

UNIT 4 WATER

4.1 Hardness of Water :-

Hard Water : The water which does not produce lather with soap.

Soft Water :- The water which produces lather with soap.

- Hardness of water is due to presence of soluble salts of calcium, magnesium and other heavier metals in water.
- Hard water does not give lather easily with soap, but produces a white scum or precipitate with soap.
- The scum or precipitate is due to the formation of insoluble soaps of calcium and magnesium ions react with soap.
- Hardness of water can be classified as temporary hardness and permanent hardness.

Types of hardness:

Temporary hardness : Temporary hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium. This can be removed by boiling.

Permanent hardness : Permanent hardness is due to presence of chlorides & sulfates of dissolved calcium , magnesium , iron & other heavy metals. The salts responsible for permanent hardening are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$. Permanent hardness cannot be removed by boiling. This is also known as non –carbonate or non – alkaline hardness. The sum of temporary and permanent hardness is referred as total hardness of water.

Although hardness of water is never presence in the form of CaCO_3 as it is insoluble in water hardness of water is conveniently expressed in terms of equivalents of CaCO_3 .

The hardness is expressed in terms of equivalent calcium carbonate.

The reason for choosing CaCO_3 as standard for report in hardness is ease in calculations on its molecular weight is exactly 100.

Units of Hardness :

1. Parts Per Million : Parts of CaCO_3 equivalent hardness per 10^6 parts of water.
1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

2. Milligrams per litre :- Number of milli grams of Calcium Carbonate equivalent hardness present in 1 litre of water.
 $1 \text{ mg / L} = 1 \text{ mg of CaCO}_3 \text{ equivalent hardness present in 1 liter of water.}$
 $1 \text{ L} = 1 \text{ Kg} = 1000 \text{ g} = 1000 \times 1000 \text{ mg} = 10^6 \text{ mg.}$
 $1 \text{ mg / L} = 1 \text{ mg of CaCO}_3 \text{ eq per } 10^6 \text{ mg of H}_2\text{O}$
 $= \text{ppm}$
3. Clarke's degree : ($^{\circ}\text{cl}$) Wo of grains (1/700 16) of CaCO_3 equivalent hardness per 70,000 parts of water.
 $1^{\circ}\text{Clarke} = 1 \text{ grain of CaCO}_3 \text{ eq hardness per gallon of water.}$
 $= 1 \text{ part of CaCO}_3 \text{ of hardness per 70,000 parts of water.}$
4. Degree French ($^{\circ}\text{Fr}$) : It is in the parts of CaCO_3 eq hardness per 10^5 parts of water.
5. Milliequivalents per litre : - No of milli equivalents of hardness present per litre.
 $1 \text{ m eq/L} = 1 \text{ meg of CaCO}_3 \text{ per / litre of water.}$
 $= 10^{-3} \times 50 \text{ g of CaCO}_3 / \text{litre}$
 $= 50 \text{ mg /L of CaCO}_3 \text{ eq} = 50 \text{ ppm}$

Relation between various units o hardness:

$$1 \text{ ppm} = 1 \text{ mg /L} = 0.1^{\circ} \text{Fr} = 0.07^{\circ}\text{CL} = 0.02 \text{ meg / L}$$

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$$1^{\circ} \text{cL} = 1.433^{\circ}\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg /L} = 0.286 \text{ meq /L}$$

$$1^{\circ}\text{Fr} = 10 \text{ ppm} = 10 \text{ mg /L} = 0.7^{\circ}\text{cL} = 0.2 \text{ meq /L}$$

$$1 \text{ meq /L} = 50 \text{ mg /L} = 50 \text{ ppm} = 5^{\circ}\text{Fr} = 0.35^{\circ}\text{Cl.}$$

4.2 Estimation of hardness of water:

Hardness of water can be estimated by the following methods:

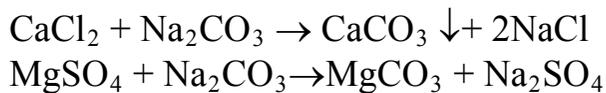
I –O.Hehner's method:

A) Temporary hardness is determined by finding the alkalinity of water before boiling and that left after boiling (temporary hardness is removed by boiling)

Procedure: Pipette out 50ml of water sample in a conical flask, 2-3 drops of methyl orange indicator is added and titrated against N/50 HCl. The volume of acid used is 'V₁ml. 100ml of water sample is taken in a pyrex beaker and evaporated to dryness. About 50ml of distilled water is added, warned,

stirred to dissolve the soluble portions left. The solution is filtered, washed the residue with distilled water. The solution is made up to 100mL. 50mL of this solution is taken in a conical flask and titrated against N/50HCl using methyl orange as indicator. The volume of acid used is 'V₂'mL.

B) Estimation of permanent hardness is based on the fact that it can be removed by boiling with a known excess of standard Na₂CO₃. The chloride and sulphates of calcium and magnesium form insoluble carbonates. The residual sodium carbonate is determined by titrating against a standard acid. The decrease in the amount of soda added is equivalent to permanent hardness.



Procedure: 50ml of the given water sample is taken in the beaker and 50ml of N/50 Na₂CO₃ solution is added. Boiled the solution for 15minutes. Cooled the solution, filtered the precipitate and the filtrate is collected in a conical flask. Titrated the unused Na₂CO₃ present in the flask against N/50 HCL. Using methyl orange as an indicator. The titre value is 'V'

II – Soap Titration Method: (or) Clarks Method:

Principle:

When soap solution is added to hard water, the hardness causing ions (Ca²⁺, Mg²⁺ and other heavy metal ions) are first to react to form a precipitate of insoluble calcium and magnesium soap is obtained.

The process takes place continuously until there is hardness in the sample of water. When all the hardness causing ions have been precipitated, further addition of soap solution gives lather.

Procedure:

Step – 1: Standardisation of sample solution:

The burette is first rinsed and filled with soap solution. In a narrow mouth 250mL glass-stoppered bottle, 50mL of standard water is taken (The hardness of standard hard water is 1g/L). Soap solution is added 0.2mL at a time to this standard hard water solution. After each addition, the contents

of the stoppered bottle are shaken vigorously until lather formation starts. Then the addition of soap solution is made at the rate of 0.1mL at a time till a lather is formed that persists for 2 minutes. Let the volume of the soap solution used is ' V_1 'mL.

Step- 2: Determination of total hardness of water:

The above procedure is repeated by taking 50mL of given water sample (Sample to be analysed.). The volume of the soap solution used in this is ' V_2 'mL.

Step -3: Determination of permanent hardness of water:

250mL of the water sample is taken in 500mL beaker. It is then boiled till the volume reduces to 50mL. (Boiling causes all the bicarbonates to decompose respectively into insoluble CaCO_3 and Mg(OH)_2). The precipitate is filtered and washed with distilled water. Simultaneously, the filtrate and washings are quantitatively collected in a 250mL conical flask. The volume is then made 250mL by adding distilled water. 50mL of this sample is taken and procedure of Step – 1 is repeated titre value of the soap solution be ' V_3 'mL.

Step -4: Determination of lather factor:

50mL of distilled water of zero hardness is titrated with soap solution. The titration is continued till lather is obtained which lasts for 2 minutes. Let the titre value be V_4 mL. This volume must be subtracted from all the litre values.

Calculations:

Step – 1: Standardisation of soap solution:

50mL of standard hard water $\equiv (V_1 - V_4)$ mL of soap solution

50mL of standard hard water contains 50mg of CaCO_3

(Standard hard water contains 1g/L or

1mg/mL CaCO_3)

Thus, $(V_1 - V_4)$ mL of soap solution = 50mg of CaCO_3 eq.

$$1 \text{ mL of soap solution} = \frac{50}{(V_1 - V_4)} \text{ mg of } \text{CaCO}_3 \text{ eq.}$$

Step – 2: Determination of total hardness of water:

50mL of hard water $\equiv (V_2 - V_4)$ mL of soap solution

$$\equiv (V_2 - V_4) \times \frac{50}{(V_1 - V_4)} \text{ mg of CaCO}_3 \text{ eq.}$$

1000mL or 1L of hard water

Determination of hardness of water:

1) Soap solution method (or) soap titration method clark's method:

Soluble soaps consist of sodium (or) potassium salts of higher fatty acids.

When soap solution is added to hard water, the hardness causing ions first react to form precipitate of calcium and magnesium soaps which are insoluble in water.

Thus, after all the hardness causing metal ions present in the hard water sample are precipitated, the further addition of soap gives lather.

The total hardness of water sample can be determined by titrating an aliquot of the sample against a standard soap solution in alcohol. The appearance of a stable lather persisting even after shaking for about 2 min marks end point.

The water sample is boiled for 30min to remove temporary hardness and then it is titrated with standard soap solution, the titre value corresponds to permanent hardness of sample.

The difference between the two measurements corresponds to the temporary hardness.

4.3 Estimation of hardness of water by EDTA Method:

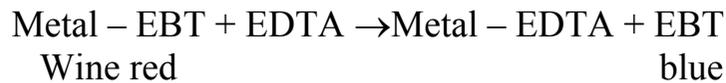
This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

Principle of EDTA titrations:

The quick, complete and 1:1 interaction of metal ions with EDTA leading to the formation of stable complex is the basis for complexometric titrations.

Theory: The hard water is buffer to a p^H value of ~ 10 using $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ buffer and few drops of EBT indicator solution are added. EBT forms a weak complex with metal ions that has a wine-red colour.

During the course of titration of water sample against EDTA, first EDTA combines with free Ca^{2+} or Mg^{2+} ions to give very stable and colour less metal-EDTA Complex. After all the free metal ions are consumed, the next drop of added EDTA solution displaces the indicator to form Metal-EBT complex.



At the equivalence point, there is change in colour from wine-red to blue.

Procedure:

Step – 1: Standardisation of EDTA solution:

The burette is filled with EDTA solution after washing and rinsing. Pipette out 50mL of standard hard water (1mL of it must contain 1mg of CaCO_3) into a 250mL conical flask, 10mL of buffer solution and 2-3 drops of EBT indicator are added and titrated against EDTA solution until the wine-red colour changes to blue. Let the volume of EDTA solution consumed be V_1 mL.

Step – 2: Determination of total hardness of water:

As per the same procedure (Step-1), 50mL of the unknown water sample is titrated against EDTA. Let the volume of EDTA solution consumed be V_2 mL.

Step -3: Determination of permanent hardness of water:

250mL of the water sample is taken in a 500mL beaker and boiled it till the volume is reduced to about 50mL. [The step causes all the bicarbonates to decompose respectively into insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$]. Filter and wash the precipitate with distilled water and quantitatively collect the filtrate and washings in a 250mL conical flask and made up the volume to 250mL with distilled water. 50mL of this water sample is titrated against EDTA solution as in Step-1. Let the volume of EDTA solution consumed be V_3 mL.

Calculations:

Step – 1: Standardisation of EDTA Solution:

$$\begin{aligned} V_1 \text{ mL of EDTA} &= 50 \text{ mL of standard hard water} \\ &= 50 \text{ mg of } \text{CaCO}_3 \text{ (1 mL contains 1 mg of } \text{CaCO}_3 \text{)} \end{aligned}$$

$$1 \text{ mL of EDTA} = 50 / V_1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness.}$$

Step -2: Determination of total hardness of water:

$$\begin{aligned} 50\text{mL of unknown hard water sample} &= V_2\text{mL of EDTA} \\ &= V_2 \times 50 / V_1 \text{mg of CaCO}_3 \text{ eq.} \end{aligned}$$

Step-3: Determination of permanent hardness of water:

$$\begin{aligned} 50\text{mL of boiled water} &= V_3\text{mL of EDTA} \\ &= V_3 \times 50 / V_1 \text{mg of CaCO}_3 \text{ eq.} \end{aligned}$$

Step-4: Determination of temporary hardness:

4.4 Scale and sludge formation:

In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively.

When the concentration of the dissolved salts reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose/slimy precipitate, it is known as sludge.

If the precipitation takes place in the form of a hard, adhering crust/coating on the inner walls of the boiler, it is known as scale.

Sludge:

It is a soft, loose and slimy precipitate formed within the boiler. It is formed at colder portions of the boiler and collects in the system where the flow rate is slow or at bends. It can be removed very easily by a wire brush. It is formed by the substances that have greater solubility values in hot water than in cold water.

Ex: MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 etc.,

Disadvantages:

- 1) Sludges are poor conductors of heat, hence there is wastage of portion of the heat generated.
- 2) If sludges are formed along with scales, then sludge gets entrapped in the scales and both get deposited as scales.
- 3) Excessive sludge formation disturbs the working of the boiler.

Preventive measures:

- 1) By using softened water
- 2) By frequently 'blow-down operation' (drawing off a portion of the concentrated water).

Scales:

Definition: Scales are hard deposits firmly sticking to the inner surfaces of the boiler.

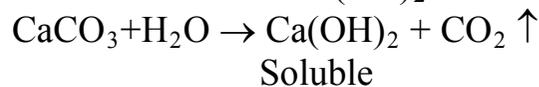
The scales are difficult to remove, even with the help of hammer and chisel and are the main source of boiler troubles.

Formation: The scales may be formed inside the boiler due to –

1) Decomposition of calcium bicarbonate:



The scale consisting of mainly CaCO_3 is soft and is the main cause of scale formation in low-pressure boilers. Whereas in high-pressure boilers, CaCO_3 is soluble due to the formation of $\text{Ca}(\text{OH})_2$.



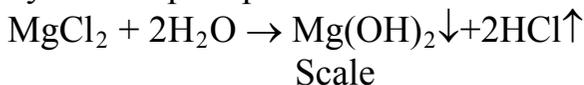
2) Deposition of calcium sulphate:

The solubility of CaSO_4 in water decreases with increase in temperature. CaSO_4 is soluble in cold water and almost insoluble in hot water [may be due to increased ionization at high temperature so $K_{sp} < K_{\text{ionic}}$ product & less availability of water molecules for solvation at high temperature.]

CaSO_4 gets precipitated as hard scale on the hotter parts of the boiler. This type of scale causes troubles mainly in high-pressure boilers. CaSO_4 scale is quite adherent and difficult to remove even with the help of hammer and chisel.

3) Hydrolysis of magnesium salts:

Dissolved magnesium salts get hydrolysed forming magnesium hydroxide precipitate that forms a soft type of scale.



4) Presence of silica:

Even if a small quantity of SiO_2 (silica) is present. It may deposit as calcium or magnesium silicate (CaSiO_3 and / or MgSiO_3). These deposits adhere 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.

Disadvantages:

1) Wastage of Fuel: Scales have low thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or, over heating is done and this causes increase in the consumption of fuel.

The wastage of fuel depends on the thickness and the nature of scale.

Ex:

Thickness of scale(mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

2) Lowering of boiler safety: Over-heating of boiler is done in order to maintain a steady supply of steam due to the formation of scales. This makes the boiler material softer and weaker. This causes the distortion of the boiler tube and also makes the boiler unsafe.

3) Decrease in efficiency: Scales may deposit in the valves and condensers of the boiler and choke them partially. This results in decrease in the efficiency of the boiler.

4) Danger of explosion: When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in the development of sudden high-pressure that may cause explosion of the boiler.

Removal of scales:

If the scales are loosely adhering, they can be removed by scraper or piece of wood or wire brush.

- If the scales are brittle, they can be removed by thermal shocks i.e, heating the boiler and then suddenly cooling with cold water.
- If the scales are loosely adhering, they can be removed by frequent blow-down operation.
- If the scales are adherent and hard, they can be removed by adding chemicals.

Ex: a) CaCO_3 scales can be removed by dissolving in 5-10% HCl.
 b) CaSO_4 scales can be removed by adding EDTA, since the Ca-EDTA complex is highly soluble in water.

Prevention of scale formation:

1) External treatment: The treatment includes efficient ‘softening of water’ (removing hardness-producing constituents of water)

2) Internal treatment: In this process, an ion is prohibited to exhibit its original character by ‘Complexing’ or converting into other more stable salt by adding appropriate reagent.

- a) Colloidal conditioning
- b) Phosphate conditioning
- c) Carbonate conditioning
- d) Calgon conditioning
- e) Treatment with sodium aluminate (NaAlO_2)
- f) Electrical conditioning
- g) Radioactive conditioning
- h) Complexometric method.

4.5 Differences between sludges and scales:

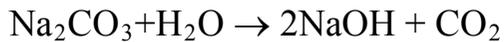
Sludges	Scales
<ol style="list-style-type: none"> 1. Sludges are soft, loose and slimy precipitate 2. Sludges are non-adherent deposits and can be removed easily. 3. Sludges are formed by substances like CaCl_2, MgCl_2, MgSO_4, MgCO_3, etc, 4. Formed at comparatively colder portions of the boiler 5. Decrease the efficiency of boiler but are less dangerous 6. Can be removed by blow-down operation. 	<ol style="list-style-type: none"> 1. Scales are hard deposits 2. Scales stick firmly to the inner surface of boiler and are very difficult to remove. 3. Scales are formed by substances like CaSO_4, Mg(OH)_2 etc., 4. Generally formed at heated portions of the boiler. 5. Decrease the efficiency of boiler and chances of explosions are also there. 6. Cannot be removed by blow-down operation.

Caustic Embrittlement:

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by lime-soda process, free Na_2CO_3 is usually present in small portion in the softened water.

In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2 . The NaOH produced makes the boiler water “Caustic”.



This caustic water flows into the minute hair-cracks, present in the inner side of the boiler, by capillary action. On evaporation of water, the concentration of dissolved caustic soda increases progressively that attacks the surrounding area, thereby dissolving iron of boiler as sodium ferrate. This causes embrittlement of boiler walls causing even failure of the boiler.

Embrittlement arises due to the setting up of a concentration cell.

With the iron surrounded by dilute NaOH is acting as the cathode whereas the iron surrounded by conc. NaOH is acting as anode. The anode in the anodic part gets dissolved or corroded.

Prevention:

Caustic embrittlement can be prevented

i) by using sodium phosphate as softening reagent instead of Na_2CO_3 in external treatment of boiled water.

ii) by adding lignin or tannin to boiler water that blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution in these areas.

iii) by adding Na_2SO_4 to boiler water:

Na_2SO_4 blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented, if Na_2SO_4 is added to boiler water so that the ratio.

$[\text{Na}_2\text{SO}_4] / [\text{NaOH}]$ is kept as 1:1, 2:1 and 3:1 in boilers working respectively at pressures upto 10, 20 and > 20 atmospheres.

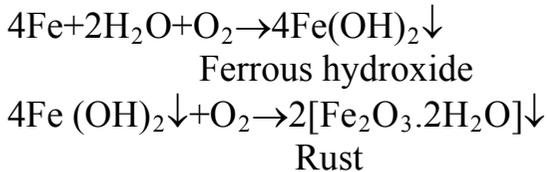
Boiler corrosion:

Boiler corrosion is ‘decay’ or ‘disintegration’ of boiler body material by either chemical or, electrochemical reaction with its environment.

Reasons for boiler corrosion:

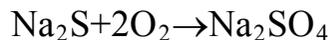
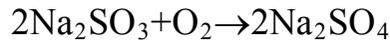
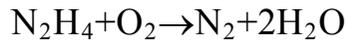
1) Dissolved oxygen: This is the most usual corrosion causing factor., water usually contains about 8ppm of dissolved oxygen at room temperature.

Dissolved oxygen reacts with iron of boiler in the presence of water and under prevailing high temperature to form ferric oxide (rust).



Removal of dissolved oxygen:

- i) By adding calculated quantity of hydrazine or, sodium sulphite or, sodium sulphide



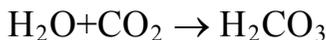
- ii) By mechanical deaeration: The process consists of spraying water over preheated perforated plates stacked in a tower. Removal of dissolved oxygen is ensured by applying high temperature and vacuum.

2) Carbon dioxide: Two sources of CO_2 in boiler water are –

- a) dissolved CO_2 in raw water and
b) CO_2 formed by decomposition of bicarbonates.

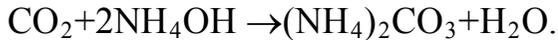


In the presence of water., CO_2 forms carbonic acid that has a corrosive effect on the boiler material like any other acid.



Removal of CO_2 :

- i) By adding calculated quantity of ammonium hydroxide



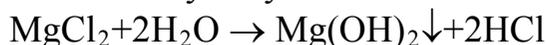
- ii) Mechanical de-aeration along with oxygen?

- iii) by filtering water through line stone

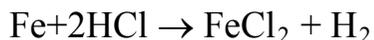


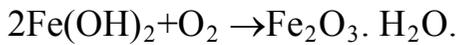
But this method increases hardness.

3) Mineral acids: Water containing dissolved magnesium salts (MgCl_2) liberate acids on hydrolysis.



The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust.





Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Presence of even a small amount of MgCl_2 cause corrosion of iron to a large extent.

Disadvantages of corrosion:

- 1) Shortening of boiler life.
- 2) Leakage of the joints and revents.
- 3) Increased cost of repairs and maintenance.

4.6 Priming and foaming:

Priming:

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along with steam. The process of 'wet-steam' formation is known as 'priming'

Priming is caused by –

- 1) the presence of large amount of dissolved salts
- 2) high steam velocities.
- 3) sudden boiling
- 4) improper boiler design
- 5) sudden increase in steam-production rate.

Priming can be avoided by-

- 1) controlling rapid change in steaming velocities.
- 2) proper design of boilers.
- 3) ensuring efficient softening
- 4) filtration of the boiler-water carried over to the boiler
- 5) by blowing off sludges or, scales from time to time.
- 6) by maintaining low water levels in boilers.

Foaming:

The formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily.

Foaming is caused by the presence of an oil and alkalis in boiler-feed water

Foaming can be avoided by

- 1)the addition of anti-foaming agents like caster oil.
- 2)the removal of foaming agent (oil)from boiler water

Reverse osmosis:

Osmosis the phenomenon by which flow of solvent takes place from a region of low concentration when two solutions of different concentrations are separated by a semi-permeable membrane. The flow continues till the concentration is equal on both the side. The driving force for osmosis is osmotic pressure.

However, if a hydrostatic pressure in addition to osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis for reverse osmosis

For practical purposes, semi-permeable membrane based on thin films of cellulose acetate, polymethyl acrylate and polyamide polymers are used, a pressure of the order of $15\text{-}40\text{kg/cm}^2$ is applied for separating the water (pure solvent) from its contaminants. The process is also known as super filtration or hyper filtration.

Advantages:

- 1)Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
- 2)Colloidal SiO_2 can be removed by reverse osmosis which even cannot be removed by demineralization.
- 3)It is a simple and reliable process.
- 4)Capital and operating expenses are low
- 5)The life of semi-permeable membrane is about 2 years and it can be easily replaced within few minutes, thereby nearly uninterrupted water supply can be provided.

Electrodialysis:

Electrodialysis is based on the fact that the ions present in saline water migrate towards their respective electrodes, through ion-selective membranes under the influence of applied EMF.

The unit consists of electrodes (cathode and anode) and thin, rigid ion-selective membranes which are permeable to either cation or anion. The anode is placed near the anion-selective membrane while the cathode is placed near the cation-selective membrane.

Under the influence of an applied emf across the electrodes, the cations (Na^+) move towards the cathodes through cation selective membrane and anions (Cl^-) move towards the anode through anion selective membrane. The net result is the depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is periodically drawn out from the central compartment while the concentrated brackish water is replaced by fresh samples.

For practical purposes, an electro dialysis cell is used.

It consists of large number of paired sets of ion-selective membranes. Under a pressure of about $5\text{-}6\text{kg/m}^2$, saline water is passed in and we get alternate streams of pure water and concentrated brackish water.

Advantages of desalination of electro dialysis:

- 1) The process is economical as per the capital cost and operational expenses are concerned.
- 2) The unit is compact and the method is best suited.

4.7. Softening of water:

Definition: The process of removing hardness-causing salts from water is known as “Softening of water”.

Internal treatment:

Internal treatment means treating the raw water inside the boiler. In this process (sequestration), an ion is prohibited to exhibit its original character by ‘complexing’ or converting it into other more soluble salt by adding appropriate reagent. This can be done by two processes.

- A) Appropriate chemicals are added to the boiler water to precipitate the scale-forming impurities in the form of ‘sludges’ which can be removed by blow-down operation.
- B) Problem causing cations are converted into compounds that will stay in “dissolved form” in water and thus do not cause any harm.

Internal treatment methods are –

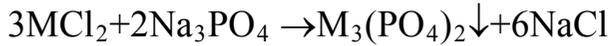
1) Colloidal conditioning:

Scale formation can be avoided in low-pressure boilers by adding organic substances like kerosene, tannin, agar-agar etc., that get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, these can be removed easily by blow-down operation.

2) Phosphate conditioning:

It is applicable to high-pressure boilers. Formation of scales is avoided by adding sodium phosphate, that reacts with magnesium and calcium salts to form non-adherent and easily removable, soft sludge of calcium and magnesium phosphate.

This can be removed by blow-down operation.



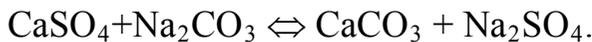
Where M = Mg²⁺ or Ca²⁺

The main phosphates employed are –

- a) NaH₂PO₄ – sodium dihydrogen phosphate (acidic)
- b) Na₂HPO₄ – disodium hydrogen phosphate (weakly alkaline)
- c) Na₃PO₄ – trisodium phosphate (alkaline)

3) Carbonate conditioning:

In low-pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water, when salts like CaSO₄ are converted into CaCO₃ in equilibrium.



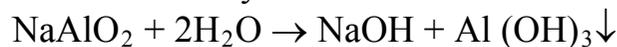
Deposition of CaSO₄ as scale does not take place and calcium is precipitated as loose sludge of CaCO₃ that can be removed by blow-down operation.

4) Calgon conditioning:

The method involves the addition of sodium hexameta phosphate (Calgon) to boiler water to prevent the formation of scale and sludge. Calgon converts the scale forming impurity like CaSO₄ into soluble complex compound.

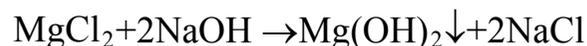
5) Treatment with sodium aluminate (NaAlO₂):

Sodium aluminate gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminium hydroxide.



Sodium aluminate gelatinous precipitate

The sodium hydroxide formed precipitates some of the magnesium as Mg(OH)₂.



The flocculent precipitate of $Mg(OH)_2 + Al(OH)_3$ produced inside the boiler, entraps finely suspended and colloidal impurities. The loose precipitate can be removed by blow-down operation.

6)Electrical conditioning:

Sealed glass bulbs having mercury connected to a battery are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, that prevents scale forming particles to adhere/stick together to form scale.

7)Radioactive conditioning:

Tablets having radioactive salts are placed inside the boiler water at a few minutes. The energy radiations emitted by these salts prevent formation of scales.

8)Complexometric method:

The method involves 1.5% alkaline(pH8.5) solution of EDTA to feed water. The EDTA binds the scale forming cations to form stable and soluble complex. As a result, the sludge and scale formation.

The treatment

- a)Prevents the deposition of iron oxides in the boiler,
- b)Reduces the carry over of oxides with steam,
- c)Protects the boiler units from corrosion by wet steam.

4.8 Methods used for softening of water:

- 1)Lime-soda process
- 2)Zeolite or, permutit process
- 3)Ion exchange process

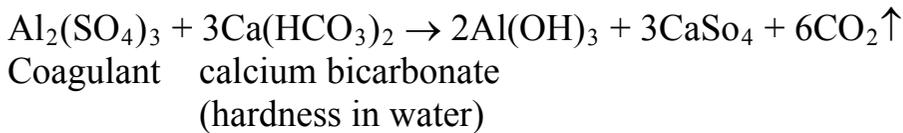
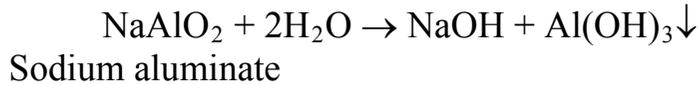
1)Lime-soda process:

In this method, the soluble calcium and magnesium salts in water are converted chemically into insoluble compounds by adding calculated amounts of lime $[Ca(OH)_2]$ and soda $[Na_2CO_3]$. Precipitates of calcium carbonate $[CaCO_3]$ and magnesium hydroxide $[Mg(OH)_2]$ formed are filtered off.

i)Cold lime-soda process:

In this method, calculated quantity of lime and soda are mixed with water at room temperature. At room temperature, the precipitates formed

are finely divided so they do not settle down easily and cannot be filtered easily. Hence, small amounts of coagulants like alum, aluminium sulphate, sodium aluminate etc, that hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide and entraps the fine precipitates. Sodium aluminate as a coagulant helps the removal of silica as well as oil. Cold Lime-soda process provides water having a residual hardness of 50-60ppm.



Method:

Raw water and calculated quantities of chemicals (lime+soda+coagulant) are fed from the top into the inner vertical circular chamber fitted with a vertical rotating shaft carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, thereby softening of water takes place. As the softened water comes into the outer co-ocial chamber, it rises upwards, the heavy sludge settles down in the outer chamber. Then the softened water passes through a filtering media to ensure the complete removal of sludge. Finally filtered soft water flows out continuously through the outlet at the top Sludge settled at the bottom of the outer chamber is drawn off.

ii) Hot Lime-soda process:

The process involves in treating water with softening chemicals at a temperature of 94-100°C. since hot process is operated at a temperature close to the boiling point of the solution. So-

- The reaction proceeds faster.
- The softening capacity of hot process is increased to many fold.
- No coagulants are needed as the precipitate and sludge formed settle down rapidly.
- Most of the dissolved gases are driven out of the water.
- Filtration of water becomes much easier as the viscosity of softened water is lower. This in turn increases the filtering capacity of filters.

Hot lime-soda process produces water of comparatively lower residual hardness of 15-30ppm.

Hot lime-soda plant consists of mainly 3 parts.

- a) a “reaction tank” in which raw water, chemicals and steam are thoroughly mixed.
- b) a “Conical sedimentation vessel” in which the sludge settles down.
- c) a “ sand filter” that ensures complete removal of sludge from the softened water.

Differences between Hot and Cold lime-soda process:

S.No	Cold Lime-Soda Process	Hot Lime-Soda Process
1	It is done at room temperature (25-30°C)	1. It is done at elevated temperature (94-100°C).
2	It is a slow process	2. It is a rapid process.
3	Use of coagulants is must.	3. Coagulants are not needed.
4	Filtration is not easy.	4. Filtration is easy as the viscosity of water becomes low at elevated temperatures.
5	Softened water has residual hardness around 60ppm	5. Softened water has residual hardness of 15-30ppm.
6	Dissolved gases are not removed	6. Dissolved gases like CO ₂ are removed to some extent.
7	Low softening capacity	7. High softening capacity

Advantages of Lime-soda process:

- Lime-soda process is economical.
- Treated water is alkaline and hence has less corrosion tendencies.
- Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.

- It removes not only hardness causing salts but also minerals.
- Iron and manganese are also removed from the water to some extent.
- If the process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.

Disadvantages:

- The process requires careful operation and skilled supervision for economical and efficient softening.
- Sludge disposal is a problem.
- The process can remove hardness only upto 15ppm, which is not good for high pressure boilers.

4.9 Zeolite or, permutit process:

Zeolites are naturally occurring hydrated sodium alumino silicate minerals (like Na_2O , Al_2O_3 , $x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x = 2-10$ and $y=2-6$) capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Zeolites are known as permutits and in greek it means “boiling stone”.

Zeolites are of two types.

i) Natural zeolites:

These are non-porous, amorphous and durable

Ex: 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 zeolites: These are porous and possess a gel structure. Prepared by heating together sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2)

Synthetic zeolites possess higher exchange capacity per unit weight compared to natural zeolites.

Process:

For softening of hard water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite.

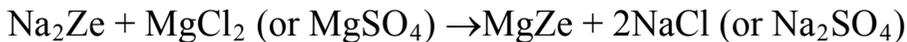
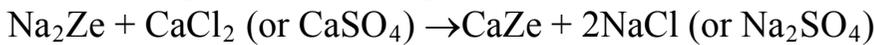
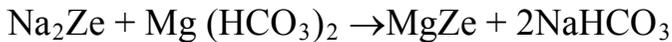
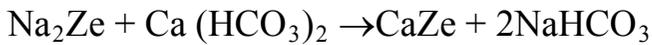
Zeolite holds sodium ions loosely and can be represented as Na_2Ze .

Where Ze =insoluble radical frame work.

The hardness causing ions (Ca^{2+} , Mg^{2+}) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts.

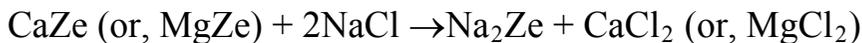
During this process, the water becomes free from Ca^{2+} and Mg^{2+} ions.

Reactions taking place during the softening process –



Regeneration:

After some time, the zeolite is completely converted into calcium and magnesium zeolites. Hence the bed ceases to soften water i.e, it gets exhausted, at this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated solution of sodium chloride(brine). The reaction taking place is



Exhausted zeolite brine reclaimed zeolite washings

The washings are led to drain and thus the regenerated zeolite bed is used again for softening purpose.

The working of zeolite softeners involve alternate cycles of softening run and the regeneration run. The scheme for softening and regeneration processes are represented as below.

Limitations of zeolite process:

- If the supplied water is turbid, the suspended matter must be removed before the water is fed to the zeolite bed. Otherwise the pores of the zeolite bed will get clogged by the turbidity, thereby making it inactive.
- If water contains large quantities of coloured ions like Mn^{2+} and Fe^{2+} , they must be removed because these ions produce manganese and iron zeolites that cannot be regenerated easily.
- If mineral acids are present in water, they destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding the water into the zeolite bed.
- The water to be softened should not be hot as the zeolite tends to dissolve in it.
- Anions are not removed by this process. The bicarbonates present in hard water get converted to NaHCO_3 that goes into soft water effluent. If it is used as boiler feed, under the boiler conditions NaHCO_3 dissociates to



- Both the products are not desirable. Since NaOH may lead to caustic embrittlement and CO₂ makes the condensed water into acidic and corrosive. Thus, it is desirable to remove temporary hardness before subjecting the raw water to zeolite process.
- Compared to ion-exchange process, water treated by zeolite process contains 25% ore dissolved salts. The higher cost of the plant and materials are also limiting factors.

Advantages:

- The hardness is nearly completely removed and water of about 10ppm hardness is produced.
- The equipment used is compact and occupies less space.
- It is quite clean and rapid process that requires less time for softening.
- Less skill is needed for maintainance as well as operations.
- Impurities are not precipitated, so there is no danger of sludge formation.
- The process automatically adjusts itself to waters of different hardness.

Comparison of zeolite process with lime-soda process:

Zeolite process	Lime-soda process
1. The process produces water of 10-15ppm residual hardness.	1. Depending on whether it is hot or cold process, water of generally, 15-50ppm residual hardness is obtained.
2. Water treated by zeolite process contains large amounts of sodium salts than in the original raw water.	2. Treated water contains lesser percentage of sodium salts.
3. The cost of plant and zeolite are higher. Hence the capital cost is higher.	3. The capital cost is lower
4. Operation expenses are lower as NaCl(cheap) is used for regeneration.	4. Operation expenses are higher as costly chemicals are consumed.
5. The method cannot be used for treating acidic water, because the zeolite undergoes disintegration	5. There is no such limitation
6. The plant occupies less space as it is compact.	6. Plant occupies more space, as it depends on the amount of water to be softened.
7. The raw water to be softened	7. The process is form such limitation
	8. The process cannot be operated under pressure.
	9. The process involves difficulty

<p>must be free from suspended matter; otherwise the pores of zeolite material are blocked and the bed loses its exchange capacity.</p> <p>8. It can operate under pressure and can be designed for fully automatic operation.</p> <p>9. The process involves no problem of settling, coagulation, filtration and removal of the sludges and precipitates.</p> <p>10. Control test comprises only in checking the hardness of treated water. The process adjusts itself to water of different hardness.</p> <p>11. Treated-water contains more NaHCO_3 that creates problem when used as feed water in boilers.</p>	<p>in settling, coagulation, filtration and removal of precipitates.</p> <p>10. In order to meet the changing hardness of incoming water, frequent control and adjustments of reagents is needed.</p> <p>11. Treated water is completely free from NaHCO_3 because it is removed in the form of insoluble CaCO_3 and Mg(OH)_2.</p>
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4.10 Ion-exchange process:

Ion exchange is “a process in which ions held on a porous, essentially insoluble solid are exchanged for ions in solution that is brought in contact with it”.

Ion exchange resins:

The ion exchange resins are insoluble, cross-linked, high molecular weight organic polymers with a porous structure. The functional groups attached to the chains are responsible for ion-exchange properties.

Classification:

The ion-exchange resins may be classified as –

A) Cation exchange resins (R^-H^+): These resins are mainly styrene divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water. Such resins have acidic functional groups like $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$ (phenolic) capable of exchanging the cationic portion of minerals by their hydrogen

ions and hence they are termed as cation exchangers. Ex: Amberlite IR-120, Dowex – 50

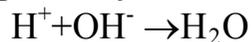
B) Anion exchange resins (R^+OH^-): These resins are styrene-divinyl benzene or amine-formaldehyde copolymers that contain basic functional groups like amino or quaternary ammonium ($-^+NR_3$) or quaternary phosphonium or tertiary sulphonium groups an integral part of the resin matrix. These resins after treatment with dilute NaOH solution, become capable of exchanging their OH^- ions with anions in water and therefore known as anion exchangers.

Ex: Amberlite – 400, Dowex-3

The hard water is first passed through cation exchange column, when all the cations like Ca^{2+} , Mg^{2+} are removed from it and the equivalent amount of H^+ ions are released from the column to water.

After passing through cation exchange column, the hard water is passed through anion exchange column, when all the anions like SO_4^{2-} , Cl^- present in the water are removed and equivalent amount of OH^- ions are released from the column to

H^+ and OH^- ions released from cation exchange and anion exchange columns respectively combine to form water molecule.



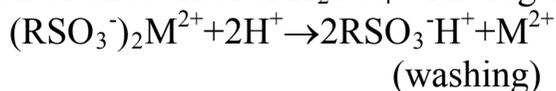
Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as deionized or demineralized water. It is also free from acidity or alkalinity. Thus it is as pure as distilled water.

Finally, the demineralized water is passed through a degasifier, a tower whose sides are heated and which is connected to a vacuum pump. High temperature and low pressure reduces the amount of dissolved gases like CO_2 and O_2 in water.

Regeneration:

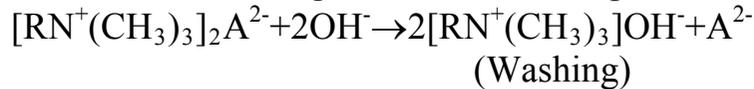
When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, then they are said to be exhausted.

The exhausted cation exchange column is regenerated by passing a solution of dilute HCl or H_2SO_4 . The regeneration can be represented as



The column is washed with deionized water and washing is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dilute NaOH solution. The regeneration can be represented as



The column is washed with deionized water and washing is passed to sink or drain.

Then the regenerated ion exchange resins are used again.

Advantages:

- i) The process can be used to soften highly acidic or, alkaline waters.
- ii) The process produces water of very low hardness (2ppm), SO, the treated water is very good for use in high pressure boilers.

Disadvantages:

- i) Capital cost is high since chemical and equipment both are costly.
- ii) If water contains turbidity then the efficiency of the process is reduced.

S.No	Characteristic	Ion-exchange process	Zeolite process	Lime-soda process
1	Requirements	Cation and anion exchangers	Zeolite	Lime, soda and coagulants
2	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place	No exchange of ions
3	Capital cost	Very high	High	Low
4	Operating expenses	High	Low	High
5	Raw water	i) Should be non-turbid ii) Both acidic or alkaline water can be treated iii) Prior knowledge of hardness not	i) Should be non-turbid ii) Should not be acidic iii) Prior knowledge of hardness not required.	Prior knowledge or hardness is essential

		required		
6	Automation	Possible	Possible	Not possible
7	Residual hardness	Least (0-2ppm)	Low (0-15ppm)	High (15-50ppm)