WELCOME
CHEMISTRY
UNIT-1
WATER

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UNIT-I

Water :i) specification for water,

ii) analysis of water for domestic use,

iii)Water softening processes-

Lime -Soda process, zeolite and ion exchange method

iv) Boiler feed water,

v) boiler problems-scale, sludge, priming and foaming, caustic embrittlement and corrosion, their causes and prevention,

vi) removal of dissolved gases, carbonate and phosphate conditioning, colloidal conditioning, calgon treatment,

v) Numerical problems on Lime-Soda process, Zeolite and Ion exchange method.

L-1 Specification of water, Hardness

Specification for Water –

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

1) Textile industry-
2) Laundries-
3) Beverages-
4) Dairies and industries-
5) Boilers-
6) Paper Industry -

2/01/2007

L-1 Specification of water, Hardness

1) Textile industry-
2) Laundries-
3) Beverages-
4) Dairies and industries-
5) Boilers-
6) Paper Industry -

L-1 Specification of water, Hardness

1) Textile industry-

Specification –

- **Water should be soft,**
- **free from turbidity.**

- **Free from colour,**
- **Fe and Mn ion.**

L-1 Specification of water, Hardness

1) Textile industry-

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Remarks –

Hard water creates

- uneven dying
- which causes stains of fabrics.

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Hard water deceases the

- solubility of dyes.

L-1 Specification of water, Hardness

2) Laundries- / washing

Specification-

- Water should be **soft,**
- free from colour.

- impurities

- Free from **organic matter.**
- **Free from Fe and Mn.**

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L-1 Specification of water, Hardness

2) Laundries-

Remarks –

- **Hard water increases**
- **consumption of soaps.**

- **Salts of Fe and Mn create**
- **gray or yellow colour on fabric.**

Washing
Nanotech
Stainfree
clothes

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L-1 Specification of water, Hardness

3) Beverages-

Specification-

- Water **should not be alkaline.**

Remarks-

- Alkalinity **destroys the taste.**
- **Neutralization** occurs.

L-1 Specification of water, Hardness

4) Dairies and industries-

Specification-

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

Remarks-

- **Organic matter** imparts foul smell.

L-1 Specification of water, Hardness

5) Boilers-

Specification-

- Water should be of **zero hardness.**

Remarks-

- **Scale formation** on using hard water.
- Loss of heat. ✓ / Energy / investment

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L-1 Specification of water, Hardness

6) Paper Industry -

Specification-

Water should be free from

- SiO_2 and turbidity.

Free from

- alkalinity and hardness.

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L-1 Specification of water, Hardness

6) Paper Industry -

Remarks-

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

ii) analysis of water for domestic use,

- **Chemical Analysis of Water**

- **Estimation of free Chlorine :**

  Excess free chlorine in water makes the municipal water **unfit for drinking purposes** because ***chlorine gas is injurious to human health.*** The estimation of free chlorine is based on the

- ***Oxidation of potassium iodide by free chlorine.***

ii) analysis of water for domestic use,

- Thus, when the sample water is **treated** with **excess of KI solution,**
- the free chlorine present in water
- liberates an equivalent amount of iodine, which forms a
- ***deep violet coloured complex (KI_3)***

with excess potassium iodide.

ii) analysis of water for domestic use,

$$Cl_2 + 2\ KI \longrightarrow 2\ KCl + I_2$$

$$KI + I_2 \longrightarrow KI_3$$

(deep violet coloured complex)

ii) analysis of water for domestic use,

- **Procedure :**
- Take about **10 ml of 10% KI** solution in a stoppered **250ml conical flask.**
- Add to it 50ml of water sample, holding the point of the pipette just above the iodine solution.
- Put on the stopper and shake the flask vigorously.

ii) analysis of water for domestic use,

- Remove the stopper and wash the adhering solution into flask, with about 5-10ml of distilled water. Then titrate the solution against
- **N/50 sodium thiosulphate solution, using starch as final indicator.**

The end point is the change in colour from ***deep-blue to just colourless.***

ii) analysis of water for domestic use,

- **Calculations:** Let 50ml of water sample = Vml N/50 $Na_2S_2O_3$ soln.

∴ 50 x Normality of free chlorine = V x (N/50)

∴ **Normality of free chlorine** $= V \times \frac{N \times 1}{50 \times 50} = \frac{V}{2500}$

- **And strength of free chlorine** $= \frac{V \times 35.5}{2500}$ **g/L** $= \frac{V \times 35.5 \times 10^6}{2500 \times 1{,}000}$ = **14.2 V ppm.**

L-9 Alkalinity of water

Determinate of Alkalinity-

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

Alkalinity of water may be due to presence of:

L-9 Alkalinity of water

Determinate of Alkalinity-

Alkalinity of water may be due to presence of:

1. **Caustic alkalinity (due to OH- and due CO_3^{-2} ions)**

2. **Temporary hardness (due to HCO^{-3})**

L-9 Alkalinity of water

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

$$\text{(i)}\quad [OH^-]+[H^+]\rightarrow H_2O$$

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

$$\text{(iii)}\quad [HCO_3^-]+[H^+]\rightarrow H_2O+CO_2$$

P

L-9 Alkalinity of water

Alkalinity :

These can be estimated separately by titration **against standard acid,**

using phenolphthalein and methyl orange as indicators.

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tors.

L-9 Alkalinity of water

Determination is based on the following reactions:

(i) $[OH\text{-}] + [H^+] \longrightarrow H_2O$

(ii) $[CO_3^{-\,-}] + [H^+] \longrightarrow [\,HCO_3^{-\,-}]$ } P

(iii) $[\,HCO_3^{-\,-}] + [H^+] \longrightarrow H_2O + CO_2$ } M

L-9 Alkalinity of water

- The titration of the water sample against a standard acid upto **phenolphthalein end point (P) marks the completion of reaction, (i) and (ii) only**

$$\left.\begin{array}{l} \text{(i)}\quad [OH^-]+[H^+]\rightarrow H_2O \\ \text{(ii)}\quad [CO_3^{2-}]+[H^+]\rightarrow[HCO_3^-] \end{array}\right\} P$$

this amount of acid used thus **corresponds to hydroxide plus ½ of normal carbonate** present.

L-9 Alkalinity of water

- **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.**

$$\text{(i)}\quad [OH^-]+[H^+]\rightarrow H_2O$$

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

$$\text{(iii)}\quad [HCO_3^-]+[H^+]\rightarrow H_2O+CO_2$$

P (reactions (i) and (ii))

M (reactions (i), (ii) and (iii))

L-9 Alkalinity of water

- The titre value up to the **end point P marks the completion of reactions (i) and (ii) only.**

- *Thus this amount of acid used **is for OH- and one half of CO3- - ions present in water**.*

- On the other hand the **end point M marks completion of all three reactions .**

L-9 Alkalinity of water

- Thus

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

-

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

- The possible combinations of ions causing alkalinity water are-

L-9 Alkalinity of water

- *. thus the total amount of acid represents the total alkalinity (due to OH^- , CO_3^{--} and HCO_3^- ions.)*
- **and the difference shows the presence of *one half of CO_3^{--} ions and all the HCO_3^- ions* present in water.**

L-9 Alkalinity of water

The possible combinations of ions causing alkalinity water are-

i) 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.

L-9 Alkalinity of water

The possible combinations of ions causing alkalinity in water are :

OH^- only or

CO_3^{--} only or

HCO_3^- only or

OH^- and CO_3^{--} together or

CO_3^{--} and HCO_3^- together.

[what about the possibility of OH^- and HCO_3^- and combination of OH^- HCO_3^- *and* CO_3^{--} *existing together?]*

L-9 Alkalinity of water

- * The possibility of OH- and HCO^{-3} ions together is ruled out because these
- combine instantaneously to from CO_3^{-2} ions.
- e.g. $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$

Alkalinity

- ***The possibility of*** **OH^-** and **HCO_3^-** ***is ruled out*** because of the following instantaneous reactions.

$$\mathbf{OH^- + HCO_3^- \longrightarrow CO_3^{--} + H_2O}$$

$$NaOH + NaH\,CO_3 \longrightarrow Na_2\,CO_3 + H_2O$$

L-9 Alkalinity of water

e.g. $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$

- thus, OH^- and HCO^{-3} ions can't exist together in water.

- On the basis of same,

all the three (OH-, CO3-2 and HCO-3 can't exist together.

Alkalinity

- **Thus OH^- and HCO_3^- ions cannot exist together in water.**

- On the basis of same reasoning, **all the three OH^- HCO_3^- *and* CO_3^{--} ions cannot exist together.**

L-9 Alkalinity of water

- **Procedure:** Pipette out 100ml of the water sample in a clean titration flask.
- **Add to it 2 to 3 drops of phenolphthalein indicator.**
- **Run in N/50 H_2SO_4(from a burette),** till *the pink colour is just discharged.*
- Then to the same solution add 2 to 3 drops of **methyl orange.** Continue the titration,
- *till the pink colour reappears.*

L-9 Alkalinity of water

Calculations

(i) $[OH^-] + [H^+] \longrightarrow H_2O$

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

P

$\longrightarrow$

(iii) $[HCO_3^{--}] + [H^+] \qquad H_2O + CO_2$

M

L-9 Alkalinity of water

(i) When P = 0, only *HCO_3^-* ions are present

both OH- and CO_3^{--} are absent and alkalinity is due to *HCO_3^-* ions only.

(ii) When P = ½ M, only CO_3^{--} is present

L-9 Alkalinity of water

- **(ii) When P = ½ M,** only CO_3^{--} is present

Because half of carbonate neutralization reaction i.e.

$$[CO_3^{--}] + [H^+] \longrightarrow [HCO_3^{--}]$$

takes place with phenolphthalein indicator;

while complete carbonate neutralization reaction i.e.

$$[CO_3^{--}] + [H+] \longrightarrow [HCO_3^{--}] \text{ and}$$

$$[HCO_3^{--}] + [H+] \longrightarrow H_2O + CO_2$$

occurs when methyl orange indicator is used.

- ***Thus alkalinity due to*** $CO_3^{--} = 2P$.

L-9 Alkalinity of water

L-10 Solved numericals
Alkalinity of water

Nu. → 100 ml of water sample, on titration with N/50 H_2SO_4 gave a titre 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 $CaCO_3$ 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.**

L-10 Solved numericals
Alkalinity of water

Further, the volume of N/50 H_2SO_4 eqiv. 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 H_2SO_4 = 50 mg of $CaCO_3$

1N CaCO3 contains 50g/L = 50,000 mg/L = 50mg/ml

11.6 ml of N/50 H_2SO_4 = 50 X 11.6 X (N/50)

= 11.6 mg of $CaCO_3$/100ml

L-10 Solved numericals
Alkalinity of water

= 11.6 mg of $CaCO_3$/100ml

This is the CO_3^{--} present in 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^{--}

L-10 Solved numericals
Alkalinity of water

- Further, the volume of N/50 H_2SO_4 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 H_2SO_4 = 50 mg of $CaCO_3$
- 11.6 ml of N/50 H_2SO_4 = 50 X 11.6 X (N/50)
- = 11.6 mg of $CaCO_3$

L-10 Solved numericals
Alkalinity of water

- This is the CO_3^{--} present in 100 ml of water
- \ Amount of CO_3^{--} present in 1 litre of water
- = 11/6 X (1000/100)
- = 116 mg/L = 116 ppm

L-10 Solved numericals
Alkalinity of water

- **Nu. (2) A water sample 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, whar are the types and amount of alkalinity present in the sample ?**

L-1 Specification of water, Hardness

HARDNESS OF WATER

- Those water which **do not produce lather with soap** are termed as **hard water.**

Definition

- On the other hand **soft water readily produce a lot of lather**

- when mixed with a little of soap.

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L-1 Specification of water, Hardness

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.**

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L-1 Specification of water, Hardness

- **Some major bivalent cations are**
- **Mg^{++}, Ca^{++} and Fe^{++}.**
- **Some important anions are**
- **HCO^{-3}, NO^{-3}, SO^{4--} Cl^{-}etc.**

(carbonate

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L-1 Specification of water, Hardness

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

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$$

Soap

Sodium stearate — **calcium stearate (insoluble)**

cheap veg. oil

Biodiesel

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

Soap — **Hardness** — **Magnesium stearate**

Hardness

L-1 Specification of water, Hardness

- 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 (<1)
70-150 mg/litre	Moderate hard water
150-300 mg/litre	Hard water (>1)
300 mg/litre and above	Very hard water (>3)

L-1 Specification of water, Hardness

Types of Hardness

HARDNESS

(A) **Temporary** Hardness or Carbonate Or **Alkaline Hardness**

(B) **Permanent** Hardness or **Non Carbonate** Or Non alkaline Hardness

CLASSIFICATION	Temp **CARBONATE HARDNESS** Alkaline	Permanent **NON CARBONATE HARDNESS**
Calcium Hardness	Calcium Bicarbonate $Ca(HCO_3)_2$ Calcium Carbonate $CaCO_3$	Calcium Sulphate $CaSO_4$ Calcium Chloride $CaCl_2$
Magnesium Hardness	Magnesium Bicarbonate $Mg(HCO_3)_2$ Magnesium Carbonate $MgCO_3$	Magnesium Sulphate $MgSO_4$ Magnesium Chloride $MgCl_2$

L-1 Specification of water, Hardness

(A) Temporary Hardness.

- It is caused by the presence of dissolved bicarbonates of
- Ca, Mg and other heavy metals.
- Salts responsible for temporary hardness
- $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$

L-1 Specification of water, Hardness

(A) Temporary Hardness.

- It can be **removed by simple boiling** of water.
- **Bicarbonates are decomposed** and are converted into
- **insoluble carbonates or hydroxides,**
- which **precipitate** and
- **settle down** at the bottom of the vessel

L-1 Specification of water, Hardness

(v) It is also known as carbonate or Alkaline hardness. –

$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} \underset{\text{(Insoluble)}}{CaCO_3} + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Heat}} \underset{\text{(Insoluble)}}{Mg(OH)_2} + 2CO_2$$

(B) Permanent Hardness-

- It is caused by the presence of
- Soluble chlorides and sulphates of
- Calcium, Magnesium, Iron and
- Other heavy metals.

L-1 Specification of water, Hardness

(B) Permanent Hardness-

Salts which are responsible for permanent hardness are –

- $CaCl_2$,
- $MgCl_2$,
- $CaSO_4$,
- $FeSO_4$,
- $Al_2(SO_4)_3$.

L-1 Specification of water, Hardness

(B) Permanent Hardness-

- It can't be removed by simply boiling of water.

It is also known as

- non carbonate or non alkaline hardness.

L-1 Specification of water, Hardness

DEGREE OF HARDNESS

- Hardness of water is expressed as equivalent of
- calcium carbonate ($CaCO_3$).
- because molecular weight of $CaCO_3$ is
- exactly 100 and
- It is the most insoluble salt.

L-1 Specification of water, Hardness

DEGREE OF HARDNESS

- **molecular weight of $CaCO_3$ is exactly 100.**
- **It is most insoluble salt that can be**
- **precipitated in water treatment.**

Equivalent of $CaCO_3$ =

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

L-1 Specification of water, Hardness

- **Multiplication factors for different salts (i) Table –**

Dissolved salt	Molar mass	Chemical equivalent	Multiplication factor for converting into equivalents of CaCO3.
$Ca(HCO3)_2$	162	81	100/162
$Mg(HCO3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$MgSO_4$	120	60	100/120
CaCl2	111	55.5	100/111
MgCl2	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO2	44	22	100/44
$Mg(NO3)_2$	148	74	100/148

L-1 Specification of water, Hardness

- **Multiplication factors for different salt are tabulated**
- **(i) Table –**

Dissolved salt	Molar mass	Chemical equivalent	Multiplication factor converting into equivalents of CaCO3.
Ca(HCO3)2	162	81	100/162
Mg(HCO3)2	146	73	100/146
CaSO4	136	68	100/136

- HCO-3OH-CO2-3NaAlO2Al2(SO4)3FeSo4.7H2OH-951008444148611760823422781817368605 5.547.5504222746117308257 1391100/162100/146100/136100/120100/111100/95100/100100/84100/44 100/148100/122100/34100/60100/164100/114100/278100/2

L-1 Specification of water, Hardness

UNITS OF HARDNESS-

– Parts per million (ppm)

– Milligrams per litre (mg/L)

– Degree Clark (^{0}Cl)

– Degree French (^{0}Fr)

L-1 Specification of water, Hardness

(a) Parts per Million (ppm) –

It is defined as the number of parts of CaCO3 equivalent hardness per 10^6 parts of water.

∴ 1ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

L-1 Specification of water, Hardness

(b) Milligrams per litre (Mg/L) –

It is defined as the number of milligrams of $CaCO_3$ persent in one litre of water.

$\therefore$ 1 mg/L = 1 mg of $CaCO_3$ equivalent hardness per litre of water.

$\therefore$ 1mg/L = 1 ppm

L-1 Specification of water, Hardness

(c) **Degree Clark (^{0}Cl)** - It is defined as the parts of CaCO3 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.

$\therefore$ 1 ^{0}Cl = 1 part of $CaCO_3$ per 70,000 parts of water.

1 ppm = 1 mg/L = 0.07 ^{0}Cl

L-1 Specification of water, Hardness

(d) Degree French) (^{0}Fr) –

It is defined as the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

$\therefore$ 1 ^{0}Fr = 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1 ppm = 1 mg/L = 0.1 ^{0}Fr

L-1 Specification of water, Hardness

Relationship between various units.

1 ppm = 1 mg/L = 0.1 ^{0}Fr = 0.07 ^{0}Cl

1 mg/l = 1 ppm = 0.1 ^{0}Fr = 0.07 ^{0}Cl

1 ^{0}Cl = 14.3 ppm = 14.3 mg/L = 1.43 ^{0}Fr

1 ^{0}Fr = 10 ppm= 10 mg/L = 0.7 ^{0}Cl

Hence ;

1 ppm = 0.1 ^{0}Fr = 0.07 ^{0}Cl = 1 mg/L

L-1 Specification of water, Hardness

(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

L-1 Specification of water, Hardness

(Solved examples based on determination of Hardness of water)

Solution:-

Hardness = (Mass of CaSO4 in mg/L) X Multiplication factor

$$= \text{Mass of } CaSO_4 \text{ in mg/L} \times \frac{\text{Chem. Eq of } CaCO_3}{\text{Chem Eq. of } CaSO_4}$$

$$= 500 \text{ mg/L} \times \frac{50}{68} = 367.65 \text{mg/L}$$

[= 312.5 mg/L= 312.5 ppm. Ans.]???

L-1 Specification of water, Hardness

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

Solution:

Hardness = (Mass of $MgCO_3$ in mg/L) x

$$\frac{\text{Chemical eq. of } CaCO_3}{\text{Chemical eq. of } MgCO_3}$$

Ex. (2)contd.

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

or

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

Or

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

Ex. (2)contd.

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

= 75.6 Mg/L = 75.6 ppm Ans.

Thus 75.6 X 10^{-3} gm of MgCO3 dissolved per litre gives 90 ppm of hardness.

L-1 Specification of water, Hardness

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

MgCl2	=	9.50 gm
CaSO4	=	13.60 gm
Ca(HCO3)2	=	16.20 gm

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

Solution:-

- $MgCl_2 = CaSO_4 = Ca(HCO_3)_2 = CaCO_3$

L-1 Specification of water, Hardness

Ex. (3) contd.

Given:

$MgCl_2$ = 9.50 gm ; $CaSO_4$ = 13.60 gm

and $Ca(HCO_3)_2$ = 16.20 gm

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 $CaCO_3$

L-1 Specification of water, Hardness

Ex. (3) contd.

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

$= \quad$ **10 gm of $CaCO_3$.**

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

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

L-1 Specification of water, Hardness

Ex. (3)contd.

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 CaCO3

= 30 gm per 70,000 C.C. (70,000 gm) of water.

L-1 Specification of water, Hardness

∴ **Ex. (3)contd.**

∴ **Clark's degree of hardness = 30^0 Cl (Clark's)**

but 1 ^{0}Cl = 14.3 ppm = 14.3 mg/L = 1.43 ^{0}Fr

∴ **30' Clark's scale = (10/7) X 30**

= 42.857^0 French

And 0.1 ^{0}Fr = 1 ppm = 1 mg/L = 0.07 ^{0}Cl

10^0 French scale = 100 ppm

∴ **42.857^0 French scale (100/10) X 42.857**

= 428.57 ppm

[7^0 Cl = 10^0 Fr = 100 ppm]

L-1 Specification of water, Hardness

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, CaSO4 = 13.6 Mg/L

Solution:-

$$\text{Temporary Hardness} = 7.3 \times \frac{100}{146} + 16.2 \times \frac{100}{162} \text{ mg/L}$$

$$\text{Permanent Hardness} = 9.5 \times \frac{100}{95} + 13.6 \times \frac{100}{136}$$

L-1 Specification of water, Hardness

Ex. (4) **Solution:-**

$$\text{Temporary Hardness} = 7.3 \times \frac{100}{146} + 16.2 \times \frac{100}{162} \text{ mg/L}$$

$= (5 + 10)$ Mg/L

$= 15$ Mg/L

$$\text{Permanent Hardness} = 9.5 \times \frac{100}{95} + 13.6 \times \frac{100}{136}$$

$= (10 + 10)$ Mg/L

$= 20$ Mg/L

Total Hardness= 15+20 = 35 Mg/L = ppm.

Types of Permitted Treatment Facilities

L-2 Water Softning, Lime-Soda Process

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-)

L-2 Water Softning, Lime-Soda Process

Water Softening :-

- Removal of hardness of water (temporary or permanent) is done through the
- process called softening of water.
- It is very essential process. Hard water is not suitable for
- domestic as well as
- industrial purposes,

L-2 Water Softning, Lime-Soda Process

Water Softening :-

- 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
  - External Treatment
  - Internal Treatment

L-2 Water Softning, Lime-Soda Process

Lime –Soda Process

PRINCIPLE :-

The solluble calcium and magnesium salts in water are

- **chemically converted into insoluble compounds, by adding calculated amount of**

- **lime [$Ca(OH)_2$]**

and

- **Soda [$Na_2\ CO_3$] .**

L-2 Water Softning, Lime-Soda Process

Lime –Soda Process

PRINCIPLE :-

- The precipitates of
- Calcium carbonate [$CaCO_3$] and
- magnesium hydroxide [$Mg(OH)_2$] ,
- are filtered off. There are two processes:

1. Cold Lime –Soda Process
2. Hot Lime –Soda Process

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,**
- **do not settle down easily and**
- **can’t be filtered easily. So…..**

L-2 Water Softning, Lime-Soda Process

(Cold Lime –Soda Process)

So small amounts of Coagulants like

- **alum,**
- **aluminium sulphate,**
- **sodium aluminate etc.**

are added.

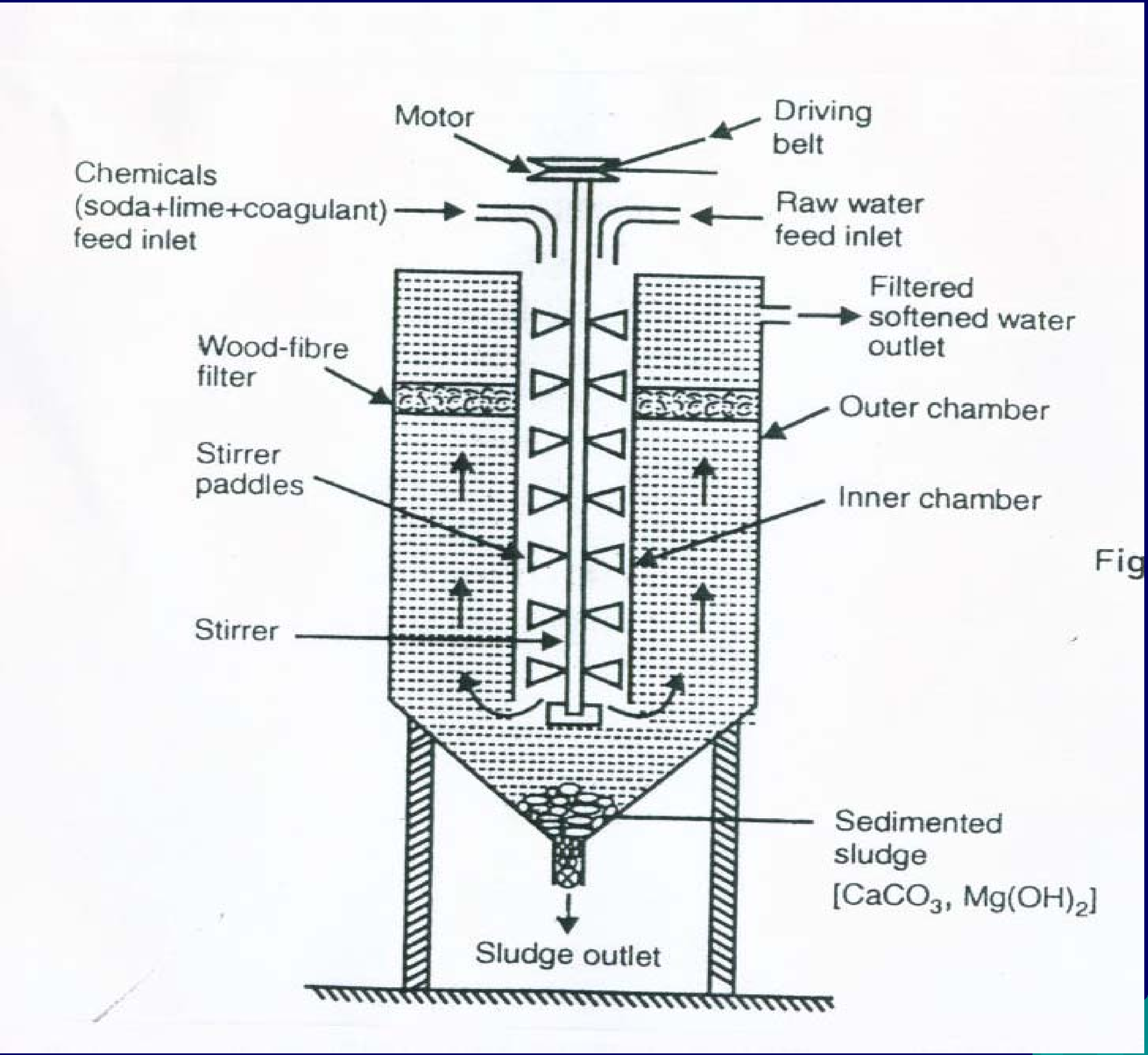
- **Which hydrolyze to …**

L-2 Water Softning, Lime-Soda Process

(Cold Lime –Soda Process)

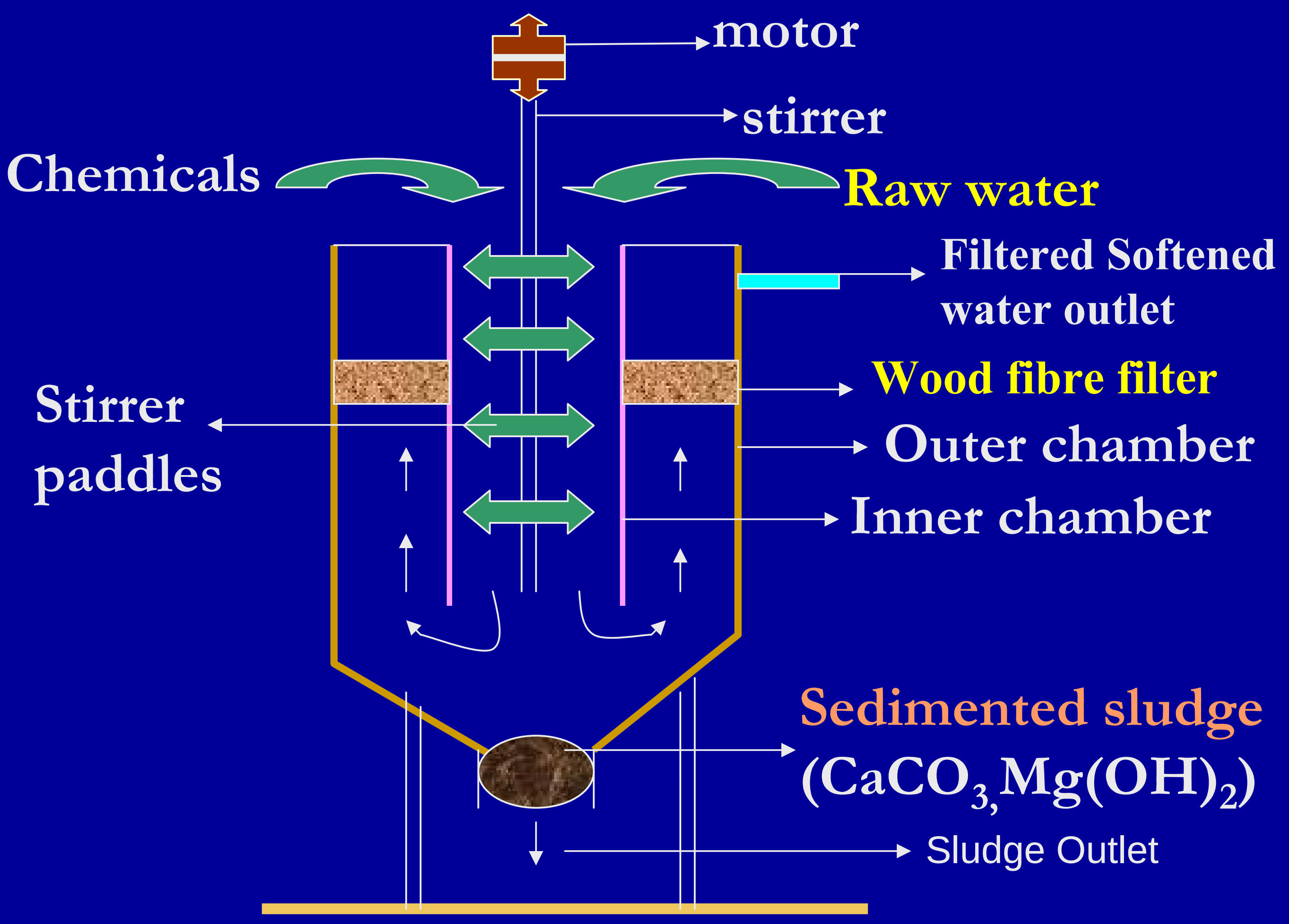
- Which hydrolyze to flocculent (precipitate),
  - gelatinous precipitate of
  - aluminum hydroxide and
  - entrap the fine precipitates.

- 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



Continuous cold lime soda softner

Continuous cold lime soda softner



L-2 Water Softning, Lime-Soda Process

- **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.**

L-2 Water Softning, Lime-Soda Process

- The heavy sludge settles down in the outer chamber and
- softened water reaches up.

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

- filtered soft water flows out continuously through the outlet at the top.

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

L-2 Water Softning, Lime-Soda Process

Hot Lime –Soda Process

- In this process water is treated with chemicals at a temperature of
- 80^0 c to 150^0 C.

- Hot L-S process provides water, containing a residual hardness of 15 –30 ppm.

The softener consists of three parts-

- 1.Reaction Tank –
- 2.Conical Sedimentation Tank –
- 3. Sand filter –

L-2 Water Softning, Lime-Soda Process

Hot Lime –Soda Process

1. Reaction Tank –

- The tank has **three separate inlets** and the third for superheated steam.
- After the entry **these are mixed.**
- The reaction starts and get completed in the reaction tank.
-

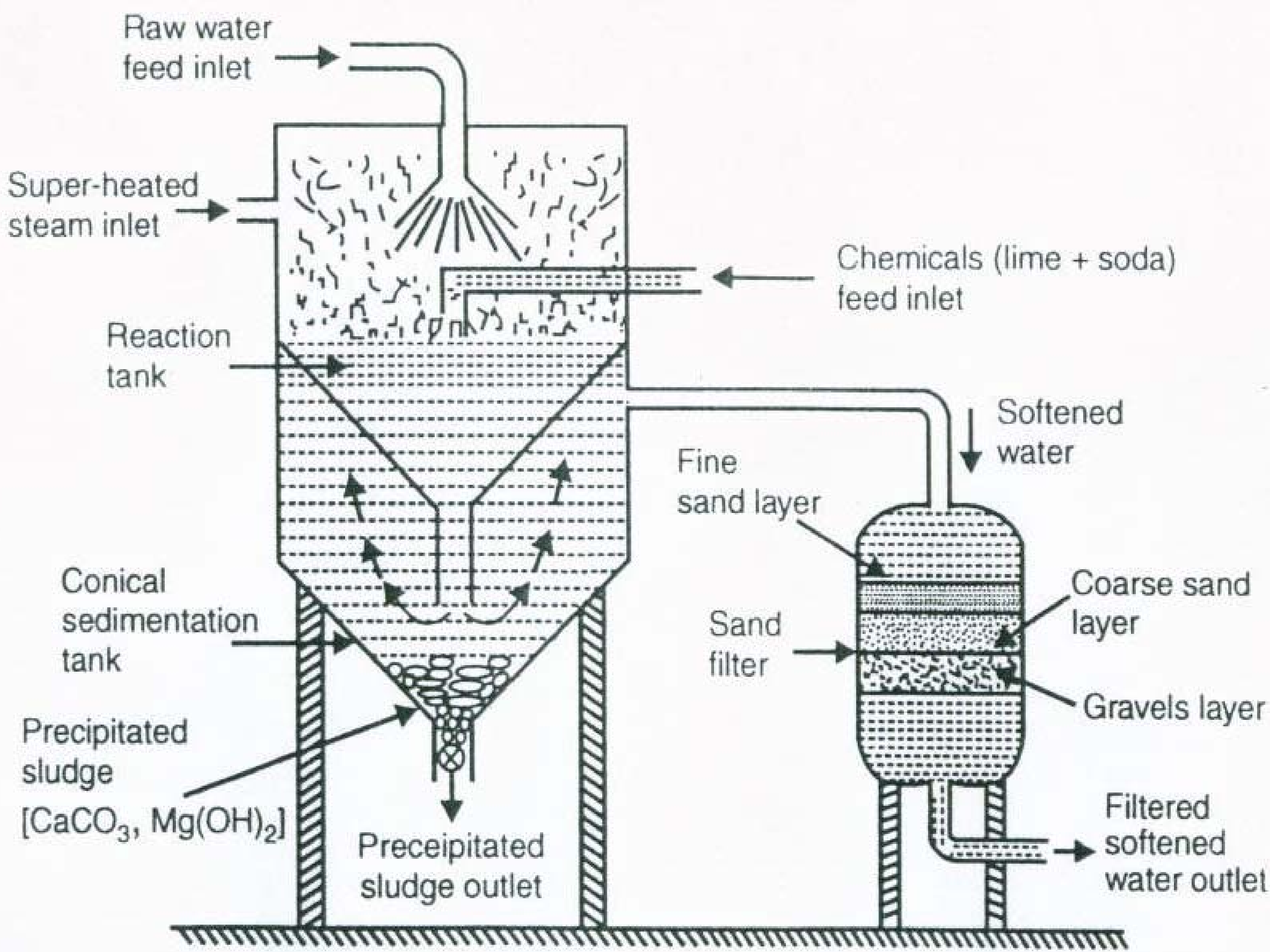
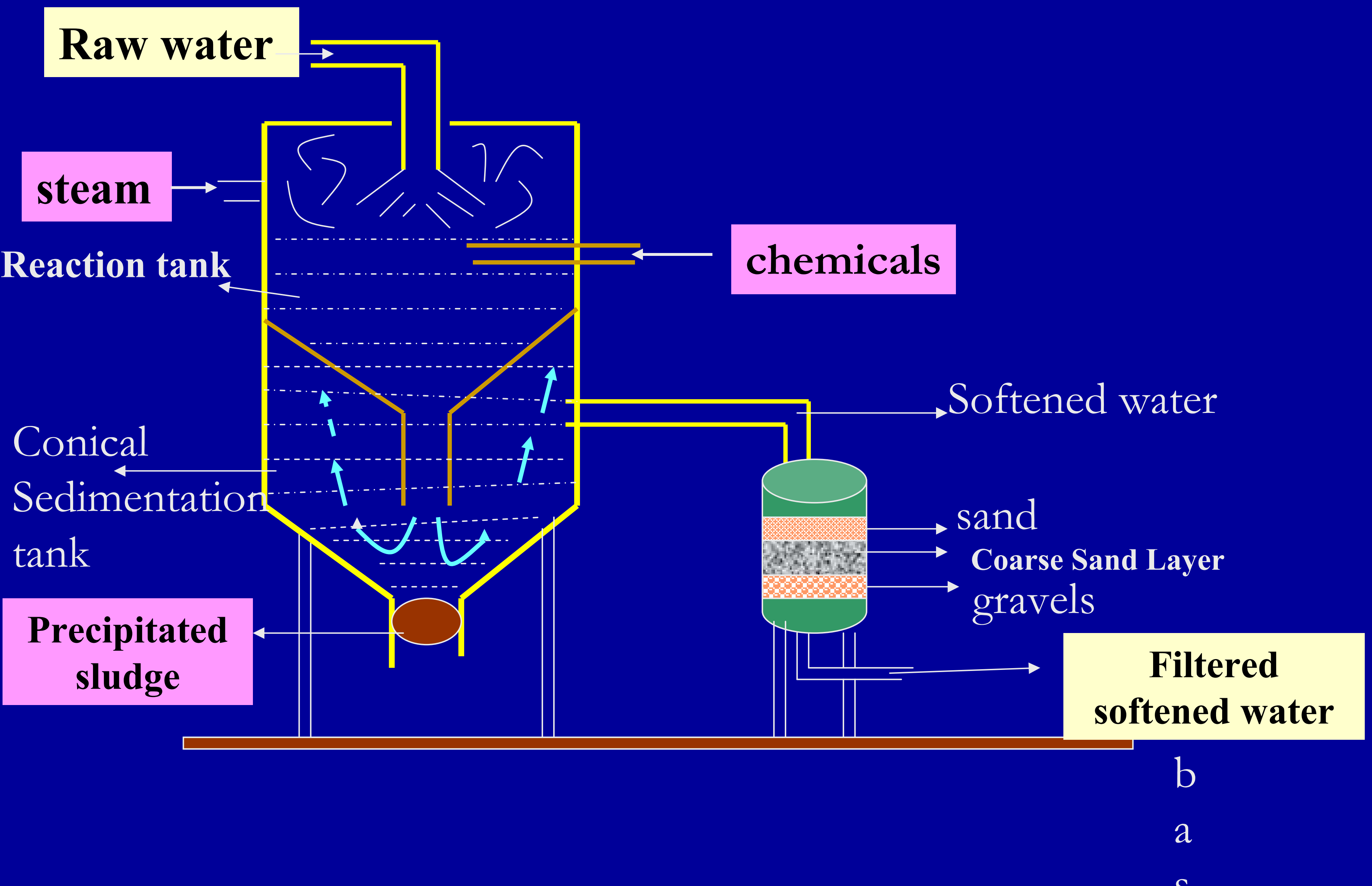


Fig. Continuous hot lime-soda softener.

Continuous Hot Lime Soda Softner



L-2 Water Softning, Lime-Soda Process

Hot Lime –Soda Process

1. Reaction Tank –

2. Conical Sedimentation Tank –

from reaction tank the reactants come in this tank and

the sludge settles down.

3. Sand filter –

L-2 Water Softning, Lime-Soda Process

Hot Lime –Soda Process

3. Sand filter –

It has layer of fine and coarse sand as filter and

it completely removes the sludge from

the softened water.

L-2 Water Softning, Lime-Soda Process

Processing –

In Hot L-S process

- **reaction proceeds faster.**

- **No coagulants are needed because sludge and precipitates settle easily.**

- **Some dissolved gases like CO_2 also driven out of the water.**

L-2 Water Softning, Lime-Soda Process

Processing –

……..

- Viscosity of softened water is lower,
- so filtration of water becomes
- much easier.
- The softening capacity of hot process is many times higher than
- that of the cold process.

L-2 Water Softning, Lime-Soda Process

Advantages of Lime –soda Process.

- Lime Soda process is very economical.
- It removes not only hardness causing salts but also minerals.
- Due to alkaline nature of treated water, pathogenic bacterias in water are reduced.
- Iron and manganese are also removed.
- Treated water is alkaline and therefore less corrosive.

L-2 Water Softning, Lime-Soda Process

Disadvantages of Lime –soda Process.

- **For efficient and economical softening, careful operation and skilled supervision is required.**
- **Disposal of large amounts of sludge causes a problem .**
- **This can remove hardness only upto 15 ppm, which is not sufficient for boilers.**

L-2 Water Softning, Lime-Soda Process

Calculation of Lime-Soda Requirement-

Constituent	Reaction	Need
Perm. Hard. Of $CaCl_2$ &/or $CaSO_4$	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$	S
	$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$	S
Perm. Hard. of $MgCl_2$ &/or $MgSO_4$	$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$	
	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$	L+S

L-2 Water Softning, Lime-Soda Process

Calculation of Lime-Soda Requirement-

Constituent	Reaction	Need
Free acids H^+ HCl & H_2SO_4	$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$ $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$	L+S
Coagulant $FeSO_4$	$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2 + CaSO_4$ $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$	L+S
$Al_2(SO_4)_3$	$2Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4$ $3CaSO_4 + 3\ Na_2CO_3 \longrightarrow 3CaCO_3 + 6Na^+$	L+S

L-2 Water Softning, Lime-Soda Process

Calculation of Lime-Soda Requirement-

Constituent	Reaction	Need
$Mg(HCO_3)_2$ (Temp)	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$	2L
$Ca(HCO_3)_2$ (Temp.)	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$	L
HCO_3^- ($NaHCO_3$)	$2HCO_3^{--} + Ca(OH)_2 \longrightarrow 2CaCO_3 + H_2O + CO_3^{2-}$	L - S

L-2 Water Softning, Lime-Soda Process

Calculation of Lime-Soda Requirement-

Constituent	Reaction	Need
Dissolved CO_2	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$	L
$NaAlO_2$	$NaAlO_2 + H_2O \rightarrow Al(OH)_3 + NaOH$	- L

L-2 Water Softning, Lime-Soda Process

Now 100 parts by mass of $CaCO_3$ are equivalent to i) 74 parts of $Ca(OH)_2$ and ii) 106 parts of Na_2CO_3

- **So Lime requirement for softening =**

$$\frac{74}{100}\left(\begin{array}{l}\text{Temp. } Ca^{2+} + 2x \text{ Temp } Mg^{2+} + \text{Perm } (Mg^{2+} + Fe^{2+} + Al3+) \\ +CO_2 + H+ (HClorH_2SO_4) + HCO_3^- - Na\ AlO_2 \\ \text{All in terms of } CaCO_3 \text{ eq.}\end{array}\right)$$

L-2 Water Softning, Lime-Soda Process

- and Soda requirement for softening =

$$\frac{106}{100}\left(\text{Perm } (Ca^{2++}\ Mg^{2+} + Fe^{2+} + Al^{3+}) + H^{+} (HCl or H_2SO_4) - HCO_3^{-} \right)$$

All in terms of CaCO3 eq.

L-3 Numericals on L-S Method

L-3 Numericals on L-S Method

L-3 Numericals on L-S Method

L-3 Numericals on L-S Method

L-3 Numericals on L-S Method

L-3 Numericals on L-S Method

Ex-1. A sample of water contains following impurities :

$Mg(HCO)_3$ =73 mg/L, $CaCl_2$ = 222mg/L,

$MgSO_4$ =120mg/L, $Ca(NO_3)_2$ =164mg/L.

Calculate the quantity of lime (74% pure) and soda(90%pure) needed for softening 5,000L of water.

SOLUTION:

Convert each into $CaCO_3$ equivalents

L-3 Numericals on L-S Method

Ex.2. explain with chemical equations and calculate the amount of lime and soda needed for softening 1,000,000 litres of water containing the following:

$Ca(HCO)_3$ = 220ppm, $Mg(HCO)_3$ = 56ppm,

$MgCl_2$ = 130ppm, $MgSO_4$ = 84ppm, and

$CaSO_4$ = 98ppm.

SOLUTION:

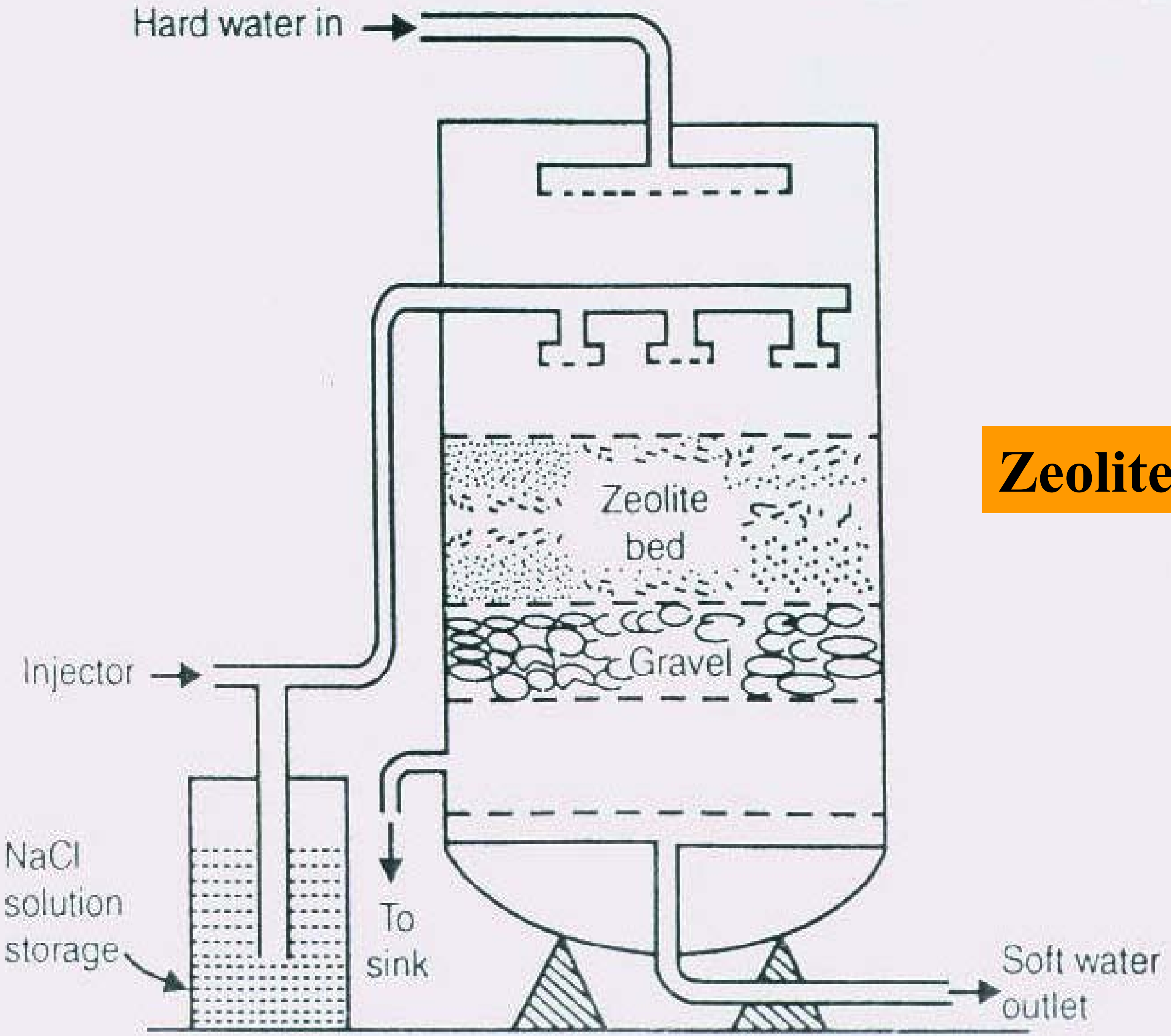
Convert each into $CaCO_3$ equivalents

L-3 Numericals on L-S Method

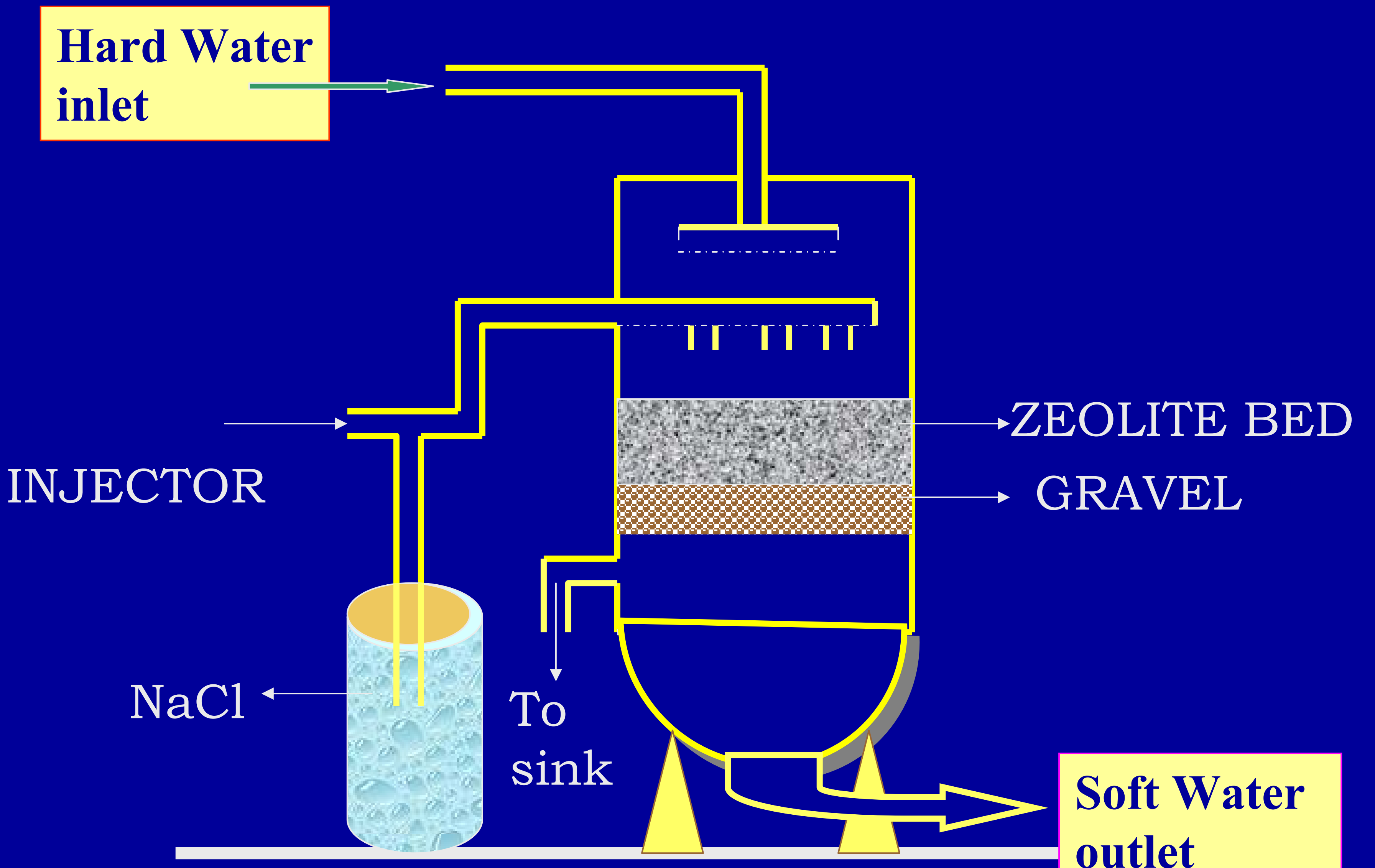
ZEOLITE OR PERMUTIT PROCESS

- 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 Softner



ZEOLITE METHOD



L- 4 Water Softning, Zeolite Process &..

- **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. –**
- **Natural Zeolites**
- **Synthetic zeolites.**

L- 4 Water Softning, Zeolite Process &..

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.**

L- 4 Water Softning, Zeolite Process &..

PROCESS :-

- $Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$
- $Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$
- $Na_2Ze + CaCl_2 + CaSO_4 \rightarrow CaZe + 2NaCl$ (or Na_2SO_4)
- $Na_2Ze + MgCl_2$ (or $MgSO_4$) $\rightarrow MgZe + 2NaCl$ (or Na_2SO_4)

Regeneration:-

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

L- 4 Water Softning, Zeolite Process &..

Regeneration:-

- Exhausted **zeolite is reclaimed** by
- treating it with a **brine (10% NaCl)** soultion.

- **regenerated zeolite** bed is

- **used again** for softening purpose.

LIMITATION:-

1. Water with turbidity should not be used as pores of zeolite get clogged.
2. PH of water should not be too high or too low.
3. Water containing Fe^{2+} and Mn^{2+} ions should be avoided because Fe^{2+} will form their zeolite .
4. Hot water can't be used as it dissolves zeolite.
5. Mineral acids, if present in water, destroy the zeolite bed.

ADVANTAGES

- Hardness is completely removed.
- Equipment used is compact and occupies less space.
- There is no danger of sludge formation.
- It is quite clean.
- It requires less time for softening.

L- 4 Water Softning, Zeolite Process &..

- ZEOLITE PROCESS
- LIME SODA PROCESS
- Water with zero hardness is produced.Capital cost is higher.Operation cost is lower because exhausted zeolite is regenerated.
- Plant is compact and occupies less space.Can not be used for hot water, acidic water or turbid water.No. problem of sludge formation.Salt causing temporary hardness are converted into $NaHCO_3$ which is present (i) soft water.
- It does not involve any secondary operation like salt, lime, coagulation, filtration. Water with 15 to 50 pm hardness is produced. Capital cost is lower.Operation cost is higher because lime and soda are consumed.Plant occupies more space.Process is free from any such limitations. There may be problem after precipitation. Temporary hardness is completely removed in the form of insoluble $CaCO_3$ and $Mg(OH)_2$.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 bed **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 X 30 g = 45 g of NaCl.**

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

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

Hardness of the water sample.

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

= 38.46 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 $CaCO_3$.

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

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

- = **32,051 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

= 400 L X 100 g/L = 40,000 g NaCl

$$= 40{,}000 \times \frac{50}{58.5}\, \mathrm{g\, CaCO_3\ eq.}$$

=34,188 g CaCO3 eq.

Hardness of 100,000 L water

= 34,188 g CaCO3 eq.

Or

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

= 0.3419 g CaCO3 eq.

= 341.9 mg

L- 5 Ion Exchange &…..

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.

L- 5 Ion Exchange &……..

ION EXCHANGE OR DE-IONIZATION PROCESS:-

- Resins containing acidic functional groups
- (-COOH, $-SO_3H$ etc.) are capable of
- exchanging their H+ ions with other cations.

- Resins containing basic functional groups (-NH2) are capable of exchanging their anion with other anion.

Ion Exchange

L- 5 Ion Exchange & ……..

- Cation exchange resins (RH_+) - are mainly styrene divinyl benzene copolymers,
- which on sulphonation or carboxylation become capable of
- exchanging their hydrogen ions with the cations in the water.

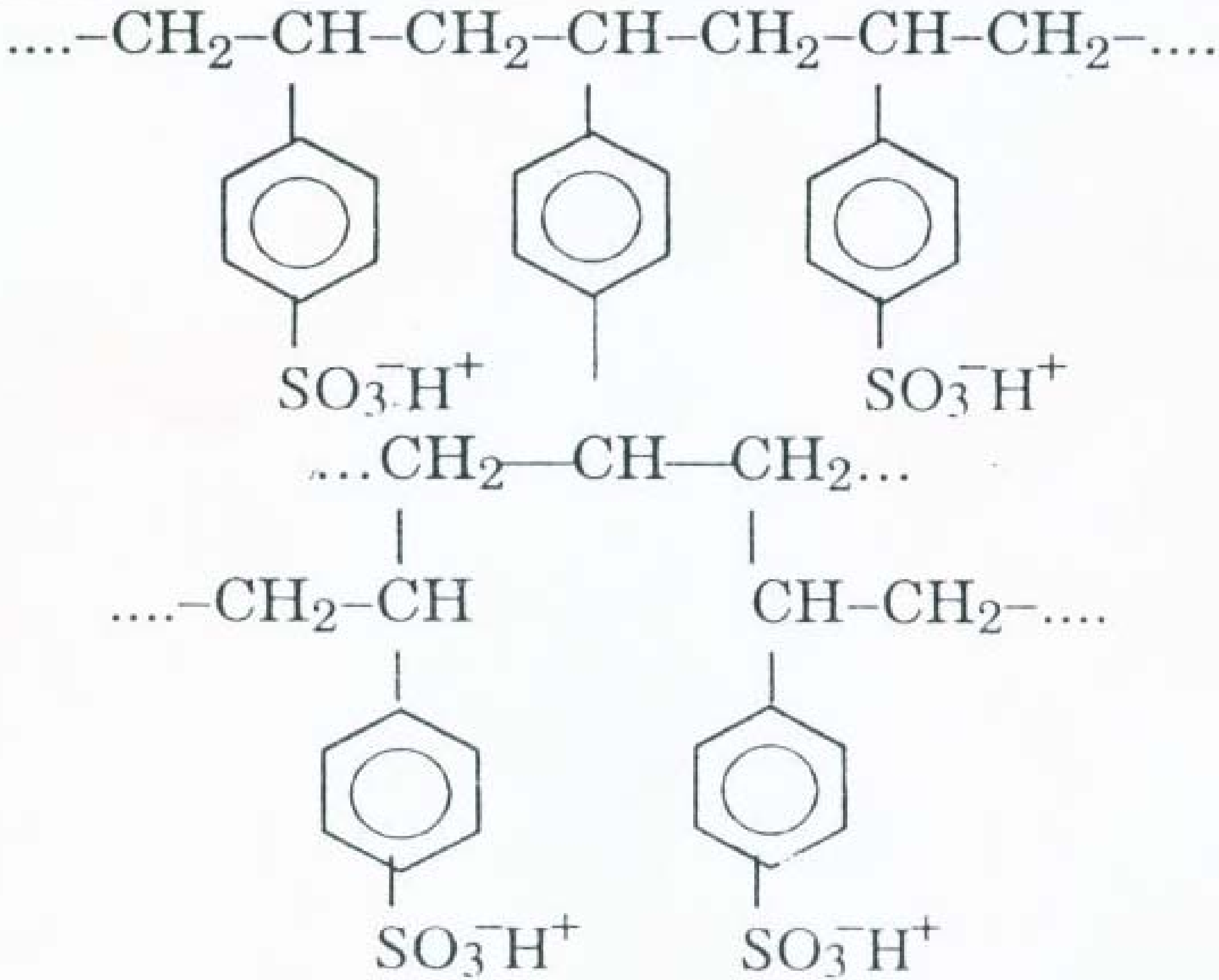


Fig. Acidic or cation exchange resin (sulphonate form).

L- 5 Ion Exchange & ……..

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

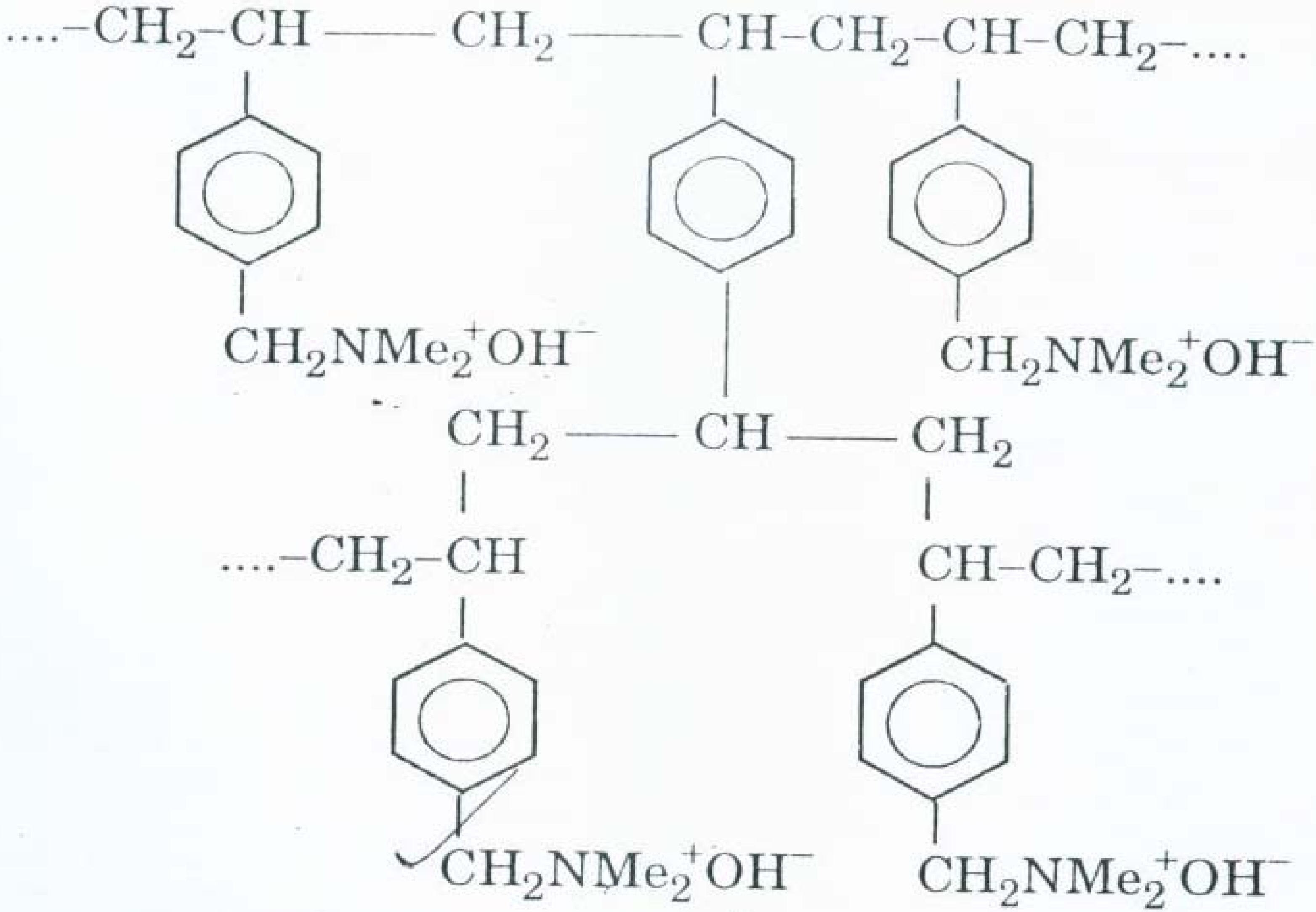


Fig. Basic or anion exchange resin (hydroxide form).

L- 5 Ion Exchange & Numericals

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 ,thus

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

$$2RH + Mg^{2+} \rightarrow R_2Mg + 2H^+$$

L- 5 Ion Exchange & Numericals

(PROCESS)

- 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.

L- 5 Ion Exchange & Numericals

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

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

- H+ and OH- ions 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.

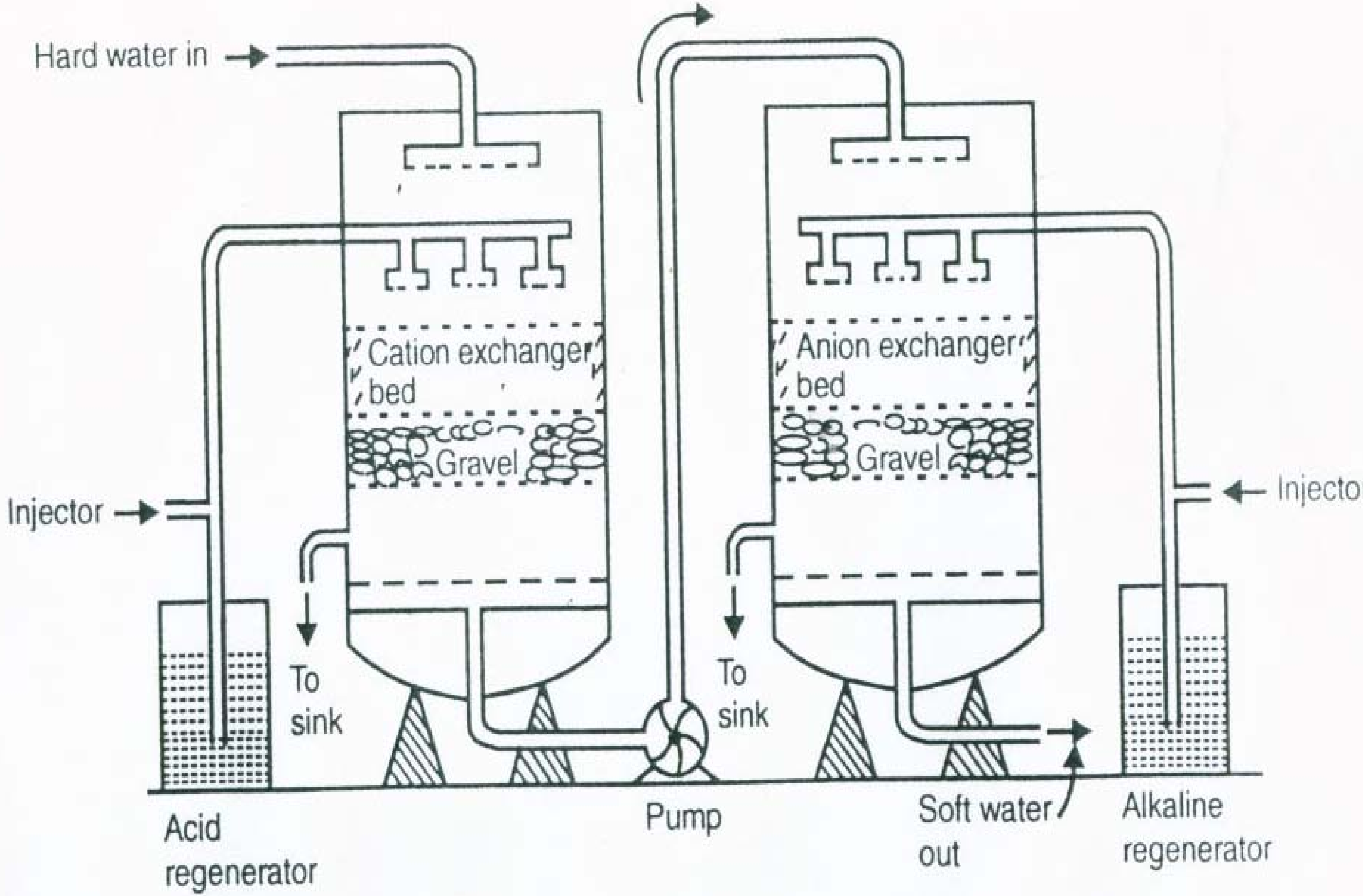


Fig. Demineralization of water.

L- 5 Ion Exchange & Numericals

REGENRATION :-

- After long use the exchange capacity of cation and anion exchange resins is lost,
- then these are called to be exhausted.
- The exhausted cation exchange column is regenerated by
- passing a solution of dil HCl or dil H_2SO_4.

L- 5 Ion Exchange & Numericals

(REGENRATION)

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

- Similarly 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)

L- 5 Ion Exchange & Numericals

Advantages :-

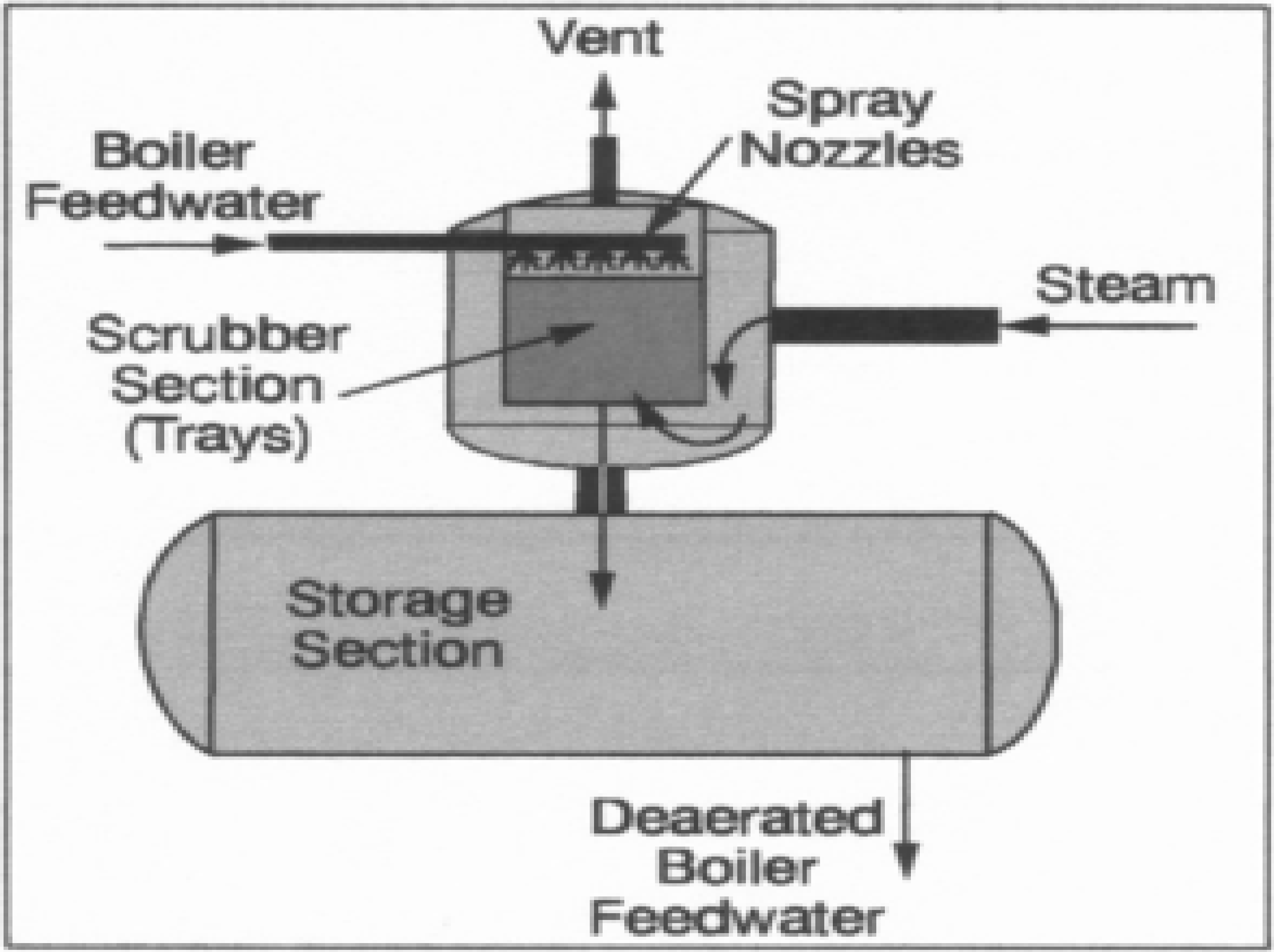
- The process can be used to soften highly acidic or alkaline water.
- It produces water of very low hardness (~2ppm).
- So it is very good for treating water for use in high pressure boiler.

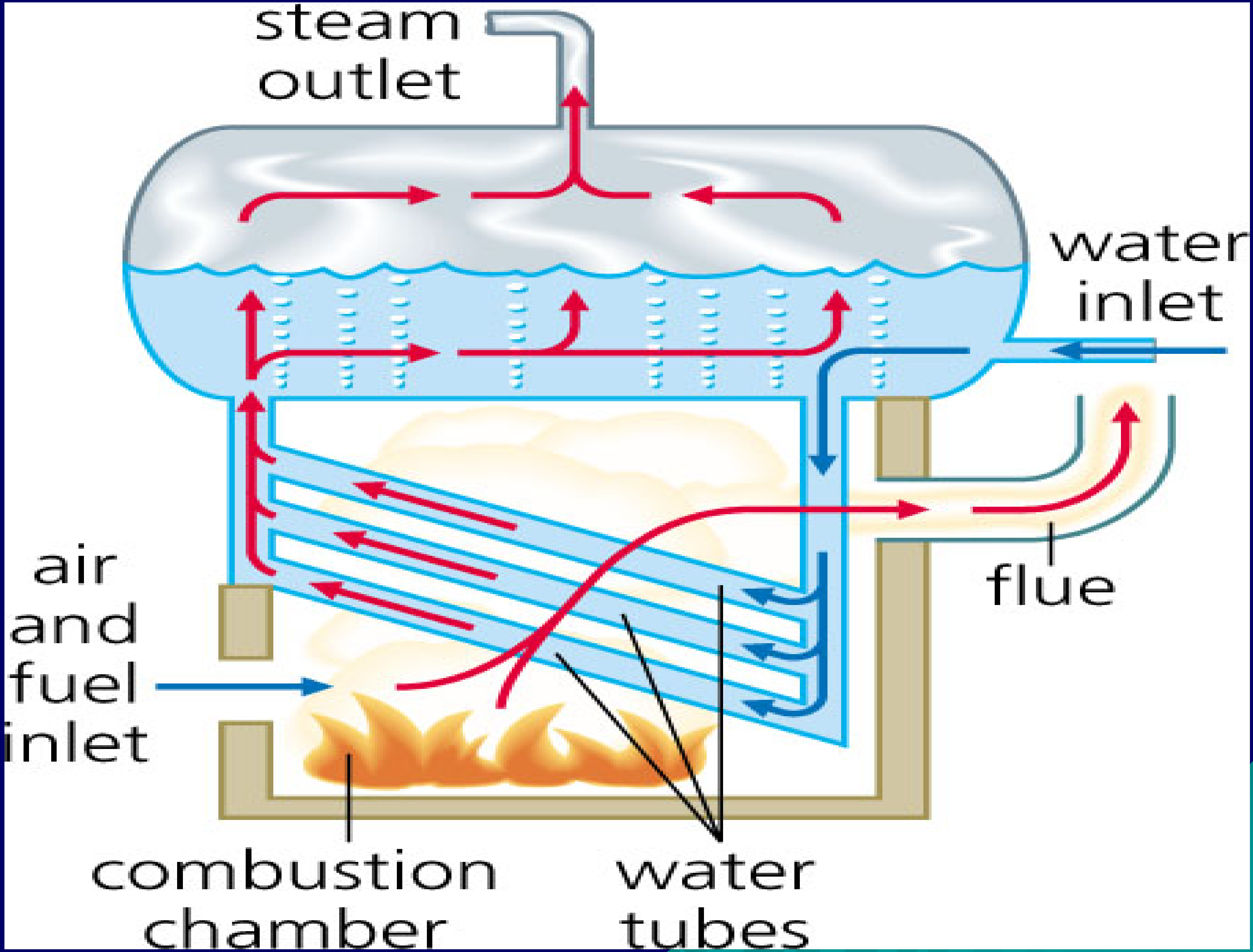
L- 5 Ion Exchange & Numericals

Disadvantages :-

- The equipment is costly and
- expensive chemicals are needed.
- If water contains turbidity,
- then the output of the process is reduced.

L- 5 Ion Exchange & Numericals


Vent
Spray Nozzles
Boiler Feedwater
Steam
Scrubber Section (Trays)
Storage Section
Deaerated Boiler Feedwater


steam
outlet
water
inlet
flue
air
and
fuel
inlet
combustion
chamber
water
tubes

L- 6 Scale, Sludge and Corrosion

BOILER TROUBLES

- A **proper quality of water** for boilers is very important.
- **Impure water** might cause following boiler problems:

1. Sludge and scale formation.
2. Corrosion of boiler metal.
3. Caustic embrittlement.
4. Priming and foaming.

L- 6 Scale, Sludge and Corrosion

(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,
- these are thrown out of water in the form of precipitates
- on the inner walls of the boiler.

L- 6 Scale, Sludge and Corrosion

(Sludge and Scale Formation)

- **If Precipitate is loose, slimy it is called as sludge.**
- **If it 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.

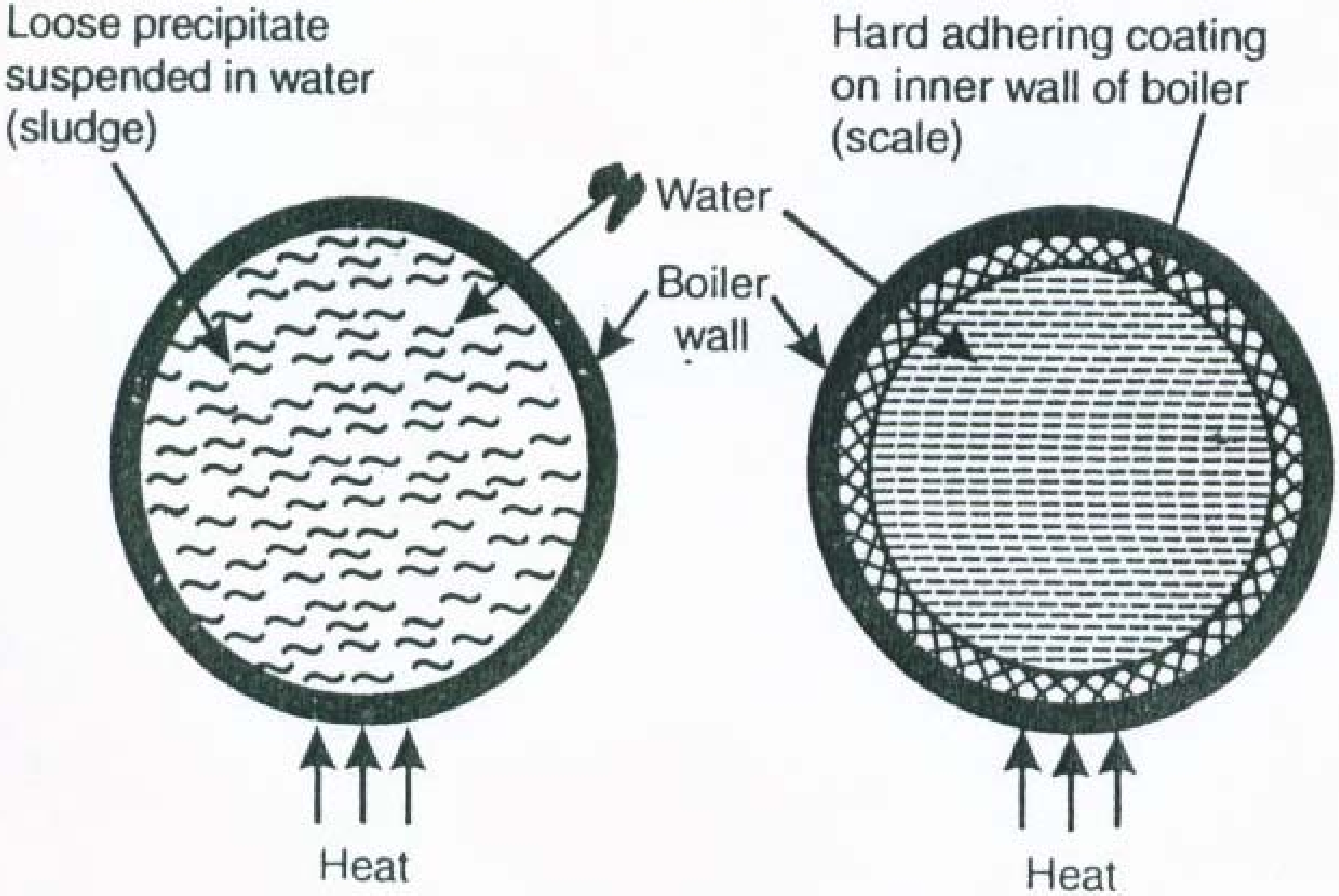
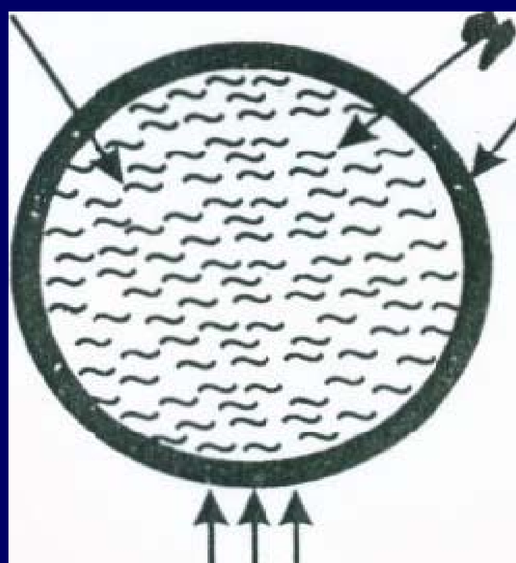

Loose precipitate suspended in water (sludge)
Water
Boiler wall
Hard adhering coating on inner wall of boiler (scale)
Heat
Heat

Fig.

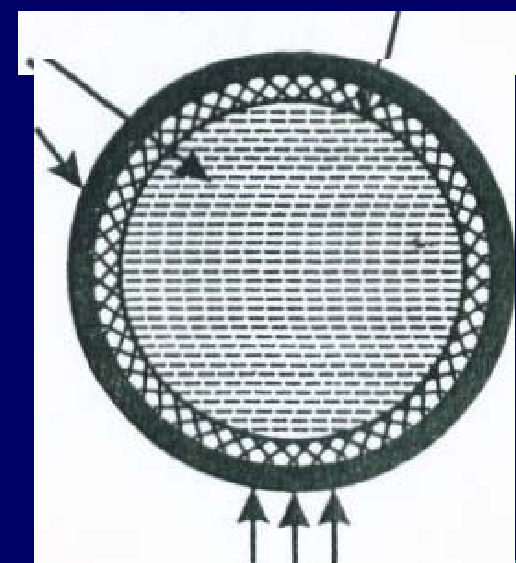
Loose precipitate suspended in water (sludge)

Hard adhering coating on inner wall of boiler (scale)

(sludge) **(scale)**



Water
Boiler wall



Heat **Heat**

Fig. Scale and sludge in boilers

L- 6 Scale, Sludge and Corrosion

Sludge

(3) Sludges are formed by substances which have greater solubility in hot water than in cold water.

Examples: $MgCO_3$, $MgCl_2$, $MgSO_4$, etc.

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

L- 6 Scale, Sludge and Corrosion

Disadvantages of Sludge formation :-

- **Sludges are poor conductors of heat, so these**
- **waste a portion of heat and thus**
- **decrease boiler efficiency.**
- **It sludge are formed along with scale,**
- **then sludge gets entrapped in the scale and**
- **both get deposited as scale.**

L- 6 Scale, Sludge and Corrosion

(Disadvantages of Sludge formation)

- **Excessive sludge formation disturbs the working of the boiler.**
- **Sludge deposited on pipe connection, plug opening due to that**
- **choking of pipes takes place.**

L- 6 Scale, Sludge and Corrosion

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."

L- 6 Scale, Sludge and Corrosion

SCALE :-

(1) Scales are hard deposit.

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

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

(4) Scales are main source of boiler trouble.

SCALING OF BOILER TUBES

L- 6 Scale, Sludge and Corrosion

Formation of Scale due to –

(1) Decomposition of Calcium bicarbonate-

(2) Deposition of $CaSO_4$

(3) Hydrolysis of Mg Salts-

(4) Presence of silica – (SiO_2)

L- 6 Scale, Sludge and Corrosion

Formation of Scale due to –

(1) Decomposition of Calcium bicarbonate-

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

(Insoluble)

- **This scale is soft and is the main cause of scale in lower pressure boiler.**
- **But in high pressure boilers $CaCO_3$ is soluble.**
- $CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$

L- 6 Scale, Sludge and Corrosion

(2) **Deposition of $CaSO_4$** – The solubility of $CaSO_4$ in water **decreases with rise of temperature.**

Temp.	15 ^{0}C	230 ^{0}C	320 ^{0}C
Solubility	3,200 ppm	55 ppm	27 ppm.

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

L- 6 Scale, Sludge and Corrosion

(3) Hydrolysis of Mg Salts-

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

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

(4) Presence of silica – (SiO_2) – Even present is small quantities deposits as $MgSiO_3$ and $CaSiO_3$.

If deposited in the inner walls of boiler is very difficult to remove.

L- 6 Scale, Sludge and Corrosion

Disadvantage of Scale formation-

(1) **Wastage of fuel –**

(2) **Lowering of boiler safety**

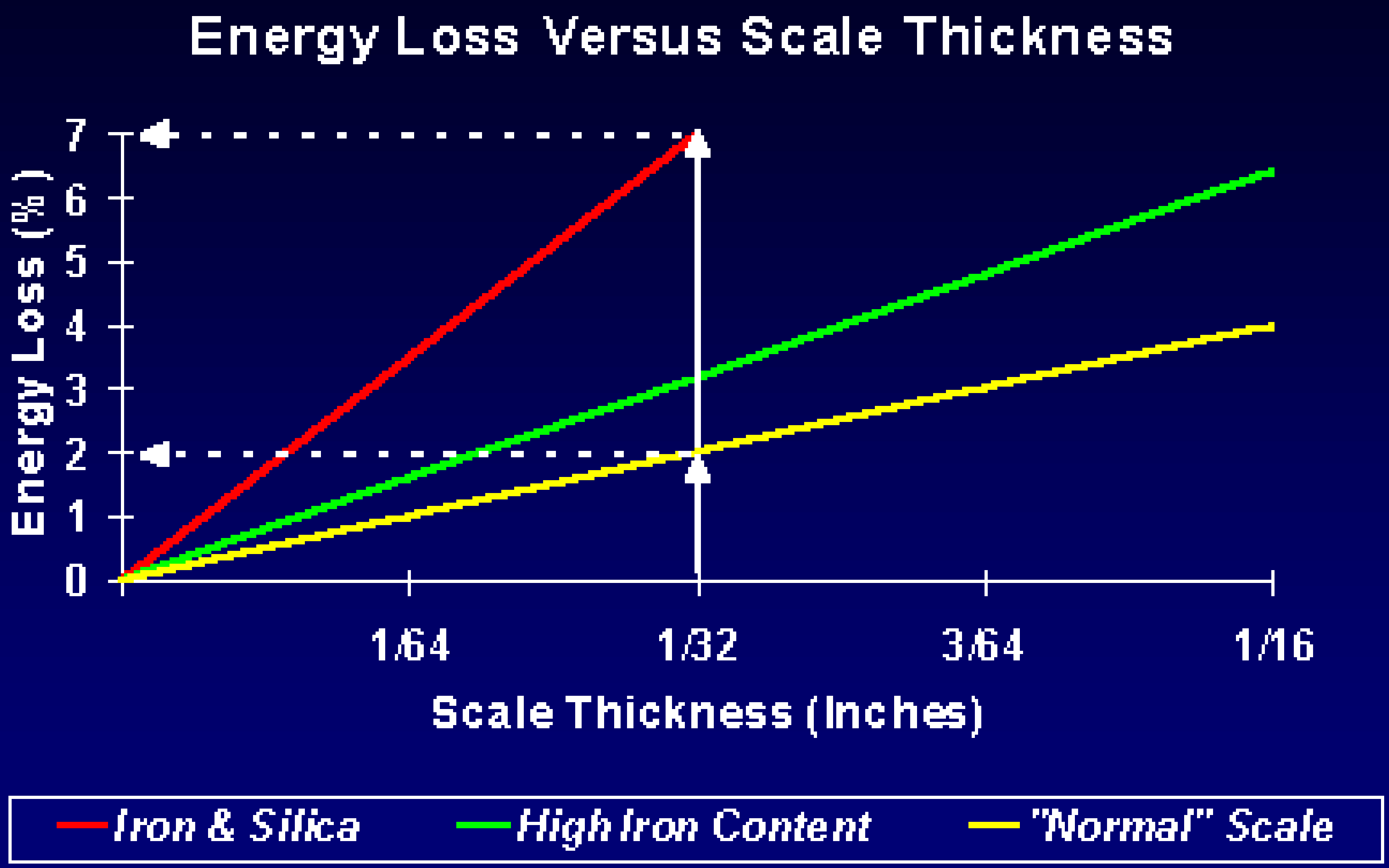
(3) **Decrease in efficiency**

L- 6 Scale, Sludge and Corrosion

Disadvantage of Scale formation-

(1) Wastage of fuel – Scales are poor conductor of heat . So excessive or over heating is needed, 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%


Energy Loss Versus Scale Thickness
Energy Loss (%)
0
1
2
3
4
5
6
7
1/64
1/32
3/64
1/16
Scale Thickness (Inches)
Iron & Silica
High Iron Content
"Normal" Scale

L- 6 Scale, Sludge and Corrosion

(2) Lowering of boiler safty –

- **The over heating of the boiler tube**
- **makes the boiler material softer and weaker**
- **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,**
- **results in decrease in efficiency.**

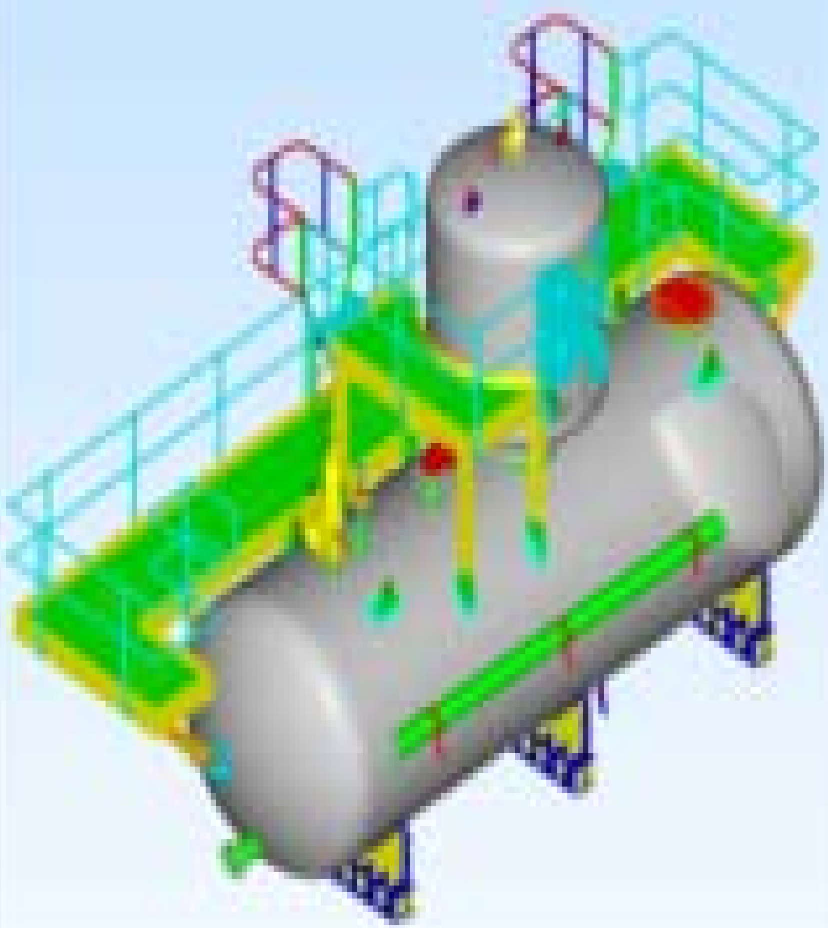
L- 6 Scale, Sludge and Corrosion

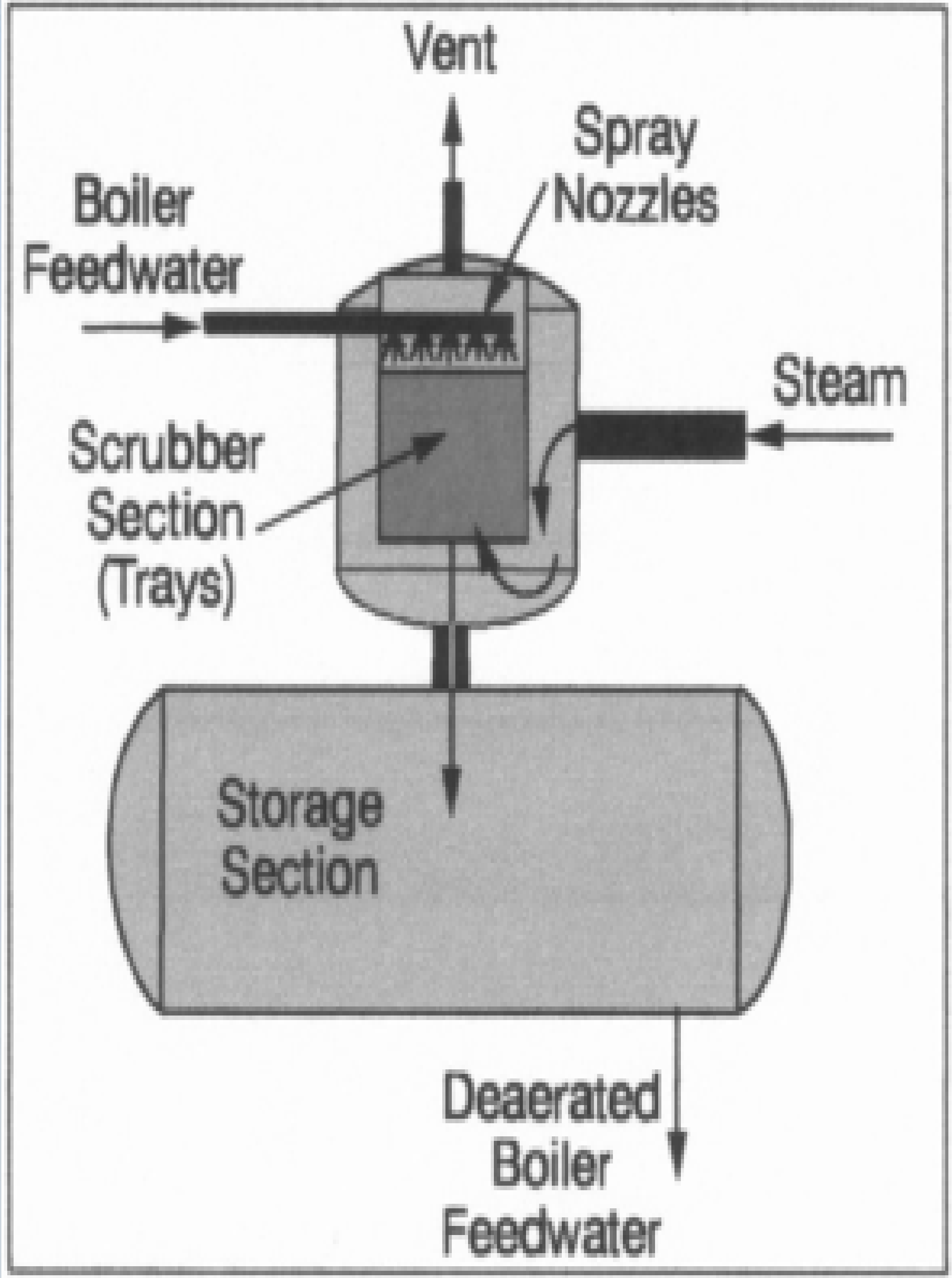
Boiler corrosion is decay of boiler material by a chemical attack by its environment. Main reasons for boiler corrosion are-

(a) Dissolved Oxygen

(b) Dissolved CO_2

© Acids from dissolved solids




Vent
Spray
Nozzles
Boiler
Feedwater
Steam
Scrubber
Section
(Trays)
Storage
Section
Deaerated
Boiler
Feedwater

L- 6 Scale, Sludge and Corrosion

(a) Dissolved Oxygen – Water usually contains above 8 mL of dissolved oxygen per litre. D.O. at high temperature, attacks boiler material-

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$$

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

Rust.

Removal of dissolved Oxygen-

$$2\ Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

sodium sulphite

- $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$

- **(b) By Mechanical de aeration –**

  In this method water is sprayed through a perforated plate – fitted above the tower is heated from sides and is connected to vacuum pump.

- **High temperature low pressure and**
- **large exposed surface area**
- **reduces the dissolved oxygen in water.**

L-7 Priming Foaming and caustic Embrittlement

(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.

caused by----

(iv) PRIMING AND FOAMING

PRIMING – caused by-

- The presence of large amount of dissolved solids.
- High steam velocities.
- Sudden boiling.
- Improper boiler design.
- Sudden increase in steam production rate.

L-7 Priming Foaming and caustic Embrittlement

Priming can be avoided by-

- Avoiding rapid change in steaming rate.
- Proper boiler design so that water level in boilers may be maintained at low level.
- Only soft water to be used.

L-7 Priming Foaming and caustic Embrittlement

- **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.

L-7 Priming Foaming and caustic Embrittlement

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

L-7 Priming Foaming and caustic Embrittlement

Foaming can be avoided By-

- **The addition of antifoaming agents which reduces the surface tension of water. Ex.- castor oil.**
- **Removing oil from boiler water by adding compound like sodium aluminate.**

L-7 Priming Foaming and caustic Embrittlement

- **(iii) CAUSTIC EMBRITTLEMENT**
- **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 fed into the boiler it may be likely that some residual Na_2CO_3 is still present in the softened water.**
- **Na_2CO_3 decomposes to give NaOH and CO_2, and NaOH thus produced makes the boiler water caustic.**

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

L-7 Priming Foaming and caustic Embrittlement

- The NaOH containing water flows 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.

L-7 Priming Foaming and caustic Embrittlement

- 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.Conc. NaOH Sol^{n} Dil. NaOH Sol^{n} Iron at Plane surfaces.

L-7 Priming Foaming and caustic Embrittlement

- Caustic Embrittlement can be avoided.
- By using sodium phosphate as softening reagent instead of sodium carbonate.
- By adding tannin or lignin to boiler water, since these blocks the hair cracks.
- By adding sodium sulphate the boiler water;

L-7 Priming Foaming and caustic Embrittlement

- 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.

L-7 Priming Foaming and caustic Embrittlement

L- 8 Internal Treatments, phosphate, carbonate, colloidal and calgon

Prevention of Scale formation-

Internal treatment – An internal treatment is done by adding a proper chemical to the boiler water.

The methods are-

(1) **Colloidal Conditioning** –

(2) **Phosphate Conditioning**

(3) **Carbonate Conditioning** –

(4) **Calgon Conditioning**

L- 8 Internal Treatments,…colloidal

Prevention of Scale formation-

Internal treatment –

(1) Colloidal Conditioning –

- **In lower pressure boiler by adding organic substance like –**
- **kerosene, tannin, agar – agar.**
- **Scale formation can be avoided.**
- **These make cover 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 form non-adherent and easily removable, soft sludge of phosphate.
- Which can be easily removed by blow – down operation.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\overline{\ } + 6NaCl$$

L- 8 Internal Treatments, phosphate,..

- $NaH_2 PO_4$ - Sodium dihydrogen phosphate (acidic)
- Na_2HPO_4 - Disodium hydrogen phosphate (weak alkali)
- Na_3PO_4 - Tri sodium phosphate (alkaline)
- The use of salt depends upon the alkalinity of water.
- Calcium is precipitated at
- pH value between 9.5 – 10.5.

L- 8 Internal Treatments,.. carbonate,..

(3) Carbonate Conditioning –

In lower pressure boiler scale formation can be avoided by adding sodium carbonate.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO3 + Na2SO4$$

$CaCO3_3$ is loose sludge which can be removed by blow down operation.

L- 8 Internal Treatments,… calgon

(4) Calgon Conditioning –

By adding calgon (Sodium hexa meta phosphate $(Na_3\ PO_4\ )6$ in boiler water.

It forms soluble complex with Ca+ ion.

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

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

(5)Treatment with sodium aluminate ($NaAlO_2$) :-

- $NaAlO_2$ gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminum hydroxide.

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

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

(5)Treatment with sodium aluminate ($NaAlO_2$) :-

- $NaAlO_2$ gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminum hydroxide.
- The ppt of $Mg(OH)_2$ plus $Al(OH)_3$ produced inside the boiler,
- entrap finely suspended and colloidal impurities, including oil drops and silica.

L-9 Alkalinity of water

Determinate of Alkalinity-

- Alkalinity of water means the total content of those substances in it,
- which **cause an increased [OH]- upon dissociation**.
- Alkalinity of water may be due to presence of:

1. Caustic alkalinity (due to OH- and due $CO2^{-3}$ ions)
2. Temporary hardness (due to HCO^{-3})

L-9 Alkalinity of water

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

$$\text{(i)}\quad \left[OH^-\right]+\left[H^+\right]\rightarrow H_2O$$

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

$$\text{(iii)}\quad \left[HCO_3^-\right]+\left[H^+\right]\rightarrow H_2O+CO_2$$

P

L-9 Alkalinity of water

- The titration of the water sample against a standard acid upto 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.

L-9 Alkalinity of water

- 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.

L-9 Alkalinity of water

- Thus

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

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

- The possible combinations of ions causing alkalinity in water are-

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.

L-9 Alkalinity of water

The possible combinations of ions causing alkalinity water are-

(i) OH^- Only or

(ii) CO_3^{2-} only or

(iii) HCO_3^- only or

(iv) OH- and CO_3^{2-} together or

(v) CO_3^{2-} and HCO_3^- together.

L-9 Alkalinity of water

- * The possibility of OH^- and HCO^-_3 ions together is **ruled out** because these
- combine instantaneously to from CO_3^{-2} ions.
- e.g. $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$

L-9 Alkalinity of water

e.g. $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$

- thus, OH^- and HCO^{-3} ions can't exist together in water.

- On the same basis,

- all the three (OH^-, $CO2^{-3}$ and HCO^{-3}) can't exist together.

L-9 Alkalinity of water

- Alkalinity OH-P=0P=MP= ½ MP> ½ MP < ½ MNilMNil(2P-M)NilNilNil 2P2(M-P)2PMNilNilNil[M-2P]
- Alkalinity is generally represented in ppm

L-10 Alkalinity of water

Nu. → 100 ml of water sample, on titration with N/50 H_2SO_4 gave a titre 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 $CaCO_3$ 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.**

L-10 Alkalinity of water

Further, the volume of N/50 H_2SO_4 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 H_2SO_4 = 50 mg of CaCO3

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

- = 11.6 mg of CaCO3

L-10 Alkalinity of water

This is the CO_3^{--} present in 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.**

L-10 Alkalinity of water

- **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 ?**

L-9 Alkalinity of water

L-9 Alkalinity of water

L-2 Water Softning, Lime-Soda Process

Calculation of Lime-Soda Requirement-

Constituent **Need** — **Reaction**

- Dissolved CO2 L

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$

Free acids H+

- HCl and H2SO4
- H2SO4 L+S

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 \downarrow + CaSO_4$$

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

- Coagulant
- Al2(SO4)3 L+S

$$2Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4$$

$$3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3 \downarrow + 6Na^+$$

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