UNIT – I Water and its treatment

HARDNESS

Definition:

If the water produces lather with soap, it is soft water. If the water does not produce lather with soap, it is called as hard water. The property is known as hardness. Hard water will produce a scummy white precipitate. The hardness is due to Ca^{2+}, Mg^{2+} and SO_4^{2-} Cl^- , CO_3^{2-}, HCO_3^- ions and their salts.

***Test for hardness*:**

a) Eriochrome Black – T indicator gives red colour in hard water.
b) With soap, hard water gives a scummy precipitate.

$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$
(Sodium stearate) (Scummy precipitate)

1. Types of Hardness:

a) Temporary Carbonate hardness: The hardness due to carbonates and bicarbonates can be removed by simple boiling. So, they are known as temporary or carbonate or alkaline hardness.

$Ca(HCO_3)_2$ (On heating) $\rightarrow CaCO_3 + H_2O + CO_2$

b) Permanent hardness (Non-carbonate): The hardness due to chlorides and sulphates cannot be removed by simple boiling. They need special methods like lime soda process and zeolite process. This hardness is called as "Permanent hardness or Non-carbonate or non alkaline hardness.

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ (Lime soda process)

$CaSO_4 + Na_2Ze$ (Zeolite) $\rightarrow CaZe + Na_2SO_4$ (Zeolite process)

2. Units of hardness:

i) ppm ii) mg/L iii) degree Clarkes iv) Degree French

1 ppm – 1 part by weight of $CaCO_3$ equivalent hardness/10^6 parts of water
1 mg/L – 1mg of $CaCO_3$ / 1 Lr of water
Clarkes Degree - ^{0}Cl-1 part of $CaCO_3$ equivalent hardness /70,000 parts of water
1 Degree French – ^{0}F - 1 part of $CaCO_3$ equivalent hardness/10^5 parts of water
Therefore, 1ppm = 1mg/L = 0.07 ^{0}Cl = 0.1^{0}F

3. $CaCO_3$ equivalence:

Hardness is expressed in $CaCO_3$ equivalence. Because,
i) It is the most insoluble and forms precipitate quite easily.
ii) Its molecular weight is 100 and equivalent weight is 50. As these are whole numbers, it is very easy to use them in calculations.

ESTIMATION OF HARDNESS BY EDTA METHOD:

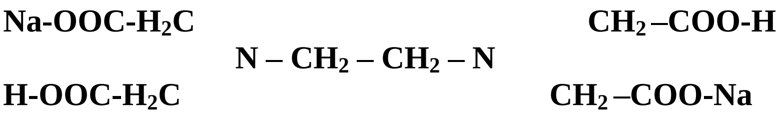
1. *Aim*:
To estimate the amount of hardness present in the given water sample.

2. *Chemicals required:*

a) Standard hard water – 1 g $CaCO_3$ + dil. HCl – made up to 1 L.
b) EDTA solution – 4 g of EDTA sodium salt / 1 L of water
c) EBT Indicator – 0.5 g EBT / 100 ml alcohol
d) Ammonia buffer - 67.5 g Ammoniumchloride +570ml Ammonia-- made up to 1L

3. *Principle:*

EDTA stands for Ethylene Diamine Tetra Aceticacid. As it is insoluble in water, we use its disodium salt.
Structure of EDTA:



$$\begin{matrix} \textbf{Na-OOC-H}_2\textbf{C} & & \textbf{CH}_2\textbf{–COO-H} \\ & \textbf{N – CH}_2\textbf{ – CH}_2\textbf{ – N} & \\ \textbf{H-OOC-H}_2\textbf{C} & & \textbf{CH}_2\textbf{–COO-Na} \end{matrix}$$

By nature, Eriochrome Black T indicator is blue in colour. When EBT indicator is added to water sample, it forms a wine red coloured unstable Ca-Mg-EBT complex.
This reaction is carried out under a basic P^H of 8- 10 using ammonia buffer.

Ca^{2+} / Mg^{2+} in water + EBT -→ [Ca / Mg –EBT] unstable wine red complex

When EDTA is titrated against the complex, EDTA replaces all the EBT and forms a stable Ca / Mg –EDTA complex. The liberated EBT indicates the end point as steel blue.

[Ca / Mg –EBT] + EDTA → [Ca / Mg –EDTA] + EBT
(Wine red/unstable) (Stable) (Steel blue)

So, the end point is the colour change from wine red to steel blue.

4. *Short Procedure:*

S.No.	Content	Titration-I Standardisation of EDTA	Titration-II Total Hardness	Titration-III permanent Hardness
1	Burette	EDTA	StandardEDTA	standardEDTA
2	Pipette(20 ml)	Std. Hardwater	Sample water	Boiled water
3	Additional solution	10ml of NH_3 buffer	10ml of NH_3 buffer	10ml of NH_3 buffer
4	Indicator	EBT	EBT	EBT
5	Endpoint	Wine red to steel blue	Wine red to steel blue	Wine red to steel blue
6	Volume	V_1	V_2	V_3

5. *Calculation*:

Step1 – Standardisation of EDTA

1 ml of Std. Hard water = 1 mg of $CaCO_3$ (Given)

So, 20 ml of Std. Hard water = 20 mg of $CaCO_3$

V_1 ml of EDTA is required for = 20 mg of $CaCO_3$

Therefore, $\boxed{1\text{ml of EDTA} = 20 / V_1 \text{ mg of } CaCO_3}$

Step 2: Finding Total hardness:

20ml of sample water required = V_2 ml of EDTA

$$= V_2 \text{ X } \frac{20}{V_1} \text{ mg of } CaCO_3$$

Therefore, 1000ml of sample requires = $V_2 \text{ X } \frac{20}{V_1} \text{ X } \frac{1000}{20}$ mg of $CaCO_3$

Hence, total hardness = $\frac{V_2}{V_1} \text{ X } 1000$ ppm

Step 3: Finding Permanent hardness:

20ml of boiled water required = V_3 ml of EDTA

$$= V_3 \text{ X } \frac{20}{V_1} \text{ mg of } CaCO_3$$

Therefore, 1000ml of boiled sample requires = $V_3 \text{ X } \frac{20}{V_1} \text{ X } \frac{1000}{20}$ mg of $CaCO_3$

Hence, permanent hardness = $\frac{V_3}{V_1} \text{ X } 1000$ ppm

Step 4 : Temporary hardness = Total hardness – permanent hardness

1.2) Boiler Troubles

1 .Definition:

The setup used to produce steam in industries is known as „Boiler‟. Water is fed to the boiler and heated to produce steam. The water fed into the boiler is known as “Boiler feed water”.

2. Requirements for boiler water

S.No.	**Requirements for boiler water**	**If not, it will cause**
1	Free from hardness causing salts	Sludge and scale
2	Free from oil and greases, silica	Foaming
3	Free from dissolved salts, suspended impurities, alkalis	Caustic embrittlement
4	Free from dissolved gases, suspended salts	Boiler corrosion

If the untreated water is fed directly to the boiler, it may cause sludge, scale, priming, foaming, caustic embrittlement and boiler corrosion which are collectively known as boiler troubles.

Sludge and scale:

Definition: If the water contains hardness causing salts like $MgSO_4$, $MgCl_2$, $CaSO_4$, $Ca(HCO_3)_2$ on evaporation, the salts are precipitated . If they form *loose, slim, non-adherent* precipitate, It is known as sludge. If they form *hard, thick, adherent* precipitate, it is known as scale.

Reasons for sludge and scale:

Sludge:
$MgCl_2$,
$MgSO_4$,
$CaCl_2$
Scale:
$CaCO_3$,
$MgCO_3$,
$Ca(HCO_3)_2$

Disadvantages of scales and sludges:

a) Wastage of fuel:

Scales have low thermal conductivity. So, the heat transfer from boiler to inside water may not be sufficient. In order to provide steady supply of heat to water, over heating is to be done which causes wastage of fuel. The wastage of fuel depends on the thickness and nature of the scale which is shown in the table.

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

b) Decrease in efficiency:

Scales sometimes deposit in the valves and condensers of the boilers and heat exchangers and cause choking. This results in decrease in efficiency of the boiler and heat exchangers.

c) Boiler explosion:

Sometimes due to overheating the thick scales may crack which causes the sudden contact of high heated boiler material with water. This causes formation of a large amount of steam and it develops high pressure. This leads to explosion.

Examples of Scale deposits:

S.No.	**Name of the deposit**	**Properties**
1	$CaCO_3$ Deposit	It is formed due to decomposition of calcium bicarbonate. It has lov solubility and forms tenacious scale. The liberated CO_2 produces carbo acid and produces boiler corrosion.
2	$CaSO_4$ deposit	At high temperature and high pressure boilers, It forms harder and dense deposit.
3	$Mg(OH)_2$ deposit	It is formed due to decomposition of magnesium bicarbonate. It reacts w water and liberates corrosive HCl.
4	SiO_2 deposit	It forms a hard, porcelain coating on the boiler surface.
5	Fe deposit	It causes dark coloured magnetic deposits.

Prevention of Scales:

1. At earlier stage, scraper, wire brush, mechanical scrubber can be used to remove scales.
2. Thermal shocks are used to remove brittle scales.
3. By external treatment methods (eg) Ion exchange demineralization, zeolite softening
4. By using boiler compounds in internal treatment (eg) Carbonate, phosphate, calgon, EDTA
5. By acid treatment

Differences between sludge and scale:

S.No.	**Sludge**	**Scale**
1	Loose, slim, non-adherent deposit on the inner walls of boiler.	Hard, thick, 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 boiler efficiency to maximum extent, ca 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, Calg conditioning iii) Mechanical hard scrubbing methods. iv) Thermal shocks
5	Diagram:	

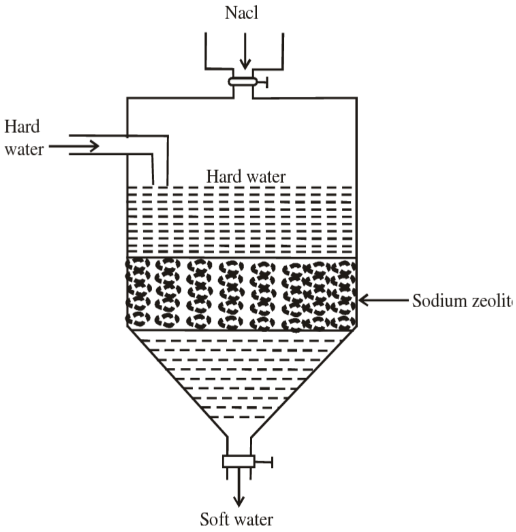
1.3) External treatment

Removal of impurities, salts from boiler feed water before feeding it to the boiler is known as external treatment.

1.3) - A) ZEOLITE (PERMUTIT) SOFTENING PROCESS

Setup

i) Hydrated sodium alumino silicates available in nature are known as zeolite.
ii) These natural zeolites are green sand. They are non porous in nature.
iii) Zeolites are having the general formula $Na_2O . Al_2O_3. xSiO_2 . yH_2O$ ($x = 2$ to 10; $y = 2$ to 6)
iv) The porous and gel structured synthetic zeolites are known as permutit.
v) These zeolites and permutits are used for water softening.
vi) Synthetic zeolite is represented as Na_2Ze.



Principle

i) The sodium ions are loosely held in these zeolites. They are easily replaced by Calcium and magnesium ions present in the water.

ii) When hard water is passed through a bed of sodium zeolite kept in a cylinder, it exchanges its sodium ion with Ca^{2+} and Mg^{2+} ions present in the water to from Calcium and Magnesium zeolites.

iii) Zeolite softeners may be of pressure type or gravity type.

Reactions:

$CaSO_4$ +

$Na_2Ze \rightarrow$

CaZe +

Na_2SO_4

$MgSO_4$ +

$Na_2Ze \rightarrow$

MgZe +

Na_2SO_4

$CaCl_2 +$

$Na_2Ze \rightarrow$

$CaZe + 2$

$NaCl$

$MgCl_2 +$

$Na_2Ze \rightarrow$

$MgZe + 2$

$NaCl$

The outcoming water is enriched with large amount of sodium salts which do not cause any hardness. But in cannot be used in boiler.

Regeneration:

i) On prolonged use, all the zeolite sodium ions are exhausted.
ii) There will be no sodium ions to exchange the Calcium and magnesium ions. So, they have to be regenerated.
iii) The exhausted zeolite is regenerated by treating with 10% solution of NaCl.

Regeneration reaction:
The regeneration step comprises of a) backwashing b) salting

c) rinsing before reuse $CaZe + 2\,NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2\,NaCl \rightarrow Na_2Ze + MgCl_2$
Advantages of zeolite process:

1. The outlet water will have least hardness around 1 – 2 ppm only.

2. As the zeolite can be regenerated, the method is cheap.

3. Operation is easy.

4. The space requirement for this setup is minimum.

5. No sludge is formed during this process.

Disadvantages of zeolite process:

1. Turbid water cannot be treated as it blocks the pores of the zeolite bed.

2. Acidic water cannot be treated as it decomposes the structure of zeolite.

3. Water containing Fe, Mn cannot be treated as the regeneration is difficult.

4. Brackish water cannot be treated because it contains Na+ ions. So, the ion exchange reaction will not occur.

5. When the softened water contains more dissolved sodium salts, it may result in boiler corrosion and caustic embrittlement.

1.3) - B).Ion exchange method - (Demineralisation)

Working:

1. Here all the cations and anions are completely removed. It uses two cylinders of cation exchange cylinder and anion exchange cylinder filled with resins.

2. Resins are long chain, insoluble, cross linked, organic polymers. There are 2 types.
   i) Cation exchange resins – RH_2 (e.g) Sulphonated coals , RSO_3H
   ii) Anion exchange resins. $R''(OH)_2$ (e.g)Ureaformaldehyde,Amines $R\text{-}NH_2$

3. The resins are prepared by copolymerization of styrene and di vinyl benzene.

The resultant polymer is treated with acid, it forms cation exchange resin. If the polymer is treated with bases and ammonium chloride, it forms anion exchange resin.

4. The water is fed into cylinder –I where all the cations are replaced by RH_2 Resins.

$$RH_2 + CaCl_2 \rightarrow R\,Ca + 2\,HCl$$

5. The cation free water is fed to cylinder II, where all the anions are replaced.

$$R'(OH)_2 + 2\,HCl \rightarrow R'Cl_2 + 2H_2O$$

6. So, the resultant water is free from all types of ions.

Regeneration:

On prolonged use, as all the resins are exhausted, there will be no H^+ orOH^- ions to exchange the unwanted ions. So, they have to be

regenerated.
Cation resins are regenerated by HCl and anion resins by NaOH.

$$R\,Ca + 2\,HCl \rightarrow RH_2 + CaCl_2$$
$$R'Cl_2 + 2NaOH \rightarrow R'(OH)_2 + 2NaCl$$

Advantages of Ion exchange method:

i) Can be used for high pressure boilers also.
ii) It can treat highly acidic or alkaline water.
iii) We can get pure water as hardness as low of 2 ppm.

Drawbacks of Ionexchange method:

i) Expensive
ii) Fe, Mn cannot be removed as they form complexes with resins
iii) Cannot be used for turbid water as they clog the resins.

Differences between soft water and demineralized water.

S. No.	**Soft water**	**Demineralized water**
1	It does not contain hardness producing calcium and magnesium ions, but it may contain other ions like K^+, Na^+, Cl^- etc.	Demineralized water does not contain any ions including hardness producing ions.
2	Softening involves removal of only hardness causing ions.	Demineralization involves removal of all the ions present in water.

Differences between Zeolite and ion exchange process:

S.No.	**Zeolite process**	**Ion exchange process**
1	It exchanges only cations.	It exchanges cations and anions
2	The cylinder is filled with zeolite. $Na_2O.\ Al_2O_3.\ xSiO_2.yH_2O$	The cylinders are using cationexchange resin - RH_2 Anion exchange resin - $R''(OH)_2$
3	NaCl is used for regeneration	HCl, NaOH are used for regeneration.
4	Softening involves removal of only hardness causing ions.	Demineralization involves removal of all the ion present in water.
5	The treated water contains relatively large amount of dissolved Na salts which causes caustic embrittlement in boilers.	The treated water does not contain any dissolved salts. They may not cause any boiler troubles.
6.	The setup and operating cost is relatively low.	The setup and operating cost high.
7	The hardness may be upto 10 ppm	The hardness may be upto 2 ppm

8	Acidic water cannot be treated because acid decomposes the zeolite.	Acidic water can be treated.

1.4. INTERNAL TREATMENT METHODS

i) The residual salts that are not removed by external methods can be removed by adding some chemicals directly into the boiler water.

ii) These chemicals are known as „*Boiler compounds'*. This method is known as „Internal treatment‟ (or) sequesterisation.

In general, internal treatment methods are followed by blow down operation.

a) Carbonate conditioning:

i) Carbonate conditioning is used for low pressure boilers.

ii) Here the salts like $CaSO_4$ are converted to easlity removable $CaCO_3$.

iii) But in high pressure boilers, the excess Na_2CO_3 undergoes hydrolysis and is converted to NaOH.

iv) It leads to caustic embrittlement and boiler corrosion. So it is less preferred.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

b) Phosphate conditioning:

i) Phosphate conditioning is used for high pressure boiler.

ii) It is superior than carbonate conditioning as there is no risk of CO_2 liberation, caustic embrittlement and boiler corrosion.

iv) For better results, a pH range of 9.5 – 10.5 is recommended.

$$3CaSO_4 + 2\ Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3\ Na_2SO_4$$

Three types of Phosphate salts are used:

S.No.	**Salt**	**Name**	**Used for treating**
1	Na_3PO_4	Tri sodium Phosphate	highly acidic water
2	Na_2HPO_4	Di sodium hydrogen Phosphate	slightly acidic water

3	NaH_2PO_4	Sodium di hydrogen phosphate	highly alkaline water

c) Calgon conditioning:

i) Calgon is the trade name of sodium hexa meta phosphate- $Na_2 [Na_4 (PO_3)_6]$.

ii) With calcium ions it forms a soluble complex .

iii) So, there is no problem of sludge disposal.

iii) It is used for high and low pressure boilers.

$$2CaSO_4 + Na_2[Na_4 (PO_3)_6] \rightarrow Na_2 [Ca_2(PO_3)_6] + 2 Na_2SO_4$$

d) Aluminate conditioning by sodium aluminate

i) Sodium aluminate (NaAlO2) gets hydrolysed inside the boiler giving aluminium hydroxide (Al(OH)3) and sodium hydroxide (NaOH).

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$

ii) The sodium hydroxide formed would react with Mg ions forming $Mg(OH)_2$.

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$

iii) The flocculant precipitates of $Mg(OH)_2$ and $Al(OH)_3$ entraped suspended particles like oil, silica and other colloidal impurities.

iv) The loose precipitate can be removed by below down operation.

e) Colloidal conditioning:

i) Colloidal conditioning is used for low pressure boilers.

ii) Here, scale formation is avoided by adding organic substances like kerosene, tannin, agar-agar etc., which get coated over the scale forming precipitates.

iii) This converts the scale into sludge and they are removed by blow down operation methods.

f) EDTA complexometric conditioning:

i) At basic P^H, EDTA is added to boiler water.

ii) EDTA binds the scale forming cations to form soluble complex. Thus scale formation is prevented.

$[Ca^{2+} / Mg^{2+}] + EDTA \rightarrow [Ca / Mg - EDTA]$

1.5) Desalination of brackish water by Reverse Osmosis method:

1. Removal of common salt (NaCl) from water is called „Desalination".

2. Based on dissolved solids, water can be classified into three types.

3. Reverse osmosis is used to convert sea and brackish water to fresh water.

4. *Osmosis*:
When two different concentrated solutions are separated by a semi permeable membrane, due to osmotic pressure, low concentrated solvent flows to higher one. This is known as osmosis.

5. *Reverse Osmosis*:
But when we apply an excess and opposite *Hydrostatic pressure of 15 – 40* kg / cm^2 to overcome the osmotic pressure, then higher concentrated solvent will flow to the lower one. This is known as reverse osmosis.

6. During this RO process, only the water flows across the membrane and it prevents the salt migration. So, this method is also called as „*Super filtration'*.

7. The membrane is madeup of *cellulose acetate, cellulose*

butyrate, polymethacrylate Advantages of Reverse Osmosis:

1. The life time of membrane is quite high. (2- 3 years)

2. Removes ionic, non-ionic and colloidal silica impurities, which can not be removed by demineralization method.

3. Low capital cost.

4. Simple operational procedure.

5. The membrane can be replaced within a few minutes, thereby providing uninterrupted water supply.

6. This method is also used to remove bio-molecules, proteins, sugar etc.,

Disadvantages:

1. Periodical cleaning of membrane is needed.

2. Pretreatment for bacterial removal is needed.