Unit–I

WATER AND ITS TREATMENT

Hardness of water – types – expression of hardness – units – estimation of hardness of water by EDTA – numerical problems – boiler troubles (scale and sludge) – treatment of boiler feed water – Internal treatment (phosphate, colloidal, sodium aluminate and calgon conditioning) external treatment-Ion exchange process, zeolite process – Desalination of brackish water - Reverse Osmosis.

CHAPTER 1 : Water and its Treatment

INTRODUCTION

The nature's most abundant supply i.e., water is essential for the survival of all the living beings on earth i.e., man, animals and plants. Water is not only essential for the survival of life, but it is also used for the operation in a large number of industries as coolant, solvent, for steam generation, for air conditioning, fire-fighting etc. Water is also used for all domestic purposes like bathing, drinking, washing, sanitary, irrigation etc.

HARDNESS OF WATER

*"Hardness of water is the characteristic of preventing lather formation of water with soap"***.** Generally salts like chlorides, bicarbonates and sulphates of Ca^{2+}, Mg^{2+} and Fe^{2+} make water hard. This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.

$$\underset{\substack{\text{Sodium Stearate}\\ \text{(soap)}}}{2C_{17}H_{35}COONa} + \underset{\substack{\text{Hardness}\\ \text{causing}\\ \text{substance}}}{CaCl_2} \longrightarrow \underset{\substack{\text{Calcium Stearate}\\ \text{(insoluble)}}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2NaCl$$

Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

TYPES OF HARDNESS

(i) *Temporary Hardness* is due to the bicarbonates of Ca^{2+} and Mg^{2+} and carbonate of Fe^{2+}. Since bicarbonates readily get precipitated on boiling the water, the temporary hardness can be easily removed, viz.

$$Ca(HCO_3)_2 \xrightarrow{\text{heat}} \underset{\text{insoluble}}{CaCO_3 \downarrow} + H_2O + CO_2$$

(ii) *Permanent Hardness* is due to the presence of chlorides and sulphates of Ca, Mg, Fe, etc. Permanent Hardness cannot be removed on boiling.

$$CaCl_2 + \underset{\text{(Soda)}}{Na_2CO_3} \longrightarrow CaCO_3 \downarrow + 2NaCl$$

EXPRESSION OF HARDNESS AND UNITS OF HARDNESS

Both temporary and permanent hardness are expressed in ppm (parts per million) as $CaCO_3$. The choice of $CaCO_3$ is due to the fact that its molecular weight is 100 and equivalent weight is 50 and it is the most insoluble salt in water.

Equivalent of $CaCO_3$

$$= \frac{\text{(Mass of hardness producing substance)} \times \text{(Chemical equivalent of } CaCO_3\text{)}}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}}$$

Hardness is principally expressed in ppm unit. Other limits include French degree of hardness, English degree of hardness or Clark, USA degree of hardness and German degree of hardness.

1. ***Parts per million (ppm):*** It is the number of parts of calcium carbonate equivalent hardness present in one million parts of water.

   1 ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

2. ***Milligram per lite (mg/L):*** It is the number of milligrams of Calcium carbonate equivalent hardness present in one litre of water.

   1 mg/lit. = 1 mg of $CaCO_3$ equivalent hardness in 1 litre of water.

3. ***Degree Clarke (°Cl):*** It is the number of parts of $CaCO_3$ equivalent hardness present in 70,000 parts of water.

4. ***Degree French (°Fr):*** It is the number of parts of $CaCO_3$ equivalent hardness present in 10^5 (1 Lakh) parts of water.

   1°F*r* = 1 part of C*a*CO_3 equivalent hardness in 10^5 parts of water.

   The above four units are correlated as given below:

   1 ppm = 1 mg/L = 0.07°C*l* = 0.1°F*r*

   $$1 \text{ ppm} = \frac{1 \text{ part of hardness}}{10^6 \text{ parts of water}}$$

Relation between various units of hardness

1 ppm	= 1 mg/*l*	= 0.1°F*r*	= 0.07°C*l*
1 mg/*l*	= 1 ppm	= 0.1°F*r*	= 0.07°C*l*
1°C*l*	= 1.43°F*r*	=14.3 ppm	= 14.3 mg/*l*
1°F*r*	= 10 ppm	= 10 mg/*l*	= 0.7 °C*l*

1.4.1 Disadvantages of Hard Water

(a) ***In domestic uses.*** For washing and bathing, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the C*a*/Mg salts get precipitated. Thus a lot of soap gets wasted also.

For cooking hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant.

Drinking of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

(b) ***In industrial uses.*** For textile industry and dyeing industry, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

- For sugar industry, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the paper industry. Iron salts interfere with the colour of the paper.
- In laundry, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- The hydration of cement and final hardening of cement are affected by use of hard water in concrete making.
- Hard water is not suitable for preparing drug solutions in pharmaceutical industry
- For steam generation in boilers, hard water creates many problems like:

  (i) scale and sludge formation,

  (ii) corrosion,

  (iii) priming and foaming and

  (iv) caustic embrittlement.

1.5 ESTIMATION OF HARDNESS OF WATER BY EDTA

Eriochrome Black-T (EBT) is the metal ionindicator used in the determination ofhardness by complexometric titration with EDTA. This dye-stuff tends to polymerize in strongly acidic solutions to a red brown product, and hence the indicator is generally used in EDTAtitration with solutions having pH greater than 6.5. The sulphuric acid gropus loses its proton much before the pH range of 7-12, which is of interest for metal ion indicator use. The dissociation of the two hydrogen atoms of the phenolic groups only should therefore be considered and hence the dye stuff may be represented by the formula H_2D^-. This functions as acid-base indicator with two colour changes as follows:

$$\underset{\text{(Red)}}{H_2D^-} \underset{\text{pH 6.3}}{\square} \underset{\text{(Blue)}}{HD^{2-}} \underset{\text{pH 11.5}}{\square} \underset{\text{(Yellowish, Orange)}}{D^{3-}}$$

In the pH range 8-10, the blue form of the indicator HD^{2-} gives a wine red complex with Mg^{2+}:

$$\underset{\text{(Blue)}}{Mg^{+2} + HD^{2-}} \longrightarrow \underset{\text{(Wine red)}}{MgD^{-} + H^{+}}$$

Now if EDTA(H_2Y^{2-}) is added to such a solution Mg^{2+} preferentially complexes with EDTA (since the metal EDTA complex is more stable than the metal-indicator complex) and liberates the free indicator HD^{2-} at the end point, thereby producing a sharp colour change from wine red to blue. These reactions during the EDTA titration may be summarized as follows:

$$\underset{\text{(Blue)}}{Mg^{+2} + HD^{2-}} \longrightarrow \underset{\text{(Wine red)}}{MgD^{-} + H^{+}}$$

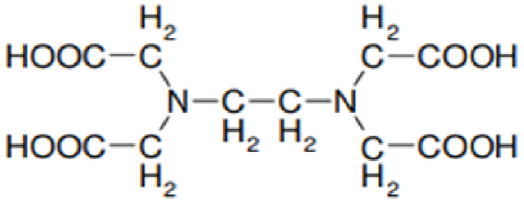
$$H_2Y^{2-} + Ca^{2+} \longrightarrow CaY^{2-} + 2H^{+}$$

$$H_2Y^{2-} + Mg^{2+} \longrightarrow MgY^{2-} + 2H^{+}$$

$$H_2Y^{2-} + \underset{\text{(Wintered)}}{Mg^{2-}} \longrightarrow MgY^{2-} + \underset{\text{(Blue)}}{HD^{2-}} + H^{+}$$

Theory: EDTA(Ethylenediamine tetra acetic acid) forms colorless stable complexes with Ca^{2+} and Mg^{2+} ions present in water at $pH = 9\text{-}10$. To maintain the pH of the solution at 9-10, buffer solution ($NH_4Cl + NH_4OH$) is used. Eriochrome Black-T (E.B.T) is used as an indicator.

The sample of hard water must be treated with buffer solution and EBT indicator which forms unstable, wine-red colored complex s with Ca^{2+} and Mg^{2+} present in water.



Structure of EDTA

Procedure

(a) Total hardness

(i) Take 25 or 50 ml or well mixed sample in a conical flask

(ii) Then add 1 to 2 ml buffer solution followed by 1 ml inhibitor

(iii) Add a pinch of Eriochrome black-T and titrate with standard EDTA (0.01M) till wine red colour changes to blue, then note down the volume of EDTArequired (A) .

(iv) Run a reagent blank. Note the volume of EDTA (B).

(v) Calculate volume of EDTA required by sample, C = A– B (from volume of EDTA required in steps (iii & iv).

(b) Calcium hardness

`(i) Take 25 or 50 ml sample in a conical flask

(ii) Add 1 ml NaOH to raise pH to 12.0 and add a pinch of muroxide indicator.

(iii) Titrate immediatelywith EDTAtill pink colour changes to purple. Note the volume of EDTAused (A1).

(iv) Run a reagent blank. Note the ml of EDTArequired (B1) and keep it aside to compare end points of sample titrations.

(v) Calculate the volume of EDTA required by sample, C1 = A1 – B1.

PROBLEMS BASED ON CALORIFIC VALUE

Problem 1: If a sample of water contains 50 mgs of Ca^{2+} ions per litre, calculate its hardness in terms of $CaCO_3$ equivalent?

Solution: Given: The amount of Ca^{2+} ions = 50 mgs/lit.

We know that, the molecular weight of calcium = 40

$$\therefore \text{ Amount equivalent to } CaCO_3 = \frac{50 \times 100}{40} = 125 \text{ mgs/lit.}$$

Problem 2: A water sample contains 204 mgs of $CaSO_4$ and 73 mgs of $m_g(HCO_3)_2$ per litre. What is the total hardness interms of $CaCO_3$ equivalent?

Solution: Given: Hardness producing salt

(i) $CaSO_4$ (molecular weight = 136)

$$\text{Amounts equivalent to } CaCo_3 = \frac{204 \times 100}{136}$$

$$= 150 \text{ mgs/lit.}$$

(ii) $Mg(HCO_3)_2$ (Molecular weight = 146)

$$\text{Amounts equivalent to } CaCO_3 = \frac{73 \times 100}{146}$$

$$= 50 \text{ mgs/lit.}$$

Temporary hardness = $Mg(HCO_3)_2$ = 50 mgs/lit

Permanent hardness = $CaSO_4$ = 150 mgs/lit

Total hardness = $Mg(HCO_3)_2 + CaSO_4$

$\Rightarrow 50 + 150 = 200$ mgs/lit.

Problem 3: Calculate the carbonate and non-carbonate hardness of a sample of water containing the dissolved salts as given below in mgs/lit. **$Mg(HCO_3)_2$ = 7.3; $Ca(HCO_3)_2$ = 40.5; $CaSO_4$ = 13.6; $MgCl_2$ = 21.75 and $NaCl$ = 50.**

Solution: Given:

(i) Hardness producing salt $Mg(HCO_3)_2$ (Mol. Wt = 146), Amount in mgs/lit = 7.3

$$= \frac{73 \times 100}{146} = 5 \text{ mgs/lit.}$$

(ii) $Ca(HCO_3)_2$ (Mol. Wt = 162), Amount in mgs/lit = 40.5

$$= \frac{40.5 \times 100}{162} = 25 \text{ mgs/lit.}$$

(iii) $CaSO_4$ (Mol. Wt. = 136), Amount in mgs/lit = 13.6

$$= \frac{13.6 \times 100}{136} = 10 \text{ mgs/lit.}$$

(iv) $MgCl_2$ (Mol. Wt. = 95), Amount in mgs/lit = 21.75

$$= \frac{21.75 \times 100}{95} = 22.9 \text{ mgs/lit.}$$

(v) $NaCl$, Amount in mgs/lit = 50.

But Nacl does not contribute any hardness to water, hence it is ignored.

Carbonate hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$

= 5 + 25 = 30 mgs/lit

Non-Carbonate hardness = $CaSO_4 + MgCl_2$

= 10 + 22.9 = 32.9 mgs/lit.

Total hardness = Carbonate Hardness + Non-Carbonate Hhardness

= 30 + 32.9 = 62.9 mgs/lit.

Problem 4: A sample of water is found no contain the following analytical data in mgs/lit. M*g*$(HCO_3)_3$ = 14.6; M*g*Cl_2 = 9.5; M*g*SO_4 = 6.0; C*a*$(HCO_3)_2$ = 16.2. Calculate the temporary and Permanent hardness of the sample of water.

Solution: Given: Hardness producing salt.

(i) M*g*$(HCO_3)_2$ (Mol. Wt. = 146), Amount in mgs/lit. = 14.6

$$= \frac{14.6 \times 100}{146} = 10 \text{ mgs/lit.}$$

(ii) M*g*C*l*$_2$ (Mol. Wt. = 95), Amount in mgs/lit. = 9.5

$$= \frac{9.5 \times 100}{95} = 10 \text{ mgs/lit.}$$

(iii) $MgSO_4$ (Mol. Wt. = 120), Amount in mgs/lit = 6.0

$$= \frac{6.0 \times 100}{120} = 5 \text{ mgs/lit.}$$

(iv) $Ca(HCO_3)_2$ (Mol. Wt. = 162), Amount in mgs/lit = 16.2

$$= \frac{16.2 \times 100}{162} = 10 \text{ mgs/lit.}$$

$$\text{Temporary hardness} = Mg(HCO_3)_2 + Ca\,(HCO_3)_2$$

$$= 10 + 10 = 20 \text{ mgs/lit.}$$

$$\text{Permanent hardness} = MgCl_2 + MgSO_4$$

$$= 10 + 5 = 15 \text{ mgs/lit.}$$

BOILER TROUBLES

Scale and Sludge

When hard water is used for boilers, on continuous evaporation, the salts present in the hard water gets saturated and are finally deposited in the areas where the flow is slow. When the precipitates formed are loose and slimy in nature, it is called *sludge,* whereas when the precipitates formed are hard and adhere strongly on the inner walls of the boiler, they are called *scale.*

Sludge can be easily removed byscrapping with a brush. Sludge is formed bythe presence of $MgCO_3$, $MgSO_4$, $MgCl_2$, $CaCl_2$ etc. These salts are more soluble in hot water.

Disadvantages of sludge formation are:

(i) poor heat conduction due to the presence of sludge on the surface;

(ii) difficulty in the operation of the boiler;

(iii) if sludge is formed along with the scale and is trapped within the scale formed and so it is difficult to remove and

(iv) it clogs the pipe lines and other connections to the vessel near the places where water circulation rate is slow.

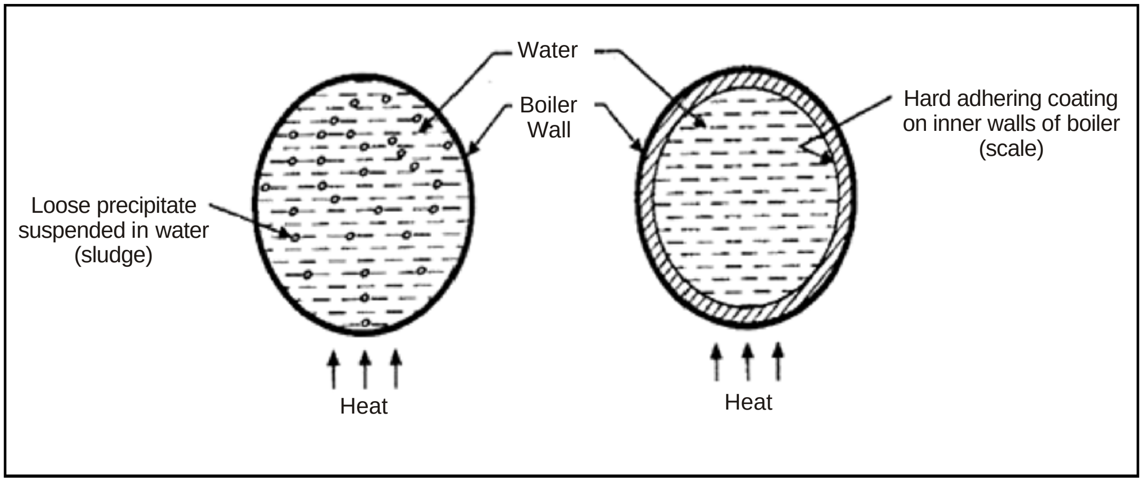


Figure 1.1: Scale and sludge formation in boilers

Removal of Sludge

Sludge formation can be prevented by:

(i) using soft water for boiler operation and

(ii) removing the concentrated salty water from time to time so that deposition of sludge is prevented. Scales are the hard deposits on the inner surface of the boilers which are difficult to remove.

This scale formation takes place due to the following reasons:

(a) In low pressure boilers scale formation occurs due to the formation of $CaCO_3$ from $Ca(HCO_3)_2$.

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

(b) In high pressure boilers this $CaCO_3$ gets converted to soluble $Ca(OH)_2$. But here $CaSO_4$ forms the hard scale. Since the solubility of $CaSO_4$ decreases with increase in temperature, and at high temperature the precipitated $CaSO_4$ forms hard scale. Similar hard scales are formed when SiO_2 is present in the hard water. It deposits as $CaSiO_3$ or $MgSiO_3$. These calcium or magnesium silicate scales are very difficult to remove. Dissolved magnesium salts also precipitate as $Mg(OH)_2$ forming soft type of scale.

Disadvantages of scale formation are similar to sludge formation but the severity is more, since its removal is more difficult.

Disadvantages include

(i) Poor heat transfer from boiler to water leading to increase in fuel consumption. The increase in thickness of the scale from 1.25 mm to 12 mm leads to increase in fuel consumption from over 50% to 150%.

(ii) Due to the overheating of the boiler, different parts of the boiler become weak and distorted and so the operation of the boiler becomes unsafe, particularly the high pressure boilers. The thick scales may sometimes lead to explosion due to sudden development of high pressure.

(iii) Valves and condensers of the boilers are chocked due to scale formation and Boiler efficiency decreases.

Removal of scales can be done by:

(i) Wooden scraper or wire brush, suitable for removing loose scales.

(ii) Blow down operations for loose scales. The operation actually involves the removal of very hard water from a tap at the bottom of the boiler and replenishing the water with softened water called ‘make up’ water.

(iii) Giving thermal shocks, which involve alternate heating and cooling to make the scales brittle.

(iv) Chemical treatment with 5-10% HCl for carbonates and EDTA treatment for Ca/Mg salts forming complexes.

Differences between Sludge and Scale

S.No.	Sludge	Scale
1.	Loose, slim , non-adherent precipitate	Hard, thick , strong adherent precipitate
2.	Due to salts like $MgSO_4$, $MgCl_2$	Due to salts like $CaSO_4$, $Ca(HCO_3)_2$
3.	Due to poor conductance, they decrease the boiler efficiency to lesser extent and causing chocking in the pipelines.	Due to poor conductance, they decrease the boiler efficiency to maximum extent, cause reduced fuel economy, improper boiling, boiler explosion etc.,
4.	It can be prevented by periodical replacement of concentrated hard water by fresh water. This process is known as *"blow down"* method.	It can be prevented by special methods like i) External treatment of ion exchange, ii) Internal carbonate, phosphate, Calgon conditioning and iii) Mechanical hard scrubbing methods.

2.Caustic embrittlement

Definition:Intercrystalline cracking of boiler material

It is a form of stress corrosion takes place in boilers operating at high temperature(200-250˚ C) and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.

$Na_2CO_3 + H_2O$ ---------2 $NaOH + CO_2$

The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water. When concentrations of the NaOH reaches a value of 10% it attacks the metal at the stressed region dissolving it in the form of sodium ferroate (Na2FeO2). Sodium ferroate undergoes hydrolysis-depositing magnetite as follows

$3Na_2FeO_2 + 4H_2O$ -------- $6NaOH + Fe_3O_4 + H_2$

$6Na_2FeO_2 + 6H_2O + O_2$ -------- $12NaOH + 2Fe_3O_4$

So NaOH is regenerated in the process and its concentration is keep on increasing maintaining a required environment. Thus corrosion process develops cracks and making the metal brittle by the deposition of the product.

3.Priming and foaming

Foaming:

Bubbles produced in the water due to heat and pass out with the steam. This is called foaming and it is caused by high concentration of impurities in the boiler water.

Priming

It is the carry over of varying amounts of droplets of water in the steam, which lowers the energy efficiency of the steam and leads to the deposit of water droplets of impurities and cause the damage of boiler.

Prevention:

To prevent it, use of chemicals like anti-foaming and anti-priming agents which prevents the formation of priming and foaming in the boiler water.

4) Boiler Corrosion

It may be due to three major reasons:

- i) Dissolved Oxygen
- ii) Dissolved CO2
- iii) Dissolved salts like MgCl2

i)Corrosion Due to dissolved oxygen :

Dissolved oxygen in presence of water, causes corrosion.

$4Fe + 6\,H_2O + 3O_2$ ……………………… $4\,Fe(OH)_3$ (Rust)

Prevention from oxygen:

a) Chemical method –

i)Adding Sodium Sulphite:

$2\,Na_2SO_3 + O_2$ ……………………… $2\,Na_2SO_4$

This method results in other precipitates which can have some side effects. So this method is less preferred.

ii)Adding Hydrazine:

$N_2H_4 + O_2$ …………………..$N_2 + 2\,H_2O$

This method results in inert gas and pure water, and has no side effects

b) Mechanical deaeration method:

1. This is based on the principle that at high temperature , low pressure and high exposed area, the solubility of gases in water is decreased. So, the gases can be expelled easily.
2. Here, the water is fed into the mechanical deaerator which is provided with vacuum pump, heaters and perforated plates.
3. The out coming water will be free from dissolved gases.

2.Corrosion due to CO_2

Salts like Calcium bicarbonate on heating produces CO2 . CO2 dissolves in water to form carbonic acid which corrodes the boiler metal. Δ

$Ca(HCO_3)_2$…………………………… $CaCO_3 + H_2O + CO_2$

$H_2O + CO_2$ ………………………………… H_2CO_3(carbonic caid)

Prevention from CO_2

1. Chemical method: By adding calculated amount of ammonium hydroxide

   $2NH_4OH + CO_2$ ……………… $(NH_4)_2CO_3 + H_2O$ 2.
2. Mechanical deaeration method (similar to oxygen method)

Corrosion due to Dissolved salts like $MgCl_2$ .Dissolved salts like $MgCl_2$

cause acid formation. .This will be prevented by alkali neutralisation.

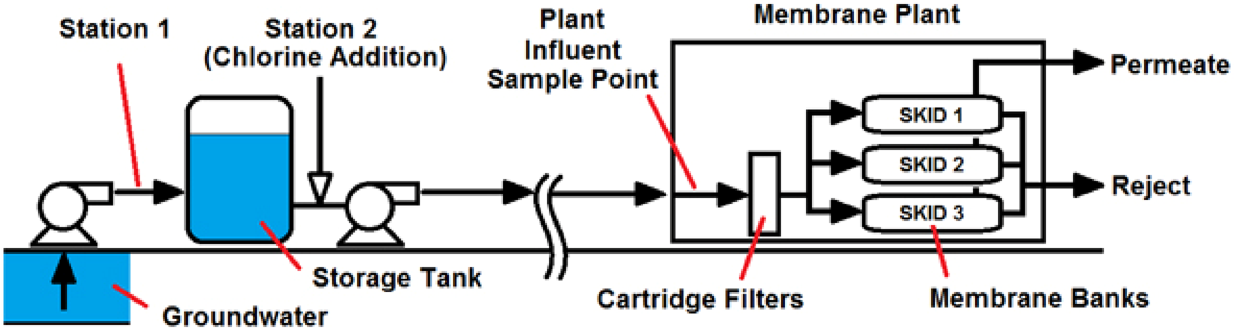
$MgCl_2 + 2\ H_2O$ ………………………$Mg(OH)_2 + 2\ HCl$ (Corrosive acid)

Neutralisation: Excess acidic nature is neutralized by adding alkalis and vice versa.

$HCl + NaOH$ ……………………….. $NaCl + H_2O$

DESALINATION PROCESS

Definition: Process of removing common salt from sea water.. Seawater desalination has the potential to reliably produce enough potable water to support large populations .



Types of process:

Reverse osmosis (RO) and Nanofiltration (NF) are the leading pressure driven membrane processes. Contemporary membranes are primarily polymeric materials with cellulose acetate still used to a much lesser degree. Operating pressures for RO and NF are in the range of 50 to 1,000 psig (3.4 to 68 bar, 345 to 6896 kPa).

Electrodialysis (ED) and Electrodialysis Reversal (EDR) processes are driven by direct current (DC) in which ions (as opposed to water in pressure driven processes) flow through ion selective membranes to electrodes of opposite charge.

Reverse osmosis

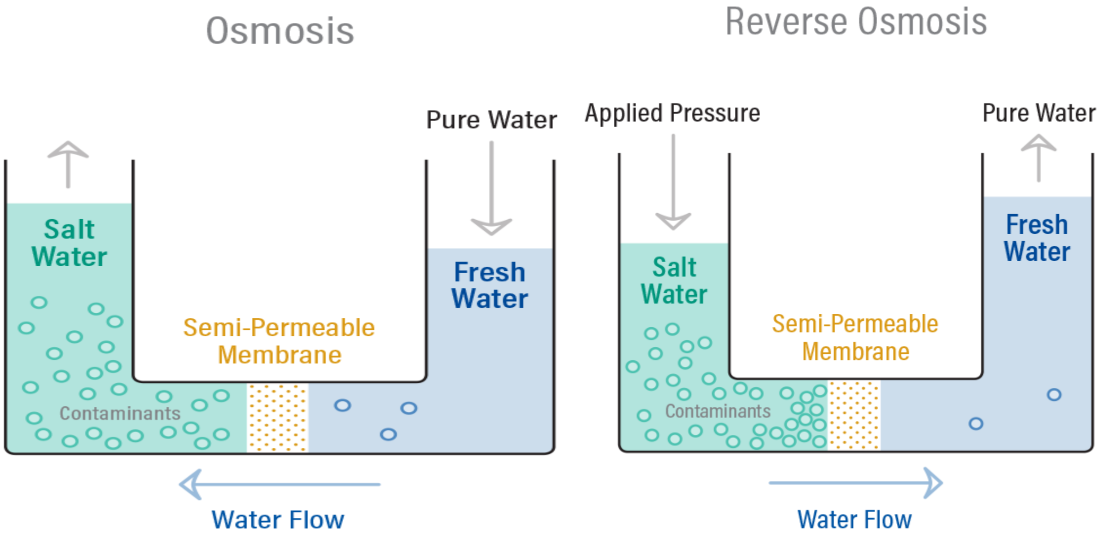
Osmosis:

If two solutions of different concentration are separated by a semi-permeable membrane which is permeable to the smaller solvent molecules but not to the larger solute molecules, then the solvent will tend to diffuse across the membrane from the less concentrated to the more concentrated solution. This process is called osmosis.

Osmosis is of great importance in biological processes where the solvent is water. The transport of water and other molecules across biological membranes is essential to many processes in living organisms. The energy which drives the process is usually discussed in terms of osmotic pressure..

Reverse osmosis

If hydrostatic pressure greater than the osmotic pressure is applied then the flow of solvent from high concentrationto low concenteration occurs. This is called reverse osmosis .thic can also be called as Superfiltration



TREATMENT OF BOILER FEED WATER

These are methods for the removal of the scales, when they are formed. There are also some methods for the prevention of scale formation by internal or external treatment.

Internal Treatment

Internal Treatment involves addition of chemical to the boiler water either to (i) precipitate the scale forming impurities in the formof sludges, which can be easily removed or (ii) convert the impurities to soluble compounds, so that scale formation can be avoided. Important internal treatments involve.

(a) ***Colloidal Conditioning*: ** Organic substances like kerosene, tannin, agar-agar are added to form gels and formloose non-sticky deposits with scale-forming precipitates, which can be easily removed by blow-down operations in low pressure boilers.

(b) ***Different Sodium Phosphates*** like NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 are added to high pressure boilers to react with the hardness forming impurities to form soft sludge of calcium and magnesium phosphates and finally this can be removed by blow down operation.

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

(c) ***Calgon Conditioning*:** Calgon i.e., sodium hexa meta phosphate when added to boiler water, reacts with scale forming $CaSO_4$ and forms soluble complex compound.

$$2CaSO_4 + [Na_4P_6O_8]^{2-} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

(d) ***Sodium Aluminate Conditioning*:** Sodium aluminate is hydrolysed yielding $NaOH$ and gelatinous $Al(OH)_3$. The NaOH formed reacts with magnesium salts to precipitate $Mg(OH)_2$. This $Mg(OH)_2$ and $Al(OH)_3$ are flocculent and entraps the colloidal as well as the finely divided impurities like silica in the boiler water and the loose precipitate is finally removed by blow down operation.

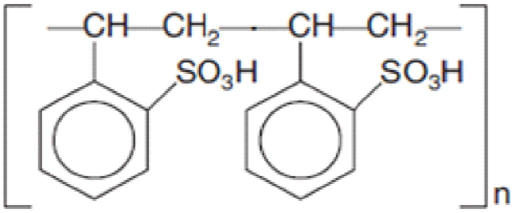
$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3 \downarrow$$
$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 \downarrow + 2NaCl$$

External Treatment

Ion Exchange or Demineralization

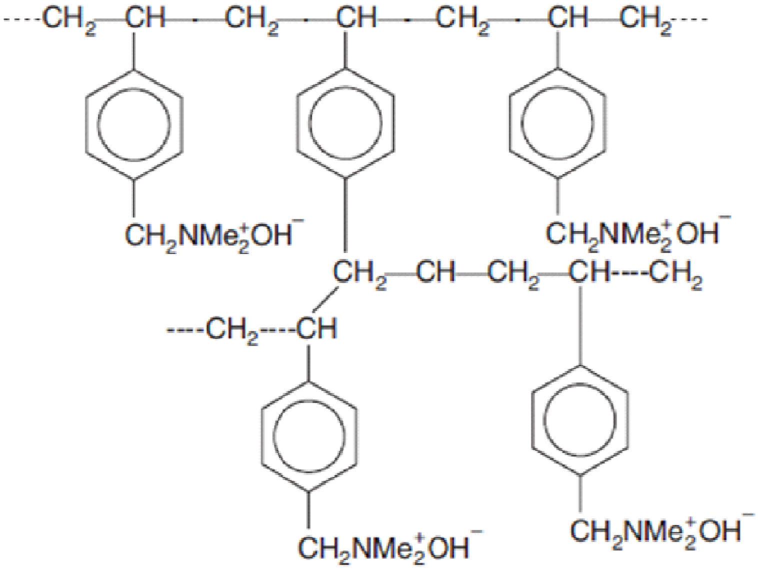
Ion Exchange Resins are organic polymers which are crosslinked having microporous structure and the functional groups are attached to the chains which are responsible for the ion exchange properties.

(i) **Cation Exchange Resins (RH^+)** are phenol-sulphonic acid-formaldehyde resin, styrene- divinyl benzene copolymers which exchange their H^+ ions with the cations present in the water i.e., Ca^{2+} and Mg^{2+}.



cation exchange resin

(ii) **Anion Exchange Resins (ROH^{-}):** The styrene divinyl benzene or amine formaldehyde copolymers contain quaternary ammonium tertiarysulphonium or amino group in the resin. The resin on treatment with hard water is capable of exchanging the OH^- with different anions of water i.e., Cl^-, SO_4^{2-} etc.



Anion exchange resin

Method

The hard water is passed first through cation exchange resin, the cations like Ca^{2+}, Mg^{2+} are removed from the hard water and exchanged with H^+ as follows:

$$2RH^+ + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2H^+$$

After this the hard water is again passed through anion exchange column, which exchanges all the anions like SO_4^{2-}, Cl^-. etc. present in the water with OH^-.

$$ROH^- + Cl^- \longrightarrow R^+Cl^- + OH^-$$

These H^+ from cation exchanger and OH^- fromanion exchanger combine to form water molecule. Thus the water coming out finally from the two exchangers is ion free and called deioinized or demineralized water.

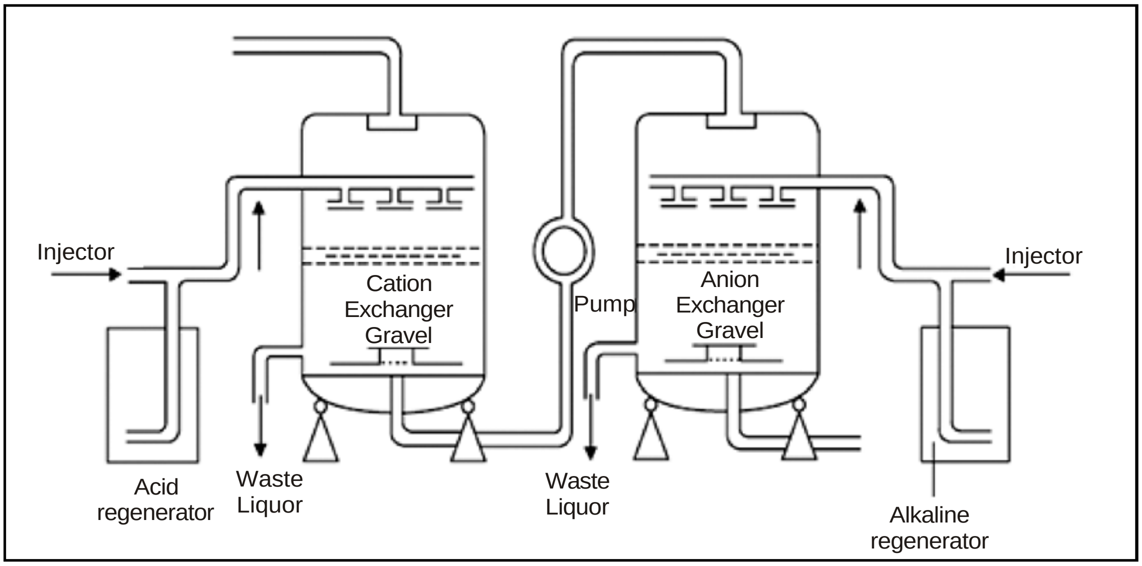


Figure 1.2: Demineralization of Water

Regeneration: The inactivated or exhausted cation exchange resin is regenerated by passing a dil. H_2SO_4/ HCl solution.

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

Similarly, the exhausted anion exchange resin is regenerated by passing a dil. NaOH solution.

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2ROH^- + SO^{2+}{}_4$$

The columns are finally washed with deionized water and the washings are discarded.

Permutit or Zeolite Process

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

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

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

Reactions taking place are:

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

$$Na_2Ze + Mg(HCO_3)_2 = 2\,NaHCO_3 + MgZe$$

$$Na_2Ze + CaSO_4 = Na_2SO_4 + CaZe$$

$$Na_2Ze + CaCl = 2NaCl + CaZe$$

Regeneration of Zeolite: The process is also commercially successful since the Ca/Mg zeolites formed by passing hard water through the bed can be easily regenerated into Na_2Ze by passing brine through the bed of inactivated zeolite.

$$CaZe \text{ or } MgZe + NaCl = Na_2Ze + CaCl_2 \text{ (or } MgCl_2\text{)}$$

The washings containing $CaCl_2$ or $MgCl_2$ are wasted. The water softened by this process can be used for laundry purposes.

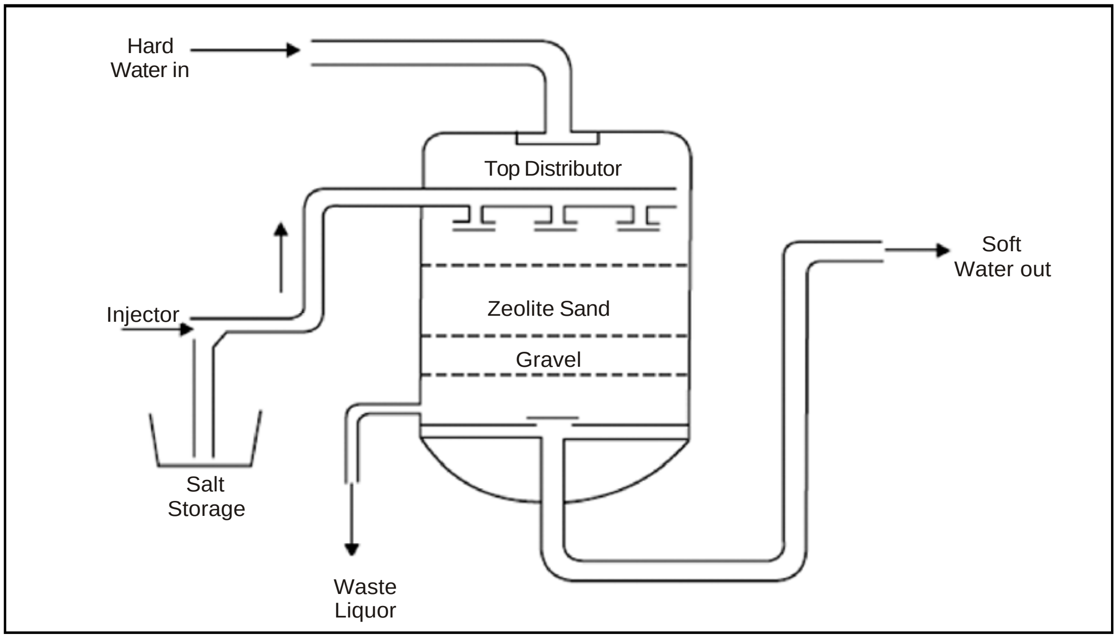


Figure 1.3: Softening of hard water by permutit process

Advantages:

(i) Hardness of water can be removed completely upto about 10 ppm.

(ii) The equipment used is small and easy to handle.

(iii) It requires less time for softening.

(iv) There is no sludge formation, hence the process is clean.

(v) Easy to regenerate.

(vi) Any hardness can be removed without any adjustment of the process.

Disadvantages:

(i) Coloured water or water containing suspended impurities cannot be used before filtration.

(ii) Water containing acid cannot be used for softening since acid may destroy the zeolite.

(iii) Since on removal of Ca^{2+} and Mg^{2+} the soft water contains large amount of $NaHCO_3$, this on heating liberates CO_2, which causes corrosion in the boilers and hence this soft water is not suitable for boilers.

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