Water Treatment

Hard water :- water which donot form lather with soap easily

Soft water :- water which form lather with soap easily.

Hardness of water :- soap consuming capacity of water to form lather is called the Hardness of water.

→ Bicarbonates of Ca^{+2} and Mg^{+2} :- $Mg(HCO_3)_2$
↳ Temporary hardness $Ca(HCO_3)_2$

→ Chlorides of Ca^{+2} & Mg^{2+} → $CaCl_2$, $MgCl_2$

→ sulphates of Ca^{+2} and Mg^{+2} → $CaSO_4$, $MgSO_4$

→ other salts :-
Fe^{+2}, Al^{3+}, HCl & H_2SO_4, CO_2, H_2S

Temporary Hardness :- which can simply be removed by boiling ~~or~~ and Filteration.

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3\downarrow + H_2O + CO_2$$

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2$$

Permanent Hardness :- Hardness which cannot simply be removed by boiling.

To remove it's hardness there are following processes :-

- R.O. Process (Reverse osmosis)

Imp
- zeolite process
- Ion - exchange process
- L.S. (Lime Soda process)
- Calgon's - conditioning.

units for measuring Hardness of water :-

1) mg/L :- 1mg of Hardness causing salt in 1 Litre.

2) PPM (Parts per million) :- 1 part of Hardness causing salt in 10^6 parts of water.

Imp ** $1 mg/L = 1 PPM$ (Proof)

3) 1 Degree Clark [$1^\circ Cl$] :- 1 Part of Hardness causing salt in 70,000 parts of water.

4) 1 Degree French [$1^\circ Fr$] :- 1 part of Hardness causing salt in 1 lakh parts of water.

Interrelationship b/w diff units of Hardness

$$[1 mg/L = 1 PPM = 0.1^\circ Fr = 0.07^\circ Cl]$$

Q 111 mg of $CaCl_2$ is present in 1 Litre of water?

Multiplication factor of $CaCl_2 = \frac{100}{111}$

Hardness in terms of $CaCO_3$ = (Amount of Actual Hardness causing salt in mg/L) × (Multiplication factor)

$= \cancel{111} \times \frac{100}{\cancel{111}} = 100$ mg/L

Multiplication factors of Some Hardness causing salts (HCS):-

Name of HCS	Mol. wt	Eq. wt.	Multiplication factor
1) $Ca(HCO_3)_2$	162	81	$M.F. = \frac{\text{mol. mass of } CaCO_3}{2 \times \text{Eq. wt. of HCS}}$ $= \frac{100}{2 \times \text{eq. HCS}}$ $= \frac{100}{2 \times 81} = \frac{100}{162}$
2) $Mg(HCO_3)_2$	146	73	$\frac{100}{2 \times 73} = \frac{100}{146}$
3) $CaCl_2$	111	$\frac{111}{2}$	$\frac{100}{111}$
4) $CaSO_4$	136	$\frac{136}{2}$	$\frac{100}{136}$
5) $MgCl_2$	95	$\frac{95}{2}$	$\frac{100}{95}$
6) $MgSO_4$	120	$\frac{120}{2}$	$\frac{100}{120}$

Ca^{++}	40	$\frac{40}{2}$	$\frac{100}{40}$
Mg^{++}	24	$\frac{24}{2}$	$\frac{100}{24}$
OH^-	17	17	$\frac{100}{2\times17} = \frac{100}{34}$
HCl	36.5	36.5	$\frac{100}{2\times36.5} = \frac{100}{72}$
$Mg(NO_3)_2$			$\frac{100}{148}$
Al_2SO_4	342	57	$\frac{100}{2\times57} = \frac{100}{114}$

Q A sample of water/L contains 16.2 ppm calcium bicarbonate, 14.6 mg/L of $Mg(HCO_3)_2$ 9.5 mg/L of $MgCl_2$ and 10 mg/L of HCl calculate the ~~temporary~~, permanent and Total Hardness of water

Hardness in terms of $CaCO_3$:- $\frac{100}{\cancel{162}} \times \overset{0.1}{\cancel{16.2}} + \frac{100}{\cancel{146}} \times \overset{0.1}{\cancel{14.6}}$

$+ \frac{100}{\cancel{95}} \times \overset{0.1}{\cancel{9.5}} + \frac{100}{72} \times 10$

$= 30 + 13.8 = 43.8$ mg/L

Imp Removal methods of Temporary hardness

1) By boiling followed by filteration

i) $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2$

↳ filter out

ii) $Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 \downarrow + H_2O + CO_2$

$\xrightarrow{filter} Mg(OH)_2 + 2CO_2$

2) Clark's method :-

↳ Addition of lime {$Ca(OH)_2$

i) $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + \cancel{2H_2O + CO_2}$

ii) $Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 + CaCO_3 + 2H_2O$

Q why the hardness of water is always expressed in terms of $CaCO_3$

There is no logical reason for that besides the two fact :-

i) $CaCO_3$ is supposed to be the most insolluble in water

ii) It's Molecular weight is 100 so it's make the calculation easier.

Method for Removal of permanent hardness

1) Reverse osmosis (R.O.) :-

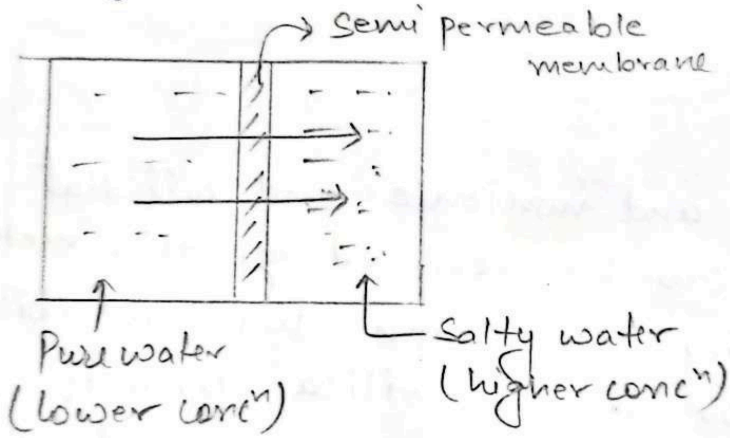
↳ (De-salination of sea or Brackish water or Hyper filteration or Superfilteration)

Principle :-

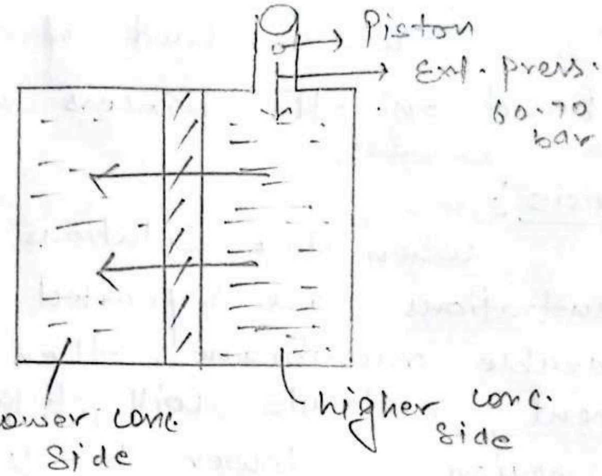
This method of water purification is based on the process of osmosis.

Osmosis :-

when two solutions of different concentrations are seperated by a semi-permeable membrane, then the flow of Solvent molecule will take place from the region of lower to Higher concn.



If however, an external pressure higher than the osmotic pressure is applied on the higher concn side then the flow of solvent is reversed i.e. now it starts flowing from higher concn side to lower concn side. This process is known as reverse osmosis process.



Reverse osmosis

Advantages :-

i) Both ionic and nonionic and collidial Impurities can be removed by this method.

ii) Low operating cost with high reliability

iii) It can also remove silica particles.

iv) Membrane can easily be removed with in few minutes.

2) Zeolite process / Permulit process

This process is used for removing both Temporary and permanent Hardness causing salt from water. In this process zeolite in the form of its sodium salt (sodium zeolite) is used as a water softening ~~Agent~~ Zeolite is chemically hydrated Sodium Alumino silicate, ($Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$) ($Na_2Ze$)

Process of water softening :-

In this process the hardwater is passed over the zeolite softener. The calcium and magnesium cations present in the hard water get exchanged by the sodium ions of the zeolite forming calcium and magnesium zeolite.

In this condition the zeolite gets exhausted and in order to regenerate it again a 10% NaCl solution (Brine solⁿ) is used for its regeneration

Removal of Ca^{++} & Mg^{++} from Hard water

A) $Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$
(Calc. zeolite)
(Exhausted zeolite)

B) $Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$
(Mag. zeolite) (Exh. zeolite)

C) $CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$
(Exh. zeolite)

D) $MgCl_2 + Na_2Ze \longrightarrow MgZe + 2NaCl$

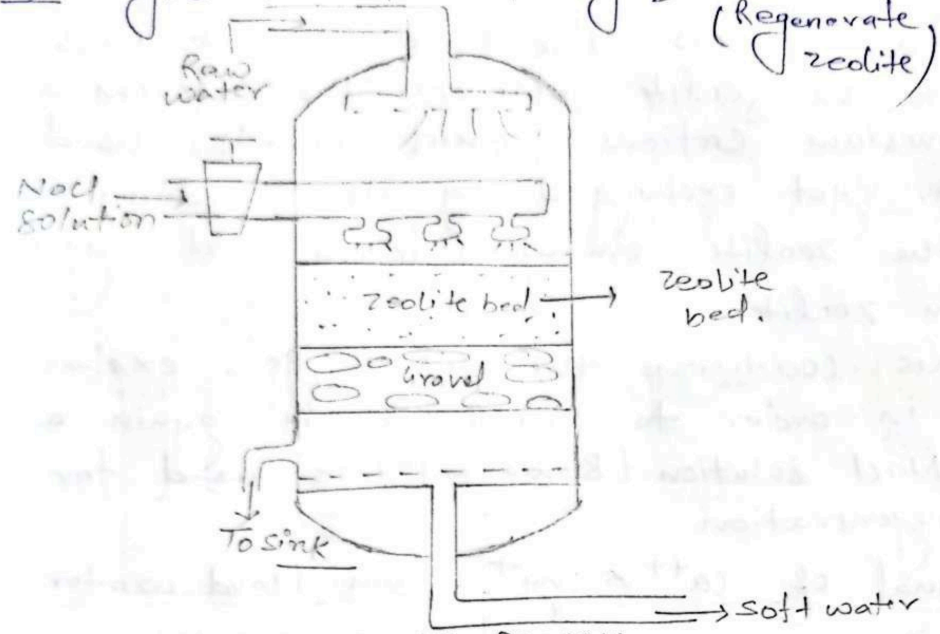
E) $CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$

F) $MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$

Regenerature of Exhausted Zeolite :-

1) $CaZe + \underset{10\%}{2NaCl} \longrightarrow Na_2Ze + CaCl_2$
(Sod. zeolite)
(Reg.)

2) $MgZe + 2NaCl \longrightarrow MgCl_2 + Na_2Ze$ (Regenerate zeolite)



Zeolite Process

Advantages :-

i) It is a cheap process as zeolite be easily regenerated.

ii) The whole setup equipment occupies less small space.

iii) upto 10 ppm of Hardness can be obtained.

iv) No sludge formation.

Disadvantages

i) This method is not suitable for water with high turbidity

ii) If mineral acid is present in water it will destroy the zeolite bed.

iii) It is not suitable for water containing Fe_2^{++} and Mn^{++} salts.

Rules for solving the numerical problems of Zeolite :-

i) Calculate the total amount of NaCl in (mg) required to regenerate the zeolite.

ii) convert this NaCl amount ~~to~~ in terms of Calcium Carbonate by multiplying by its multiplication factor $\left(\frac{100}{117}\right)$.

iii) Finally deride the above amount by the total volume of Hard water in Litres. This will give you the formula ~~of~~ for Calculating the hardness of water sample in mg/L.

$$\left\{\frac{\left(\begin{array}{c}\text{Total Amount of}\\ \text{NaCl in mg}\end{array}\right)\times\frac{100}{117}}{\begin{array}{c}\text{Total Vol. of Hard water}\\ \text{in (L)}\end{array}} = \begin{array}{c}\text{Hardness}\\ \text{of water in}\\ \text{terms of } CaCO_3\\ \text{in mg/L}\end{array}\right\}$$

Q The Hardness of 50,000 Litres of Hard water is removed by passing it over zeolite. The zeolite required 250 Litres of NaCl Having concn. (130 gm NaCl / L) for its regeneration. calculate the hardness of the water sample in zeolite.

$$\frac{(130\times1000\times250)\times\frac{100}{117}}{50,000} = 555.56\ ppm$$

Q An exhausted zeolite softener was regenerated by passing 150 Litres of 5% NaCl How many Litres of Hardness water having hardness 600ppm will softened by this zeolite.

** 5% NaCl $\longrightarrow$ 5gm/100 ml

$= 50 gm/L$

so
$$\frac{(50 \times 150 \times 1000 \text{ mg NaCl}) \times \frac{100}{117}}{x} = 600$$

$= 10683.76$ Litre.

Q Calculate the amt of NaCl required in gm to regenerate 60,000 litres of Hard water having hardness 600 ppm

$$\frac{x \times \frac{100}{117}}{60{,}000} = 600$$

$x = 42120$ gm

Ion- Exchange Method

(or)

Deionization or Demineralization of Hard water

This process is most commonly used for the purification/softening of both temporary and permanent hardness. In this process the hard water is softened by using ion-exchange Resins (both Cationic & Anionic).

→ **Cationic Resin :-** They are represented as $[R-H^+]$ these are complex organic molecules with Acidic functional groups like $-COOH$, $-SO_3H$ etc. These are capable of exchanging their (H^+) ions with the cations present in Hard water

→ **Anionic Resin :-** They are represented as $[R-OH^-]$ they are complex organic molecules with Basic functional group.
They are capable of exchanging the (OH^-) ions with the anions present in the Hard water.

→ **Process :-** The Hard water is first passed through Cationic Resign where all the cations of Calcium and magnesium (Ca^{++} and Mg^{++}) are taken by the Resign and equivalent amount of H^+ ion are released from the resign to the water.

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

$2RH^+ + Mg^{++} \longrightarrow \underset{\text{Exhausted Cationic Resin}}{R_2-Mg} + 2H^+$

Now, the water (cation free) is passed through anionic Resin where all the anions present in Hard water by chloride, sulphate and absorbed by the resin and eq. ~~atom~~ amount of OH ions gets released into water

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

$R-OH^- + SO_4^{--} \longrightarrow R_2SO_4 + 2OH^-$

(Exhausted Anionic Resin)

<u>Regeneration</u> of <u>cationic and Anionic Resins</u>

For the regeneration of cationic Resin (HCl and H_2SO_4) is needed and for Regeneration of Anionic Resign we need NaOH.

<u>Rxn</u>:- a) cationic <u>Resin</u>:-

$R_2Ca + 2HCl \longrightarrow 2RH^+ + CaCl_2$

$R_2Mg + 2HCl \longrightarrow 2RH^+ + MgCl_2$

b) <u>Anionic Resin</u>:-

$R-Cl + NaOH \longrightarrow R-OH^- + NaCl$

$R_2SO_4 + NaOH \longrightarrow 2R-OH^- + Na_2SO_4$

Advantages :-

i) water upto a very low Hardness of 2ppm can be obtained.

ii) Highly Acidic and Highly Alkaline water can also be softened.

Disadvantages

i) The equipments are costly

ii) The chemical req. for regeneration is expensive

iii) Highly turbid water decrease/decline the efficiency of this process.

Lime soda process
→ only for Numerical problems.

Salts resins Lime only $\{Ca(OH)_2\}$	Salts Resins soda Na_2CO_3	Salts need both lime soda.
$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2L$	$CaCl_2 + Na_2CO_3 \rightarrow 1S$	$MgCl_2 + \rightarrow (1L + 1S)$
$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow 2L$	$CaSO_4 + Na_2CO_3 \rightarrow 1S$	$MgSO_4 \rightarrow (1L + 1S)$
$CO_2 + Ca(OH)_2 \rightarrow 1L$		$Fe^{++} \rightarrow (1L + 1S)$
$H_2S + Ca(OH)_2 \rightarrow 1L$		$Al^{3+} \rightarrow (1L + 1S)$
$HCO_3^- + Ca(OH)_2 \rightarrow 1L$		$HCl/H_2SO_4 \rightarrow (1L + 1S)$

Formula Req. for Lime in mg $= \frac{74}{100}\left[Ca(HCO_3)_2 + 2(Mg(HCO_3)_2) + CO_2 + H_2S + HCO_3^- + MgCl_2 + MgSO_4 + Fe^{++} + Al^{3+} + HCl/H_2SO_4\right]$

↓

All are concⁿ of salts in mg/L but in terms of $CaCO_3$.

$\times$ (Total vol. of Hard water (L)).

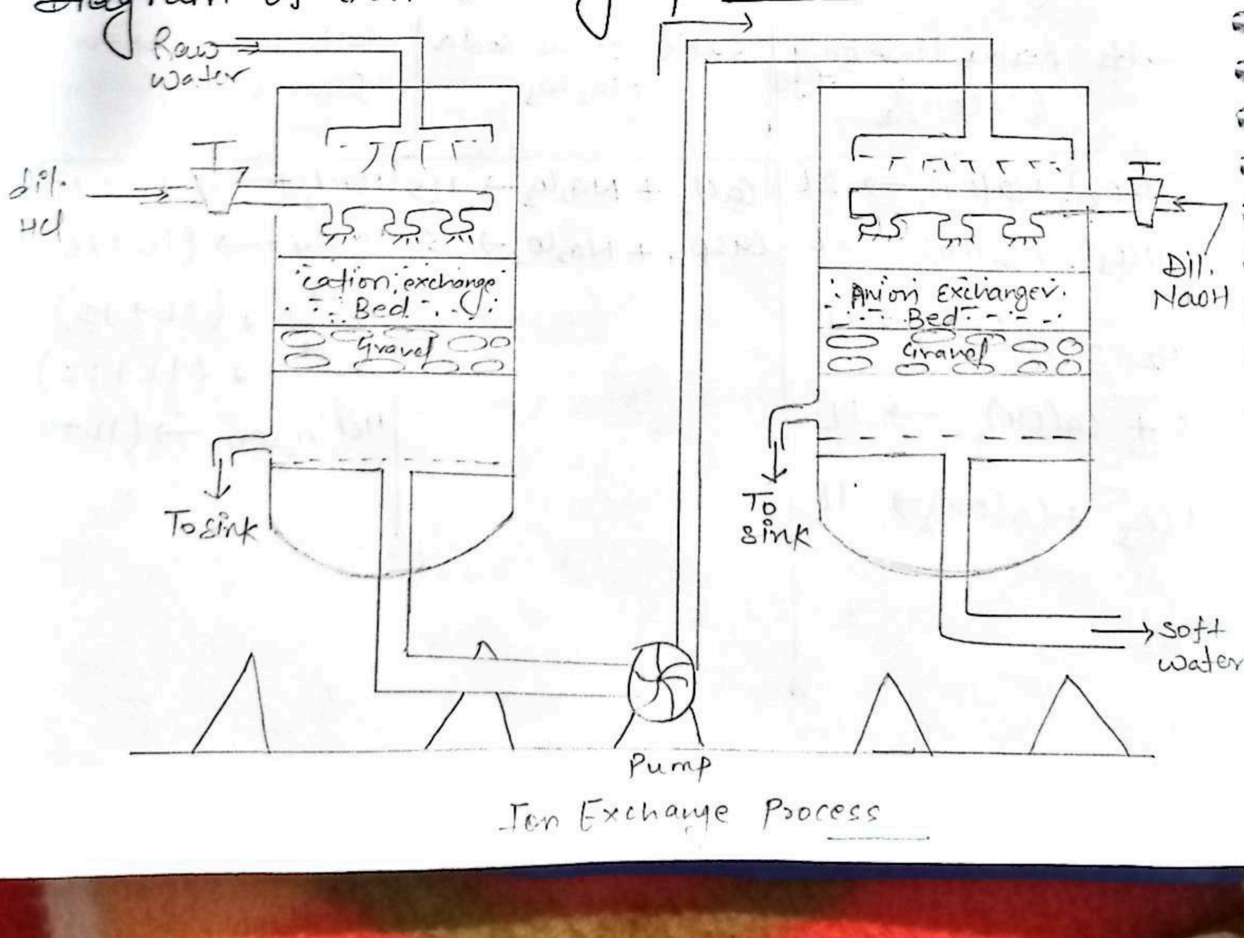
$\times \frac{100}{\text{\% purity of Lime}}$

Soda Req. in mg $= \frac{106}{100}\left[CaCl_2 + CaSO_4 + MgCl_2 + MgSO_4 + Fe^{++} + Al^{3+} + HCl/H_2SO_4 - HCO_3^-\right] \times$ Total vol. of Hard water

All in terms of $CaCO_3$

$\times \frac{100}{\text{\% purity of soda}}$

Diagram of Ion-Exchange process :-



Ion Exchange Process

Q calculate the amount of lime 90% pure and soda 90% pure required for treatment of 10^6 Litres of Hard water containing following salts

$Ca(HCO_3)_2$ = 8.1 PPm , HCO_3^- = 91.5 PPm , $Mg(HCO_3)_2$ = 14.6 ppm
$CaCl_2$ = 50 PPm , $MgCl_2$ = 40 PPm , $Al_2(SO_4)_3$ = 20 mg/L

concentration in terms of $CaCO_3$:-

$$Ca(HCO_3)_2 = 8.1 \times \frac{100}{162}$$

$$CaCl_2 = 50 \times \frac{100}{111}$$

$$HCO_3^- = 91.5 \times \frac{100}{}$$

$$Mg(HCO_3)_2 = 14.6 \times \frac{100}{146}$$

$$MgCl_2 = 40 \times \frac{100}{95}$$

$$Al_2(SO_4)_3 = 20 \times \frac{100}{114}$$

Lime Needed in mg :-

Boiler Problems

As water (Hard water) in the boiler is boiled to generate steam, The concn. of salts present in the water increases and it get precipitated out to cause certain problem in the efficiency of the boiler such problems are known as Boiler problem.

i) Sludge and scale ~~pr~~ formation

ii) Boiler corrosion.

iii) Primming and Foaming formation

iv) Caustic Embrittlement

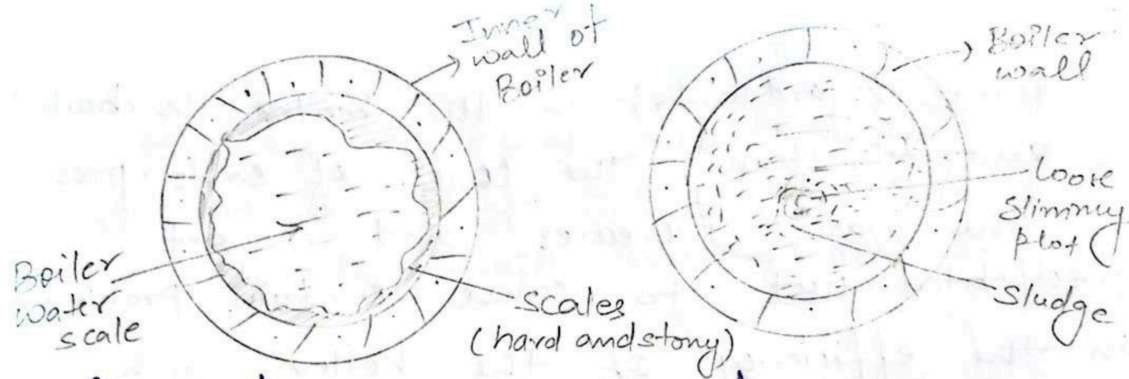
i) Sludge and Scale Formation :-

Sludge :- Sludge is a loose, soft and slimmy precipitate formed with in the boiler and is not adhere to the walls of the boiler.

Salts responsible :- $MgCl_2$, $MgSO_4$, $CaCl_2$

Scale :- Scales are hard and stony precipitate which firmly adhere to the forms of the boiler

Salt :- $CaSO_4$, $CaCO_3$, $CaSiO_3$, $MgSiO_3$



Remonal of sludge and scale

Sludge :- Remoned by wire brush

scale :- Remoned by chiesel & hammer and shocks to boiler

Disadvantanges

i) chocking of boiler pipes

ii) wastage of fuel.

scale :-

i) wastage of fuel.

ii) Lowering of Boiler safety.

Boiler corrosion

The distruction of Boiler Material by chemical or electrochemical Intraction with its enviornment called Boiler Corrosion.

causes :-

i) Presence of dissolved gases such as CO_2, H_2S, SO_2, SO_3, dissolved O_2 etc.

Disadvantages

i) The life of boiler gets decreased.

ii) The Joints and rivets of boiler starts leaking.

iii) The maintainence and repairing costs of boiler gets increased.

Prevention of boiler corrosion

i) By Adding certain chemicals like Sodium-sulphide (Na_2S), Sodium sulphite (Na_2SO_3), Hydrazine (NH_2-NH_2)

Priming & foaming

Priming:- The Formation of wet steam in a boiler is called priming.

foaming:- The continious formation of bubbles or foams on the surface of boiler water and which do not break easily.

Causes of Priming:-

i) Presence of suspended impurities in water.

ii) Sudden rapid boiling

iii) Due to high steam velocity.

Causes of foaming

Due to the presence of oil and alkali in the boiler water

Disadvantages of Priming & foaming

i) It reduces the steam pressure in the boiler, thus the wastage of fuel.

ii) The actual hieght of water coloumn in the boiler cannot be ~~adjused~~ adjudged properly.

iii) The water droplets enters the machinery part and decreases the life of boiler.

Prevention of Priming & foaming

i) use of chemicals like caster oil in water

ii) use of chemicals like Sodium Aluminate and $FeSO_4$.

Caustic Embrittlement:-

Caustic Embrittlement is the corrosion of boiler material which is caused by using Highly inclined in water.

$$Na_2CO_3 + H_2O \longrightarrow \underset{\text{caustic soda.}}{2NaOH} + CO_2\uparrow$$

Prevention of caustic Embrittlement

i) By using sodium phosphate and sodium Sulphate as softening reagent

ii) By Adding Tanin & Lignin to the boiler water.

Calgon Process :-

Calgon is the commercial name of a chemical compound ~~p~~ called sodium hexameta phosphate $[Na_2(Na_4(PO_3)_6)]$.

The salt present in the hard water reacts with the calgon to foarm meta phosphate of ~~cher~~ calcium and magnesium which are not harmful for water and the calcium and magnesium hardnen causing salts gets converted to their Sodium Salts.

$$Na_2[Na_4(PO_3)_6] + 2CaCl_2 \longrightarrow \underset{\text{Calcium meta phosphate}}{Na_2[Ca_2(PO_3)_6]} + \underset{\text{Sodium chloride}}{4NaCl}$$

$$Na_2[Na_4(PO_3)_6] + MgCl_2 \longrightarrow \underset{\text{magnesium meta phosphate}}{Na_2[Mg_2(PO_3)_6)} + 4NaCl$$