

# CO-3: Water technology



**K L University**

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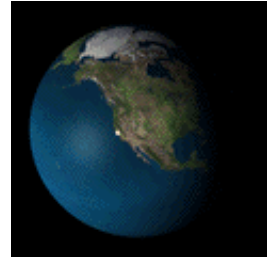
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# Overview Syllabus



## 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**

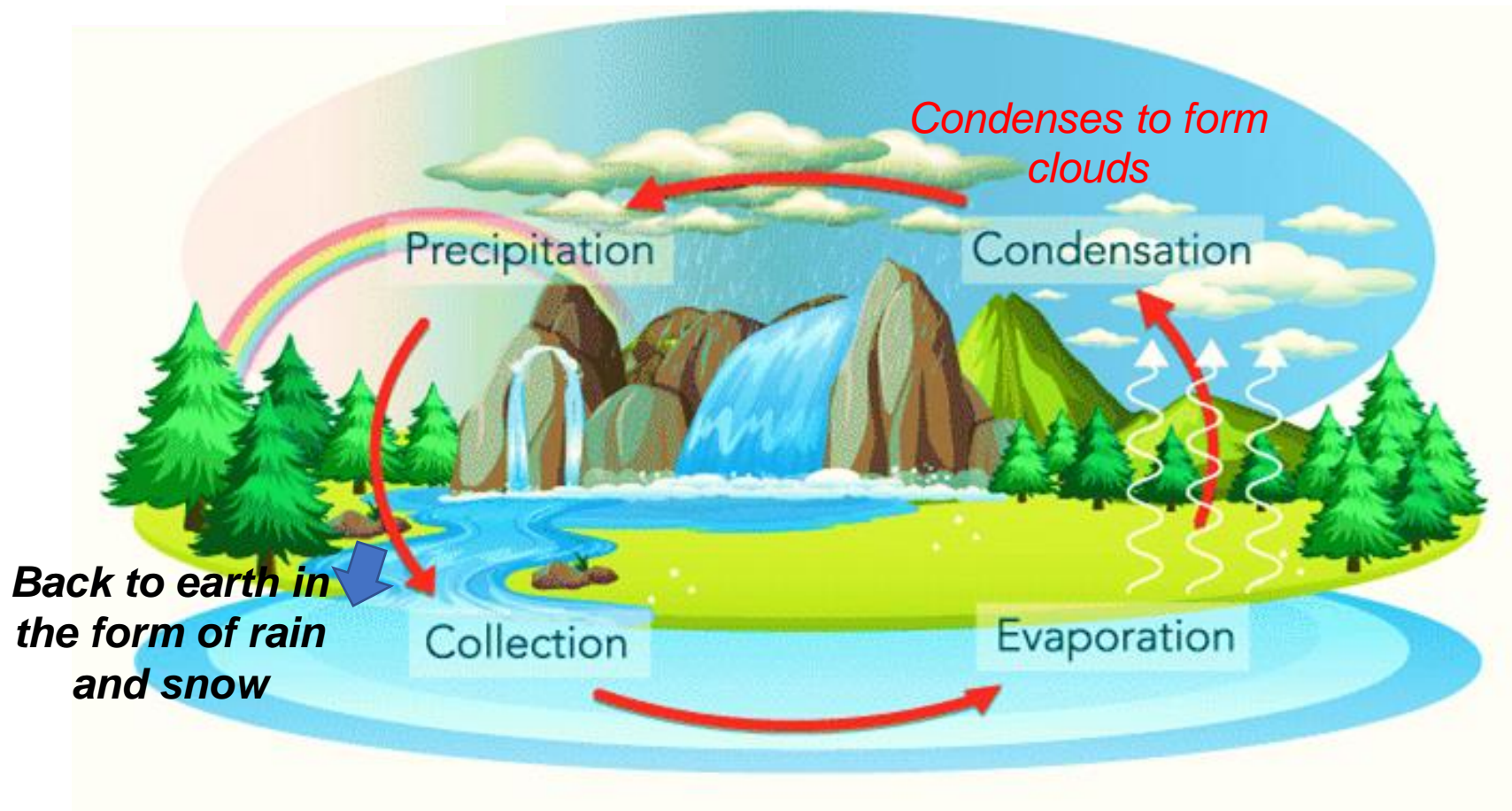


# Why water essential?

- 👉 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

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



Surface water

Rainwater

Sea water

Ground water

*Purest form of natural water, but contaminated with gases*

*large amounts dissolved salts; high salinity*

*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 ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$ ) c) Minerals; d) Salinity; e) Alkalinity; f) Hardness**

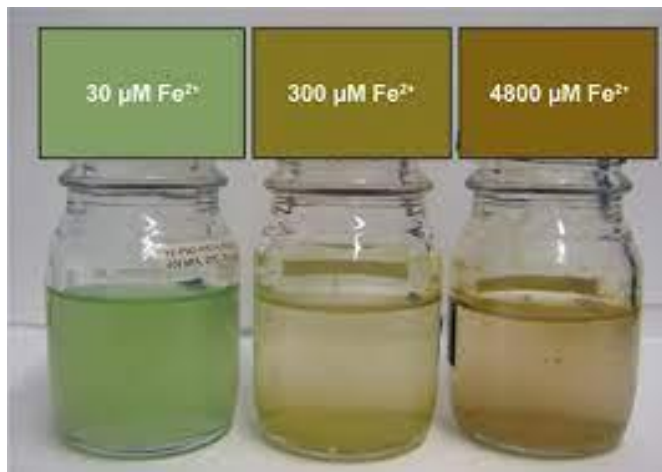
## 3) Biological Impurities - Pathogens, algae, fungi, viruses.

**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*



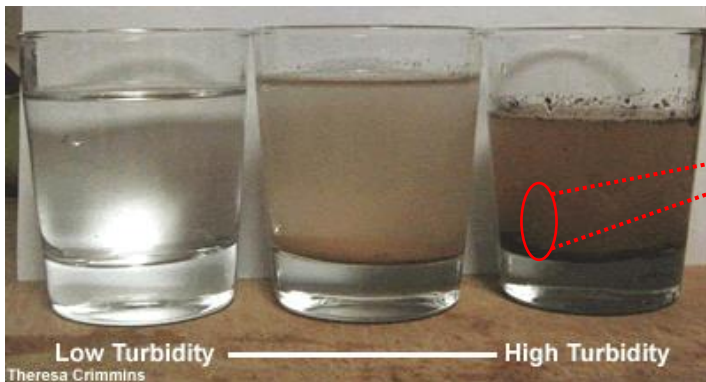
## Industrial activities





# Physical Impurities: Turbidity

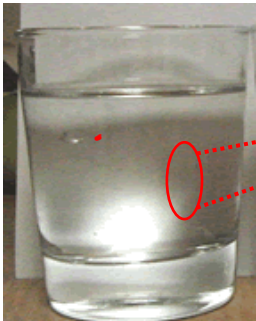
- ☞ It is the measure of relative clarity of a liquid ( water, oils)
- ☞ A turbidity occurs when particles suspended in a liquid ~create a cloudy or hazy appearance.
- ☞ It is due to colloidal, extremely fine suspension (clay, slit, microorganisms).
- ☞ Instead of transmitting light straight ahead, it 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 siemens/cm<sup>3</sup> ( $\mu\text{S}/\text{cm}$ ).
- ☞ It tells you how much dissolved substances, chemicals, and minerals are in it.
- ☞ It enhances if its ion concentration increases.



Conductometry

Water Type	Conductivity ( $\mu\text{S}/\text{cm}$ )
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,  $\text{SO}_4$ ,  $\text{Ca(OH)}_2$ )
- ✓ Soapy ( $\text{NaHCO}_3$ )
- ✓ Brackish (High salt content- $\text{NaCl}$ )
- ✓ Palatable ( $\text{CO}_2$  and  $\text{NO}_3$ )

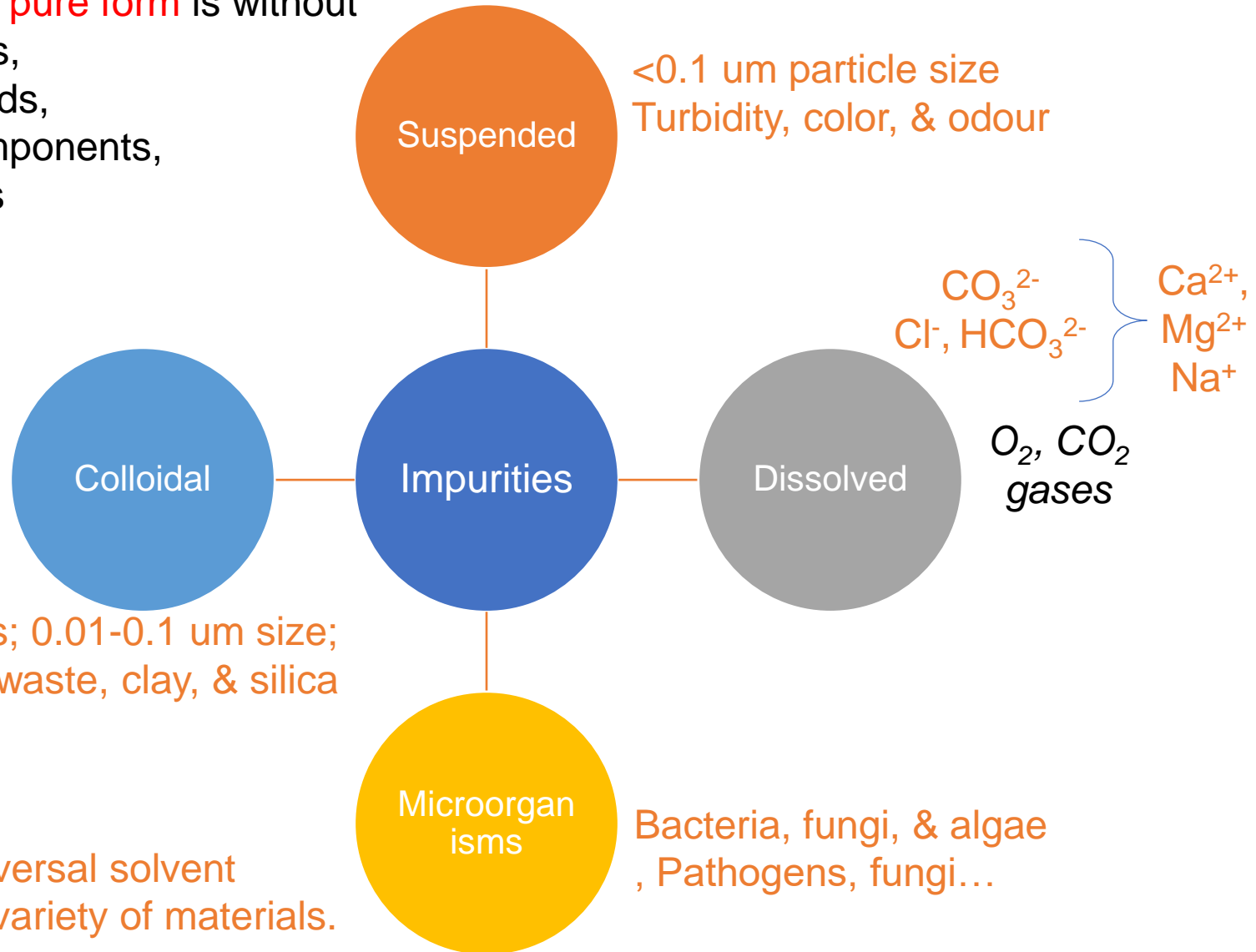
## odor

- 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

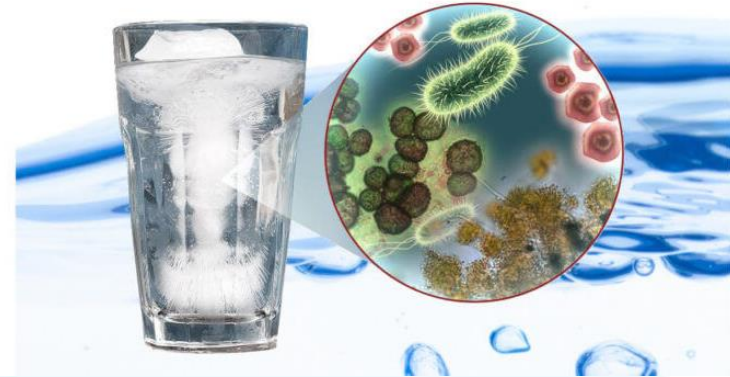


- ✓ Water is a universal solvent
- ✓ It dissolves a variety of materials.

# What Causes Water Impurity and its types?

Water in its **most pure form** is without

- Any chemicals,
- Dissolved solids,
- Biological components,
- Even minerals



**Bacteria**

**Viruses**

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

**Sodium**

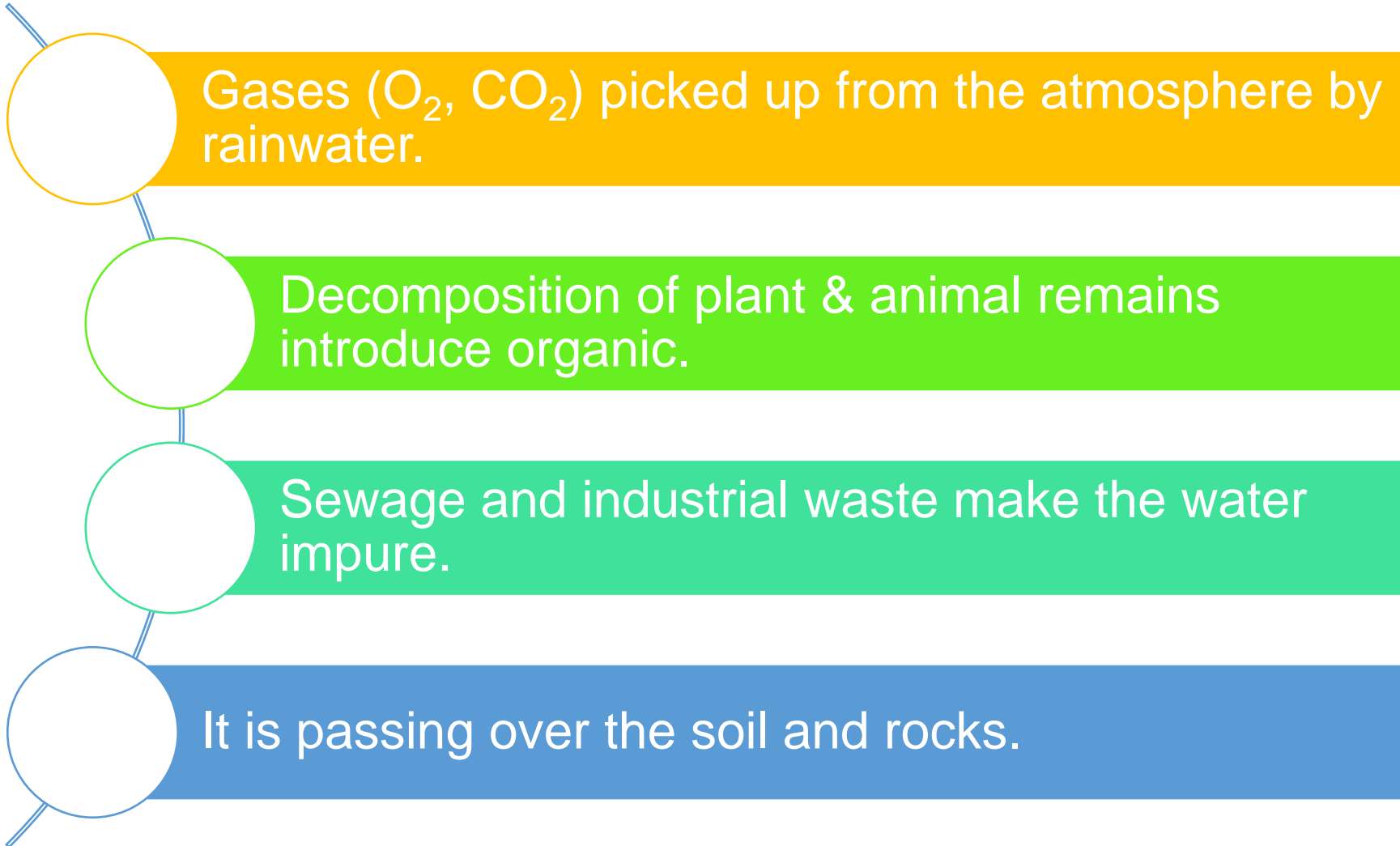
**Dissolved Solids**

**Chlorine**

**Industrial Wastes**









# What Causes Water Impurity and its types?





# Drinking water – W.H.O Parameters

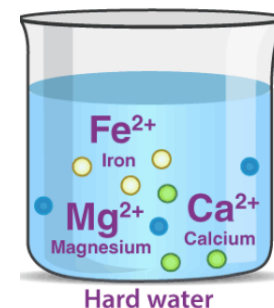
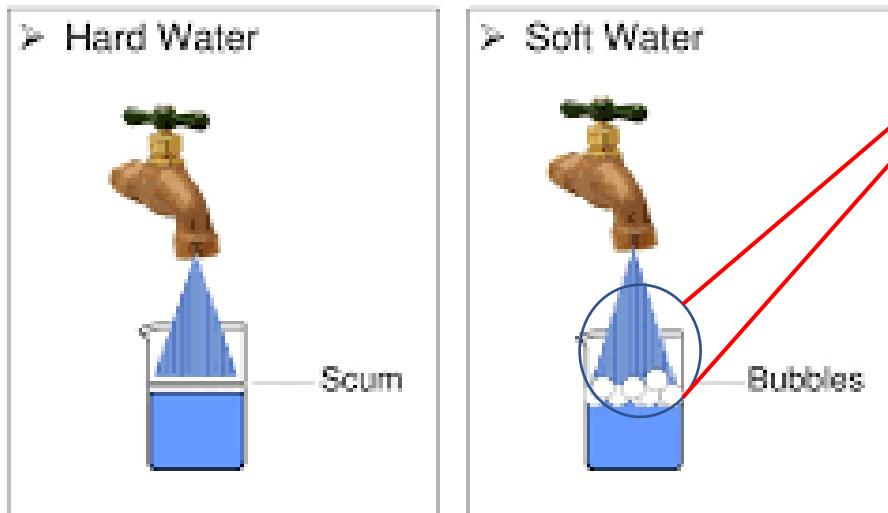
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-  It should be colorless, odorless and tasteless.
-  Its turbidity should be less than 10 ppm
-  It should not contain poisonous metals (Pb, As, Cr).
-  pH should be in the range of 7.0-8.5.
-  Total hardness should be less than 500 ppm.
-  It should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

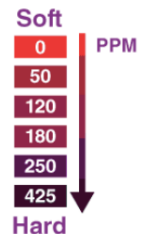
# Hardness of water

- ☞ 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.

## Water Hardness



Salts are less

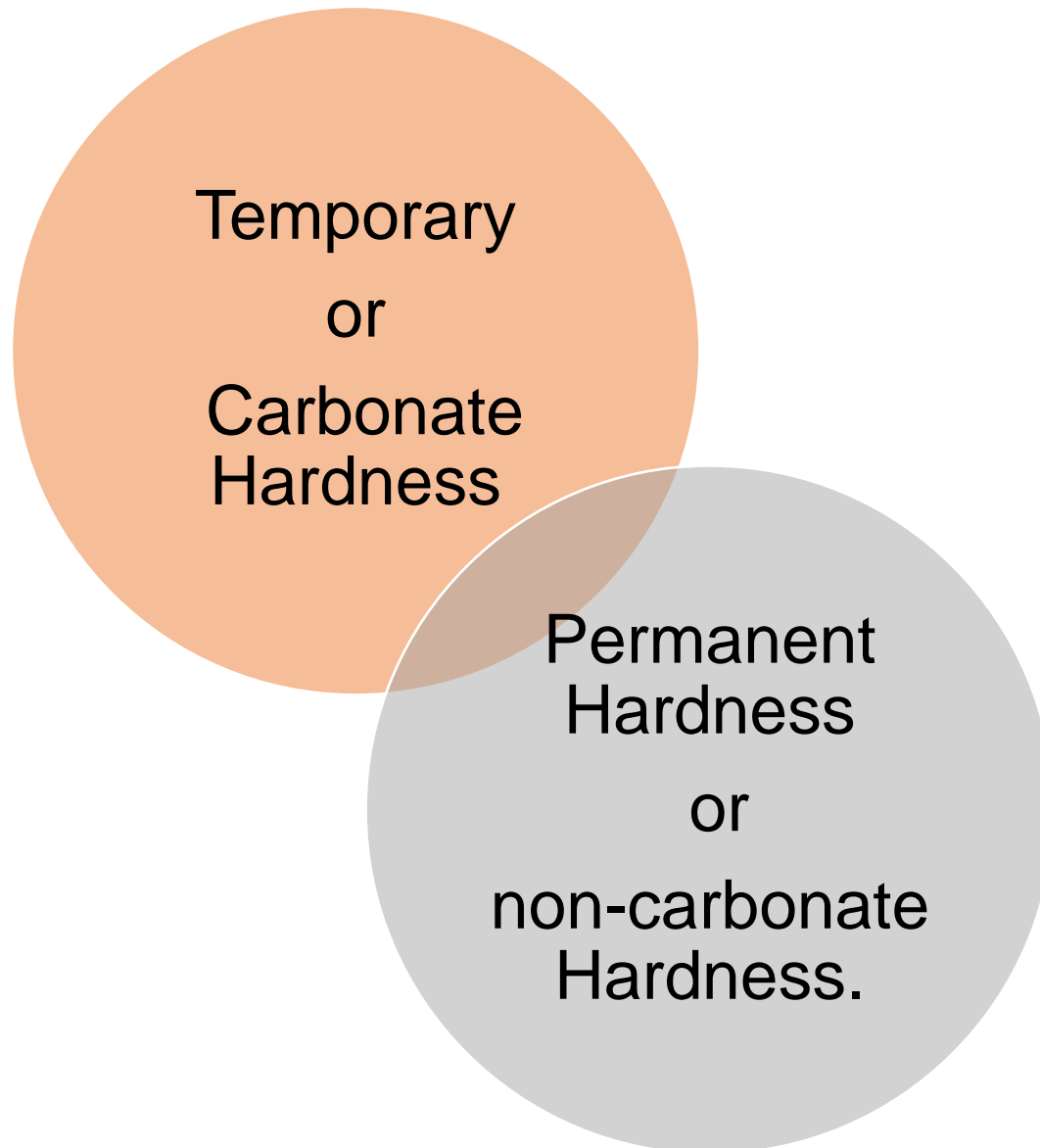


Salts are more

Based on consuming capacity of water is two types

# Type of hardness

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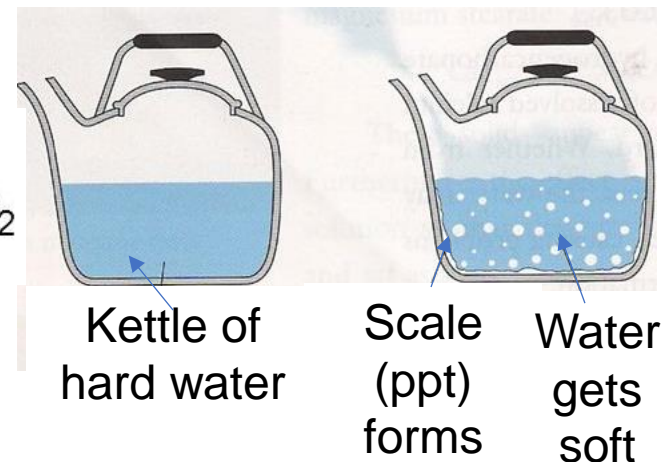


# Type of hardness

## 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:

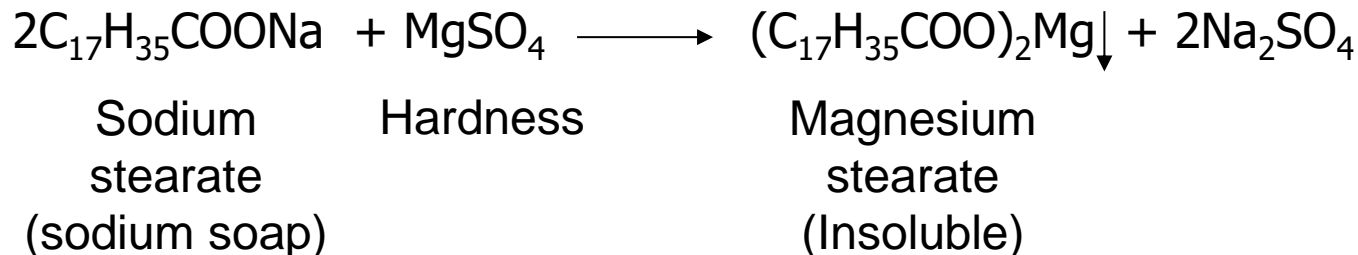
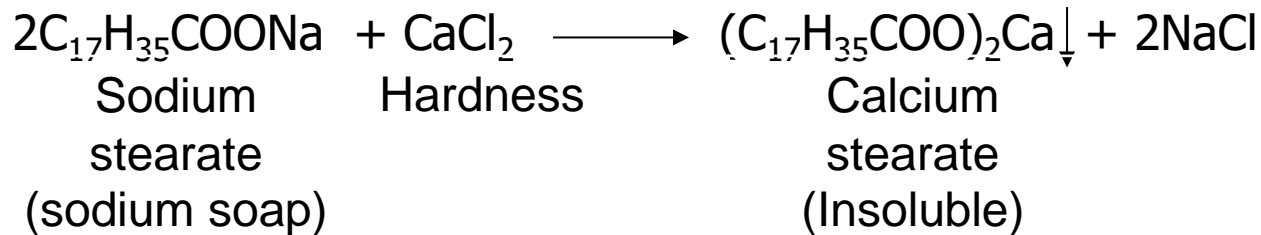


Almost insoluble  $\text{Ca/MgCO}_3$  are formed and are deposited as a scale at the bottom of the vessel, while carbon dioxide escapes.

# Type of hardness

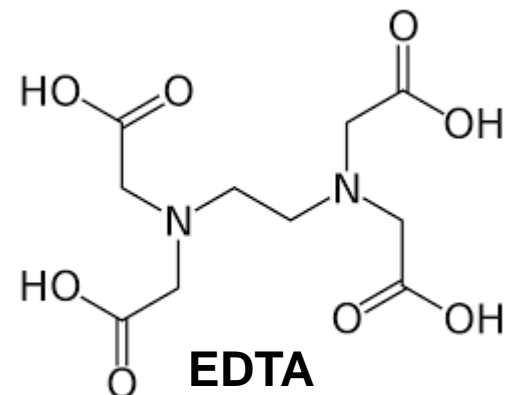
## Permanent hardness

- 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.



# Determination of hardness of water by EDTA method

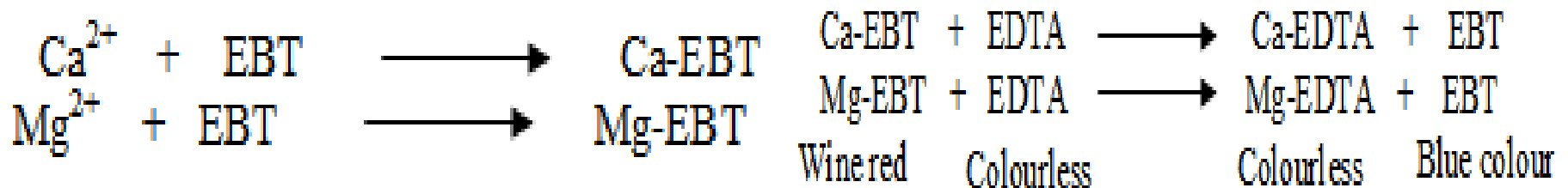
- ◇ By titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent.
- ◇ Since EDTA is insoluble in water, the disodium salt of EDTA is taken for this experiment.
- ◇ EDTA can form four or six coordination bonds with a metal ion.
- ◇ From the amount of the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



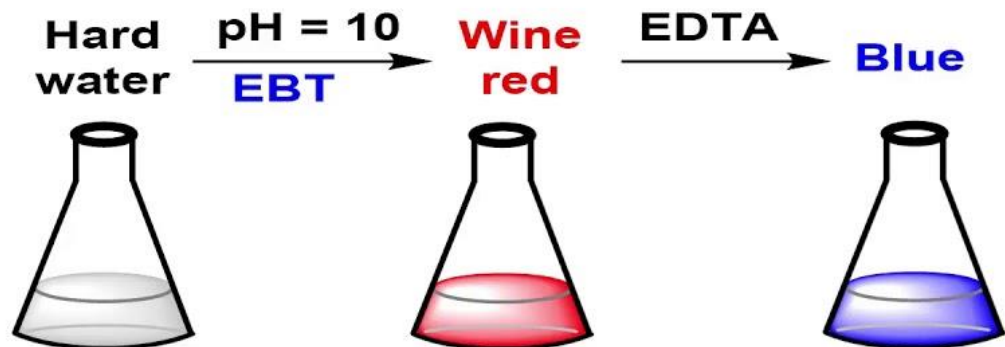
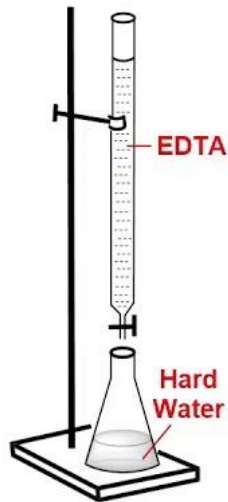
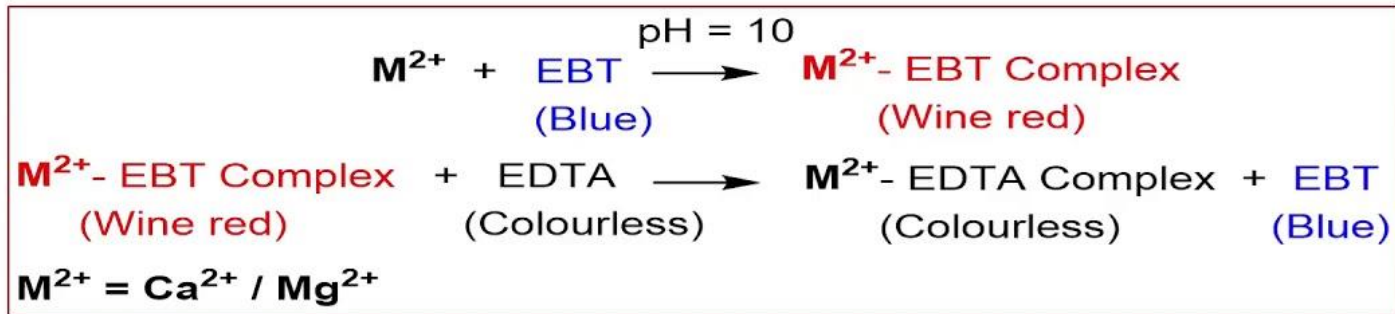


# Determination of hardness of water by EDTA method: *theory*

- ◇ 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.



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



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  $\text{CaCO}_3$  equivalence hardness causing substance present in  $10^6$  parts of water

- Milligrams per liter (mg/liter)

1 mg/L = 1 mg of  $\text{CaCO}_3$  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  $\text{CaCO}_3$  eq per  $10^6$  mg of water

= 1 part of  $\text{CaCO}_3$  eq per  $10^6$  parts of water = 1ppm

- Clare's Degree( $^{\circ}\text{Cl}$ )

1 $^{\circ}$  Clarke = 1part of  $\text{CaCO}_3$  equivalent hardness in 70000 parts of water

- Degrees French ( $^{\circ}\text{Fr}$ )

1 $^{\circ}$  Fr = 1 part of  $\text{CaCO}_3$  eq per  $10^5$  parts of water

## CaCO<sub>3</sub> 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<sub>4</sub> per liter

### Solution :

$$\text{Calcium carbonate equivalent hardness} = \frac{204 \times 100}{136} = 150 \text{ mg of CaCO}_3/\text{L} = 150 \text{ ppm}$$

Note : Mol. Weight of CaCO<sub>3</sub> = 100

Mol. Weight of CaSO<sub>4</sub> = 136

# Equivalence conversion during hardness calculation

Hardness producing substance	Molecular weight as $\text{CaCO}_3$	Equivalent weight as $\text{CaCO}_3$
$\text{Ca}(\text{HCO}_3)_2$	162/100	81/50
$\text{Mg}(\text{HCO}_3)_2$	146/100	73/50
$\text{CaSO}_4$	136/100	68/50
$\text{CaCl}_2$	111/100	55.5/50
$\text{MgSO}_4$	120/100	60/50
$\text{MgCl}_2$	95/100	47.5/50
$\text{CaCO}_3$	100/100	50/50
$\text{MgCO}_3$	84/100	42/50
$\text{CO}_2$	44/100	22/50
$\text{HCO}_3^-$	61/100	61/50
$\text{OH}^-$	17/100	17/50
$\text{CO}_3^{2-}$	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

$\text{Mg}(\text{HCO}_3)_2 = 16.8\text{mg/L}$ ,  $\text{MgCl}_2 = 19\text{ mg/L}$ ,  $\text{CaCO}_3 = 20\text{ ppm}$ ,  $\text{MgSO}_4 = 24.0\text{mg/L}$  and  $\text{KOH} = 1\text{ ppm}$ .

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

**Solution** Step 1: Conversion in to  $\text{CaCO}_3$  equivalent

Constituent present	Quantity (mg/L)	Conversion factor	Hardness
$\text{Mg}(\text{HCO}_3)_2$	16.8	100/146	$16.8 * 100/146 = 11.5\text{ppm}$
$\text{MgCl}_2$	19.0	100/95	$19.0 * 100/95 = 20\text{ppm}$
$\text{CaCO}_3$	20	100/100	$20.0 * 100/100 = 20\text{ ppm}$
$\text{MgSO}_4$	24.0	100/120	$24.0 * 100/120 = 20\text{ ppm}$

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
<p>1. Ca for healthy teeth and bones</p> 	<p>1. Limescale -blocks pipes and leaves a scale on kettles.</p>  
<p>2. Good for Brewing</p> 	<p>2. Wastes soap</p> 
<p>3. Tastes better</p> 	<p>3. Scum produced with soap</p> 

# 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

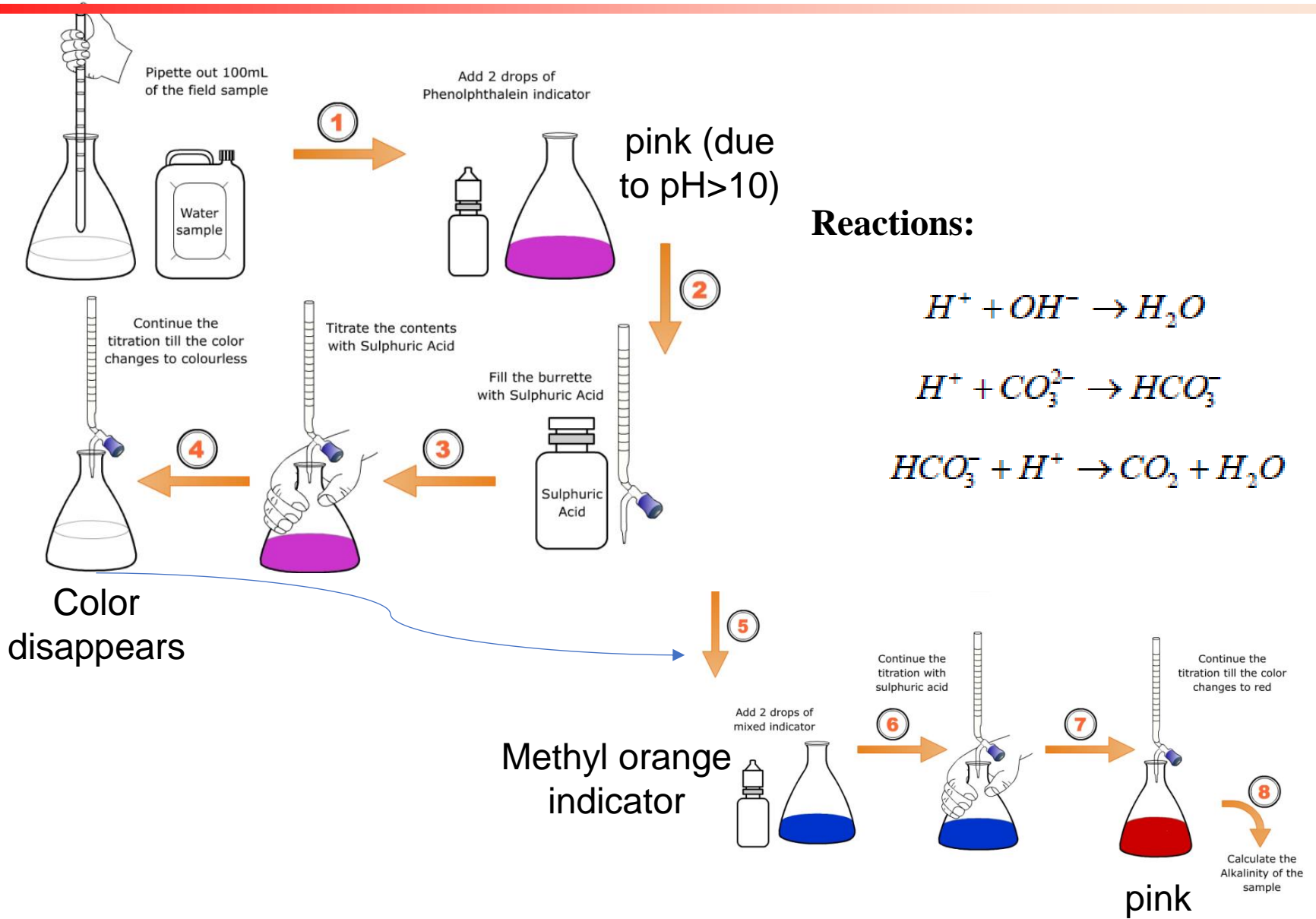
*Def:*

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

## Factors

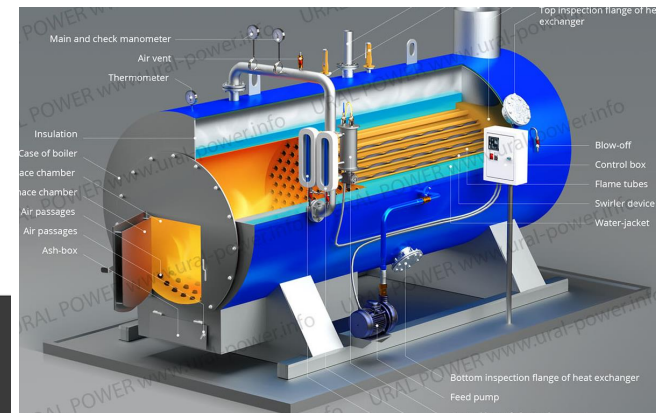
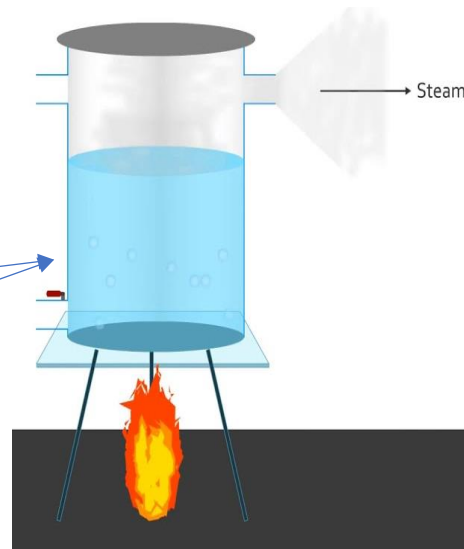
- The presence of salts of weak organic acids which undergo hydrolysis and consume H<sup>+</sup> ions of water. As a result, concentration of OH<sup>-</sup> ions increases in water and water becomes alkaline.
- The presence of HCO<sub>3</sub><sup>-</sup>, HSiO<sub>3</sub><sup>-</sup> and SiO<sub>3</sub><sup>-2</sup> ions in water which makes the water alkaline because they have tendency to take up H<sup>+</sup> ions from water.

# Alkalinity of water

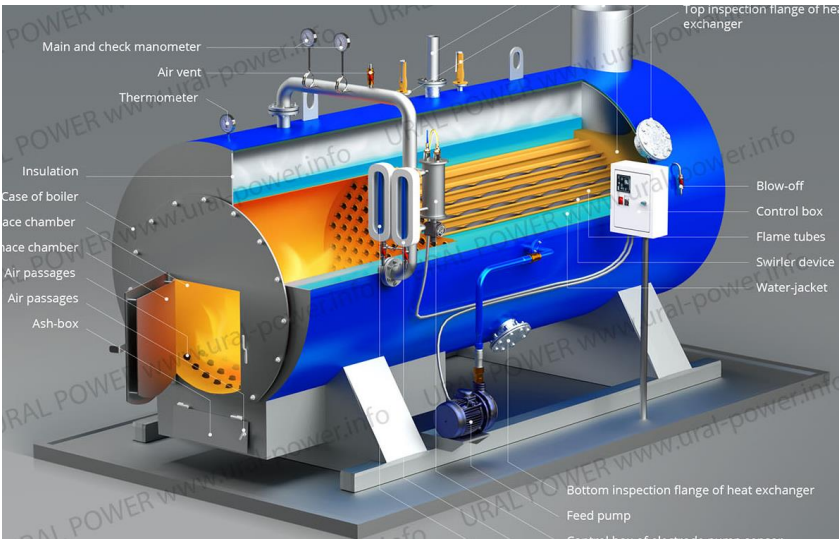


# Boiler troubles

- ☞ 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

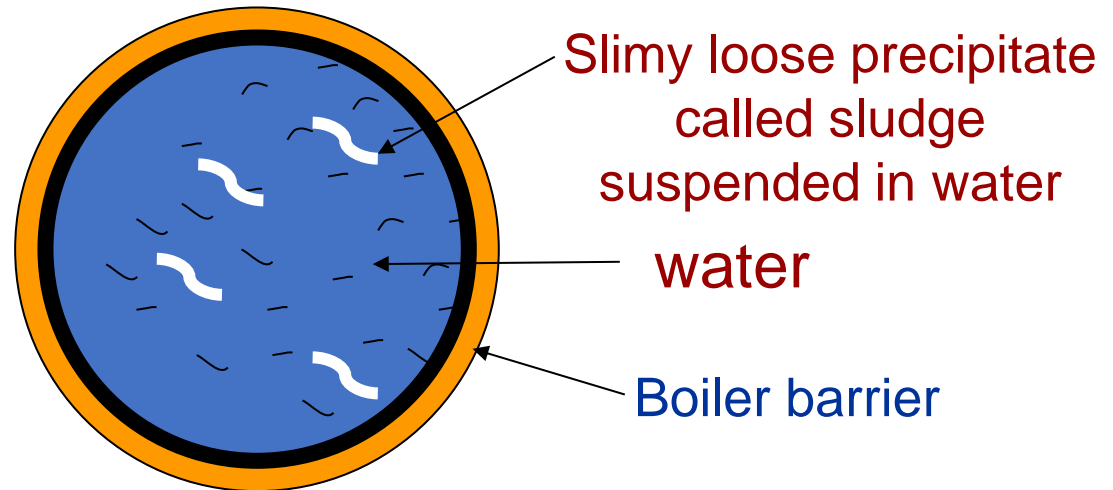


# Common impurities of water and their effect

Name	Common Name	Effect
Calcium carbonate, $\text{CaCO}_3$	Chalk, limestone	Soft scale
Calcium bicarbonate, $\text{CaHCO}_3$	-	Soft scale, $\text{CO}_2$
Calcium sulphate, $\text{CaSO}_4$	Gypsum, plaster of paris	Hard scale
Calcium chloride $\text{CaCl}_2$	-	Corrosion
Magnesium carbonate, $\text{MgCO}_3$	Magnesite	Soft scale
Magnesium bicarbonate, $\text{MgHCO}_3$	-	Scale, Corrosion
Magnesium sulphate, $\text{MgSO}_4$	Epsom salt	Corrosion
Sodium Chloride, $\text{NaCl}$	Common salt	Electrolysis

# Scale & sludge formation

## 1. Sludge

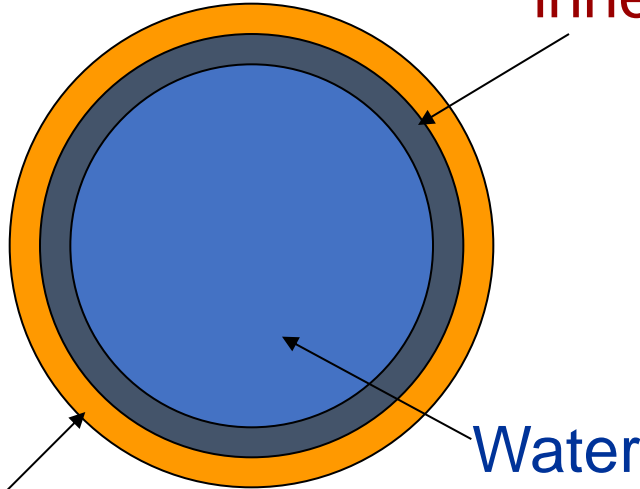


- Sludge is a **soft, loose and slimy precipitate** formed within the boiler.
- It can be easily scrapped off with a wire brush.
- It is formed at **comparatively colder portions** of the boiler and collects in areas of the system, where the flow rate is slow or at bends.
- It is formed by substances which have greater solubilities in hot water than in cold water, e.g.,  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  etc.,

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

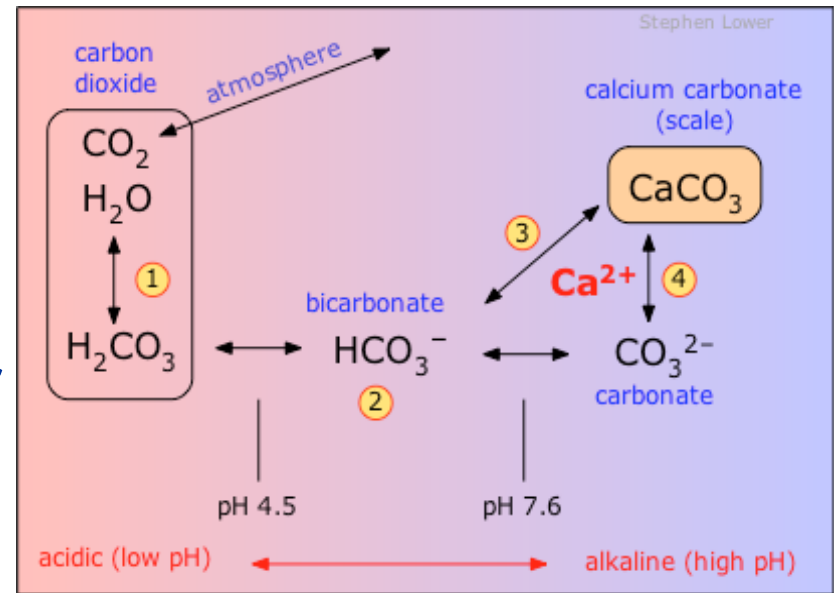
# I. Scale & Sludge formation

## 1. Scale



Hard adherent coating on inner walls of boiler

Boiler wall

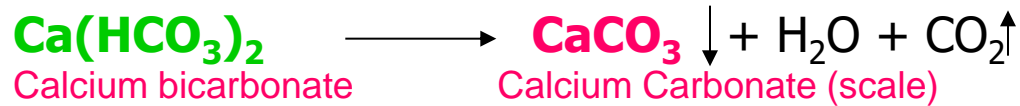


- Scales are hard substances which **sticks very firmly** to the inner surfaces of the boiler wall.
- Scales are difficult to remove even with the help of a hammer and chisel.
- Examples:  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$



# Reasons for formation of scale

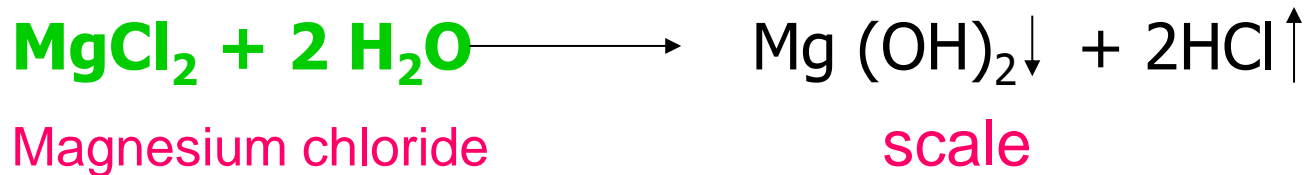
## 1. Presence of $\text{Ca}(\text{HCO}_3)_2$ in low pressure boilers



## 2. Presence of $\text{CaSO}_4$ in high pressure boilers

On continuous heating,  $\text{CaSO}_4$  present in boiler water gets precipitated as scales

## 3. Presence of $\text{MgCl}_2$ in high temperature boilers



$\text{Mg}(\text{OH})_2$  can also be generated by thermally decomposing  $\text{Mg}(\text{HCO}_3)_2$

## 4. Presence of $\text{SiO}_2$

It forms insoluble hard adherent  $\text{CaSiO}_3$  &  $\text{MgSiO}_3$  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

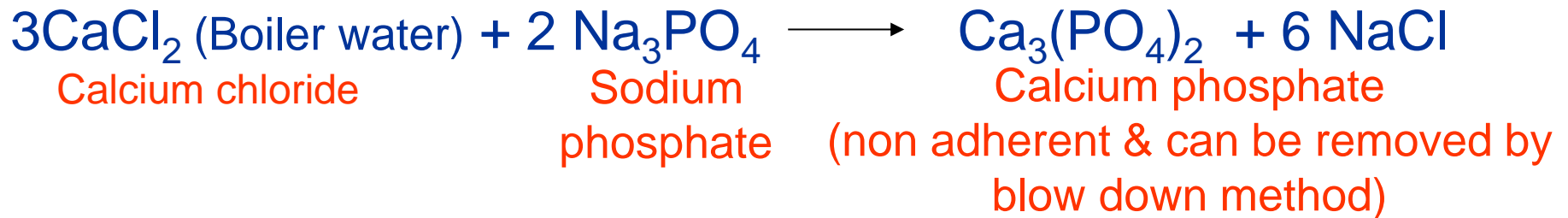
Carbonate conditioning: Addition of carbonate compound

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.



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.

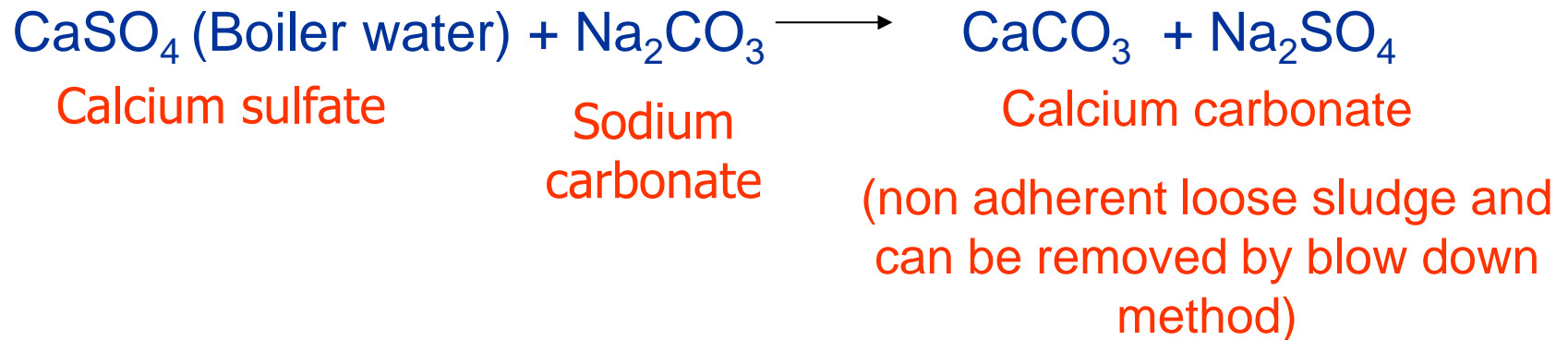
$\text{NaH}_2\text{PO}_4$  (acidic in nature),

$\text{Na}_2\text{HPO}_4$  (weakly alkaline in nature),

$\text{Na}_3\text{PO}_4$  (Alkaline in nature)

# Selection of Phosphate compound

## 2. Carbonate conditioning



Caution: Excess  $\text{Na}_2\text{CO}_3$  can result in caustic embrittlement



# Prevention of scale formation

## 3. Calgon conditioning



Calgon – sodium hexa  
meta phosphate



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 .



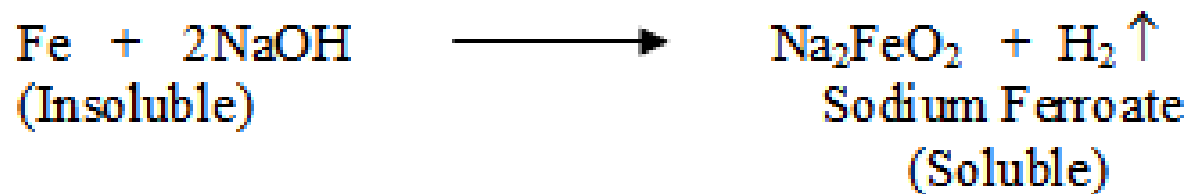
- Extent of hydrolysis increases with the temperature.
- NaOH has better mobility and can penetrate in fine cracks present in boiler walls.

*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



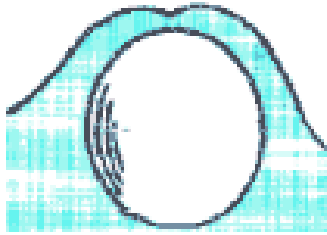
### Prevention of Caustic embrittlement

- (i) Use phosphate salts instead of sodium carbonate
- (ii) use  $\text{Na}_2\text{SO}_4$  or agar-agar gel compounds to fill the fine cracks.

### III. Priming and foaming



Foaming



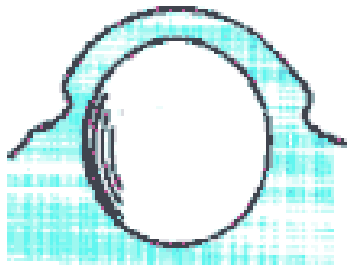
Normal bubble

#### Foaming

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



Priming

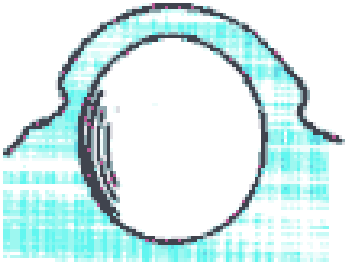


Carry over  
bubble

#### 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  $CO_2$

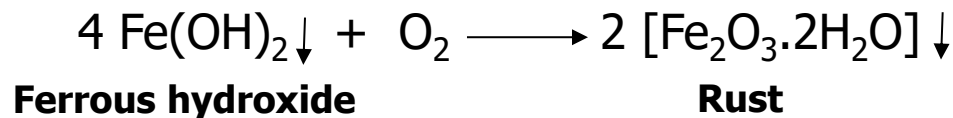
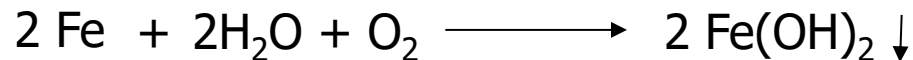


Acids formed by dissolved salts

## IV. Boiler corrosion

### 1. Corrosion due to dissolved oxygen (DO)

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



### Removal of dissolved oxygen

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



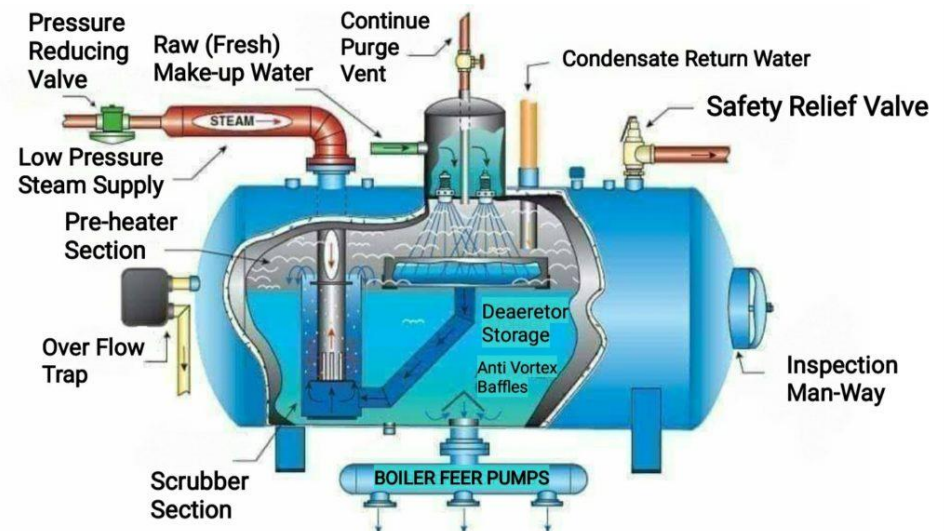
**2)** Dissolved oxygen can be removed by adding Hydrazine.



## 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<sub>2</sub>.*

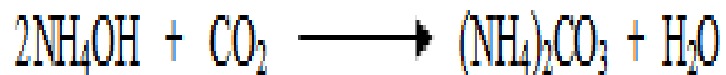


CO<sub>2</sub> reacts with water produces carbonic acid. It is corrosive.



### Removal of carbon dioxide:

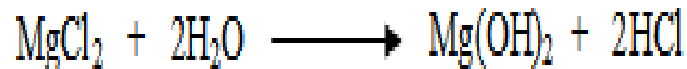
- Dissolved CO<sub>2</sub> is also removed by mechanical de-aeration method.
- Dissolved CO<sub>2</sub> is removed by adding ammonium hydroxide.



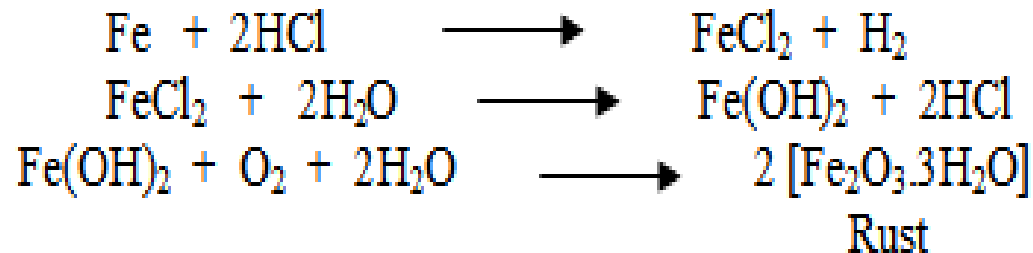
## IV. Boiler corrosion

### 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.*



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



### 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

# External treatment of water – External Conditioning of water

## 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 ( $\text{Ca(OH)}_2$ ) and soda ( $\text{Na}_2\text{CO}_3$ ) are added to the hard water to convert the soluble calcium and magnesium salts **to insoluble compounds** by a chemical reaction.
- $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$  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

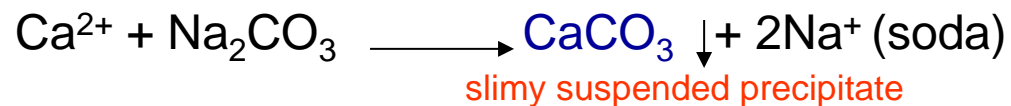
# Softening of hard water-External treatment

## 1. Lime soda process

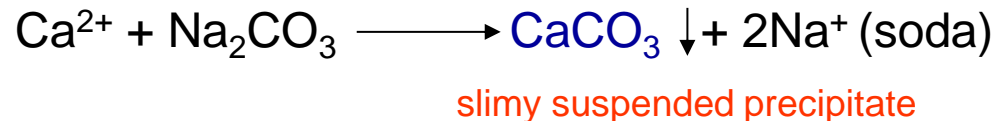
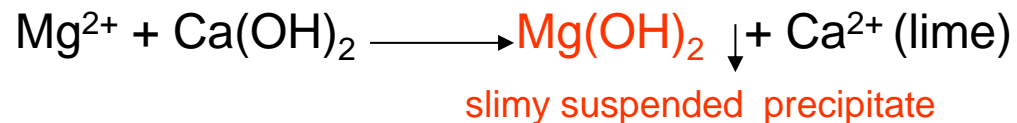
### I. Cold lime soda process

- In this process a calculated quantity of  $\text{Ca(OH)}_2$  (lime) and  $\text{Na}_2\text{CO}_3$  (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



If it is due to Magnesium salt



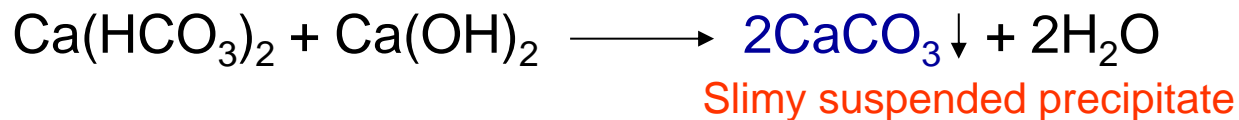
# Softening of hard water-External treatment

## 1. Lime soda process

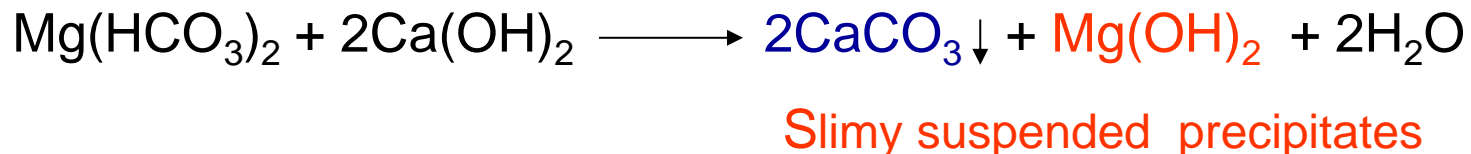
### I. Cold lime soda process

#### Step 1

If it is Temporary hardness and due to calcium salt



If it is due to Magnesium salt



# Softening of hard water-External treatment

## 1. Lime soda process

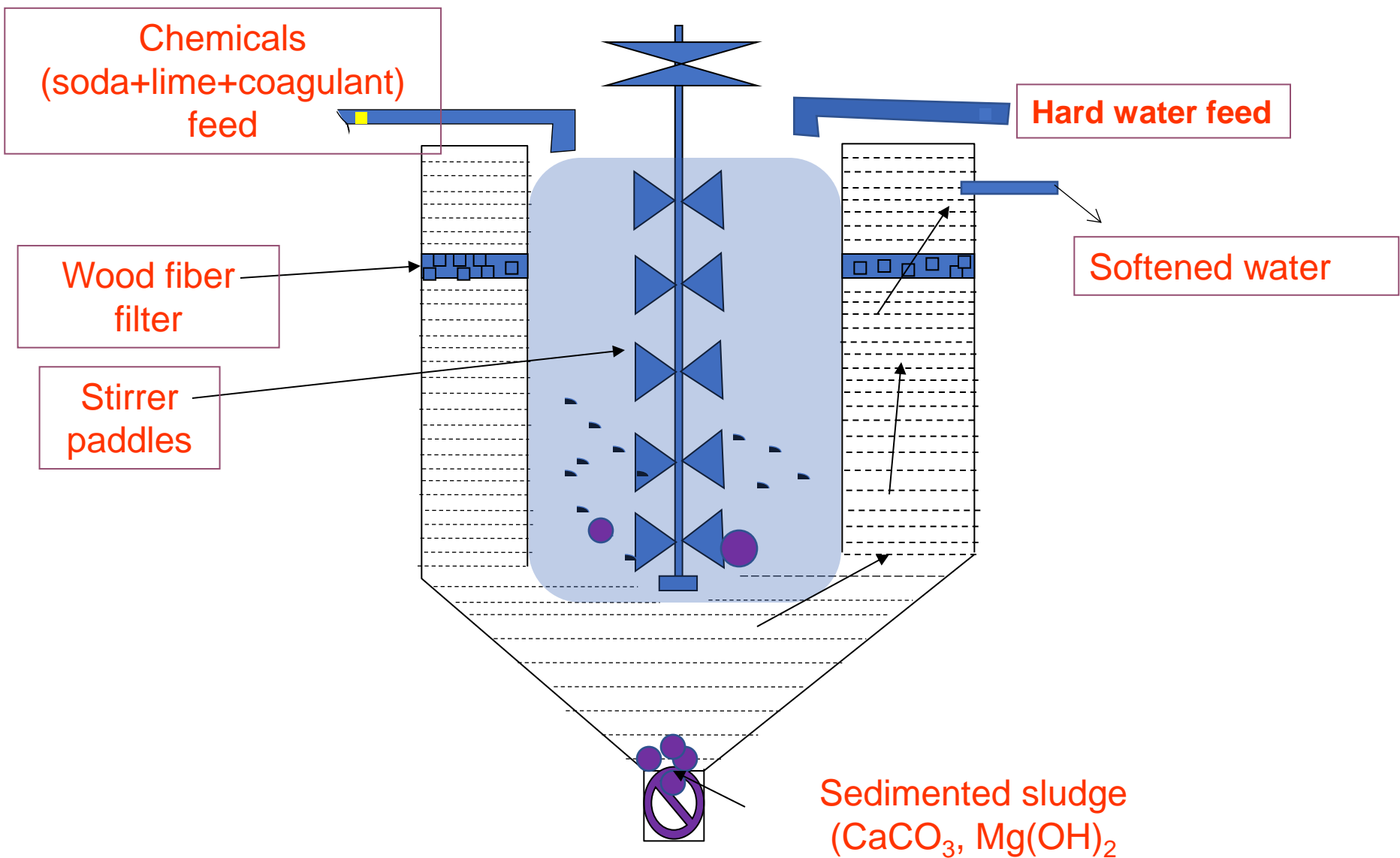
### I. Cold lime soda process

#### Step 2

- Precipitates  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  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  $\text{Al}(\text{OH})_3$  which entraps the fine precipitates.



# Continuous cold lime soda softener



## 2. Hot lime soda Process

In this process a calculated quantity of  $\text{Ca(OH)}_2$  (lime) and  $\text{Na}_2\text{CO}_3$  (soda) are mixed with hot water at a temperature range of 80 to 150°C and added to the hard water. The following reactions takes place depending on the nature of hardness

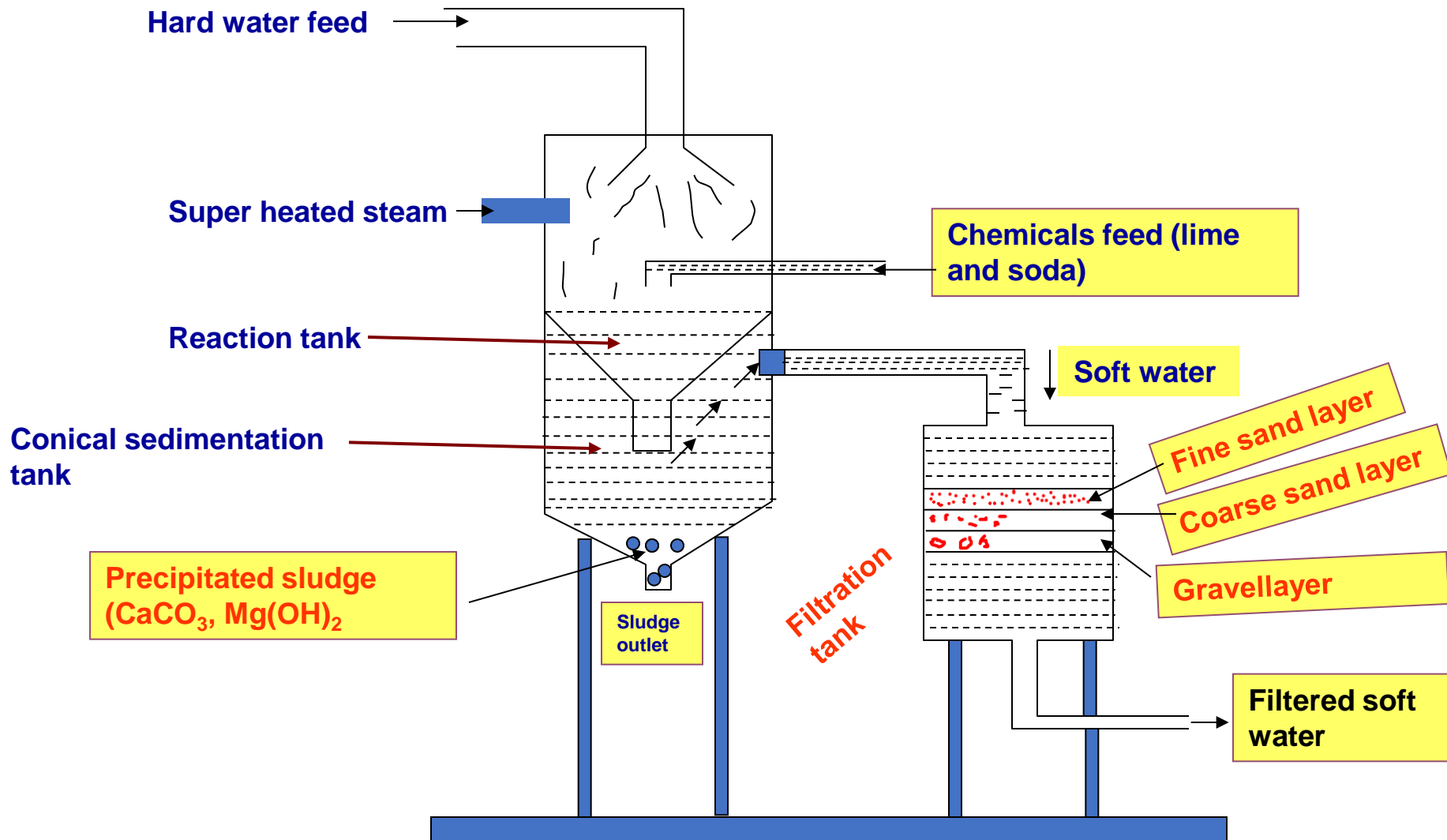
### Advantages of Hot Lime Soda Process

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 ( $\text{CO}_2$  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



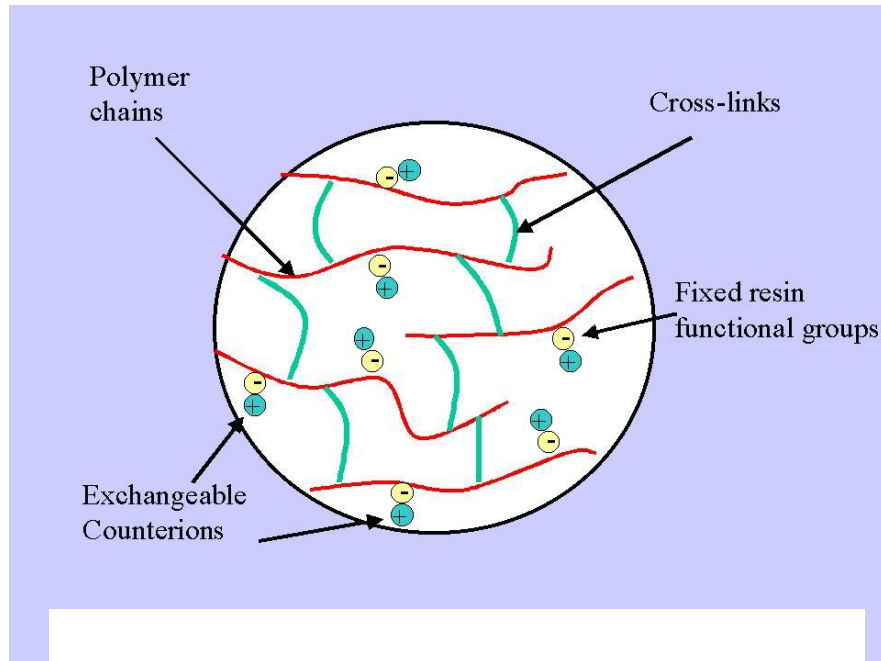
### **Advantages of Lime soda process**

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

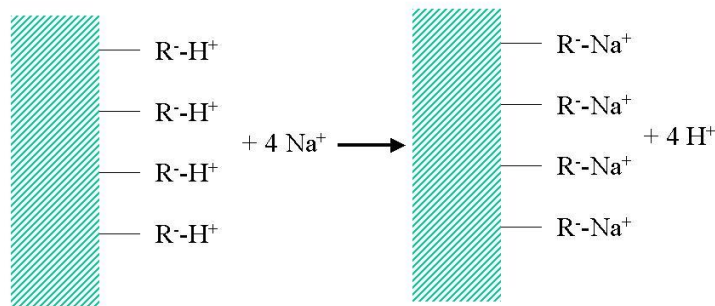
### **Disadvantages of Lime soda process**

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 ( $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  etc) are capable of exchanging their  $\text{H}^+$  ions with other cations, which comes in their contact; whereas those containing basic functional groups ( $-\text{NH}_2$ ,  $=\text{NH}$  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 ( $\text{RH}^+$ ) –

Strongly acidic ( $\text{SO}_3^-\text{H}^+$ ) and weakly acidic ( $\text{COO}^-\text{H}^+$ ) cation exchange resins

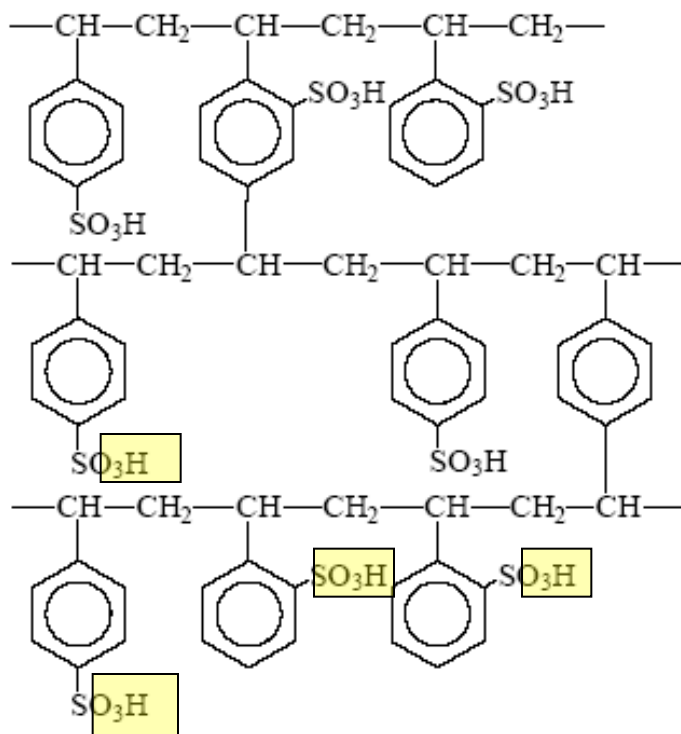
2. Anion Exchange resin ( $\text{ROH}^-$ ) –

Strongly basic ( $\text{R}_4\text{N}^+\text{OH}^-$ ) and weakly basic ( $\text{RNH}_2^+\text{OH}^-$ ) anion exchange resins

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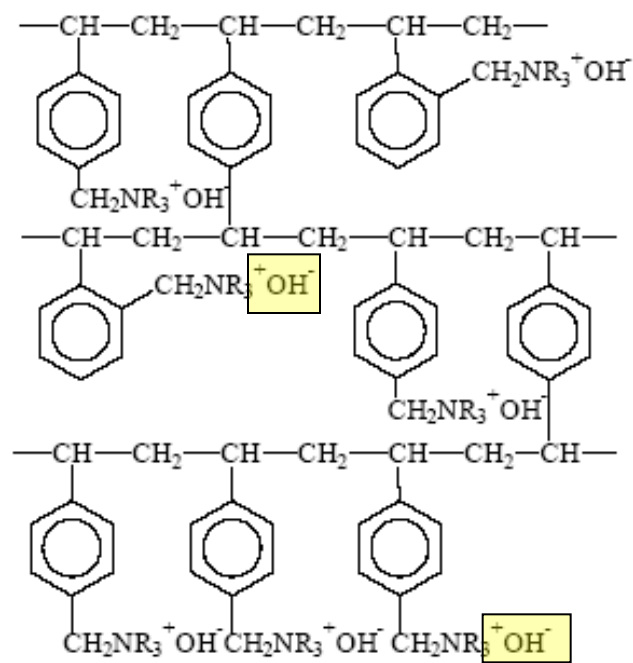
## Structure of Cation and Anion exchange resins

### Cation exchange resin



A strongly acidic sulphonated polystyrene cation exchange resin

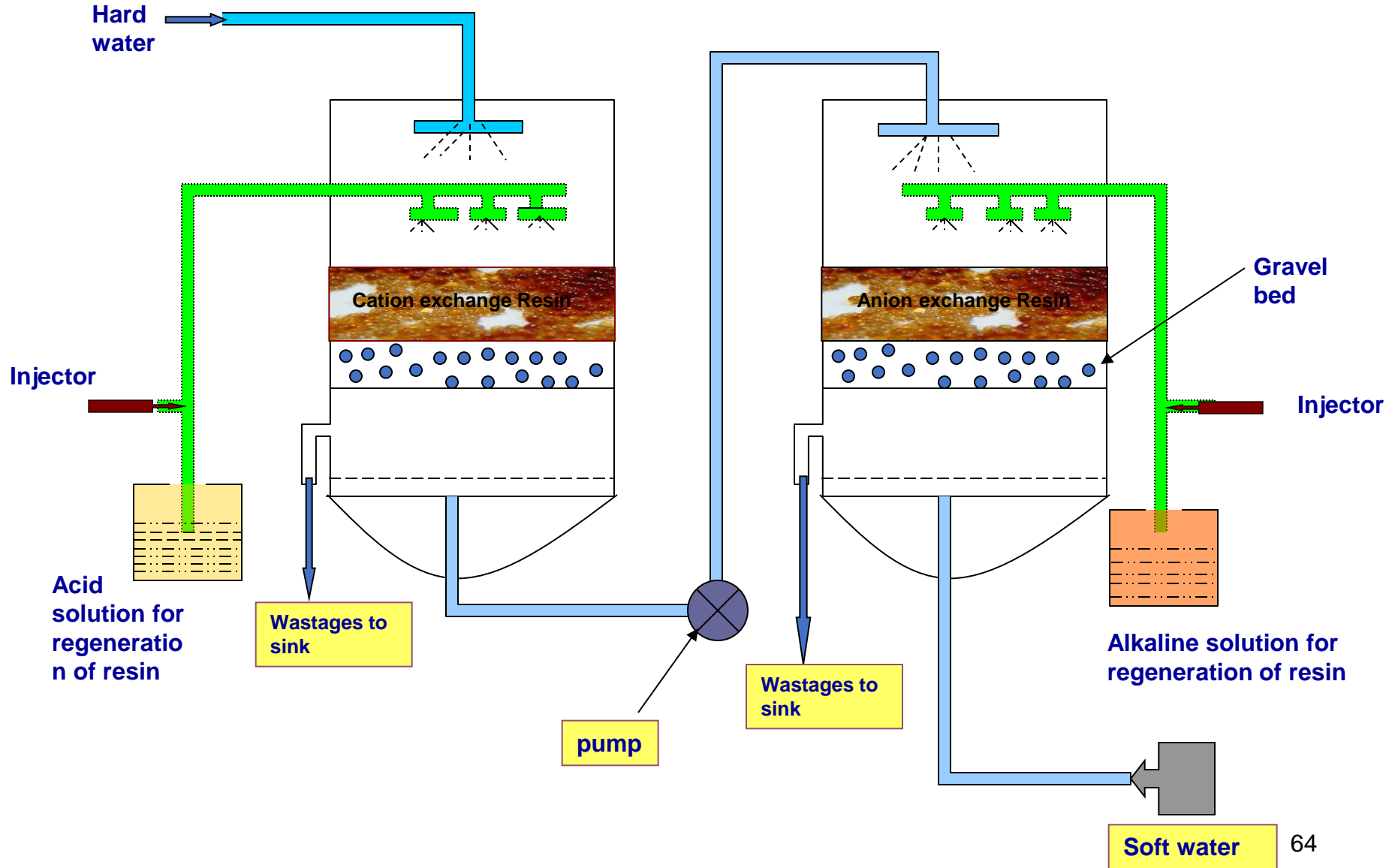
### Anion exchange resin



A strongly basic quaternary ammonium anion exchange resin

$\text{R} = \text{CH}_3$

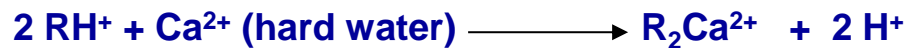
## Ion exchange purifier or softener



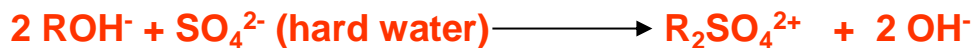


# Process or Ion-exchange mechanism involved in water softening

Reactions occurring at Cation exchange resin



Reactions occurring at Anion exchange resin

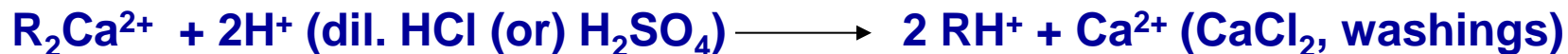


At the end of the process

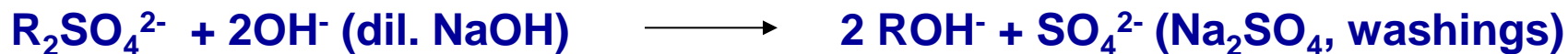


# Regeneration of ion exchange resins

## Regeneration of Cation exchange resin



## Regeneration of Anion exchange resin



## 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

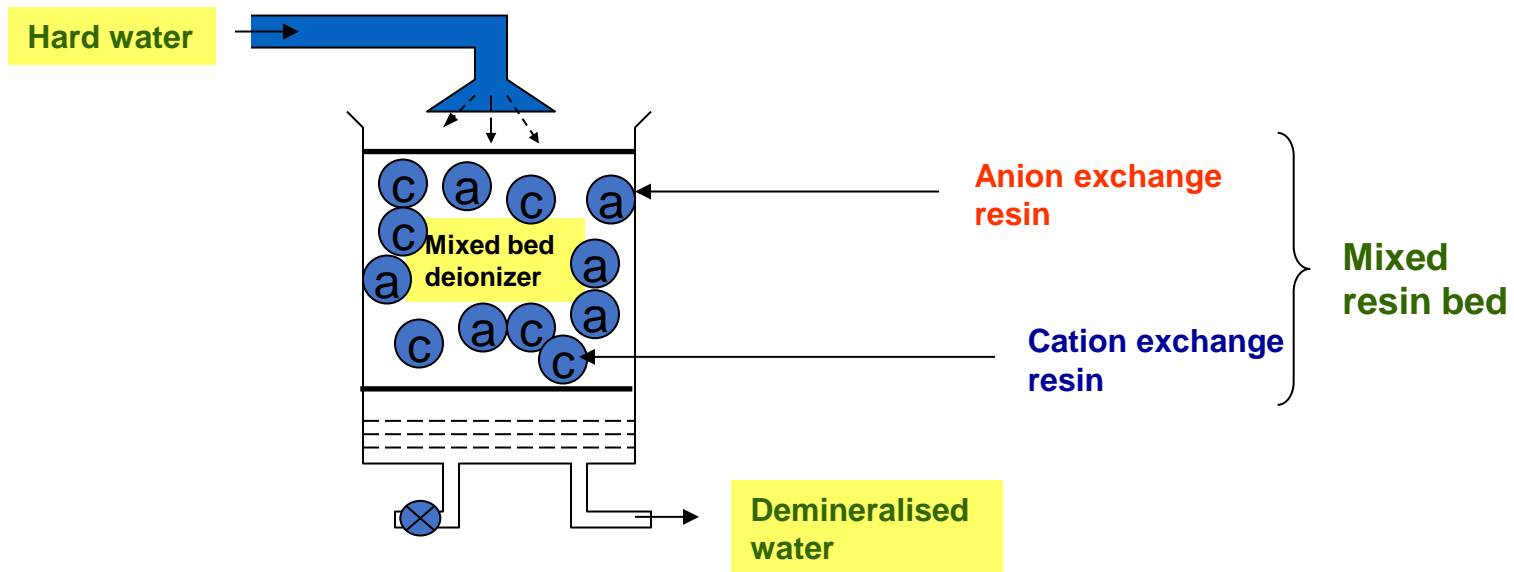
## Disadvantages

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

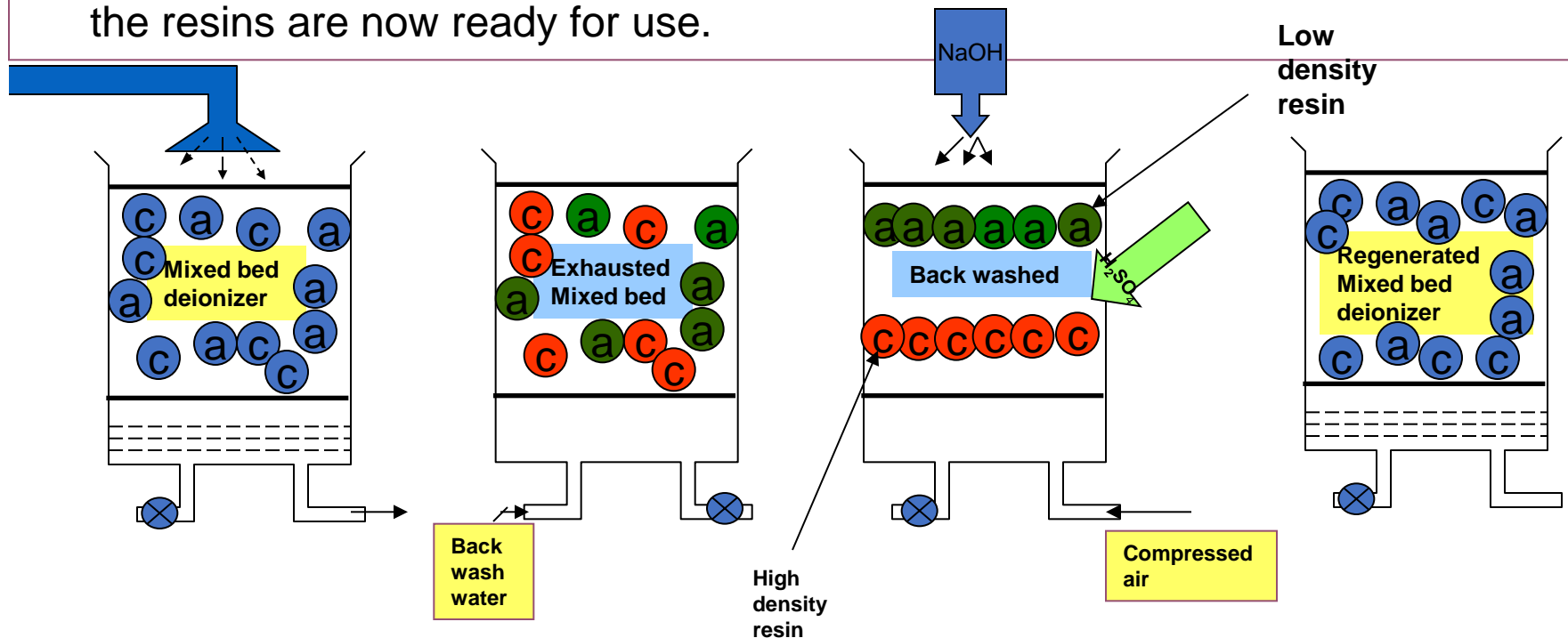
### Description and process of mixed bed deionizer

- 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 anions 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.  $\text{H}_2\text{SO}_4$  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

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- 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

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## **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

# DE-SALINATION OF BRACKISH WATER

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## ELECTRO DIALYSIS

### **Principle:**

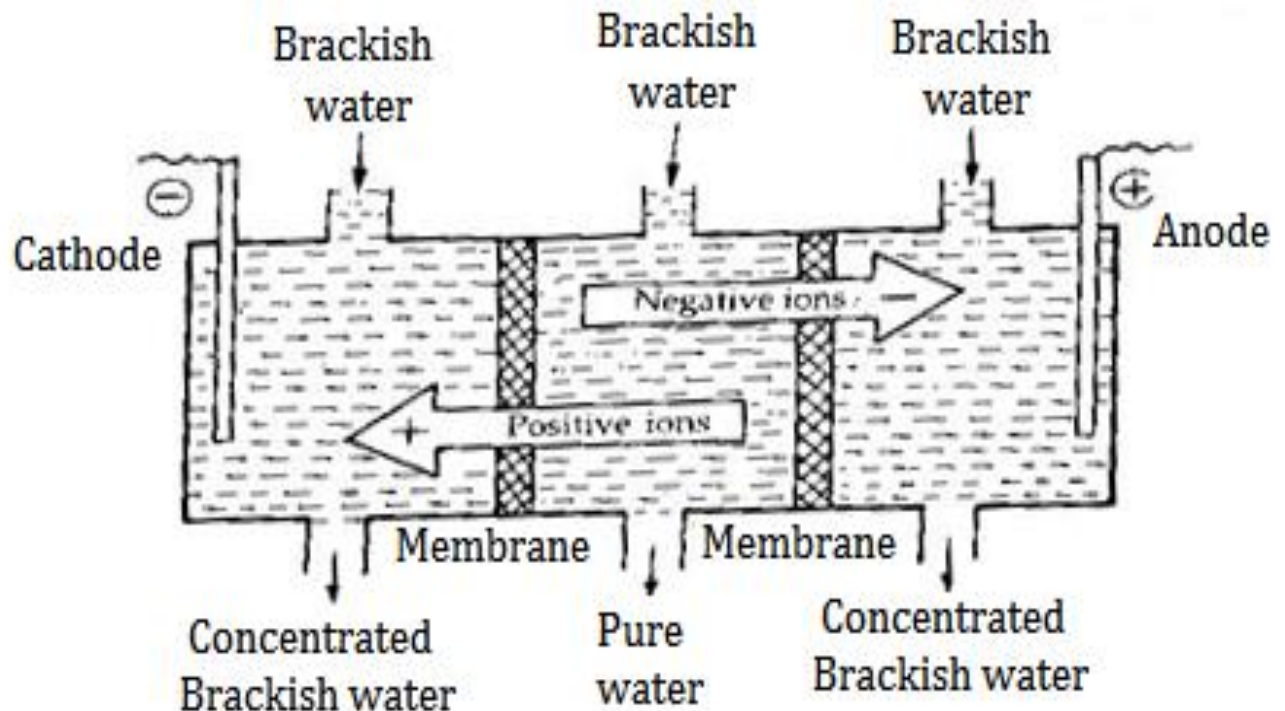
It is based on the principle that when **direct current is passed through saline water** using electrodes, salt ions present in saline water migrate towards their respective electrodes through ion selective membrane, under the influence of applied EMF.

# DE-SALINATION OF BRACKISH WATER

## ELECTRO DIALYSIS

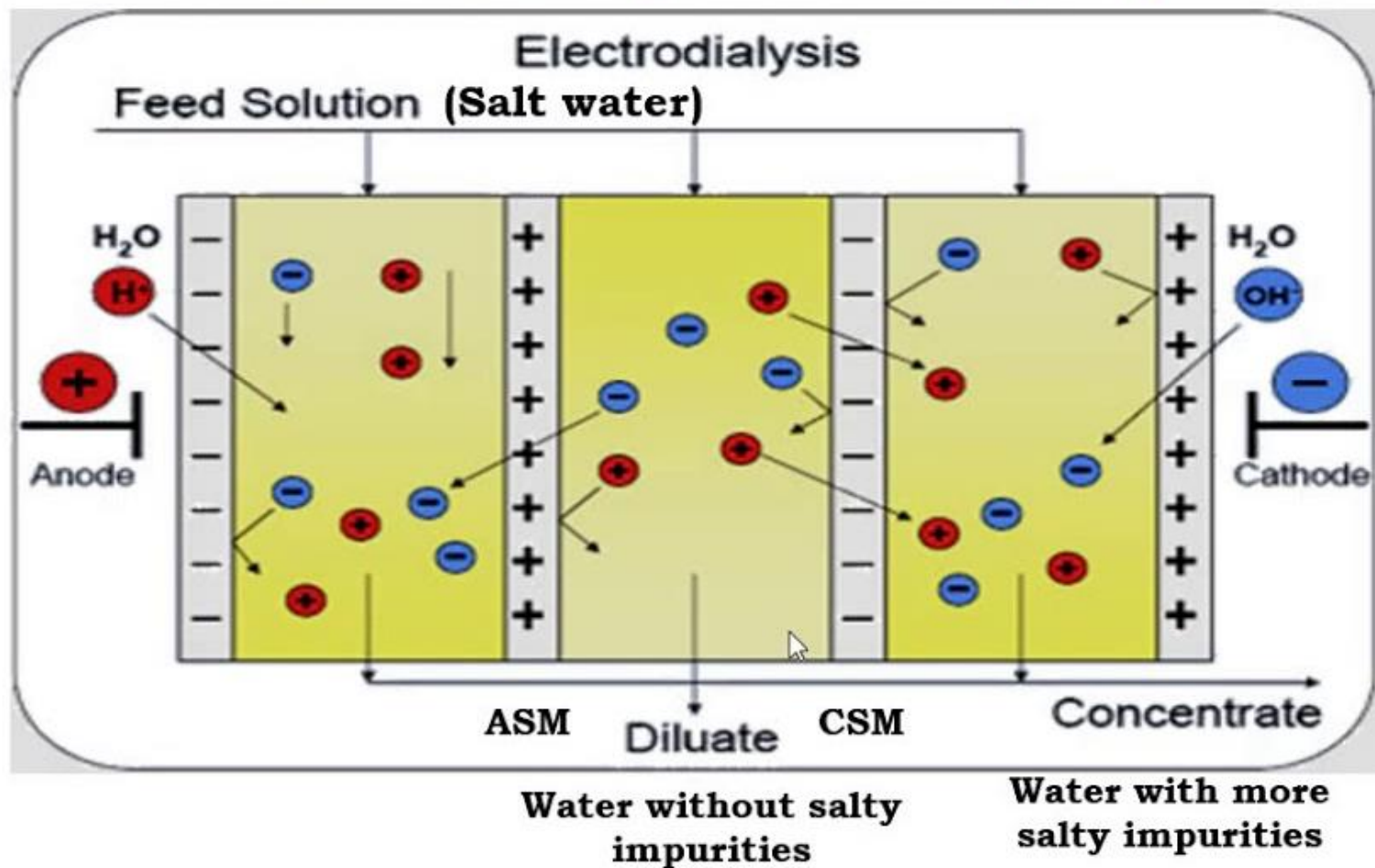
### Apparatus:

- 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:



# DE-SALINATION OF BRACKISH WATER

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## ELECTRO DIALYSIS

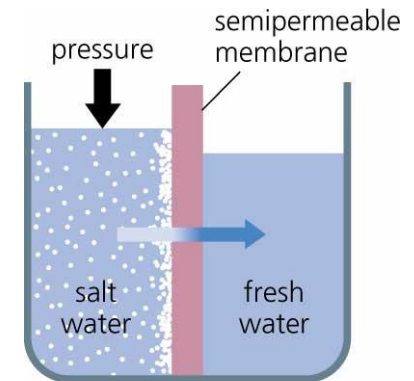
### **Advantages:**

- 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

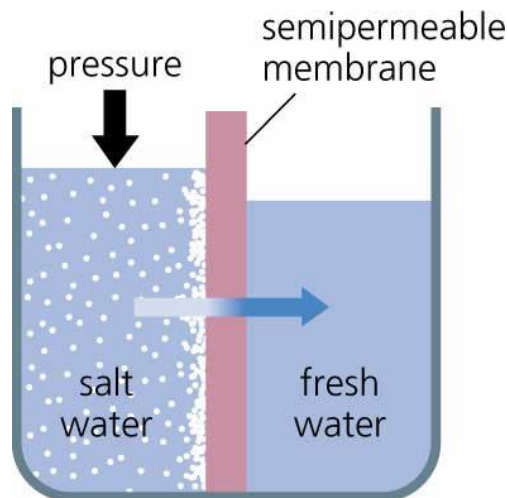


# DE-SALINATION OF BRACKISH WATER

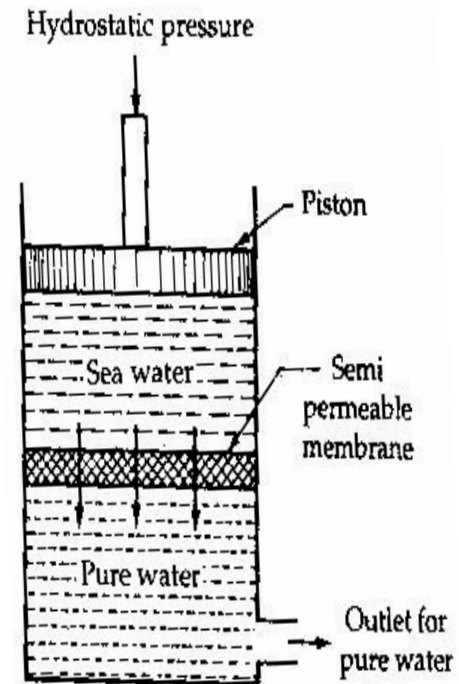
## Process:

- 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/cm<sup>2</sup> is applied on the sea water or impure water, the pure water is forced through the semi permeable membrane.

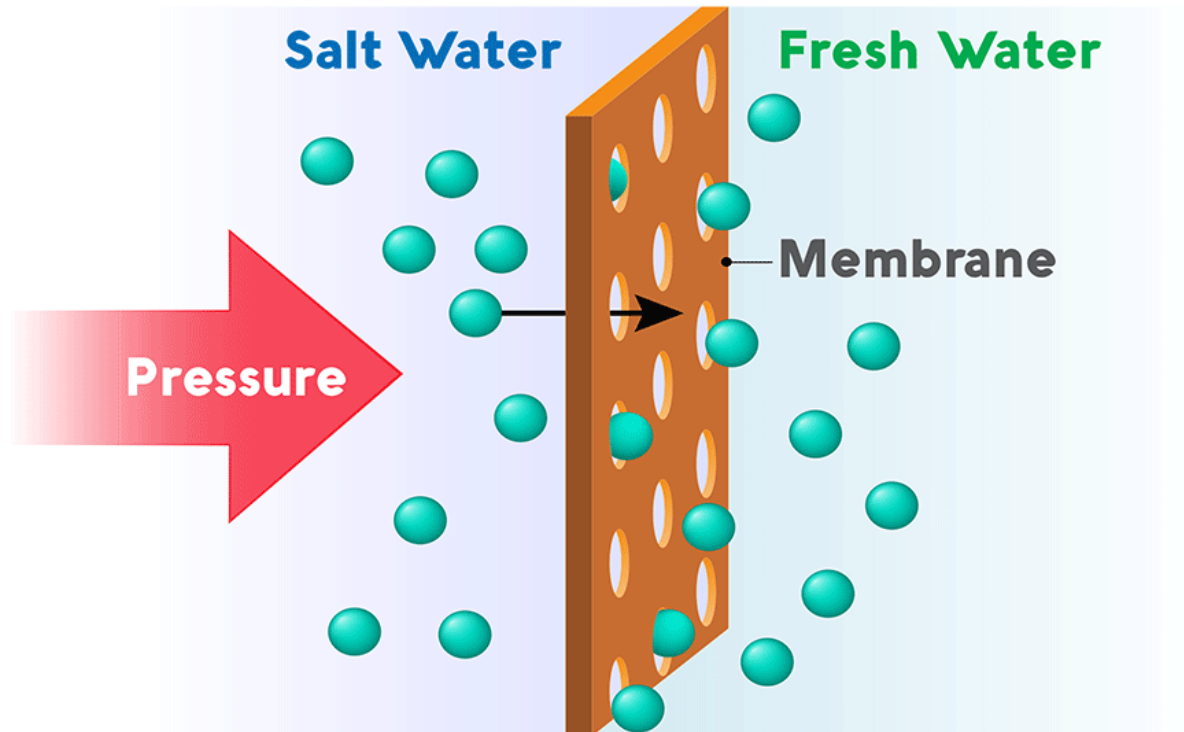
## REVERSE OSMOSIS



Precision Graphics



# Reverse Osmosis

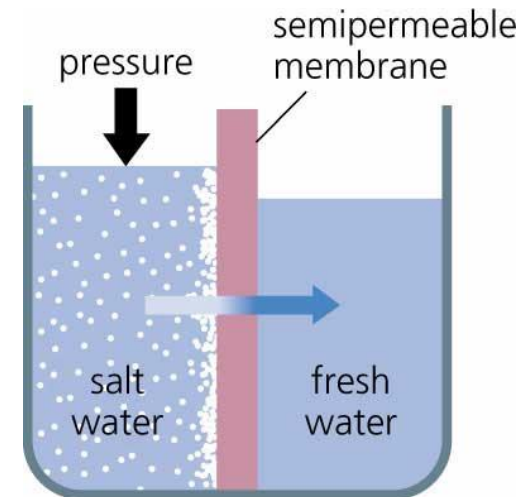


# DE-SALINATION OF BRACKISH WATER

## 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.

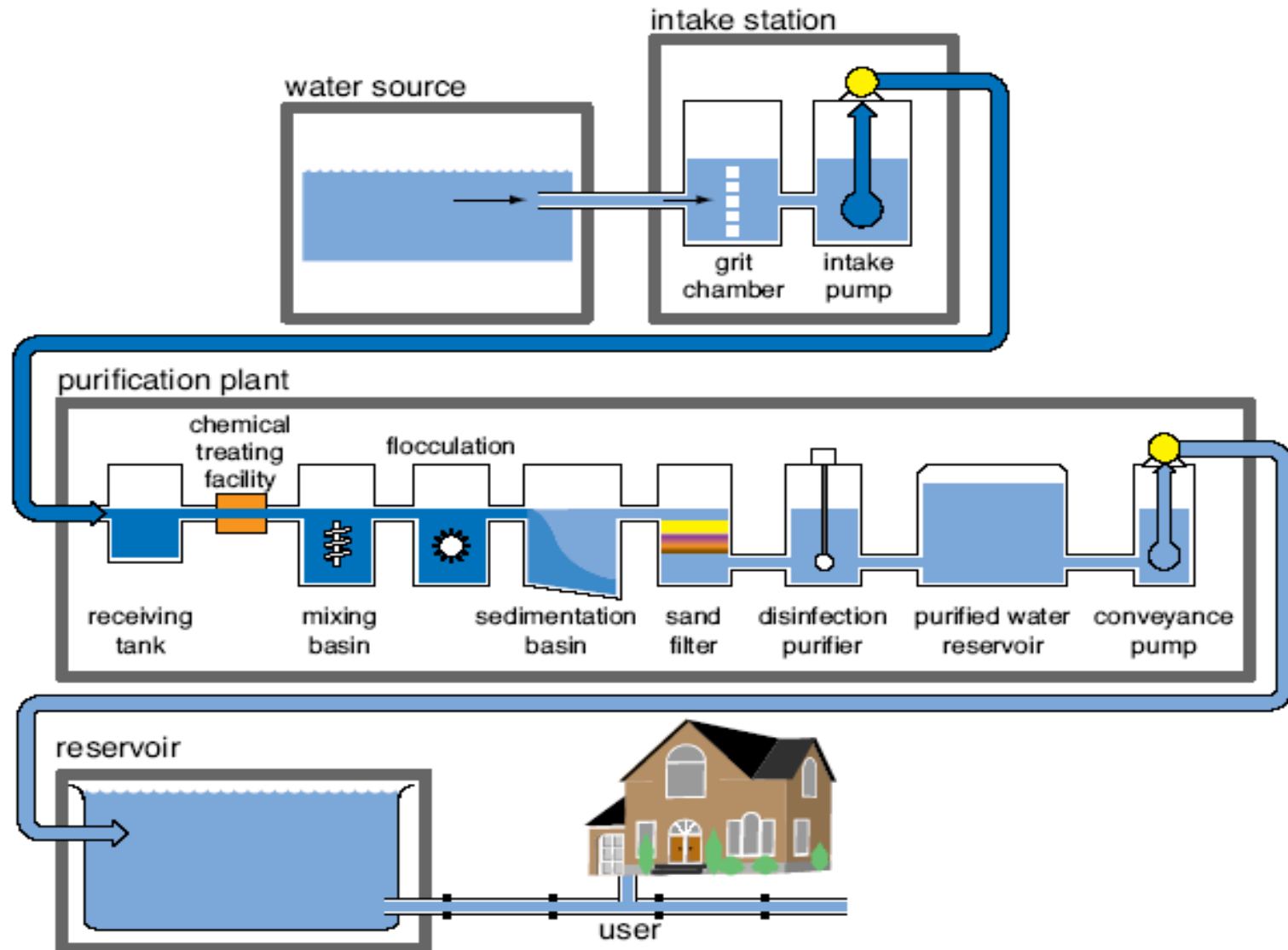


# Treatment of Municipal Drinking Water

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- 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





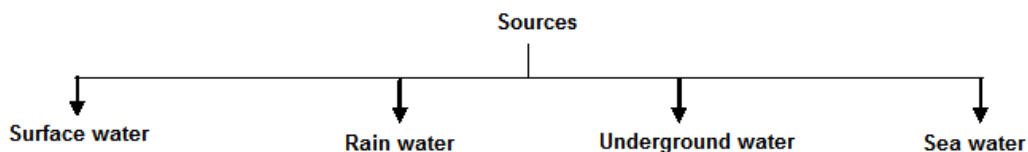
# WATER TECHNOLOGY

## INTRODUCTION

Water is highly essential for the existence of all living beings. One cannot survive without water. Water is required for all activities like domestic, agricultural and industrial purposes.

### Sources of Water

There are 4 main sources for water.



**River Water:** It contains minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron. It also contains suspended impurities like sand, rock, and organic matter. The composition of river water change from river to river based on the nature of surrounding soil.

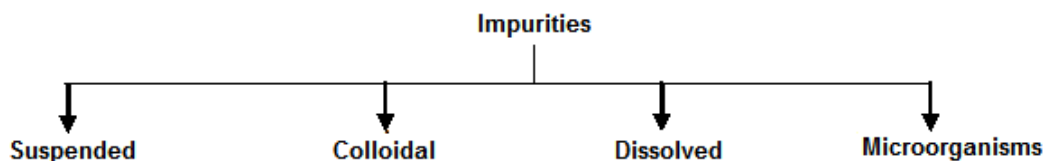
**Rain Water:** It is the purest form of natural water. But it also becomes impure while coming down.

**Underground water:** It is free from organic impurities and is clear in appearance due to the filtering action of soil. It also contains large amount of dissolved salts.

**Sea Water:** It is very impure. It contains large amounts dissolved salts.

### Impurities in water

The following types of impurities are present in water.



**Suspended impurities:** They impart turbidity, colour and odour to the water. They may be organic (or) inorganic.

**Colloidal impurities:** Organic waste, clay and silica form colloidal impurities.

**Dissolved impurities:** Carbonates, bicarbonates, chlorides and sulphates of calcium and magnesium, iron and sodium are responsible. Dissolved gases like O<sub>2</sub>, CO<sub>2</sub> etc also come under this type.

**Micro organisms:** They include bacteria, fungi and algae.

## Sources of impurities in water

1. Gases like O<sub>2</sub>, CO<sub>2</sub> etc are picked up from the atmosphere by rain water.
2. Decomposition of plant and animal remains introduce organic impurities in water.
3. Water takes impurities while it is passing over the soil and rocks.
4. Sewage and industrial waste make the water impure.

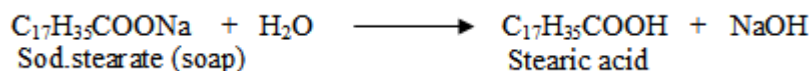
## Drinking water – W.H.O Parameters

Potable water is fit for human consumption. The common specifications (or) standards prescribed for drinking water are as follows.

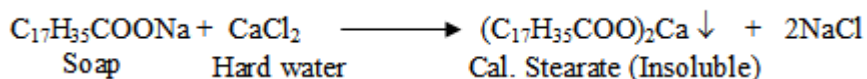
1. It should be colourless, odourless and tasteless.
2. Its turbidity should be less than 10ppm.
3. It should not contain poisonous metals like lead, arsenic, chromium and manganese.
4. P<sup>H</sup> should be in the range of 7.0-8.5.
5. Total hardness should be less than 500ppm.
6. It should be free from disease causing microorganisms.

## HARDNESS OF WATER

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



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



**Causes of Hardness** Hard water contains more number of salts like CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub> and MgSO<sub>4</sub> etc.

**Units of hardness:** Hardness is caused by many salts. It is expressed in terms of equivalents of CaCO<sub>3</sub>.

Degree of hardness is expressed in ppm or degree clark (°cl) or degree French (°fr).

**Parts per million (or) mg/litre:** ppm means one part of CaCO<sub>3</sub> equivalent to hardness causing salt present in 1 million parts of water.

$$\begin{aligned} 1 \text{ ppm} &= 1 \text{ part per } 10^6 \text{ parts of water} \\ &= 1 \text{ mg per } 10^6 \text{ mg of water} \end{aligned}$$

$$= 1 \text{ mg per 1 kg of water}$$

$$= 1 \text{ mg per 1 litre of water (1 kg = 1 litre)}$$

So, the unit of hardness of water in ppm or mg/lit

Degree Clarke ( $^{\circ}\text{cl}$ ): It is the British unit of hardness of water. One degree Clarke means one part of  $\text{CaCO}_3$  per 70,000 parts of water.

Degree French ( $^{\circ}\text{fr}$ ): It is the French unit of hardness of water. One degree French means one part of  $\text{CaCO}_3$  per  $10^5$  parts of water.

Grains per gallon (gpg):

It is the English unit of hardness of water. One grain of  $\text{CaCO}_3$  present in 1 gallon of water is known as gpg.

$$1 \text{ grain} = \frac{1}{7000} \text{ lb} \qquad 1 \text{ gallon} = 10 \text{ lb}$$

Therefore 1 gpg is nothing but one part of  $\text{CaCO}_3$  per 70,000 parts of water and it is also called as degree Clarke.

### Relation between these units of degree hardness

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

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

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

The most common and universal expression of hardness of water is ppm or mg/L.

Hardness due to any dissolved salt is obtained by multiplying the amount of dissolved salt (mg) with the multiplication factor which is the ratio of Equivalent weight of  $\text{CaCO}_3$  to the Equivalent weight of the dissolved salts present in water as given below.

$$\text{Hardness of water} = \text{Weight of dissolved salt (mg/L)} \times \frac{\text{Equivalent .wt of CaCO}_3}{\text{Equivalent .wt of dissolved salt}}$$

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

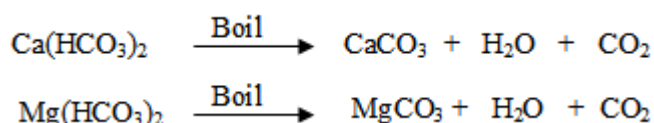
Dissolved salt	Molecular weight	Equivalent weight
$\text{Ca}(\text{HCO}_3)_2$	162 = 100 of $\text{CaCO}_3$	81 = 50 of $\text{CaCO}_3$
$\text{Mg}(\text{HCO}_3)_2$	146 = 100 of $\text{CaCO}_3$	73 = 50 of $\text{CaCO}_3$

CaSO <sub>4</sub>	136 = 100 of CaCO <sub>3</sub>	68 = 50 of CaCO <sub>3</sub>
MgSO <sub>4</sub>	120 = 100 of CaCO <sub>3</sub>	60 = 50 of CaCO <sub>3</sub>
CaCl <sub>2</sub>	111 = 100 of CaCO <sub>3</sub>	55.5 = 50 of CaCO <sub>3</sub>
MgCl <sub>2</sub>	95 = 100 of CaCO <sub>3</sub>	47.5 = 50 of CaCO <sub>3</sub>

**Types of hardness:** There are two types.

**Temporary hardness;**

This is due to presence of bicarbonates of calcium and magnesium. Water containing these salts is boiled; they readily dissociate to give insoluble carbonates.



Hardness which is easily removed by boiling is called temporary hardness.

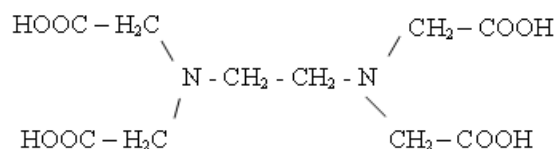
**Permanent hardness;** It is due to chlorides and sulphates of calcium and magnesium. This type of hardness cannot be removed by simple boiling.

### **DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD**

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

**Principle:**

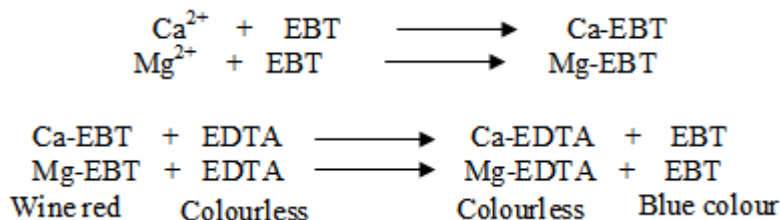
- ✓ EDTA acts as complexing agent or chelating agent.
- ✓ It forms complexes with various metal ions present in water.
- ✓ From the amount of the EDTA consumed during complex formation, the hardness of the water sample can be calculated.
- ✓ Structural formula of EDTA, ethylene diamine tetra acetic acid is



**Theory:**

- Water is colourless and EDTA is also colourless.

- So in order to know the formation of the complexes Eriochrome black-T indicator is used along with EDTA.
- Eriochrome black-T (EBT) is first added to water, then it forms wine red colour complex with the metal ions present in water.
- This complex is less stable.
- After the addition of EDTA, EDTA is added.
- EDTA forms stable complex with the metal ions and EBT is released which has blue colour.
- EDTA replaces EBT from the complex.



### Solutions required:

- \* Standard EDTA solution, Water sample, Eriochrome black- T indicator and ammonia – ammonium chloride buffer solution ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ,  $\text{P}^{\text{H}} = 10$ )
- \* To maintain  $\text{P}^{\text{H}}10$ , buffer solution is used. Instead of EDTA solution,  $\text{Na}_2\text{EDTA}$  is used because it is more soluble.

### Procedure:

- ☞ Burette is filled with standard EDTA solution.
- ☞ Pipette out 10ml of the water sample into a conical flask. Add 2ml of ammonia-ammonium chloride buffer solution and 2 or 3 drops of **Eriochrome black-T indicator**.
- ☞ Now the solution is wine red in color.
- ☞ Titrate this solution with standard EDTA solution from a burette until the color changes from **wine red to blue**.
- ☞ Repeat the titration until the concurrent value is obtained.

Total hardness of water sample can be calculates as follows

$$\text{Total Hardness} = \frac{\text{Volume of EDTA} \times \text{Molarity of EDTA} \times 100 \times 1000}{\text{Volume of water sample}} \text{ mg of CaCO}_3/\text{L or ppm}$$

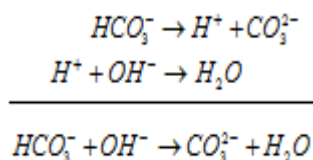
### NUMERICAL PROBLEMS

- (a) Four samples of water are collected at Kunchanapalli (KB), Gundimeda (GM), Vaddeswaram (VB) and the other at Green Fields (GF). 100 ml of each water sample collected at KB, GM, VB and GF requires 28, 26, 20 and 18 ml of EDTA solutions on titrations respectively. 100 ml of SHW (0.28 g of  $\text{CaCO}_3$  per liter) requires 22 ml of EDTA solution on titration. Calculate and compare the degree of hardness and write the chemical reactions involved in titrations.

(b) Learner wants to evaluate the accuracy of the EDTA method for estimation of water hardness. He took a sample of water containing dissolved salts as given below in mg/liter.  $\text{Ca}(\text{HCO}_3)_2 = 32.4$ ;  $\text{CaSO}_4 = 27.2$ ;  $\text{Mg}(\text{HCO}_3)_2 = 29.2$ ;  $\text{MgCl}_2 = 19$ ; and  $\text{KCl} = 20$  and calculated Temporary hardness and permanent hardness. Now he carried out EDTA titration and observed that 100 ml of this water sample consumed 8 ml of 0.01M EDTA before boiling and 4.5 ml of 0.01M EDTA after boiling. Calculate, compare and discuss the result (your answer should contain why or why not the results are same).

### ALKALINITY OF WATER

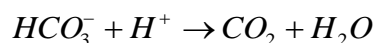
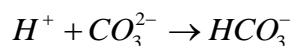
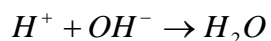
- ✓ Alkalinity of water is mainly due to the presence of anions like  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{OH}^-$ .
- ✓ The estimation of alkalinity in water is done by titrating water sample against standard acid using phenolphthalein and methyl orange as indicators.
- ✓ In this titration, two indicators are used as the different anions give end points at different PH values.
- ✓ Out of the three anions  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{OH}^-$ , any two of them can exist in water together.
- ✓  $(\text{CO}_3^{2-}, \text{HCO}_3^-)$  and  $(\text{CO}_3^{2-}, \text{OH}^-)$
- ✓  $\text{HCO}_3^-$  and  $\text{OH}^-$  cannot be present together because  $\text{H}^+$  ion of  $\text{HCO}_3^-$  neutralizes  $\text{OH}^-$ .



### Experimental Procedure:

- A known volume of water sample is taken into a conical flask and adds two drops of phenolphthalein indicator.
- The colour will become pink (due to  $\text{pH} > 10$ ). This solution is titrated against HCl solution until pink colour disappears. This end point is termed as P.
- Now add two drops of methyl orange indicator to the same water ( $\text{pH}$  falls below 7) and titrate with HCl. At the end point, pink colour reappears. This end point is taken as M.

### Reactions:



**Calculations:**

Phenolphthalein alkalinity in terms of  $\text{CaCO}_3$  is calculated by using the formula

$$\frac{P \times \text{Molarity of HCl} \times 50 \times 1000}{\text{Volume of water sample}} \text{ ppm}$$

Methyl Orange alkalinity in terms of  $\text{CaCO}_3$  is calculated by using the formula

$$\frac{M \times \text{Molarity of HCl} \times 50 \times 1000}{\text{Volume of water sample}} \text{ ppm}$$

**Conclusions:**

Burette reading	$\text{OH}^-$ alkalinity	$\text{CO}_3^{2-}$ alkalinity	$\text{HCO}_3^-$ alkalinity
$P = 0$	-	-	M
$P = M$	P	-	-
$P = \frac{1}{2} M$	-	2P	-
$P < \frac{1}{2} M$	-	2P	$M - 2P$
$P > \frac{1}{2} M$	$2P - M$	$2(M - P)$	-

**NUMERICAL PROBLEMS ON ALKALINITY:**

- (a) A water sample is alkaline to both phenolphthalein and methyl orange. From this water sample 100 ml on titration with 0.02N HCl required 4.7 ml of acid to reach phenolphthalein end point. When 4 drops of MO are added to the same solution and titration is further continued, the yellow color of the solution just turned red after addition of another 10.5 ml of acid solution. Report the type of and extent of alkalinity present in the water sample. Also write the chemical reactions involved in the titration.

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

**BOILER TROUBLES: III Effects of Water in Steam Generation**

In our daily life we use water for various purposes like domestic, industrial and

agricultural. Most important industrial use of water is as an engineering material for generating steam. In industries boiler is used to produce steam. Hardly, we find any industry without boiler. Any natural source of water does not supply perfectly suitable feed water. It is generally believed that a boiler feed water should satisfy the following requirements. Hardness less than 0.2 ppm, caustic alkalinity: 0.15 – 0.45 ppm, soda alkalinity: 0.15 to 1 ppm, excess soda ash: 0.3 to 0.55 ppm. Directly any source of water can't be fed into the boiler. If we do so it leads to boiler troubles.

The major boiler troubles are

- Scale and Sludge formation
- Caustic embrittlement
- Boiler corrosion
- Priming and foaming

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### Scale and sludge for steam generation

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

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

**SLUDGE:** Sludges are formed by substances which have greater solubilities in hot water than in cold water, e.g.  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , etc. They are formed at comparatively at colder portions of the boiler and get collected at places where the flow rate is slow. They can be easily removed by wire brush.

Disadvantages:

Sludges are poor conductors of heat, so they tend to waste a portion of heat generated and thus decrease the efficiency of the boiler. Excessive sludge formation disturbs the working of the boiler. Prevention:

- ☐ By using softened water
- ☐ By blow down operation (i.e. partial removal of concentrated hard water through a tap at bottom of the boiler, at equal intervals of time)

**SCALES:** Scales are hard deposits firmly sticking to the inner surfaces of the boiler. The scale formation is due to

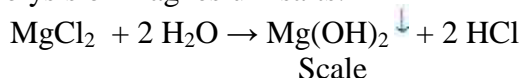
- a) Decomposition of Calcium bicarbonate:





b) Deposition of Calcium sulphate: The solubility of  $\text{CaSO}_4$  in water decreases with increase in temperature.  $\text{CaSO}_4$  is soluble in cold water, but almost completely insoluble in superheated water. Consequently,  $\text{CaSO}_4$  gets precipitated as hard scale on the hotter parts of the boiler.

c) Hydrolysis of Magnesium salts:



d) Presence of silica: If silica is present in boiler feed water, it reacts with Calcium and Magnesium ions forming Calcium silicate and Magnesium silicate which are very hard scales.

Disadvantages of scale formation:

Wastage of fuel: Being dependent on the thickness and the nature of the scale.

Lowering of boiler safety: Due to excessive heating

Decrease in efficiency: As scales block the valves and condensers

Danger of explosion: Due to sudden high pressures.

Removal of scales:

Mechanical methods: Loosely adhering scales can be removed with the help of scrapper or wire brush. Brittle scales are removed by giving thermal shocks.

Chemical methods: Adherent and hard scales can be removed by dissolving them by adding chemicals such as EDTA or N/50 HCl solutions.

Prevention: By using softened water

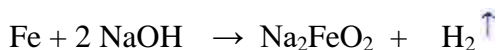
## CAUSTIC EMBRITTLEMENT

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**Caustic embrittlement** was first used to describe the cracking of riveted mild steel boiler plates due to local deposition of concentrated hydroxide at temperatures of 200 to 250°C. It was later known as stress corrosion cracking which was in turned replaced by environmental cracking. Cause of caustic embrittlement: It results from the conjoint action of three components:

- i) a susceptible material (carbon steel),
- ii) a specific chemical species (Conc. NaOH), and
- iii) Stress (around the riveted holes).

Caustic soda (NaOH) was added in small amounts to boiler water to prevent scaling. But the presence of caustics (alkalis), usually concentrated in crevices around rivet heads and hot spots, combined with the considerable fabrication stresses around rivet holes to caused cracking of steel boiler shells and tube plates. Finally, concentrated alkali dissolves the iron of the boiler around rivet holes as sodium ferroate ( $\text{Na}_2\text{FeO}_2$ ).



This dissolution of loss of the boiler body material is caustic embrittlement.

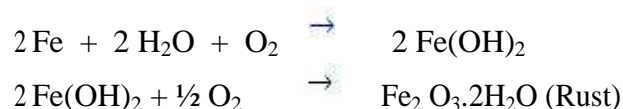
It can be prevented through:

- ☐ Control of stress level (residual or load) and hardness
- ☐ Avoid alkalis
- ☐ Use of materials known not to track in the specified environment
- ☐ Control temperature and or potential

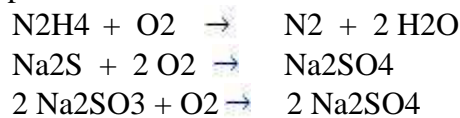
## BOILER CORROSION

Boiler corrosion is the decay or loss of the boiler body material by the chemical or electrochemical reactions. Corrosion in boilers is due to the presence of dissolved oxygen, carbon dioxide and mineral acids in the feed water.

Dissolved oxygen: Usually natural water contains 8 ppm of dissolved oxygen. At high temperatures dissolved oxygen comes out of the water and they attack the iron of the boiler as



Dissolved oxygen can be removed by adding chemicals like hydrazine, sodium sulphite or sodium sulphide.

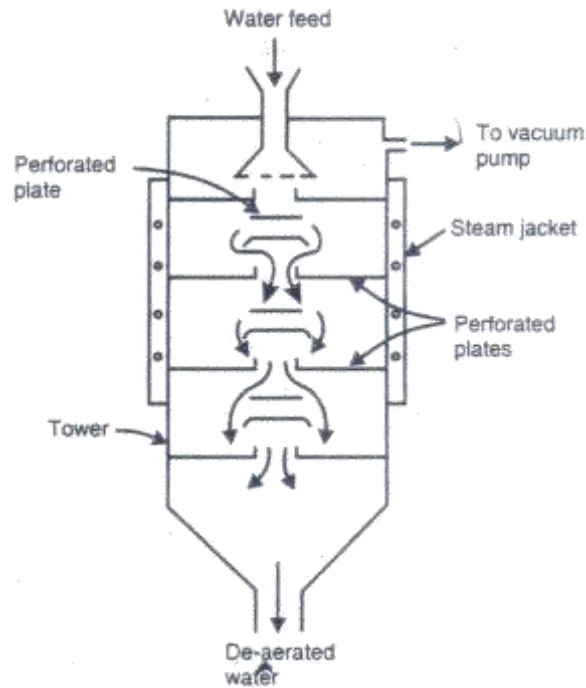


Also, dissolved oxygen can be removed along with CO<sub>2</sub> and other gases, if any by mechanical deaeration process.

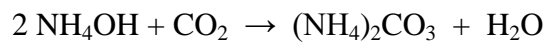
**Dissolved CO<sub>2</sub>:** If carbon dioxide is already present in water or introduced by the decomposition of bicarbonates [ $\text{Ca(HCO}_3)_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ ] present in water has slow corrosive effect on boiler material.

- a) By mechanical deaeration process: A deaerator is a device that is widely used for the removal of air and other dissolved gases from the feed water to steam generating boilers. Most deaerators are designed to remove oxygen down to levels of 7 ppb by weight (0.005 cm<sup>3</sup> per liter or less). There are many different horizontal and vertical designs available from a number of manufacturers, and the actual construction details will vary from one manufacturer to another.

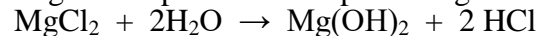
So by increasing temperature, decreasing pressure and exposing large surface area of water much of the dissolved gases are driven out of water.



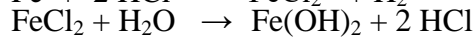
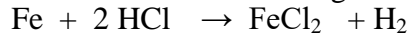
b) By using calculated amount of ammonia:



**Acids producing salts:** If  $\text{MgCl}_2$  is present in feed water it undergoes hydrolysis at higher temperatures and producing acid.



Acid attacks the iron of the boiler forming HCl again and again.



And corrosion continues in a chain like reaction. So even small quantities of salt causes severe corrosion of the boiler.

#### Disadvantages:

- Shortening of boiler life
- Leakages of joints and reverts, increased cost of repairs and maintenance.

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## PRIMING AND FOAMING

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**Priming** is the carryover of varying amounts of droplets of water in the steam (wet steam), which lowers the energy efficiency of the steam and leads to the deposit of salt crystals on the super heaters and the turbines. Cause of Priming:

- ☐ Improper construction of boiler
- ☐ Excessive ratings

- ☐ Sudden fluctuations in steam demand
- ☐ High levels of boiler water
- ☐ Large quantities of dissolved solids

**Foaming:** Boiler water carry - over is the contamination of the steam with boiler water solids. Bubbles or froth actually build up on the surface of the boiler water and pass out with the steam. This is called foaming. Foaming is caused by high concentration of any solids in boiler water. It is generally believed, however, that specific substances such as oils, fats, greases and alkalis are particularly conducive to foaming. It is believed that the finer the suspended particles the greater their collection in the bubble to make it tougher.

The most common measure to prevent foaming and priming is:

- ☐ To maintain the concentration of solids in boiler water at reasonably low levels
- ☐ Avoiding high water levels
- ☐ Excessive boiler loads, avoiding sudden load changes
- ☐ The chemicals anti foaming and anti priming agents are added to prevent carry – over.

## **SOFTENING OF WATER**

The process of removing or reducing hardness producing substances from water is called water softening. Boiler feed water is given two types of water treatments – internal treatment and external treatment. Internal treatments are especially given for correcting the mistakes committed in external treatments only in case of preventing scales.

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## **INTERNAL TREATMENTS**

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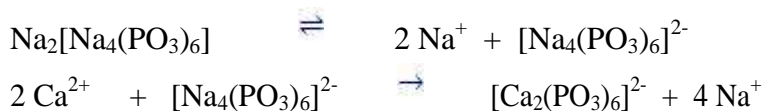
In internal treatment, suitable chemicals are added to convert scale forming substances into sludge or to keep them in dissolved form in boiler feed water. In case of sludge, they are removed by blow down operation. So every internal treatment is followed by blow down operation.

- a) Colloidal conditioning: In this method, colloidal agents like kerosene, tannin, agar- agar gel are added to boiler water. These substances get coated over scale forming substances and make them non adherent converting scale into sludge.
- b) Carbonate conditioning: In this method,  $\text{Na}_2\text{CO}_3$  added to boiler water will react with the  $\text{CaSO}_4$  present in dissolved state in boiler water.

The reaction is:  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + \text{Na}_2\text{SO}_4$

The reaction is favoured in forward direction only when the concentration of  $[\text{CO}_3^{2-}] > [\text{SO}_4^{2-}]$ .

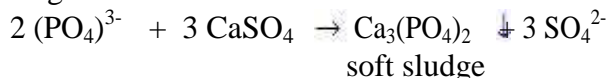
- c) Calgon conditioning: Calgon is sodium hexa metaphosphate with the composition  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ . During the process of softening of water, four sodium ions are replaced by double salts containing calcium inside the complex. Since the complex formed is highly soluble, there is no problem of sludge disposal.



Scale forming ion

Highly soluble complex

- d) Phosphate conditioning: In high pressure boilers,  $\text{CaSO}_4$  forms hard type scale. This is because the solubility of  $\text{CaSO}_4$  decreases with increase of temperature. It can be converted into soft sludge by adding excess of soluble phosphates. The optimum pH for the precipitation  $\text{Ca}_3(\text{PO}_4)_2$  soft sludge is 9.5 – 10.5.



There are three types of phosphate are employed for this purpose.

- (i) Tri sodium phosphate –  $\text{Na}_3\text{PO}_4$  (too alkaline)
- (ii) Disodium hydrogen phosphate –  $\text{Na}_2\text{HPO}_4$  (weakly alkaline)
- (iii) Monosodium dihydrogen phosphate –  $\text{NaH}_2\text{PO}_4$  (acidic)

When the alkalinity of boiler feed water is too low,  $\text{Na}_3\text{PO}_4$  is used. If the feed water is alkaline,  $\text{NaH}_2\text{PO}_4$  is used. For feed waters with the correct alkalinity, the neutral  $\text{Na}_2\text{HPO}_4$  is used.

- e) EDTA conditioning: Phosphate treatment fails to prevent the cuprous and iron depositions. EDTA forms soluble complexes with scale and sludge forming substances and corrosion impurities.



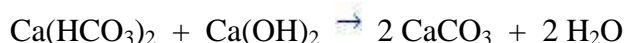
## EXTERNAL TREATMENT

This treatment is given outside the boiler by the following methods. Lime soda process, ion-exchange process and zeolite process.

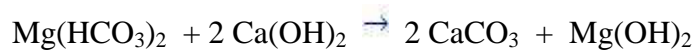
- i) Lime Soda process: In this process, the dissolved salts present in water are chemically converted into insoluble precipitates [such as  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$ , etc] by adding calculated amounts of lime  $[\text{Ca}(\text{OH})_2]$  and soda  $[\text{Na}_2\text{CO}_3]$ .

Chemistry of lime soda process:

**Reactions with lime  $[\text{Ca}(\text{OH})_2]$ :**



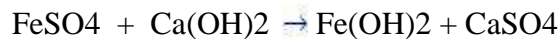
One equivalent of temporary Calcium hardness requires one equivalent of lime.



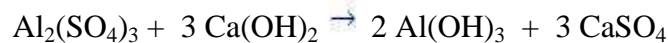
One equivalent of Mg temporary hardness requires two equivalent of lime.



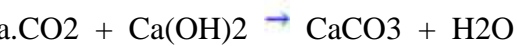
One equivalent of Mg permanent hardness requires one equivalent of lime and one equivalent of soda.



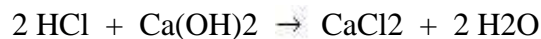
One equivalent of Fe requires one equivalent of lime and one equivalent of soda.



One equivalent of Aluminium sulphate requires three equivalents of lime and three equivalent of soda.



One equivalent of CO<sub>2</sub> requires one equivalent of lime.



Two equivalents of HCl requires one equivalent of lime.



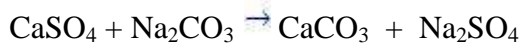
Two equivalents of HCO<sub>3</sub><sup>-</sup> require one equivalent of lime.



One equivalent of sodium meta aluminate produces half equivalent of lime.

#### **Reactions with soda (Na<sub>2</sub>CO<sub>3</sub>):**

Permanent calcium hardness already present and permanent calcium hardness introduced while removing permanent Mg, FeSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, HCl is removed by adding soda.



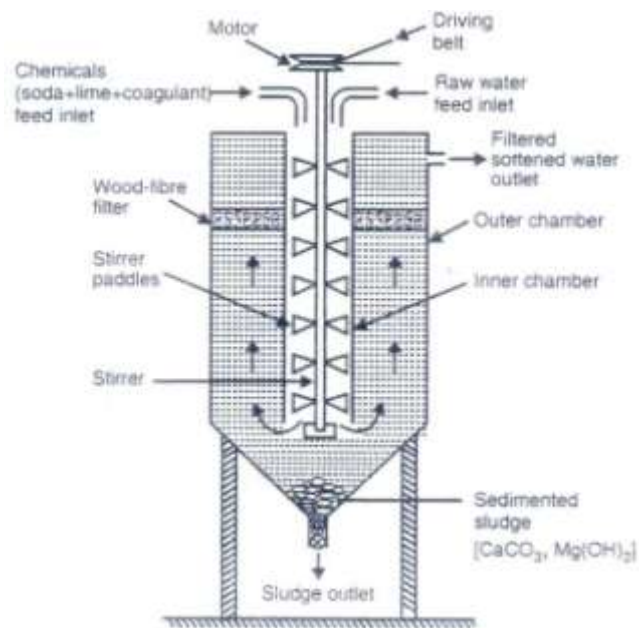
#### **LIME SODA PROCESS:**

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Lime soda process can be carried out either at room temperature or near the boiling point of water. The process carried at room temperature is called cold lime soda process

Chemistry of lime soda process: On the basis of the various reactions taking place in lime soda process the following deductions can be made. One equivalent of calcium temporary hardness requires one equivalent of lime.

**Lime soda process:** Lime soda process can be carried either at room temperature or near the boiling point of water known as cold lime soda process and hot lime soda process respectively.



- i) **Cold lime soda process:** Since this process is carried at room temperature reactions are slow. Then the precipitates formed are finely divided. So they can not be settle down easily. In order to aid the sedimentation process certain coagulants such as alum, Al and Iron salts are added. These substances dissolve in water to form hydroxides which are gelatinous nature. Gelatinous precipitate having positive charge attracts the finely divided precipitates (negatively charged) and brings them down when weight increases.

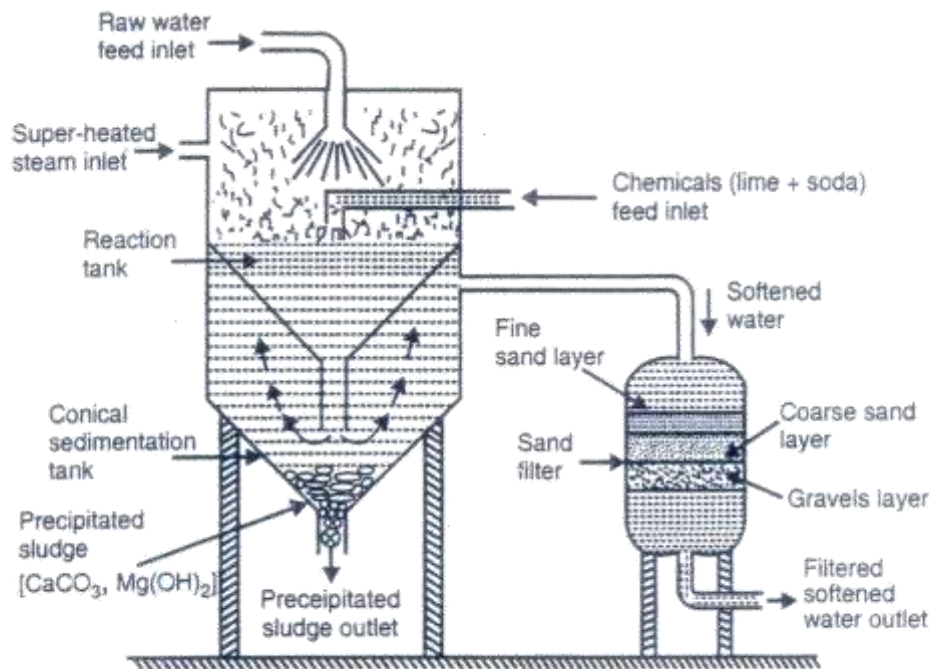
**Process:** The raw water and softening chemicals lime, soda and coagulants are fed from top into the inner vertical circular tank attached with a peddle stirrer. Due to the continuous mixing raw water and softening chemicals come in contact with each other and reaction takes place. As a result of reaction, precipitates are formed. When these precipitates are settle down water flows into the outer coaxial tank and is allowed to pass through wooden filter. Wooden filter ensures the complete removal of sludge from the softened water and softened water is supplied from the top continuously. Water softened by cold lime soda process contains 15 – 30 ppm residual hardness.

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- ii) **Hot lime soda process:** As the process is carried at the boiling point of water:
- a) reactions proceed fast.
  - b) precipitates formed granular in nature and settle down easily. No need of coagulants.
  - c) Much of the dissolved gases are driven out from the water.
  - d) Viscosity of water decreases. So filtering process become easy and life of the filter increases.
  - e) Finally, softening capacity increases to a many fold.

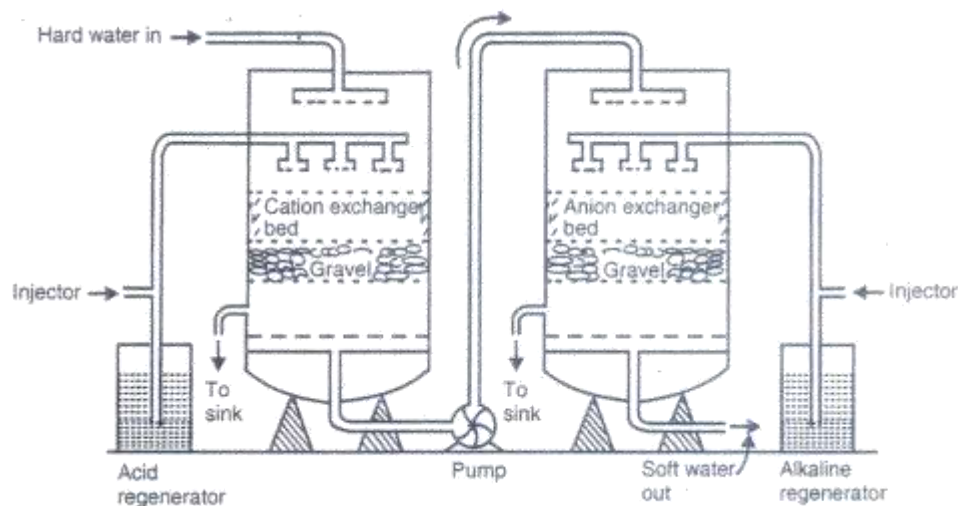
**Process:** Continuous Hot lime soda softener consists of mainly three parts.

- i) reaction tank in which softening chemicals and raw water are thoroughly mixed with steam,
- ii) conical sedimentation tank in which sludge formed will settle down.
- iii) sand filter consists of three layers i.e. fine sand layer, coarse layer and gravel layer.

It ensures the complete removal of the sludge. Water softened by hot lime soda process contains 15 – 30 ppm residual hardness.







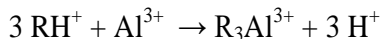
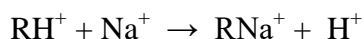
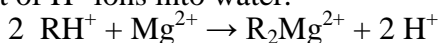
## ION EXCHANGE PROCESS (OR) DEIONISATION PROCESS

The ion exchange resins are long chain organic polymers with micro porous structure and the functional groups attached to the resins are responsible for the exchanging properties.

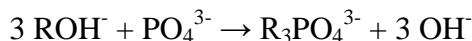
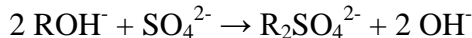
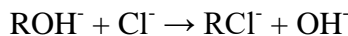
**Cation exchange resins:** It is a styrene – divinyl benzene copolymer which on sulphonation or carboxylation becomes capable to exchange the  $H^+$  ions with cations present in water.

**Anion exchange resins:** It is styrene – divinyl benzene copolymer which contains quarternary ammonium or quarternary phosphonium groups as an integral part of the resin. This on treatment with dil. NaOH becomes capable to exchange  $OH^-$  ions with anions present in water.

**Process:** First hard water is allowed to pass through cation exchange resin which takes up all the cations (such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ , etc...) and releases equivalent amount of  $H^+$  ions into water.



Then water containing anions and  $H^+$  ions is allowed to pass through anion exchange resin which removes all the anions (such as  $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ , etc...) and releases equivalent amount of  $OH^-$  ions into water.



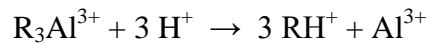
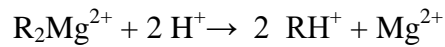
The water coming out of the anion exchange resin contains  $H^+$  and  $OH^-$  ions.

They combine to form water.

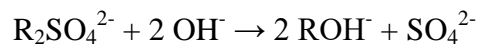
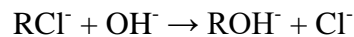


Ion free water is known as demineralised water or deionised water.

**Regeneration:** Once the cation exchanger resin and anion exchange resin to exchange cations and anions are lost then the resins are said to be exhausted. The exhausted cations exchange resin is regenerated by passing dil. HCl solution through it.



The exhausted anion exchange resin can be regenerated by passing dil. NaOH solution through it.



The regenerated resins can be used again.

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## DESALINATION METHODS

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Water with peculiar salty taste is called saline water.

Ex: Sea water

The process of removing salts present in water is known as desalination of water. The two important desalination methods are: Electrodialysis and Reverse osmosis.

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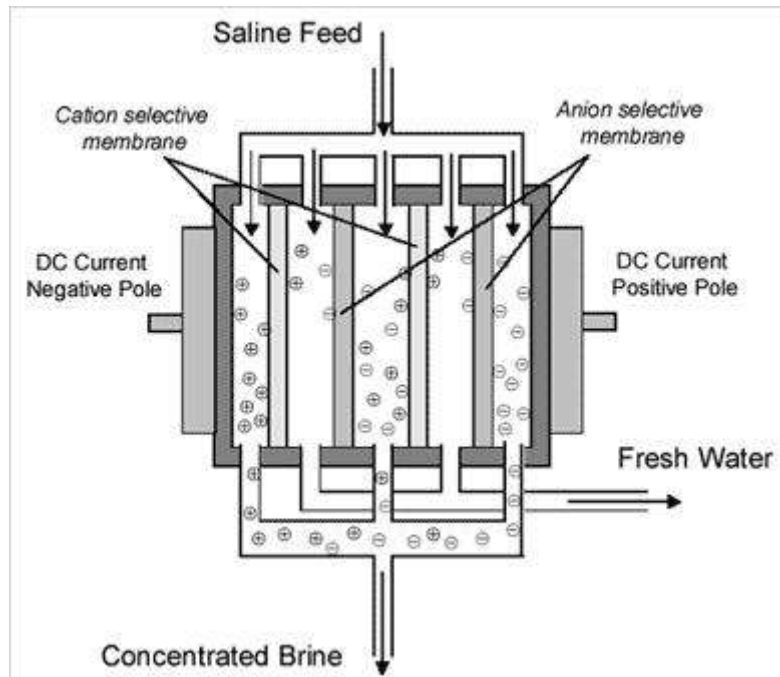
### Electrodialysis

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**Principle:** In this process, the ions present in water are removed by passing direct current through sea water using electrodes and thin rigid plastic membrane (may be natural and synthetic).

Electrodialysis process is carried out using electrodialysis cell. The two membranes divide the cell into three compartments, two side compartments and one central compartment. Sea water is taken in all the three compartments. On passing direct current, the cations present in central compartment pass through membrane and travel towards cathode and anions travel towards anode.

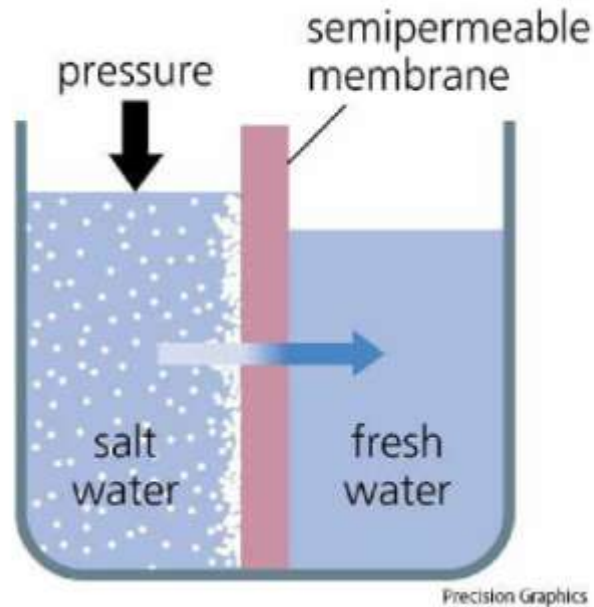
As a result, the water present in the central compartment becomes free from ions. The pure water is collected through the outlet placed at the bottom. The concentration of sea water increases in the two side compartments. The concentrated sea water is removed from the respective outlets.



For effective separation, nowadays a modified electrodialysis cell is used. It contains large no. of sets of ion selective membranes. Cation selective membrane contains some fixed negatively charged groups (such as  $\text{COO}^-$ ,  $\text{SO}_3^-$ , etc...) in it which allow positively charged cations to pass through and repel anions. Similarly, the anion selective membrane contains some fixed positively charged groups in it which allow negatively charged anions to pass through and repel cations. Thus the water becomes free from ions and become pure.

## REVERSE OSMOSIS

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When two different concentrated solutions are separated by semipermeable membrane (allows only solvent molecules to pass through but not ions) then the flow of solvent takes place from dilute solution side to concentrated solution side is known as **osmosis**. Examples of semipermeable membrane are cellulose acetate, polyamide, etc.

Let us say sea water and pure water are separated by a semipermeable membrane. A pressure higher than osmotic pressure of the order  $15\text{--}40\text{ kg/cm}^2$  is applied on sea water side. The water present in sea water side is forced to pass through the membrane and enter into pure water side leaving behind all the impurities (like dissolved salts, organic impurities, etc.). Such a process of reversal of osmosis is called reverse osmosis.

### **Advantages:**

- 1) The water obtained by this process is used for high pressure boilers.
- 2) Due to low capital and operating costs, high reliability, this is used for converting sea water into drinking water.