CO-3: Water technology

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Overview Syllabus

Outcomes

CO3; Topic 3

- Generalize water quality parameters & analysis of Hardness & alkalinity.
- Understand operational troubles of the boiler for the given water analysis report.
- Apply appropriate water softening and desalination methods.

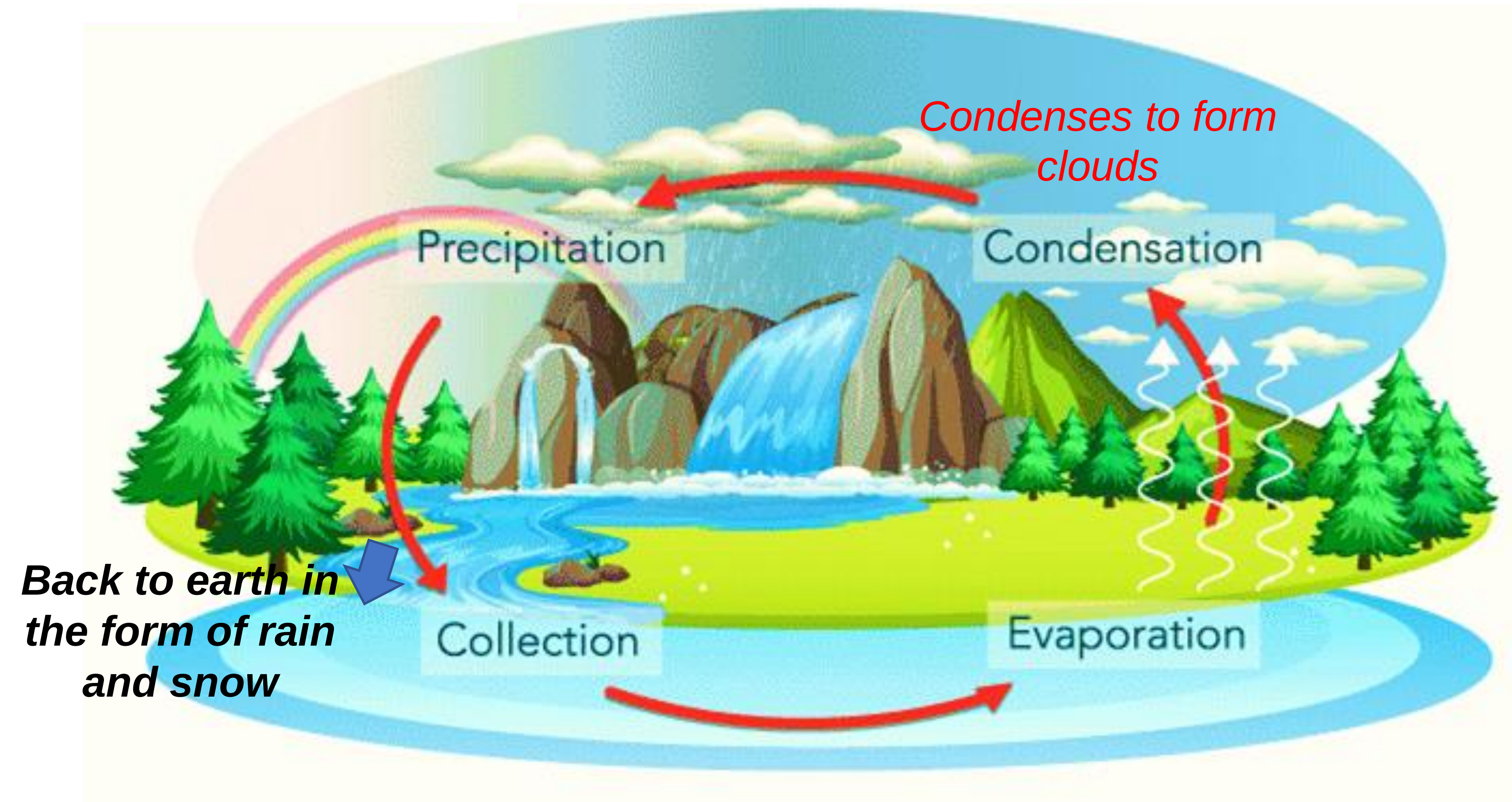
Water technology: Outlines

- Introduction
- Causes of water impurity & its types
- Hardness of water
- Alkalinity of water
- Boiler troubles & its control
- Softening of water
- Desalination methods

Why water essential?

- ☞Living beings require water to survive.
- ☞Water in our plant atmosphere helps to keep the plant warm
- ☞Our bodies are composed of 70% dependent on water
- ☞Humans can survive for many days without food, but without water, they cannot survive.
- ☞Your brain is 75-85% water and plays a vital role in your body's response to dehydration.
- ☞Domestic, agricultural, and industrial activities require water.

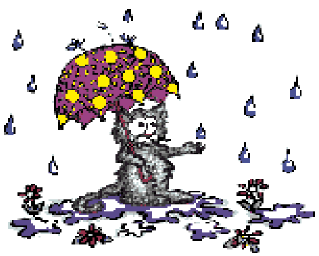
Water cycle



Water continuously moves within the Earth and atmosphere.

Sources of Water

- **Surface water**
  - *Rivers, streams, lakes, & ponds*
  - *Reservoirs & dams*



- **Rainwater** → *Purest form of natural water, but contaminated with gases*

- **Sea water** → *large amounts dissolved salts; high salinity*

- **Ground water** → ***more specifically well water***

No organic impurities
is crystal clear
large number of DS.

Classification of Impurities in water

1) Physical Impurities - Dissolved Solids/Salts

i) Color ii) Turbidity iii) Taste iv) Odour v) Conductivity

2) Chemical Impurities - Inorganic & Organic Chemicals

a) Acidity (pH); b) Gases (CO_2, O_2, NH_3) c) Minerals; d) Salinity; e) Alkalinity; f) Hardness

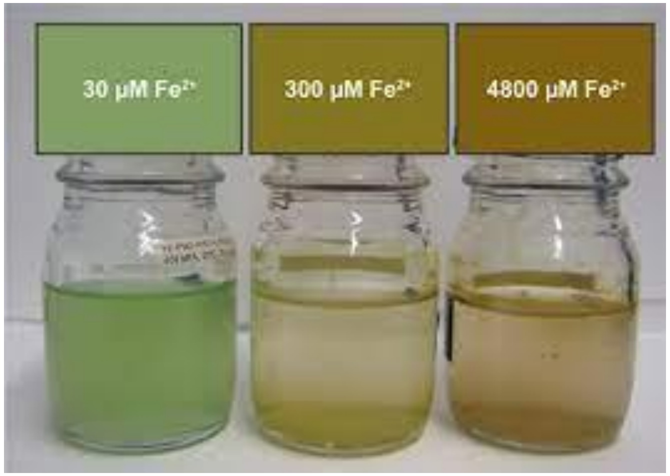
3) Biological Impurities - Pathogens, algae, fungi, viruses.

i) Microorganisms (Bacteria, fungi, & algae) ii) Pathogens; iii) Water Bodies

Physical Impurities: color

- Color in water is due to metallic salts of Fe, Mn or organic substances (humus, peat, algae, weed)
- Industrial activities such as textile, paper & pulp, dyeing, tanneries.
- Color intensities of water sample can be measured using tintometer using Platinum cobalt standard color complex

Metallic salts of Fe & Mn

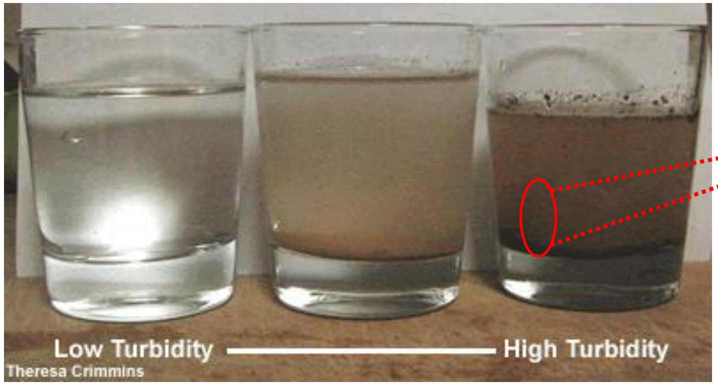


Textile dyeing

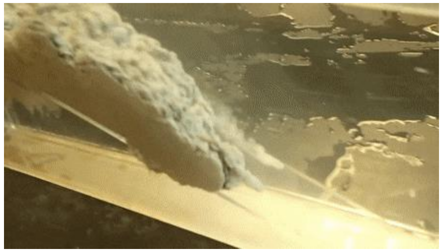
Industrial activities

Physical Impurities: Turbidity

- It is the measure of relative clarity of a liquid (water, oils)
- A turbidity occurs when particles suspended in a liquid create a cloudy or hazy appearance.
- It is due to colloidal, extremely fine suspension (clay, slit, microorganisms).
- Instead of transmitting light straight ahead, it reflects the optical properties of water in terms of its ability to scatter light.
- Turbid levels of water sample can be measured using turbidimetry:

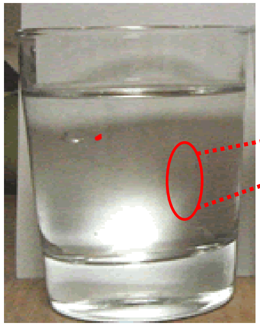


Turbidimetry



Physical Impurities: Conductivity

- The conductivity of a solution is a measure of its ability to conduct electricity, sound, and transmit heat.
- Conductivity measured in micro mhos/cm or micro siemns/cm^3 (μS/cm).
- It tells you how much dissolved substances, chemicals, and minerals are in it.
- It enhances if its ion concentration increases.



Conductometry

Water Type	Conductivity (μS/cm)
totally pure water	0.055
typical deionized water	0.1
distilled water	0.5-3.0
reverse osmosis water	50-100
domestic "tap" water	500-800
potable water	1,055 max
sea water	56,000
brackish water	100,000

Physical Impurities: Taste & odor

Taste

Dissolved salts and gases impart a bitter, soapy, brackish, palatable taste which is normally associated with odor, but this is not always the case.

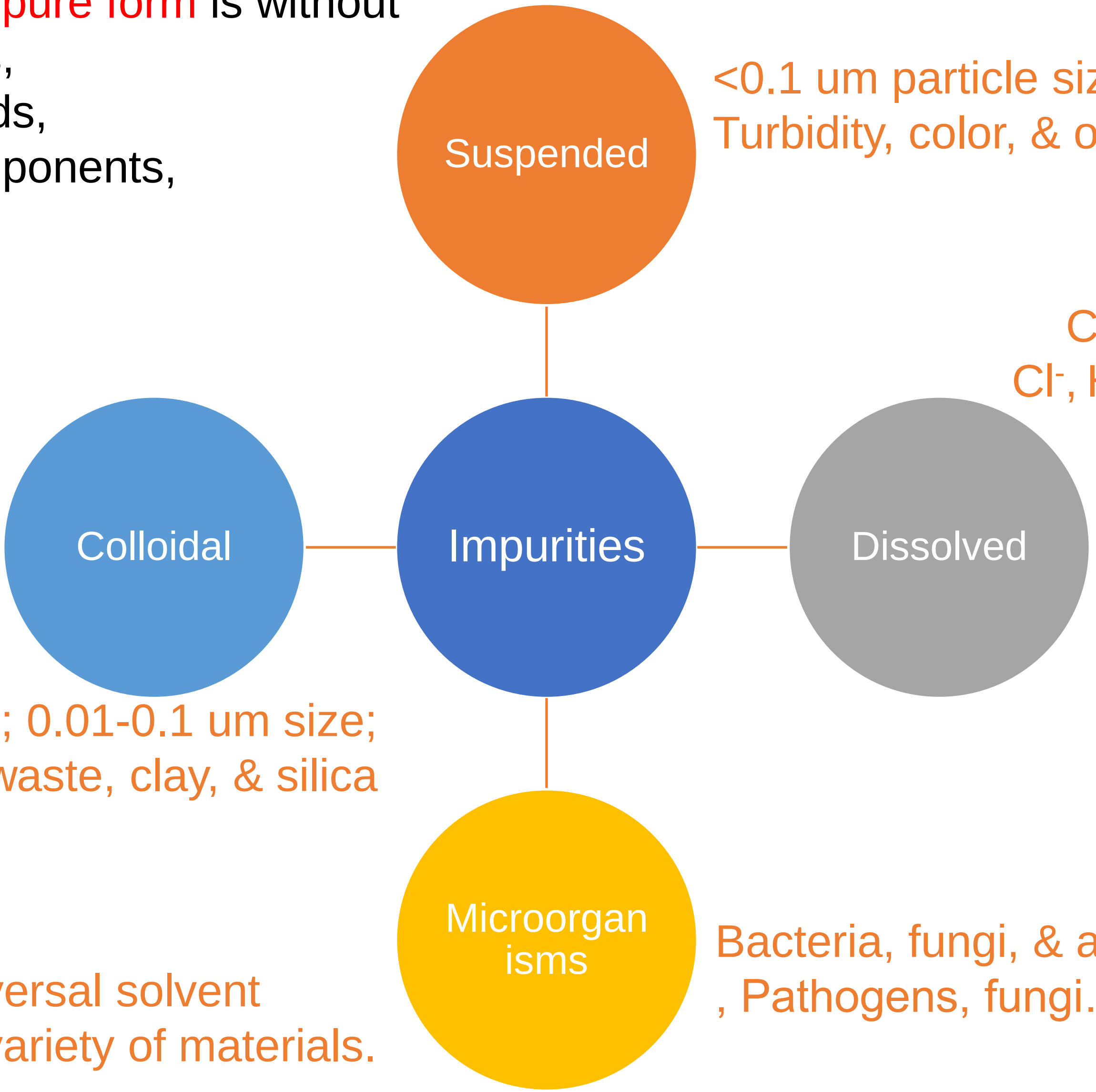
- ✓ Bitter (Fe, Al, Mn, SO_4, $Ca(OH)_2$)
- ✓ Soapy ($NaHCO_3$)
- ✓ Brackish (High salt content-NaCl)
- ✓ Palatable (CO_2 and NO_3)

odor

- Water is subjected to undesirable odors due to domestic and industrial activities.
- Industrial effluents with organics, sewage discharges with compounds containing nitrogen, sulfur, and phosphorous, and metal ions such as iron
- Substances like algae, peat, bacteria's

What Causes Water Impurity and its types?

Water in its most pure form is without
- → Any chemicals,
- → Dissolved solids,
- → Biological components,
- → Even minerals



<0.1 um particle size
Turbidity, color, & odour

CO_3^{2-}
Cl^-, HCO_3^{2-}

Ca^{2+},
Mg^{2+}
Na^+

O_2, CO_2 gases

Tiny particles; 0.01-0.1 um size;
Ex: Organic waste, clay, & silica

Bacteria, fungi, & algae
, Pathogens, fungi…

- ✓ Water is a universal solvent
- ✓ It dissolves a variety of materials.

What Causes Water Impurity and its types?

Water in its most pure form is without
→ Any chemicals,
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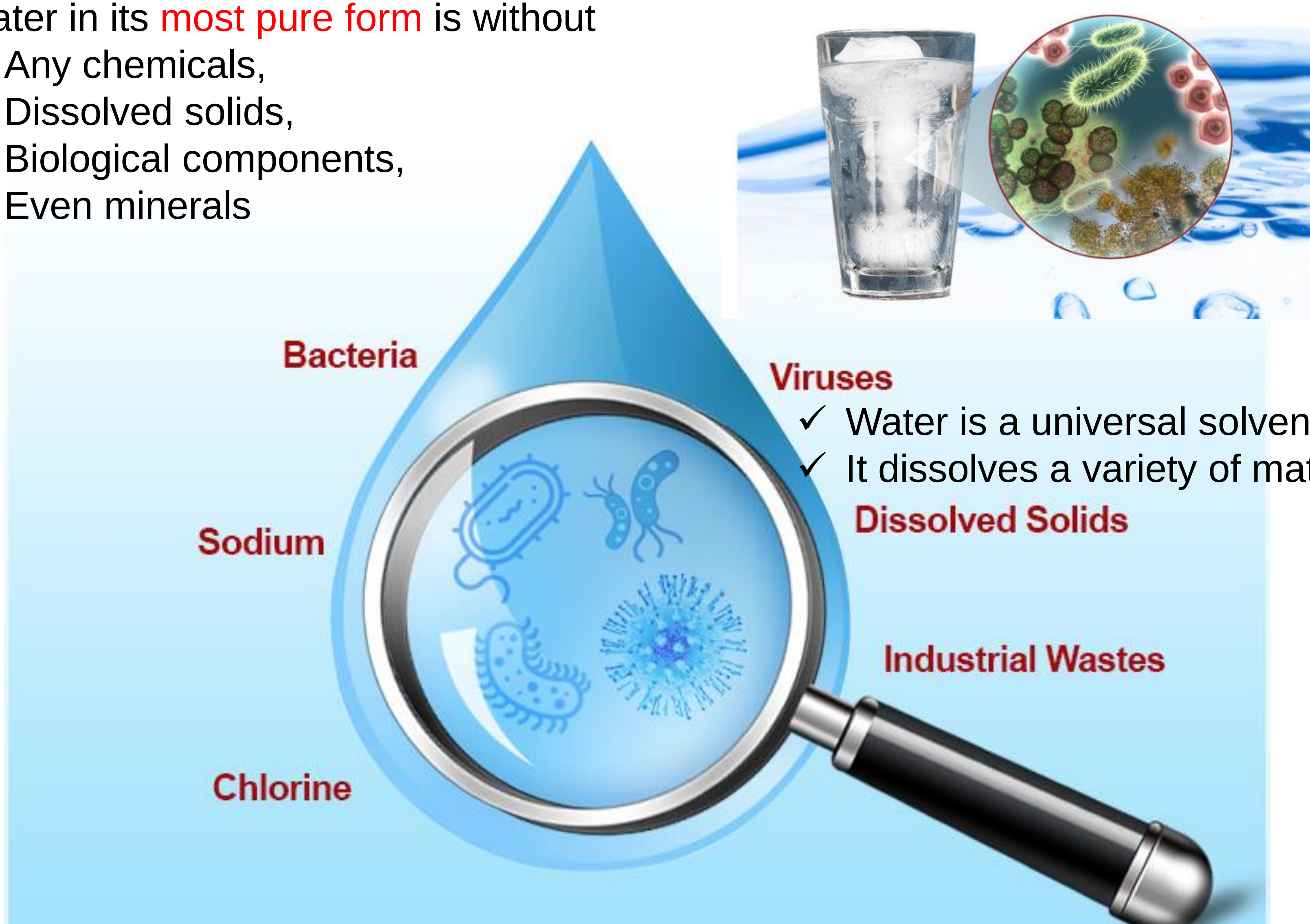


✓ Water is a universal solvent
✓ It dissolves a variety of materials.

What Causes Water Impurity and its types?

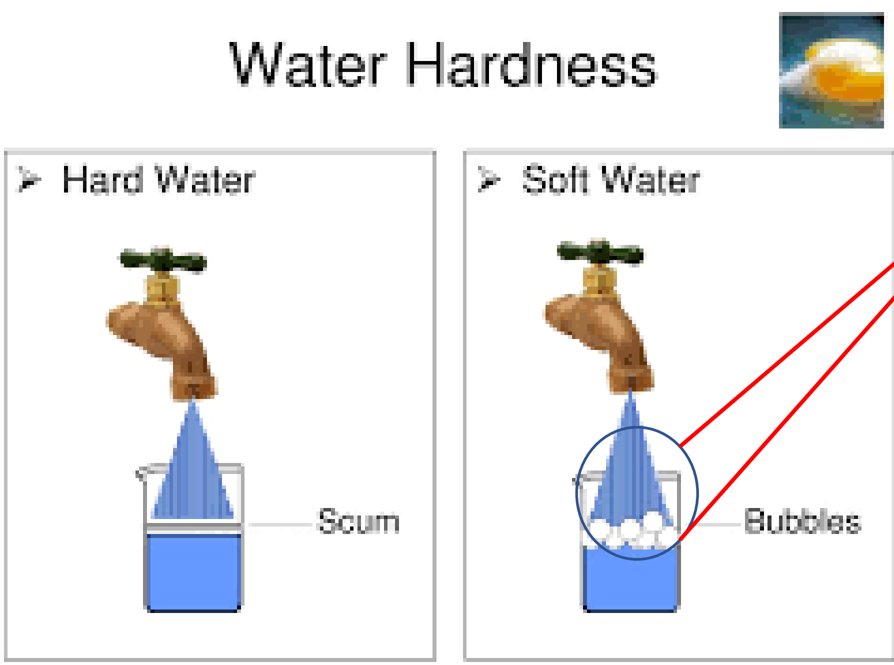
- Gases (O_2, CO_2) picked up from the atmosphere by rainwater.
- Decomposition of plant & animal remains introduce organic.
- Sewage and industrial waste make the water impure.
- It is passing over the soil and rocks.

Drinking water – W.H.O Parameters

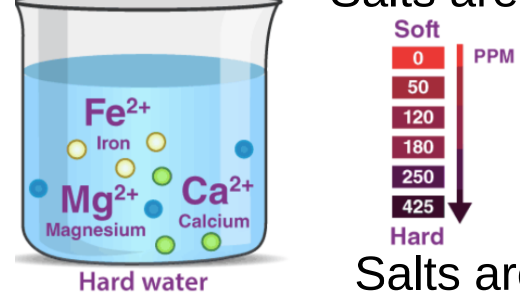
- It should be colorless, odorless and tasteless.
- Its turbidity should be less than 10 ppm
- It should not contain poisonous metals (Pb, As, Cr).
- pH should be in the range of 7.0-8.5.
- Total hardness should be less than 500 ppm.
- It should be free from disease causing microorganisms.

Hardness of water

- The property of water to form an insoluble curd with soap instead of lather (foam).
- A water sample's ability to **consume soap**, or **precipitate soap** as a characteristic property.



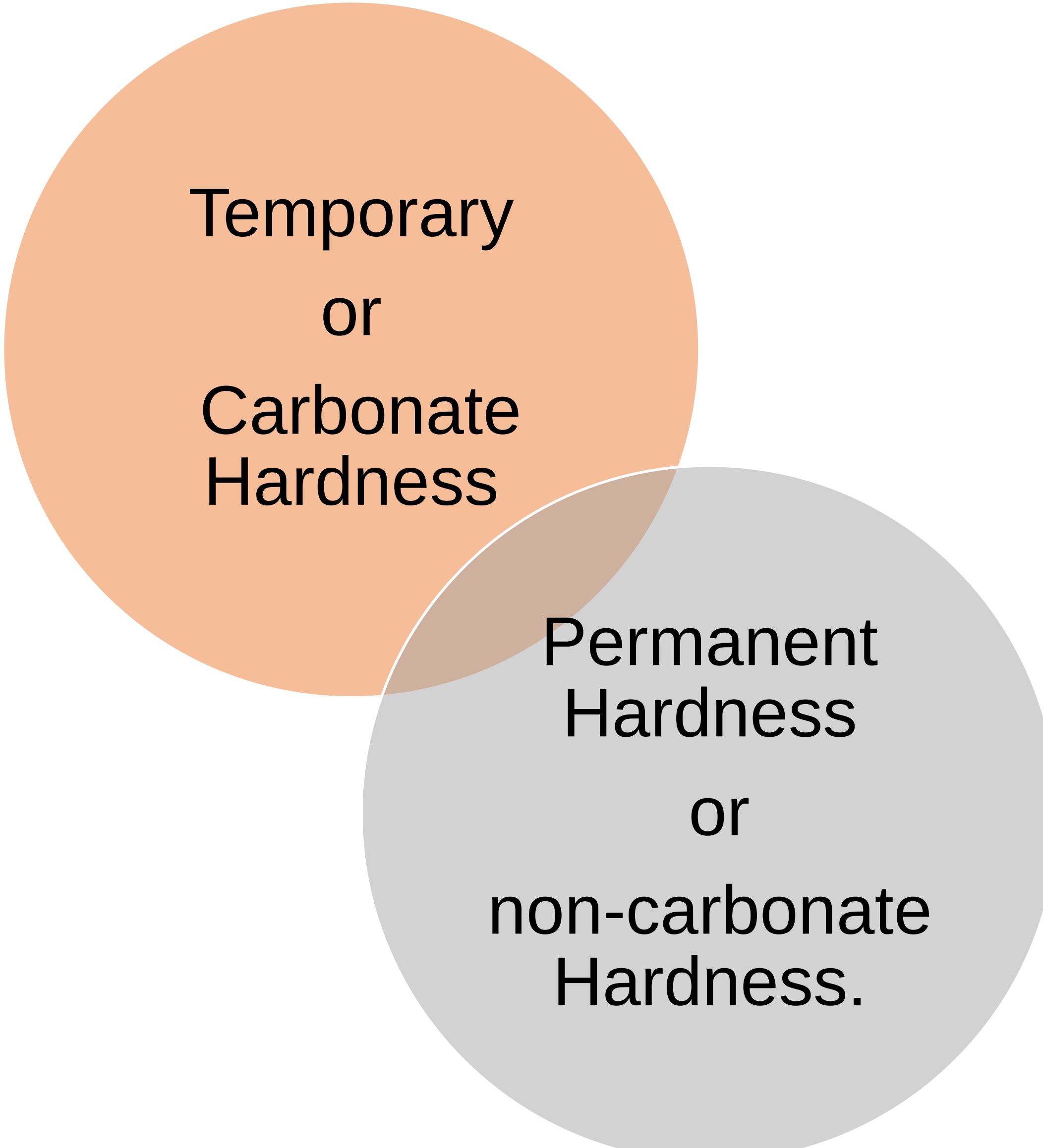
Salts are less



Salts are more

Based on consuming capacity of water is two types

Type of hardness



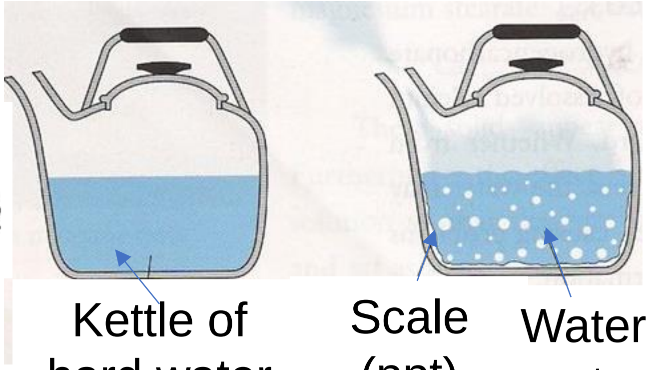
Type of hardness

Temporary hardness

- It is caused by the presence of dissolved bicarbonate of calcium (Ca), magnesium (Mg), and the carbonate of iron (Fe).
- Dissolved bicarbonates destroyed by boiling of water, when bicarbonates are decomposed yielding insoluble carbonates.

This reaction occurs:

- $Ca(HCO_3)_2 + \text{heat} \longrightarrow CaCO_3 + H_2O + CO_2$



Almost insoluble $Ca/MgCO_3$ are formed and are deposited as a scale at the bottom of the vessel, while carbon dioxide escapes.

Type of hardness

Permanent hardness

- It is due to chlorides and sulphates of calcium and magnesium.
- This type of hardness cannot be removed by simple boiling.
- It is removed by ion exchange, zeolite process etc.

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$$

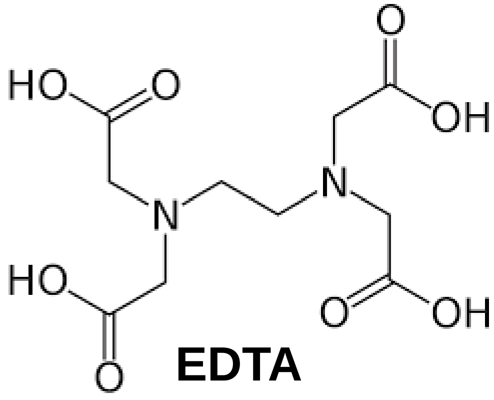
Sodium stearate (sodium soap) — Hardness — Calcium stearate (Insoluble)

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

Sodium stearate (sodium soap) — Hardness — Magnesium stearate (Insoluble)

Determination of hardness of water by EDTA method

- By titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent.
- Since EDTA is insoluble in water, the disodium salt of EDTA is taken for this experiment.
- EDTA can form four or six coordination bonds with a metal ion.
- From the amount of the EDTA consumed during complex formation, the hardness of the water sample can be calculated.



EDTA

Determination of hardness of water by EDTA method: *theory*

- EDTA and water are both colorless.
- As a result, Eriochrome black-T (EBT) indicator is used in conjunction with EDTA to determine the formation of color complexes.
- EBT is first added to water, after which it forms a complex with the metal ions present in the water. There is less stability in this complex.
- EDTA is added after the addition of EBT.
- A stable complex is formed between EDTA and the metal ions and EBT is released, displaying a blue color.
- EBT is replaced by EDTA.

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

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

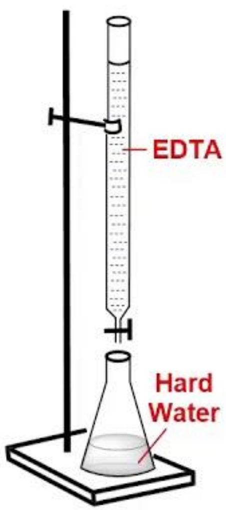
Wine red | Colourless | Colourless | Blue colour

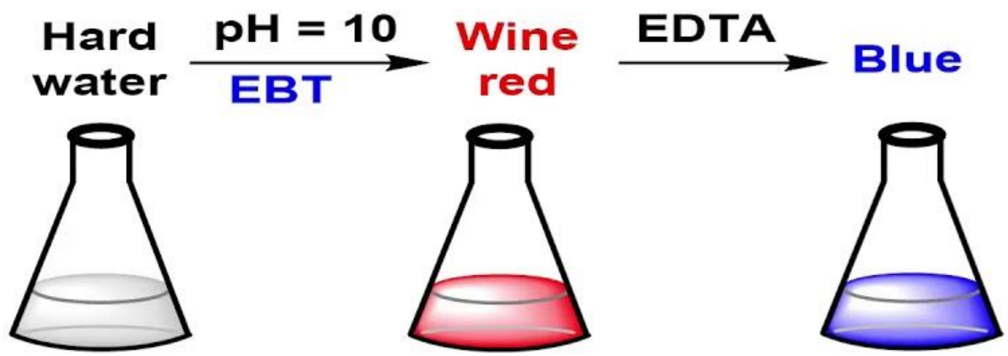
Determination of hardness of water by EDTA method: *Procedure*

$$M^{2+} + \underset{\text{(Blue)}}{\text{EBT}} \xrightarrow{\text{pH} = 10} \underset{\text{(Wine red)}}{M^{2+}\text{- EBT Complex}}$$

$$\underset{\text{(Wine red)}}{M^{2+}\text{- EBT Complex}} + \underset{\text{(Colourless)}}{\text{EDTA}} \longrightarrow \underset{\text{(Colourless)}}{M^{2+}\text{- EDTA Complex}} + \underset{\text{(Blue)}}{\text{EBT}}$$

$M^{2+} = Ca^{2+} / Mg^{2+}$





Total hardness of water sample can be calculating as follows

$$\text{Total Hardness} = \frac{\text{Volume of EDTA} \times \text{Molarity of EDTA} \times 100 \times 1000}{\text{Volume of water sample}}$$

Unit of hardness

Most used

- Parts per million (ppm)

1 ppm = 1 part of $CaCO_3$ equivalence hardness causing substance present in 10^6 parts of water

- Milligrams per liter (mg/liter)

1 mg/L = 1 mg of $CaCO_3$ equivalence hardness causing substance present in one liter of water

1mg/L=1ppm

Relationship; 1L water = 1Kg = 1000 g = 1000 X 1000 mg = 10^6 mg

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

= 1 part of $CaCO_3$ eq per 10^6 parts of water = 1ppm

- Clare's Degree(°*Cl*)

1° Clarke = 1part of $CaCO_3$ equivalent hardness in 70000 parts of water

- Degrees French (°*Fr*)

1° Fr = 1 part of $CaCO_3$ eq per 10^5 parts of water

$CaCO_3$ equivalent hardness

$$\text{Calcium carbonate equivalent} = \frac{\text{Mass of hardness producing substance} \times \text{Molecular weight of } CaCO_3}{\text{Molecular weight of hardness producing substances}}$$

Problem 1

Calculate the calcium carbonate equivalent hardness of a water sample containing 204 mg of $CaSO_4$ per liter

Solution :

$$\text{Calcium carbonate equivalent hardness} = \frac{204 \times 100}{136} = 150 \text{ mg of } CaCO_3/L$$

$$= 150 \text{ ppm}$$

Note : Mol. Weight of $CaCO_3$ = 100

Mol. Weight of $CaSO_4$ = 136

Equivalence conversion during hardness calculation

Hardness producing substance	Molecular weight as $CaCO_3$	**Equivalent weight** as $CaCO_3$
$Ca(HCO_3)_2$	162/100	81/50
$Mg(HCO_3)_2$	146/100	73/50
$CaSO_4$	136/100	68/50
$CaCl_2$	111/100	55.5/50
$MgSO_4$	120/100	60/50
$MgCl_2$	95/100	47.5/50
$CaCO_3$	100/100	50/50
$MgCO_3$	84/100	42/50
CO_2	44/100	22/50
HCO^-_3	61/100	61/50
OH^-	17/100	17/50
CO_3^{2-}	60/100	30/50

Molecular weight of any dissolved salts is equivalent to the molecular weight of calcium carbonate.

Problems

Water sample from an industry in Vijawada had the following data

$Mg(HCO_3)_2$ = 16.8mg/L, $MgCl_2$ = 19 mg/L, $CaCO_3$ = 20 ppm, $MgSO_4$ =24.0mg/L and KOH = 1 ppm.

Calculate the temporary, permanent and total hardness of the water sample.

Solution Step 1: Conversion in to $CaCO_3$ equivalent

Constituent present	Quantity (mg/L)	Conversion factor	Hardness
$Mg(HCO_3)_2$	16.8	100/146	**16.8 *100/146 = 11.5ppm**
$MgCl_2$	19.0	100/95	**19.0*100/95 = 20ppm**
$CaCO_3$	20	100/100	**20.0*100/100 = 20 ppm**
$MgSO_4$	24.0	100/120	**24.0*100/120 = 20 ppm**

Calculation

Temp. Hardness = 31.5 ppm

P. Hardness = 40 ppm

Tot. Hardness = 71.5 ppm

Advantages or disadvantages hardness of water

Advantages of Hard Water	Disadvantages of Hard Water
1. Ca for healthy teeth and bones 	1. Limescale -blocks pipes and leaves a scale on kettles.  
2. Good for Brewing 	2. Wastes soap 
3. Tastes better 	3. Scum produced with soap 

Draw backs (or) Disadvantages of Hard Water

Domestic Use

1. **Washing**
2. **Bathing**
3. **Drinking**
4. **Cooking**

The sticky precipitate adheres on the fabric/cloth and gives spots & streaks. Fe salts stain the cloths.

Produces sticky scum on the bathtub and the body

Bad to the digestive system and calcium oxalate formation is possible in urinary tracts

Requires more fuel and time. Certain food don't cook soft and also gives unpleasant taste

Industrial Use

1. **Textile Industry**
2. **Sugar Industry**
3. **Dyeing Industry**
4. **Paper Industry**
5. **Pharmaceutical Industry**
6. **In Steam generation in Boilers**

Alkalinity of water

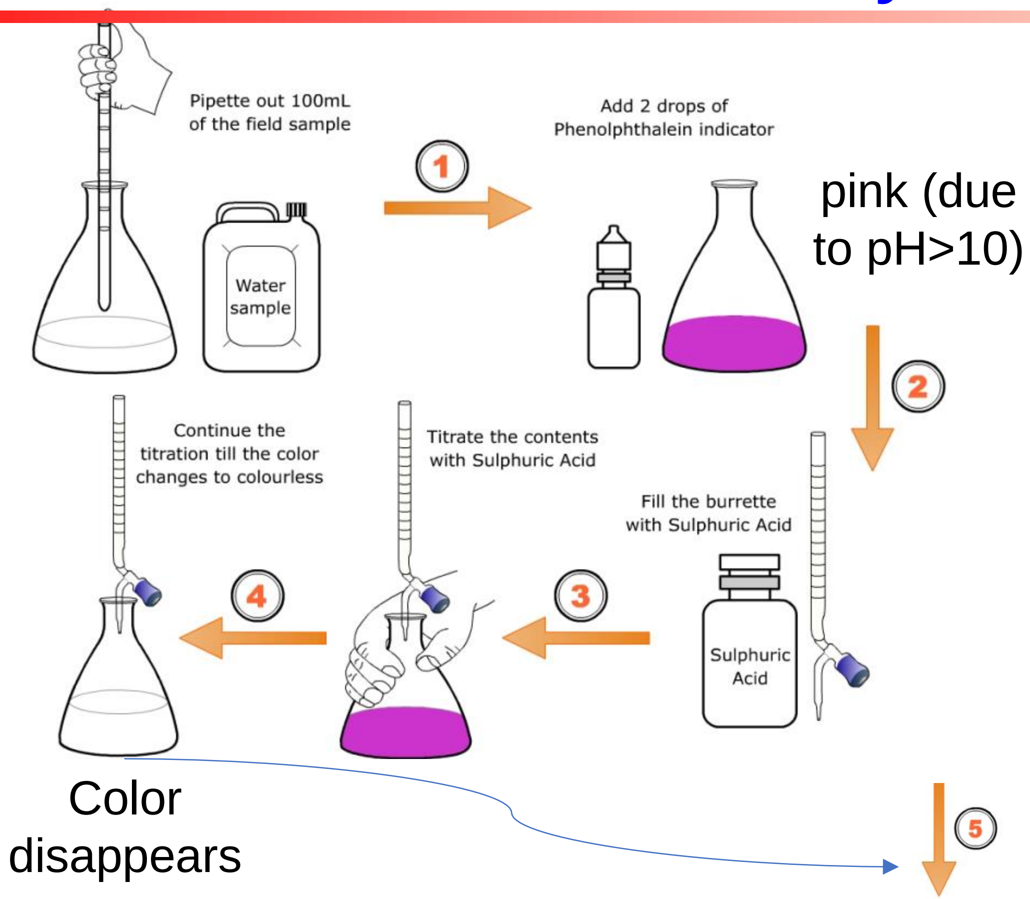
Def:

It is due to the presence of those types of substances in water which have tendency to increase the concentration of OH- ions either by hydrolysis or by dissociation of water.

Factors

- The presence of salts of weak organic acids which undergo hydrolysis and consume H+ ions of water. As a result, concentration of OH- ions increases in water and water becomes alkaline.
- The presence of HCO_3^-, $HSiO_3^-$ and SiO_3^{-2} ions in water which makes the water alkaline because they have tendency to take up H+ ions from water.

Alkalinity of water

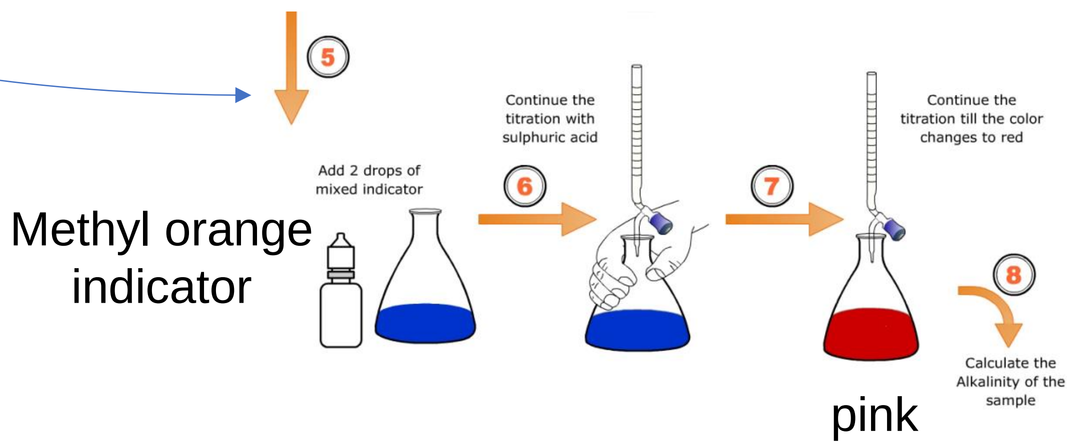


Reactions:

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

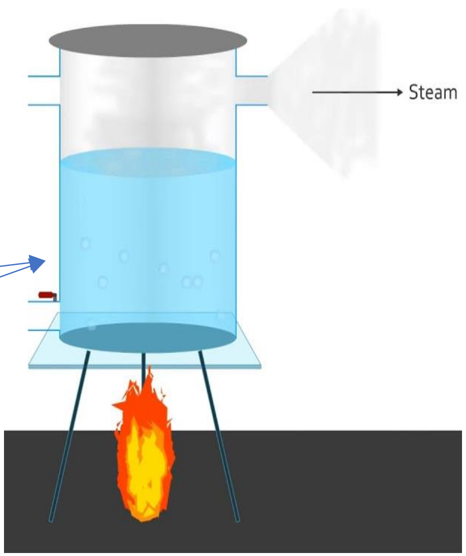
$$H^+ + CO_3^{2-} \rightarrow HCO_3^-$$

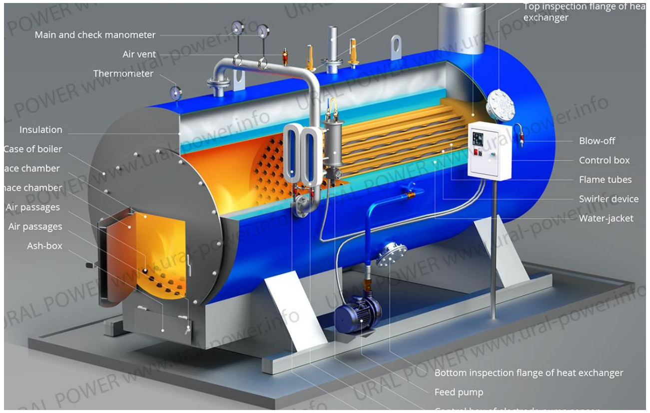
$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$



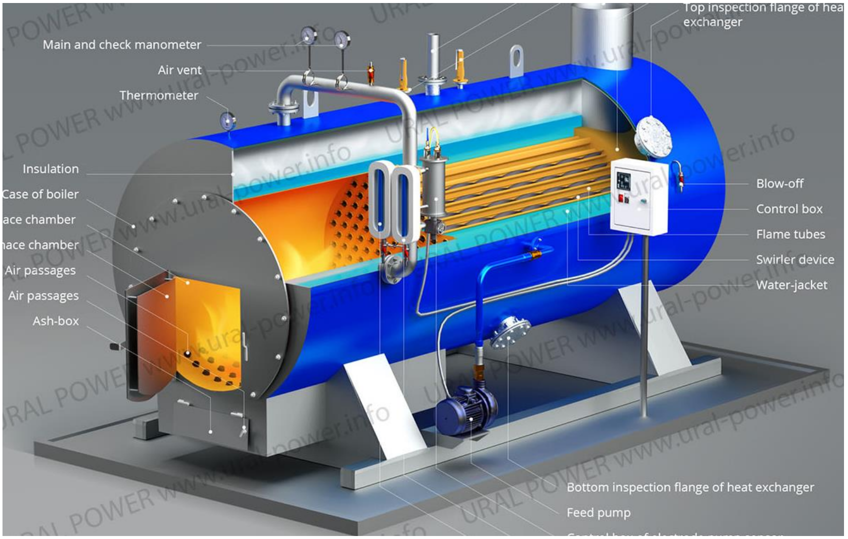
Boiler troubles

- A **boiler** is a closed vessel in which fluid (generally water) is heated
- Boilers heat water or other suitable liquid to produce steam.
- Steam can be used for heating uses, power generation & even cooking.
- It works like a pressure cooker, but much larger.
- A boiler feed water should satisfy the following requirements.
- Directly feeding water into the boiler causes issues.





Major boiler troubles



It impairs the effective use of boilers and affects the quality of steam produced

Boiler troubles

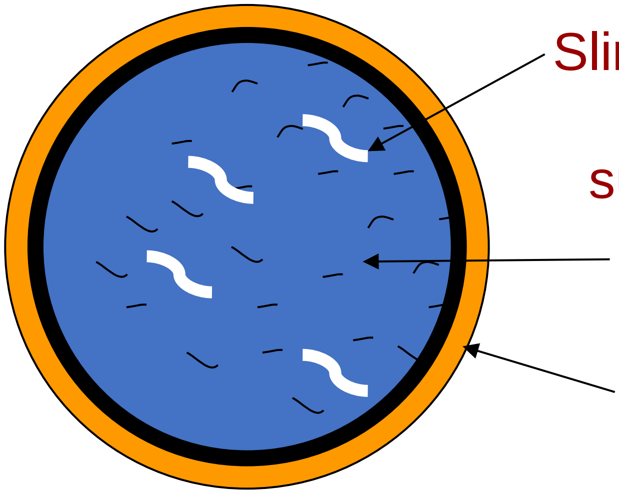
- Scale & Sludge
- Caustic embrittlement
- Priming & foaming
- Boiler corrosion

Common impurities of water and their effect

Name	Common Name	Effect
Calcium carbonate, $CaCO_3$	Chalk, limestone	Soft scale
Calcium bicarbonate, $CaHCO_3$	-	Soft scale, CO2
Calcium sulphate, $CaSO_4$	Gypsum, plaster of paris	Hard scale
Calcium chloride $CaCl_2$	-	Corrosion
Magnesium carbonate, $MgCO_3$	Magnesite	Soft scale
Magnesium bicarbonate, $MgHCO_3$	-	Scale, Corrosion
Magnesium sulphate, $MgSO_4$	Epsom salt	Corrosion
Sodium Chloride, NaCl	Common salt	Electrolysis

Scale & sludge formation

1. Sludge

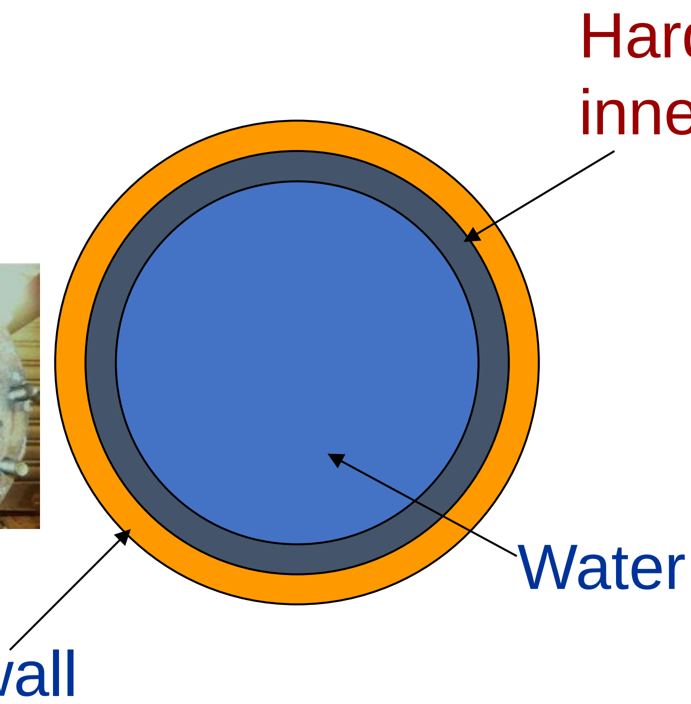


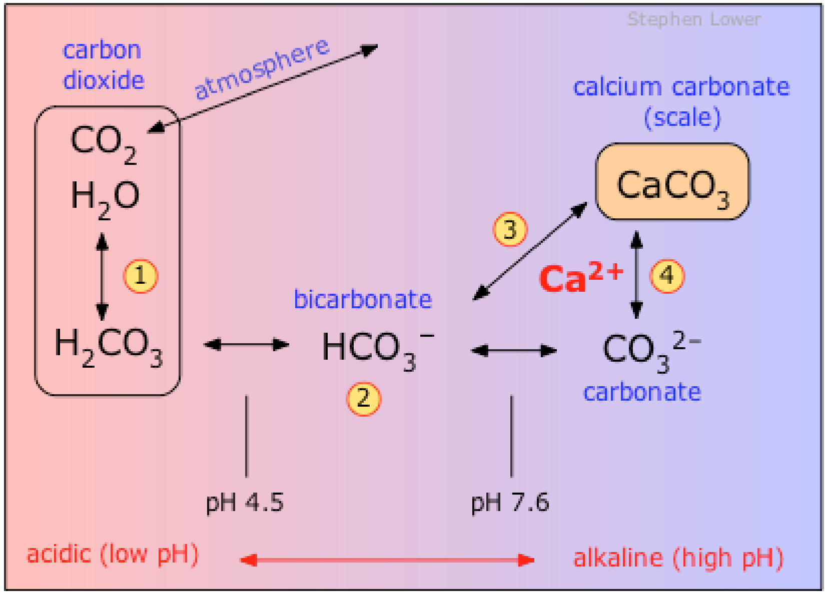
- Sludge is a soft, loose and slimy precipitate formed within the boiler.
- It can be easily scrapped off with a wire brush.
- It is formed at comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow or at bends.
- It is formed by substances which have greater solubilities in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.,

Remedy: Sludges can be removed using wire brush or mild acid

I. Scale & Sludge formation

1. Scale





- Scales are hard substances which sticks very firmly to the inner surfaces of the boiler wall.
- Scales are difficult to remove even with the help of a hammer and chisel.
- Examples: $CaSO_4$, $CaCO_3$, $Mg(OH)_2$

Reasons for formation of scale

1. Presence of $Ca(HCO_3)_2$ in low pressure boilers

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \longrightarrow \underset{\text{Calcium Carbonate (scale)}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

2. Presence of $CaSO_4$ in high pressure boilers

On continuous heating, $CaSO_4$ present in boiler water gets precipitated as scales

3. Presence of $MgCl_2$ in high temperature boilers

$$\underset{\text{Magnesium chloride}}{MgCl_2 + 2\,H_2O} \longrightarrow \underset{\text{scale}}{Mg(OH)_2} \downarrow + 2HCl \uparrow$$

$Mg(OH)_2$ can also be generated by thermally decomposing $Mg(HCO_3)_2$

4. Presence of SiO_2

It forms insoluble hard adherent $CaSiO_3$ & $MgSiO_3$ as scales

Disadvantages of scale formation

1. Fuel wastage – scales have low thermal conductivity
2. Degradation of boiler material and increases of risk of accident
3. Reduces the efficiency of the boiler and- deposit on the valves and condensers
4. Both cause chocking of pipes.
5. The boiler may explode – if crack occurs in scale

Remedies: Removal of scale

1. Using scrapper, wire brush often
2. By thermal shock- heating and cooling suddenly with cold water
3. Using chemicals – 5-10% HCl and by adding EDTA

Prevention of scale formation

Scale formation can be prevented by two methods

1. Internal conditioning or Internal Treatment

2. External conditioning or External treatment

1. Internal conditioning methods of boiler water to prevent scale formation

Phosphate conditioning: Addition of phosphate compound

Carbonate conditioning: Addition of carbonate compound

Calgon conditioning: Addition of sodium hexa meta phosphate

Prevention of scale formation

1. Phosphate conditioning

*Scale formation can be prevented by **adding sodium phosphate** to the boiler water which reacts with the hardness producing ions and forms easily removable phosphate salts of respective ions.*

$3CaCl_2$ (Boiler water) + $2\ Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6\ NaCl$

Calcium chloride — Sodium phosphate — Calcium phosphate (non adherent & can be removed by blow down method)

Calcium can not be precipitated below a pH = 9.5, hence the selection of phosphate must be based on the pH of the boiler feed water.

NaH_2PO_4 (acidic in nature),

Na_2HPO_4 (weakly alkaline in nature),

Na_3PO_4 (Alkaline in nature)

Selection of Phosphate compound

2. Carbonate conditioning

$CaSO_4$ (Boiler water) + $Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$

Calcium sulfate

Sodium carbonate

Calcium carbonate

(non adherent loose sludge and can be removed by blow down method)

Caution: Excess Na_2CO_3 can result in caustic embrittlement

Prevention of scale formation

3. Calgon conditioning

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

Calgon – sodium hexa meta phosphate

$$2CaSO_4 \text{ (Boiler water)} + [Na_4P_6O_{18}]^{2-} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

Calcium sulfate

Soluble complex ion of calcium-can be removed easily

Calgon tablets are used in the cleaning of washing machine drums.

II. Caustic embitterment

- Cracking of boiler material due to high concentration of NaOH in boiler feed water is known as caustic embrittlement.

- NaOH content in boiler feed water is due to the hydrolysis of dissolved salts like sodium carbonate which is added during external treatment of water to remove hardness .

$$\boxed{Na_2CO_3 + H_2O \rightarrow 2\,NaOH + CO_2}$$

- Extent of hydrolysis increases with the temperature.
- NaOH has better mobility and can penetrate in fine cracks present in boiler walls.

When caustic substances accumulate in a boiler, the material becomes brittle.

II. Caustic embitterment

- NaOH gets **concentrated in the fine cracks** present in the boiler walls.
- A concentration cell corrosion is established between the conc. NaOH and dilute NaOH solution in contact with boiler walls.
- Since concentrated NaOH acts as an anode, sodium ferroate is formed in the boiler as a result of corrosion.
- Thus, it makes the cracks bigger in bents, joints and crevices of boiler

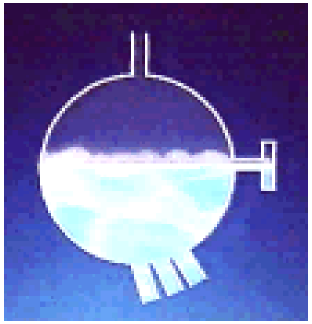
$$\underset{\text{(Insoluble)}}{Fe} + 2NaOH \longrightarrow \underset{\substack{\text{Sodium Ferroate} \\ \text{(Soluble)}}}{Na_2FeO_2} + H_2\uparrow$$

Prevention of Caustic embrittlement

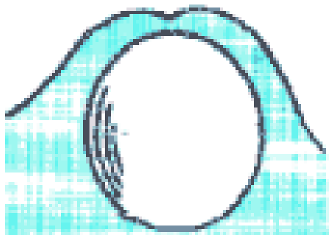
(i) Use phosphate salts instead of sodium carbonate

(ii) use Na_2SO_4 or agar-agar gel compounds to fill the fine cracks.

III. Priming and foaming



Foaming

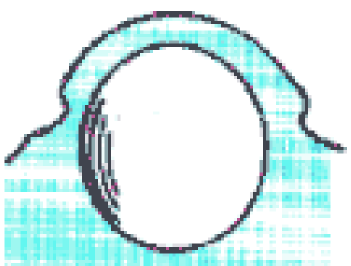


Normal bubble

Foaming

It is the production of continuous foam or hard bubblers in boilers. Foaming is due to the presence of substance like oil in boiling water.

Priming

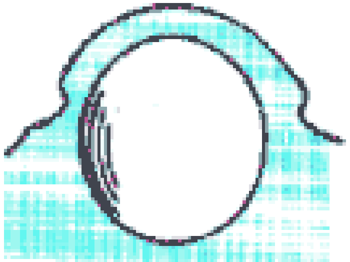


Carry over bubble

Priming

- It is the process in which some particles in water are carried along with the steam.
- Resulting process is called as wet steam or carry over.
- Process of formation of wet steam in boilers is called as priming.

III. Priming and foaming



Causes of Priming

- Very high level of water
- Uneven heating
- Presence of large quantity of dissolved salts, organic matter, alkalies and suspended matter etc.
- Improper design of the boiler.
- High steam velocity

Prevention of Priming

- Maintaining proper water level in the boiler.
- Removing dissolved salts and oily matter.
- Avoiding sudden changes in temperature.
- Proper design of the boiler.

IV. Boiler corrosion

- Degradation or destruction of boiler materials (Fe) due to the chemical or electrochemical attack of dissolved gases or salts is called boiler corrosion.

The corrosion in boilers is due to

- Dissolved O_2
- Dissolved CO_2
- Acids formed by dissolved salts

IV. Boiler corrosion

1. Corrosion due to dissolved oxygen (DO)

Water containing dissolved oxygen attacks boiler material at high temperature and causes corrosion.

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

$$4\,Fe(OH)_2 \downarrow + O_2 \longrightarrow 2\,[Fe_2O_3.2H_2O] \downarrow$$

Ferrous hydroxide **Rust**

Removal of dissolved oxygen

1) Chemical method: a) Dissolved oxygen can be removed by adding sodium sulphite.

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

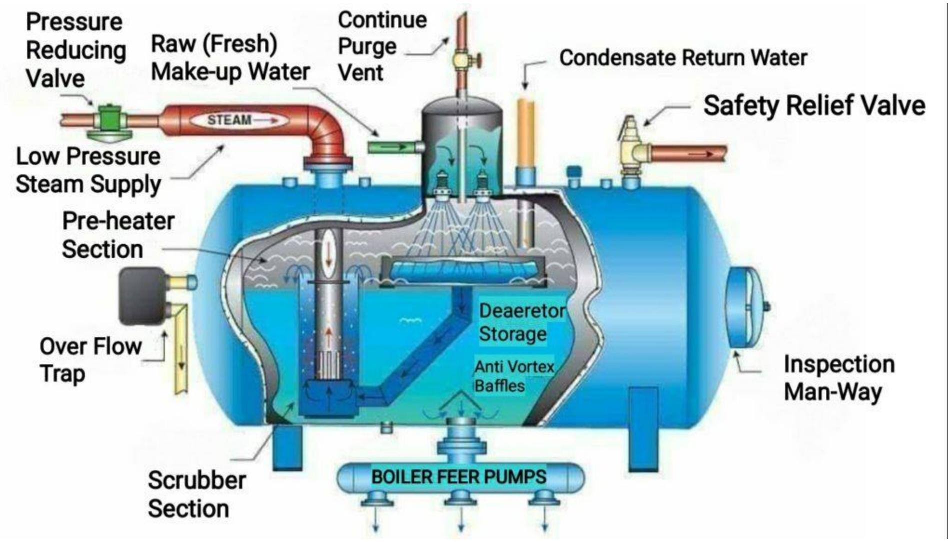
2) Dissolved oxygen can be removed by adding Hydrazine.

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

IV. Boiler corrosion

2) Mechanical de-aeration method:

- This is based on the principle that at high temperature, low pressure and high exposed area, solubility of gases in water decreases.
- So, water is fed into the mechanical de-aerator which is provided with vacuum pump, heaters and perforated plates.
- The out coming water will be free from dissolved gases.



IV. Boiler corrosion

2. Corrosion due to Dissolved Carbon dioxide:

When water containing bicarbonates is heated, bicarbonates decompose to evolve CO_2.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boil}} MgCO_3 + H_2O + CO_2$$

CO_2 reacts with water produces carbonic acid. It is corrosive.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Removal of carbon dioxide:

- Dissolved CO_2 is also removed by mechanical de-aeration method.
- Dissolved CO_2 is removed by adding ammonium hydroxide.

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

IV. Boiler corrosion

3. Hydrolysis of dissolved salts

Certain salts like $MgCl_2$, $CaCl_2$ etc present in water undergo hydrolysis at higher temperature to produce acids which cause corrosion of boiler.

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

The acids produced reacts with iron of the boiler and decay metal.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

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

$$Fe(OH)_2 + O_2 + 2H_2O \longrightarrow \underset{\text{Rust}}{2\,[Fe_2O_3.3H_2O]}$$

Removal of magnesium chloride

- HCl so formed can be removed by adding alkali to the boiler water.
- Softening of water before it fed into boiler.
- Addition of inhibitors like sodium silicate, sodium phosphate and sodium chromate.

Softening of hard water – External treatment

Softening of hard water-External treatment

Softening of hard water can be done by the following methods

2. Lime soda process
3. Zeolite methods
4. Ion exchange resin method
5. Mixed bed deionizer method

Softening of hard water-External treatment

1. Lime soda process

- It is a process in which Lime ($Ca(OH)_2$) and soda (Na_2CO_3) are added to the hard water to convert the soluble calcium and magnesium salts ***to insoluble compounds*** by a chemical reaction.
- $CaCO_3$ and $Mg(OH)_2$ so precipitated are filtered off and removed easily.

It is further divided in to two types

1. Cold lime soda process
2. Hot lime soda process

Softening of hard water-External treatment

1. Lime soda process

I. Cold lime soda process

- In this process a calculated quantity of $Ca(OH)_2$ (lime) and Na_2CO_3 (soda) are mixed with water at room temperature and added to the hard water.
- Following reactions takes place depending on the nature of hardness.

If it is permanent hardness and due to calcium salt

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2Na^{+} \text{ (soda)}$$

slimy suspended precipitate

If it is due to Magnesium salt

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + Ca^{2+} \text{ (lime)}$$

slimy suspended precipitate

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2Na^{+} \text{ (soda)}$$

slimy suspended precipitate

Softening of hard water-External treatment

1. Lime soda process

I. Cold lime soda process

Step 1

<u>If it is Temporary hardness and due to calcium salt</u>

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

Slimy suspended precipitate

<u>If it is due to Magnesium salt</u>

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

Slimy suspended precipitates

Softening of hard water-External treatment

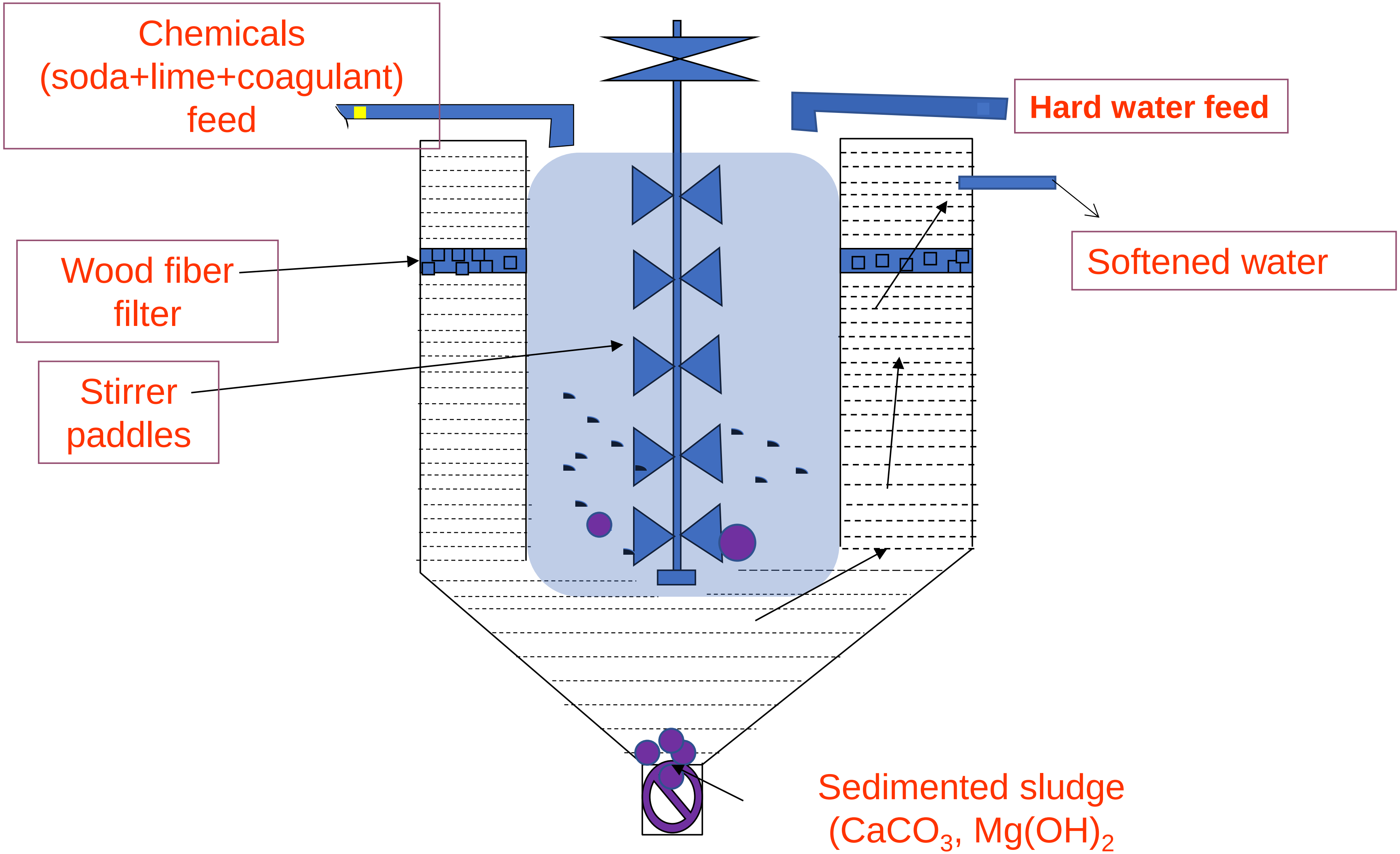
1. Lime soda process

I. Cold lime soda process

Step 2

- Precipitates $CaCO_3$ and $Mg(OH)_2$ are very fine and forms sludge like precipitates in the boiler water.
- Which are difficult to remove because it does not settle easily making it difficult to filter and the removal process. Finally reduces the efficiency of the boiler.
- Thus, it is essential to add small amount of coagulant (such as Alum, Aluminum sulfate, sodium aluminate etc.) which hydrolyses to flocculent precipitate of $Al(OH)_3$ which entraps the fine precipitates.

Continuous cold lime soda softener



2. Hot lime soda Process

In this process a calculated quantity of $Ca(OH)_2$ (lime) and Na_2CO_3 (soda) are mixed with hot water at a temperature range of 80 to 150^oC and added to the hard water. The following reactions takes place depending on the nature of hardness

Advantages of Hot Lime Soda Process

1. Reaction between hardness producing **substance and lime soda** proceeds at a faster rate.

2. Precipitates and sludges formed are settled at the bottom easily and hence No coagulants are required

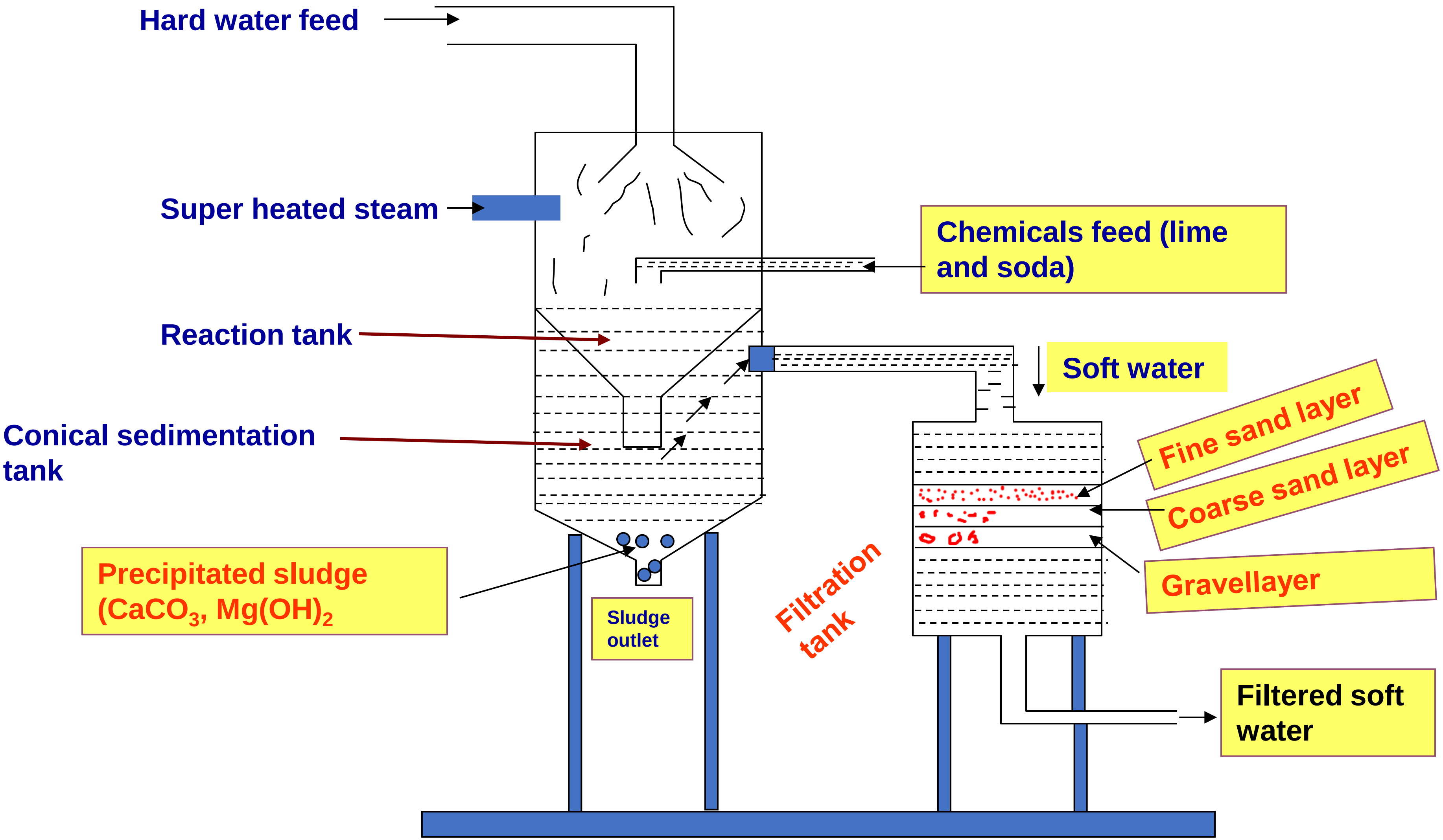
3. Dissolved gases (CO_2 escapes) and the water becomes free from dissolved gases

4. It produces soft water with the residual hardness of 15-30ppm in contrast to the cold lime soda process which produces soft water with 50-60ppm of residual hardness

Hot lime soda Plant consists of three parts

1. **Reaction tank**: water, chemicals and steam are mixed
2. **Conical sedimentation tank** : sludge settles down
3. **Sand filter** : complete removal of sludge from the soft water is ensured

Continuous Hot Lime soda Process



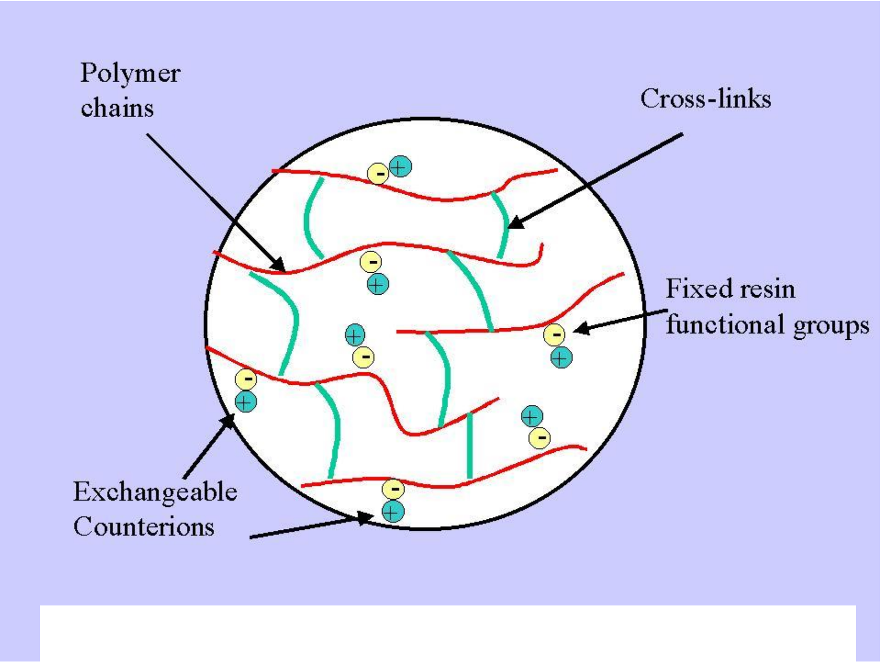
Advantages of Lime soda process

1. It is very economical compared to other methods
2. Iron and manganese salts are also removed by this process
3. It increases the pH of the softened water hence corrosion is minimized also pathogenic bacteria

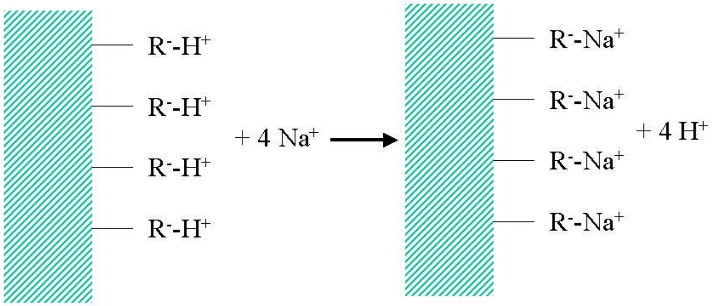
Disadvantages of Lime soda process

1. Disposal of large amount of sludge (insoluble precipitates) poses a problem
2. This can remove hardness to the extent of 15ppm which is not good for boilers

III. Ion-Exchange resin (or) deionization (or) demineralization process



Ion exchange resin



Cation exchange Resin

Resin after treatment

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a microporous structure, and the functional groups attached to the chain is responsible for the "ion-exchange" properties.

In general the resins containing acidic functional groups (-COOH, $-SO_3H$ etc) are capable of exchanging their H^+ ions with other cations, which comes in their contact; whereas those containing basic functional groups ($-NH_2$, =NH as hydrochlorides) are capable of exchanging their anions with other ions, which comes in their contact.

Based on the above fact the resins are classified into two types

1. Cation exchange resin (RH^+) –
   Strongly acidic ($SO_3^-H^+$) and weakly acidic (COO^-H^+) cation exchange resins
2. Anion Exchange resin (ROH^-) –
   Strongly basic ($R_4N^+OH^-$) and weakly basic ($RNH_2^+OH^-$) anion exchange resins

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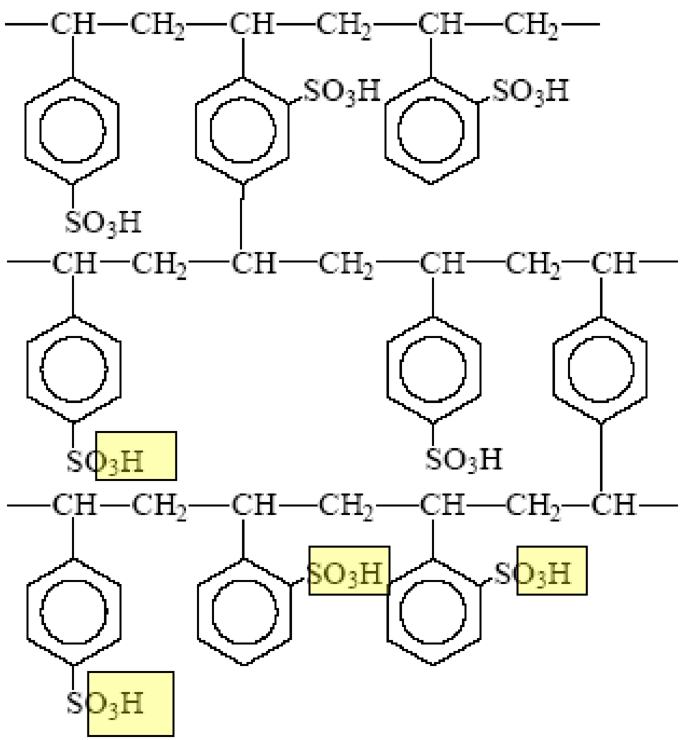
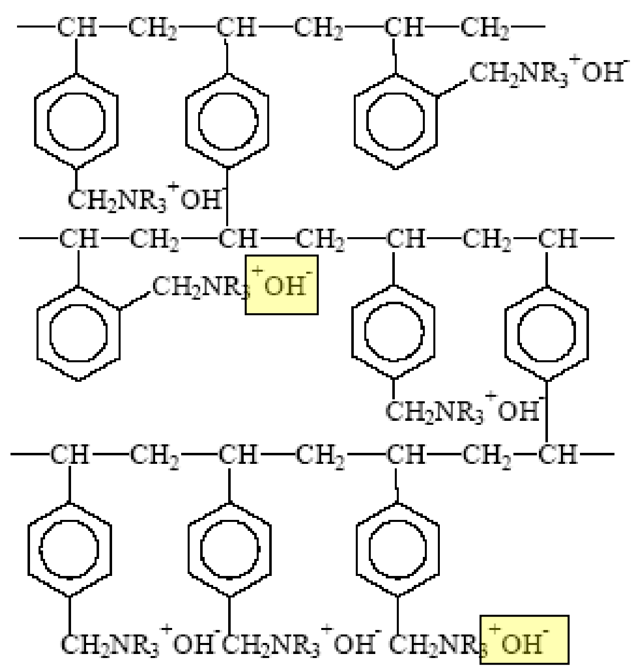
Structure of Cation and Anoin exchange resins

Cation exchange resin



A strongly acidic sulphonated polystyrene cation exchange resin

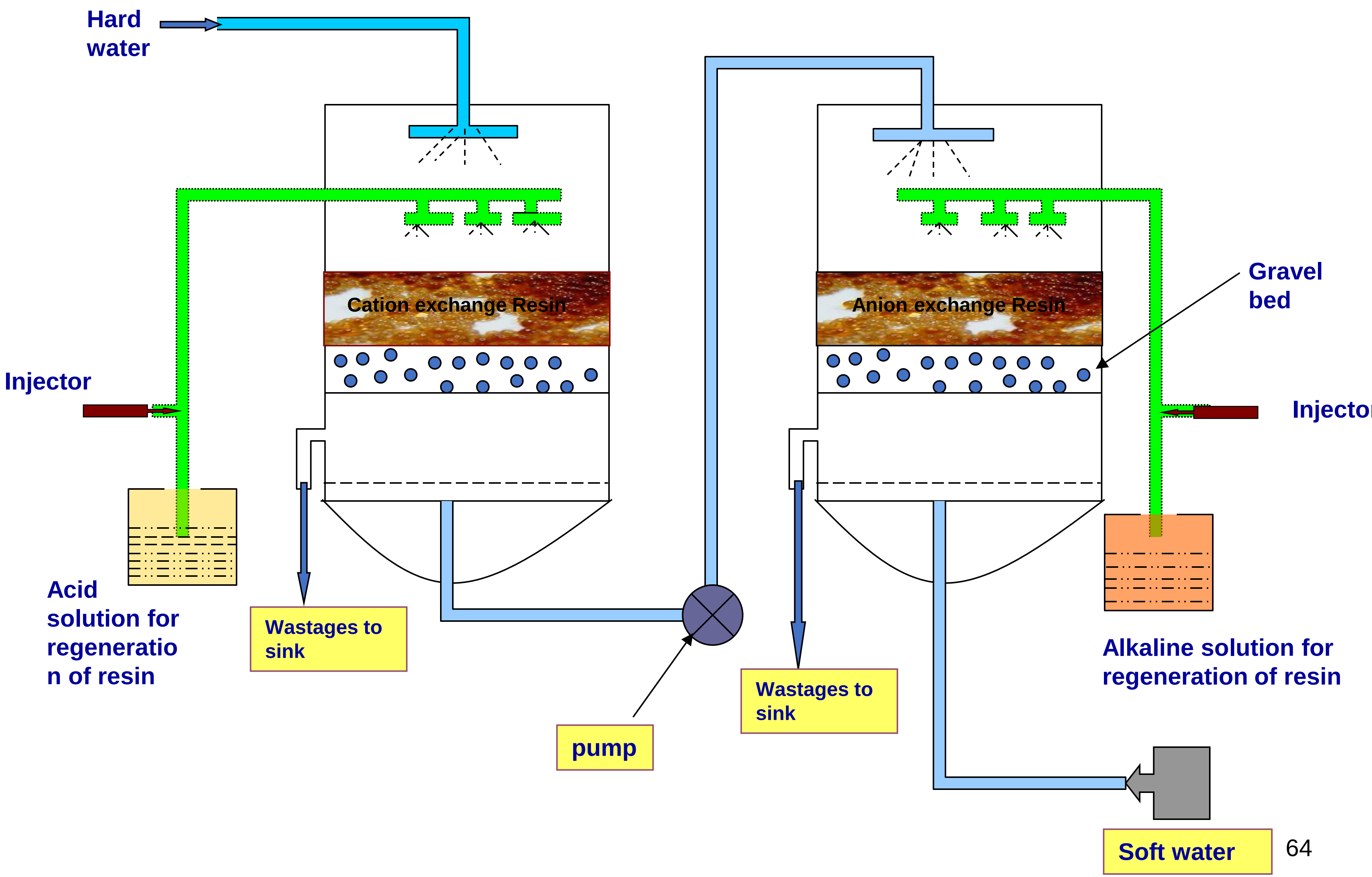
Anion exchange resin



A strongly basic quaternary ammonion anion exchange resin

R = CH_3

Ion exchange purifier or softener



Process or Ion-exchange mechanism involved in water softening

Reactions occurring at Cation exchange resin

$2\ RH^+ + Ca^{2+}$ (hard water) $\longrightarrow R_2Ca^{2+} + 2\ H^+$

$2\ RH^+ + Mg^{2+}$ (hard water) $\longrightarrow R_2Mg^{2+} + 2\ H^+$

Reactions occurring at Anion exchange resin

$2\ ROH^- + SO_4^{2-}$ (hard water) $\longrightarrow R_2SO_4^{2+} + 2\ OH^-$

$2\ ROH^- + Cl^-$ (hard water) $\longrightarrow R_2Cl^- + 2\ OH^-$

At the end of the process

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

Regeneration of ion exchange resins

Regeneration of Cation exchange resin

R_2Ca^{2+} + $2H^+$ (dil. HCl (or) H_2SO_4) $\longrightarrow$ 2 RH^+ + Ca^{2+} ($CaCl_2$, washings)

Regeneration of Anion exchange resin

$R_2SO_4^{2-}$ + $2OH^-$ (dil. NaOH) $\longrightarrow$ 2 ROH^- + SO_4^{2-} (Na_2SO_4, washings)

Advantages

1. The process can be used to soften highly acidic or alkaline waters
2. It produces water of very low hardness of 1-2ppm. So the treated waters by this method can be used in high pressure boilers

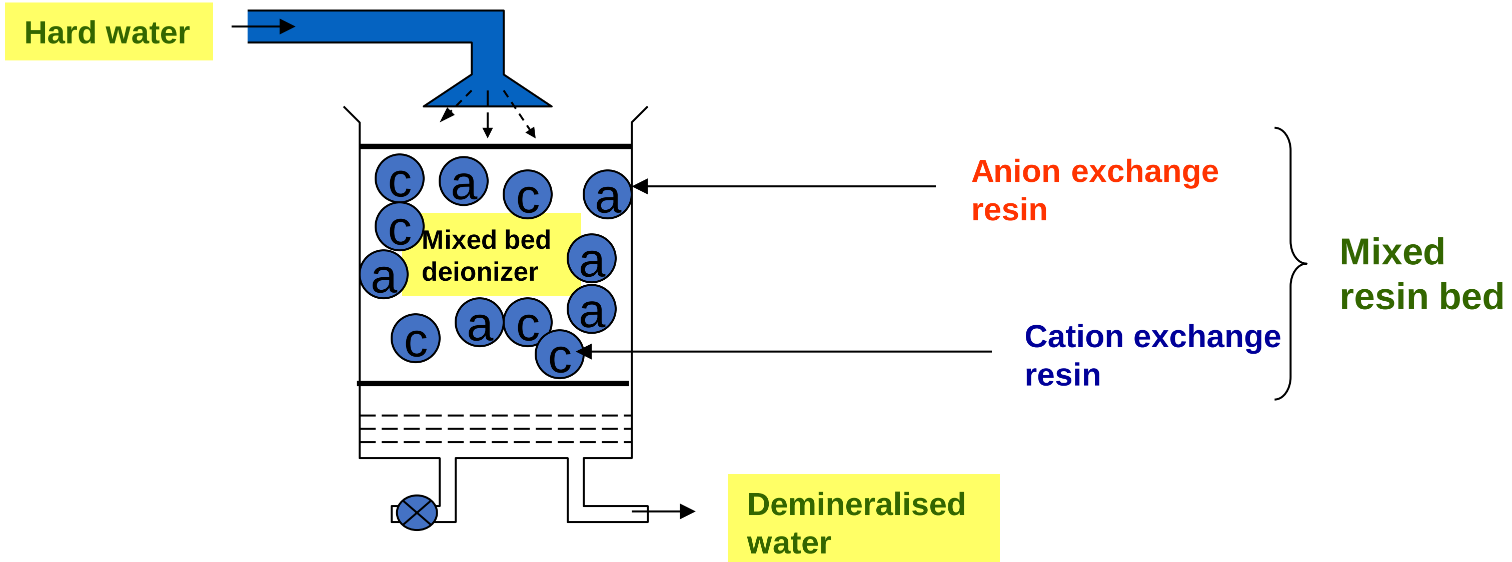
Disadvantages

1. The setup is costly, and it uses costly chemicals
2. The water should not be turbid, and the turbidity level should not be more than 10ppm.

IV. Softening of water by Mixed Bed deioniser

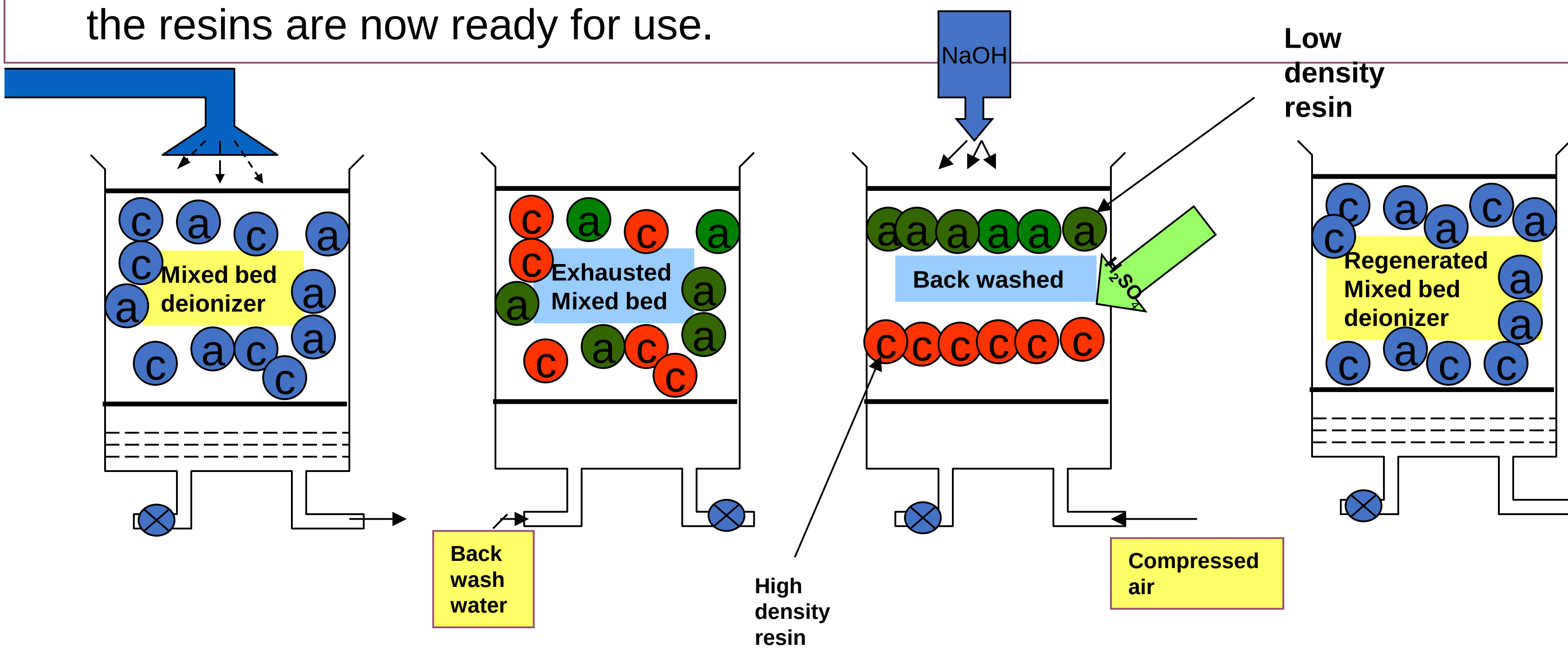
Description and process of mixed bed deionizer

- It is a single cylindrical chamber containing a mixture of anion and cation exchange resins bed
- When the hard water is passed through this bed slowly the cations and anioins of the hard water comes in to contact with the two kind of resins many number of times
- Hence, it is equivalent to passing the hard water many number of times through a series of cation and anion exchange resins.
- The soft water from this method contains less than 1ppm of dissolved salts and hence more suitable for boilers



Regeneration of mixed bed deionizer

- When the bed (resins) are exhausted or cease to soften the water, the mixed bed is back washed by forcing the water from the bottom in the upward direction
- Then the lightweight anion exchanger move to the top and forms a upper layer above the heavier cation exchanger
- Then the anion exchanger is regenerated by passing caustic soda solution (NaOH) from the top and then rinsed with pure water
- The lower cation exchanger bed is then washed with dil.H_2SO_4 solution and then rinsed.
- The two beds are then mixed again by forcing compressed air to mix both and the resins are now ready for use.



DE-SALINATION OF BRACKISH WATER

- The water containing dissolved salts with a particular salty or brackish taste is called brackish water, which contains about 3.5% of dissolved salts.

- This water cannot be used for domestic and industrial applications.

Classification of water under the concentration of dissolved salts.

1. Fresh water-0-100 ppm
2. Brackish water-1000-35000 ppm
3. Sea water- >35000 ppm

DE-SALINATION OF BRACKISH WATER

Desalination:

The process of removal of dissolved salt from the water is known as desalination.

Sea water is brackish water.

Desalination can be done in many ways.

1. Electro dialysis
2. Reverse Osmosis

ELECTRO DIALYSIS

Principle:

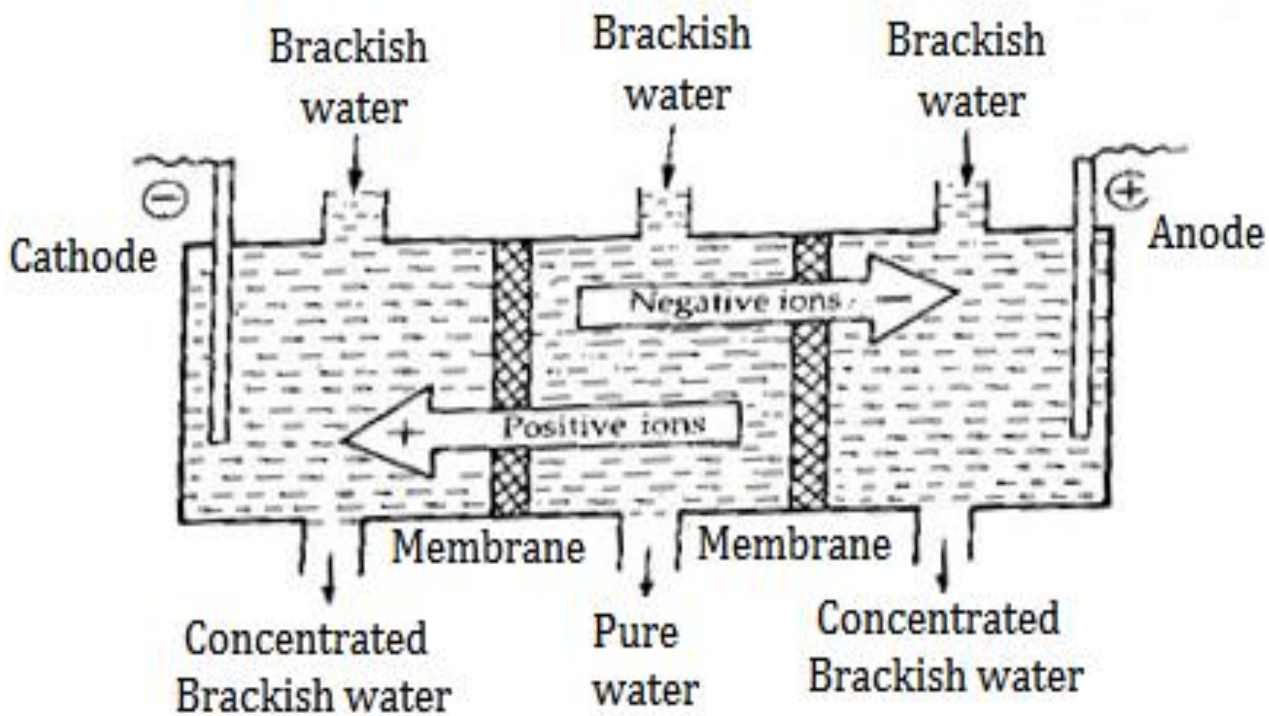
It is based on the principle that when direct current is passed through saline water using electrodes, salt ions present in saline water migrate towards their respective electrodes through ion selective membrane, under the influence of applied EMF.

ELECTRO DIALYSIS

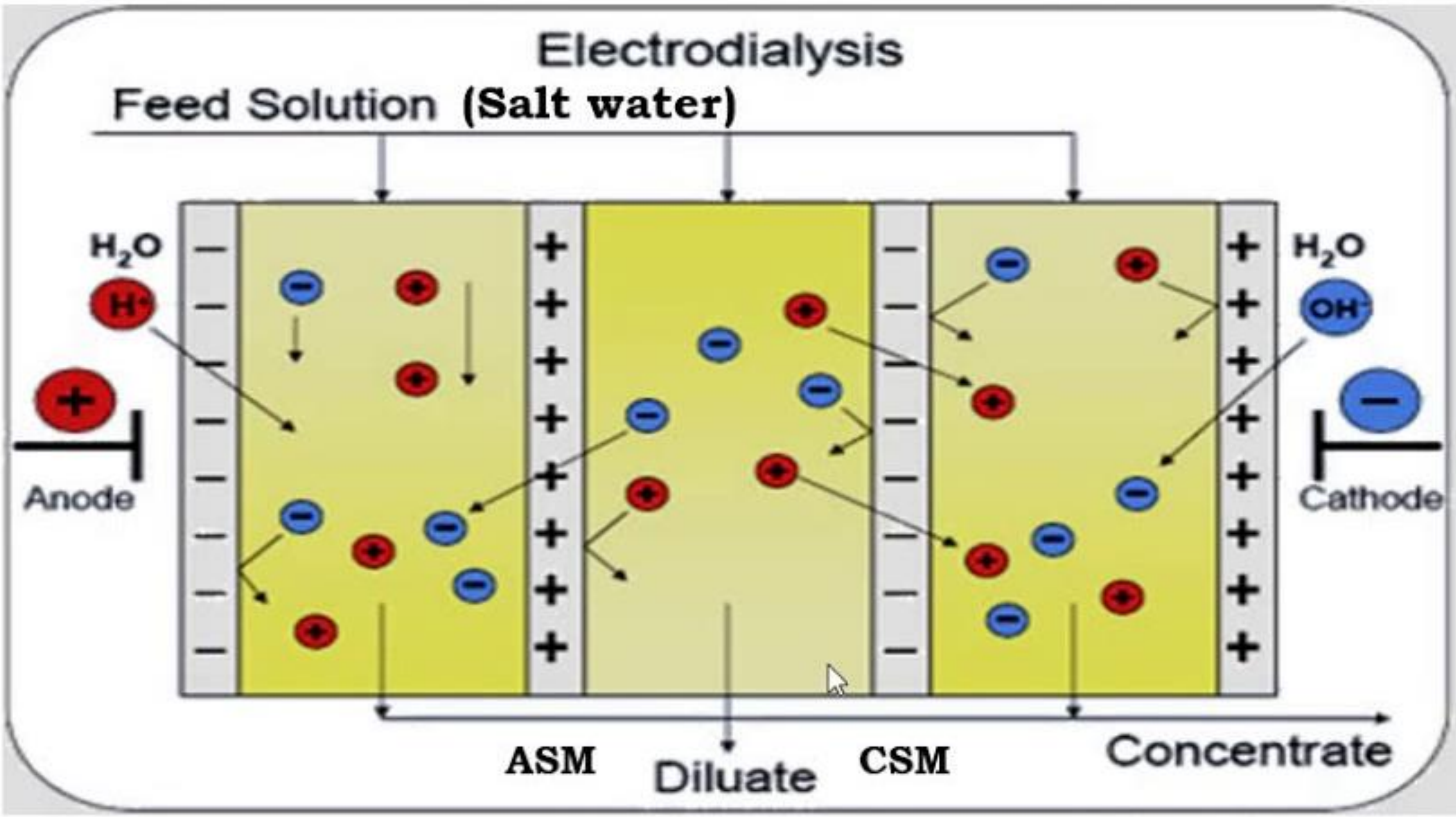
Apparatus:

•The electro dialysis unit consists of a chamber, two electrodes a cathode and an anode.

•The chamber is divided into three compartments with the help of thin, ion selective membranes which are permeable to either cation or anion.



Purification of Water by Electrodialysis process:



Water without salty impurities

Water with more salty impurities

ELECTRO DIALYSIS

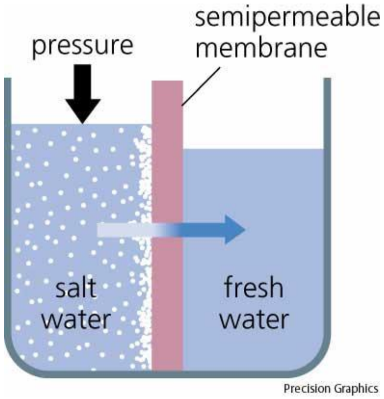
Advantages:

- It is a most compact unit.
- The cost of installation of the plant and its operation is economical.
- If electricity is easily available, it is best suited.

DE-SALINATION OF BRACKISH WATER

REVERSE OSMOSIS

- The flow of solvent molecules from a dilute solution to the concentrated solution when these two are separated by a semi permeable membrane is called osmosis.
- The pressure developed on the membrane is called osmotic pressure.
- If a pressure higher than the osmotic pressure is applied on the concentrated side, **solvent flows in reverse direction** i.e., from higher concentrated region to lower concentrated region.
- This process is known as reverse osmosis

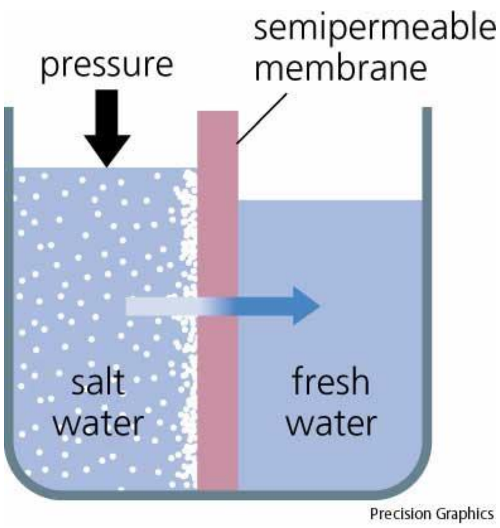


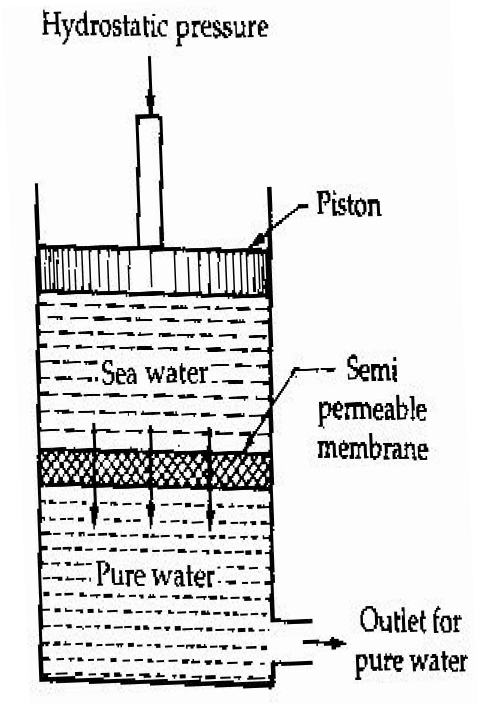
DE-SALINATION OF BRACKISH WATER

REVERSE OSMOSIS

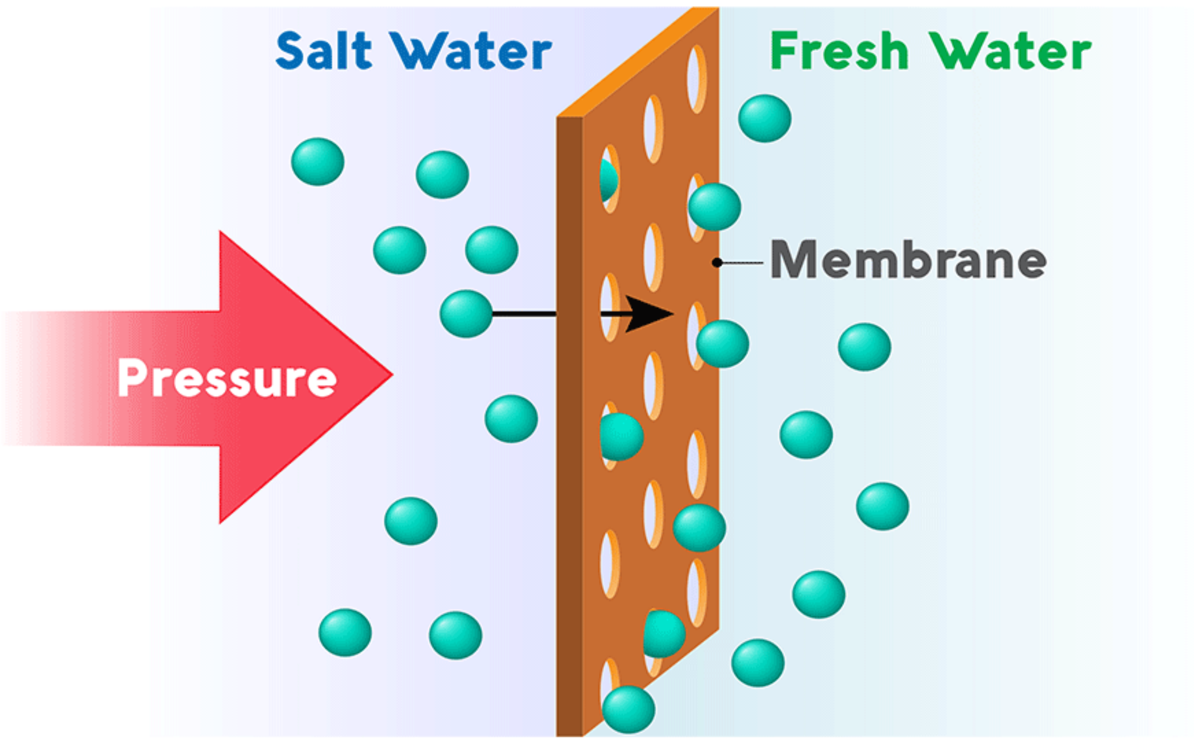
Process:

- The reverse osmosis cell consists of a chamber fitted with a semi permeable membrane, above which, sea water or impure water is taken.
- Pressure of 15 to 40 Kg/cm2 is applied on the sea water or impure water, the pure water is forced through the semi permeable membrane.





Reverse Osmosis

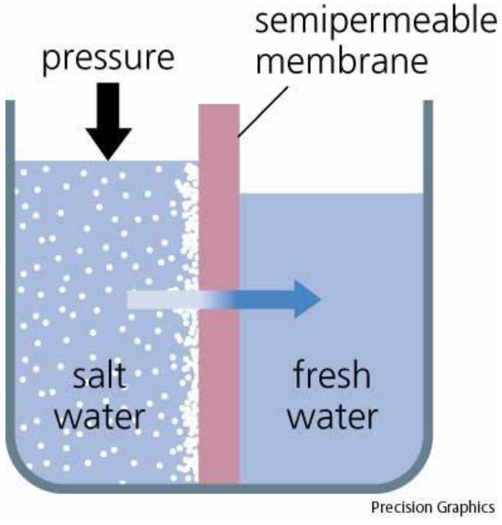


DE-SALINATION OF BRACKISH WATER

REVERSE OSMOSIS

Advantages:

- Maintenance cost is low.
- Lifetime of membrane is high.
- It removes ionic, non-ionic, colloidal and organic matter from water.
- The water used in high pressure boilers is produced by reverse osmosis.



Treatment of Municipal Drinking Water

- Screening :- to remove floating matters
- Aeration:- to remove dissolved gas & improve taste of water
- Sedimentation & Coagulation:–After chemical treatment (L-S)
- Filtration:– Gravity (or) Pressure sand filters
- Sterilization and disinfection
- Storage and distribution

Treatment of Municipal Drinking Water