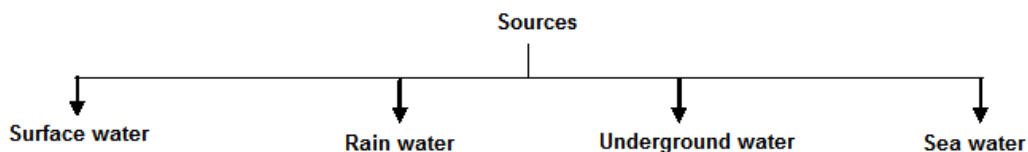# WATER TECHNOLOGY

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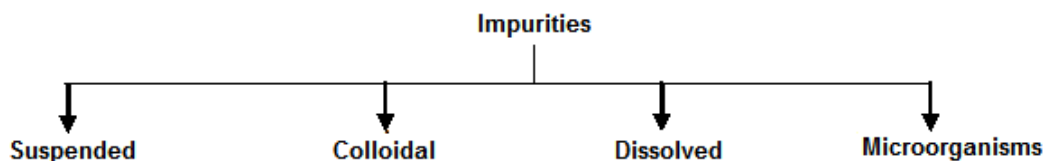
Suspended impurities: They impart turbidity, colour and odour to the water. They may be organic (or) inorganic.

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_2, CO_2 etc also come under this type.

Micro organisms: They include bacteria, fungi and algae.

Sources of impurities in water

1. Gases like O_2, CO_2 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.
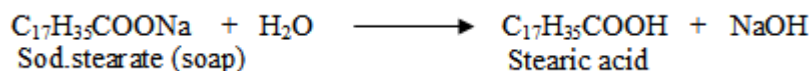4. Sewage and industrial waste make the water impure.

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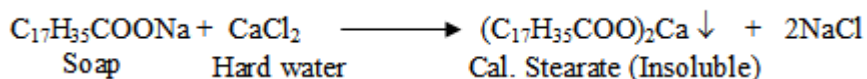
1. It should be colourless, odourless and tasteless.
2. Its turbidity should be less than 10ppm.
3. It should not contain poisonous metals like lead, arsenic, chromium and manganese.
4. P^H should be in the range of 7.0-8.5.
5. Total hardness should be less than 500ppm.
6. It should be free from disease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

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

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

$$C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca \downarrow + 2NaCl$$
$$\text{Soap} \qquad \text{Hard water} \qquad \text{Cal. Stearate (Insoluble)}$$

Causes of Hardness Hard water contains more number of salts like $CaCl_2$, $MgCl_2$, $CaSO_4$ and $MgSO_4$ etc.

Units of hardness: Hardness is caused by many salts. It is expressed in terms of equivalents of $CaCO_3$.

Degree of hardness is expressed in ppm or degree clark (^{o}cl) or degree French (^{o}fr).

Parts per million (or) mg/litre: ppm means one part of $CaCO_3$ equivalent to hardness causing salt present in 1 million parts of water.

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

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

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

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

Degree Clarke (^{o}cl): It is the British unit of hardness of water. One degree Clarke means one part of $CaCO_3$ per 70,000 parts of water.

Degree French (^{o}fr): It is the French unit of hardness of water. One degree French means one part of $CaCO_3$ per 10^5 parts of water.

Grains per gallon (gpg):

It is the English unit of hardness of water. One grain of $CaCO_3$ present in 1 gallon of water is known as gpg.

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

Therefore 1 gpg is nothing but one part of $CaCO_3$ per 70,000 parts of water and it is also called as degree Clarke.

Relation between these units of degree hardness

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

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

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

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 $CaCO_3$ 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	
$Ca(HCO_3)_2$	162	$= 100$ of $CaCO_3$	81	$= 50$ of $CaCO_3$
$Mg(HCO_3)_2$	146	$= 100$ of $CaCO_3$	73	$= 50$ of $CaCO_3$

CaSO$_4$	136 = 100 of CaCO$_3$	68 = 50 of CaCO$_3$
MgSO$_4$	120 = 100 of CaCO$_3$	60 = 50 of CaCO$_3$
CaCl$_2$	111 = 100 of CaCO$_3$	55.5 = 50 of CaCO$_3$
MgCl$_2$	95 = 100 of CaCO$_3$	47.5 = 50 of CaCO$_3$

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.

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

$$Mg(HCO_3)_2 \xrightarrow{\text{Boil}} MgCO_3 + H_2O + CO_2$$
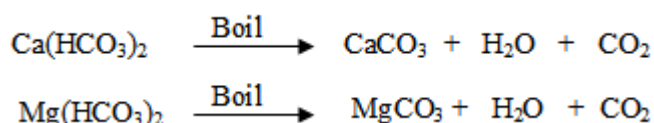
      Hardness which is easily removed by boiling is called temporary hardness.
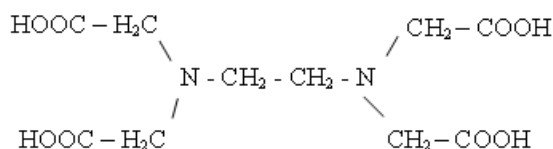
Permanent hardness; It is due to chlorides and sulphates of calcium and magnesium. This type of hardness cannot be removed by simple boiling.

DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD

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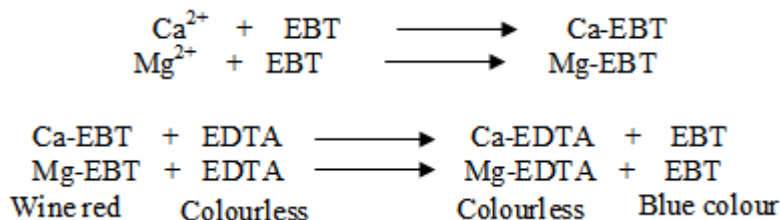✦ This method is called complexometric method.

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

$$\begin{array}{ccc} HOOC-H_2C & & CH_2-COOH \\ \diagdown & & \diagup \\ & N-CH_2-CH_2-N & \\ \diagup & & \diagdown \\ HOOC-H_2C & & CH_2-COOH \end{array}$$

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 EBT, 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.

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

$$\underset{\text{Wine red}}{Ca\text{-}EBT} + \underset{\text{Colourless}}{EDTA} \longrightarrow \underset{\text{Colourless}}{Ca\text{-}EDTA} + \underset{\text{Blue colour}}{EBT}$$
$$Mg\text{-}EBT + EDTA \longrightarrow Mg\text{-}EDTA + EBT$$

Solutions required:

❈ Standard EDTA solution, Water sample, Eriochrome black- T indicator and ammonia – ammonium chloride buffer solution ($NH_4Cl + NH_4OH$, $P^H = 10$)

❈ To maintain $P^H 10$, buffer solution is used. Instead of EDTA solution, Na_2EDTA 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

$$\text{Total Hardness} = \frac{\text{Volume of EDTA} \times \text{Molarity of EDTA} \times 100 \times 1000}{\text{Volume of water sample}} \text{ mg of } CaCO_3/L \text{ or ppm}$$

NUMERICAL PROBLEMS

1. (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 $CaCO_3$ 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. $Ca(HCO_3)_2$ = 32.4; $CaSO_4$ = 27.2; $Mg(HCO_3)_2$ = 29.2; $MgCl_2$ = 19; and 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).
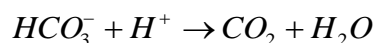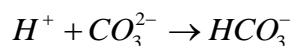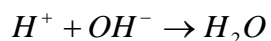
ALKALINITY OF WATER

✓ Alkalinity of water is mainly due to the presence of anions like CO_3^{2-}, HCO_3^-, and OH^-.
✓ The estimation of alkalinity in water is done by titrating water sample against standard acid using phenolphthalein and methyl orange as indicators.
✓ In this titration, two indicators are used as the different anions give end points at different PH values.
✓ Out of the three anions CO_3^{2-}, HCO_3^-, and OH^-, any two of them can exist in water together.
✓ (CO_3^{2-}, HCO_3^-) and (CO_3^{2-}, OH^-)
✓ HCO_3^- and OH^- cannot be present together because H^+ ion of HCO_3^- neutralizes OH^-.

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$
$$H^+ + OH^- \rightarrow H_2O$$
$$\overline{HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O}$$
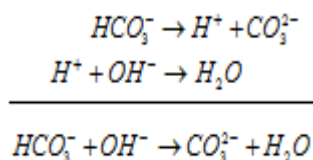
Experimental Procedure:

- 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 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 (pH falls below 7) and titrate with HCl. At the end point, pink colour reappears. This end point is taken as M.

Reactions:

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

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

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

Calculations:

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

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

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

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

Conclusions:

Burette reading	OH⁻ alkalinity	CO₃⁻ alkalinity	HCO₃⁻ 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:

1. (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: Ill 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

Scale and sludge for steam generation

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. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, 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:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$
<div align="center">Scale</div>

b) Deposition of Calcium sulphate: The solubility of $CaSO_4$ in water decreases with increase in temperature. $CaSO_4$ is soluble in cold water, but almost completely insoluble in superheated water. Consequently, $CaSO_4$ gets precipitated as hard scale on the hotter parts of the boiler.

c) Hydrolysis of Magnesium salts:

$$MgCl_2 + 2\,H_2O \rightarrow Mg(OH)_2 \downarrow + 2\,HCl$$
<div align="center">Scale</div>
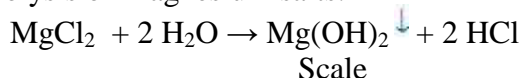
d) Presence of silica: If silica is present in boiler feed water, it reacts with Calcium and Magnesium ions forming Calcium silicate and Magnesium silicate which are very hard scales.

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

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 (Na_2FeO_2).

$$Fe + 2\,NaOH \rightarrow Na_2FeO_2 + H_2 \uparrow$$
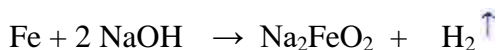
This dissolution of loss of the boiler body material is caustic embrittlement.

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

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

$$2\,Fe(OH)_2 + \tfrac{1}{2}\,O_2\ \rightarrow\ Fe_2\,O_3.2H_2O\ (Rust)$$
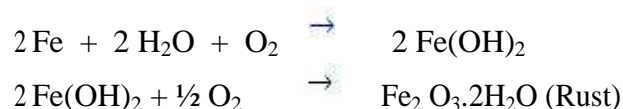
Dissolved oxygen can be removed by adding chemicals like hydrazine, sodium sulphite or sodium sulphide.

$$N2H4\ +\ O2\ \rightarrow\ N2\ +\ 2\,H2O$$
$$Na2S\ +\ 2\,O2\ \rightarrow\ Na2SO4$$
$$2\,Na2SO3 + O2 \rightarrow\ 2\,Na2SO4$$
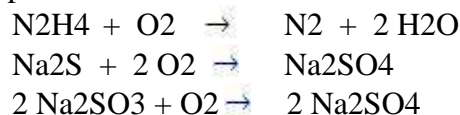
Also, dissolved oxygen can be removed along with CO_2 and other gases, if any by mechanical deaeration process.

Dissolved CO$_2$: If carbon dioxide is already present in water or introduced by the decomposition of bicarbonates [$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$] 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^3 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.
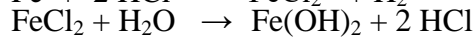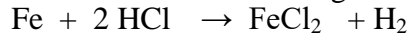
Water feed

Perforated plate

To vacuum pump

Steam jacket

Perforated plates

Tower

De-aerated water
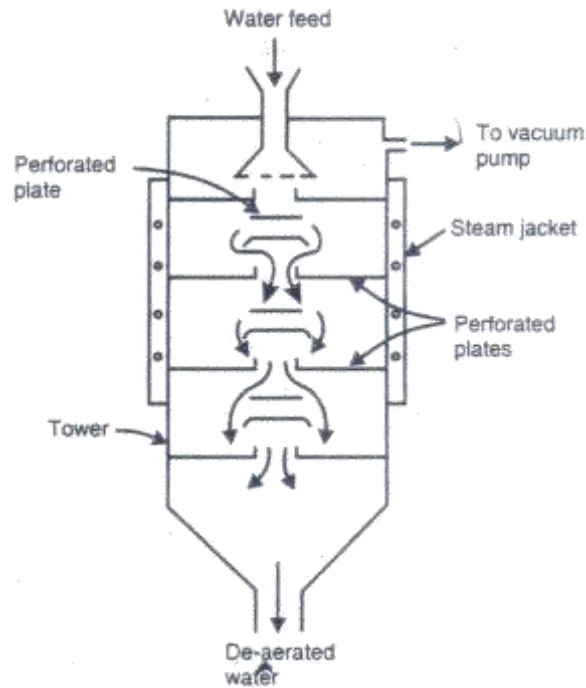
b) By using calculated amount of ammonia:
$$2\,NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$
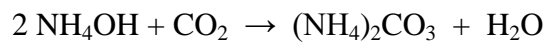
Acids producing salts: If $MgCl_2$ is present in feed water it undergoes hydrolysis at higher temperatures and producing acid.
$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2\,HCl$$
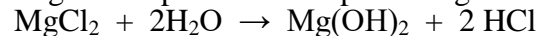
Acid attacks the iron of the boiler forming HCl again and again.
$$Fe + 2\,HCl \rightarrow FeCl_2 + H_2$$
$$FeCl_2 + H_2O \rightarrow Fe(OH)_2 + 2\,HCl$$

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

Disadvantages:
a) Shortening of boiler life
b) Leakages of joints and reverts, increased cost of repairs and maintenance.

PRIMING AND FOAMING

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 conductive 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.
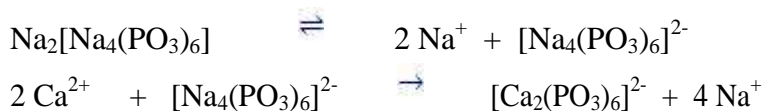
INTERNAL TREATMENTS

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, Na_2CO_3 added to boiler water will react with the $CaSO_4$ present in dissolved state in boiler water.

The reaction is: $CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$

The reaction is favoured in forward direction only when the concentration of $[CO_3^{2-}] > [SO_4^{2-}]$.

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

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

$$2\,Ca^{2+} + [Na_4(PO_3)_6]^{2-} \rightarrow [Ca_2(PO_3)_6]^{2-} + 4\,Na^+$$

Scale forming ion $\qquad\qquad\qquad\qquad$ Highly soluble complex

d) Phosphate conditioning: In high pressure boilers, $CaSO_4$ forms hard type scale. This is because the solubility of $CaSO_4$ decreases with increase of temperature. It can be converted into soft sludge by adding excess of soluble phosphates. The optimum pH for the precipitation $Ca_3(PO_4)_2$ soft sludge is $9.5 – 10.5$.

$$2\,(PO_4)^{3-} + 3\,CaSO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 3\,SO_4^{2-}$$
$$\text{soft sludge}$$
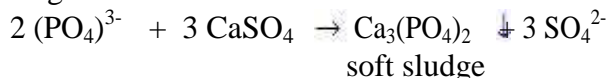
There are three types of phosphate are employed for this purpose.
(i) Tri sodium phosphate – Na_3PO_4 (too alkaline)
(ii) Disodium hydrogen phosphate – Na_2HPO_4 (weakly alkaline)
(iii) Monosodium dihydrogen phosphate – NaH_2PO_4 (acidic)
When the alkalinity of boiler feed water is too low, Na_3PO_4 is used. If the feed water is alkaline, NaH_2PO_4 is used. For feed waters with the correct alkalinity, the neutral Na_2HPO_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.

$$EDTA + Cu^{2+} \rightarrow [Cu^{2+} \text{ - EDTA}]$$

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 $CaCO_3$, $Mg(OH)_2$, etc] by adding calculated amounts of lime [$Ca(OH)_2$] and soda [Na_2CO_3].

Chemistry of lime soda process:
Reactions with lime [$Ca(OH)_2$]:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3 + 2\,H_2O$$
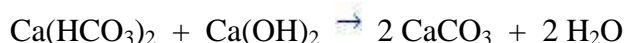
One equivalent of temporary Calcium hardness requires one equivalent of lime.

$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \rightarrow 2\,CaCO_3 + Mg(OH)_2$$
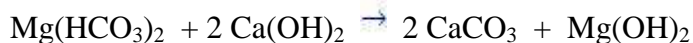
One equivalent of Mg temporary hardness requires two equivalent of lime.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

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

$$FeSO4 + Ca(OH)2 \rightarrow Fe(OH)2 + CaSO4$$
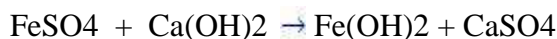
One equivalent of Fe requires one equivalent of lime and one equivalent of soda. $$Al_2(SO_4)_3 + 3\,Ca(OH)_2 \rightarrow 2\,Al(OH)_3 + 3\,CaSO_4$$
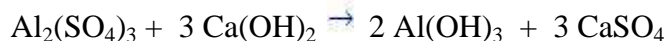
One equivalent of Aluminium sulphate requires three equivalents of lime and three equivalent of soda. $$CO2 + Ca(OH)2 \rightarrow CaCO3 + H2O$$
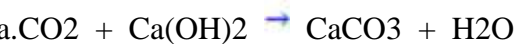
One equivalent of CO2 requires one equivalent of lime.

$$2\,HCl + Ca(OH)2 \rightarrow CaCl2 + 2\,H2O$$
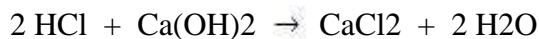
Two equivalents of HCl requires one equivalent of lime.

$$2\,HCO3- + Ca(OH)2 \rightarrow CaCO3 + CO32- + 2\,H2O$$

Two equivalents of HCO3- require one equivalent of lime.

$$NaAlO2 + 2\,H2O \rightarrow NaOH + Al(OH)3$$

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

Reactions with soda (Na_2CO_3):

Permanent calcium hardness already present and permanent calcium hardness introduced while removing permanent Mg, $FeSO_4$, $Al_2(SO_4)_3$, HCl is removed by adding soda. $$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
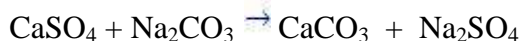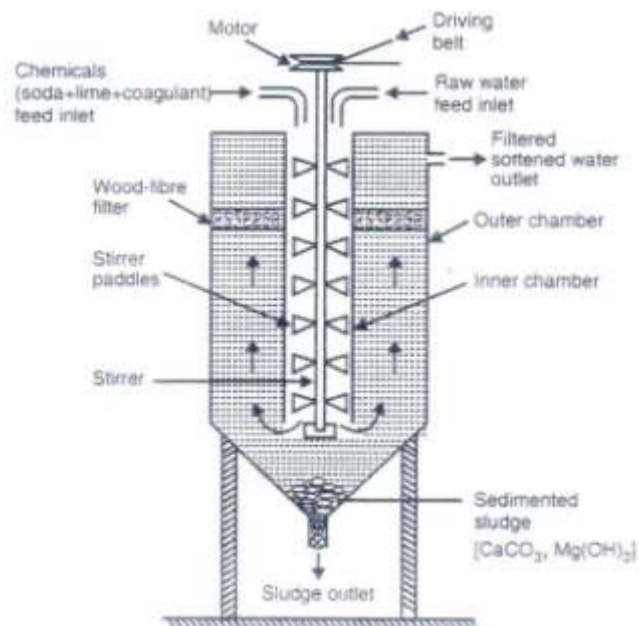
LIME SODA PROCESS:

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.

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
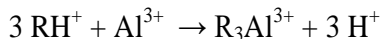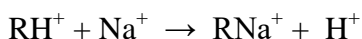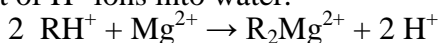
contains 15 – 30 ppm residual hardness.
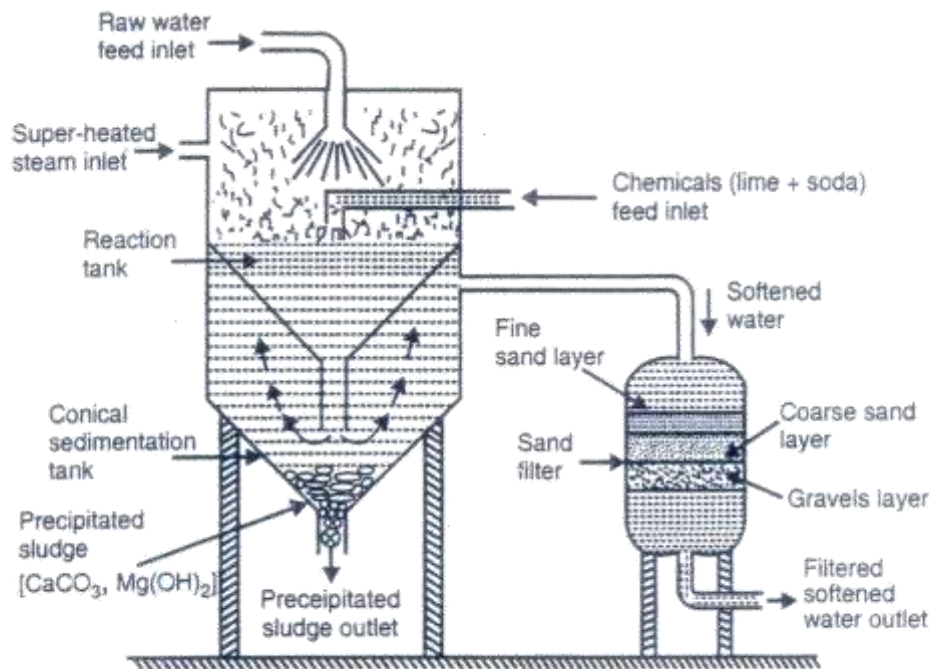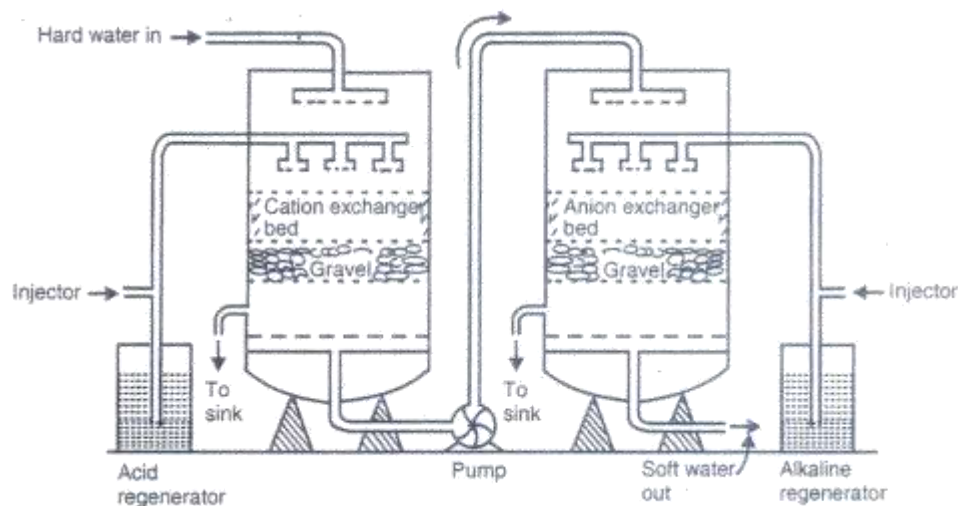
ION EXCHANGE PROCESS (OR) DEIONISATION PROCESS

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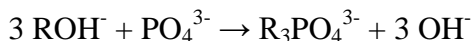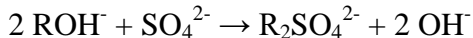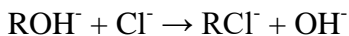
Cation exchange resins: It is a styrene – divinyl benzene copolymer which on sulphonation or carboxylation becomes capable to exchange the H^+ ions with cations present in water.

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.

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

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

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

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.

$$ROH^- + Cl^- \rightarrow RCl^- + OH^-$$
$$2\ ROH^- + SO_4^{2-} \rightarrow R_2SO_4^{2-} + 2\ OH^-$$
$$3\ ROH^- + PO_4^{3-} \rightarrow R_3PO_4^{3-} + 3\ OH^-$$

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

They combine to from water.
$$H^+ + OH^- \rightarrow H_2O$$

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.

$$R_2Mg^{2+} + 2\ H^+ \rightarrow 2\ RH^+ + Mg^{2+}$$
$$R_3Al^{3+} + 3\ H^+ \rightarrow 3\ RH^+ + Al^{3+}$$
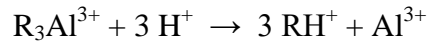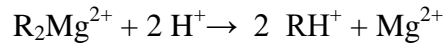
The exhausted anion exchange resin can be regenerated by passing dil. NaOH solution through it.

$$RCl^- + OH^- \rightarrow ROH^- + Cl^-$$
$$R_2SO_4^{2-} + 2\ OH^- \rightarrow 2\ ROH^- + SO_4^{2-}$$
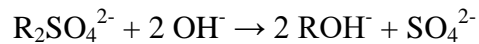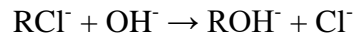
The regenerated resins can be used again.

DESALINATION METHODS

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.

Electrodialysis

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.
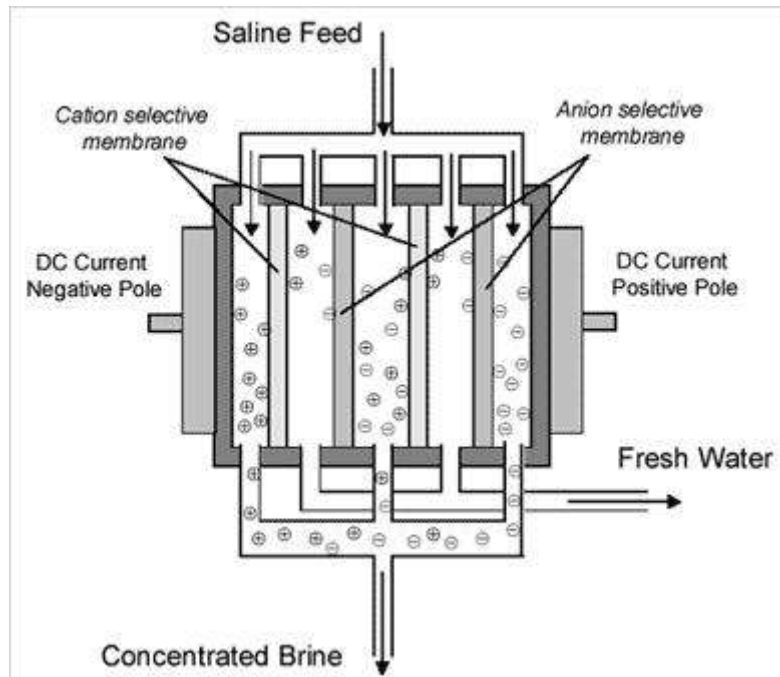
For effective separation, now a days modified electrodialysis cell is used. It contains large no. of sets of ion selective membranes. Cation selective membrane contains some fixed negatively charged groups (such as COO^-, SO_3^-, etc…) in it which allow positively charged cations to pass through and 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
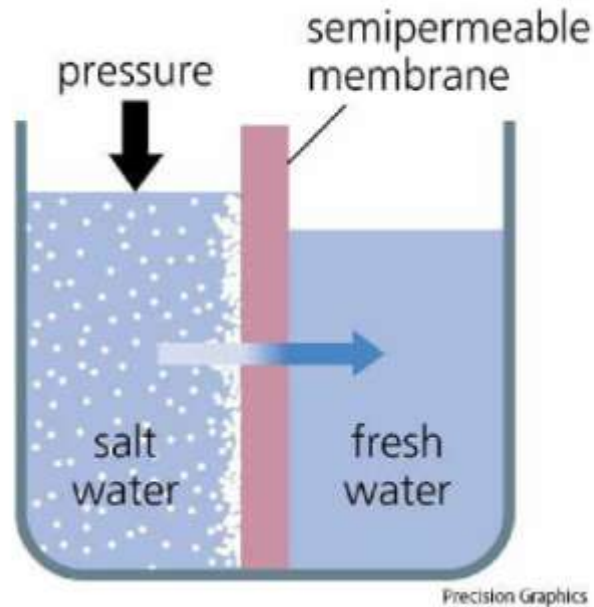
When two different concentrated solutions are separated by semipermeable membrane (allows only solvent molecules to pass through but not ions) then the flow of solvent takes place from dilute solution side to concentrated solution side is known as **osmosis**. Examples of semipermeable membrane are cellulose 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 15-40 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.