + CO_3^{2-} \rightarrow R'CO_3^{2-} + 2OH^-$$

H$^+$ and OH$^-$ ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.

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

Thus, water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as **deionized or demineralized water.**

Regeneration:

After the deionization of certain amount of raw water the cation and anion exchangers will be exhausted.

Regeneration of cation exchanger is carried out by passing dil. HCl or H_2SO_4 solution into the bed.

$R_2Ca^{+2} + 2H^+ \rightarrow 2RH^+ + Ca^{+2}$ (washing)

The column is washed with deionized water and the washings (Ca^{+2}, Mg^{+2} etc and Cl^- or SO_4^{2-}) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH.

$R_2 SO_4^{2-} + 2 OH^- \rightarrow 2R'OH^- + SO_4^{2-}$ (washing)

The column is washed with deionized water and washings containing Na^+ and SO_4^{2-} or Cl^- ions is passed to sink or drain.

The regenerated ion exchange resins are then used again.

Fig. Deionisation of water
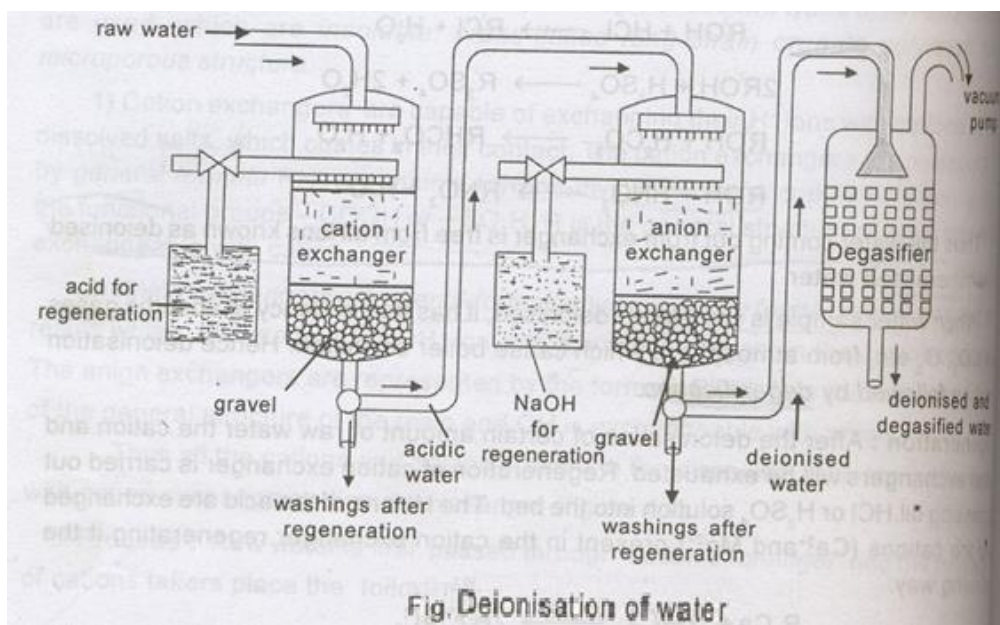
Advantages:

1)   Highly acidic or alkaline water samples can be purified by this process.

2)   The hardness possessed by the deionised water is 2ppm.

3)   The deionised water is most suitable for high pressure boilers.

Disadvantages:

1)   The ion exchanging resins are expensive hence the cost of purification is high.

2)   Raw water should contain turbidity below 10ppm. Otherwise pores in the resin will be blocked and output of the process is reduced.

MIXED-BED DEIONIZER:

- In mixed-bed deionizers the cation-exchange and anion-exchange resins are intimately mixed and contained in a single pressure vessel. The thorough mixture of cation-exchangers and anion-exchangers in a single column makes a mixed-bed deionizer equivalent to a lengthy series of two-bed plants. As a result, the water quality obtained from a mixed-bed deionizer is appreciably higher than that produced by a two-bed plant.
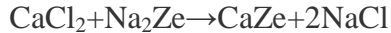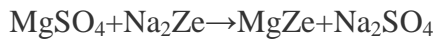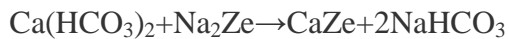
Permutit or Zeolite Process

Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly its sodium ions for Ca^{2+} and Mg^{2+}, having the general formula $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. Common zeolite is $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$ and is known as natrolith. Others gluconites, green sand etc. are used for water softening. Zeolites are represented as Na_2Ze

Artificial Zeolite used for softening purpose is permutit. These are porous and glassy and have greater softening capacity than green sand. They are prepared by heating together with china clay, feldspar and soda ash.

Method of Softening: Hard water is passed through a bed of zeolite at a specific rate at ordinary temperature; the hardness causing cations i.e., Ca^{2+} and Mg^{2+} are exchanged for Na^+ and it is converted to $CaZe$ and $MgZe$.

The reactions taking place the softening process are as follows-

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

$MgSO_4 + Na_2Ze \rightarrow MgZe + Na_2SO_4$

$CaCl_2 + Na_2Ze \rightarrow CaZe + 2NaCl$

After some time, when the zeolite is completely changed into calcium and magnesium zeolites, then it gets exhausted (saturated with Ca^{2+} and Mg^{2+} ions) and it ceases to soften water. It can be regenerated and reused by treating it with a 10% brine (sodium chloride) solution. Regeneration reactions are

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$
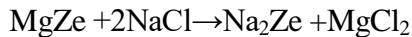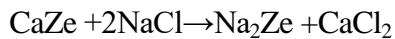
Advantages-

It removes the hardness almost completely (about 10 ppm hardness). The process automatically adjust itself for variation in hardness of incoming water.

This process does not involve any type of precipitation, thus, no problem of sludge formation occurs.

Limitations-

1) Raw material must be free from turbidity and suspended impurities.

2) Highly acidic water is not suitable as it affects mineral.

3) Zeolites of iron and manganese cannot be easily regenerated by passing NaCl solution. Hence iron and manganese impurities in the water to be treated must be minimum.
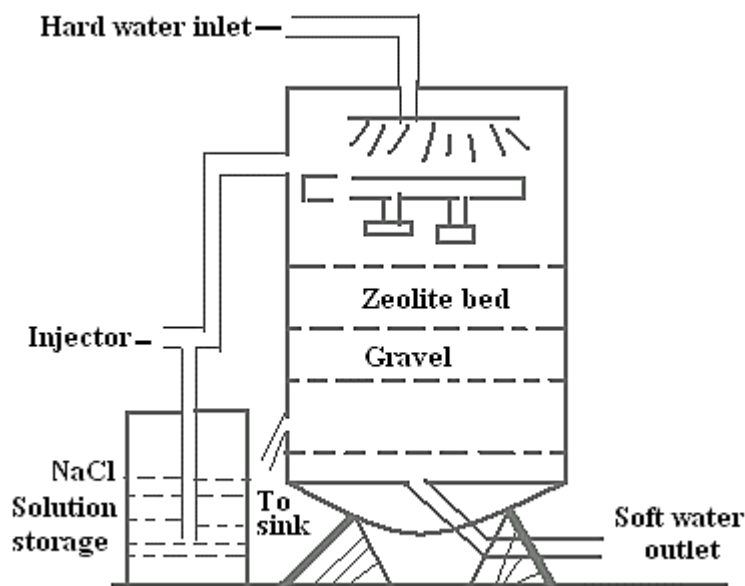

Fig: Zeolite process

Sterilization by ozonation: Water sterilization is recommended whenever drinking water is to be consumed, when retrieving water from a contaminated well or other sources, or any time surface water is treated prior to consumption. Ozone is the most excellent and effective water sterilizing method available today.
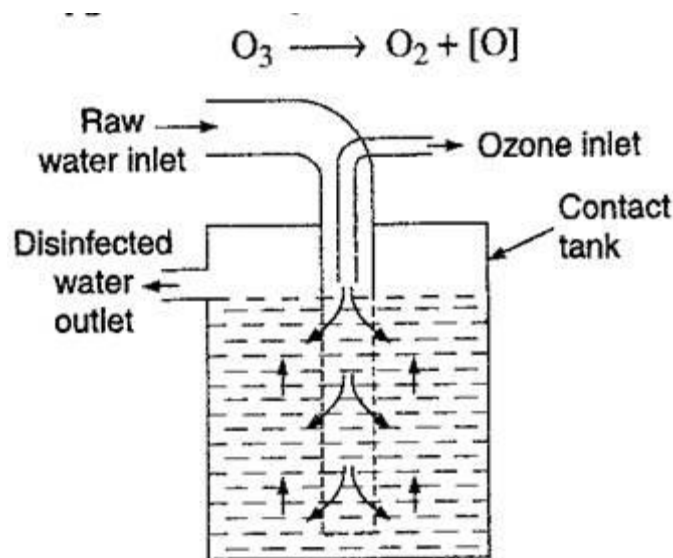
Ozone is a very reactive and unstable gas with a short half-life before it reverts back to oxygen. Ozone is the most powerful and rapid acting oxidizer man can produce, and will oxidize all bacteria, mold and yeast spores, organic material and viruses given sufficient exposure. It is said to be:

- *50 times more powerful than chlorine* and

- *3000 times faster at killing bacteria* and other microbes

- *Does not leave any by-products* such as, with chlorine which creates tri halo methanes (THM's).

Ozone is an unstable allotropic form of oxygen. When added to water, ozone breaks up into oxygen and nascent oxygen.

Ozone is made up of three oxygen atoms (O_3) a "free radical" of oxygen. It will readily give up one atom of oxygen providing a *powerful oxidising agent (Nascent oxygen)* which is toxic to most waterborne organisms such as bacteria, mold and yeast spores, viruses or harmful protozoa that form cysts.

This single Oxygen atom binds with these substances causing them to oxidize (think iron tuning into Iron Oxide - Rust). The by-product of this oxidation is a single Oxygen atom.

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

Raw water inlet → Ozone inlet
Disinfected water outlet ← Contact tank

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The advantages of using Ozone Water Purification include:

- Ozone is primarily a disinfectant that effectively kills biological contaminants.

- Ozone also oxidizes and precipitates iron, sulphur, and manganese so they can be filtered out.

- Ozone will oxidize and break down many organic chemicals including many that cause odour and taste problems.

- Ozonation removes taste colour and odour in the water.
- Ozone is made of oxygen and reverts to pure oxygen and it vanishes without a trace once it has been used.

The disadvantages of using Ozone Water Purification include:

- Ozone treatment can create undesirable by products, formaldehyde and bromate, that can be harmful to health if they are not controlled.

- The process of creating ozone in the home requires electricity. Loss of power means no purification.

- Ozone is ineffective at removing dissolved minerals and salts.

- Water companies that use ozone to disinfect the water must add chlorine or another disinfectant must be added to minimize microbial growth during storage and distribution.

Characteristics of potable water and steps involved in treatment of municipal water

Standards required for Potable water:

Potable water is generally obtained from rivers and lakes. Water obtained from these sources are never pure and as such it is unfit for drinking.

Characteristics:

1. It should be safe.

2. It should be clear and odour less.

3. It should be pleasant in taste.

4. It should be perfectly cool.

5. Its turbidity should not exceed 10 ppm.

6. It should be free from objectional dissolved gases like H_2S.

7. It should be free from minerals such as lead, arsenic, chromium, manganese salts.

8. Its alkalinity should not be high.

9. It should be reasonably soft.

10. Its total dissolved solids should be less than 500ppm.

11. It should be free from disease producing microorganisms.

Municipal Water Treatment:

The type of treatment is given to water largely depends upon the quality of raw water and also upon specified standards.

In general water treatment for municipal supply or domestic use consists of following stages:
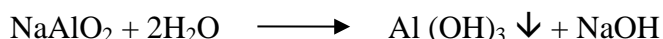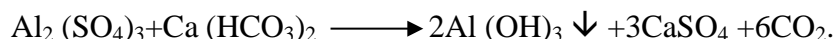*1. Removal of suspended impurities:*

a) **Screening:** The raw water is passed through screens having large no. of holes where floating materials are retained.

b) **Sedimentation:** It is a process of allowing water to stand undisturbed in big tanks about 5m deep for 5-6 hours, when most of suspended particles settle down at the bottom due to force of gravity.

c) **Coagulation:** Sedimentation with coagulation is the process of removing fine suspended and colloidal impurities by addition of coagulants (chemicals) to water before sedimentation.

Coagulant when added to water form insoluble gelatinous, flocculent precipitate which adsorbs and entangles very fine suspended impurities forming bigger flocs, and facilitate easy settling of finely divided particles.

Eg. Alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$], $NaAlO_2$, $FeSO_4 \cdot 7H_2O$.

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

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

The aluminium hydroxide floc causes sedimentation. The sodium hydroxide thus produced, precipitates magnesium salts such as $Mg(OH)_2$.

$$MgSO_4 + 2NaOH \longrightarrow Mg(OH)_2 + Na_2SO_4$$
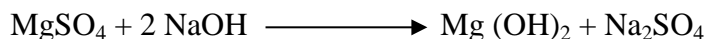
d) **Filtration:** The process of removing colloidal matter and most of the bacteria, microorganism by passing water through a bed of fine sand and other proper sized granular materials.

A sand filter consists of a thick top layer of fine sand placed over coarse sand layer and gravels. It is provided with an inlet for water and an under drain channel at the bottom for exit of filtered water. Sedimented water entering the sand filter is uniformly distributed over the entire fine sand bed. During filtration, the sand pores get clogged, due to retention of impurities in the pores.

When the rate of filtration become slow the working of filter is stopped and about 2-3cm of the top fine sand layer is scrapped off and replaced with clean sand and the filter is put back into use again. The scrapped sand is washed with water, dried and stored for reuse at the time of next scrapping operation.
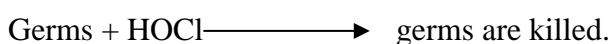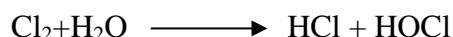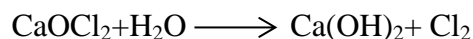
2. *Removal of microorganisms:*

Water used particularly for drinking purpose must be freed from diseases producing bacteria, microorganism etc from the water and making it safe for use, is called disinfection.

The chemicals or substances which are added to water for killing the bacteria are known as disinfectants.

a) Boiling: water boiled for 10-15 minutes kills all the disease producing bacteria.

b) Adding bleaching powder: 1 kg of bleaching powder per 1000 kilo litres of water is mixed and water is allowed to stand undisturbed for several hours.

The chemical action produces hypochlorous acid, a powerful germicide.

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

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$Germs + HOCl \longrightarrow germs\ are\ killed.$$

The disinfecting action of bleaching powder is due to the chlorine made available by it.

Drawbacks:

Bleaching powder introduces calcium in water which makes it harder.

Bleaching powder deteriorates due to its continuous decomposition during storage.

Excess of bleaching powder gives bad taste and smell to treated water.

c) By chlorination: chlorine (either in gas or in concentrated solution form) produces hypochlorous acid which is a powerful germicide.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$Bacteria + HOCl \longrightarrow bacteria\ are\ killed.$$
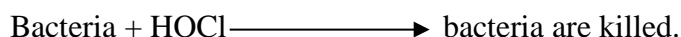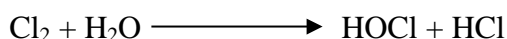
Liquid Cl_2 is most effective when applied to filtered water at such a point where adequate mixing is done.

Cl_2 is the most widely used disinfectant throughout the world.

Mechanism of action: **According to Gleen and Stumpt**, the death of microorganisms, bacteria etc., result from *chemical action of hypochlorous acid* with the enzymes in the cells of the organisms, etc. since enzyme is essential for the metabolic processes of the microorganisms, so death of microorganisms results due to inactivation of enzyme by hypochlorous acid, producing OCl^- which cannot combine with enzymes in the cells of microorganisms.

$$HOCl \longrightarrow H^+ + OCl^-$$
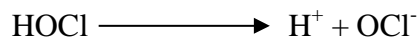
This explains the fact that chlorine is found to be more effective disinfectant at lower pH values (below 6.5). This is due to the fact that HOCl is about 80 times more destructive to bacteria than OCl⁻.

The apparatus used for this purpose is known as chlorinator.

Chlorinator: It is a high tower having a no. of baffle plates. Water and proper quantity of conc. Cl_2 treated water is taken out from the bottom. For filtered water about 0.3-0.5 ppm of Cl_2 is sufficient.

Factors affecting efficiency of chlorine:

1. Time of contact: it has been experimentally shown that no. of microorganism destroyed by Cl_2 per unit time is proportion al to the no. of microorganisms remaining alive. Consequently the death rate is maximum to start with and it goes on decreasing with the time.

2. Temperature of water: the rate of reaction with enzymes increase with temperature. Consequently death rate of microorganism by Cl_2 increases with rise in water temperature.

3. pH: at lower pH values (5-6.5) a small contact period is required to kill same percentage of organisms.

Advantages of chlorine: It is effective and economical, requires little space for storage, stable, used at low and high temperatures and an ideal disinfectant.

Disadvantages: Excess of chlorine if added produces a characteristic unpleasant taste and

odour. It causes irritation on mucus membrane.

The quantity of free chlorine in treated water should not exceed 0.1-0.2 ppm.

It is more effective below 6.5 pH and less effective at higher pH values.
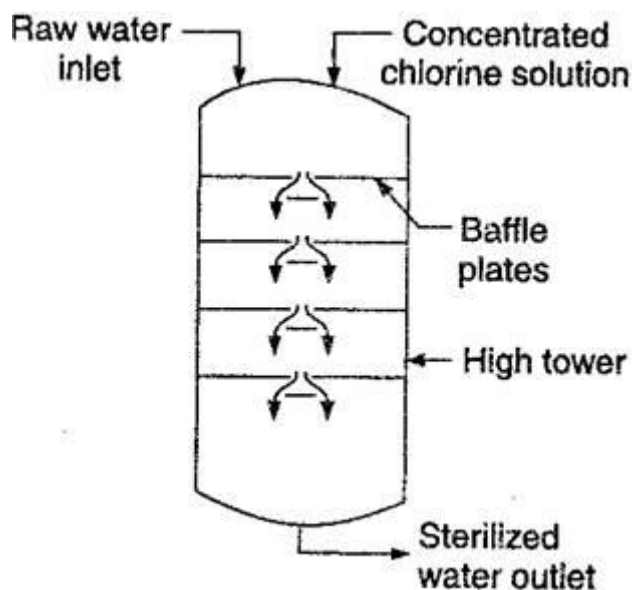
Break point Chlorination:

The process of applying calculated amounts of chlorine to water in order to kill the pathogenic bacteria and to oxidize organic impurities is called chlorination.

Chlorine also reacts with water and generates hypochlorous acid, which kills bacteria.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
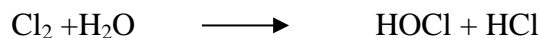
Chlorine is a powerful disinfectant than chloramine and bleaching powder. Calculated amount of chlorine must be added to water because chlorine after reaction with bacteria and organic impurities or ammonia, remains in water as residual chlorine which gives bad taste, odour and toxic to human beings.

The amount of chlorine required to kill bacteria and to remove organic matter is called ***break point chlorination.***

The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted as a graph as shown below which gives the break point chlorination.

From the graph it is clear that the area under represents,

1-2 : chlorine added oxidises reducing impurities of water.

2-3: chlorine added forms chloramine and chloro compounds.
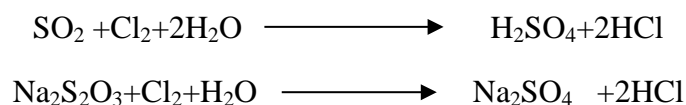
3-4: chlorine added causes destruction of bacteria.

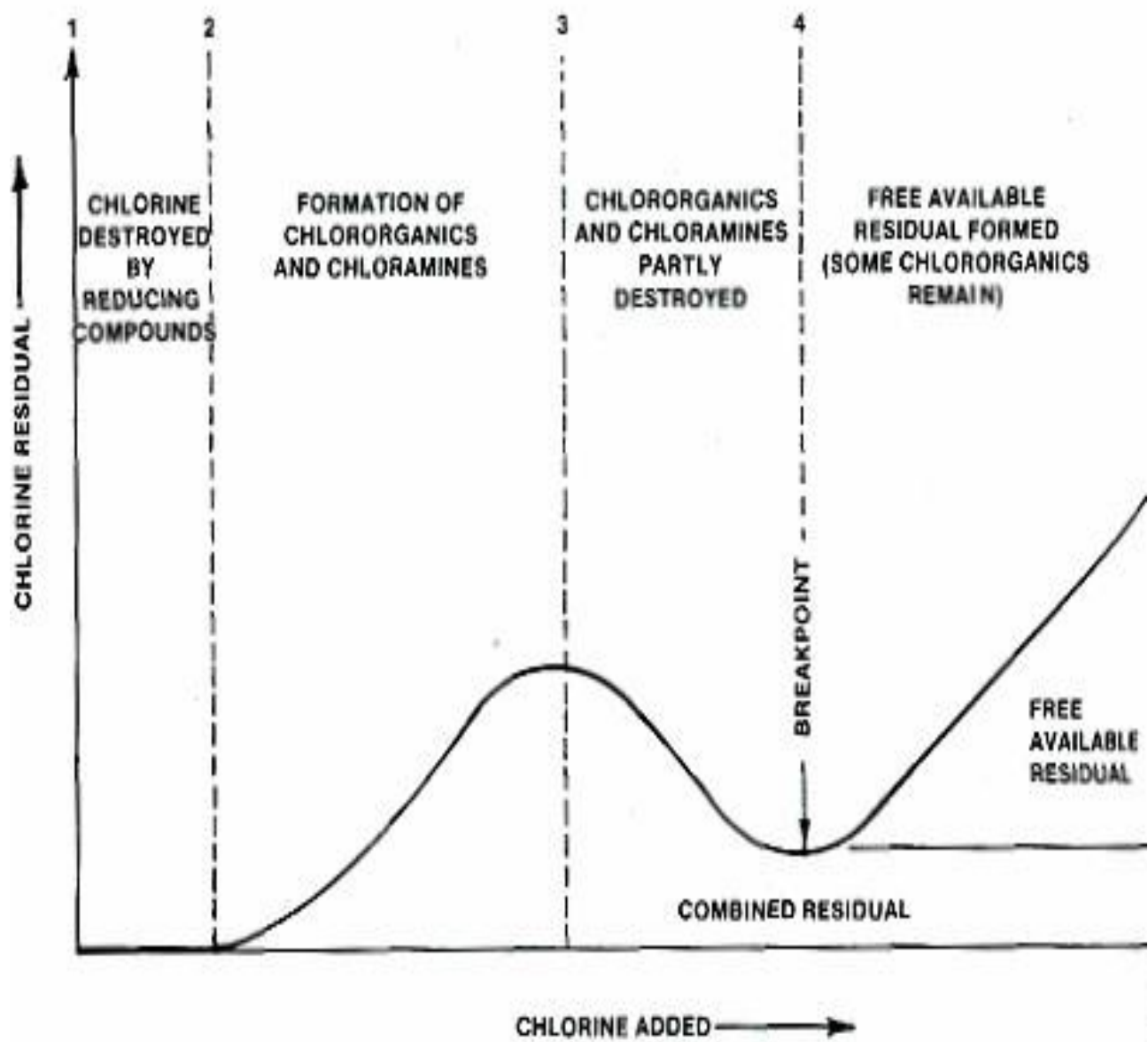After 4: chlorine is residual chlorine.

So, **4 is the break point** for the addition of chlorine to water. This is called **break point chlorination**.

Advantages of break point chlorination:

1. It removes taste, colour, oxidise completely organic compounds, ammonia and other reducing impurities.

2. It destroys completely (100%) all disease producing bacteria.

3. It prevents growth of any weeds in water.

4. De chlorination:

    The over chlorination is removed by passing the water through a bed of granular carbon and also by addition of SO_2 and sodium thiosulphate.

    $$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

    $$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

Y-axis: CHLORINE RESIDUAL →

X-axis: CHLORINE ADDED →

1 CHLORINE DESTROYED BY REDUCING COMPOUNDS

2 FORMATION OF CHLORORGANICS AND CHLORAMINES

3 CHLORORGANICS AND CHLORAMINES PARTLY DESTROYED

4 FREE AVAILABLE RESIDUAL FORMED (SOME CHLORORGANICS REMAIN)

BREAKPOINT

FREE AVAILABLE RESIDUAL

COMBINED RESIDUAL

Desalination of brackish water:-

The process of removing common salt (sodium chloride) from the water is known as **"Desalination".** The water containing dissolved salts with a peculiar salty or brackish taste is called **"Brackish water".** Ex. Sea water (contains an average of about 3.5% salts) is an example of brackish water.

It is totally unfit for drinking purpose.

Commonly used methods for desalination of brackish water are:-

1) Electro dialysis

2) Reverse Osmosis

Reverse osmosis:-

When two solutions of unequal concentrations are separated by a semipermeable membrane (which does not permit selectively the passage of dissolved solute particles i.e., molecules, ions etc) flow of solvent takes place from dilute to concentrated sides, due to Osmosis.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses i.e., solvent is forced to move from concentrated side to dilute across the membrane. This is the principle of reverse osmosis.

Thus, in reverse osmosis, pure solvent (water) is separated from its contaminants, rather than removing contaminants from water. This membrane filtration is also called **"Super/ Hyper filtration".**

Method:

In this process, pressure (15-40 kg/cm^2) is applied to sea water/impure water (to be treated) to force its pure water through the semi-permeable; leaving behind the dissolved solids (both ionic and non-ionic). The principle of reverse osmosis as applied for treating saline/sea water is as follows: given in fig above.

The membrane consists of very thin film of cellulose acetate, affixed to either side of a perforated tube. Superior membranes recently developed are made of polymethacrylate and polyamide polymers have come into use.

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Advantages:

1) Reverse osmosis process has distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.

2) It removes colloidal silica, which is not removed by demineralization.

3) The life time of membrane is quite high, about 2 years.

4) The membrane can be replaced within a few minutes thereby providing nearly uninterrupted water supply.

5) Low capital cost, simplicity, low operating cost and high reliability.

6) The reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.
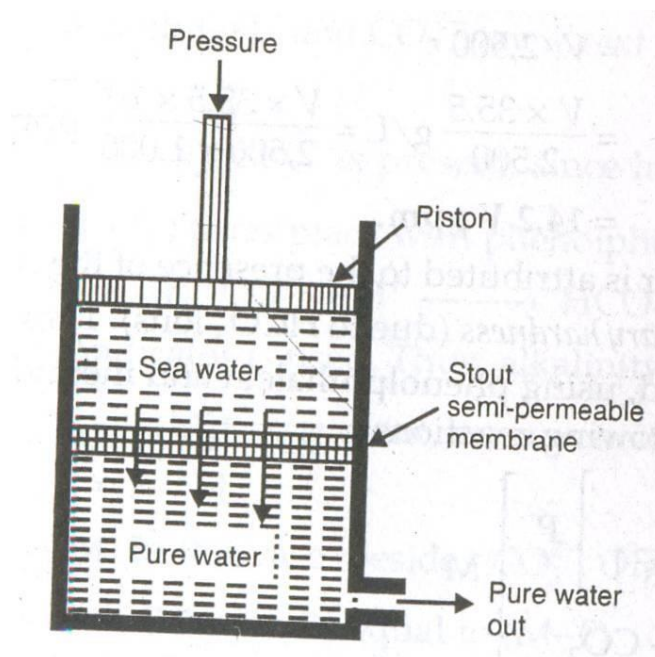

Diagram for Reverse Osmosis

Electrodialysis:

It is a method in which the ions are pulled out of the salt water by passing direct current, using electrodes and thin ion selective membrane pair.

An Electro-dialysis cell consists of a large number of paired sets of Ion selective membranes. Hard water is passed between the membrane pairs and an electric field is applied perpendicular to the direction of water flow. Positively charged membrane and negatively charged membrane repel positively charged ions and negatively charged ions respectively to pass through. So, in one compartment of the cell, the salt concentration decreases while in the adjacent compartment it increases. Thus, we get alternative stream of pure water and concentrated brine.
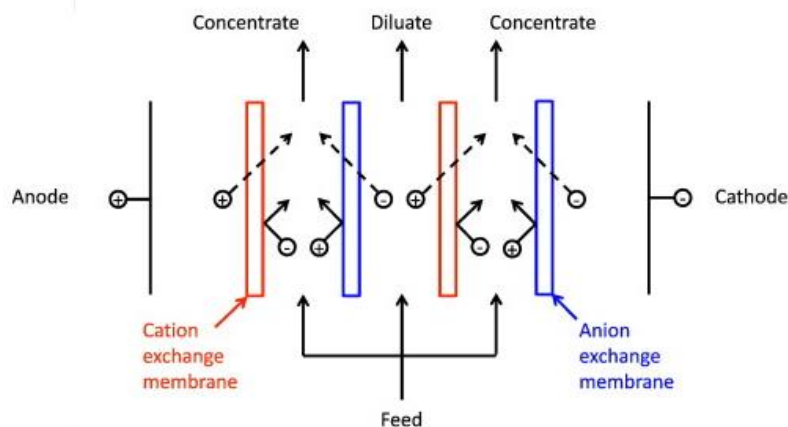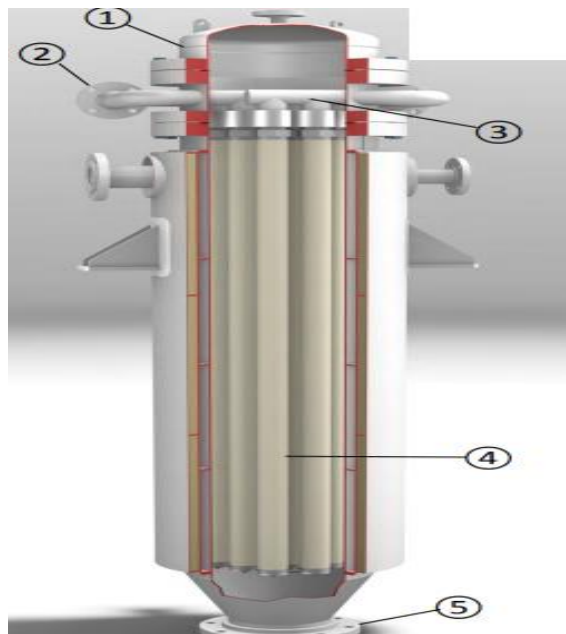

Electrodialysis –An experimental setup

Advantages: 1. It is most compact unit

2.Using this method,brackish water containing 2000 ppm can be reduced to 250-300 ppm.

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Candle filtration

1.) Filter Vessel
2.) Filtrate Nozzle
3.) Header
4.) CANDLE Element
5.) Discharge Nozzle

Construction:

1. Candle filter are cylindrical shape either as single tube or arranged in a group inside of a larger vessel.
2. These candle tubes are connected with header.

3. The headers are connected to main manifold through valves.
4. During operation, the formation of CAKES occurs by separation of solids from water and the cake removed water is further subject to filtration to remove slurry and thin cakes which are formed in this process.
5. The cake grows on the outer side of the candle and form a thick coating. The thickness of CAKE varies from 5mm -25mm . As the process ends, the discharging of cake is done by blowing hot air from inner side to outer walls of candle filter.
6. Thus toxic solids, germs, bacteria, mud,flue gas ,mineral oils and TiO_2 can be filtered from water as CAKE.
7. Candle filters remove chlorine and E. coli bacteria by up to 99%.

Activated Carbon (Charcoal) Filters

1. Activated charcoal is charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atoms.
2. In Carbon filtering , a bed of activated carbon is used to remove contaminants and impurities via chemical adsorption.
3. Each granule of carbon provides a large surface area due its porous structure, allowing contaminants to get adsorbed onto this pores.

E.g., One pound (450 g) of activated carbon contains a surface area of approximately 100 acres (40 hectares)

4. Carbon filtering is commonly used for water purification, in air purifiers and industrial gas processing, for example the removal of siloxanes and hydrogen sulfide from biogas.

5. It is also used in respirator masks, the purification of sugarcane and in the recovery of precious metals, especially gold. It is also used in cigarette filters.

6. It removes chlorine, sediment, volatile organic compounds (VOCs), taste and odor from water most effectively.

7. Typical particle sizes that can be removed by carbon filters range from 0.5 to 50 micrometres.

8. They are not effective at removing minerals, salts, and dissolved inorganic compounds.


Treated Water

Activated Carbon Filter

Contaminated Water
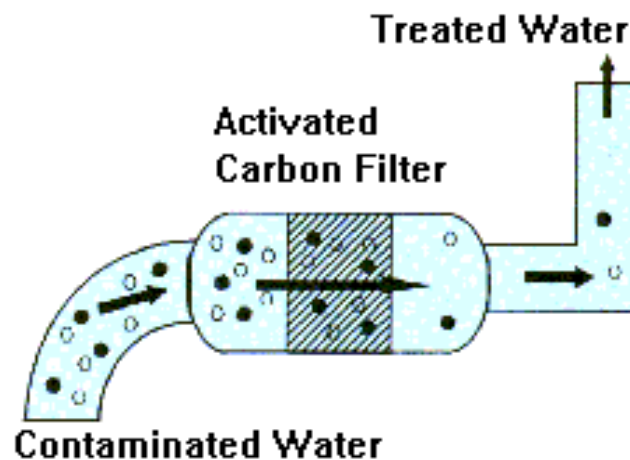
Ultraviolet water purification

It is the most effective method for disinfecting bacteria from the water. Ultraviolet (UV) rays penetrate harmful pathogens and destroy harmful microorganisms by deactivating their enzyme metabolic (DNA). UV rays are extremely efficient in eliminating the ability of Bacteria reproduction.

UV light occurs in the wavelength region of 200 to 390 nm. From the point of view of microbial disinfection, the most effective wavelength frequency is 254 nm as this is where the optimum energy intensity is obtained.
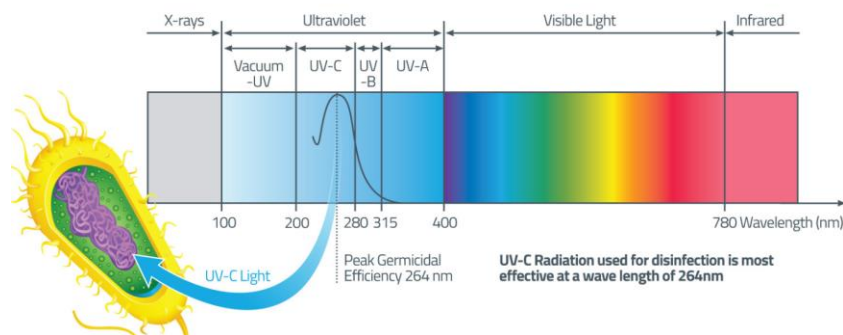
Working

1. Typical UV disinfection systems involve the flow of water through a vessel containing UV Lamp.

2. As the water passes through this vessel, microorganisms are exposed to intense ultraviolet light energy which causes damage to genetic molecules(DNA or RNA) required for reproductive functions.
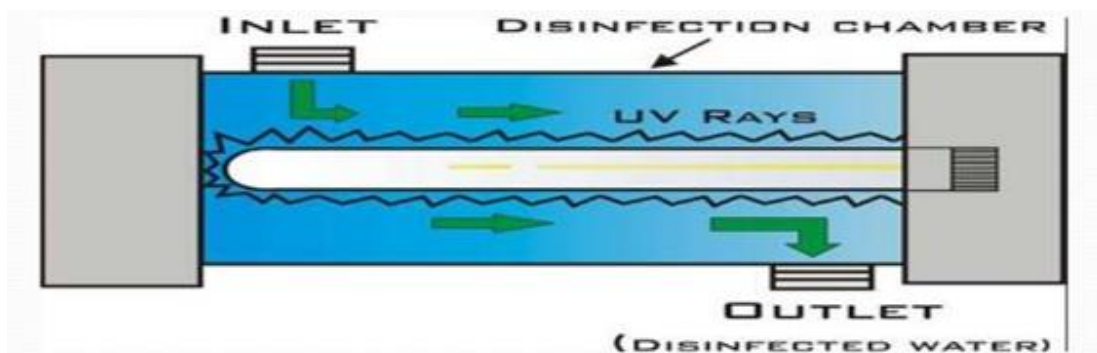
Advantages

- UV systems destroy 99.99% of harmful microorganisms without adding chemicals or changing water's taste or odour.
- <u>It</u> is always used with other forms of filtration such as reverse osmosis systems or carbon block filters.
- It's maintenance cost is low.
- This process has no impact on the chemical composition or the dissolved oxygen content of the water.

Limitations

1. UV radiation is only effective for treating bacteria and viruses.

2. UV light does not work to eliminate contaminants such as chlorine, heavy metals and VOC's (Volatile Organic Compounds).

3. UV systems are often paired with Reverse Osmosis Systems to provide a complete purification process for the safest drinking water.

References:

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2. Teh.Fu.Yen, Chemistry for Engineers, Imperial College Press, 2008.

3. O.V. Roussak and H.D. Gesser, Applied Chemistry-A Text Book for Engineers and Technologists, Springer Science Business Media, New York, 2nd Edition, 2013.