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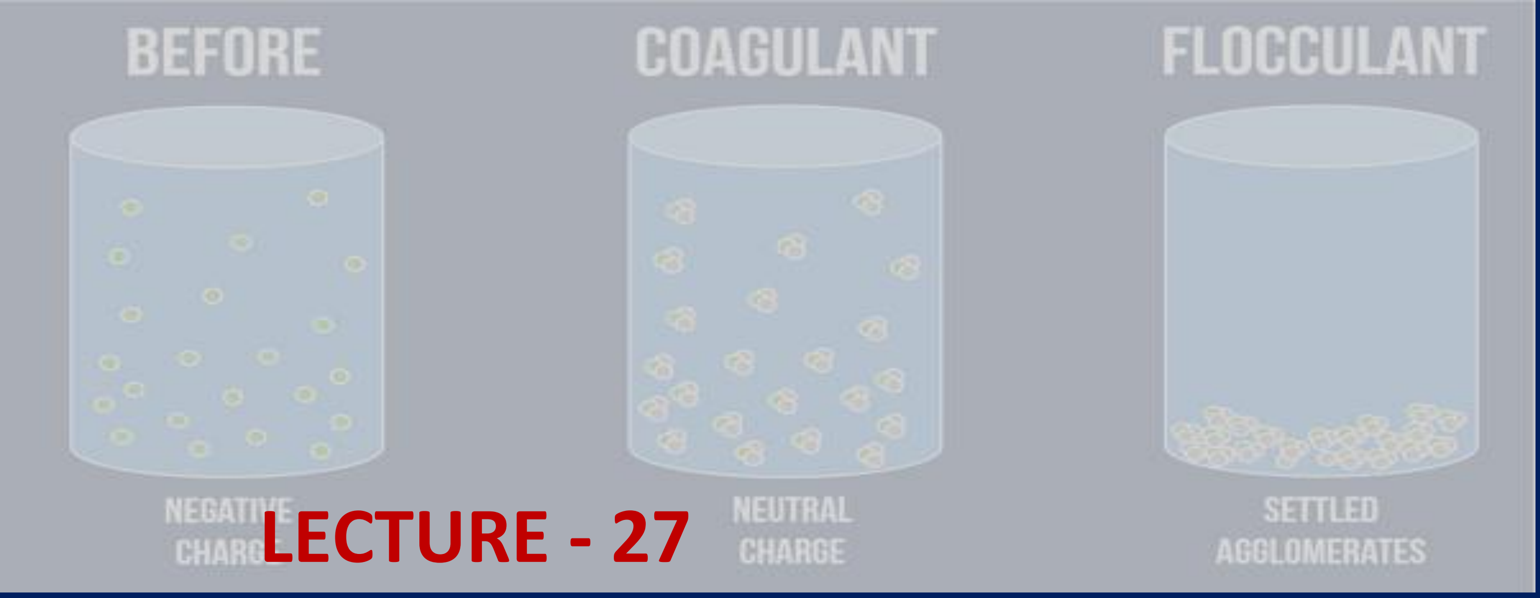
ENGINEERING- CHEMISTRY (BAS- 102/ 202)
B. TECH. I YEAR

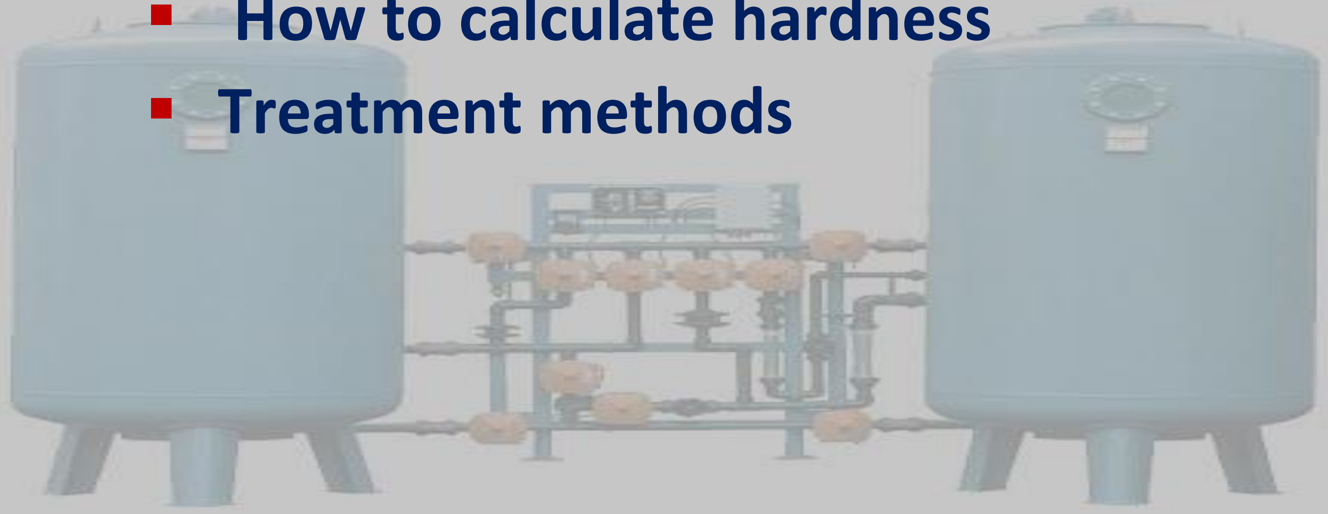
WATER TREATMENT

A Scientific Approach Towards the Purification of H_2O



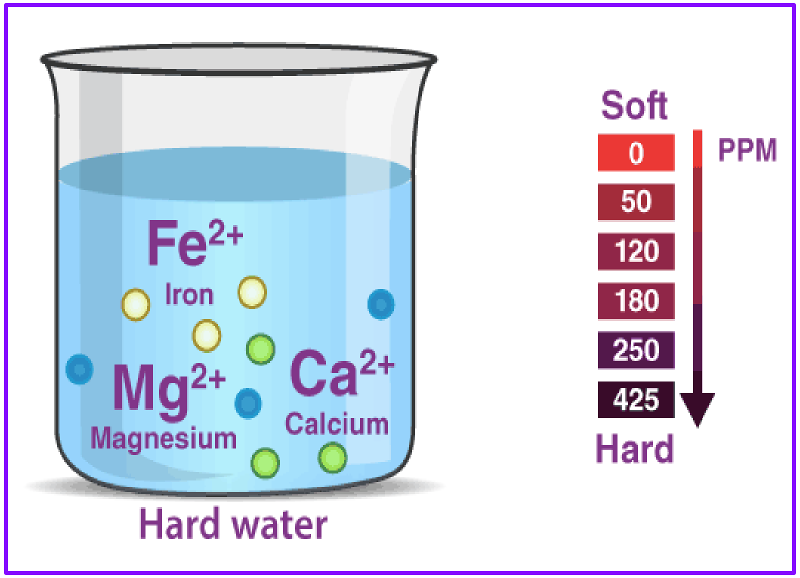
LECTURE - 27

- Hardness, its units and types
- How to calculate hardness
- Treatment methods



Why water is not always pure and what makes it hard or soft?

The dissolved salts of calcium like $CaCl_2$, $Ca(HCO_3)_2$, $CaSO_4$ etc. and that of magnesium like $MgCl_2$, $Mg(HCO_3)_2$, $MgSO_4$ etc. and traces of other salts makes the water hard.



Reaction of hard water with soap

$$Ca^{++}/Mg^{++} + 2C_{17}H_{35}COONa$$

Hard water Soap(sodium stearate)

$$\downarrow$$

$$(C_{17}H_{35}COO)_2Ca\ /\ (C_{17}H_{35}COO)_2Mg + 2Na^{+}$$

Calcium stearate / Magnesium stearate Sodium ions released in water

Scum (white curdy ppt)

- The water which does not give lather with soap is called hard water. The Hard water contains dissolved calcium & magnesium salts.
- **So Hardness** of water is defined as the soap consuming capacity of water **or** The amount of dissolved salts in water is known as its hardness”.

Types of Hardness

Hardness of Water

Temporary hardness

Ca and Mg carbonates & bicarbonates

Permanent Hardness

1. Calcium sulphate
2. Magnesium sulphate
3. Calcium nitrate
4. Magnesium nitrate
5. Chlorides of Ca and Mg.
6. Sulphides of ca and Mg.

Difference between temporary and permanent hardness

Temporary Hardness	Permanent Hardness
▪ Temporary Hardness is caused by the presence of dissolved bicarbonate of Ca, Mg and traces of other heavy metals.	It is caused due to the chlorides, sulphates, nitrates of Ca, Mg and traces of other heavy metals
▪ It can be removed by mere boiling of water, when bicarbonates are decomposed yielding insoluble carbonates. $Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$ **Insoluble ppt** $Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2$ **Insoluble ppt**	Permanent hardness cannot be removed by boiling. It needs special treatment methods like zeolite process, lime soda process and ion exchange

Expression of Hardness

Hardness of water is expressed in terms of $CaCO_3$ because of the following reasons:

- Molecular weight of $CaCO_3$ is 100 (Equivalent wt. is 50) which makes the calculation easy.
- $CaCO_3$ is most insoluble salt that can be precipitated in water treatment.

Units of hardness

Hardness of water is expressed in following units:

1. PPM
2. Milligrams per litre
3. Degree Clark
4. Degree French

- ***Parts per million (ppm)***

  It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

- ***Milligrams per litre (mg/L)***

  It is defined as the number of milligrams of $CaCO_3$ equivalent hardness per 1 litre of water.

- ***Clarke's degree (^oCl)***

  It is defined as the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

- ***French degree (^oFr)***

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

Relationship between various units

1Mg/lit = 1 ppm = 0.1 ^{0} Fr = 0.07 ^{0} Cl

CALCULATION OF HARDNESS

$$\text{Hardness} = \text{Amount of salt in mg/lit} \times \frac{\text{Equivalent Weight of } CaCO_3}{\text{Equivalent weight of hardness causing salt.}}$$

(Equivalent weight of $CaCO_3$ = 50)

Total Hardness = Total Temporary Hardness + Total Permanent Hardness

Let us take some numericals on hardness.

Q1. A water sample contains 400 mg of $CaSO_4$ per liter. Calculate the hardness in terms of $CaCO_3$ equivalent.

Solution:

$$\text{Hardness} = \text{Amount of salt} \times \frac{\text{Equivalent Weight of } CaCO_3}{\text{Equivalent Weight. of salt}}$$

$$= 400 \text{ mg/L} \times 50/68$$

$$= 295 \text{mg/L} \quad = 295 \text{ppm}$$

Q.2. How many grams of $MgCO_3$ dissolved per litre gives 84 ppm hardness?

Solution.

Hardness =

$$\text{Amount of } MgCO_3 \text{ in mg/L} \times \frac{\text{Equivalent Weight of } CaCO_3}{\text{Equivalent Weight of } MgCO_3}$$

$$= 84 \text{ ppm} \times 50/42$$

$$= 100 \text{ ppm}$$

So, 100 mg of $MgCO_3$ dissolved per litres gives 84 ppm of hardness.

Q3. A sample of water on analysis was found to contain the following impurities:

Impurity	Quantity (mg/L)	Mol. Wt.
$Ca(HCO_3)_2$	4	162
$Mg(HCO_3)_2$	6	146
$CaSO_4$	8	136
$MgSO_4$	10	120

Calculate the temporary, permanent and total hardness of water in ppm, degree french and degree clarke

Sol. Conversion into $CaCO_3$ equivalent.:

Constituents	Amount (mg/L)	Multiplication factor	$CaCO_3$ equivalent
$Ca(HCO_3)_2$	4	50/81	4 × 50/81 = 2.47 mg/L
$Mg(HCO_3)_2$	6	50/73	6× 50/73 = 4.11 mg/L
$CaSO_4$	8	50/68	8× 50/68 = 5.88 mg/L
MgSO4	10	50/60	10× 50/60 = 8.33 mg/L

Temporary hardness is due to bicarbonates of Ca and Mg. So,

Temporary hardness = 2.47 + 4.11 = 6.58 mg/L

As, 1 mg/L= 1 ppm = 0.1 °Fr = 0 .07°Cl

Hence temporary hardness = 6.58 mg/L = 6.58 ppm

= 6.58 × 0.1 = 0.658°Fr

= 6.58 × 0.07 =0.46°Cl

Permanent hardness is due to $CaSO_4$ and $MgSO_4$. So,

Permanent hardness = 5.88 +8.33

= 14.21mg/L

= 14.21 ppm = 14.21 × 0.1 °Fr

= 1.421°Fr

= 14.21 × 0.07 = 0.995°Cl

BOILER FEED WATER

The water used in boilers for steam generation is known as boiler feed water. It should have the following composition:

- **Hardness**: below 0.2 ppm.
- **Caustic alkalinity** (due to OH^-): 0.15 to 0.45ppm.
- **Soda alkalinity** (due to Na_2CO_3): 0.45 to 1ppm.
- **Excess soda ash**: 0.3 to 0.55ppm.
- **pH**: 8 to 9.
- **Oxygen:** Below 0.02ppm

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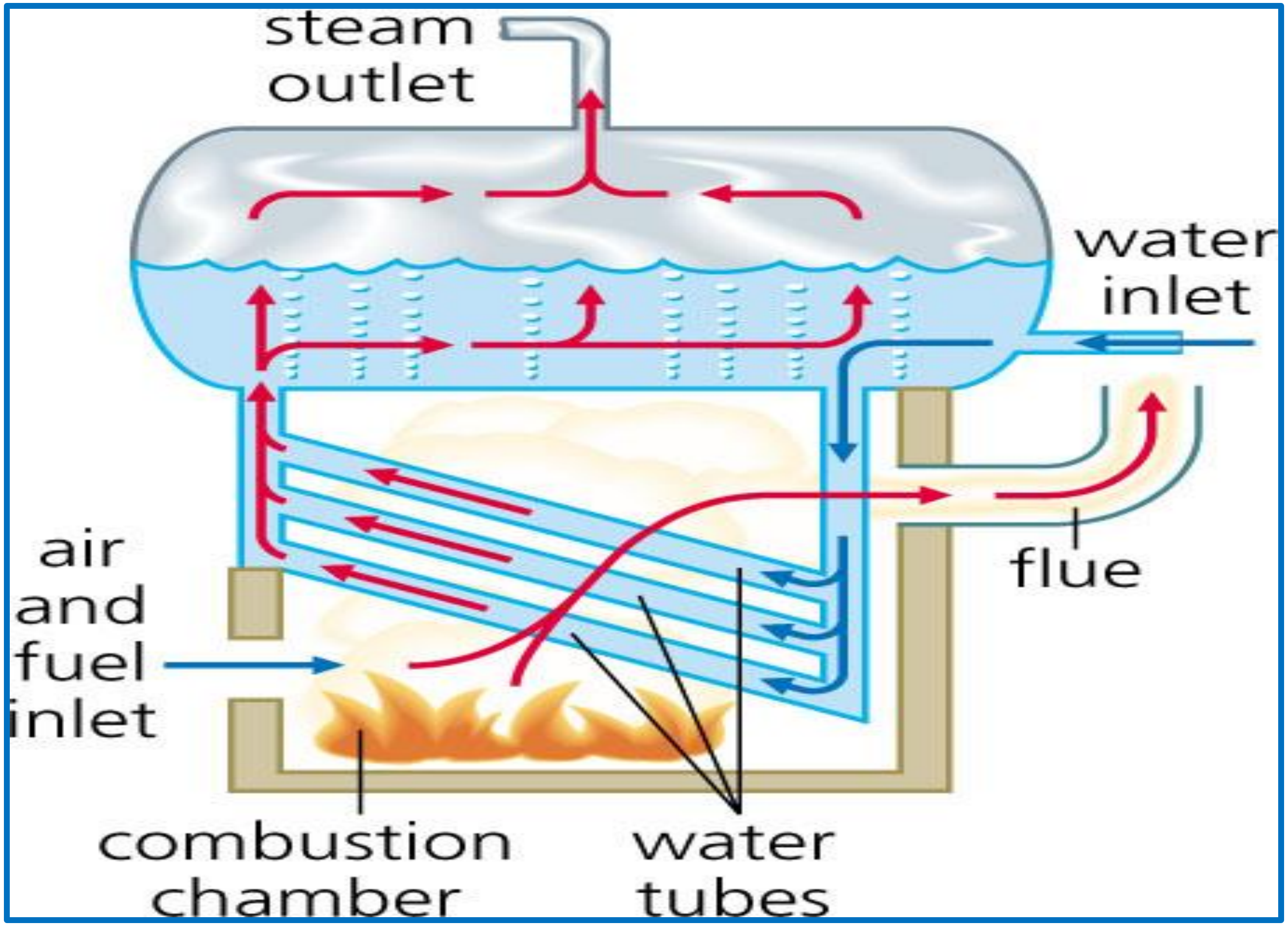
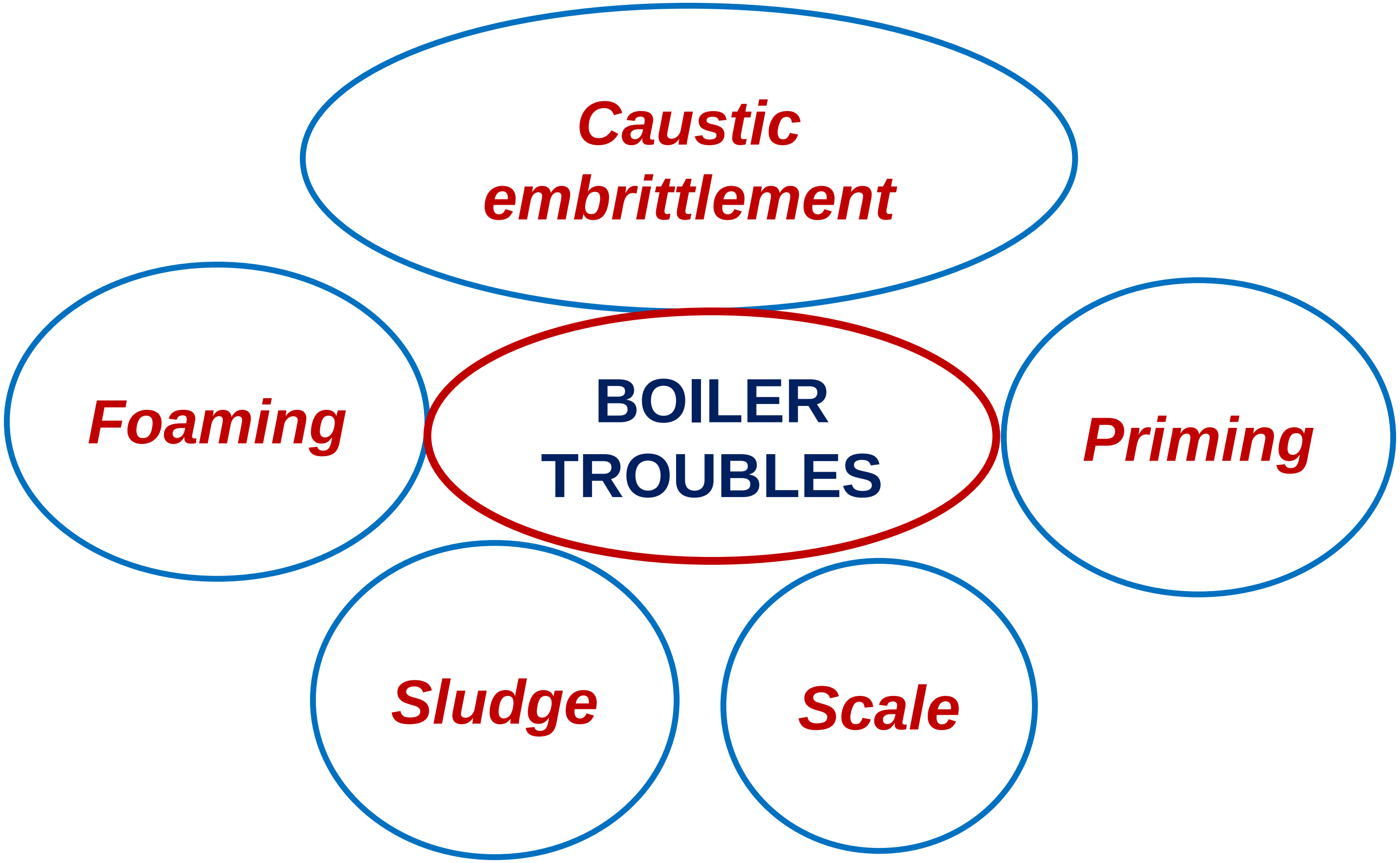
View of an Industrial Boiler

Boilers are used in Industries for the purpose of steam generation.

Schematic view inside a boiler





BOILER TROUBLES

Caustic embrittlement

Foaming

Priming

Sludge

Scale

1. Priming or Wet Steam Formation:

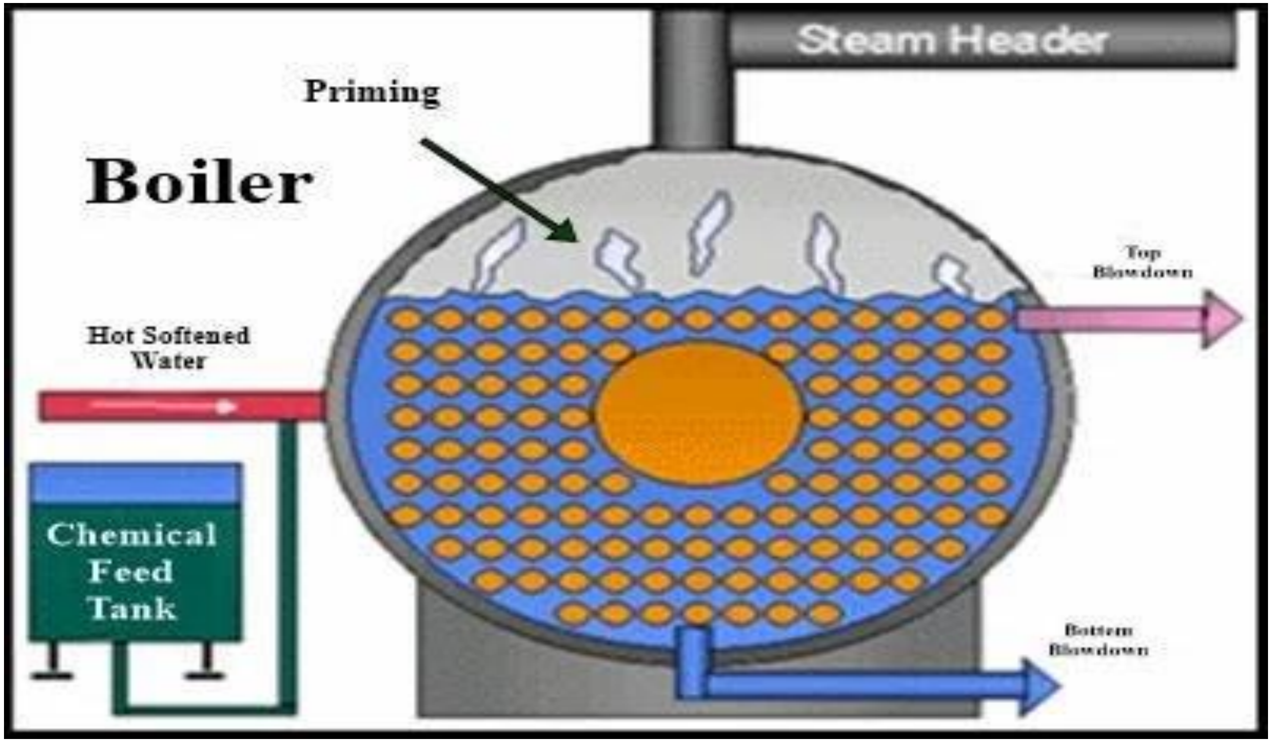
Small droplets of liquid water associated with steam are carried to steam drum. These droplets of water carry some suspended and dissolved solids along with them.

Causes:

- Large amount of dissolved solids.
- High steam velocities.
- Sudden boiling.
- Faulty boiler design.
- Sudden increase in stream production rate.
- The high levels of water in boilers.

Prevention of priming:

- Fitting mechanical steam purifiers.
- Avoiding rapid change in steaming rate.
- Maintaining low water levels in boilersand.
- Using soft water



2. Foaming

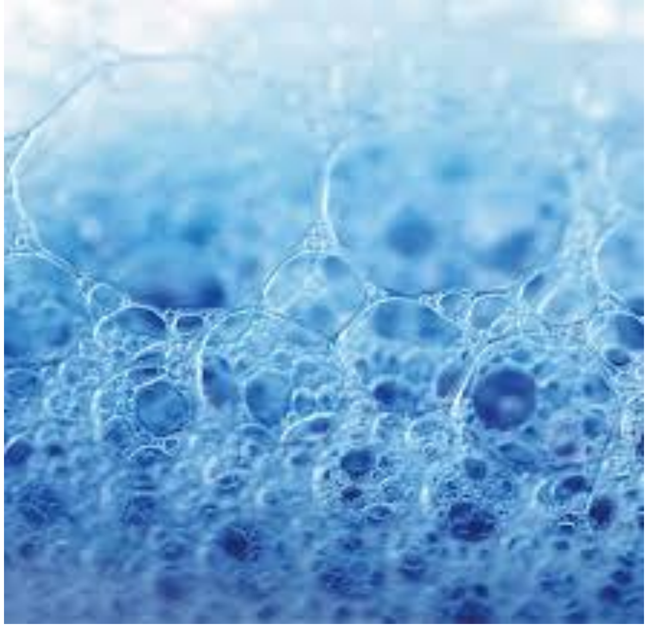
Formation of stable bubbles at the surface of water in the boiler which do not break easily and passes out with the steam is calling foaming.

Reason:

- Due to the presence of oil drops, alkalies etc.
- Oils and alkalies reacts to form soaps which greatly lowers the surface tension of water and thus increases the foaming tendency of water.

Prevention of Foaming:

- Adding antifoaming chemicals like castor oil, tannic acid etc.
- Oil can be removed by adding sodium aluminates or alum.
- Using soft water



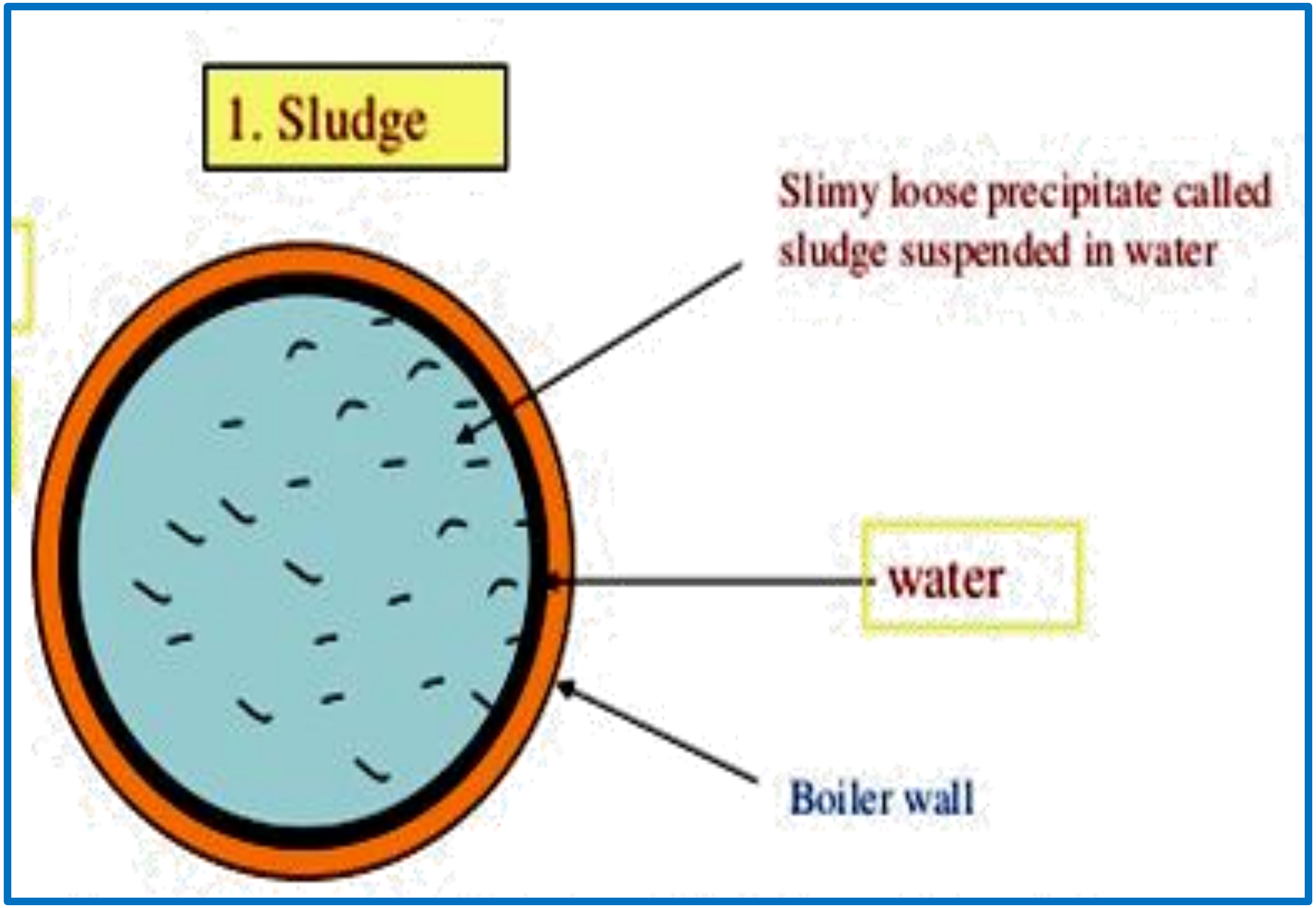
3. Scale & sludge formation

Sludge:

The muddy solid deposited at the bottom of the boiler is called sludge. It is formed at comparatively colder portion of the boiler and collects in the areas of the system, where the flow rate is slow or at bends.

Causes of the sludge:

The sludge is caused by substances that have greater solubility in hot water than in cold water like ***$MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.***


1. Sludge
Slimy loose precipitate called sludge suspended in water
water
Boiler wall

Disadvantages of sludges:

- Wastage of heat and fuel.
- Chocking of the pipes.

Prevention of sludge formation:

- By using soft water.
- Blow down operation.

Scales

Scales are hard sticky deposits on the inner walls of boiler. The scales are very difficult to remove.

Causes of Scale formation:

i) Due to the decomposition of $Ca(HCO_3)_2$ at high temperature & pressure present in boiler, It forms $CaCO_3$ (insoluble salt) which settles as precipitate in the boiler.

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

ii) $CaSO_4$ precipitates out as hard scale, whenever the temperature of boiler increases.

iii) The dissolved $MgCl_2$ present in water precipitates as $Mg(OH)_2$ at high temperature, which deposits as scale.

$$\mathbf{MgCl_2 + 2H_2O \xrightarrow{\Delta} Mg(OH)_2 + 2HCl}$$

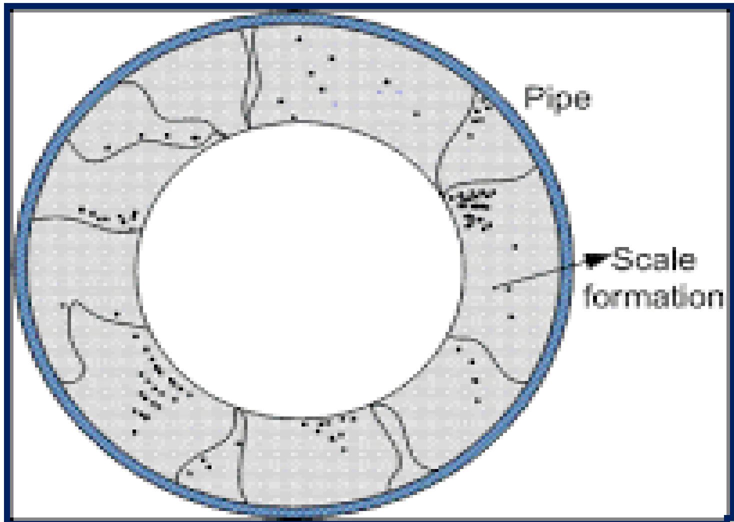
iv) SiO_2 present in water deposits as calcium silicate or magnesium silicate.

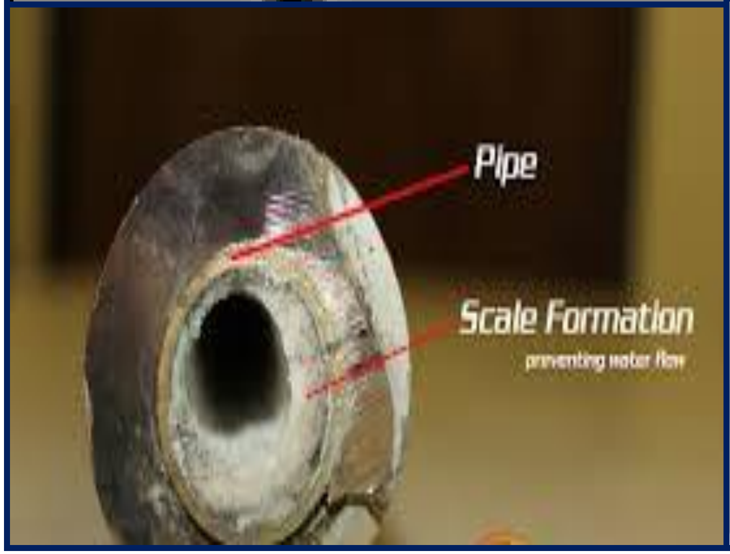
Disadvantages of Scale:

- Loss of heat and fuel.
- Heating the boiler to high temperatures causes the weakening of boiler material.
- Chocking of boiler.
- Cracks in Scale causes sudden steam and high pressure resulting in explosion of boiler.

Removal of Scales:

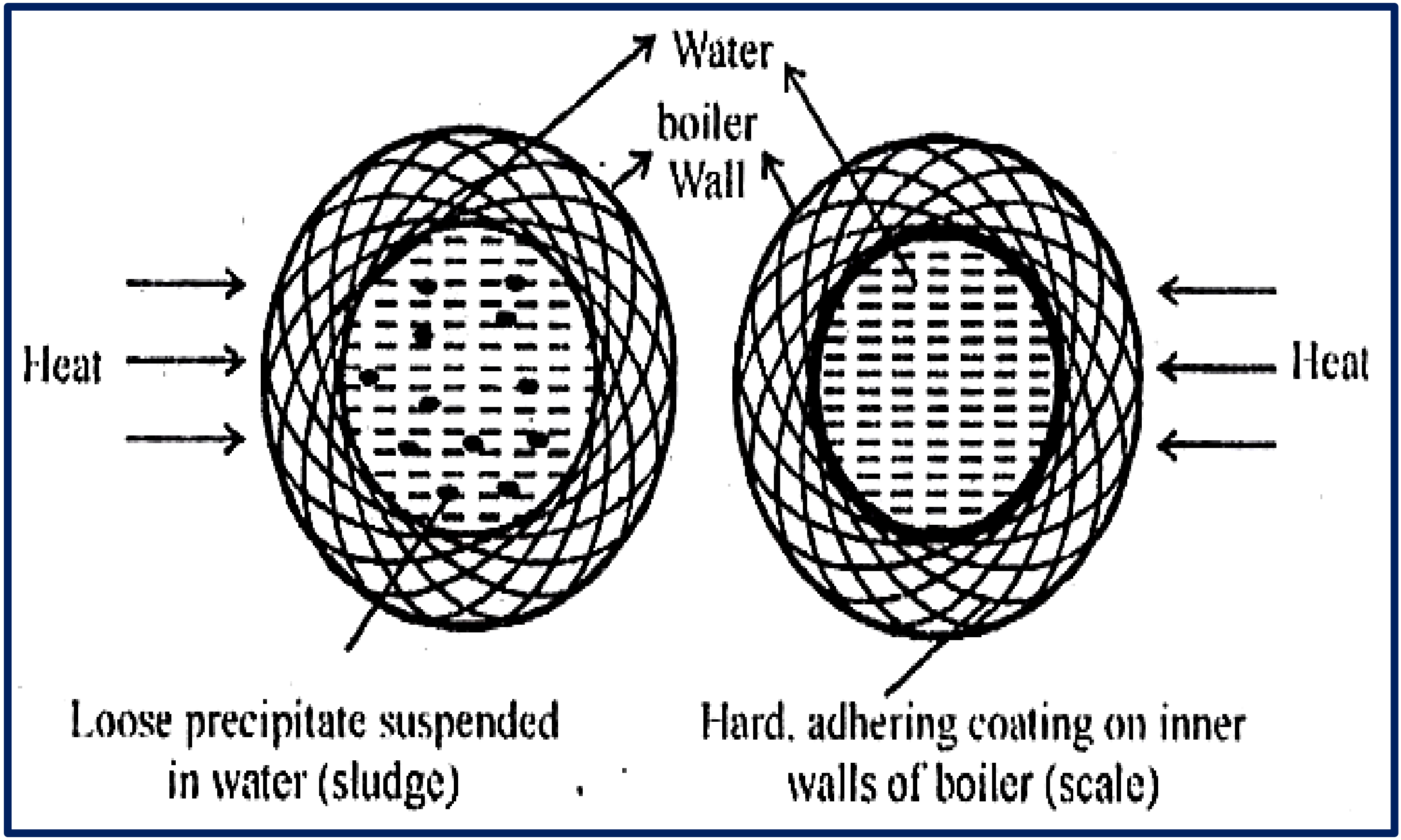
- If the scale is soft. It can be removed by scrapper.
- By giving thermal shocks (by heating to higher temperature and suddenly cooling.)
- The $CaCO_3$ scale is removed by the washing with 5-10% HCl Solution and $CaSO_4$ scale is removed by washing with EDTA solution


Pipe
Scale formation


Pipe
Scale Formation
preventing water flow


PIPE PLUGGED WITH SCALE

Sludge	Scale
1. It is soft, loose and slimy precipitate.	It forms hard deposits.
2. Do not stick to boiler walls and can be easily removed.	They stick to the inner surface of the boiler and are very difficult to remove.
3. They are formed by substances like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$, etc.	They are formed by substances like $CaSO_4$, $Mg(OH)_2$ etc.
4. Formed at comparatively colder portions of the boiler.	Formed at heated portions of the boiler.
5. Less dangerous.	Chances of explosion are there.
6. They can be removed by blow down operation.	Removed by use of EDTA, thermal shock treatment.



Scale and sludge formation in boilers

4. Caustic embrittlement:

- The formation of cracks in boilers due to NaOH is called caustic embrittlement.

- The Na_2CO_3 present in water hydrolysed to NaOH at high pressures in boilers.

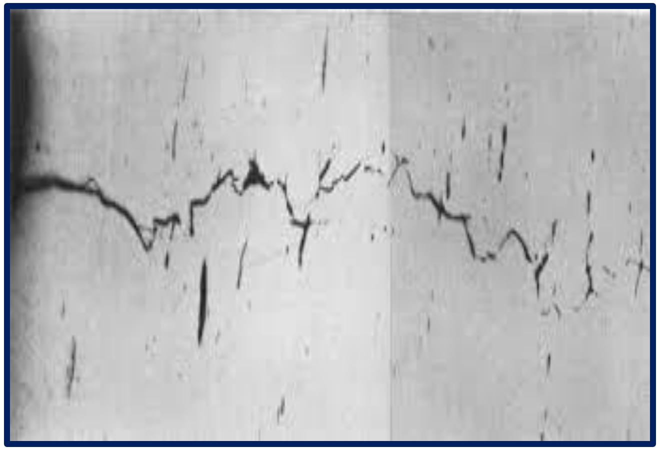
$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

- The NaOH formed concentrates after long use. It causes cracks on the boiler walls, especially at the stress points.

Prevention of caustic embrittlement:

- By using sodium phosphate as softening agent instead of Na_2CO_3.
- By adding tannin or lignin to boiler water which block the hair cracks and pits in boiler.
- By adding sodium sulphate to soften the water and this also blocks the hair cracks present on the surface of the boiler plate.


CAUSTIC EMBRITTLEMENT
CRACKS
INCRUSTATIONS



5) Boiler Corrosion

It is the decay of the boiler body material ***due to environmental factors.***

Disadvantages

- Reduced life of boiler.
- Increased cost of repairs and maintenance.
- Leakage of joints.

Prevention:

- By removal of oxygen using hydrazine, Na_2SO_4 etc.
- By removal of CO_2: By adding ammonia CO_2 .
- pH should be adjusted between 8.5 to 9.

Treatment of boiler feed water (softening of water)

Treatment of Boiler feed water is of two types.

- External Treatment Method.
  - Zeolite method
  - Lime soda method
  - Ion Exchange Process
- Internal Treatment Method.
  - Calgon conditioning
  - Phosphate conditioning
  - Carbonate conditioning

INTERNAL TREATMENT OF WATER

- Internal treatment is ***corrective method***.
- It is also called ***conditioning method***.
- In internal treatment, water in treated inside the boiler. Some chemicals are added inside the boilers for water conditioning, which reacts with scale forming substances in water and converts them into sludge (loose slimy precipitate) which remains in the dissolved state in water and is harmless for the boilers and can be conveniently removed by ***blow down operation*** when required.

Various internal treatment methods

1. *Carbonate conditioning:*

In low pressure boilers, scale formation can be avoided by treating the boiler water with Na_2CO_3. Where, $CaSO_4$ is converted into $CaCO_3$. $CaCO_3$ is precipitated as loose sludge in the boiler which can be removed by blow down operation.

$$Na_2CO_3 + CaSO_4 \longrightarrow \underset{\text{(sludge)}}{CaCO_3} + Na_2SO_4$$

Caution: ***Excess sodium carbonate can result in caustic embrittlement.***

2. Calgon Conditioning:

- Calgon means calcium gone i.e. the removal of Ca^{2+}.
- ***Sodium hexa-meta phosphate*** ***$(NaPO_3)_6$*** is called calgon.
- Calgon reacts with calcium ion and forms a water soluble compound.
- Involves adding Calgon i.e. sodium hexa meta phosphate $(NaPO_3)_6$ to boiler water.
- It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

$$Na_2[Na_4(PO_3)_6] \longrightarrow 2Na^+ + [Na_4P_6O_{18}]^{-2}$$

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

3. Phosphate conditioning:

It is applied to high pressure boilers. scale formation can be avoided by treating the boiler water with ***Na_3PO_4*.** Where, scale forming salts are converted into sludge forming salts. Loose sludge in the boiler can be removed by blow down operation.

$$3\,CaCl_2 + 2Na_3PO_4 \longrightarrow \underset{\text{sludge}}{Ca_3(PO_4)_2} + 6NaCl$$

$$3\,MgCl_2 + 2Na_3PO_4 \longrightarrow \underset{\text{sludge}}{Mg_3(PO_4)_2} + Na_2SO_4$$

LECTURE - 28

- Zeolite Process
- Ion exchange resins
- Numericals on zeolite process.

ZEOLITE METHOD OF WATER TREATMENT

Zeolites are ***hydrated sodium alumino silicates***. They are also known as permutit (permutit means boiling stone).

They have porous structure with molecular formula **$Na_2O.Al_2O_3.xSiO_2.yH_2O$ (X=2 to 10 & Y=2 to 6)**.

They are ***represented as Na_2Ze***

(Ze = insoluble framework; Na= loosely held sodium ions).

Principle of zeolite process:

They exchange their loosely held sodium ions reversibly with the hardness producing cations in water (Ca^{+2} and Mg^{+2}).

WORKING OF ZEOLITE FOR WATER TREATMENT

Working- It involves two steps:

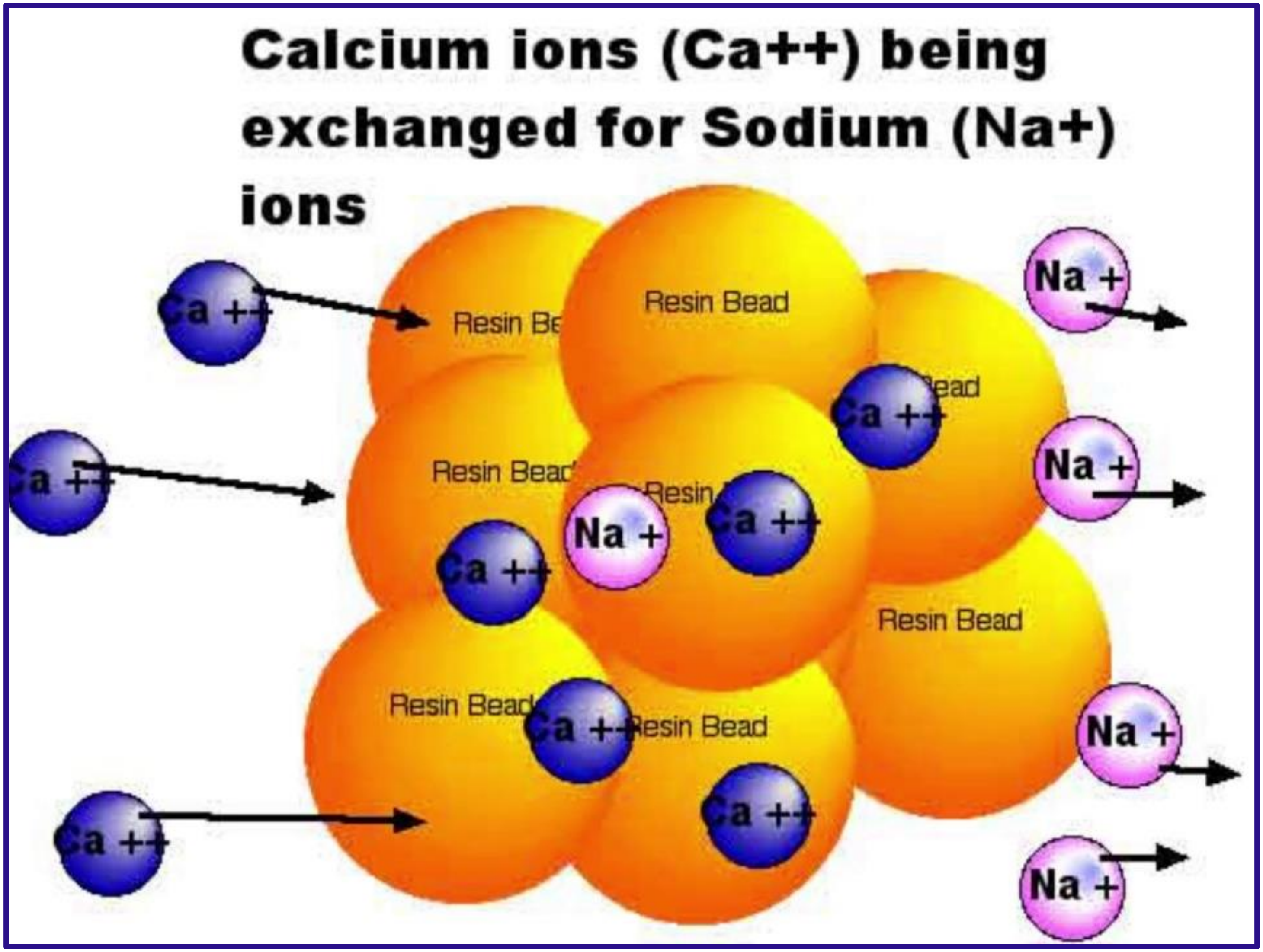
1. ***Water softening:*** When Ca^{2+} and Mg^{2+} ions containing hard water is passed through a bed of sodium zeolite, the ***sodium ions are replaced by the calcium and magnesium ions.***

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow 2NaHCO_3 + CaZe$$

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow 2NaHCO_3 + MgZe$$

$$Na_2Ze + CaSO_4 \rightarrow Na_2SO_4 + CaZe$$

$$Na_2Ze + MgSO_4 \rightarrow Na_2SO_4 + MgZe$$



Calcium ions (Ca++) being exchanged for Sodium (Na+) ions

2. Regeneration:

When all sodium ions are replaced by Ca and Mg ions, The zeolite becomes inactive. Then the zeolite needs to Be regenerated. ***Brine solution*** is passed through the bed of inactivated zeolite. Na_2Ze is regenerated.

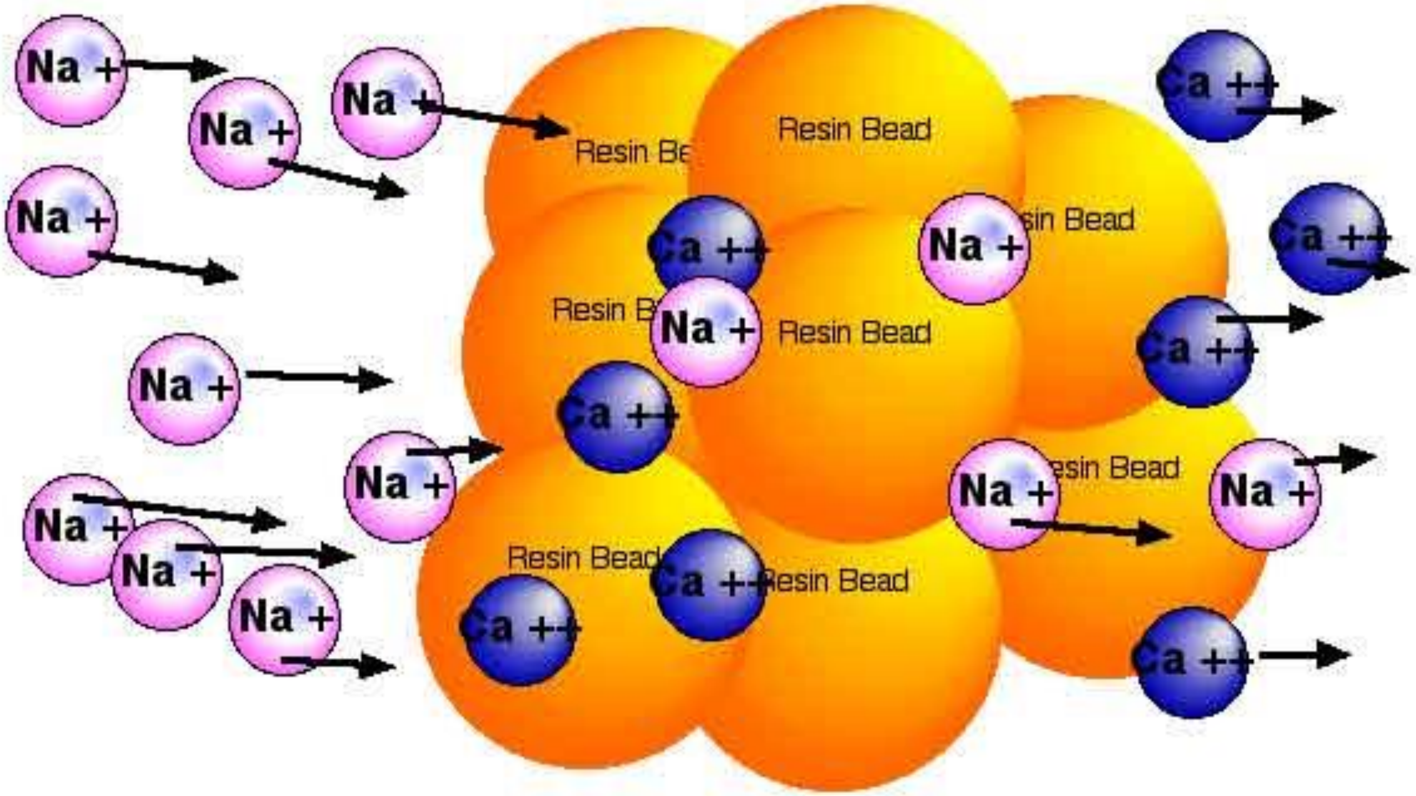
$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

Exhausted zeolite **Brine Solution** **Regenerated zeolite**

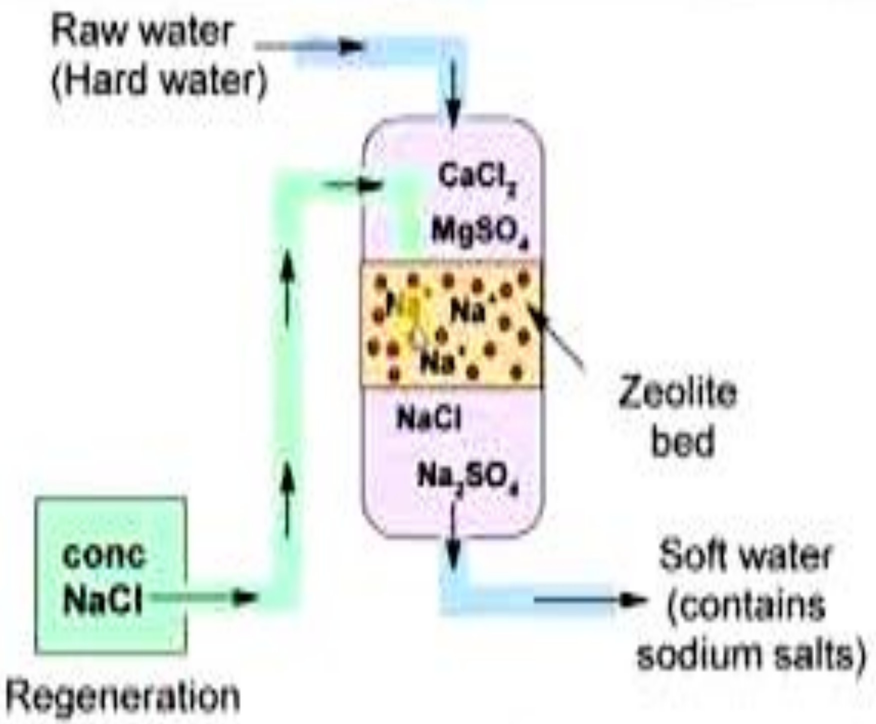
$$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$$

Exhausted zeolite **Brine Solution** **Regenerated zeolite**

Resin which is being regenerated



ZEOLITE METHOD OF WATER TREATMENT



The calcium (ca) & magnesium (mg) salts present in hard water react with sodium zeolite (Na+) forming insoluble calcium & magnesium zeolite. these salts present or retain in zeolite bed while the outgoing water contains only sodium salts

Advantages

- About only 10 ppm residual hardness is left.
- No sludge formation.
- Requires less time and operation is clean.
- Automatic process.
- Equipment is compact and maintenance and operation is easy.

Disadvantages

- This method replaces cationic impurities; anions are left behind in water.
- Treated water contains more sodium salts, so this water cannot be used in boilers.

Limitations:

- Turbid water cannot be used as it will clog the pores of zeolite
- Acidic water cannot be used as it will destroy the zeolite bed.
- Hot water cannot be used as zeolite tends to dissolve in it.
- If Fe and Mn impurities are present, then they bind tightly to the zeolite bed and hence the zeolite can not be regenerated.

NUMERICALS ON ZEOLITE SOFTENER

Q1. The hardness of 10,000 L of sample of water was completely removed by passing it through a zeolite softener. The zeolite softener then required 200 L of NaCl solution containing 150 gm/L of NaCl for regeneration. Find out the hardness of water sample.

Solution: 200 L of NaCl has = 200 L × 150 gm/L = 30,000 g NaCl

$$CaCO_3 \text{ eq.} = \text{Amount of NaCl} \times \frac{\text{Eq. wt. of } CaCO_3}{\text{Eq. wt. of NaCl}}$$

$$= 30{,}000 \times \frac{50}{58.5} = 25641.025 \text{ gm/L}$$

$$= 25641.025 \text{ gm/L} \times 1000 = 25641025 \text{ ppm}$$

$$\text{Hardness of 1 L of water} = \frac{25641025}{10{,}000} = 2564.1 \text{ ppm}$$

Q2. By passing 50 liters of NaCl solution containing 250 gm/ litre of NaCl, an exhausted zeolite softener bed was regenerated. Calculate the litres of hard water sample (hardness equal to 200 ppm as $CaCO_3$) which can be softened by regenerated bed of zeolite softener.

Solution: Total amount of NaCl used= 50 × 250 = 12,500 gm

$$CaCO_3 \text{ equivalents} = 12{,}500 \times \frac{50}{58.5} \times \frac{1000}{\text{Vol. of water}}$$

$$200 = 12{,}500 \times \frac{50}{58.5} \times \frac{1000}{\text{Vol. of water}}$$

$$\text{Vol. of water} = 12{,}500 \times \frac{50}{58.5} \times \frac{1000}{200}$$

$$= 53418.80 \text{ L}$$

ION EXCHANGE METHOD OF WATER TREATMENT

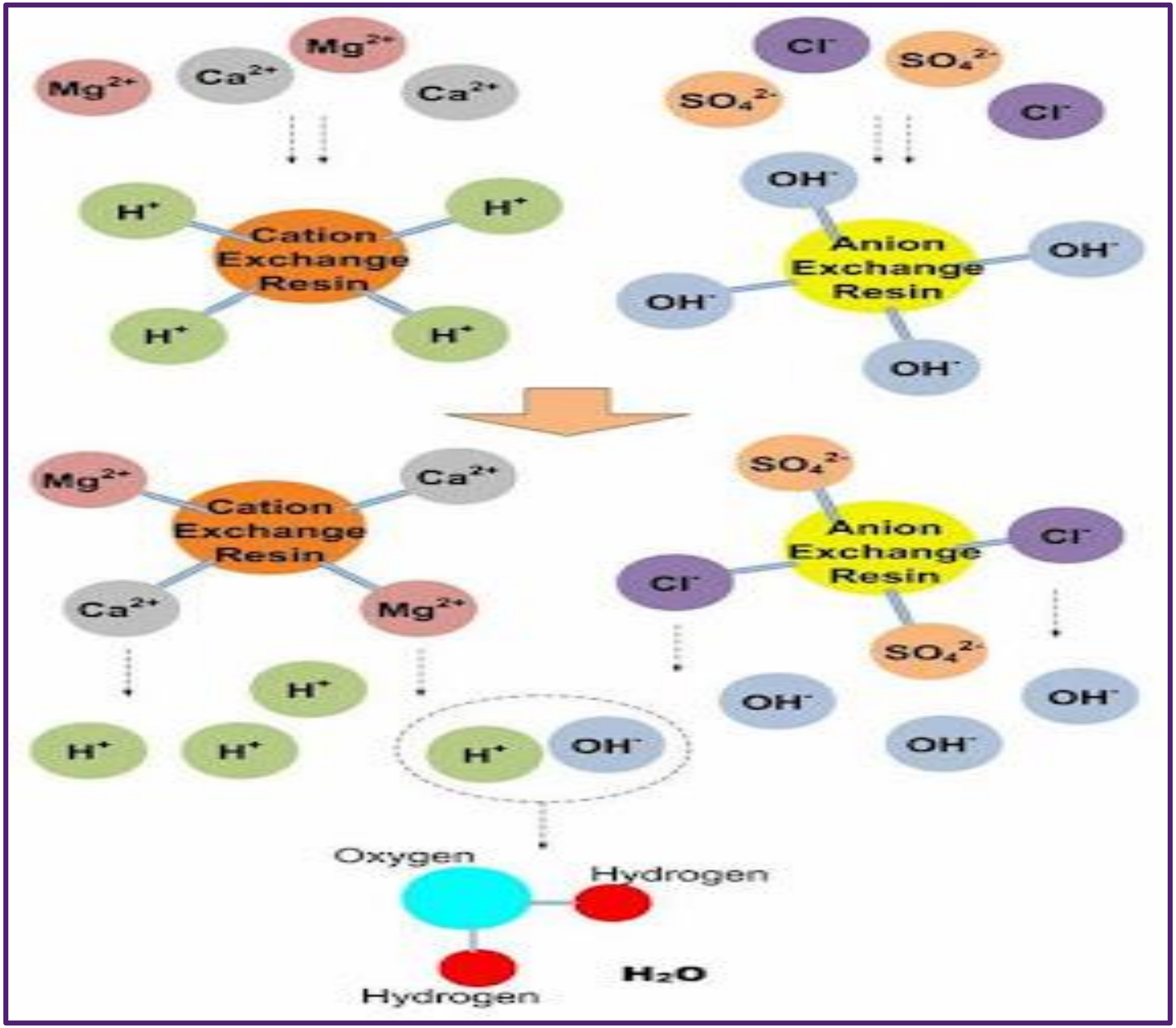
Used for producing demineralised or deionised water.

- Ion exchange resins are:
- High molecular weight, cross linked, organic polymers
- Have porous structure
- Capable of exchanging their H^+ and OH^- ions with hardness producing ions in water.

There are two types of ion exchangers:

Cation Exchange resins: Have ***loosely held H^+ ions*** which are reversibly exchanged by hardness producing cations (Ca^{2+} and Mg^{+2}) in water.

Anion Exchange resins: Have ***loosely held OH^-*** ions which are reversibly exchanged by hardness producing anions (Cl^-, SO_4^{-2} and HCO_3^-) in water.


Mg²⁺
Ca²⁺
Mg²⁺
Ca²⁺
Cl⁻
SO₄²⁻
SO₄²⁻
Cl⁻
H⁺
Cation Exchange Resin
H⁺
H⁺
H⁺
OH⁻
Anion Exchange Resin
OH⁻
OH⁻
OH⁻
Mg²⁺
Cation Exchange Resin
Ca²⁺
Ca²⁺
Mg²⁺
SO₄²⁻
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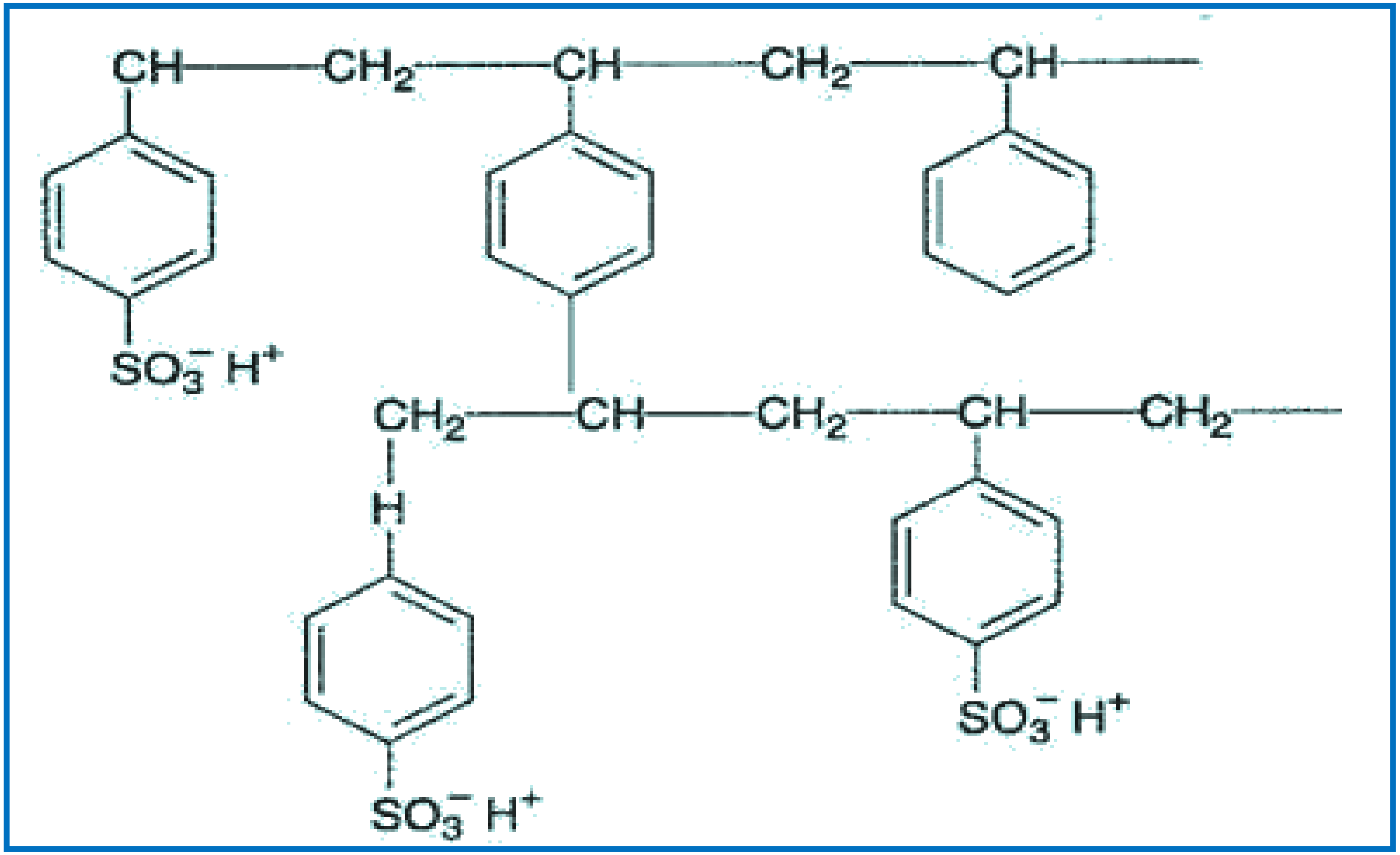
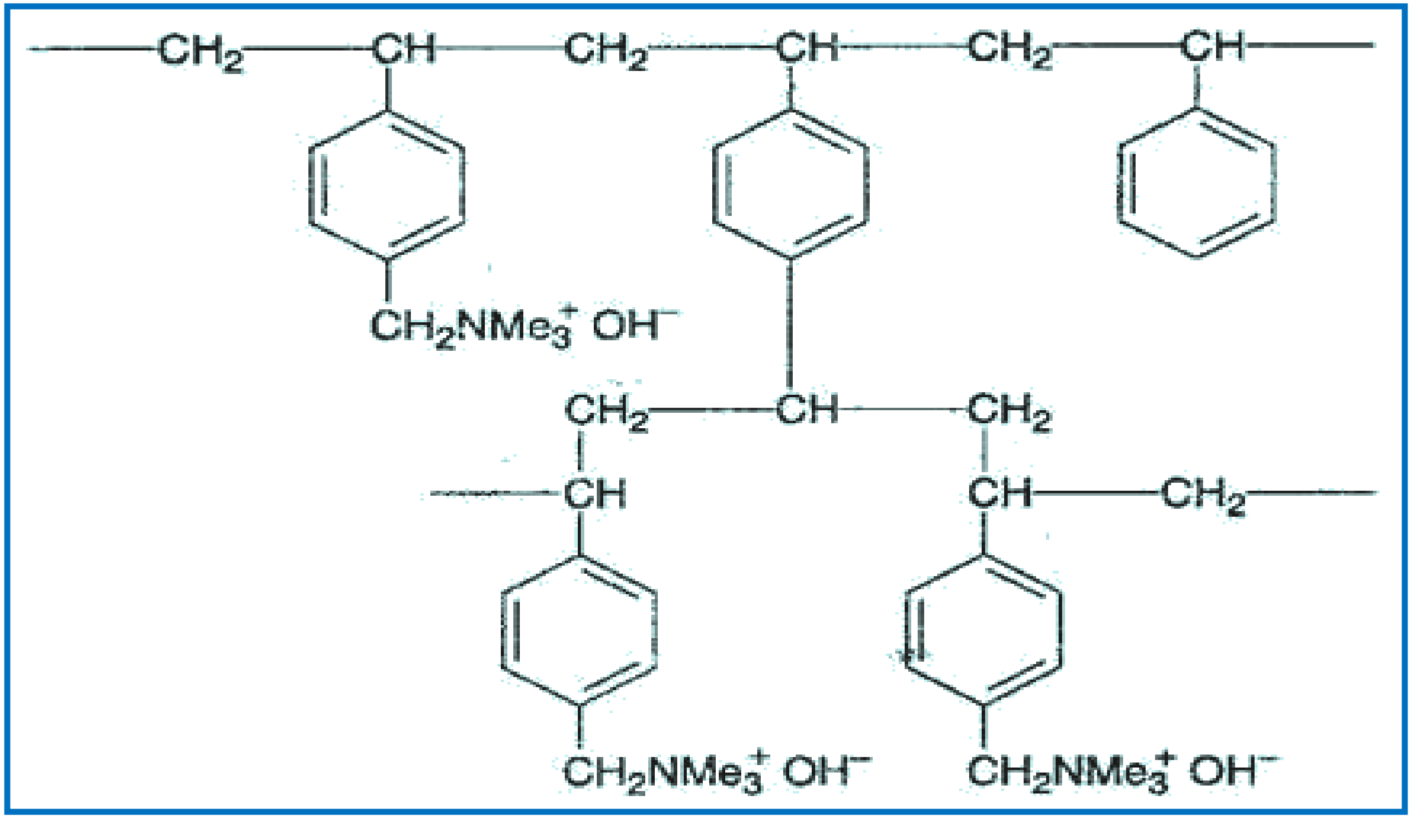


Cation Exchange resins



Anion Exchange resins

Principle:

These are capable of exchanging hardness producing ions (cations as well as anions) in water with their H^+ and OH^- ions.

Working of ion exchange resins for water softening:

Ion exchange process consists of two columns- ***Cation exchanger column and anion exchanger column.***

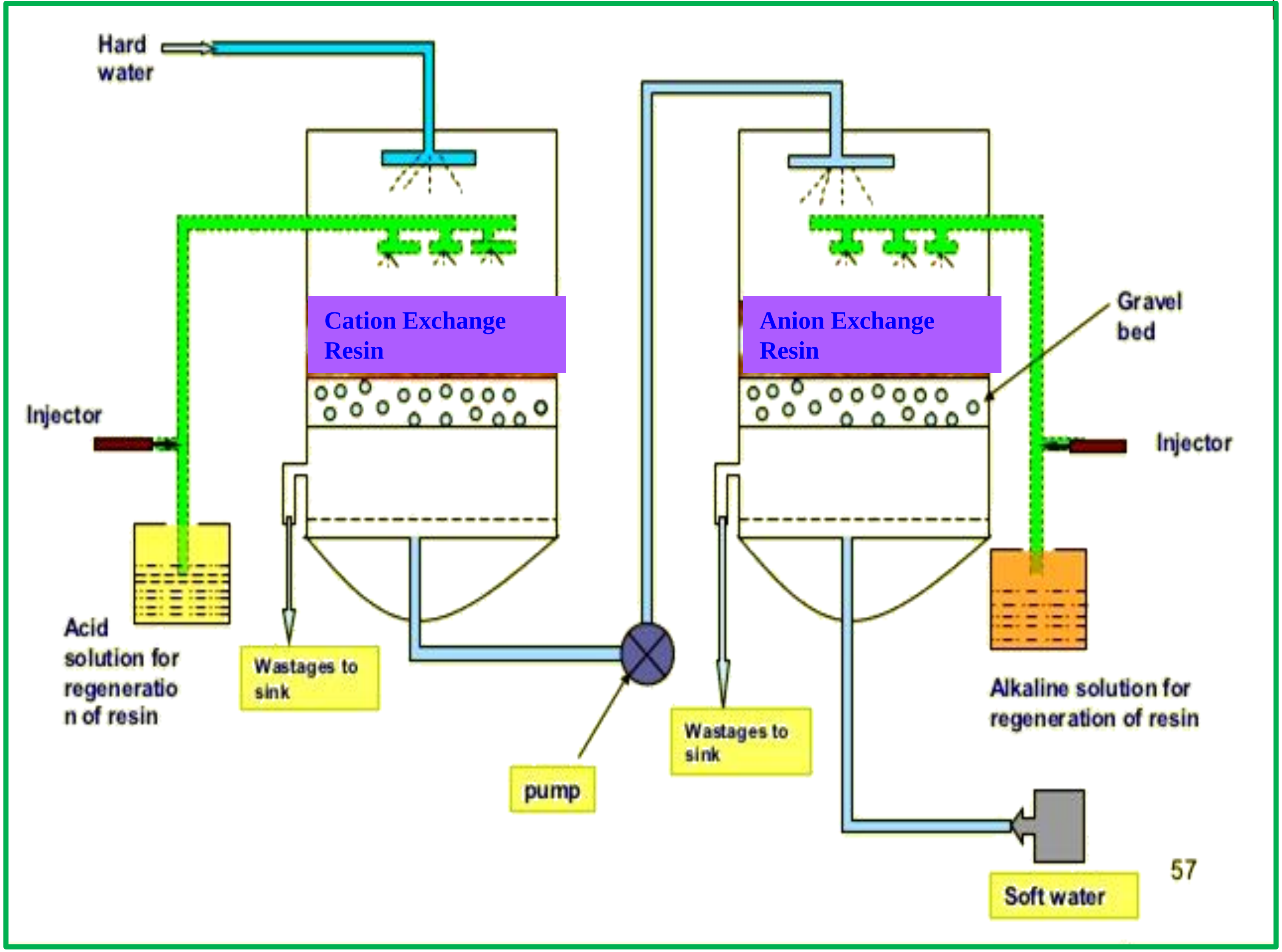
- First hard water is passed through cation exchanger which exchanges hardness causing cations like Ca^{+2}, Mg^{+2}, Fe^{+2} etc in water with H^+ ions of cation exchange resin.

- Then hard water is passed through anion exchanger which exchanges hardness causing anions like SO_4^{2-}, Cl^- etc in water with OH^- ions of anion exchange resin.

- The H^+ and OH^- ions thus released in water combine to form water molecule.

- Hence water coming out of the columns is free from hardness causing cations as well as anions and thus it is known as ***deionised or demineralised water.***

ION EXCHANGE METHOD OF WATER TREATMENT



Working:

Ion exchange process consists of two columns- ***Cation exchanger column*** *and* ***anion exchanger column.***

Step 1: Water Softening

Cation exchanger- $2R{-}H + Ca^{+2} \rightleftharpoons R_2{-}Ca + 2H^+$

(R = insoluble matrix)

$2R{-}H + Mg^{+2} \rightleftharpoons R_2{-}Mg + 2H^+$

Anion exchanger- $R{-}OH + Cl^- \rightleftharpoons RCl + OH^-$

(R= insoluble matrix)

$2\ R{-}OH + SO4^{-2} \rightleftharpoons R_2SO_4 + OH^-$

Step 2: Regeneration of ion exchangers:

- After some time these two exchangers are exhausted when all their H^+ and OH^- ions are replaced by hardness causing ions.
- Therefore, Cation and anion exchangers are regenerated by treating with acid and base respectively.

Regeneration of cation exchanger by acid:

$$\underset{\text{Exhausted resin}}{R_2{-}Ca} + 2H^+ \rightleftharpoons \underset{\text{Regenerated resin}}{2R{-}H} + Ca^{+2}$$

Regeneration of anion exchanger by base:

$$\underset{\text{Exhausted resin}}{RCl} + OH^- \rightleftharpoons \underset{\text{Regenerated resin}}{R{-}OH} + Cl^-$$

Advantages:

- Gives water of almost zero hardness and no ionic impurities.
- Removes pathogens from water.
- Occupies less space and easy to operate.
- Negligible running cost.

.

Disadvantages:

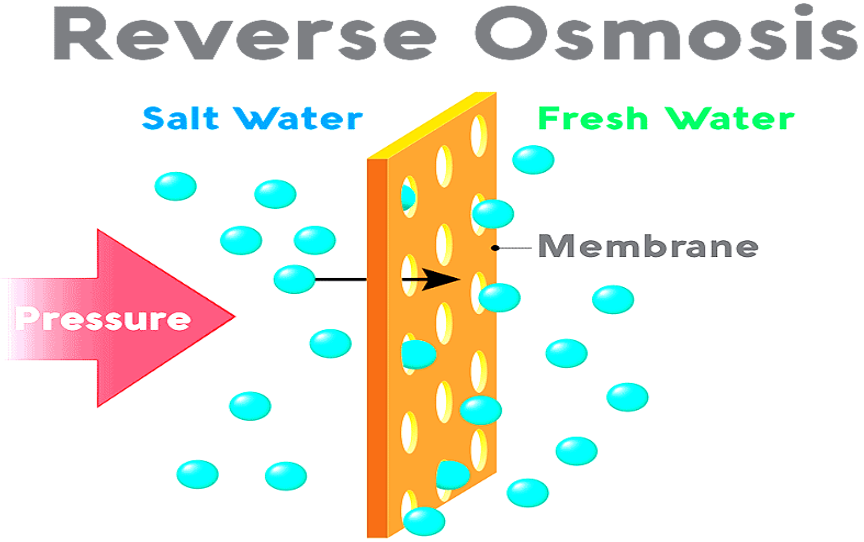
- The setup is costly and it uses costly chemicals.
- The water should not be turbid and the turbidity level should not be more than 10 ppm.

Limitations:

- Initial cost is high.
- Used for small scale treatment of water.

LECTURE - 29

- Lime soda process and its numericals.
- Reverse osmosis



Lime Soda Process For Water Softening

In this process lime and soda are used to remove the hardness from water.

Principle:

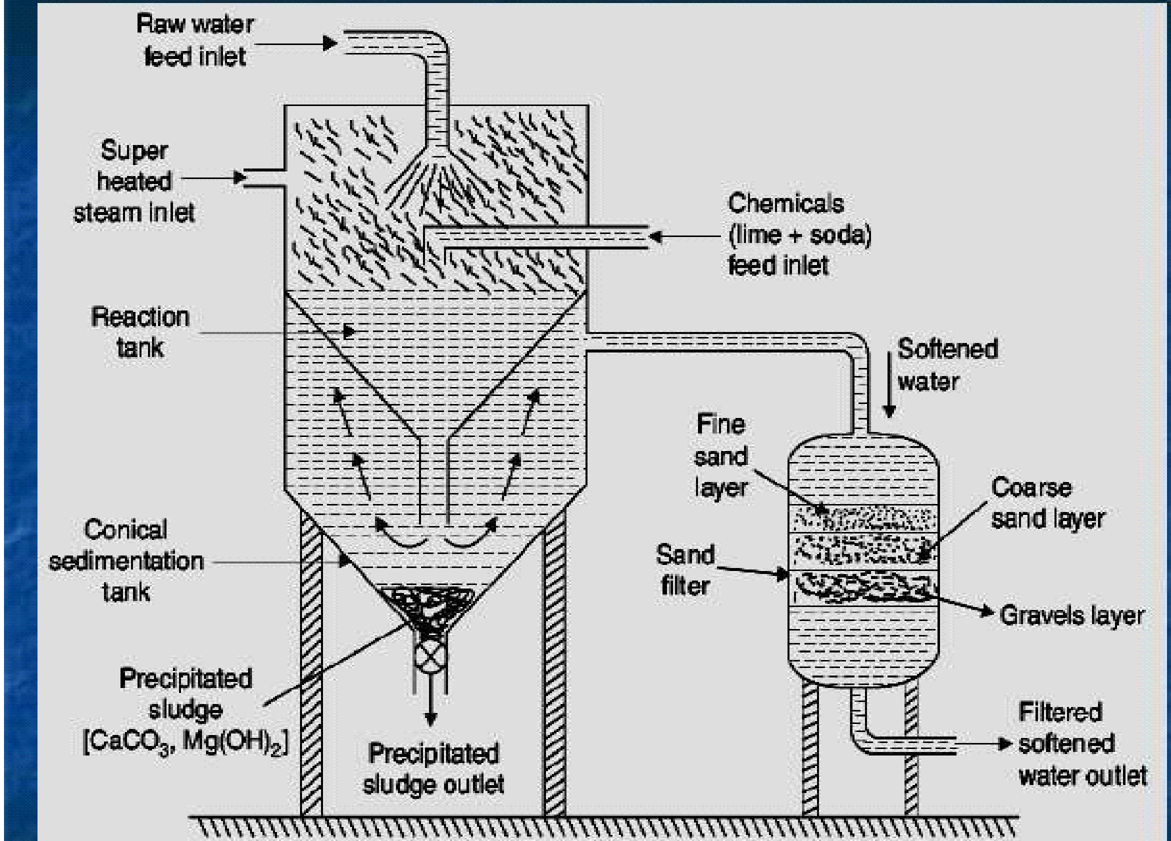
- By adding calculated amounts of lime [$Ca(OH)_2$] and soda [Na_2CO_3], all the calcium salts are precipitated out as calcium carbonate $CaCO_3$ and all the magnesium salts are precipitated as magnesium hydroxide $Mg(OH)_2$ which can be easily filtered off.
- Lime [$Ca(OH)_2$] and soda [Na_2CO_3] are the reagents used to precipitate the dissolved salts of Ca^{+2} and Mg^{+2} as $CaCO_3$ and $Mg(OH)_2$.

- Lime reacts with temporary hardness, CO_2, acids, bicarbonates and alums.
- Lime cannot remove the calcium permanent hardness which should be removed by soda.
- Only calculated amounts of lime and soda are to be added. Excess amount of lime & soda causes boiler troubles like caustic embrittlement.

There are two types of lime soda processes:
Cold soda lime process and Hot soda lime process.

Cold Soda Lime Process	Hot Soda Lime Process
It is carried out at room temperature (25-30°C).	It is carried out at high temperature (95-100°C).
It is a slow process.	It is a rapid process.
Use of coagulant is necessary.	No coagulant is required.
Filtration is not easy.	Filtration is easy as viscosity of water is low.
Residual hardness is 60 ppm.	Residual hardness is 15-30 ppm.
Dissolved gases are not removed.	Dissolved gases are removed.
It has low softening capacity.	It has high softening capacity.

Lime Soda Process (Hot) For Water Softening



Continuous hot lime-soda softener.

Construction and working:

Consists of treating water with softening chemicals at temp. of 80 ˚c to 150˚C (close to the boiling point). The hot lime soda apparatus consists three parts:

- ***Reaction tank:***

  In the reaction tank raw water, chemicals & steam are mixed and the reactions takes place.

- ***Conical sedimentation vessel:***

  In the conical sedimentation vessel sludge settles down.

- ***Sand filter:***

  In sand filter sludge is completely removed from softened water.

Working Lime soda process of water softening

Following reactions are involved:

1. ***Lime removes all the temporary hardness.***

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

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

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow$$

2. Lime removes bicarbonates of Na and K

$$2NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + Na_2CO_3 + 2H_2O$$

$$2KHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + K_2CO_3 + 2H_2O$$

3. Lime removes all the permanent hardness of magnesium salts

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2\downarrow$$

4. *Lime removes the dissolved gases*

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

$$H_2S + Ca(OH)_2 \longrightarrow CaS\downarrow + 2H_2O$$

5. *Lime removes free mineral acids*

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$$

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O$$

6. Lime removes dissolved alums:

$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2 + CaSO_4$$

$$2Fe(OH)_2 + H_2O + O_2 \longrightarrow 2Fe(OH)_3 \downarrow$$

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

If sodium aluminate is present in water then it reacts with water to form sodium hydroxide which in turn reacts with permanent calcium salts to form Lime.

$$\boxed{NaAlO_2} + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

$$2NaOH + CaCl_2 \longrightarrow \boxed{Ca(OH)_2} + 2NaCl$$

7. Soda removes all soluble calcium permanent hardness.

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$

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

$Ca(NO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaNO_3$

$Ca^{++} + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2Na^{+}$

Note:

Ca^{++} is to be considered as permanent calcium salt.

Advantages of L.S. Process:

- It is a very economical.
- The quantity of minerals in the water is reduced.
- Some iron and manganese ions are also removed from the water.
- Pathogenic bacteria in water is also reduced.
- Acidic impurities can also be removed.
- Colloidal impurities can also be removed.
- pH of the treated water is nearly 8.5

Disadvantages of L.S. Process

- Careful operation and skilled supervision is required
- Disposal of large amounts of sludge poses a problem.
- This can remove hardness only up to 15ppm, which is not good for boilers.
- Thorough study of water is required before treating

Points to be remembered while solving Numerical problems on lime-soda requirements for softening of hard water:

- The units in which the impurities are analyzed and expressed are to be noted.
- Substances which do not contribute towards hardness (K^+, Na^+, KCl, NaCl, SiO_2, K_2SO_4, Na_2SO_4 etc.) should be ignored.
- A substance causing hardness should be converted into their respective $CaCO_3$ equivalents.

- $CaCO_3$ equivalent of hardness causing impurity

  = 50 × wt. of the impurity/chemical equiv. of impurity

  or

  = Multiplication factor x wt. of impurity

Multiplication factor

= Equiv. wt. of $CaCO_3$ / Equiv. wt. of impurity

- Consider Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+} as permanent hardness causing ions.

General formula for calculating amount of lime and soda required for water softening.

Lime = (74/100) {temporary calcium hardness + (2 × temporary magnesium hardness) + Perm Mg hardness + CO_2 + HCl + H_2SO_4 + HCO_3^- + salts of Fe^{2+}+ Al^{3+} – $NaAlO_2$} × 100 / % purity × volume of water(L)

Soda = (106/100) {Perm Ca hardness + Perm Mg hardness + salts of Fe^{2+} + Al^{3+} + HCl + H_2SO_4 – HCO_3^-} × 100/% purity x volume of water.

NOTE: Its not compulsory that you will be always given with all the types of salts mentioned above.

Calculations of the requirement of lime and soda

Salt	Lime	Soda
$Ca(HCO_3)_2$,$CaCO_3$	+L	
$Mg(HCO_3)_2$	+2L	
$CaSO_4$,$CaCl_2$, Ca^{2+}		+ S
$MgSO_4$,$MgCl_2$,$Mg(NO_3)_2$, Mg^{2+}	+L	+ S
H_2S, CO_2	+L	
$NaHCO_3$, $KHCO_3$, HCO_3^-	+L	-S
OH^- (treated water)	+L	+S
CO_3^{2-} (treated water)		+S
$NaAlO_2$	-L	
$Al_2(SO4)_3$, $FeSO_4.7H_2O$, Fe^{2+}, Al^{3+}	+L	+S
H^+, HCl, H_2SO_4	+L	+S

Q1. Calculate the quantities of lime and soda required for softening of 20,000 litres of water containing salts in ppm (16.4 ppm $NaAlO_2$ used as a coagulant): Ca^{+2} = 160 ppm; Mg^{+2} = 72 ppm; HCO_3^- = 73.2 ppm; CO_2 = 44 ppm; $Al_2(SO_4)_3$ = 34.2 ppm and HCl = 36.5 ppm.

Impurity	Quantity (mg/L)	Eq. Wt.	$CaCO_3$ Eq. (mg/l)	L or S
Ca^{++}	160	20	$160 \times \frac{50}{20} = 400$	S
Mg^{++}	72	12	$72 \times \frac{50}{12} = 300$	L + S
CO_2	44	22	$44 \times \frac{50}{22} = 100$	L
HCO_3^-	73.2	61	$73.2 \times \frac{50}{61} = 60$	L – S

$Al_2(SO_4)_3$	**34.2**	**57**	**$34.2 \times \frac{50}{57} = 300$**	**L +S**
$NaAlO_2$	**16.4**	**82**	**$16.4 \times \frac{50}{82} = 100$**	**-L**
HCl	**36.5**	**36.5**	**$36.5 \times \frac{50}{36.5} = 50$**	**L + S**

Lime =

$$\frac{74}{100}\left[Mg^{++} + CO_2 + HCO3^- + Al_2(SO_4)_3 + HCl - NaAlO_2\right] \text{ all as } CaCO_3 \text{ eq.} \times \frac{\text{vol. of water}}{10^6}$$

$$= \frac{74}{100}[300 + 100 + 60 + 300 + 50 - 100] \times \frac{20{,}000}{10^6}$$

$$= \frac{74}{100}[710] \times \frac{20000}{10^6}$$

$$= 10.508 \text{ Kg}$$

Soda =

$$\frac{106}{100}\left[\,Ca^{++} + Mg^{++} - HCO_3^{-} + Al_2(SO_4)_3 + HCl\,\right] \text{ all as } CaCO_3 \text{ eq.} \times \frac{\text{vol. of water}}{10^6}$$

$$= \frac{106}{100}\,[400 + 300 - 60 + 300 + 50] \times \frac{20{,}000}{10^6}$$

$$= \frac{106}{100}\,[990] \times \frac{20000}{10^6}$$

$$= 20.988 \text{ kg}$$

Q2: Write the different chemical reactions taking place in a lime soda process. A sample of water on analysis give following result :

Analysis of raw water : Ca^{2+}= 24mg/L , CO_2 = 33mg/L ,
HCO_3^-= 132mg/L, H^+= 10mg/L and NaCl= 4.3ppm
Analysis of treated Water : CO_3^{2-} = 12mg/L and OH^- = 34mg/L

Calculate the quantity of lime (74%pure) and soda (92%pure) needed for softening 50000L of water.

Constituents	Amount (in mg/L)	Equivalent Weight	$CaCO_3$ Equivalent	L or S
Raw Water				
Ca^{2+}	80	20	$80\times\frac{50}{20} = 200$	S
Mg^{2+}	24	12	$24\times\frac{50}{12} = 100$	L+S
CO_2	33	22	$33\times\frac{50}{22} = 75$	L
H^+	10	1	$10\times\frac{50}{1} = 500$	L+S
HCO_3^-	132	61	$132\times\frac{50}{61} = 108.19$	L-S

Treated Water				
OH^-	34mg/l	17	$34\times\frac{50}{17}=100$	L+S
CO_3^{2-}	12mg/l	30	$12\times\frac{50}{30}=20$	S

Lime(74%pure)

$=(\frac{74}{100})$ [(Mg^{2+} + HCO_3^-+CO_2+H^+ + OH^-) as $CaCO_3$ equivalents]$(\frac{100}{74})$ ×50000mg

$= \frac{74}{100}[100 + 108.19 + 75+500+100\ ](\frac{100}{74})\times 50000$mg

= 44.16×10^6 mg = 44.16Kg.

Soda (92%pure)

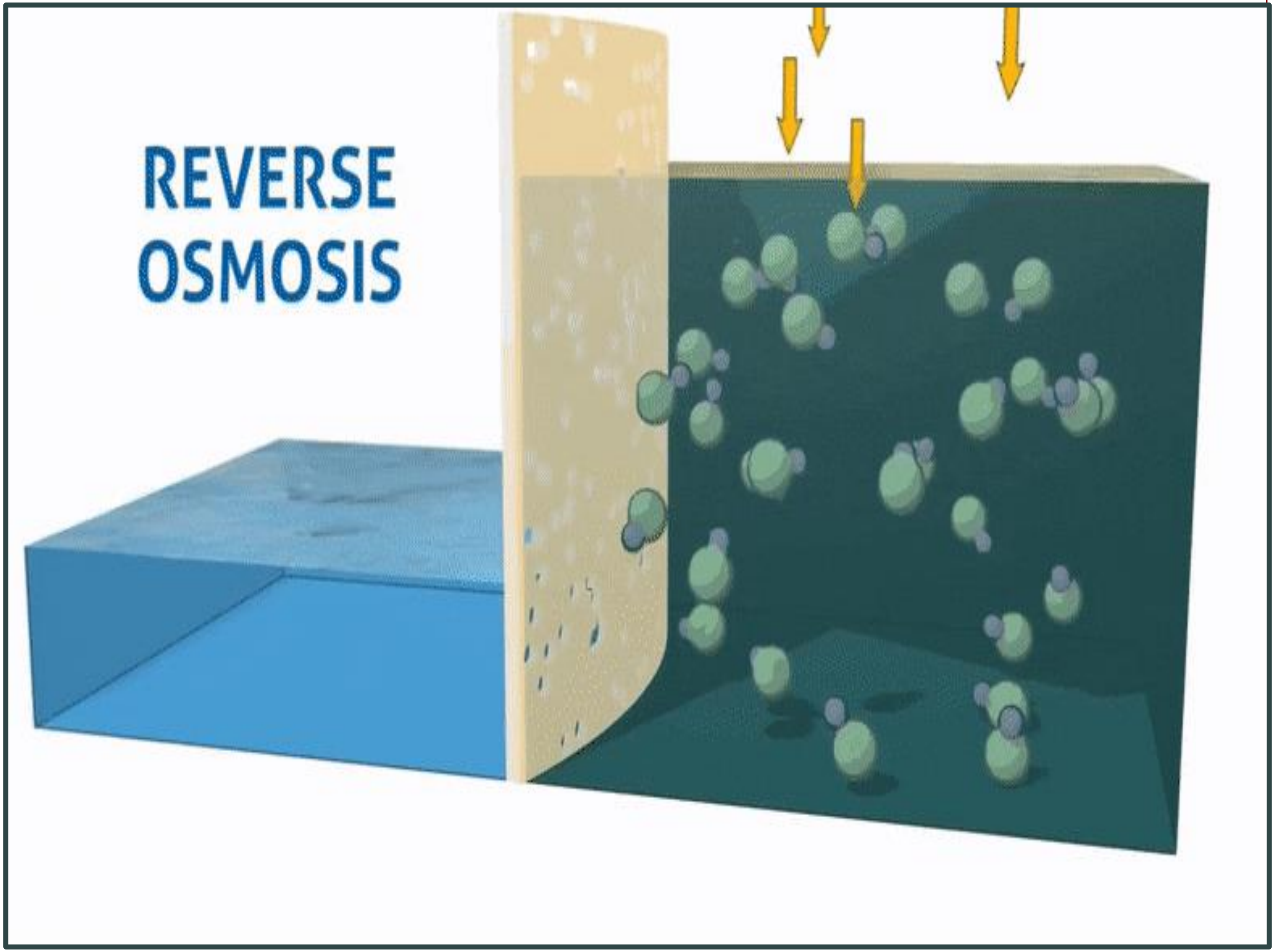
$= (\frac{106}{100})[(Ca^{2+} + Mg^{2+} + H^{+} + OH^{-} + HCO_3^{-})$ as $CaCO_3$ equivalents]$(\frac{100}{92})$ ×50000 mg

$= (\frac{106}{100})[(200+100+500+100+20-108.19)](\frac{100}{92}) \times 50000$ mg

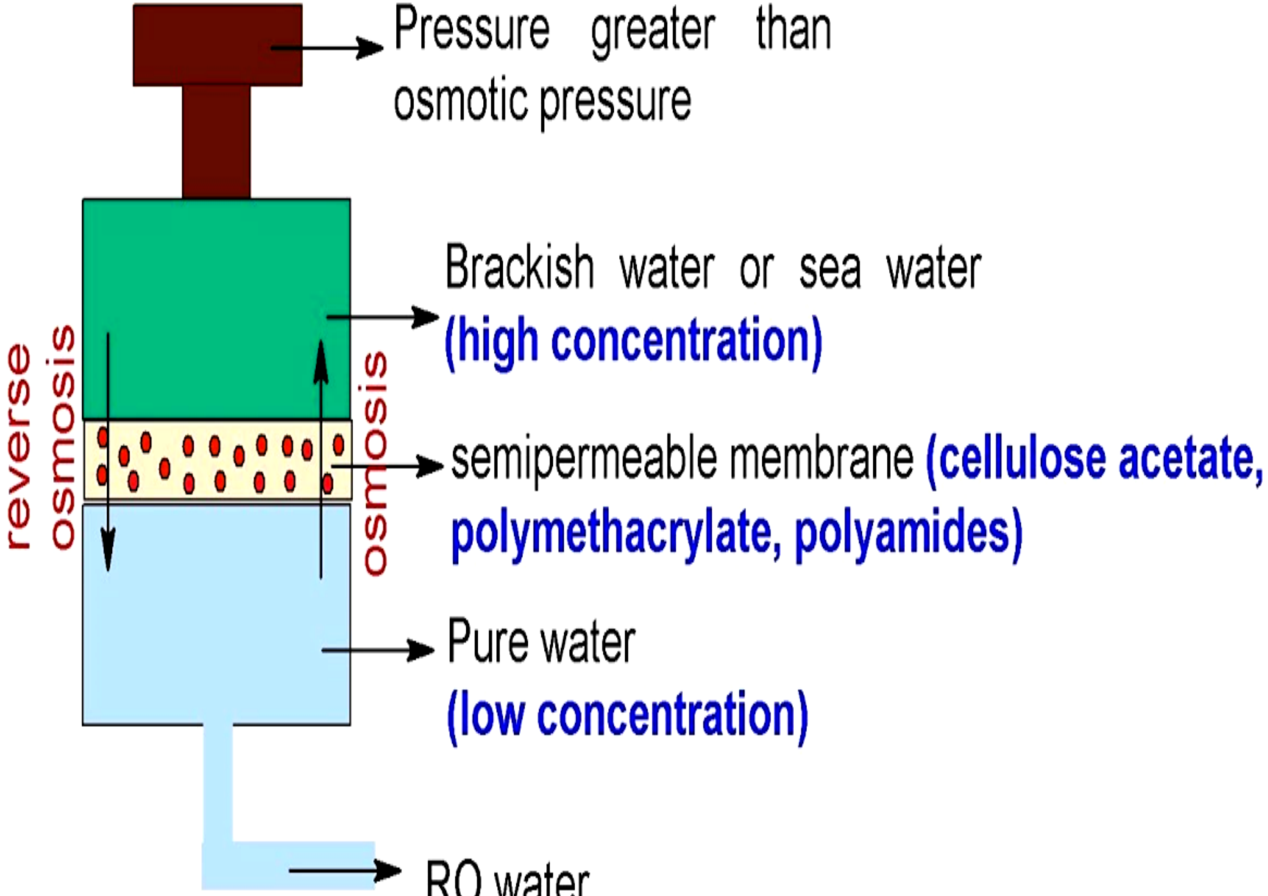
$= 46.8 \times 10^6$ mg = 46.8 Kg

DESALINATION OF BRACKISH WATER

- The removal of dissolved solids (NaCl) from water is known as desalination process. It can be carried out by Reverse osmosis.
- Reverse Osmosis or super filtration is commonly referred to as RO.


REVERSE
OSMOSIS

REVERSE OSMOSIS PROCESS



Pressure greater than osmotic pressure

Brackish water or sea water **(high concentration)**

semipermeable membrane **(cellulose acetate, polymethacrylate, polyamides)**

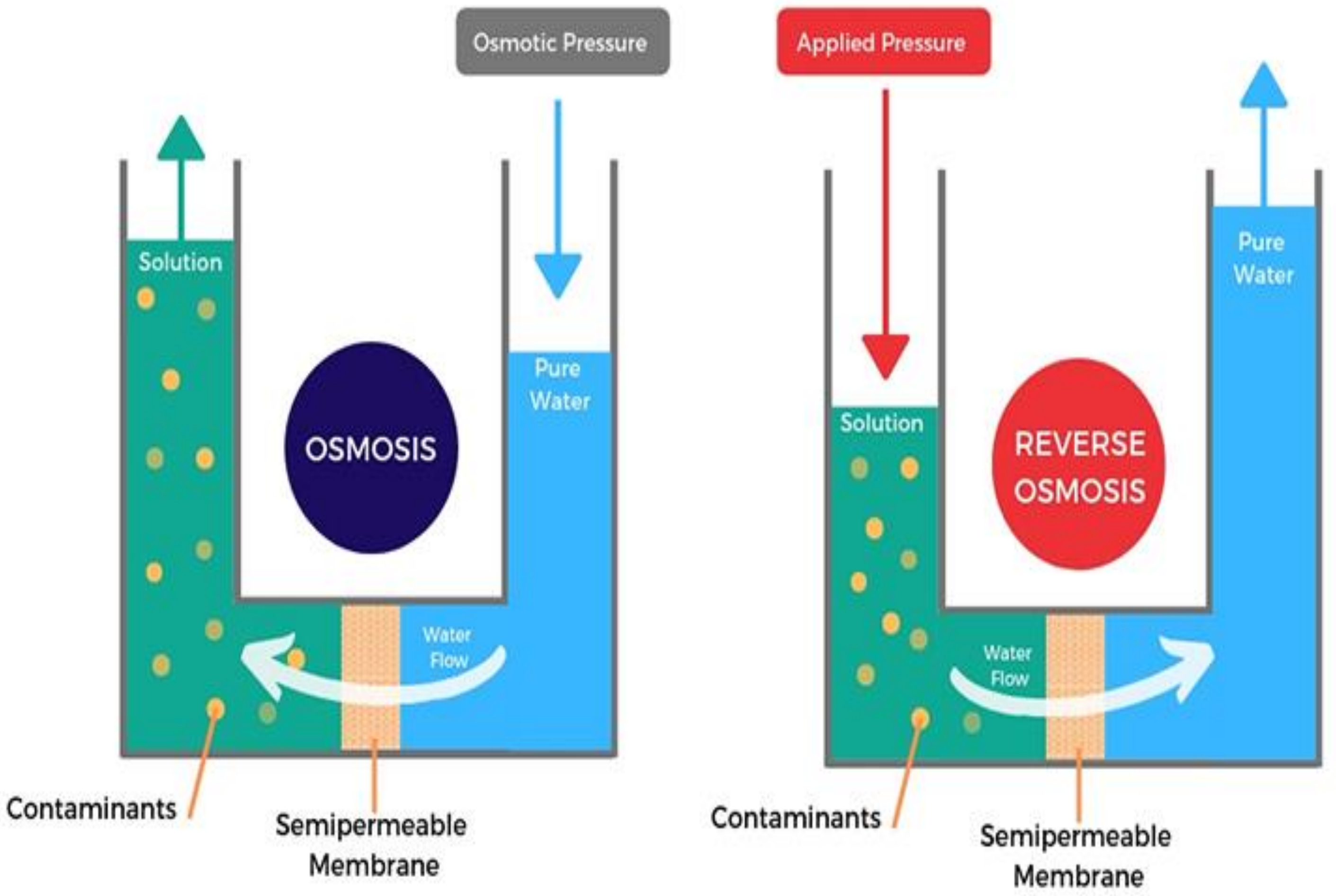
Pure water **(low concentration)**

RO water

- **Osmosis** is a process to deionize water by pushing it under pressure through a semi-permeable membrane from the lower concentration to the higher concentration.
- But in the **Reverse Osmosis (R.O.)**, pressure higher than osmotic pressure is applied from the higher concentration side so that solvent moves from higher concentration to lower concentration. Reverse osmosis or ***Super Filtration*** is a water purification process that uses a partially permeable membrane to remove ions, unwanted molecules and larger particles from drinking water.

- This method is applicable mainly for the ***desalination of sea water.***
- Sea water and pure water are separated by a ***semi-permeable membrane.***
- The process is very easy.
- It is used to make pure water.
- The life of a membrane is nearly 2 years and it should be replaced after this period.
- By this process, ***sea water is made to fit for drinking.***
- Water obtained after being treated by this process is used in boilers.

Osmosis And Reverse Osmosis



Advantages:

- Removes up to 99% of the dissolved salts (ions), particles, colloids, organics, bacteria and pathogens from water.
- Removes both ionic and non-ionic impurities.
- Requires extremely low energy.
- Low cost process.
- Very effective in treating brackish, surface and groundwater.
- Simple to operate.
- Pure water for high pressure boilers can be obtained.

Applications or Uses for Demineralised Water:

- Industrial uses.
- Lab applications and testing.
- Used by computer chip manufacturers and other microelectronics.
- In lead acid batteries and cooling systems.
- High-pressure boilers.
- Laser cutting.
- Cosmetics.
- Aquariums.
- Fire extinguishers

POTABLE (DRINKING) WATER

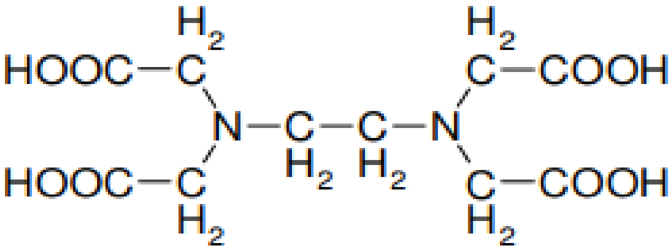
- It should be clear, colourless and odourless.
- It should be cool and pleasant to taste.
- t should be free from bacteria and impurities.
- It should be free from dissolved gases like CO_2, H_2S, NH_3, etc., and poisonous minerals like lead, arsenic, manganese, etc.,
- Hardness should be less than 500 ppm.
- Chloride ion content should be less than 250 ppm.
- Fluoride ion content should be less than 1.5 ppm.
- Total Dissolved Solids (TDS) should be less than 500 ppm.
- pH of the potable water should be 6.5 – 8.5.

LECTURE - 30

- Determination of Hardness and alkalinity

ESTIMATION OF HARDNESS OF WATER BY EDTA METHOD

- The estimation of hardness of water is done by complexometric titration using standard EDTA as titrant and EBT as indicator.
- EDTA is tetraprotic acid represented by the symbol H_4Y.
- Hardness of water is determined by titrating with a standard solution of ethylenediamine tetra acetic acid (EDTA) which is a complexing agent. Since EDTA is insoluble in water, the disodium salt of EDTA is taken for this experiment. EDTA can form four or six coordination bonds with a metal ion.



Structure of EDTA

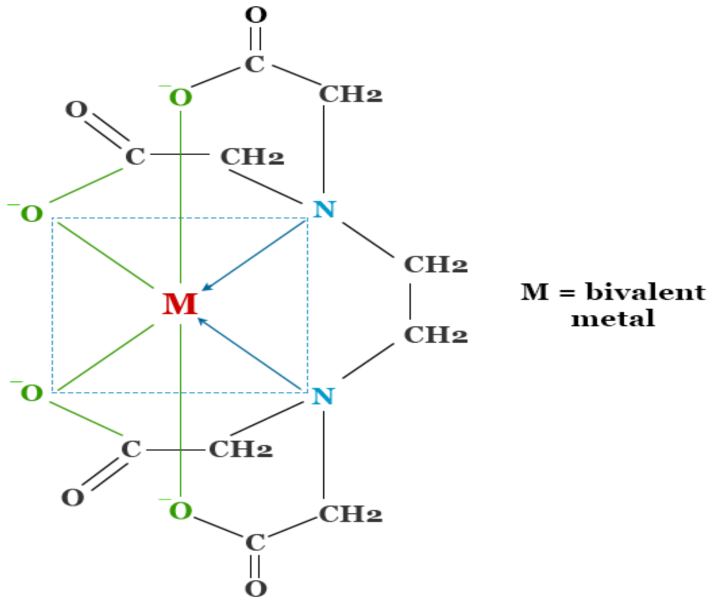
EDTA (Ethylenediamine tetra acetic acid) forms colorless stable complexes with Ca^{2+} and Mg^{2+} ions present in water at pH = 9-10. To maintain the pH of the solution at 9-10, buffer solution (NH_4Cl + NH_4OH) is used and Eriochrome Black-T (EBT) is used as an indicator.

Ca^{2+}	+	EBT	→	[Ca-EBT]
(from hard water) complex		Indicator(blue)	pH-10 (buffer)	Metal-indicator less stable (wine-red)

Ca^{2+}	+	EDTA	→	[Ca-EDTA]
Free hardness			pH -10	Metal-EDTA stable complex (Colourless and water soluble)

$[Ca^{2+}$-EBT]	+	EDTA	→	[Ca-EDTA]	+	EBT
(wine-red)			pH-10	(Colourless)		Free indicator (blue)

- Whenever we are adding EDTA solution to the wine- red color (M-In) solution, EDTA first combines with free Ca^{2+} or Mg^{2+} ions to give very stable, colourless and water soluble metal-EDTA complex. After all the free metal ions are consumed, the next drop of added EDTA solution displaces the indicator, EBT, from metal-EBT complex.
- When all the metal ions in the sample complexed with EDTA, further addition of EDTA liberates the free indicator solution at pH-10 which in blue color indicates the end point of the titration.



Calculations

Step 1: Normality of $CaCO_3$ $(N_1) = \frac{\text{Mass of } CaCO_3}{\text{eq.mass of } CaCO_3 \times \text{volume of distilled water}}$

Step 2: Calculation of Normality of EDTA :$N_2 = N_1 \times \frac{V_1}{V_2}$

Where, V_1 : Volume of EDTA required for standardization

V_2 : Volume of water sample taken

Step 3: Total hardness normality calculation:$N_3 = N_2 \times \frac{V_2}{V_3}$

V_2 : Volume of EDTA required for water sample

Step 4: Total hardness in ppm = $N_3 \times eq.mass\ of\ CaCO_3 \times 1000$

Step 5: Permanent hardness normality calculation:$N_4 = \mathrm{N}_2 \times \frac{\mathrm{V}_2}{V_4}$

V_2 : Volume of EDTA required for water sample after boiling

Step 6: Permanent hardness in ppm = $\mathrm{N}_4 \times \mathrm{eq.\,mass\ of\ CaCO_3} \times 1000$

Step 7: Temporary hardness = Total hardness - Permanent hardness

Q.1 0.28 g of $CaCO_3$ was dissolved in HCl and the solution was made to one litre with distilled Water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample required 35 ml of the same EDTA solution on titration. After boiling 100 ml of the water, cooling, filtering and then titration required 10 ml of EDTA solution. Calculate temporary hardness, permanent hardness and total hardness.

Standardization of EDTA solution:

$$\text{Normality of } CaCO_3\ (N_1) = \frac{\text{Mass of } CaCO_3}{\text{eq. mass of } CaCO_3 \times \text{volume of distilled water}}$$

$$N_1 = \frac{0.28}{50 \times 1} = \frac{0.28}{50} = 0.0056\ \text{N}$$

Calculation of Normality of EDTA :$N_2 = N_1 \times \frac{V_1}{V_2}$

$$N_2 = \frac{0.28}{50} \times \frac{100}{28} = \frac{28}{1400} = 0.02\ \text{N}$$

Determination of total hardness of water : $N_3 = N_2 \times \frac{V_2}{V_3}$

$$N_3 = 0.02 \times \frac{35}{100} = 0.007\text{N}$$

Total hardness in ppm = $N_3 \times \text{eq. mass of CaCO}_3 \times 1000$

= 0.007× 50 × 1000

= 350 ppm

Determination of Permanent hardness:

Permanent hardness normality calculation: $N_4 = N_2 \times \frac{V_2}{V_4}$

$N_4 = 0.02 \times \frac{10}{100} = 0.002$ N

Permanent hardness in ppm = $N_4 \times \text{eq. mass of CaCO}_3 \times 1000$

= 0.002× 50 × 1000

= 100 ppm

Determination of Temporary hardness:

Temporary hardness = Total hardness – Permanent hardness

= 350-100 = 250 ppm

Temporary hardness = 250 ppm

Q.2 100 ml of a sample of water required 15 ml of 0.01 M EDTA for titration. In another experiment, 100 ml of the same sample after boiling required 8 ml of 0.01 M EDTA . Calculate

(i) the total hardness, (ii) permanent hardness,

Calculate hardness in terms of ppm of $CaCO_3$.

Titration of EDTA solution with sample of hard water

$(M_1V_1)_{\text{hard water}} = (M_2V_2)_{\text{EDTA solution}}$

$M_1 * 100 = 0.01 * 15$

$M_1 = 0.0015\ M$

Total hardness = (Molarity * Molecular mass of CaCO3 * 1000) ppm

= 150 ppm

Titration of EDTA solution with sample of hard water after removal of temporary hardness

$M_1' * 100 = 0.01 * 8$

$M_1' = 0.0008\ M$

Therefore, Permanent hardness = (M_1' * 100 * 1000) ppm

= 80 ppm

Estimation of Temporary hardness

Temporary hardness = Total hardness – Permanent hardness

= 150 – 80 = 70 ppm

Detemination of Alkalinity

Alkalinity

Alkalinity is a measure of the ability of water to neutralize the acids.

The alkalinity of water is due to the presence of the:

i. OH^-

ii. CO_3^{2-}

iii. HCO_3^-

With respect to the constituents causing alkalinity in water, the following situations may arise:

i. OH^- and CO_3^{2-} together

ii. CO_3^{2-} and HCO_3^- together.

The possibility of OH^- and HCO_3^- together is ruled out, as they will combine instantaneously to form CO_3^{2-} ions.

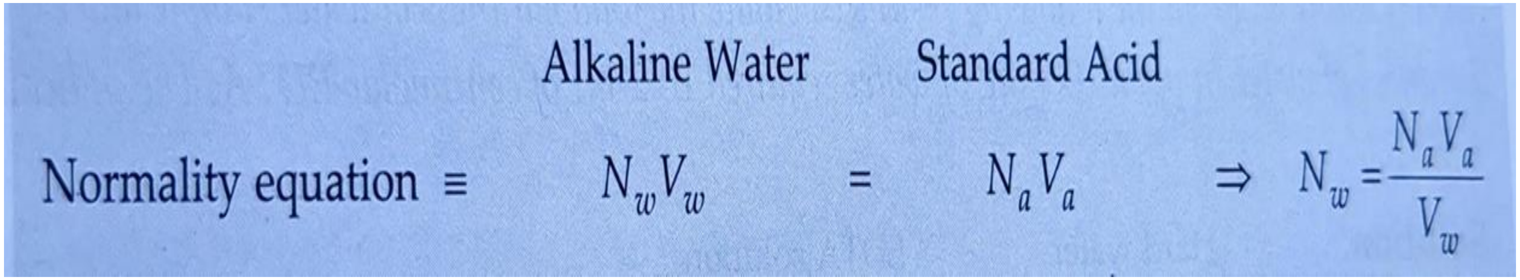
$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$

Due to this, all three ions cannot exist together.

OH^- , CO_3^{2-} and HCO_3^- can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators.

Calculations:

- **Titration of water sample against a standard acid upto phenolphthalein end point**



Alkaline Water Standard Acid

Normality equation ≡ $N_w V_w = N_a V_a \Rightarrow N_w = \frac{N_a V_a}{V_w}$

Therefore strength of alkalinity upto phenolphthalein end-point in terms of $CaCO_3$ equivalent,

$$(\mathbf{P}) = N_w \times \text{ Eq. weight of } CaCO_3 \text{(g/L)}$$

$$P = (N_w \times \text{ Eq. weight of } CaCO_3 \times 1000)\text{ppm}$$

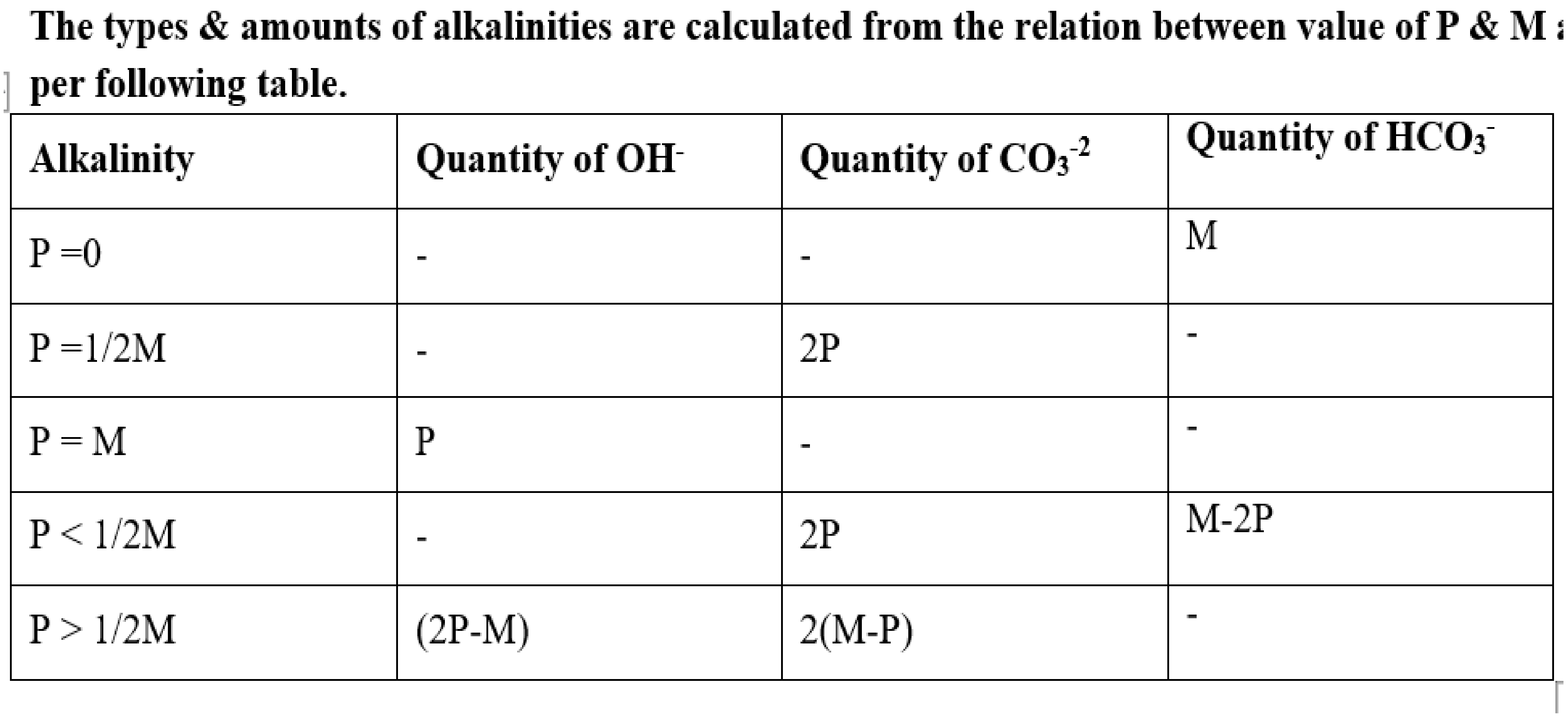
Hence, $\mathbf{P} = \dfrac{\mathbf{N_aV_a \times 50 \times 1000}}{\mathbf{V_w}}$ ppm

- **Titration of water sample against a standard acid upto methyl orange end point**

Since, $N_w' = N_a \times \dfrac{V_a'}{V_w}$

Therefore, $\mathbf{M} = \dfrac{\mathbf{N_aV_a' \times 50 \times 1000}}{\mathbf{V_w}}$ppm

Type and Extent of Alkalinity due to various anions



The types & amounts of alkalinities are calculated from the relation between value of P & M per following table.

Alkalinity	Quantity of OH^-	Quantity of CO_3^{-2}	Quantity of HCO_3^-
P =0	-	-	M
P =1/2M	-	2P	-
P = M	P	-	-
P < 1/2M	-	2P	M-2P
P > 1/2M	(2P-M)	2(M-P)	-

Q.1 A sample of water was alkaline to both phenolphthalein and methyl orange. 100 ml of this water sample required 6 ml of N/50 HCl for phenolphthalein end point and 10 ml of the acid to methyl orange end point. Determine the types and extent of alkalinity present.

100 ml of water upto phenolphthalein end point = 6 ml of acid

$100 \times N_p = 6 \times \frac{1}{50}$

$N_p = 0.0012$ N

$P = N_p \times 50 \times 1000$

$= 0.0012 \times 50 \times 1000 = 60$ppm

100 ml of water upto methyl orange end point = 10 ml of acid

$100 \times N_m = 10 \times \frac{1}{50}$

$N_m = 0.002$ N

$M = N_m \times 50 \times 1000 = 100$ ppm

Since P > M/2, hence OH^- and CO_3^{2-} ions are present.

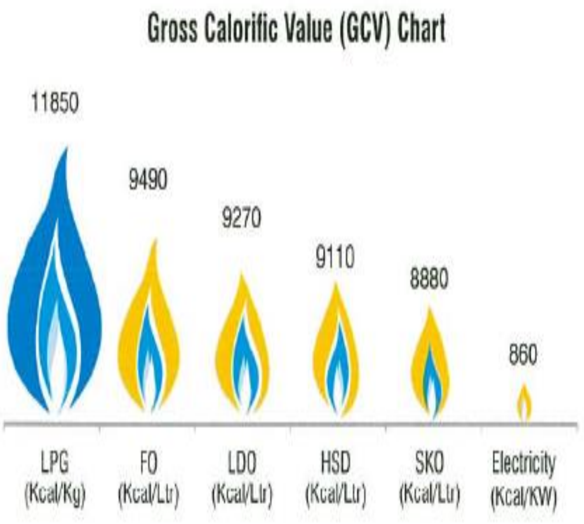
Therefore, alkalinity due to OH^- = 2P-M = 2 × 60-100 = 20 ppm

alkalinity due to CO_3^{2-} = 2(M-P) = 2(100-60) = 80 ppm

Hence, the given water sample contains

OH^- Alkalinity = 20 ppm

CO_3^{2-} Alkalinity = 80 ppm



MIET GROUP OF INSTITUTIONS

Lecture – 31

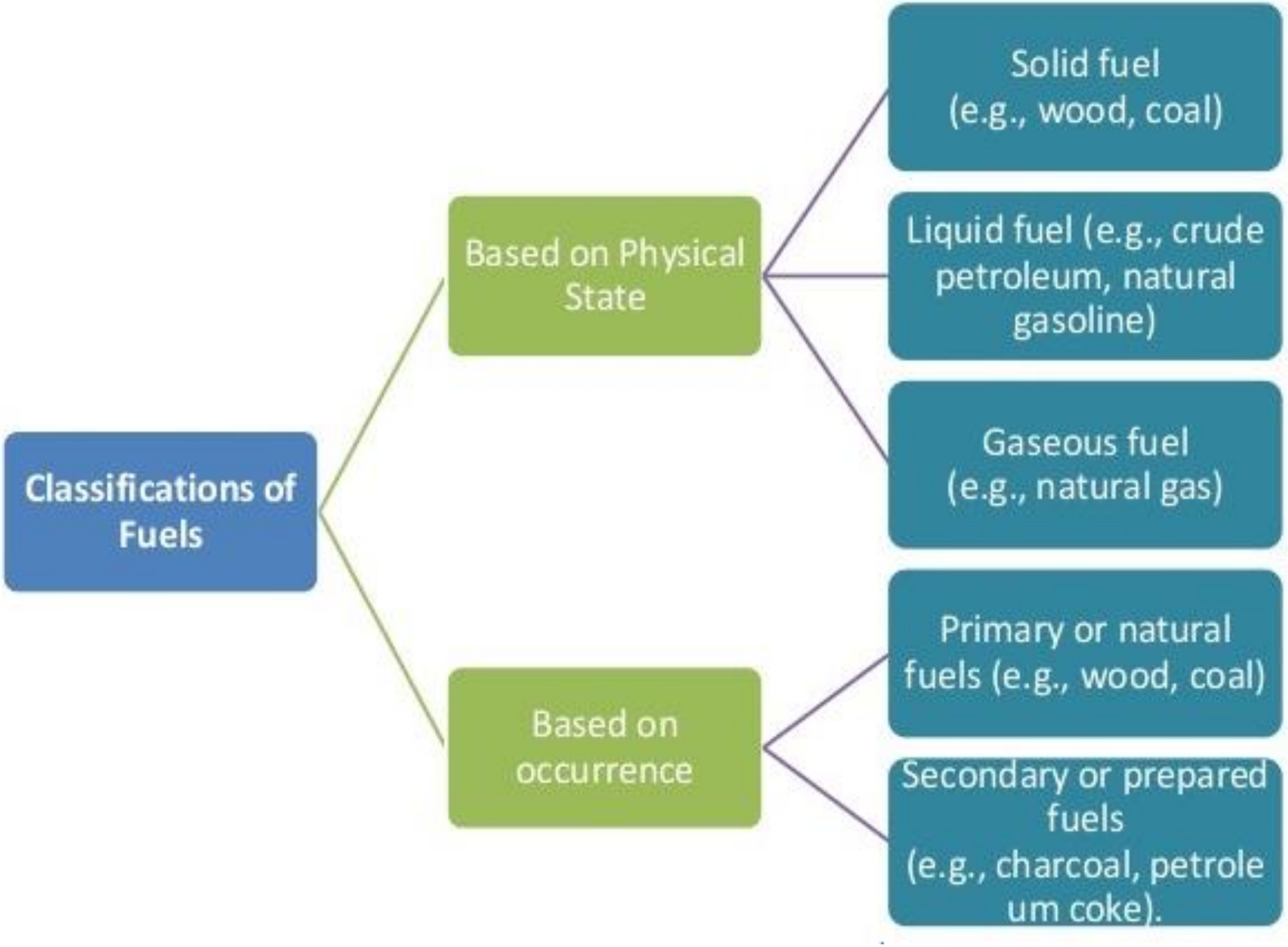
- Classification of fuels
- Comparison between solid, liquid and gaseous fuels
- Characteristics of good fuel
- Coal and its classification
- Calorific value and its types
- Determination of calorific value

Fuels

Any compound which on burning in the presence of air or oxygen (combustion) produce a large amount of heat that can be used economically for industrial and domestic purpose is known as fuel.

Fuel + Oxidant → Combustion Products + Energy

Classification of fuels



- Classifications of Fuels
  - Based on Physical State
    - Solid fuel (e.g., wood, coal)
    - Liquid fuel (e.g., crude petroleum, natural gasoline)
    - Gaseous fuel (e.g., natural gas)
  - Based on occurrence
    - Primary or natural fuels (e.g., wood, coal)
    - Secondary or prepared fuels (e.g., charcoal, petroleum coke).


Solid fuels
Liquid fuels
Gaseous fuels

Comparison Between Solid, Liquid and Gaseous Fuels

Property	Solid fuel	Liquid fuel	Gaseous fuel
Calorific value	Low	higher	highest
Cost	Very cheap	costly	costly
Ash	High	negligible	Nil
Rate of combustion	Not controllable	controllable	controllable
Air used	Large excess	Small excess	Just sufficient
Space for storage	Small	smaller	Very large
Thermal Efficiency	Low	high	high

Characteristics of Good Fuel

- ***Suitability:*** The fuel selected should be most suitable for the process.

- ***Calorific value:*** Fuel should have high carbon content i.e. high calorific value.

- ***Ignition Temperature:*** Ignition temperature is the temperature at which fuel starts igniting. A good fuel should have moderate ignition temperature. If the ignition temperature is low then it may cause fire hazards, whereas if the ignition temperature is high then fuel would not ignite easily.

- ***Moisture content:*** It should be low as it reduces the calorific value of fuel and high moisture content also quenches the fire in the furnace.

- ***Non combustible matter (ash content):*** Ash content should be low as it reduces the calorific value of the fuel, lowers the rate of combustion, results in high heat losses and also results in the formation of ash lumps.

- ***Rate of combustion:*** It should be moderate. Too high rate of combustion can result in fire hazards and too low rate of combustion would consume lot of time and fuel.

- ***Volatile matter:*** The high volatile content gives long flames, high smoke and relatively low heating values. It also reduces the calorific value of fuel.

- ***Cost:*** Cost of fuel should be reasonable.

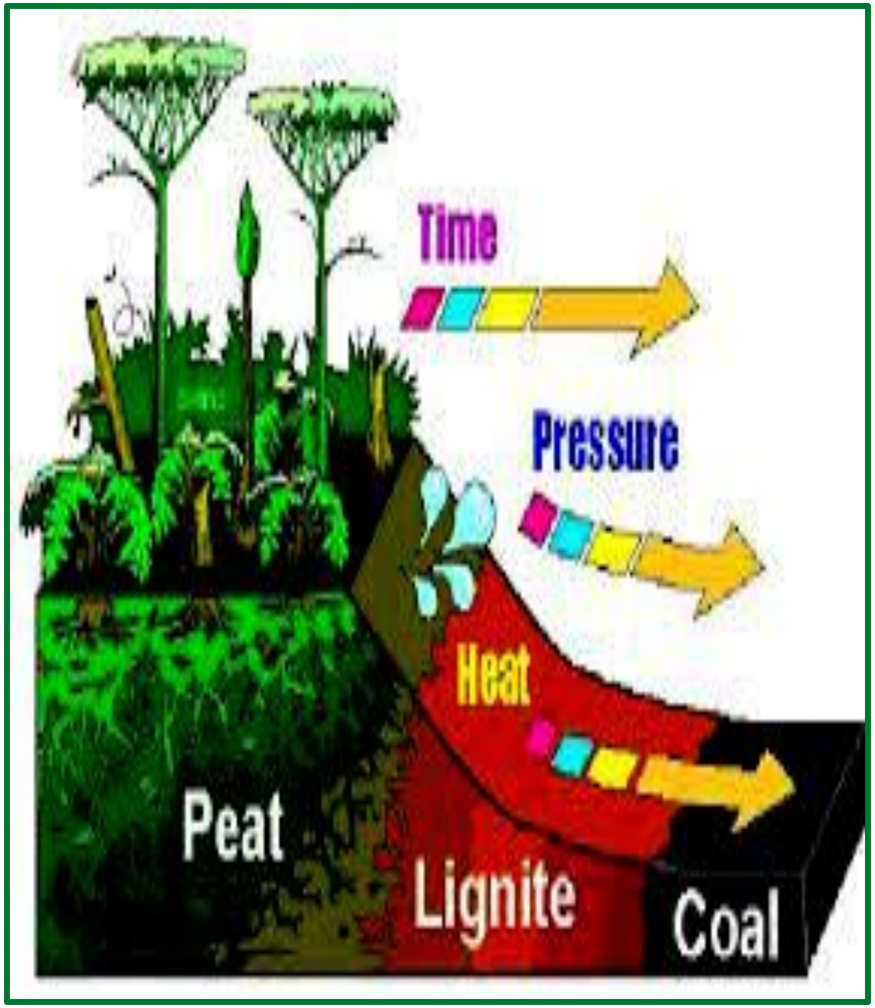
- ***No pollution:*** Good fuel should not produce any harmful by-products or pollution.

- ***Transportation and storage:*** Transportation and storage of fuel should be easy.

Coal

Coal is regarded as a fossil fuel produced from the vegetable buried under conditions of high temperature and pressure over millions of years.

Coal is given a ranking depending upon the carbon content of the coal from the wood to anthracite.



Classification of coal

Types of coal	% of carbon	Calorific value	Characteristics	Applications
Wood	50	4000-4500	Dried wood of trees	Domestic fuel
Peat	50-60	4125-5400	Brown fibrous jelly like mass	Used if deficiency of high rank coal is prevailing
Lignite	60-70	6500-7100	Soft, brown coloured, lowest ranked coal	For steam generation in thermal power plants
Bituminous	80-90	8000-8500	Pitch black to dark grey coal	In making coal gas and Metallurgical coke
Anthracite	90-98	8650-8700	Highest ranked coal	In households and for steam raising

Anthracite

Bituminous

Sub-bituminous

Lignite

Peat

Different Forms of Coal

Calorific Value

Calorific value of a fuel is "the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely."

Units of heat:

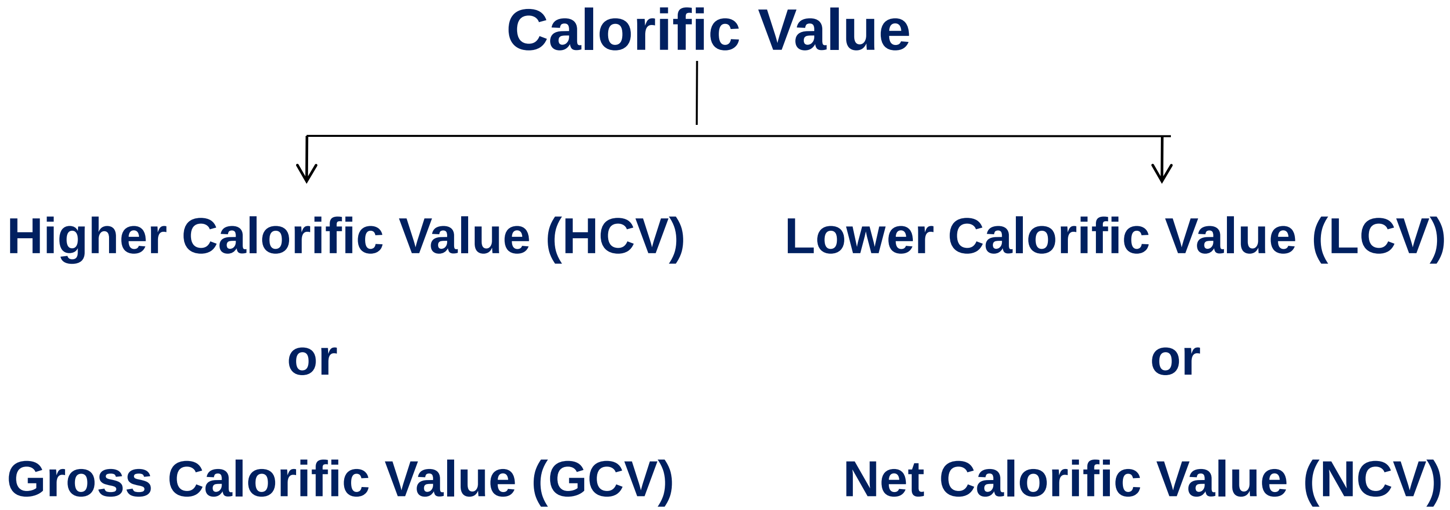
- ***Calorie:*** It is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).

- ***Kilocalorie:*** It is equal to 1,000 calories. It may be defined as 'the quantity of heat required to raise the temperature of one kilogram of water through one degree Centigrade. Thus: 1 kcal = 1,000 cal

- ***British Thermal unit (B.T.U.):*** is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.

1 B.T.U. = 252 cal = 0.252 kcal
1 kcal = 3.968 B.T.U.

Types of Calorific Value



Calorific Value

Higher Calorific Value (HCV)

or

Gross Calorific Value (GCV)

Lower Calorific Value (LCV)

or

Net Calorific Value (NCV)

Higher or Gross Calorific Value

HCV is "the total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature“ (i.e., 15° C or 60°F). HCV of a fuel can be calculated by the use of Bomb Calorimeter or by using Dulong’s formula.

Lower or net calorific value

LCV is "the net heat produced, when unit mass /volume of the fuel is burnt completely and the products are permitted to escape".

NVC is given by:

NCV = GCV - % H x (0.09) x Latent heat of steam

LCV will be equal to GCV when the percentage of hydrogen is zero.

LCV is given as:

LCV = GCV – 0.09(%H) x Latent heat of steam

LCV = GCV – 0.09 (0) x Latent heat of steam

LCV = GCV – 0

LCV = GCV

Determination of Calorific Value

- Experimentally the Higher calorific value for solid as well as non volatile liquid fuels can be determined by using ***Bomb Calorimeter***.

- Theoretical calculation of Higher calorific value for a fuel is done by using ***Dulong's formula***.

Theoretical Calculation of Calorific value of a Fuel

- The calorific value of a fuel can be calculated by **Dulong's Formula**.
- According to Dulong, the calorific value of a fuel is the sum of the calorific values of all the elements present. The calorific values of different elements are given as under:

Calorific Value of C = 8080 cal/g

Calorific Value of H = 34500 cal/g

Calorific Value of S = 2240 cal/g

Dulong's formula

GCV= 1/100 [8,080 %C + 34,500 (% H – % O/8)+ 2,240 % S] kcal/kg

[If both oxygen and hydrogen are present in fuel then it is assumed that all the oxygen combines with 1/8 of its weight of hydrogen to form water. So, this fraction is deducted from the hydrogen content of the fuel in the calculation]

BOMB CALORIMETER

It is used for experimental calculation the calorific value (GCV) of solid and non volatile liquid fuels.

Principle:

A known amount of the fuel is burnt in excess of oxygen and heat liberated is transferred to a known amount of water. The calorific value of the fuel is then determined by applying the principle of calorimetery i.e.

Heat gained = Heat lost

Construction

Bomb calorimeter consists of:

- A strong stainless steel pot fitted with a lid.
- Two electrodes.
- One oxygen inlet.
- One of the electrodes is attached to the crucible having fuel.
- Fuel sample is weighed and burnt in high pressure oxygen (25-30 atm).

- Stainless steel or copper calorimeter.
- Stirrer for uniform circulation of water.
- Beckmann thermometer (0.01 ˚C changes in temperature can be easily noticed).
- Water and air jackets to avoid heat losses.
- A 6 Volt battery to start combustion of fuel.

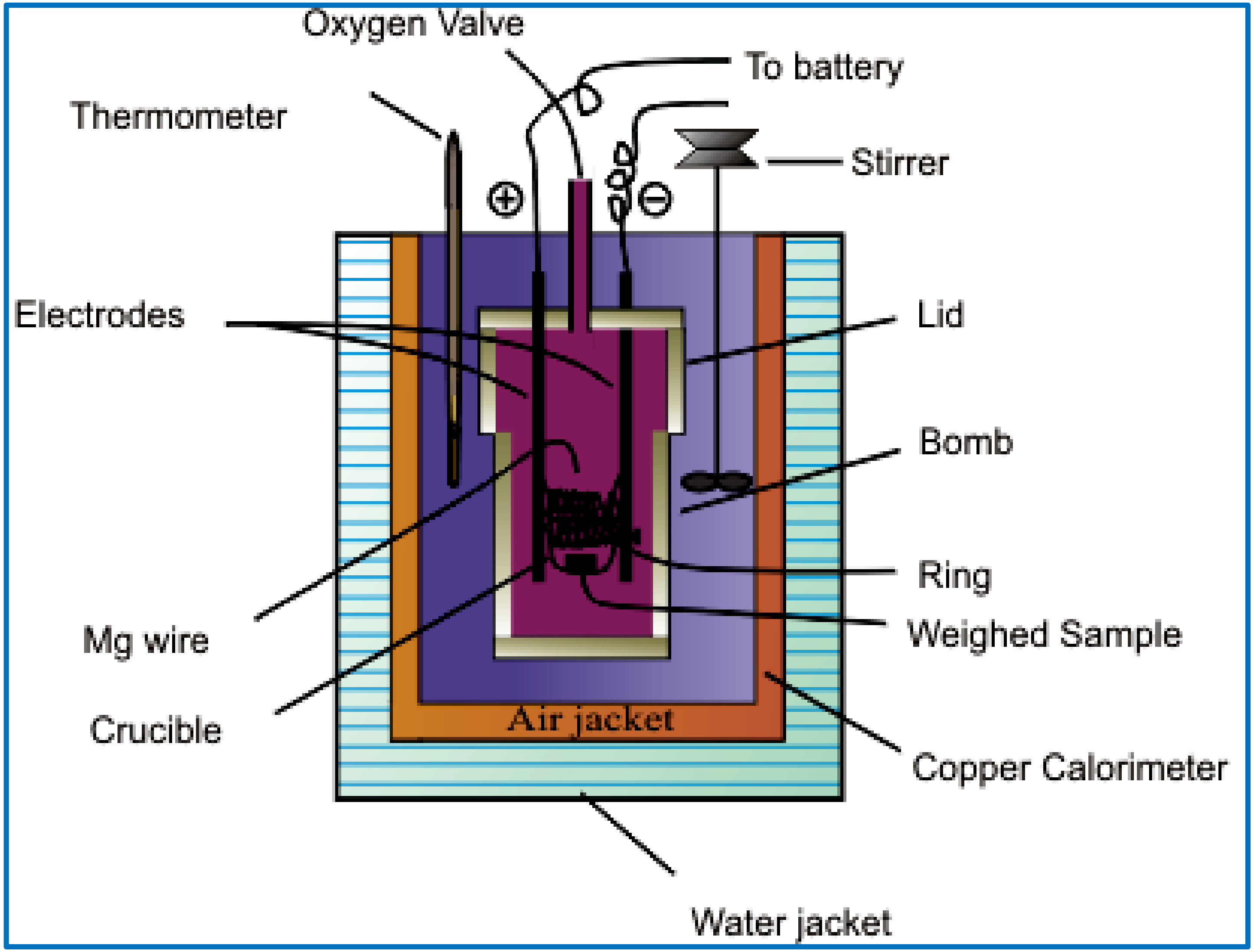
Working of bomb calorimeter:

Weigh fuel sample and keep it in crucible.

- Stainless steel bomb’s lid is fixed tightly.
- Fill the bomb with oxygen (25-30 atm pressure).
- Place the bomb in calorimeter.
- Add known volume of water in the calorimeter.
- Keep the thermometer and stirrer in the water.

- Place the calorimeter in the water jacket.
- Put the plastic cover on top and make electrical connections.
- Stir for 5 minutes and note the initial temperature of water.
- Pass the current to heat the wire so that the fuel catches fire.
- Note the maximum temperature reached.

Bomb Calorimeter



Calculations:

Let weight of the fuel sample taken = x g

Weight of water in the calorimeter = W g

Water equivalent of the Calorimeter,

stirrer,bomb,thermometer = w g

Initial temperature of water = t_1ºC

Final temperature of water = t_2ºC

GCV= Gross calorific value

$$GCV = \frac{(W+w)\ (t_2-t_1)}{x}$$

NCV = GCV - % H x (0.09) x Latent heat of steam

Corrections

For accurate results the following corrections are also included.

- ***Acid corrections (C_A):*** It must be made for the heat liberated in the bomb by the formation of H_2SO_4 and HNO_3
- ***Cooling correction (C_C):*** As the temperature rises above the room temperature, the loss of heat does occur due to radiation, and the highest temperature recorded will be slightly less than that obtained. A temperature correction is therefore necessary.

- ***Fuse wire correction (C_F):*** Heat liberated by combustion of magnesium wire must be subtracted.
- ***Cotton thread correction (C_{CT}):*** For the proper combustion of fuel some cotton threads are kept in the crucible, so heat liberated due to this must be subtracted.

So,

$$GCV = \frac{(W + w)(t_2 - t_1 + C_c) - (C_A + C_f + C_{CT})}{X}$$

C_A = Acid correction

C_F = fuse wire correction

C_{CT} = cotton thread correction

C_C = cooling correction

LECTURE - 32

- Analysis of Coal
- Proximate Analysis
- Ultimate Analysis

Analysis of coal

In order to assess the quality of coal the following two types of analysis are made: Proximate analysis and Ultimate analysis.

Proximate Analysis

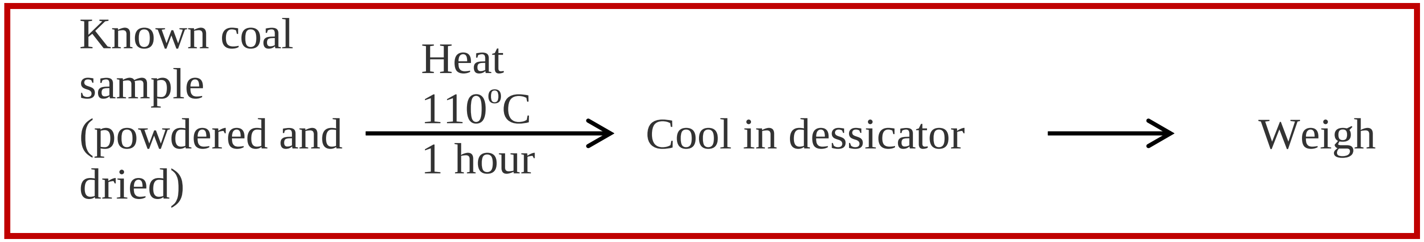
It includes the determination of :

- Moisture
- Volatile matter
- Ash and
- Fixed carbon

This gives quick and valuable information for commercial classification and determination of suitability for a particular industrial use.

Moisture%

All moisture in coal escapes on heating coal at 110ºC for 1h.



Known coal sample (powdered and dried) → Heat 110°C 1 hour → Cool in dessicator → Weigh

$$\text{Moisture \%} = \frac{\text{weight of moisture}}{\text{weight of coal sample}} \times 100$$

Volatile matter %

At 925°C in muffle furnace, coal undergoes thermal degradation to form volatile matter.

Moisture free coal left in first experiment $\xrightarrow[925^{\circ}C,\ 7\ \text{min}]{\text{heat}}$ Cool the crucible in dessicator $\longrightarrow$ Weigh

$$\boxed{\text{VM \%} = \frac{\text{weight of volatile matter}}{\text{weight of coal sample}} \times 100}$$

Ash %

The residual coal in the above experiment is heated and burned above $750^{o}C$ for 30 min. The ash is left behind. Cool and weigh.

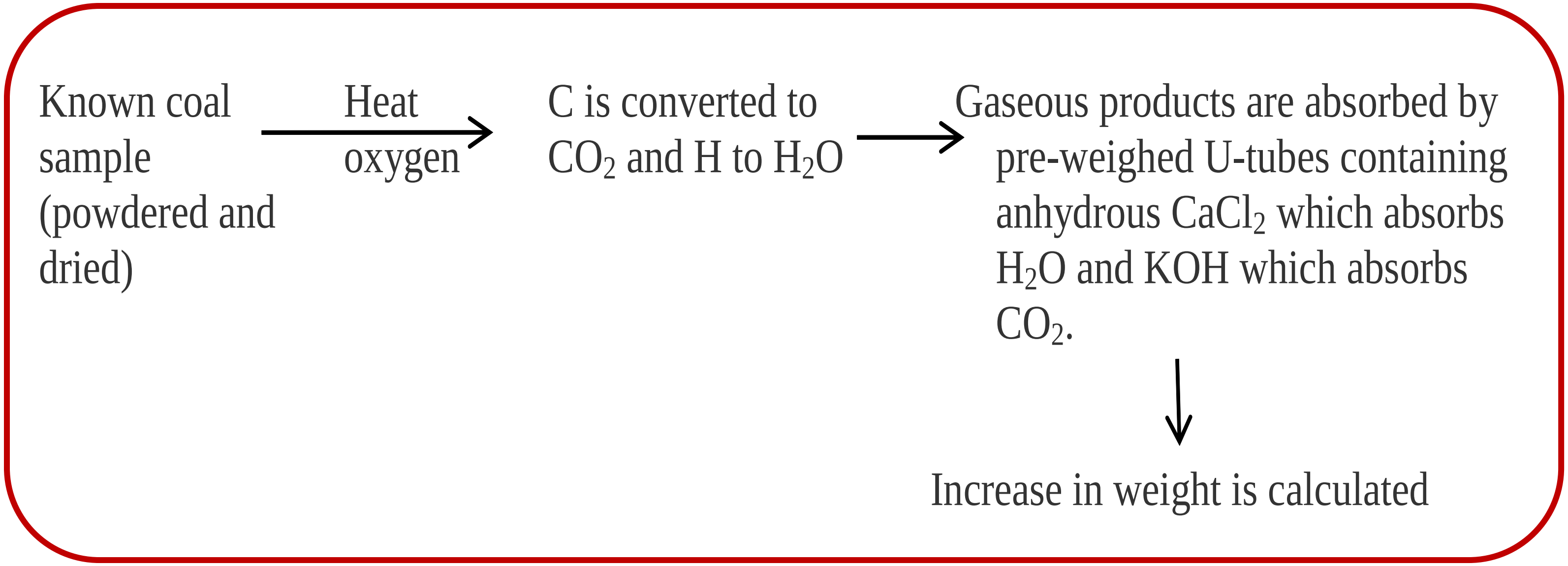
Ash % = weight of Ash x 100
Weight of coal sample

%Fixed carbon

%C= 100 – (moisture % + volatile matter % + ash%)

ULTIMATE ANALYSIS OF COAL

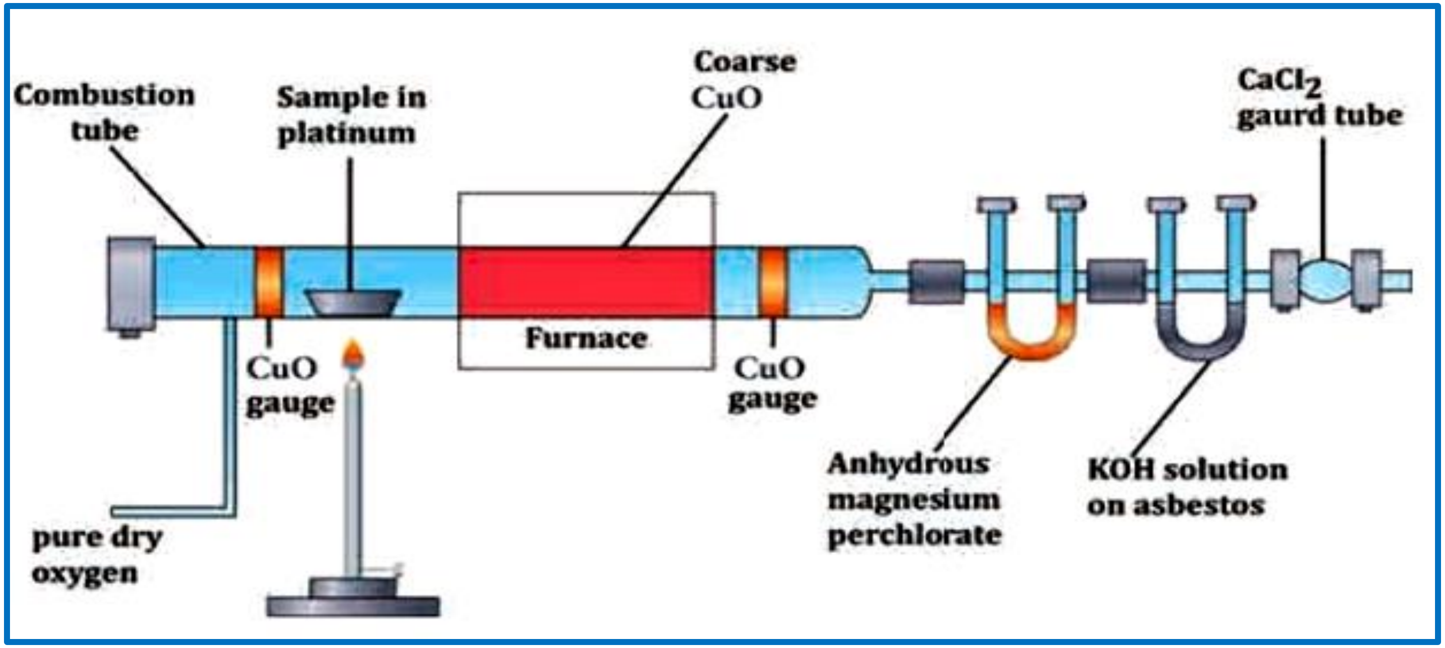
Analysis of coal in which % of C, H, O, N, S elements are found out is known as ultimate analysis.



Known coal sample (powdered and dried) $\xrightarrow[\text{oxygen}]{\text{Heat}}$ C is converted to CO_2 and H to H_2O → Gaseous products are absorbed by pre-weighed U-tubes containing anhydrous $CaCl_2$ which absorbs H_2O and KOH which absorbs CO_2.

↓

Increase in weight is calculated



$$\% \text{ C} = \frac{12}{44} \times \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of coal sample}} \times 100$$

$$\% \text{ H} = \frac{2}{18} \times \frac{\text{Increase in Weight of } CaCl_2 \text{ tube}}{\text{Weight of coal sample}} \times 100$$

Determination of N (kjeldahl method):

Known coal sample (powdered and dried) in kjeldahl flask $\xrightarrow[\text{conc. } H_2SO_4 \;\; K_2SO_4]{\text{heat}}$ clear solution → Alkali → NH_3 is liberated.

↓

Pass through known volume of standard acid

↓

Unused acid is determined by back titration with NaOH

$$\%N = 1.4 \times \frac{\text{Volume of acid} \times \text{Normality}}{\text{weight of coal sample}}$$

Determination of S:

$S \xrightarrow{O_2} SO_2 \xrightarrow{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 + 2HCl$

$BaSO_4$ is filtered, dried and weighed.

$$\%\ S = \frac{32}{233} \times \frac{\text{Weight of } BaSO_4 \text{ precipitate}}{\text{Weight of coal sample}} \times 100$$

% Ash

Known coal sample (powdered and dried) → 750°C(heat) 30 min in a muffle furnace → Residue left → weigh

$$\% \text{ Ash} = \frac{\text{Weight of residue}}{\text{Weight of coal sample}} \times 100$$

$$\%O = 100-(C\% + H\% + N\% + ash\% + S\%)$$

Importance of Ultimate Analysis

- ***Carbon:*** greater the % carbon in coal, better is the coal quality and calorific value.
- ***Hydrogen:*** Hydrogen is in the form of moisture and volatile matter. It decreases the calorific value and quality of coal.
- ***Nitrogen:*** Nitrogen has no calorific value. A good quality coal should have negligible N%.
- ***Sulphur:*** Though has good calorific value but has corrosive effect and act as a pollutant. A good quality coal should have low S%.
- ***Oxygen:*** Decreases the calorific value of coal, decreases the coal quality.

LECTURE - 33

- Numericals on Calorific value
- Numericals on Proximate Analysis
- Numericals on Ultimate Analysis

Que1. A sample of coal contains C= 70%, O= 20%, H= 8%, S= 1%, N= .5% and ash= .5%. Calculate GCV and NCV of coal.

Solution:

$$GCV = \frac{1}{100}\left[8080\%C + 34500\left(\%H - \frac{\%O}{8}\right) + 2240\%S\right]$$

$$GCV = \frac{1}{100}\left[8080\,(70) + 34500\left(8 - \frac{20}{8}\right) + 2240\,(1)\right]$$

$$= 7575.9 \text{ cal/g}$$

$$NCV = GCV - 0.09\,(\%H)\,(587)$$

$$= 7575.9 - 0.09\,(8)\,(587) = 7153.26 \text{ cal/g}$$

Ques 2. Calculate GCV and NCV of coal having the following compositions: C = 85%, H = 7%, S = 1%, N= 2%, ash = 4% and heat capacity of steam = 2458 J/g.

Solution:

$$GCV = \frac{1}{100}\left[8080\%C + 34500\left(\%H-\frac{\%O}{8}\right) + 2240\%S\right]$$

$$\%O = 100 – (C\% + N\% + S\% + H\% + ash\%)$$

$$= 100 – (85+2+1+7+4) = 1\%$$

$$GCV = \frac{1}{100}\left[8080\,(85) + 34500\left(7-\frac{1}{8}\right) + 2240\,(1)\right]$$

$$= 9262.27 \text{ cal/g} \quad = 9262.27 \times 4.18$$

$$= 38716.30 \text{ J/g}$$

$$NCV = GCV – 0.09(\%H)(2458)$$

$$= 38716.30 - 0.09(7)(2458) = 37167.76 \text{ J/g}$$

Ques 3. On burning 0.83 g of a fuel in a bomb calorimeter, temperature of 3500 g of water increased from 26.5 to 29.2^oC. Water equivalent of calorimeter and Latent heat of water are 385 g and 587 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific value.

Solution:

$x = 0.83$ g, $w = 385$ g, $W = 3500$ g, %H = 0.7

Latent heat of water = 587 cal/g, $t_2-t_1 = 29.2-26.5 = 2.7^oC$

$$HCV = \frac{(W+w)\ (t_2-t_1)}{x}$$

$$= \frac{(3500+385)\ (2.7)}{0.83} = 12637.95 \text{ cal/g}$$

$$LCV = HCV-0.09\ (\%H)\ (587)$$

$$= 12637.95 - 0.09\ (0.7)\ (587) = 12600.97 \text{ cal/g}$$

Ques 4. A sample of coal contains C= 93%, H=6%, ash= 1%. The following data was obtained when the above coal was tested in bomb calorimeter: wt. of coal burnt= 0.92 g, wt. of water taken= 2200 g, water equivalent of bomb calorimeter= 550 g, rise in temp is 2.42 ° C, Fuse wire correction= 10.0 cal, acid correction= 50.0 cal. Calculate gross and net calorific value of coal, assuming the latent heat of condensation of steam as 580 cal/g.

Solution: HCV and LCV are given as:

$$\text{HCV} = \frac{(W+w)\,(t_2-t_1) - (C_A + C_F)}{X}$$

$$\text{LCV} = \text{GCV} - 0.09\ \%\text{H} \times \text{latent heat of steam}$$

Solution:

$$HCV = \frac{(W+w)\ (t_2-t_1) - (C_A + C_F)}{X}$$

$$= \frac{(2200 + 550)\ (2.42) - (50 + 10)}{0.92}$$

$$= \frac{(2750)\ (2.42) - (60)}{0.92} \quad = 7168.48 \text{ cal/g}$$

$$LCV \quad = GCV - 0.09\ \%H \times \text{latent heat of steam}$$

$$= 7168.4782 - 0.09 \times 6 \times 580$$

$$= 7168.4782 - 313.2 \quad = 6855.28 \text{ cal/g}$$

Ques 5: 3.25 g of coal was kjeldahlized and NH_3 gas thus evolved was absorbed in 45 ml of 0.1 N H_2SO_4. To neutralize excess of acid, 11.5 ml of 0.1N NaOH was required. Calculate N%.

Solution:

Weight of coal = 3.25 g

Volume of H_2SO_4 consumed = 45 - 11.5 = 33.5 ml

$$\% \text{ N} = \frac{\text{Volume of acid} \times \text{Normality}}{\text{Weight of coal sample}} \times 1.4$$

$$= \frac{33.5 \times 0.1 \times 1.4}{3.25} = 1.44\%$$

Ques 6. 1g of coal loses 0.03 g at 110°C and then complete combustion leaves 0.08 g residue . 1 g of same coal loses 0.22 g at 950°C. Calculate fixed carbon %.

Solution: Weight of moisture in 1 g coal = 0.03 g

Weight of ash in 1 g coal = 0.08 g

Weight of (moisture + volatile matter) in 1 g coal = 0.22 g

Weight of volatile matter = 0.22-0.03 = 0.19 g

$$\textbf{Moisture \% } = \frac{\textbf{weight of moisture}}{\textbf{Weight of coal sample}} \textbf{ x 100}$$

$$= \frac{0.03}{1} \text{ x } 100 \quad =3\%$$

$$\textbf{Ash \%} = \frac{\textbf{weight of ash}}{\textbf{Weight of coal sample}} \times 100$$

$$= \frac{0.08}{1} \times 100 = 8\%$$

$$\textbf{VM \%} = \frac{\textbf{weight of volatile matter}}{\textbf{Weight of coal sample}} \times 100$$

$$= \frac{0.19}{1} \times 100 = 19\%$$

% Fixed carbon = 100 - (19+3+8) = 70%

Ques 7. 0.25 g coal sample on burning in combustion chamber in current of pure O_2 was found to increase weight of $CaCl_2$ U-tube by 0.08 g and KOH U-tube by 0.5 g. Find % of carbon and hydrogen in coal.

Solution: Weight of coal = 0.25 g

Increase in wt. of KOH tube (Wt. of CO_2) = 0.5 g

Increase in wt. of $CaCl_2$ tube (Wt. of H_2O) = 0.08 g

$$\% \text{ C} = \frac{\text{Weight of } CO_2 \text{ formed} \times 12 \times 100}{\text{Weight of coal sample} \times 44}$$

$$= \frac{0.5 \times 12 \times 100}{0.25 \times 44} = 54.5\%$$

$$\% \text{ H} = \frac{\text{Increase in Weight of CaCl}_2\text{ tube x 2}}{\text{Weight of coal sample x 18}} \text{ x } 100$$

$$= \frac{0.08 \text{ x } 2 \text{ x } 100}{0.25 \text{ x } 18}$$

$$= 3.55\%$$

Ques 8. Calculate %S in coal sample when 0.55 g of coal is combusted in bomb calorimeter. Solution from bomb on treatment with $BaCl_2$ forms 0.025 g $BaSO_4$.

Solution:

Weight of coal sample = 0.55 g

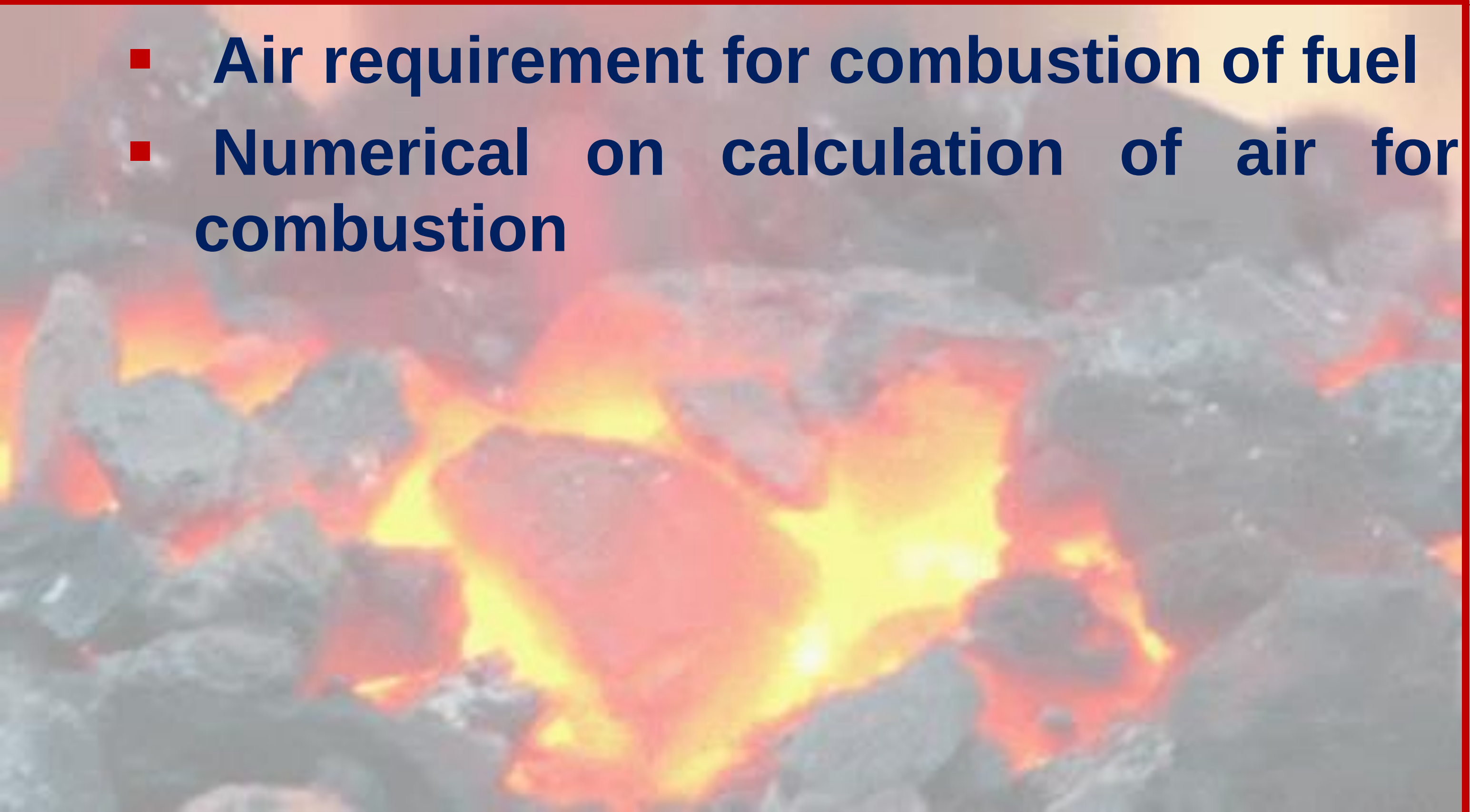
Weight of $BaSO_4$ = 0.025 g

$$\% S = \frac{\text{Weight of } BaSO_4 \text{ precipitate} \times 32}{\text{Weight of coal sample} \times 233} \times 100$$

$$= \frac{0.025 \times 32}{0.55 \times 233} \times 100$$

$$= 0.62\%$$

LECTURE - 34



- Air requirement for combustion of fuel
- Numerical on calculation of air for combustion

Air requirement for combustion of fuel

- Combustion refers to the rapid oxidation of fuel accompanied by the production of heat, or heat and light. Complete combustion of a fuel is possible only in the presence of an adequate supply of oxygen.

- At STP (273 K, 1 atm) one mole of all gases occupy a volume of 22.4 litres.

- Hence at S.T.P. 22.4 liters of CO_2 will have a weight of 44gm, its molecular weight.

- Minimum oxygen required

  = (Theoretical O_2 required) - (O_2 present in fuels).

- If fuel does not contain oxygen then theoretical oxygen is considered as Net oxygen.

- Air contains 21 % of oxygen by volume and 23 % of oxygen by weight,
- Hence 1 m^3 of oxygen will be supplied by

$$\frac{1 \times 100}{21} = 4.76 \text{ m}^3 \text{ of air}$$

- Similarly 1 kg of oxygen will be supplied by $\frac{1\text{x } 100}{23}$

  $= 4.35$ kg of air

- Molecular weight of air is 28.94 mol $^{-1}$

CONVERSIONS

To convert liters of air into grams:

22.4 L of air at STP = 28.97 g

y L of air at STP = $\frac{28.97}{22.4}$ x y = 1.29 x y grams

To convert grams of oxygen into liters:

y g of air = $\frac{22.4}{32}$ x y = 0.7 x y L (**1000 Litres = 1 m^3**)

Ques 1. A sample of coal was found to have the following percentage composition: C = 75%, H= 5.2%, O = 12.1%, N = 3.2%, ash = 4.5%. Calculate minimum amount of air required for complete combustion of 1 kg of coal sample.

Sol. (N is not combustible, so no calculations required for nitrogen)

Weight of C in 1 kg coal = $\frac{75}{100} \times 1000\ \text{g} = 750\ \text{g}$

$H = \frac{5.2}{100} \times 1000\ \text{g} = 52\ \text{g}$

$O = \frac{12.1}{100} \times 1000\ \text{g} = 121\ \text{g}$

(N is not combustible)

$$O_2 \text{ quantity} = \left[\frac{32}{12} C + (8 \times H) + S - O\right] \text{ g}$$

$$= \left[\frac{32}{12} \times (750) + (8 \times 52) - 121\right] \text{ g} = 2295 \text{ g}$$

$$\text{Minimum amount of air} = \text{Net } O_2 \times \frac{100}{23} = 2295 \times \frac{100}{23}$$

$$= 9978.2 \text{ g air}$$

Ques 2. Calculate the volume of air required for complete combustion of 1m³ of gaseous fuel having the composition: CO=46%, methane=10%, hydrogen = 4%, C_2H_4 = 2%, N_2 = 1% and remaining being CO_2.

Solution.

Fuel	Composition	Combustion reaction	Vol of O_2 (m3)
CO	$\frac{46}{100} \times 1 = 0.46\ m^3$	$CO + 1/2\ O_2 \longrightarrow CO_2$	$0.46 \times \frac{1}{2} = 0.23$
CH_4	$\frac{10}{100} \times 1 = 0.1\ m^3$	$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2H_2O$	$0.1 \times 2 = 0.2$
H_2	$\frac{4}{100} \times 1 = 0.04\ m^3$	$H_2 + 1/2\ O_2 \longrightarrow H_2O$	$0.04 \times \frac{1}{2} = 0.02$
C_2H_4	$\frac{2}{100} \times 1 = 0.02\ m^3$	$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$	$0.02 \times 3 = 0.06$

O_2 Quantity = 0.23 + 0.20 + 0.02 + 0.06 = 0.51 m^3

Volume of air needed for complete combustion

$$= 0.51 \times \frac{100}{21} = 2.43 \text{ m}^3 \text{ air}$$

Ques 3. Calculate the weight and volume of air required for complete combustion of 3 kg of carbon.

Solution:

$$C + O_2 \longrightarrow CO_2$$

12 g carbon requires oxygen = 32 g

$$3000g\ (3\ kg)\ \text{requires oxygen} = \frac{32}{12} \times 3000 = 8000\ g$$

$$\text{Therefore, weight of air required} = \text{Net } O_2 \times \frac{100}{23}$$

$$= 8000 \times \frac{100}{23}$$

$$=34782.6g$$

Since at S.T.P. , 32 g of oxygen = 22.4 L

1g oxygen = $1 \times \frac{22.4}{32}$ L

($1000\ L = 1\ m^3$)

8000 g of oxygen = $\frac{22.4}{32} \times 8000 = 5600\ L = 5.6\ m^3$

Therefore, volume of air required = $\frac{100}{21} \times 5.6$

$= 26.67\ m^3$

Ques 4. A gas was found to have the following percentage composition by volume: methane=14%, hydrogen = 32%, N_2 = 40%, O_2 = 14%. If 25% excess air is used, Calculate minimum weight of air required for complete combustion of this gas.

Solution:

Fuel	Composition	Combustion reaction	Vol of O_2 (m^3)
CH_4	(14/100)x 1 =0.14 m^3	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$	0.14 x 2 = 0.28
H_2	(32/100)x 1 = 0.32 m^3	$H_2 + 1/2\ O_2 \rightarrow H_2O$	0.32 x (1/2)=0.16

O_2 Quantity = O_2 required for combustion – O_2 in fuel sample

$$= (0.28+0.16)-0.14 = 0.3\ m^3 = 300\ L$$

Volume of air required for 1 m^3 of gas using 25% excess air

$$= 300 \times \frac{(100+25)}{21} = 1785.7\ L$$

22.4 L of air at STP = 28.97 g

1785.7 L of air at STP $= \frac{28.97}{22.4} \times 1785.7 = 2309.5\ g$

Ques 5. A sample of fuel having following percentage composition C = 70%, H = 6%, O = 4%, N = 3%, S = 3%, ash = 6% and moisture = 8%. Calculate the quantity of air required for complete combustion of 1kg of fuel.

(N is not combustible, so no calculations required for nitrogen)

Weight of C in 1 kg coal = $\frac{70}{100}$ x 1000 g = 700 g

H = $\frac{6}{100}$ x 1000 g = 60 g

O = $\frac{4}{100}$ x 1000 g = 400 g

S = $\frac{3}{100} \times 1000g = 30g$

(N is not combustible)

$$O_2 \text{ quantity} = \left[\frac{32}{12}C + (8 \times H) + S - O\right] g$$

$$= \left[\frac{32}{12}\times(700) + (8\times60) + 30 - 400\right] g = 1976.67\ g$$

$$\text{Minimum amount of air} = \text{Net } O_2 \times \frac{100}{23} = 1976.667 \times \frac{100}{23}$$

$$= 8594.2\ g \text{ air}$$

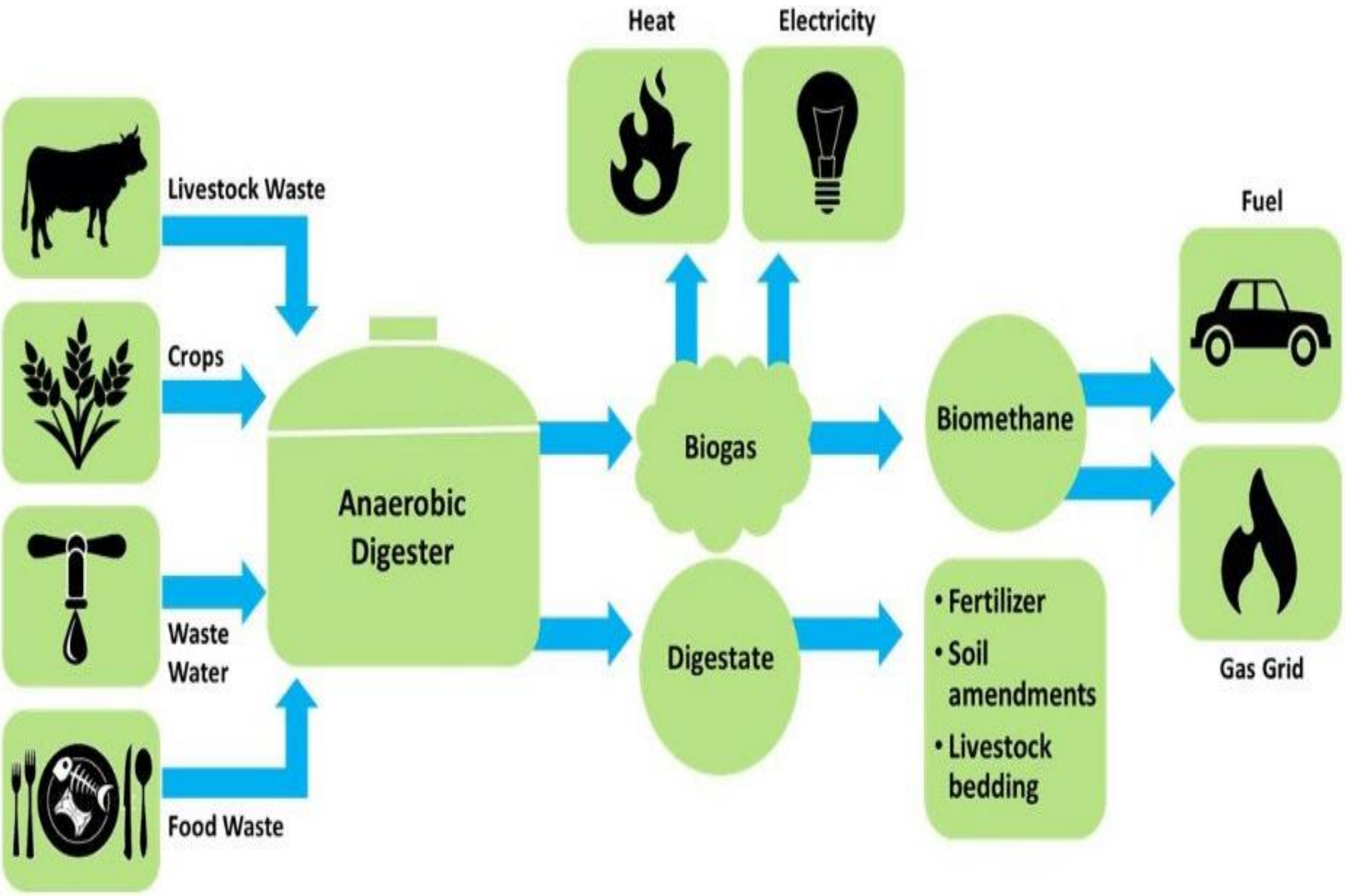
LECTURE - 35

- Chemistry of Biogas production from organic waste materials
- Its environmental impact on society

Biogas plant

- It’s a mixture of gas produced by the microorganisms during the anaerobic fermentation of biodegradable materials. Anaerobic fermentation is a biochemical process in which particular kinds of bacteria digest biomass in an oxygen-free environment resulting in production of CH_4, CO_2, H_2 and traces of other gases along with decomposed mass
- BIOENERGY :- Bio-energy refers to various forms of energy generated from biomass by using biotechnological methods.
- For example :- Biogas, oil, ethanol, methanol, charcoal etc.

Production of biogas from organic waste



Composition of biogas

Gases	Formula	Percentage present
Methane	CH_4	50-70
Carbon dioxide	CO_2	25-50
Nitrogen	N_2	0-9
Hydrogen	H_2	0-1
Hydrogen sulfide	H_2S	0.1-0.5
Oxygen	O_2	0-0.5

Substrates required in biogas production

Animal Wastes	Dung and urine of cattle, buffalo, goat, sheep, slaughterhouses
By-products	Tobacco waste, bagasse, bran
Aquatic plants	Algae, water hyacinth
Crop Residues	Straw, fodder, weed, crop stubble, sticks of cotton and jute
Forest Residues	Branches, leaves, twigs, bark
Urban solid waste	Paper, domestic waste
Human waste	Night soil

Biogas Plant Types

1. Floating dome type

   Eg. KVIC-type (KVIC- Khadi Village Industries Commission)

2. Fixed dome type

   Eg. Deenabandu model

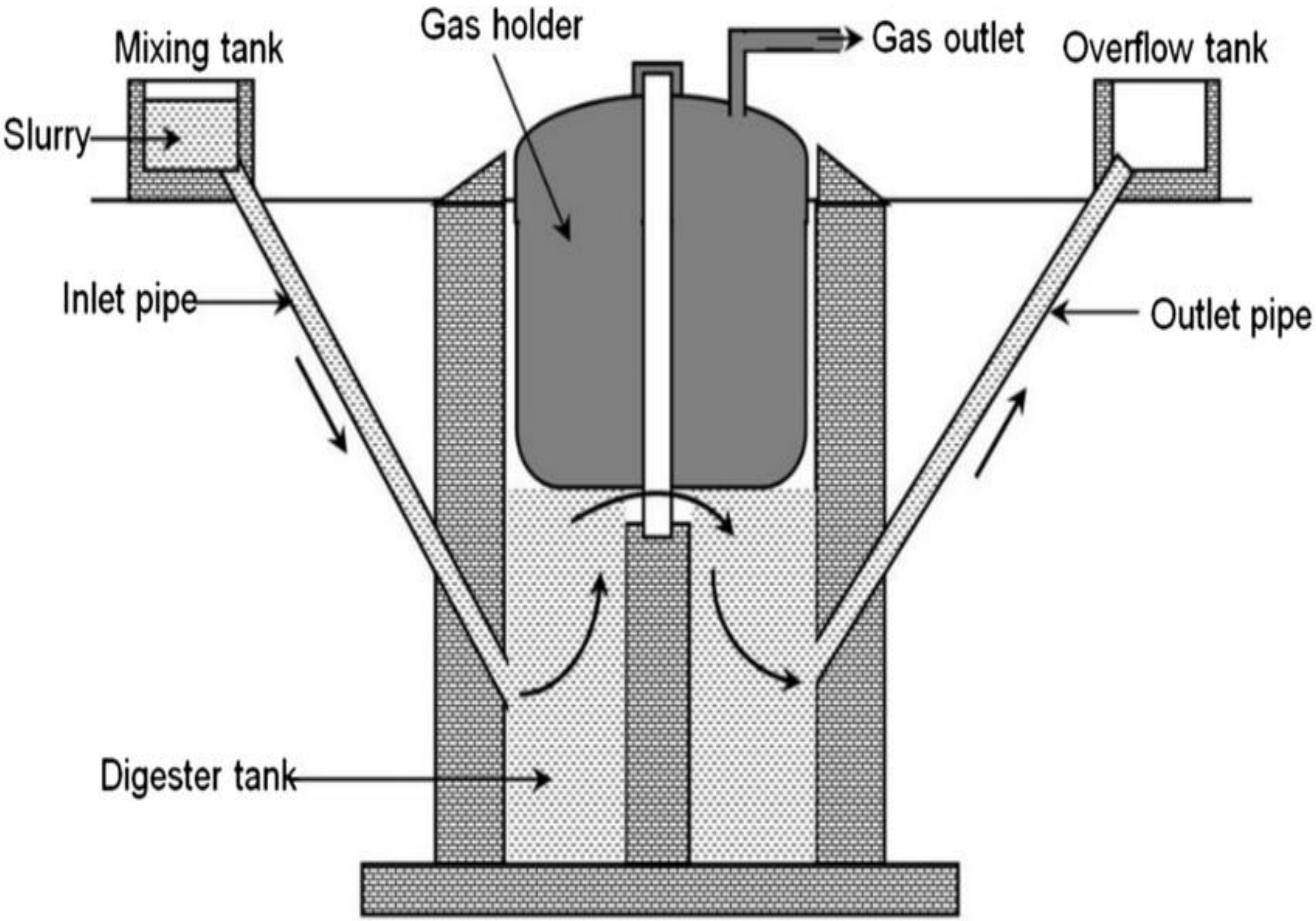
Floating dome type

- The floating gas holder type bio gas plant consists of a dome shaped gas holder made of steel for collecting bio gas.
- The dome shaped gas holder is not fixed but is moveable and floats over the slurry present in the digester tank.
- Due to this reason, this biogas plant is called floating gas holder type biogas plant
- Slurry is prepared by mixing water in cattle dung in equal proportion in mixing tank.
- The slurry is then injected into a digester tank with the help of inlet pipe

Floating dome type

- The digester tank is a closed underground tank made up of bricks. Inside the digester tank, the complex carbon compounds present in the cattle dung breaks into simpler substances by the action of anaerobic microorganisms in the presence of water.
- This anaerobic decomposition of complex carbon compounds present in cattle dung produces bio gas and gets completed in about 60 days.
- The bio gas so produced starts to collect in floating gas holder and is supplied to homes through pipes. And the spent slurry is replaced from time to time with fresh slurry to continue the production of bio gas

Floating dome type



Fixed dome type

- This type of biogas plant is very economical is design. It works with the constant volume principle.
- The main structure is made up of brick and cement masonry. This type of plant doesn't have any moving parts so it is safe from wear and tear
- The operating pressure varies from 0 to 100 cm of water column.
- It is also known as Janata model.

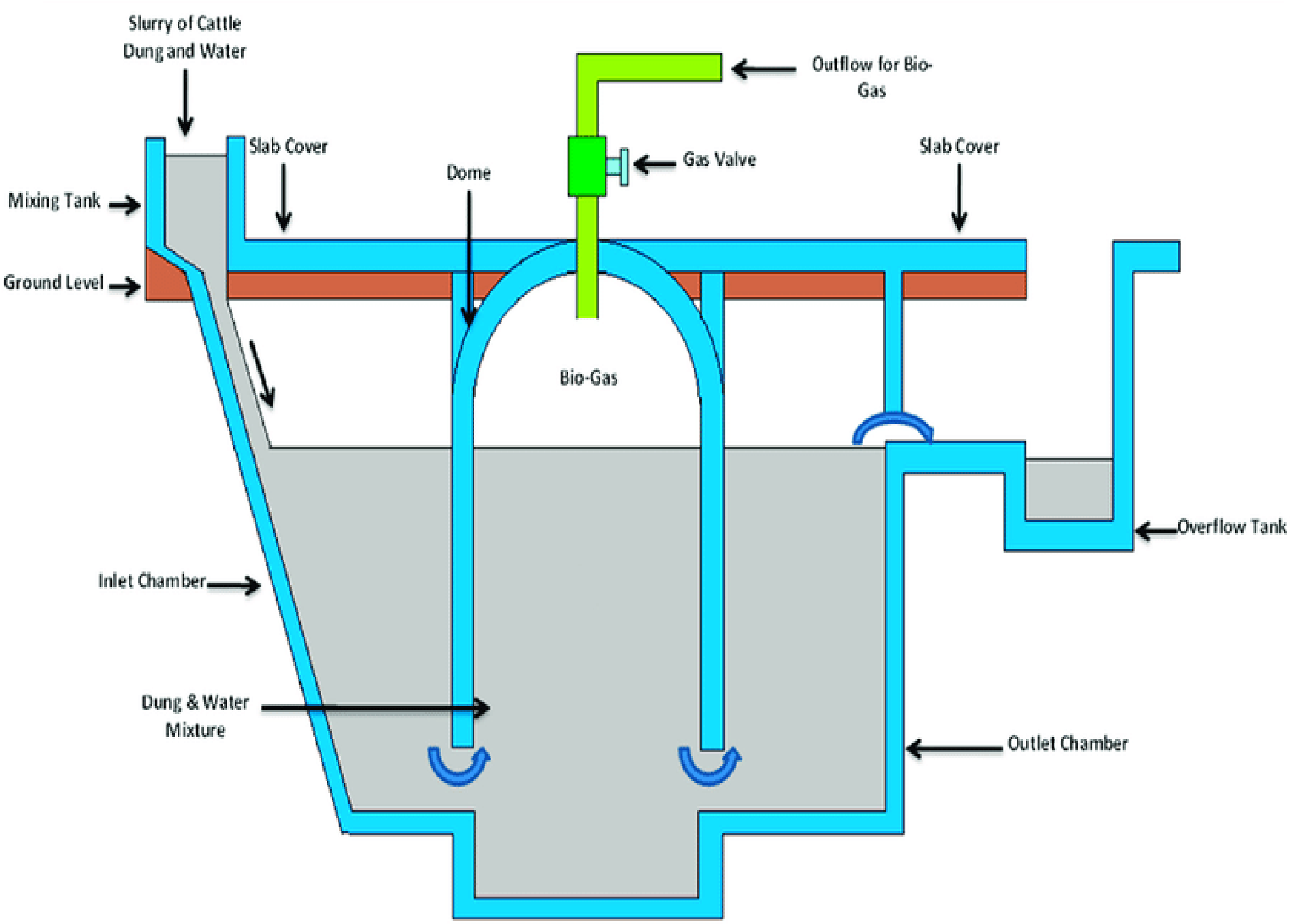
Working of Fixed Dome type Biogas Plant

- The various forms of biomass are mixed with an equal quantity of water in the mixing tank and this forms the slurry.
- The slurry is fed into the digester through the inlet chamber. When the digester is partially filled with the slurry, the introduction of slurry is stopped and the plant is left unused for about two months.
- During these two months, anaerobic bacteria present in the slurry decomposes or ferments the biomass in the presence of water.
- As a result of anaerobic fermentation, biogas is formed, which starts collecting in the dome of the digester.

Working of Fixed Dome type Biogas Plant

- As more and more biogas starts collecting, the pressure exerted by the biogas forces the spent slurry into the outlet chamber.
- From the outlet chamber, the spent slurry overflows into the overflow tank. The spent slurry is manually removed from the overflow tank and used as manure for plants.
- The gas valve connected to a system of pipelines is opened when a supply of biogas is required. To obtain a continuous supply of biogas, a functioning plant can be fed continuously with the prepared slurry.

Fixed dome type



Impact of biogas on society

- The use of Biogas technology reduces the CO_2 emission through the reduction of the demand for fossil fuels.
- Anaerobic digestion of animal waste significantly reduces nitrous oxide emissions by avoiding emissions during the storage/disposal of animal waste.
- The processing of animal and human excrement in biogas system obviously improves sanitary conditions in the locality. The initial pathogenic capacity of the starting materials is greatly reduced by the fermentation process since most of the diseases causing microbes are aerobic in nature.

Impact of biogas on society

- Since biogas slurry does not attract flies or other vermin, the vectors for contagious diseases, for humans and animals alike, are minimized.
- Biogas system leads to permanent availability of cooking energy in a household as long as the organic waste is available.
- In rural areas the use of fire wood for cooking can be replaced by biogas and there by reducing deforestation.