Unit - 1 (Mrs. Samta Deshpande)

WATER

Specification for Water –

Surface and ground water normally used for domestic purposes. Each industry has its own specification for water.

1) **Textile industry-**

Specification –

- Water should be soft, free from turbidity.
- Free from colour, Fe and Mn ion.

Remarks –

- Hard water creates uneven dying which causes stains of fabrics.
- Hard water decreases the solubility of dyes.

2) **Laundries-**

Specification-

- Water should be soft, free from colour.
- Free from organic matter. Free from Fe and Mn.

Remarks –

- Hard water increases consumption of soaps.
- Salts of Fe and Mn creates gray or yellow colour on fabric.

3) **Beverages-**

Specification-

- Water should not be alkaline.

Remarks-

- Alkalinity destroys the taste.
- Neutralization occurs.

4) **Dairies and industries-**

Specification-

- Water should be colorless, tasteless, odorless.
- Free from pathogenic organism.

Remarks-

- Organic matter imparts foul smell.

5) **Boilers-**

Specification-

- Water should be zero hardness.

Remarks-

- Scale formation on using hard water.
- Loss of heat.

6) **Paper Industry -**

Specification-

- Water should be free from SiO_2, turbidity,
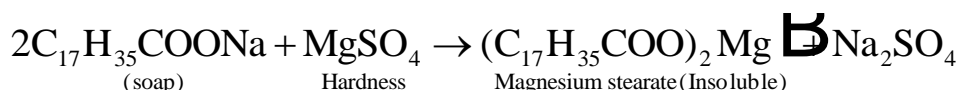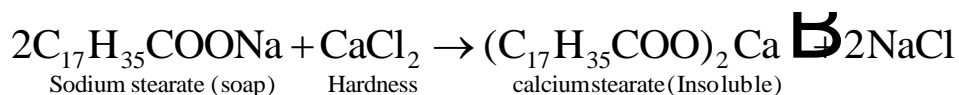- Free from alkalinity.
- Free from hardness.

Remarks-

- SiO_2 produces cracks on paper.
- Brightness and colour of the paper affected.

HARDNESS OF WATER

Those water which does not produce lather with soap are termed as hard water. On the other hand soft water readily produce a lot of lather when mixed with a little of soap. The hard water causes boiler troubles like scale formation etc. the hardness is mostly due to the presence of bivalent metallic ions which react with soap and form precipitates. Some major bivalent cations are Mg^{++}, Ca^{++} and Fe^{++}. Some important anions are HCO^-_3, NO^-_3, SO_4^{--} etc.

Example :- A reaction of soap (Sodium stearate) with calcium chloride and Magnesium sulphate is as follows-

$$2\underset{\text{Sodium stearate (soap)}}{C_{17}H_{35}COONa} + \underset{\text{Hardness}}{CaCl_2} \rightarrow \underset{\text{calcium stearate (Insoluble)}}{(C_{17}H_{35}COO)_2 Ca} \downarrow 2NaCl$$

$$2\underset{\text{(soap)}}{C_{17}H_{35}COONa} + \underset{\text{Hardness}}{MgSO_4} \rightarrow \underset{\text{Magnesium stearate (Insoluble)}}{(C_{17}H_{35}COO)_2 Mg} \downarrow Na_2SO_4$$

The water are commercially classified on the basis of degree of hardness as follows-

Hardness	Name of the water
0-70 mg/litre	Soft water
70-150 mg/litre	Moderate hard water
150-300 mg/litre	Hard water
300 mg/litre and above	Very hard water

Types of Hardness

HARDNESS

(A) Temporary Hardness   (B) Permanent Hardness
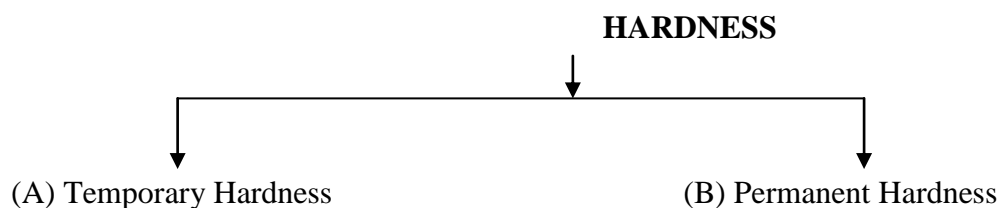
Carbonate Or Alkaline Hardness   Non Carbonate or Non alkaline Hardness

(A) Temporary Hardness -	(B) Permanent Hardness-
(i) It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals.	(i) It is caused by the presence of soluble chlorides and sulphates of calcium, Magnesium, iron and other heavy metals.
(ii) Salts which are responsible for temporary hardness are – $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$	(ii) Salts which are responsible for permanent hardness are – $CaCl_2$, $MgCl_2$, $CaSO_4$, $FeSO_4$, $Al_2(SO_4)_3$.
(iii) It can be removing by simple boiling of water.	(iii) It can't be removed by simply boiling of water.
(iv) Bicarbonates are decomposed and are converted into insoluble carbonates or hydroxides, which precipitate and settle down at the bottom of the vessel. $Mg(HCO_3)_2 \xrightarrow{\text{Heat}} Mg(OH)_2 \downarrow 2CO + CO_2 \uparrow$ (v) It is also known as carbonate or Alkaline hardness.	(iv) It is also known as non carbonate or non alkaline hardness.

DEGREE OF HARDNESS	

Hardness of water is expressed as **equivalent of calcium carbonate (CaCO₃).**

The reason for choosing CaCO₃ as standard is – CaCO₃ is the ease in calculations as its molecular weight is exactly 100.

It is most insoluble salt that can be precipitated in water treatment.

Equivalent of CaCO₃ =

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

Multiplication factors for different salt are tabulated

(i) Table -

Dissolved salt	Molar mass	Chemical equivalent	Multiplication factor for converting into equivalents of CaCO₃.
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$MgSO_4$	120	60	100/120
$CaCl_2$	111	55.5	100/111

$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Mg(NO_3)_2$	148	74	100/148
HCO^-_3	61	61	100/122
OH^-	17	17	100/34
$CO_2^-{}_3$	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al_2(SO_4)_3$	342	57	100/114
$FeSo_4.7H_2O$	278	139	100/278
H^-	1	1	100/2

UNIT OF HARDNESS-

UNIT

(A)   Parts per million (ppm)

(B)   Milligrams per litre (Mg/L)

(C)   Degree Clark (^oCl)

(D)   Degree French (^oFr)

(A)   Parts per Million (ppm) – It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

∴**1ppm = 1 part of CaCO₃ equivalent hardness in 106 parts of water.**

(B)   Milligrams per litre (Mg/L) – It is defined as the number of milligrams of $CaCO_3$ persent in one litre of water.

∴**1 Mg/L = 1 mg of CaCO₃ equivalent hardness per litre of water.**

   1Mg/L = 1 ppm

(C)   Degree Clark (^oCl) - It is defined as the parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

      Or

   It is the number of grains of $CaCO_3$ equivalent hardness for a gallon of water.

∴ **1 ᵒCl = 1 part of CaCO₃ per 70,000 parts of water.**

(D)   Degree French) (^{o}Fr) – It is defined as the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

∴ **1 ^{o}Fr = 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.**

Relationship between various units.

1 ppm = 1 Mg/L   =   0.1 ^{o}Fr   = 0.07 ^{o}Cl

1 mg/l = 1 ppm   =   0.1 ^{o}Fr   = 0.07 ^{o}Cl

1 ^{o}Cl = 1.43^{o}Fr   =   14.3 ppm   = 14.3 mg/L

1 ^{o}Fr = 10 ppm   =   10 Mg/L   = 0.7 ^{o}Cl

Hence ;

1 ppm = 0.1 ^{o}Fr = 0.07 ^{o}Cl = 1 mg/L

Solved examples based on determination of Hardness of water

Ex.(1) A water sample contains 500 mg of $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalents.

Solution:-

Hardness = (Mass of $CaSO_4$ in Mg/L) X Multiplication factor

$$= \left(\text{Mass of } CaSO_4 \text{ in Mg/L} \right) \times \left\{ \frac{\text{chemical eq. of } CaCO_3}{\text{chemical eq. of } CaSO_4} \right\}$$

$$= 500 mg/L \times \left\{ \frac{50}{80} \right\}$$

= 312.5 Mg/L =   312.5 ppm. Ans

Ex. (2) How many grams of $MgCO_3$ dissolved per litre gives 90 ppm of hardness.

Solution-

$$\text{Hardness} = \left(\text{Mass of } MgCO_3 \text{ in mg/L} \right) \times \left\{ \frac{\text{chemical eq. of } CaCO_3}{\text{chemical eq. of } MgCO_3} \right\}$$

$$\text{Mass of } MgCO_3 = \text{Hardness} \times \frac{\text{chemical eq. of } MgCO_3}{\text{chemical eq. of } CaCO_3}$$

$$\text{Mass of } MgCO_3 = 90 ppm \times \left\{ \frac{42}{50} \right\}$$

=   75.6 Mg/L   = 75.6 ppm   Ans.

Thus 75.6 X 10^{-3} gm of $MgCO_3$ dissolved per litre gives 90 ppm of hardness.

Ex. (3) A sample of 70,000 c.c. of hard water baring dissolved impurities gave on analysis the following results-

$MgCl_2$ = 9.50 gm

$CaSO_4$ = 13.60 gm

$Ca(HCO_3)_2$ = 16.20 gm

Calculate the degree of hardness in clark's, French and in ppm scales.

Solution:-

$MgCl_2$ =	$CaSO_4$ =	$Ca(HCO_3)_2$ =	$CaCO_3$
24+71	40+32+64	40+2(1+12+48)	40+12+48
= 95	= 126	= 162	= 100

95 gm of $MgCl_2$ = 100 gm $CaCO_3$

$$9.50 \text{gm of } MgCl_2 = \frac{100}{95} \times 9.5$$

= 10 gm of $CaCO_3$.

$\therefore$ 136 gm of $CaSO_4$ = 100 gm of $CaCO_3$

$$13.6 \text{gm of } CaSO_4 \frac{100}{136} \times 13.6 = 10 \text{gm} CaCO_3$$

162 gm of $Ca(HCO_3)_2$ = 100 gm of $CaCO_3$

$$\therefore 16.2 \text{gm of } CA(HCO_3)_2 \frac{100}{162} \times 16.2 = 10 \text{gm} CaCO_3$$

Total weight of hardness causing substance in terms of $CaCO_3$ = 10 + 10 + 10 = 30 gm

Thus total hardness of water in terms of $CaCO_3$ in 30 gm per 70,000 C.C. (70,000 gm) of water.

(i) Clark's degree of hardness = 30^oCl (Clark's)

(ii) 7° Clark's scale = 10° French scale

30' Clark's scale = (10/7) X 30

= 42.857^o French

10° French scale = 100 ppm

42.857^o French scale (100/10) X 42.857 = 428.57 ppm

Ex. (4) Calculate temporary hardness and total hardness of sample of water containing $Mg(HCO_3)_2$ = 7.3 Mg/L, $Ca(HCO_3)_2$ = 16.2 Mg/L, $MgCl_2$ = 9.5 Mg/L, $CaSO_4$ = 13.6 Mg/L

Solution:-

$$\text{Temporary Hardness} = \left[\times \frac{100}{146} + 16.2 \times \frac{100}{162} \right] g / L$$

= (5 + 10) Mg/L

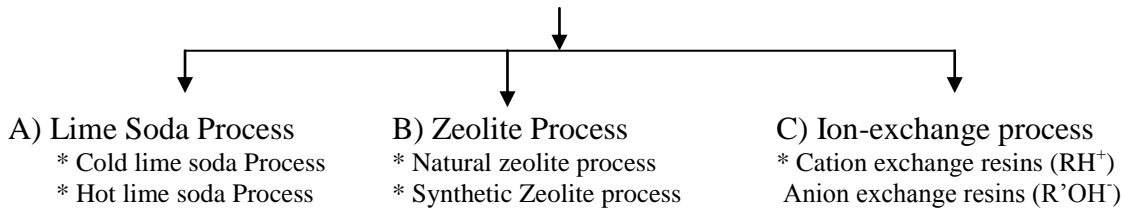$$= \quad 15 \text{ Mg/L}$$

$$\text{Permanent hardness} = \left(19 \times \frac{100}{95} + 13.6 \times \frac{100}{136} \right) \text{Mg/L}$$

$$= \quad (10 + 10) \text{ Mg/L}$$

$$= \quad 20 \text{ Mg/L}$$

Total Hardness $\quad = 15 + 20 = 35 \text{ Mg/L} = \text{ppm.}$

SOFTENING METHODS

A) Lime Soda Process
* Cold lime soda Process
* Hot lime soda Process

B) Zeolite Process
* Natural zeolite process
* Synthetic Zeolite process

C) Ion-exchange process
* Cation exchange resins (RH^+)
Anion exchange resins ($R'OH^-$)

Water Softening :-

Removal of hardness of water whether temporary or permanent hardness is done through the process called softening of water. It is very essential process since hard water is unsuitable for domestic as well as industrial purposes, In steam generation hard water creates number of problems like scale and sludge formation, priming and foaming etc.

Hardness can be removed by two methods

(1) **External Treatment**

(2) **Internal Treatment**

Lime –Soda Process

This is the most important method of water softening.

PRINCIPLE :- The principle involved in this process the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amount of **lime [$Ca(OH)_2$]** and **soda [$NaCO_3$]** . **Calcium carbonate [$CaCO_3$]** and **magnesium hydroxide [$Mg(OH)_2$]** , so precipitated, are filtered off.

Cold Lime –Soda Process

In this method-calculated amount of chemical (lime and soda) are mixed with water at room temperature. The precipitates formed are finely divided, so they do not settle down easily and can't be filtered easily. So it is essential to add small amounts of Coagulants (like alum, aluminum sulphate, sodium acuminate etc.). Which hydrolyze to flocculent (precipitate), gelatinous precipitate of aluminum hydroxide and entraps the fine precipitates.

Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.

→ Raw water and calculated amount of chemicals (lime + soda + coagulant) are fed on top into the inner vertical circular chamber, fitted with a vertical rotating shaft varying a number of paddles.

→ As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, so softening of water takes place.

→ The heavy sludge settles down in the outer chamber by the time and softened water reaches up.

→ The softened water then passes through a filtering media to ensure complete removal of sludge.

→ Filtered soft water finally flows out continuously through the outlet at the top.

→ Sludge settings at the bottom of the outer chamber are drawn of occasionally.

Hot Lime –Soda Process

In this process water is treated with required chemicals at a temperature of 80 ^{o} c to 150 ^{o}C.

Hot L-S process provides water, containing a residua hardness of 15 –30 ppm. The softener consists of following three parts-

(a) **Reaction Tank** – The tank has three separate inlets and third for superheated steam. After their entry they are mixed. The reaction starts and get completed in the reaction tank.

(b) **Conical Sedimentation Tank** – from reaction tank the reactants come in this tank and the sludge settles down.

(c) **Sand filter** – It has layer of lime and coarse sand, which works as filter and makes its possible to completely remove the sludge from the softened water.

Processing -

(i) In Hot L-S process reaction proceeds faster.

(ii) No coagulants are needed because sludge and precipitates settle easily.

(iii) Some dissolved gases like CO_2 also driven out of the water.

(iv) Viscosity of softened water is lower, so filtration of water becomes much easier.

(v) The softening capacity of hot process is many times higher than that of the cold process.

Advantages of Lime –soda Process.

(i) Lime Soda process is very economical.

(ii) It removes not only hardness causing salts but also minerals.

(iii) Due to alkaline nature of treated water, pathogenic bacteria's in water are reduced.

(iv) Iron and manganese are also removed.

(v) Treated water is alkaline and therefore less corrosive.

Disadvantages of Lime –soda Process.

(i) For efficient and economical softening, careful operation and skilled supervision is required.

(ii) Disposal of large amounts of sludge poses a problem.

(iii) This can remove hardness only upto 15 ppm, which is not good for boilers.

Calculation of Lime-Soda Requirement-

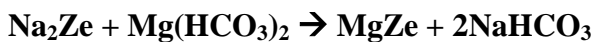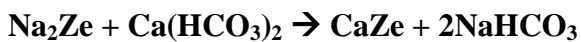| Constituent	Reaction	Need
Permanent Hardness of CaCl$_2$ and CaSO$_4$	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow 2NaCl$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow Na_2SO_4$	S S
Perm. Hard. Of MgCl$_2$ and MgSO$_4$	$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow CaCl_2$ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow 2NaCl$	L + S
Ca(HCO$_3$)$_2$ (Temp. Ca)	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow 2H_2O$	L
Mg(HCO$_3$)$_2$ (Temp. Mg)	$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow 2H_2O$	2L
HCO$_3^-$ (NaHCO$_3$)	$2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow H_2O + CO_3^{2-}$	L - S
Dissolved CO$_2$	$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow H_2O$	L
Free acids H$^+$ HCl and H$_2$SO$_4$	$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow 2NaCl$	L+S
H$_2$SO$_4$	$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow Na_2SO_4$	L+S
Coagulant FeSO$_4$	$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 \downarrow CaSO_4$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow Na_2SO_4$	L+S
Al$_2$(SO$_4$)$_3$	$2Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4$ $3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3 \downarrow 6Na^+$	L+S
NaAlO$_2$	$NaAlO_2 + H_2O \rightarrow Al(OH)_3 + NaOH$	-L

ZEOLITE OR PERMUTIT PROCESS

The word zeolite is derived from two Greek word (zein + lithos) means 'boiling stone'. Natural zeolite are non porous in nature. Chemical structure of sodium zeolite May be represented by Na_2O. Al_2O_3. x SiO_2. Y H_2O.   Where x   = 2 – 10, Y = 2 – 6.
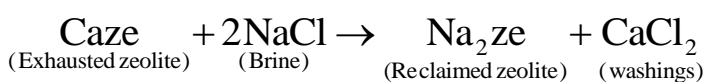
Zeolite is **hydrated sodium alumino silicate**, capable of exchanging reversibly its sodium ions for hardness – producing ions in water. Zeolites are also known as permutits. Zeolites are of two types. –

(i)   Natural Zeolites

(ii)   Synthetic zeoliets.

(i)   Natural Zeolite – are non porous. Ex.

Natrolite Na_2O, Al_2O_3 $3SiO_2$. $2H_2O$

Thomsonite (Na_2O, CaO). Al_2O_3. 2 SiO_2. 2 ½ H_2O

(ii)   Synthetic Zeolite – They are porous are posses gel structure. Such zeolile passes higher exchange capacity than natural zeolite but they are less durable.

PROCESS :- Hard water is percolated at a specific rate through a bed of zeolite, kept in a cylinder. Hardness causing ions (Ca^{2+}, Mg^{2+} etc) are retained by the zeolite as CaZe and MgZe, while outgoing water contains sodium salts.

Na_2Ze + $Ca(HCO_3)_2$ → $CaZe$ + $2NaHCO_3$

Na_2Ze + $Mg(HCO_3)_2$ → $MgZe$ + $2NaHCO_3$

Na_2Ze + $CaCl_2(CaSO_4)$ → $CaZe$ + $2NaCl$ (or Na_2SO_4)

Na_2Ze + $MgCl_2$ (or $MgSO_4$) → $MgZe$ + $2NaCl$ (or Na_2SO_4)

Regeneration:- When the zeolite bed is exhaused (saturated with Ca^{2+} and Mg^{2+}), it can be regenrated and reused. **Exhausted zeolite is reclaimed by treating the bed with a brine (10% NaCl) soultion.**

$$\underset{(Exhausted\,zeolite)}{Caze} + \underset{(Brine)}{2NaCl} \rightarrow \underset{(Re\,claimed\,zeolite)}{Na_2ze} + \underset{(washings)}{CaCl_2}$$

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

LIMITATION:-

(i)   Water with turbidity should not be used as pores of zeolite get clogged.

(ii)   PH of water should not be too high or too low as it affects zeolites.

(iii) Water containing Fe^{2+} and Mn^{2+} ions should be avoided because Fe^{2+} will form their zeolite which can't be easily regenerated.

(iv) Hot water can't be used as it dissolves zeolite.

(v) Mineral acids, if present in water, destroy the zeolite bed.

ADVANTAGES

(i) Hardness is completely removed.

(ii) Equipment used is compact and occupies less space.

(iii) There is no danger of sludge formation.

(iv) It is quite clean.

(v) It requires less time for softening.

ZEOLITE PROCESS	LIME SODA PROCESS
(i) Water with zero hardness is produced.	(i) Water with 15 to 50 pm hardness is produced.
(ii) Capital cost is higher.	(ii) Capital cost is lower.
(iii) Operation cost is lower because exhausted zeolite is regenerated.	(iii) Operation cost is higher because lime and soda are consumed.
(iv) Plant is compact and occupies less space.	(iv) Plant occupies more space.
(v) Can not be used for hot water, acidic water or turbid water.	(v) Process is free from any such limitations.
(vi) No. problem of sludge formation.	(vi) There may be problem after precipitation.
(vii) Salt causing temporary hardness are converted into $NaHCO_3$ which is present (i) soft water.	(vii) Temporary hardness is completely removed in the form of insoluble $CaCO_3$ and $Mg(OH)_2$.
(viii) It does not involve any secondary operation like salt, lime, coagulation, filtration.	(viii) This involves all problems associated with setting coagulation and filtration.

Solved Examples Based on Hardness.

Ex. (1) The hardness of 1000 litres of a water sample was completely removed by a zeolite softener. The zeolite had required 30 litres of NaCl solution, containing 1,500 mg/L of NaCl for regeneration. Calculate the hardness of the water sample.

Solution-

30 litres of NaCl solution contains

$$= 1.50 \times 30 \text{ g} = 45 \text{ g of NaCl.}$$

$$= \frac{45 \times \frac{50}{58.5} \text{ g}}{} \text{ of CaCO3 equivalent hardness.}$$

This much hardness may be deemed to be present in 1000 litres of water sample.

$\therefore$ Hardness of the water sample.

$$= 45 \times \frac{50}{58.5} \times \frac{1,000}{1,000} \text{ Mg / L}$$

$$= \quad 38.46 \text{ ppm}$$

Ans.

Ex. (2) An exhausted zeolite softener was regenerated by passing 150 litres of NaCl solution, 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 softener ?

Solution-

150 litres of NaCl solution contains

150 X 150 g $=$ 22,500 g NaCl

$$= 22,500 \times \frac{50}{58.5} \text{ g of CaCO}_3 \text{ eq. hardness}$$

Given that 1 litre of hard water contains 600 ppm hardness = 600 mg of $CaCO_3$ = 0.6 g of $CaCO_3$.

$\therefore$ The amount of hard water that can be softened by this softener

$$= \frac{22,500 \times 50}{0.6 \times 58.5}$$

$$= \quad 32,051 \text{ litres.}$$

Ex. (3) The hardness of 100000 litres of a sample of water was completely removed by passing it through a zeolite softener. The softener then required 400 litres of sodium chloride solution containing 100 g/litre of NaCl for regeneration. Calculate the hardness of the water sample.

Solution –

400 L of NaCl solution

$= \quad$ 400 L X 100 g/L $\quad = 40,000$ g NaCl

$$= 40,000 \times \frac{50}{58.5} \text{ g CaCO}_3 \text{ eq.}$$

$$= 34,188 \text{ g CaCO}_3 \text{ eq.}$$

$\therefore$ Hardness of 100,000 L water $= 34,188$ g $CaCO_3$ eq.

Or

$$\text{Hardness of 1L water} = \frac{34,188}{100,000}$$

$$= \quad 0.3419 \text{ g } CaCO_3 \text{ eq.}$$

$$= \quad 341.9 \text{ mg}$$

ION EXCHANGE OR DE-IONIZATION PROCESS:-

→ 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.

→ Resins containing acidic functional groups (-COOH, -SO$_3$H etc) are capable of exchanging their H^+ ions with other cations.

→ Resins containing basic functional groups (-NH$_2$) are capable of exchanging their anion with other anion.

(i) **Cation exchange resins (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.

(ii) **Anion exchange resins (R' OH$^-$) are styrene** – divinyl benzene or amine formaldehyde copolymers, which contain amino groups as an integral part of the resin. These after treatment with dil NaOH solution become capable to exchange their OH$^-$ anions with other anions of water.

PROCESS :- The hard water is passed first through cation exchange column, which removes all the cations like Ca^{2+}, Mg^{2+} etc. from it, and equivalent amount of H^+ ions are released from this column to water. Thus;

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

$$2RH + Mg^{2+} \rightarrow R_2Mg + H^+$$
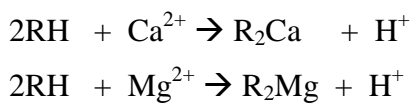
After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-}, Cl^- etc. present in the water and equivalent amount of OH^- ions are released from this column.

$$R'OH + Cl^- \rightarrow R'Cl + OH^-$$

$$2R'OH + SO_4^{2-} \rightarrow R_2'SO_4 + 2OH^-$$
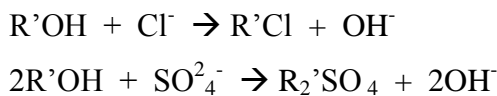
H^+ and OH^- ions get combined to produce water molecule.

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

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

REGENRATION :-

After long use the exchange capacity of cation and anion exchange resins is lost, they are then called to be exhausted.

The exhausted cation exchange column is regenerated by passing a solution of **dil HCl** or **dil H$_2$SO$_4$**.

$R_2Ca + 2H^+ \rightarrow 2RH + Ca^{2+}$ (washing)

The exhausted anion exchange column is regenerated by passing a solution of dil NaOH.

$R_2'SO_4 + 2OH^- \rightarrow 2R'OH + SO_4^{2-}$ (washings)

Advantages :-

    <u>(i)</u>   The process can be used to soften highly acidic or alkaline water.

    <u>(ii)</u>   It produces water of very low hardness (~2ppm). So it is very good for treating water for use in high pressure boiler.

Disadvantages :-

    (i)   The equipment is costly and more expensive chemicals are needed.

    (ii)   If water contain turbidity, then the output of the process is reduced.
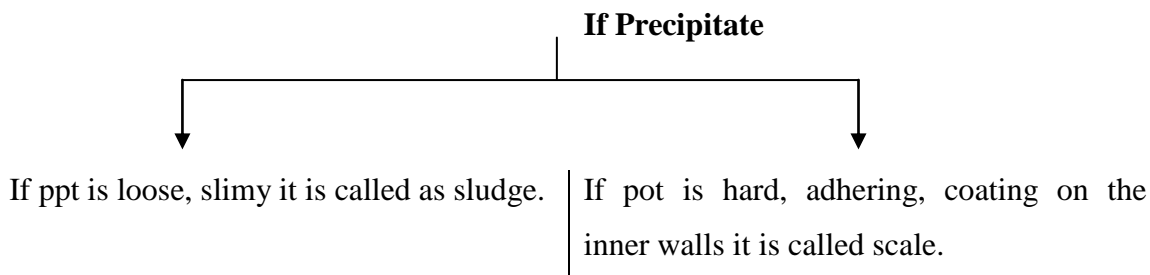
BOILER TROUBLE

A proper quality of water for use in boilers is very important. If impure water is made use of as boiler feed water, then following boiler problems may occurs.

    (i)   **Sludge and scale formation.**

    (ii)   **Corrosion of boiler metal.**

    (iii)   **Caustic embrittlement.**

    (iv)   **Priming and foaming.**

(i)   **Sludge and Scale Formation.**

    In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler.

If Precipitate

If ppt is loose, slimy it is called as sludge.	If pot is hard, adhering, coating on the inner walls it is called scale.

Sludge :-

(1)   It is a soft, loose, slimy precipitate.

(2)   It can be easily scrapped off with a wire brush.

(3)   Sledges are formed by substances which have greater solubility in hot water than in cold water. Ex. MgCO$_3$, MgCl$_2$, MgSO$_4$, etc.

(4)   It is formed at colder portions of the boiler and collects in areas, where flow rate is slow.

Disadvantages of Sludge formation :-

(1)   Sludge is poor conductors of heat, so they tend to waste a portion of heat and thus decrease boiler efficiency.

(2)   It sludge are formed along with scale, then sludge gets entrapped in the scale and both get deposited as scale.

(3)   Excessive sludge formation disturbs the working of the boiler.

(4)   Sludge deposited on pipe connection, plug opening so choking of pipes takes place.

Prevention of sludge formation:-

(1)   By using well softened water.

(2)   By frequent 'Blow down operation'

        Blow down operation is "Partial removal of concentrated water through a outlet at the bottom."

SCALE :-

(1)   Scales are hard deposit.

(2)   They stick very firmly to the inner surface of the boiler.

(3)   They are difficult to remove, even with the help of hammer and chisel.

(4)   Scales are main source of boiler trouble.

Formation of Scale due to –

(1)   Decomposition of Calcium bicarbonate-

$$Ca(HCO_3)_2 \rightarrow \underset{(Soluble)}{Ca(OH)_2} + Co_2 \uparrow$$
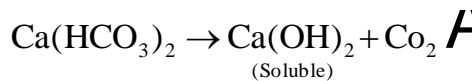
        This scale is soft and is the main cause of scale in lower pressure boiler. But in high pressure boilers $CaCO_3$ is soluble.

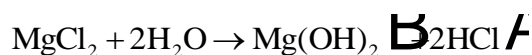$$CaCO_3 + H_2O \rightarrow \underset{(Soluble)}{Ca(OH)_2} + CO_2 \uparrow$$
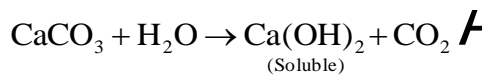
(2)   Deposition of $CaSO_4$ – The solubility of $CaSO_4$ in water decreases with rise of temperature.

Temp.	15^oC	230^oC	320^oC
Solubility	3,200 ppm	55 ppm	27 ppm.

Means $CaSO_4$ is soluble in cold water but almost completely insoluble in super heated water.

(3)   Hydrolysis of Mg Salts-

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 \downarrow 2HCl \uparrow$$

It forms $Mg(OH)_2$ ppt. This forms a soft type of scale.

(4) **Presence of silica – (SiO_2)** – Even present is small quantities deposits as $MgSiO_3$ and $CaSiO_3$. It deposited in the inner walls of boiler and very difficult to remove.

Disadvantage of Scale formation-

(1) **Wastage of fuel** – Scales are poor conductor of from boiler to inside water is decreased. So excessive or over heating is deeded, this causes increase in fuel consumption.

Thickness of Scale	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(2) **Lowering of boiler safety** – The over heating of the boiler tube makes the boiler material softer and weaker this causes distortion of boiler tube and make boiler unsafe.

(3) **Decrease in efficiency** – Scales sometimes deposited in the valves and condensers of the boiler and choke them, this results in decrease in efficiency.

Prevention of Scale formation-

Internal treatment – An internal treatment is accomplished by adding a proper chemical to the boiler water. Some methods are-

(1) **Colloidal Conditioning** – In lower pressure boiler by adding organic substance like – kerosene, tannin, agar – agar. Scale formation can be avoided. They get converted over the scale, so scale will be non sticky and loose deposits, which can easily be removed by blow down operation.

(2) **Phosphate Conditioning** – In high pressure boilers by adding sodium phosphate scale formation can be avoided. They formed non-adherent and easily removable, soft sludge of phosphate. Which can easily removed by blow – down operation.

$3cacl_2 + 2Na3SO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$
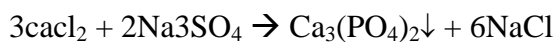
   (i) NaH_2PO_4 - Sodium elihydrogen phosphate (acidic)

   (ii) Na_2HPO_4 - Disodium hydrogen phosphate (weak alkaliz)

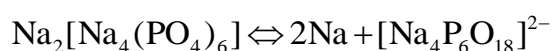   **(iii)** Na_3PO_4 - Tri sodium phospate (alkaline)

       The use of salt depends upon the alkalinity of water. Calcium precipitated at PH value b/w 9.5 – 10.5.
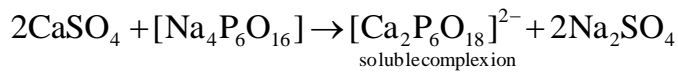
(3) **Carbonate Conditioning** – In lower pressure boiler scale formation can be avoided by adding sodium carbonate.

$CaSO_4 + Na_2CO \Leftrightarrow CaCO_3 + Na_2SO_4$

$CaCO_3$ is loose sludge which can be removed by blow down operation.

(4) **Calgon Conditioning** – By adding calgon (Sodium hexa meta phosphate ($NaFO_3)_6$ in boiler water. It forms soluble complex with Ca^+ ion.

$Na_2[Na_4(PO_4)_6] \Leftrightarrow 2Na + [Na_4P_6O_{18}]^{2-}$

$$2CaSO_4 + [Na_4P_6O_{16}] \rightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$
$$\text{soluble complex ion}$$

(5) **Treatment with sodium aluminate ($NaAlO_2$) :-** $NaAlO_2$ gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminum hydroxide.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \quad\text{(ppt)}$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$
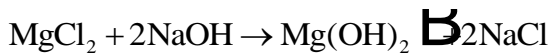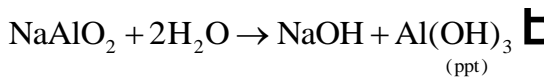
The ppt of $Mg(OH)_2$ plus $Al(OH)_3$ produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica.
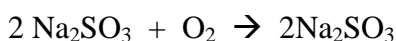
(ii) **CORROSION OF BOILER METAL**

Boiler corrasion is deeay of boiler material by a chemical a Hack by its environment Main resons for boiler corrasion are-

(a) **Dissolved Oxygen –** Water usually contains above 8 mL of dissolved oxygen per litre. Dissolved oxygen in presence of high temperature, attacks boiler material-
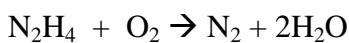
$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2\downarrow$

$4Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3 . 2H_2O]\downarrow$
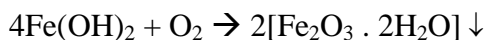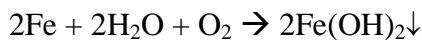
$\qquad\qquad$ Rust.

Removal of dissolved Oxygen-

$2 Na_2SO_3 + O_2 \rightarrow 2Na_2SO_3$

so, sulphite

$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$

**(b)** **By Mechanical de aeration –** Water spraying ina perforated plate – fitted tower, heated from sides and commeeted to veccum pump. High temperature low pressure and large expased surface reduees the dissolved oxygen in water.

(iii) **CAUSTIC EMBRITTLEMENT**

$\qquad$ This type of boiler corrosion is caused because of use of high alkaline water in high pressure boilers. When water is softened by lime and soda process and is ped into the boiler it may be likely that some residual Na_2CO_3 is still present in the softened water. Na_2CO_3 decomposer to give NaOH and CO_2, and NaOH thus produced makes the boiler water caustic.

$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\downarrow$
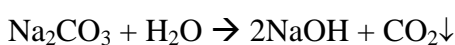
The NaOH containing water floues into the minute hair cracks always present in the inner side of boiler by capillary action. Here water evaporates and the dissolved caustic soda concentration increases progressively and attacks the surrounding boiler material and iron is dissolved as sodium ferrate. This causes embrittlement of boiler walls more particularly stressed parts. Like bends, joints   rivets etc. causing even boiler failure.

Embitterment arises due to setting up of a concetration cell, with the iron surrounded by dil NaOH acts as a cathode while the iron surrounded by conc. NaOH acting as the Anode.

Iron at + rivets, bends Joints, etc.	Concentrated NaOH Solution	Dilute NaOH Solution	- Iron at Plane surfaces.

Caustic Embrittlement can be avoided.

   (i)   By using sodium phosphate as softening reagent instead of sodium carbonate.
   (ii)   By adding tannin or lignin to boiler water, since these blocks the hair cracks.
   (iii)   By adding sodium sulphate the boiler water;

It has been observed that caustic cracking can be prevented, it Na2SO4 is added to boiler water so that the ratio-

$$\frac{Na_2SO_4 \text{ concentration}}{NaOH \text{ concentration}}$$

Is kept as 1 : 1 : 2 : 1 and 3 : 1 in boilers working respectively at pressure up to 10,20 and above 20 atmosphere.

(iv)   PRIMING AND FOAMING

PRIMING – When steam is generated rapidly in the boilers, some droplets of the liquid water are carried along with the steam. This process is called wet steaming or priming.

Priming is caused by-

   (i)   The presence of large amount of dissolved solids.
   (ii)   High steam velocities.
   (iii)   Sudden boiling.
   (iv)   Improper boiler design.
   (v)   Sudden increase in steam production rate.

Priming can be avoided by-

   (i)   Avoiding rapid change in steaming rate.
   (ii)   Proper boiler design so that water level in boilers may be maintained at low level.

(iii)   Only soft water to be used.

FOAMING – Foaming is the formation of small but stable bubbles above the surface of water, which do not break easily.

Foam formation takes place when concentration of solids in the surface layer is different from that in the mass of the liquid.

Foaming is caused by – The presence of substances like oil (which greatly reduce the surface tension of water.)

Foaming can be avoided By-

(i)   The addition of antifoaming agents which reduces the surface tension of water. Ex.- caster oil.

(ii)   Removing oil from boiler water by adding compound like sodium aluminate.


Determinate of Alkalinity-

Alkalinity of water means the total content of those substances in it, which causes an increased $[OH]^-$ upon dissociation.

Alkalinity of water may be due to presence of:

(i)   Caustic alkalinity (due to OH^- and due CO^{2-}_3 ions)

(ii)   Temporary hardness (due to HCO^-_3

These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicator. The determinations are based on following reaction.

(i) $OH^- + H^+ \rightarrow H_2O$

(ii) $CO_3^{2-} + H^+ \rightarrow [HCO_3^-]$

(iii) $HCO_3^- + H^+ \rightarrow H_2O + CO_2$

P

M
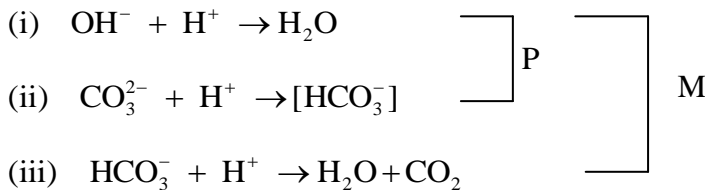
The titration of the water sample against a standard acid up to phenolphthalein end point (P) marks the completion of reaction, (i) and (ii) only this amount of acid   used thus corresponds to hydroxide plus ½ of normal carbonate present.

On the other hand, titration of water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii) and (iii). Hence the total amount of acid used represent the total alkalinity.
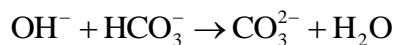
Thus

$P = OH^-$ and $\dfrac{1}{2} CO_3^{2-}$

$M = OH^-$, CO_3^{2-} and HCO_3^-

The possible combinations of ions causing alkalinity

(i)   water are-

(ii)   OH⁻ Only or (ii) CO_3^{2-} only or (iii) HCO_3^- only or (iv) OH⁻ and CO_3^{2-} together (v) CO_3^{2-} and HCO_3^- together.

*   The possiblility of OH⁻ and HCO_3^- ions together is ruled out because they combine instantaneously to from CO_3^{2-} ions.

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$$

e.g.   NaOH + NaHCO₃ → NaCO₃ + H₂O

thus, OH- and HCO_3^- ions can't exist together in water. On the basis of same, all the three (OH⁻, CO_3^{2-} and HCO_3^-) can't exist together.

→ Table is as follows.

Alkalinity	OH-	CO_3^{2-}	HCO_3^-
P=0	Nil	Nil	M
P=M	M	Nil	Nil
P= ½ M	Nil	2P	Nil
P> ½ M	(2P-M)	2(M-P)	Nil
P < ½ M	Nil	2P	[M-2P]

Alkalinity is generally represented in ppm.

Nu. → 100 ml of water sample, on titration with N/50 H₂SO₄ gave a litre value of 5.8 ml to [P] end point and 11.6 ml to [M] end point. Calculate the alkalinity of the water sample in terms of CaCO₃ and comment on the type of alkalinity present.

Solⁿ → P = 5.8 ml,   M = 11.6 ml

Since   P = ½ M,   it means all alkalinity is due to CO_3^- only.

Further, the volume of N/50 H₂SO₄ eq. To Co_3^{2-} present in 100 ml of water sample.

    =   2 P

    =   2 X 5.8=   11.6 ml

Since 1 ml of 1N H₂SO₄   =   50 mg of CaCO₃

    11.6 ml of N/50 H₂SO₄ =   50 X 11.6 X (N/50)

            =   11.6 mg of CaCO₃

This is the CO_3^- present om 100 ml of water

∴ Amount of CO_3^- present in 1 litre of water

    =   11/6 X (1000/100)

    =   116 mg/L   =   116 ppm

Result = The alkalinity of water sample is 116 ppm which is only due to CO_3^-.

Nu. (2) A water saple is not alkaline to [P] However, 100 ml of the sample, on titration with N/50 HCl, required 16.9 ml to obtain the end point, using [M] as indicatar, are tlu types and amount of alkalinity present in the sample ?