



Module 7: Water

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Module outline:

Introduction

Hardness of water

Disadvantage of hard water

Techniques for water softening

Calgon, Zeolite, Lime-Soda, Ion exchange resin

Reverse osmosis

Water treatment method for boiler feed by internal process

7.1. INTRODUCTION

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table.

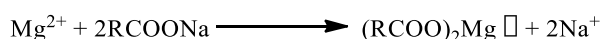
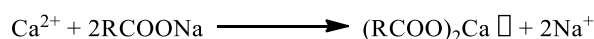
Table 7.1: Estimated World Water Supply

Source	% of Total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

It is a colourless and tasteless liquid. The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

7.2. HARDNESS OF WATER

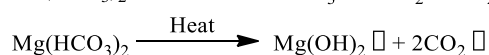
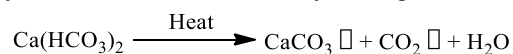
The soap consuming capacity of water is called hardness of water. The hardness of water is due to the presence of soluble salts of calcium, magnesium and other heavy metal ions, which reacts with soap giving insoluble salts as follows:



Due to these reactions water cannot form lather with soap.

Hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

1. Temporary Hardness: This type of hardness is due to presence of soluble bicarbonate salt of calcium and magnesium (e.g. $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$). Temporary hardness can be removed by boiling as follows:



2. **Permanent Hardness:** This type of hardness is due to presence of soluble salts of calcium and magnesium other than bicarbonates (e.g. CaSO_4 , MgSO_4 , CaCl_2 , MgCl_2 , FeSO_4). It does not remove by boiling of water.

7.3. UNITS OF HARDNESS

The hardness of water is expressed in following units.

1. **Parts per million (ppm):** ppm is the parts of calcium carbonate equivalent hardness per 10^6 parts of water.

2. **Milligrams per litre (mg/L):** It is the number of milligram of CaCO_3 equivalent hardness present per litre of water.

$1\text{mg/L} = 1\text{mg of CaCO}_3$ equivalent hardness per litre of water

But 1L of water weight = 1000gm = 1000×1000 mg

$1\text{mg/L} = 1\text{mg}/10^6 \text{ mg} = 1\text{ppm}$

3. **Degree French ($^\circ\text{Fr}$):** It is the parts of CaCO_3 equivalent hardness per 10^5 parts of water.

4. **Degree Clark ($^\circ\text{Cl}$):** It is the parts of CaCO_3 equivalent hardness per 70,000 parts of water.

These are related to each other as follows:

$1\text{ppm} = 1\text{mg/L} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl}$

$1^\circ\text{Fr} = 10\text{ppm} = 10\text{mg/L} = 0.7^\circ\text{Cl}$

$1^\circ\text{Cl} = 14.3\text{ppm} = 14.3\text{mg/L} = 1.43^\circ\text{Fr}$

7.4. DISADVANTAGE OF HARD WATER

Hard water does not give lather with soap. It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler.

7.5. TECHNIQUES FOR WATER SOFTENING

7.5.1. External Treatment of Boiler Feed Water

To remove temporarily and permanent hardness simultaneously certain methods like Permutit or Zeolite process, lime-soda process and ion exchange process.

1. Permutit or Zeolite process

Permutit or Zeolite is an inorganic resin having chemical formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ (Where $x = 2 - 10$ and $y = 2 - 6$). It is also represented as Na_2Ze (where $\text{Ze} = \text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$). Zeolite is hydrated sodium alumina silicate, capable of exchanging reversibly its sodium ions for hardness producing ions in water. Zeolites are also known as permutits. Zeolites are of two types.

(i). Natural zeolites are non-porous. For example natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

(ii). Synthetic zeolite are porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash. Such zeolite possesses higher exchange capacity per unit weight than natural zeolite.

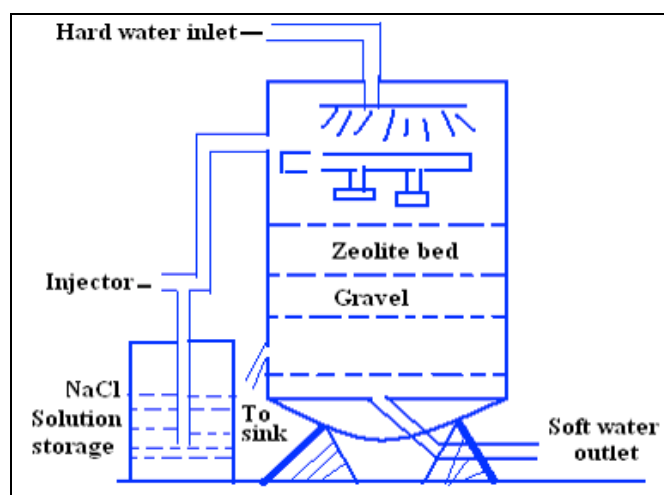
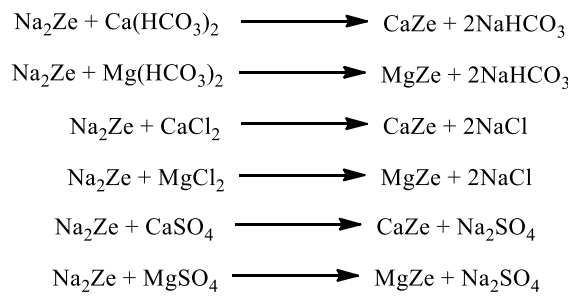


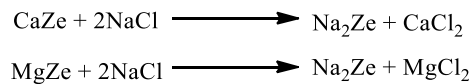
Fig. 7.1 Zeolite process for water softening

Permutit or Zeolite exchanges sodium ions with hardness causing ions present in hard water. When hard water is passed through zeolite resin, the sodium ions of zeolite are replaced by hardness causing ions present in water as follows:

E-Content: Water

**Regeneration**

When all the sodium ions are replaced by hardness causing ions, then it is said to be exhausted and it stops water softening process. It is regenerated by passing 10% solution of NaCl (called brine) as follows:

**Advantages of Zeolite Process**

- It removes hardness in water almost completely.
- There is no formation of precipitates as impurities.
- It is more efficient and less skilled process.
- The process is self-adjusting with variation of hardness in water.

Limitations of Zeolite Process

- Turbid water cannot be softened, because it blocks the pores of zeolite.
- If hard water is acidic then it destroys the zeolite.
- Hot water may dissolve the zeolite.
- The soft water obtained from zeolite process cannot be used as boiler feed water.

2. Lime-Soda Process

In this process the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$. Calcium carbonate $[\text{CaCO}_3]$ and magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ so-precipitated, are filtered off. The lime-soda process may be broadly classified into two categories:

- Cold Lime-Soda Process:** In this process, calculate quantity of chemicals is mixed with water at room temperature. Since precipitation does not take place at room temperature completely A small quantity of coagulant like alumina, ferrous sulphate, aluminium sulphate are added for complete precipitation.

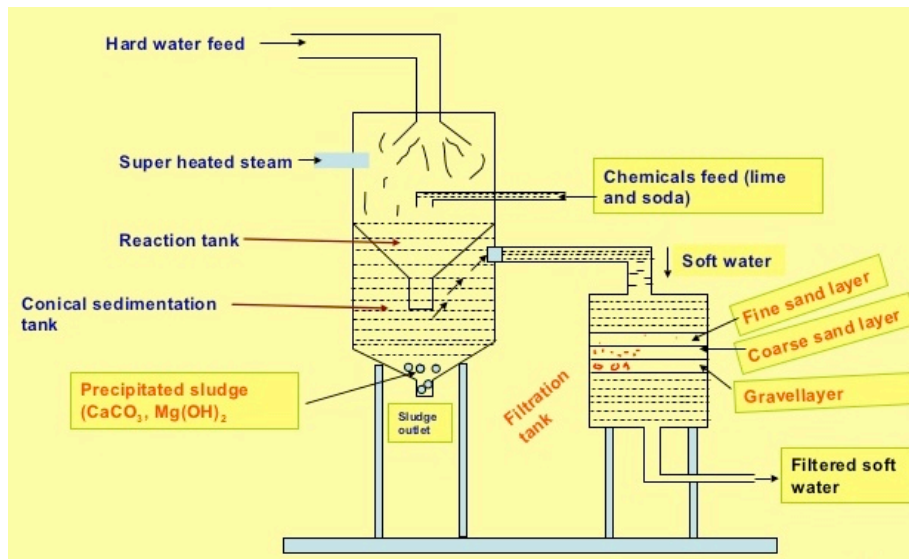


Fig. 7.2 A continuous type hot lime soda process

- Hot Lime-Soda Process:** This method is used specially for boiler feed water. This process is more efficient than cold lime soda process the softening reactions are made to occur almost at the boiling point of water the high temperature of water increases the rate of precipitation, decreases the viscosity of water and eliminates the need of adding coagulants. A continuous type hot lime soda process is described by the Fig. 7.2.

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Chemical reactions involved in lime soda process

Constituent	Reaction	Required
Lime removes the temporary (Ca and Mg) hardness	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	L
	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
Lime removes the permanent hardness	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$	L + S
	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$	
	$\text{MgSO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaSO}_4$	L + S
	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	
	$\text{FeSO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{Fe}(\text{OH})_2 \downarrow + \text{CaSO}_4$	L + S
	$2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Fe}(\text{OH})_3 \downarrow$	
	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	
	$\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \longrightarrow 2\text{Al}(\text{OH})_3 \downarrow + 3\text{CaSO}_4$	L + S
	$3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \longrightarrow 3\text{CaCO}_3 \downarrow + 3\text{Na}_2\text{SO}_4$	
	Lime removes free mineral acids	$2\text{HCl} + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$		
$\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$		L + S
$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$		
$\text{CO}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$		L
$\text{H}_2\text{S} + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaS} \downarrow + 2\text{H}_2\text{O}$		
Soda removes all the soluble Ca permanent hardness	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$	S
	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	S
	$\text{NaAlO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + \text{NaOH}$	-L
	2NaOH is eq to $\text{Ca}(\text{OH})_2$	

Calculation of the Amount of Lime and Soda Required

From the above chemical reactions it becomes clear that only required amount of lime and soda are to be added. The calculations and amount of lime and soda are based on the amounts of the salts present in water. Now 100 parts by mass of CaCO_3 are equivalent to: (i) 74 parts of $\text{Ca}(\text{OH})_2$, and (ii) 106 parts of Na_2CO_3 .

∴ Lime requirement for softening

$$= \frac{74}{100} \left[\begin{array}{l} \text{Temp. Ca}^{2+} + 2 \downarrow \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) \\ + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \\ \text{all in terms of CaCO}_3 \text{ eq} \end{array} \right]$$

∴ Soda requirement for softening

$$= \frac{106}{100} \left[\begin{array}{l} \text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- \\ \text{all in terms of CaCO}_3 \text{ eq} \end{array} \right]$$

Advantages of Lime-Soda Process

- i. It is very cheap and economical.
- ii. Lesser amount of coagulants will be required, if this process is combined with sedimentation and coagulation.
- iii. Iron and manganese are also removed from water.
- iv. The number of pathogenic bacteria in water is considerably reduced, due to alkaline nature of treated water.

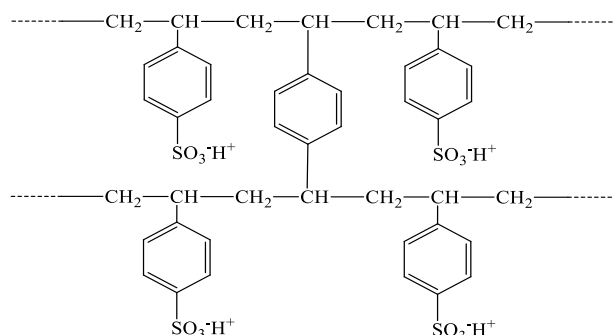
Disadvantages of Lime-Soda Process

- i. Careful operation and skilled supervision is required in lime-soda process for softening of water.
- ii. Formation of large amount of sludge creates its disposal problem.
- iii. Lime-soda softeners do not produce water of zero hardness.
- iv. Softened water from lime-soda softeners is not good for boilers.

3. Ion Exchange Process

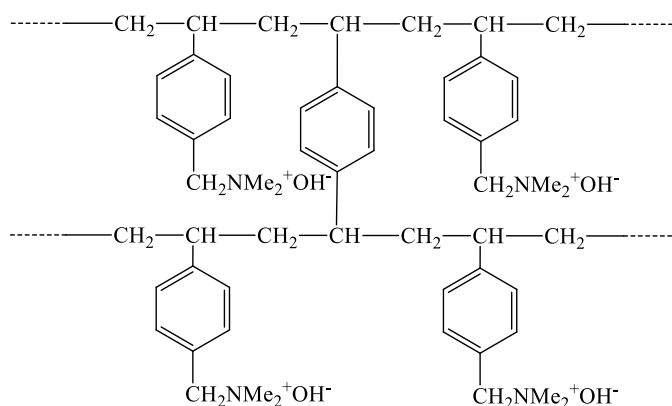
This process is based on exchange of cations and anions present in hardness causing molecules of water with ion exchange resin. In this method, firstly we describe about ion exchange resins and after that about the process. The ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure, and the 'functional groups' attached to the chains are responsible for the ion exchanging properties. It is categorised into two types viz., Cation exchange resin and anion exchange resin. Resins containing acidic functional groups (-COOH, -SO₃H, etc.) are capable of exchanging their H⁺ ions with other cations, which comes in their contact; whereas those containing basic functional groups (-NH₂ = NH₂ as hydrochloride) are capable of exchanging their anions with other anions, which comes in their contact. The ion exchange resins may be classified as:

i. Cation exchange resin (RH⁺) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water.



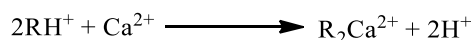
Acidic or cationic exchange resins (sulphonate form)

ii. Anion exchange resins (R'OH) are styrene divinyl benzene or amine formaldehyde copolymers, which contain amino or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH⁻ anions with anions in water.



Basic or anionic exchange resins (hydroxide form)

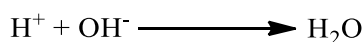
In exchange process hard water is passed through cation exchanger where hardness causing ion is exchange by H⁺ ion as follows:



The water coming out from cation exchanger passes through anion exchanger, where the anions are exchanged by OH⁻ as follows:



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



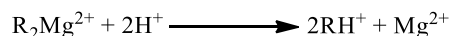
Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as deionized or demineralized water.

Regeneration

When cation and anion exchange resins get exhausted, then they are regenerated as follows:

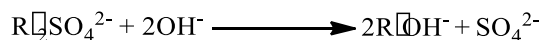
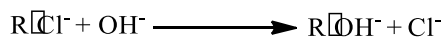
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1. Cation exchange resin is regenerated by passing dil. HCl or dil. H₂SO₄. The regeneration can be represented as:



The column is washed with deionised water and washing (which contains Ca²⁺, Mg²⁺, etc. and Cl⁻ and SO₄²⁻ ions) is passed to sink or drain.

2. Anion exchange resin is regenerated by passing dil. NaOH solution. The regeneration can be represented as:



The column is washed with deionised water and washing (which contains Na⁺, SO₄²⁻, etc. or Cl⁻ and SO₄²⁻ ions) is passed to sink or drain. The regenerated ion exchange resins are then used again. The typical diagram of ion exchange equipment is given as follows:

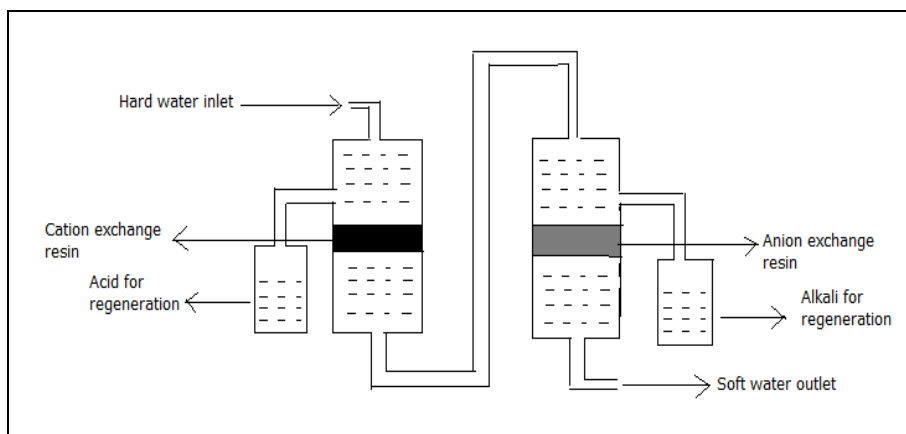


Fig.7.3 Ion exchange equipment

Advantages of Ion Exchange Resin

- i. The process can be used to soften highly acidic or alkaline water.
- ii. It produces water of very low hardness (2 ppm). So it is very good for treating water for use in high pressure boilers.

Disadvantages of Ion Exchange Resin

- i. The equipment is costly and more expensive chemicals are needed.
- ii. If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

7.5.2. Water Treatment Method for Boiler Feed by Internal Process

In many industries water is used for generation of steam in boilers. The water obtained from natural sources in sometimes supplied as such without treatment. The boiler feed water requires following conditions:

1. The hardness of water should be below 0.2 ppm.
2. The caustic alkalinity should be in the range of 0.15 to 0.45 ppm.
3. The soda alkalinity should from 0.45 to 1.0 ppm.
4. Excess soda ash should be 0.3 to 0.5 ppm.

If boiler feed water contains excess of impurities then it causes the following effects.

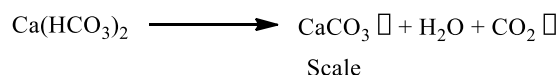
1. Scale or sludge formation
2. Boiler corrosion
3. Priming and foaming
4. Caustic embrittlement
5. Scale due to presence of silica

Scale and Sludge Formation in Boilers

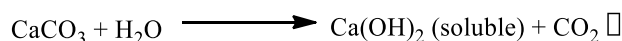
Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludge can easily be scrapped off with a wire brush. It is formed at comparatively colder portion of the boiler and collects in areas of the system, where the flow rate is slow or at bends. Sludge are formed by substances which have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

Scales are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer and chisel. Scales are the main source of boiler troubles. Formation of scales may be due to:

1. Decomposition of calcium bicarbonate:



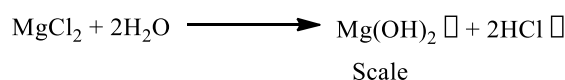
2. However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low pressure boilers. But in high pressure boilers, $CaCO_3$ is soluble.



3. Deposition of calcium sulphate: $CaSO_4$ is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, $CaSO_4$ gets precipitated as hard scale on the heated portion of boiler. This is the main cause of scale in the high- pressure boilers.

Note: Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

1. Hydrolysis of magnesium salts: Dissolved magnesium salts undergo hydrolysis (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a soft type scale, e.g.,



2. Presence of silica: (SiO_2), even present in small quantities, deposits as calcium silicate ($CaSiO_3$) and/ or magnesium silicate ($MgSiO_3$). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

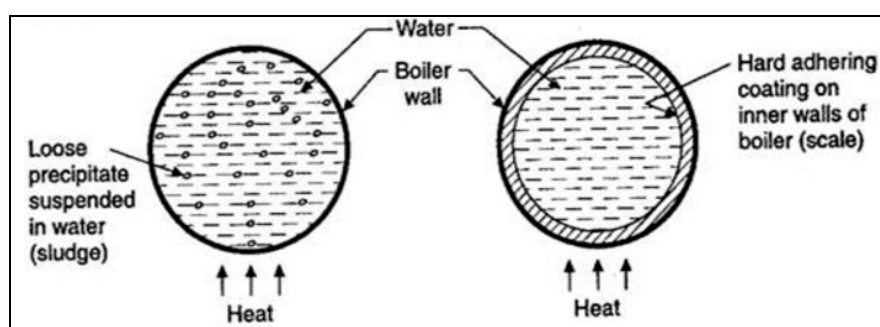


Fig. 7.4 Scale and sludge in boilers

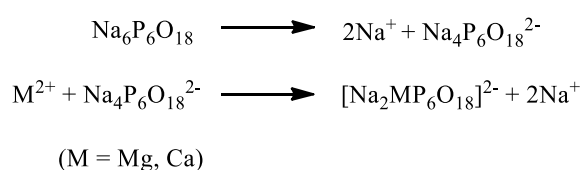
Caustic embrittlement

Development of certain types of cracks resulting from excessive stress and chemical attack leading to boiler failures is called embrittlement. Chemicals, like NaOH are believed to be responsible for embrittlement in a steam boiler operation. These cracks appear like a brittle fracture and hence called caustic embrittlement.

Some of the important methods used in the internal treatment of water softening include calgon conditioning, colloidal conditioning, carbonate conditioning, phosphate conditioning, etc.

Calgon's Method

Sodium hexametaphosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.



The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution. This method is not applicable for the prevention of iron oxide and copper deposition.

7.6. REVERSE OSMOSIS

Osmosis describes flow of the solvent from dilute to concentrated solution through a semipermeable membrane. Whereas reverse osmosis describes the flow of solvent in opposite direction i.e. from concentrated solution to dilute solution across a semipermeable membrane by applying hydrostatic pressure in excess of osmotic pressure. The cellulose acetate and the more recently used polymethacrylate and polyamide membranes do not allow the solute to pass, while the solvent is forced through and collected as a pure solvent in a direction as shown in Fig.7.5.

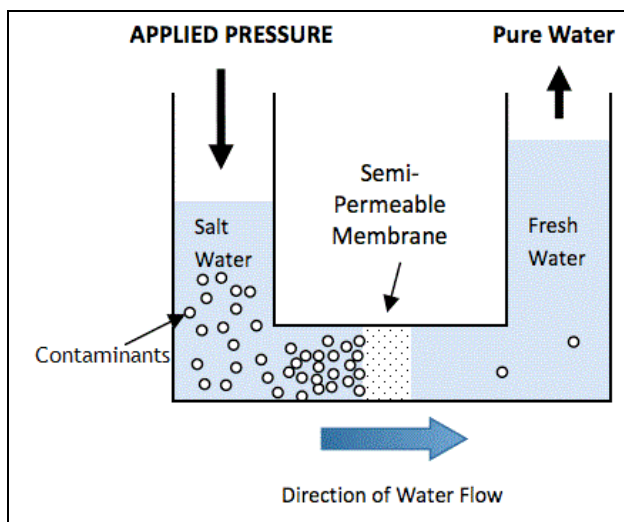


Fig.7.5 Reverse Osmosis

7.7. ADVANTAGES OF REVERSE OSMOSIS

- i. Easy maintenance and economical, as the membrane lifespan is high.
- ii. Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
- iii. It removes colloidal silica, which is not removed by demineralization.
- iv. The main tenancy cost is almost entirely on the replacement of the semipermeable membrane.
- v. The life time of membrane is quite high, about two years.
- vi. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.

Example 7.1. A sample of hard water has hardness 500 ppm. Express the hardness in $^{\circ}\text{Fr}$ and $^{\circ}\text{Cl}$.

Solution

Since, $1\text{ppm} = 0.1^{\circ}\text{Fr}$
 Hence, $500\text{ ppm} = 0.1 \times 500 = 50^{\circ}\text{Fr}$
 Again, $1\text{ppm} = 0.07^{\circ}\text{Cl}$
 $500\text{ppm} = 0.07 \times 500 = 35^{\circ}\text{Cl}$

Example 7.2. Calculate temporary and total hardness of water sample of water containing $\text{Mg}(\text{HCO}_3)_2 = 9.3\text{mg/L}$, $\text{Ca}(\text{HCO}_3)_2 = 17.4\text{mg/L}$, $\text{MgCl}_2 = 8.7\text{mg/L}$ and $\text{CaSO}_4 = 12.6\text{mg/L}$.

Solution

To calculate the temporary and total hardness in water sample we have to express the hardness causing salt into CaCO_3 equivalent.

$$\text{Strength in term of CaCO}_3 \text{ equivalent} = \frac{\text{strength of hardness causing salt} \times \text{equivalent wt. of CaCO}_3}{\text{Equivalent wt. of hardness causing salt}}$$

$$\begin{aligned} \text{Temporary hardness} &= \text{CaCO}_3 \text{ equivalent of } [\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2] \\ &= \frac{9.3 \times 50}{73} + \frac{17.4 \times 50}{81} \\ &= 6.37 + 10.74 = \mathbf{17.11 \text{ mg/L}} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness} &= \text{CaCO}_3 \text{ equivalent of } [\text{MgCl}_2 + \text{CaSO}_4] \\ &= \frac{8.7 \times 50}{47.5} + \frac{12.6 \times 50}{68} \\ &= 9.16 + 9.26 = \mathbf{18.42 \text{ mg/L}} \end{aligned}$$

$$\text{Total hardness} = 17.11 + 18.42 = \mathbf{35.53 \text{ mg/L}}$$

Example 7.3. 100 mL of water sample has a hardness equivalent of 12.5 mL of 0.08N MgSO₄. What is its hardness in ppm.

Solution.

$$\begin{aligned} N_1 V_1 (\text{water sample}) &= N_2 V_2 (\text{MgSO}_4 \text{ solution}) \\ N_1 &= ?, N_2 = 0.08, V_1 = 100 \text{ mL}, V_2 = 12.5 \text{ mL} \\ N_1 \times 100 &= 0.08 \times 12.5 \\ &= \frac{0.08 \times 12.5}{100} = 0.01 \text{ N} \end{aligned}$$

$$\begin{aligned} \text{Hardness of water sample} &= \text{Normality} \times \text{Equivalent wt. of CaCO}_3 \\ &= 0.01 \times 50 = 0.5 \text{ g/L} \\ \text{Hardness in ppm} &= 0.05 \times 1000 = 500 \text{ ppm} \end{aligned}$$

Example 7.4. Calculate temporary and permanent of a water sample which analysed as: Ca(HCO₃)₂ = 21.0mg/L, Mg(HCO₃)₂ = 25.0 mg/L, CaCl₂ = 16.4 mg/L, MgCl₂ = 5.2mg/L (**Odd sem. 2011 - 2012**)

Solution.

$$\text{Strength in term of CaCO}_3 \text{ equivalent} = \frac{\text{strength of hardness causing salt} \times \text{equivalent wt. of CaCO}_3}{\text{Equivalent wt. of hardness causing salt}}$$

$$\begin{aligned} \text{Temporary hardness} &= \text{CaCO}_3 \text{ equivalent of } [\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2] \\ &= \frac{25 \times 50}{73} + \frac{21 \times 50}{81} \\ &= 17.12 + 12.96 = \mathbf{30.08 \text{ mg/L}} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness} &= \text{CaCO}_3 \text{ equivalent of } [\text{MgCl}_2 + \text{CaSO}_4] \\ &= \frac{5.2 \times 50}{47.5} + \frac{16.4 \times 50}{55.5} \\ &= 5.45 + 14.77 = \mathbf{20.22 \text{ mg/L}} \end{aligned}$$

Example 7.5. Calculate the quantity of lime and soda required for softening 50,000 litres of water containing the following salts per litre. Ca(HCO₃)₂ = 9.2 mg; Mg(HCO₃)₂ = 7.9 mg; CaSO₄ = 15.3 mg; MgSO₄ = 15.0 mg; MgCl₂ = 3.0 mg and NaCl = 4.3 mg.

Solution:

Constituent	Amount mg/L	Multiplication Factor	CaCO ₃ Equivalent mg/L
Ca(HCO ₃) ₂	9.2	100/162	5.68
Mg(HCO ₃) ₂	7.9	100/146	5.41
CaSO ₄	15.3	100/136	11.25

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MgSO ₄	15.0	100/120	12.5
MgCl ₂	3.0	100/95	3.16
NaCl	4.3	Neglected	-

$$\therefore \text{Lime requirement} = \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2\text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2 \text{ in terms of CaCO}_3 \text{ eq.}]$$

$$= \frac{74}{100} [5.68 + 2(5.41) + 12.5 + 3.16] \text{ mg/L} = 23.39 \text{ mg/L}$$

Lime required for softening

$$50,000 \text{ litres} = 23.40 \times 50,000 \text{ mg} = 11.70 \text{ g} = 1.17 \text{ kg.}$$

$$\text{Soda requirement} = \frac{106}{100} [\text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ eq.}]$$

$$= \frac{106}{100} [11.25 + 12.5 + 3.16] = 28.5 \text{ mg/L}$$

Soda required for softening

$$50,000 \text{ litres} = 28.52 \times 50,000 \text{ mg} = 14.26 \text{ g} = 1.426 \text{ kg}$$

Example 7.6. Calculate the amount of lime and soda required per litre for chemical treatment of water containing: Ca²⁺ = 80 ppm; Mg²⁺ = 32 ppm; HCO₃⁻ = 195 ppm; FeSO₄·7H₂O added as coagulant = 73.5 ppm.

Solution

Conversion to CaCO₃ eq.

Constituent	Amount (ppm)	Multiplication Factor	CaCO ₃ Equivalent (ppm)
Ca ²⁺	80	100/40	200
Mg ²⁺	32	100/24	133.3
HCO ₃ ⁻	195	100/122	159.8
FeSO ₄ ·7H ₂ O	73.5	100/278	26.44

$$\text{Lime requirement} = \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \text{ as CaCO}_3 \text{ eq.}]$$

$$= \frac{74}{100} [133.3 + 159.8 + 26.44] \text{ ppm} = 236.6 \text{ ppm}$$

$$\text{Soda requirement} = \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{FeSO}_4 \cdot 7\text{H}_2\text{O} - \text{HCO}_3^- \text{ as CaCO}_3 \text{ eq.}]$$

$$= \frac{106}{100} [200 + 133.3 + 26.44 - 159.8] = 211.94 \text{ ppm}$$

Note: If analytical report shows the quantities of Ca²⁺ and Mg²⁺, then 1 eq. of lime and 1 eq. of soda is required for Mg²⁺, whereas 1eq. of soda is required for Ca²⁺. In other words, the ions Ca²⁺ and Mg²⁺ are treated as permanent hardness due to calcium and magnesium.

Example 7.7. Calculate the amount of lime (92% pure) and soda (98% pure) required for treatment of 30,000 litres of water whose analysis is as follows:

Ca(HCO₃)₂ = 40.5 ppm; Mg(HCO₃)₂ = 36.5 ppm; CaSO₄ = 34.0 ppm; MgSO₄ = 30.0 ppm; CaCl₂ = 27.75 ppm and NaCl = 10.0 ppm.

Solution

Conversion to CaCO₃ eq.

Constituent	Amount (ppm)	Multiplication Factor	CaCO ₃ Equivalent (ppm)
Ca(HCO ₃) ₂	40.5	100/162	25
Mg(HCO ₃) ₂	36.5	100/146	25
CaSO ₄	34.0	100/136	25
MgSO ₄	30.0	100/120	25
CaCl ₂	27.75	100/111	25
NaCl	-	-	-

$$\begin{aligned} \text{Lime requirement} &= \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2\text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4 \text{ in terms of CaCO}_3 \text{ eq.} \times \text{volume of water}] \\ &= \frac{74}{100} [25 + (2 \times 25) + 25] \text{ mg/L} \times 30,000 \text{ L} = 74 \times 30,000 \text{ L} = 2220 \text{ g} \end{aligned}$$

Since lime is 92% pure, therefore lime required will be

$$= \frac{100}{92} \times 2220 \text{ g} = 2.413 \text{ kg}$$

$$\text{Soda requirement} = \frac{106}{100} [\text{CaSO}_4 + \text{MgSO}_4 + \text{CaCl}_2 \text{ as CaCO}_3 \text{ eq.}]$$

$$= \frac{106}{100} [25 + 25 + 25] \text{ mg/L} \times 30,000 \text{ L} = 2385 \text{ g}$$

98% pure soda, required for softening 30,000 L

$$= \frac{100}{98} \times 2385 = 2433 \text{ g} = 2.433 \text{ kg}$$

Note: If the lime and soda are impure, then the actual requirement is calculated accordingly. In the above example as lime and soda are 92% and 98% pure respectively, therefore, the values obtained in each case are multiplied by purity factor ($\frac{100}{92}$ for lime; $= \frac{100}{98}$ for soda).

Example 7.8. Calculate the amount of lime (74% pure) and soda (92% pure) required for treatment of 20,000 litres of hard water containing, $\text{MgCO}_3 = 84 \text{ mg/L}$; $\text{CaCO}_3 = 40 \text{ mg/L}$; $\text{MgCl}_2 = 95 \text{ mg/L}$; $\text{CaCl}_2 = 111 \text{ mg/L}$; $\text{Mg}(\text{NO}_3)_2 = 37 \text{ mg/L}$ and $\text{KCl} = 30 \text{ mg/L}$.

Solution:

Conversion to CaCO_3 eq.

Constituent	Amount (ppm)	Multiplication Factor	CaCO ₃ Equivalent (ppm)
MgCO ₃	84	100/84	100
CaCO ₃	40	100/100	40
MgCl ₂	95	100/95	100
CaCl ₂	111	100/111	100
Mg(NO ₃) ₂	37	100/148	25
KCl	-	-	-

$$\text{Lime requirement} = \frac{74}{100} [2 \times \text{MgCO}_3 + \text{CaCO}_3 + \text{MgCl}_2 + \text{Mg}(\text{NO}_3)_2 \text{ in terms of CaCO}_3 \text{ eq.}] \times \text{volume of water} \times \text{purity factor}$$

$$= \frac{74}{100} [2 \times 100 + 40 + 100 + 25] \text{ mg/L} \times 20,000 \text{ L} \times \frac{100}{74} = 7300 \text{ g} = 7.3 \text{ kg}$$

$$\text{Soda requirement} = \frac{106}{100} [\text{MgCl}_2 + \text{CaCl}_2 + \text{Mg}(\text{NO}_3)_2 \text{ in terms of CaCO}_3 \text{ eq.}] \times \text{volume of water} \times \text{purity factor}$$

$$= \frac{106}{100} [100 + 100 + 25] \text{ mg/L} \times 20,000 \text{ L} \times \frac{100}{92} = 5184 \text{ g} = 5.2 \text{ kg}$$

Note: CaCO_3 and MgCO_3 are regarded as being present in the form of their bicarbonates, only their weights have been expressed in terms of CaCO_3 and MgCO_3 . So the lime requirement for MgCO_3 is 2 eq. as in the case of $\text{Mg}(\text{HCO}_3)_2$ whereas for CaCO_3 it is one eq. No soda is required for either Ca or Mg if they are given as CaCO_3 and MgCO_3 .

Example 7.9. A zeolite softener was 95% exhausted, when 10,000 L of hard water was passed through it. The softener required 150 L of NaCl solution of strength 50 g NaCl/L of solution to regenerate. What is the hardness of water?

Solution:

$$\begin{aligned} 10,000 \text{ L of hard water} &= 150 \text{ L of NaCl solution} \\ &= 150 \text{ L} \times 50 \text{ g/L of NaCl} \\ &= 7500 \text{ g of NaCl} \\ &= 7500 \times \frac{100}{58.5 \times 2} \text{ g of CaCO}_3 \text{ eq.} \\ &= 6410.26 \text{ g of CaCO}_3 \text{ eq} \\ 1 \text{ L of hard water} &= 6410.26 \text{ g of CaCO}_3 \text{ eq}/10,000 \\ &= 0.6410 \text{ g of CaCO}_3 \text{ eq.} \\ &= 641 \text{ mg of CaCO}_3 \text{ eq} \end{aligned}$$

Hence hardness of water = 641 mg/L

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Example 7. 10. A zeolite softener was completely exhausted and then regenerated by passing 200 litres of NaCl solution containing 100 g per litre of NaCl. How many litres of a sample of water of hardness 500 ppm can be softened by the softener.

Solution:

$$\begin{aligned} 200 \text{ litre of NaCl} &= 100 \text{ L} \times 200 \text{ g/L} = 20000 \text{ g of NaCl} \\ &= 20000 \times \frac{100}{58.5 \times 2} \text{ g of CaCO}_3 \text{ eq.} \\ &= 17094 \text{ g of CaCO}_3 \text{ eq.} \end{aligned}$$

Now 500 mg of hardness is present in = 1 litre of water

$$\begin{aligned} 17094 \times 10^3 \text{ mg of CaCO}_3 \text{ eq. hardness is present in} &= \frac{1}{500} \times 17094 \times 10^3 \text{ L} \\ &= 34188 \text{ litre of hard water.} \end{aligned}$$

Hence, the softener can soften 34188 litres of hard water.

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EXERCISE

1. What is hardness of water? Describe ion exchange process for making soft water from hard water.
2. What do you mean by the term permutit? Describe the softening of water by permutit process.
3. Describe Zeolite Process for making soft water from hard water.
4. Write a short note on softening of water by Zeolite Process.
5. Explain why Alkalinity of water cannot be due to simultaneous presence of OH^- , CO_3^{2-} and HCO_3^- ?
6. Water contains 408 mg CaSO_4 per litre. Calculate the hardness in litres of CaCO_3 equivalent.
7. Give a brief account of the treatment of boiler feed water of calgon process.
8. What are scales? What are their disadvantages?
9. What is calgon conditioning? How is it better than phosphate conditioning?
10. Explain scale and sludge formation in boilers. How are they removed?
11. 100 mL of water sample has a hardness equivalent of 12.5 mL of 0.08 N MgSO_4 . What is its hardness in ppm?
12. An exhausted Zeolite softener was regenerated by passing 150 litres of NaCl, having a strength of 150 g/L of NaCl. How many litres of hard water sample, having hardness of 600 ppm, can be softened, using the softener?
13. A water sample contains the following impurities: $\text{Ca}^{2+} = 20$ ppm, $\text{Mg}^{2+} = 18$ ppm, $\text{HCO}_3^- = 183$ ppm and $\text{SO}_4^{2-} = 24$ ppm. Calculate the lime and soda needed for softening ($\text{Ca} = 40$, $\text{Mg} = 24$).
14. Calculate the amount of lime and soda required for the treatment of 15,000 litres of water, which analysed as follows: temporary hardness = 20 ppm; permanent hardness = 15 ppm; permanent Mg hardness = 10 ppm.
15. Write a note on reverse osmosis.