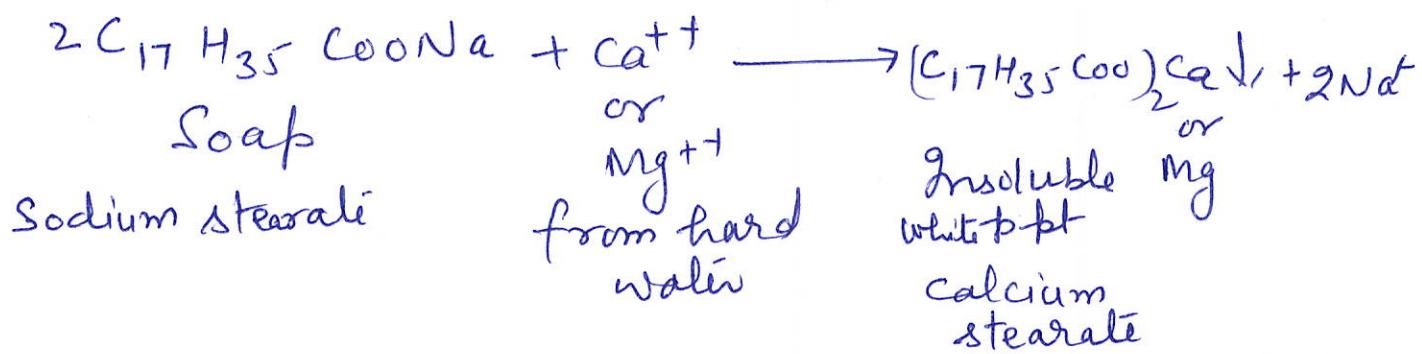


## Water treatment

Hardness :- Hardness is the property of water which prevents the lather formation with soap. or Soap consuming capacity of water



Lather is not produced until the cations causing the ppt of soap are completely removed

Types of Hardness :- 1. Temporary hardness  
2. Permanent hardness

Temporary hardness :- It is due to the presence of bicarbonates of calcium, Magnesium and other heavy metals. This hardness is also known as carbonate hardness. It can be removed by boiling which converts bicarbonates into insoluble carbonates or hydroxides.





(2)

2. Permanent hardness :- It is due to the presence of chlorides and sulphates of calcium, magnesium and other heavy metals. This hardness is also known as non-carbonate hardness.

Permanent hardness cannot be removed by boiling. These are removed by special chemical method like

- i) Redite process
- ii) Ion-Exchange process
- iii) Lime-Soda process

Units of Hardness :-

① Parts per million :- Parts of  $\text{CaCO}_3$  equivalent hardness per million ( $10^6$ ) parts of the

② Miligrams per litre :- Number of milligrams of  $\text{CaCO}_3$  equivalent hardness present in 1 litre of the

$1 \text{ mg/L} \equiv 1 \text{ mg CaCO}_3 \text{ equivalent hardness per litre of the}$

$$1 \text{ mg/L} \equiv 1 \text{ mg of CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of H}_2\text{O} \quad [1 \text{ Kg H}_2\text{O} = 1 \text{ L of H}_2\text{O}]$$

$$10^3 \times 10^3 \text{ mg} \\ \equiv 1 \text{ part of CaCO}_3 \text{ equivalent per } 10^6 \text{ parts of H}_2\text{O} \quad 10^6 \text{ mg} = 1 \text{ L}$$

$$1 \text{ mg/L} \equiv 1 \text{ ppm}$$

③ Degree French ( ${}^{\circ}\text{Fr}$ ) Parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of  $\text{H}_2\text{O}$

$$1 {}^{\circ}\text{Fr} = 1 \text{ part of CaCO}_3 \text{ equivalent hardness per } 10^5 \text{ parts of H}_2\text{O}$$



(3)

④ Clark's degree :- Parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

Relation between Various units :-

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1^\circ \text{Fr} = 0.07^\circ \text{Cl}$$

Degree of Hardness :-

Hardness of water is expressed in terms of  $\text{CaCO}_3$  equivalent because of

1. Its  $(\text{CaCO}_3)$  molecular weight is 100 which makes calculation easy
2. It is the most insoluble salt that can be precipitated in water treatment

$$\text{Hardness in terms of } \text{CaCO}_3 \text{ Equivalent} = \frac{\text{Strength of hardness causing substance mg/L}}{\text{Chemical equivalent of hardness producing substance}}$$

Example A sample of water contains 204 mg of  $\text{CaSO}_4$  per litre. calculate the hardness in terms of  $\text{CaCO}_3$  equivalent

Solution :-

$$\frac{204 \times 50}{68} = 150 \text{ mg/L}$$

$$\text{Hardness} = 150 \text{ ppm}$$



(4)

# Calculation of $\text{CaCO}_3$ Equivalent

Dissolved Salt/Ion	Molar mass	Chemical equivalent
$\text{Ca}(\text{HCO}_3)_2$	$162/2$	81
$\text{Mg}(\text{HCO}_3)_2$	$146/2$	73
$\text{CaSO}_4$	136	68
$\text{MgSO}_4$	120	60
$\text{CaCl}_2$	111	55.5
$\text{MgCl}_2$	95	47.5
$\text{CaCO}_3$	100	50
$\text{MgCO}_3$	84	42
$\text{HCO}_3^-$	61	61
$\text{CO}_3^{--}$	60	30
$\text{Al}_2(\text{SO}_4)_3$	342	57
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	13.9



(5)

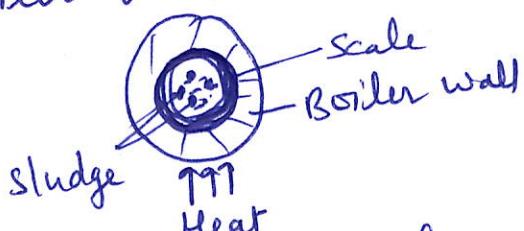
Boiler troubles or Problems:- Boilers are used for steam generation in industries and power houses. If hard water is directly fed into the boilers it may lead to the following problems.

- i) scale and sludge formation
- ii) Caustic embrittlement
- iii) Boiler corrosion
- iv) Priming and foaming

scale and sludge formation :- In boilers steam

is generated continuously by the evaporation of water. As water evaporates continuously, the concentration of dissolved salt increases, finally the solution becomes saturated. The point at which ionic product exceeds the solubility product, they are thrown out as precipitates.

If the precipitate formed is soft, loose and floats in boiler water it is called sludge.



Scale and sludge formation in boiler

example:-  $Mg(OH)_2$ ,  $MgCO_3$ ,  $CaCO_3$ ,  $MgSO_4$

scale:- Scales are the hard deposits firmly sticking on the inner wall of the boiler and can't be removed easily by scrapping. example:-  $CaCO_3$ ,  $CaSO_4$



## Disadvantages of sludge formation :-

1. Decreases the efficiency of boiler
2. Excessive sludge may cause chocking of pipe

Prevention of sludge formation :- frequent blow-down operation

## Disadvantage of scale formation :-

- i) wastage of fuel
- ii) Decrease in efficiency
- iii) Lowering of boiler safety
- iv) Danger of explosions

## Removal of scale formation:-

- i) Brittle scales can be removed by giving thermal shocks
- ii) Hard and adherent scales can be removed by adding chemicals. (Calc<sub>3</sub>O<sub>4</sub> scale can be removed by using 10% HCl solution)

Prevention of scale formation :- scale formation can

be prevented by

- 1.) External treatment
- 2.) Internal treatment



Boiler corrosion :- Loss of boiler body material or its useful properties by chemical or electrochemical interaction with its environment is known as boiler corrosion.

Corrosion in boiler may be due to the following reasons

- i) presence of dissolved  $\text{CO}_2$
- ii) presence of dissolved  $\text{O}_2$
- iii) formation of acids by dissolved salts

Caustic Embrittlement :- During the softening of

water by lime-soda process, the free  $\text{Na}_2\text{CO}_3$  decomposes to give  $\text{NaOH}$  and  $\text{CO}_2$



This makes the boiler water slightly alkaline due to caustic formation.

Prevention :- Caustic embrittlement can be prevented by sodium phosphate.

Priming and foaming :- The process of priming is

Passage of water particle with steam from the boiler. This is caused due to the presence of excess alkali sulphate and chlorides in water.

The foaming is persistent formation of foam of bubbles in the boiler, which do not break easily due to this the water film enclosing the steam around solid particles, passes out from the boiler along with steam. The foaming is due to the presence of oil which greatly reduces the surface tension of water in boiler.

Prevention :- By the addition of compounds like sodium aluminate



Water Softening :- The process of removing or reducing the hardness (temporary or permanent) from water is known as softening of water.

Important method for the softening of water are:-

- (1) Zeolite process
- (2) Ion-Exchange process
- (3) Lime-soda process

All these are the external treatments

Zeolite process or Permutit process

Zeolite are hydrated sodium aluminosilicates capable of exchanging its sodium ion reversibly with the hardness producing cations in water.



$$\text{where } x = 2 \text{ to } 10 \\ y = 2 \text{ to } 6$$

Zeolites are of two types

(1) Natural Zeolite :- Natural zeolites are amorphous and non-porous in nature. They are derived from green sands by washing, heating and treating with  $\text{NaOH}$   
eg. Natrolite -  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

(2) Synthetic Zeolite :- are porous and gel structure  
synthetic zeolites are prepared by heating together solution of sodium silicate, aluminium sulphate and sodium aluminate



Q. An exhausted zeolite softener required 500L of NaCl solution containing 100 g/L of NaCl for regeneration. If the hardness of water is 600 ppm, calculate the volume of water softened by this softener.

$$\text{Hardness} = \frac{\text{Concentration of NaCl} \times \text{Vol. of NaCl}}{\text{Vol. of H}_2\text{O}} \times \frac{50}{58.5}$$

$$600 = \frac{100 \times 1000 \times 500}{\text{Vol. of H}_2\text{O}} \times \frac{50}{58.5}$$

$$\text{Ans.} = 7.116 \times 10^4 \text{ L}$$

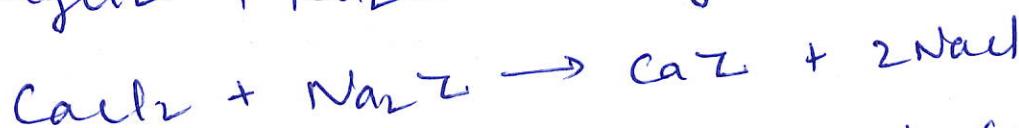
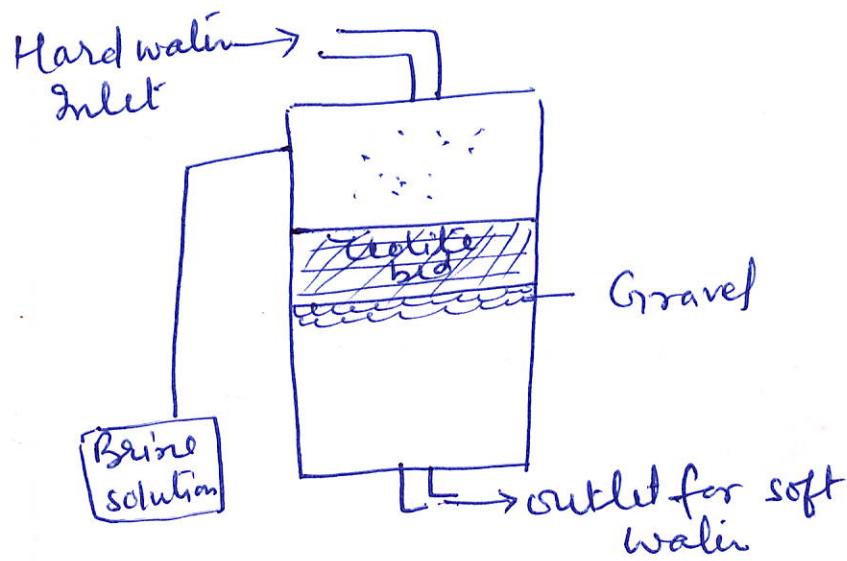
Q. A zeolite softener was 95% exhausted, when 10,000L of hard water was passed through it, the softener required 150L of NaCl soln. of strength 50g NaCl/L of soln. to regenerate. What is the hardness of water.

Soln.

$$\text{Hardness} = \frac{\text{Concentration of NaCl} \times \text{Vol. of NaCl}}{\text{Vol. of H}_2\text{O}} \times \frac{50}{58.5}$$

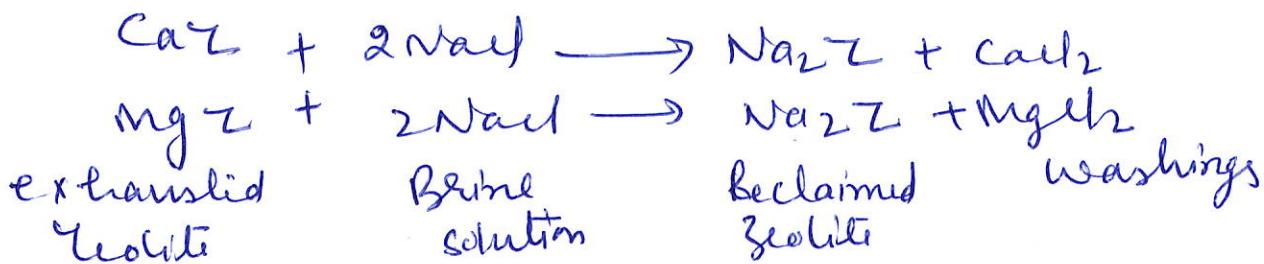
$$= \frac{50 \times 1000 \times 150}{10,000} \times \frac{50}{58.5} = 641 \text{ mg/L}$$

Principle :- Zeolite can be represented as  $\text{Na}_2\text{Z}$  where  $\text{Z}$  represents insoluble radical framework. They hold sodium ion loosely. When hard water passes through a bed of zeolite, the hardness causing ions are retained by zeolite as  $\text{CaZ}$  or  $\text{MgZ}$ . Therefore water becomes free from the main hardness producing cations but gets more concentrated with respect to sodium salts and eventually zeolite gets exhausted.



Regeneration :- During softening, zeolite exchange its sodium ions with magnesium and calcium ions and after some time they are completely converted into  $\text{Ca}$  &  $\text{Mg}$  zeolite.

and the Zeolite bed ceases to soften water i.e gets exhausted.



The regenerated zeolite is again used for softening

Advantage of Real-life process:-

1. Hardness is almost completely removed and water of about 15 ppm hardness is produced
  2. It requires less time for softening
  3. There is no danger of sludge formation because impurities are not precipitated

Disadvantage of reolite process:-

1. Only cations are replaced by sodium ions and not the anionic ions.
  2. Treated water contains more sodium salts than in lime-soda process.

Limitations :- ① If water is turbid it will cause the clogging of pores of zeolite bed, thereby making it inactive.

- ② Mineral acids destroy the zeolite bed
  - ③ soft water obtained by zeolite process contains about 25% more dissolved solids than that obtained by lime-soda process



Ion-Exchange process :- Ion-exchange resins are high molecular weight, insoluble crosslinked organic polymers containing functional groups which are responsible for the ion exchange properties.

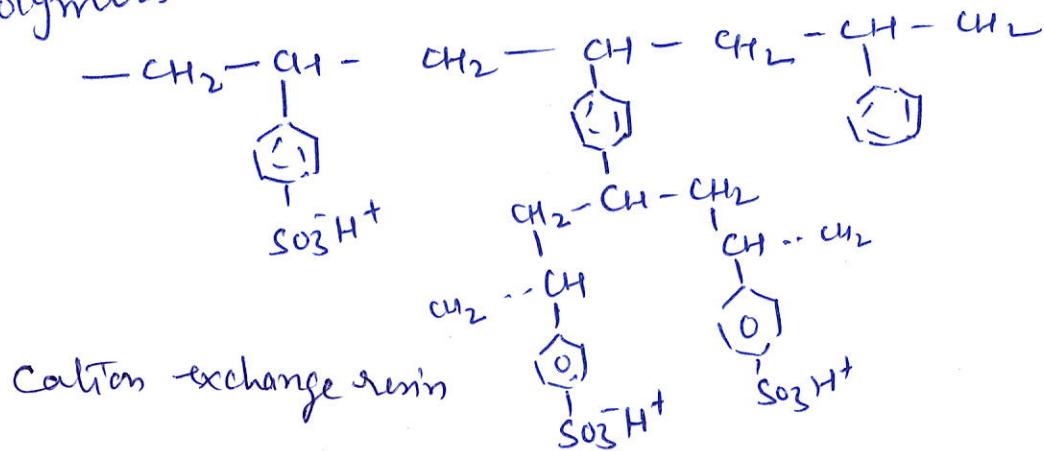
1) Cation Exchange resin    2) Anion exchange resin

## 1) Cation Exchange resin :- Ion exchange resins

1) Cation Exchange resin :- Ion exchange resins

Containing acidic functional groups like  $-COOH$ ,  $-SO_3H$  etc. are capable of exchanging their  $H^+$  ions with other cations and are known as cation exchange resin. They are generally denoted by  $R^+$ . They are mainly sulphonated or

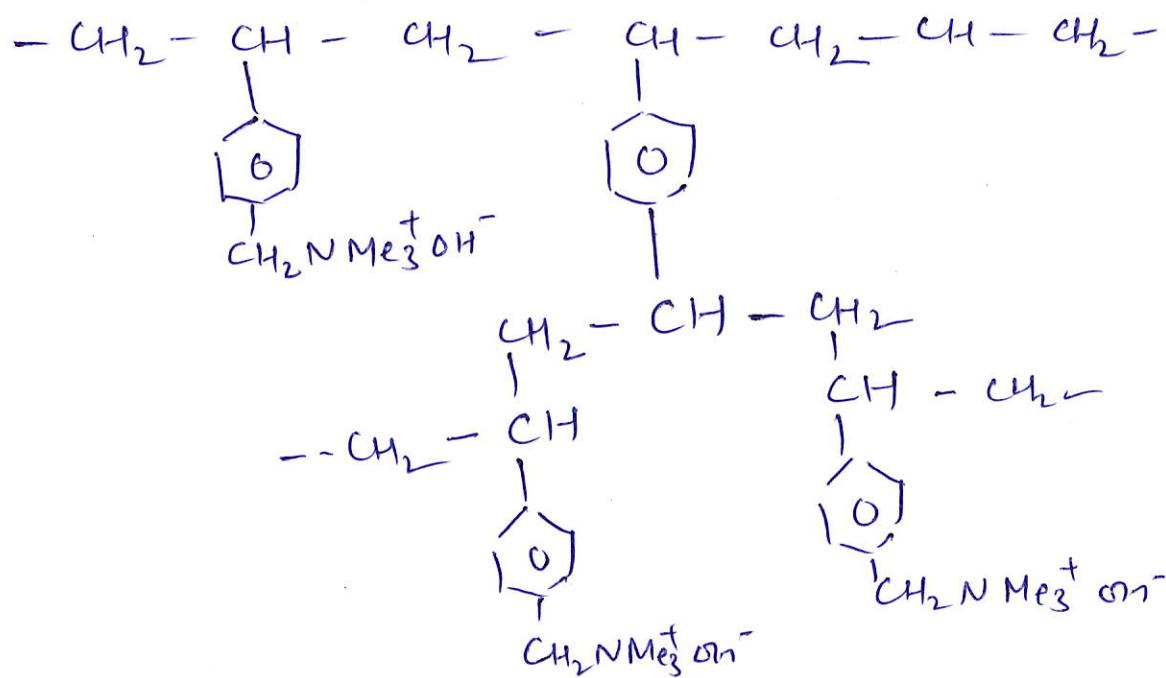
exchange resin may be of the type  $RH^+$ . They are mainly sulphonated or carboxylated styrene and divinyl benzene copolymers.



② Anion exchange resin: Ion exchange resins containing basic functional groups like  $-NH_2$ ,  $=NH$  as hydroxide are capable of exchanging their anions with other anions are known as anion exchange resin. They are represented  $R^+OH^-$  where  $R^+$  represent the insoluble organic matrix.

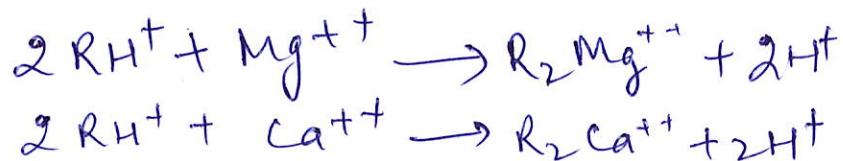


They are mainly styrene - divinyl benzene or Amine formaldehyde copolymers which contain amino or quaternary ammonium groups. These after treatment with dilute solution of NaOH soln. become capable of exchanging their  $\text{OH}^-$  ion with the anion of hard water.



### Anion Exchange resin

Principle:- when hard water is passed through cation exchange tank all the cations are taken up by the resin and an equivalent amount of  $\text{H}^+$  is released from the resin to water

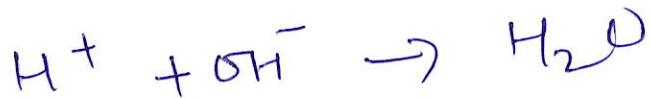




Therefore, all the cations are removed from water 13  
 After cation exchange tank, this water is passed  
 through anion exchange column when all the  
 anion like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc. are taken up by  
 the resin and equivalent amount of  $\text{OH}^-$   
 ion is released from this tank to water



Thus water becomes free from all anions.  
 The  $\text{H}^+$  &  $\text{OH}^-$  ions released from cation and  
 anion exchange tank respectively will combine  
 to form water.

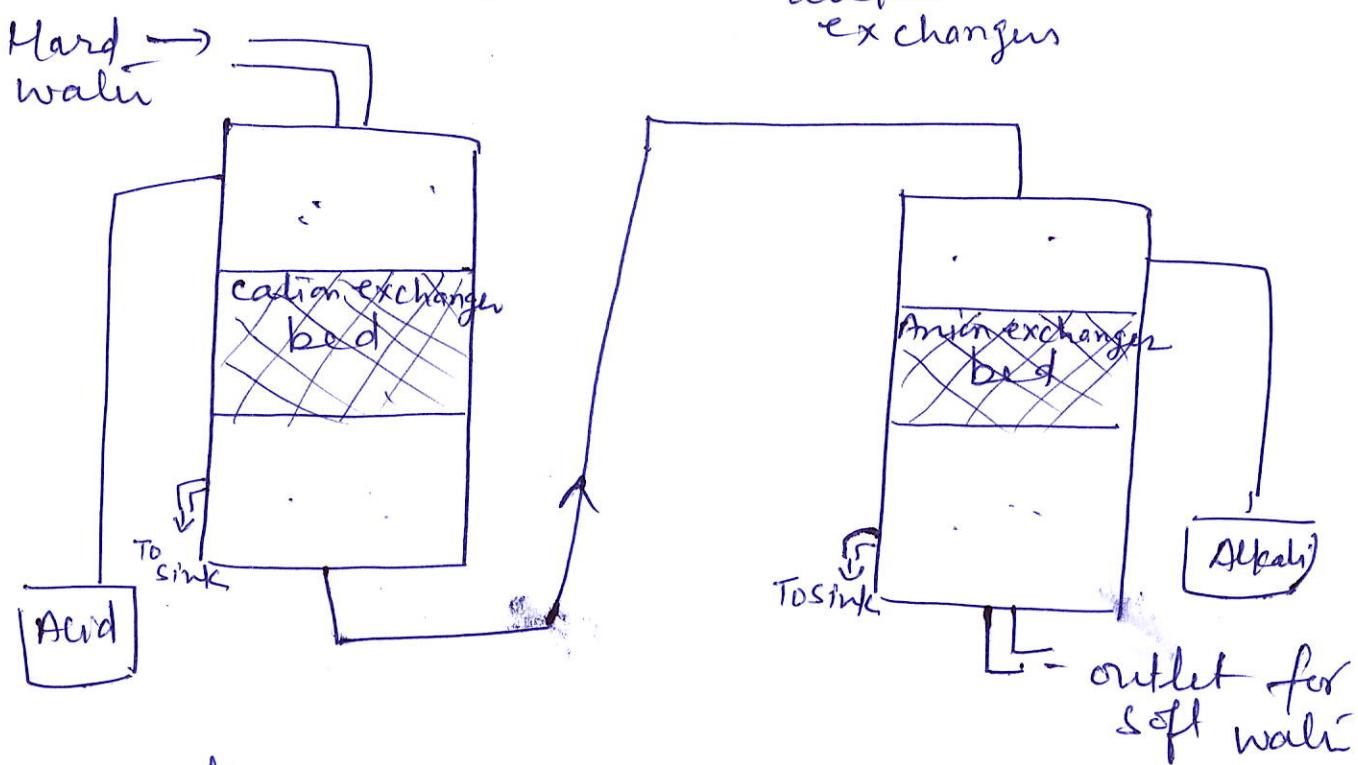
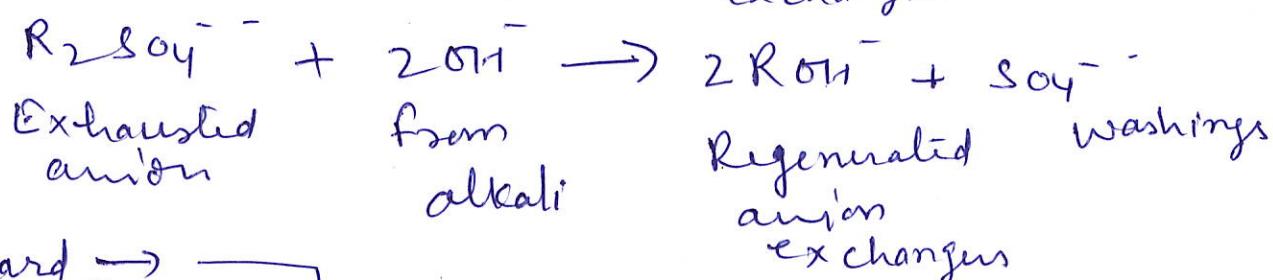
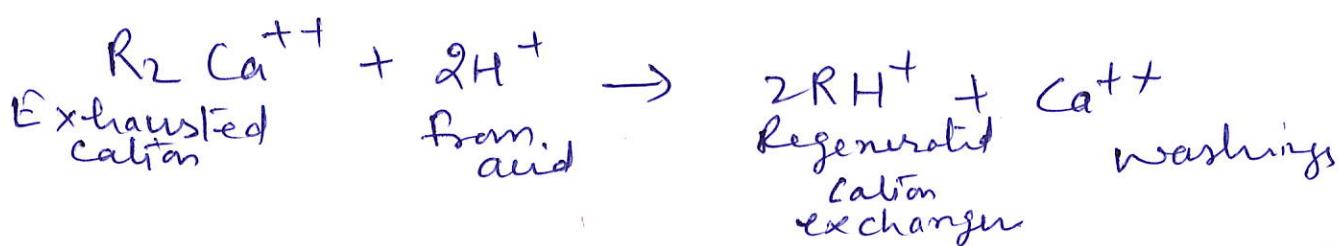


Therefore water obtained from this process  
 is free from all cations and anions  
 and the water is known as deionised or demin-  
 eralised water

Regeneration :- As the cation and anion  
 exchangers are used continuously they  
 loose their ion exchanging capacity and  
 become exhausted.



The reclamation of Ion exchanging capacity of exhausted cation and anion exchangers by treating it with a solution of dil HCl/H<sub>2</sub>SO<sub>4</sub> and dil NaOH respectively is known as Regeneration.



Advantage :-

- ① The process can be used to soften slightly acidic or alkaline waters.
- ② It produces water of very low hardness (2 ppm) so the treated water is very good for use in high pressure boilers.



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Disadvantages :- ① The cost of plant and equipment is very high.

② If water contains turbidity then efficiency of the process is reduced.

Note :- During the process water will be passed first through cation exchanger then anion exchanger because water which comes from cation exchanger is slightly acidic in nature and it will not affect the anion resin but if reverse happens then alkaline water will destroy the cation exchanger.

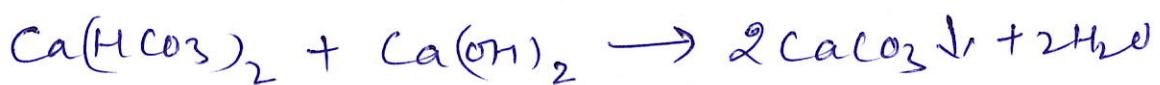


Lime-Soda process :- Chemically convert all the soluble hardness causing substance into insoluble precipitates which are then removed by settling and filtration.

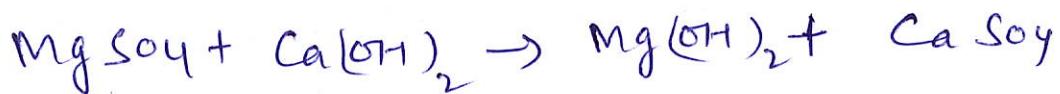
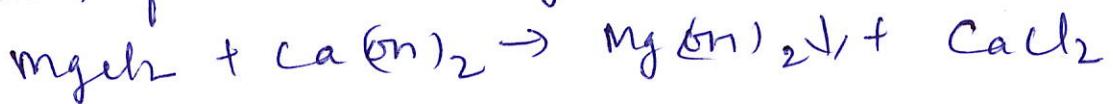
In this process, calculated amount of lime and soda ( $\text{Na}_2\text{CO}_3$ ) are added to  $\text{Ca}(\text{OH})_2$  hard water which react with the calcium and magnesium salts so as to form insoluble precipitates of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ .

### Reaction with lime

#### (a) Removal of temporary hardness



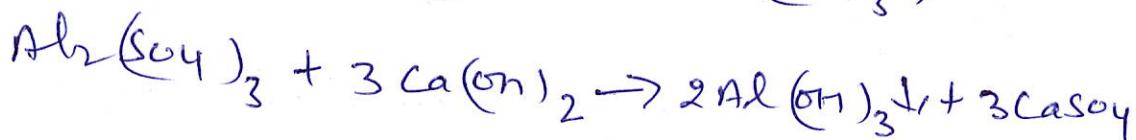
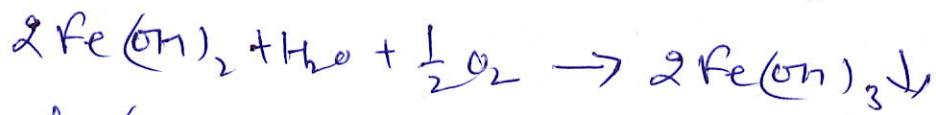
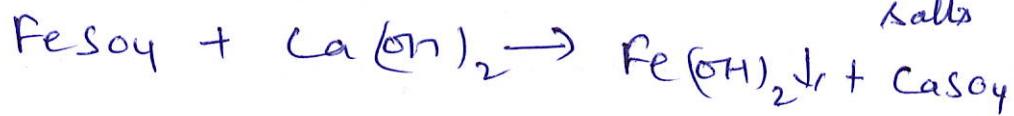
#### (b) Removal of permanent Mg hardness



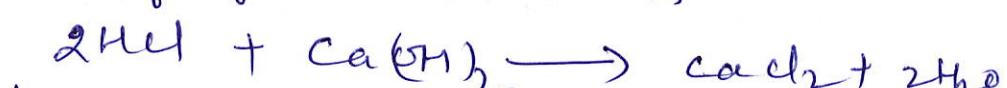
#### (c) Removal of dissolved $\text{CO}_2$ and $\text{H}_2\text{S}$



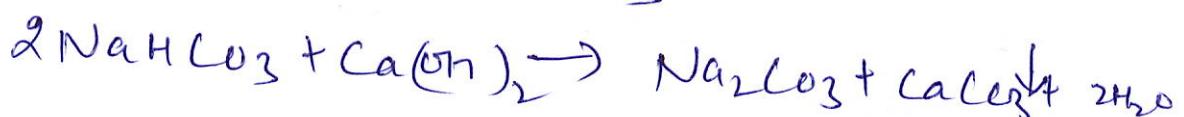
(d) Removal of dissolved Iron and aluminium



(e) Removal of free mineral acid



(f) Reaction with  $Na_2CO_3$



Reaction with Soda



Calculation of the amount of lime & soda required

lime requirement =

$$\frac{74}{100} \left( 2 \times \text{Temp. Mg} + \text{Temp. Ca} + \text{Permanent Mg} + \text{salt of Ret'd} \right)$$



terms of  $CaCO_3$  equivalent

$$\text{Soda requirement} = \frac{106}{100} \left( \text{Perm. Ca} + \text{Perm. Mg} + \text{Salt of Fe + Al} \right) + \text{HCO}_3^-$$

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$\text{H}_2\text{SO}_4 - \text{HCO}_3^-$  all in terms of  $\text{CaCO}_3$  equivalent  $\times \text{Vol. of H}_2\text{O}$

Example :- calculate the quantity of lime 74% fine and soda 90% fine required for softening 50,000 litres of water containing -

$$\text{Mg}(\text{HCO}_3)_2 = 50 \text{ mg/L} \quad \text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/L} \quad \text{MgCl}_2 = 6 \text{ mg/L}$$

$$\text{HCO}_3^- = 73 \text{ mg/L} \quad \text{CO}_2 = 44 \text{ mg/L} \quad \text{Al}_2(\text{SO}_4)_3 = 57 \text{ mg/L}$$

Solution :- Conversion into  $\text{CaCO}_3$  Equivalent

$$\text{Mg}(\text{HCO}_3)_2 = \frac{50 \times 50}{73} = 34.26 \text{ ppm}$$

$$\text{Ca}(\text{HCO}_3)_2 = \frac{81 \times 50}{81} = 50 \text{ ppm}$$

$$\text{MgCl}_2 = \frac{6 \times 50}{47.5} = 6.31 \text{ ppm}$$

$$\text{CO}_2 = \frac{44 \times 50}{22} = 100 \text{ ppm}$$

$$\text{HCO}_3^- = \frac{73 \times 50}{36.5} = 100 \text{ ppm}$$

$$\text{Al}_2(\text{SO}_4)_3 = \frac{57 \times 50}{57} = 50 \text{ ppm}$$

$$\text{Lime requirement} = \frac{74}{100} \left( \text{Ca}(\text{HCO}_3)_2 + 2 \times \text{Mg}(\text{HCO}_3)_2 + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 + \text{CO}_2 + \text{HCO}_3^- \text{ as } \text{CaCO}_3 \text{ eq.} \right)$$

$$\times \frac{100}{74} \times \frac{\text{Vol. of H}_2\text{O}}{106} \text{ kg}$$

$$= \frac{74}{100} \left( 50 + 2 \times 34.26 + 50 + 6.31 + 100 + 100 \right) \times \frac{100}{74} \times \frac{50,000}{106} \text{ kg} \\ = 18.74 \text{ kg}$$

Soda requirement =  $\frac{106}{100} \left( \text{MgCl}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O as} \right) \times \frac{100}{90} \times \frac{50,000}{106} \text{ kg}$

calories, x. purity

$$= \frac{106}{100} \left( 6.31 + 50 + 100 \right) \times \frac{100}{90} \times \frac{50,000}{106} \text{ kg}$$

$$= 9.20 \text{ kg}$$

Lime requirement = 18.74 kg

Soda requirement = 9.20 kg

Q. A water sample has the following analysis  
⑧  
 $Mg(HCO_3)_2 = 83 \text{ mg/L}$  calculate temp. Permanant hardness in  
 $^{\circ}\text{C}$ .

$$Ca(HCO_3)_2 = 134 \text{ mg/L}$$

$$CaSO_4 = 124 \text{ mg/L}$$

$$MgCl_2 = 84 \text{ mg/L}$$

$$CaCl_2 = 94 \text{ mg/L}$$

NaCl = 50 mg/L Does not produce hardness

So/ln:

$$Mg(HCO_3)_2 = \frac{83 \times 50}{73} = 56.8 \text{ mg/L}$$

$$Ca(HCO_3)_2 = \frac{134 \times 50}{81} = 82.7 \text{ mg/L}$$

$$CaSO_4 = \frac{124 \times 50}{68} = 91.2 \text{ mg/L}$$

$$MgCl_2 = \frac{84 \times 50}{47.5} = 88.4 \text{ mg/L}$$

$$CaCl_2 = \frac{94 \times 50}{55.5} = 84.7 \text{ mg/L}$$

$$\begin{aligned} \text{Temporary hardness} &= Ca(HCO_3)_2 + Mg(HCO_3)_2 \\ &= 82.7 + 56.8 \\ &= 139.5 \text{ mg/L} = 139.5 \times 0.07 \text{ }^{\circ}\text{C} \\ &= 9.77 \text{ }^{\circ}\text{C} \end{aligned}$$

$$\begin{aligned} \text{Permanant hardness} &= CaSO_4 + MgCl_2 + CaCl_2 \\ &= 91.2 + 88.4 + 84.7 \\ &= 264.3 \text{ mg/L} = 264.3 \times 0.07 = 18.50 \text{ }^{\circ}\text{C} \end{aligned}$$

Q. calculate the quantity of lime & soda required for softening 50,000 litres of water containing the following salts per litres :

$$\text{Ca}(\text{HCO}_3)_2 = \frac{9.2 \times 50}{100} = 5.68 \text{ mg/L}$$

$$\text{Mg}(\text{HCO}_3)_2 = \frac{7.9 \times 50}{73} = 5.41 \text{ mg/L}$$

$$\text{CaSO}_4 = \frac{15.3 \times 50}{68} = 11.25 \text{ mg/L}$$

$$\text{MgSO}_4 = \frac{15 \times 50}{60} = 12.5 \text{ mg/L}$$

$$\text{MgCl}_2 = \frac{3.0 \times 50}{47.5} = 3.16 \text{ mg/L}$$

Lime  
requirement =  $\frac{74}{100} \left( \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2 \right) \times$   
all in terms of  
CaCO<sub>3</sub> eq. Vol of H<sub>2</sub>O

$$\frac{74}{100} \left( 5.68 + 2 \times 5.41 + 12.5 + 3.16 \right) = 23.39 \text{ mg/L}$$

$$= 23.39 \times 50,000 = 1170 \text{ g} = 1.17 \text{ kg}$$

Soda  
Requirement =  $\frac{106}{100} \left( \text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \right)$   
all in  
terms of  
CaCO<sub>3</sub> eq.

$$= \frac{106}{100} \left( 11.25 + 12.5 + 3.16 \right) \times 50,000$$

$$= 14.28 = 1.426$$

Types of lime-soda process:- Lime-soda process are<sup>19</sup> of two types-

- ① Cold lime-soda process
- ② Hot lime-soda process

Cold lime-soda process :- In this process

calculated amount of lime and soda are mixed with <sup>hard</sup> water at room temperature.

Since the precipitates formed are finely divided they remain suspended in water and do not settle down easily. Therefore they can't be filtered easily. Hence it

is necessary to add a small amount of coagulant like aluminium sulphate, sodium

aluminate or alums etc. These get hydrolysed to form gelatinous ppt of  $\text{Al}(\text{OH})_3$

which entraps the finely suspended particles of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . Therefore coagulants help in the formation of coarse ppt.

There are two types of softeners used for softening water by this process

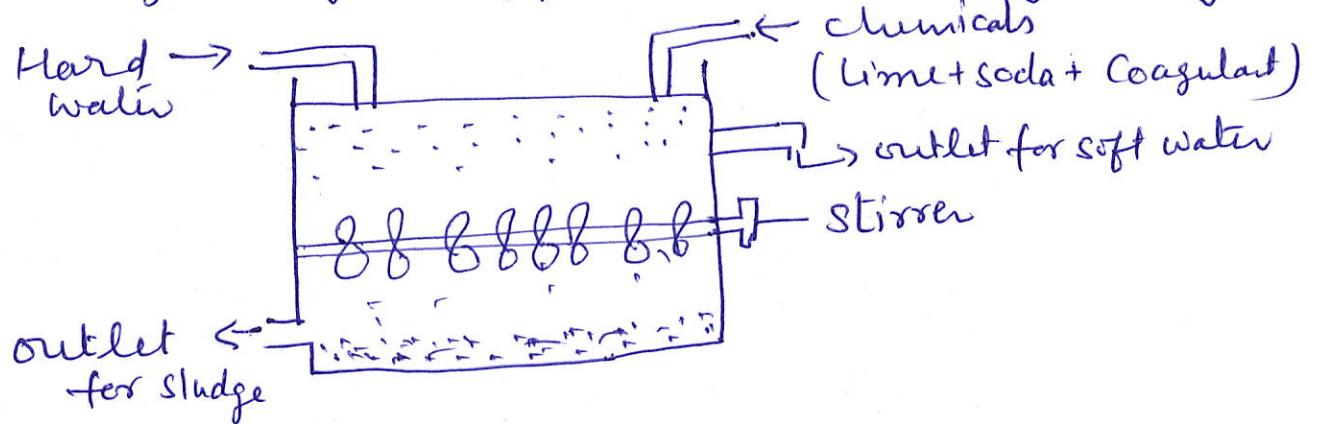
- (a) Intermittent type (Batch process) :-

Intermittent consists of a pair of tanks. Each tank is used in turn for softening of water.

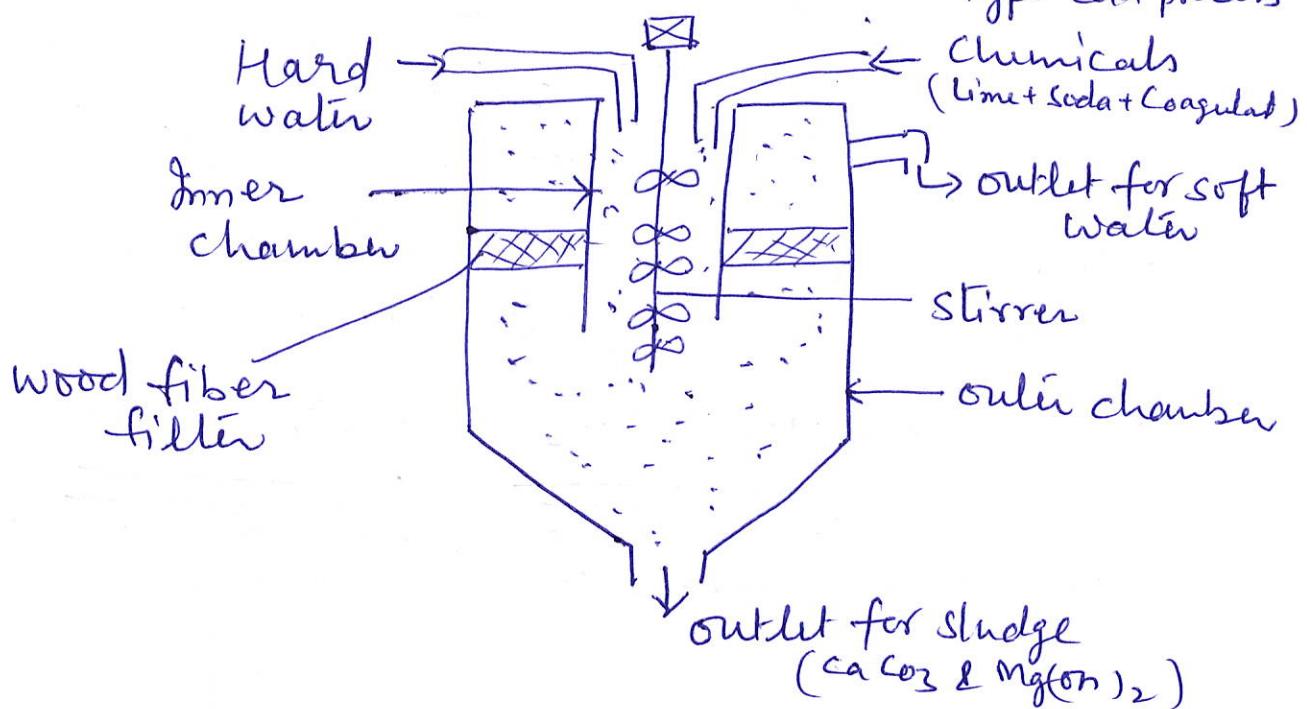
Each tank is provided with inlets for raw water and chemicals, outlets for softened water and sludge, and a mechanical stirrer.

Raw water and the calculated quantities of lime and soda are allowed to run in simultaneously and stirring is started.

Stirring is stopped, when the reaction is complete and the sludge formed is allowed to settle. The sludge formed in the tank is removed through the outlet and clear softened water is collected through a float pipe and filtered by filtering unit.



② Continuous cold lime-soda process: Conventional type cold process



This is a continuous process in which the hard water and the chemicals in calculated amount are continuously fed from the top into an inner chamber at room temperature. As the hard water and chemicals flow down the chamber a continuous mixing takes place due to vigorous stirring. Softening of water takes place in the inner chamber and ppt (sludge) settles down at the bottom in the outer chamber. The soft water goes upwards in the outer chamber where it passes through a filtering media (made up of wood fibres) to ensure the complete removal of sludge. Filtered soft water finally comes out continuously through the outlet.

Hot-lime soda process :- In this process hard water is treated with chemicals at temperature of  $80-150^{\circ}\text{C}$ . Since the reaction takes place at higher temperature, no coagulant is needed in this process.

The softener may be of   
 ① Intermittent  
 ② Continuous

① Intermittent type Hot-lime soda process :- Hot lime-soda intermittent type softener is similar to the Intermittent cold-lime soda process except that heating coils are installed in it for heating.

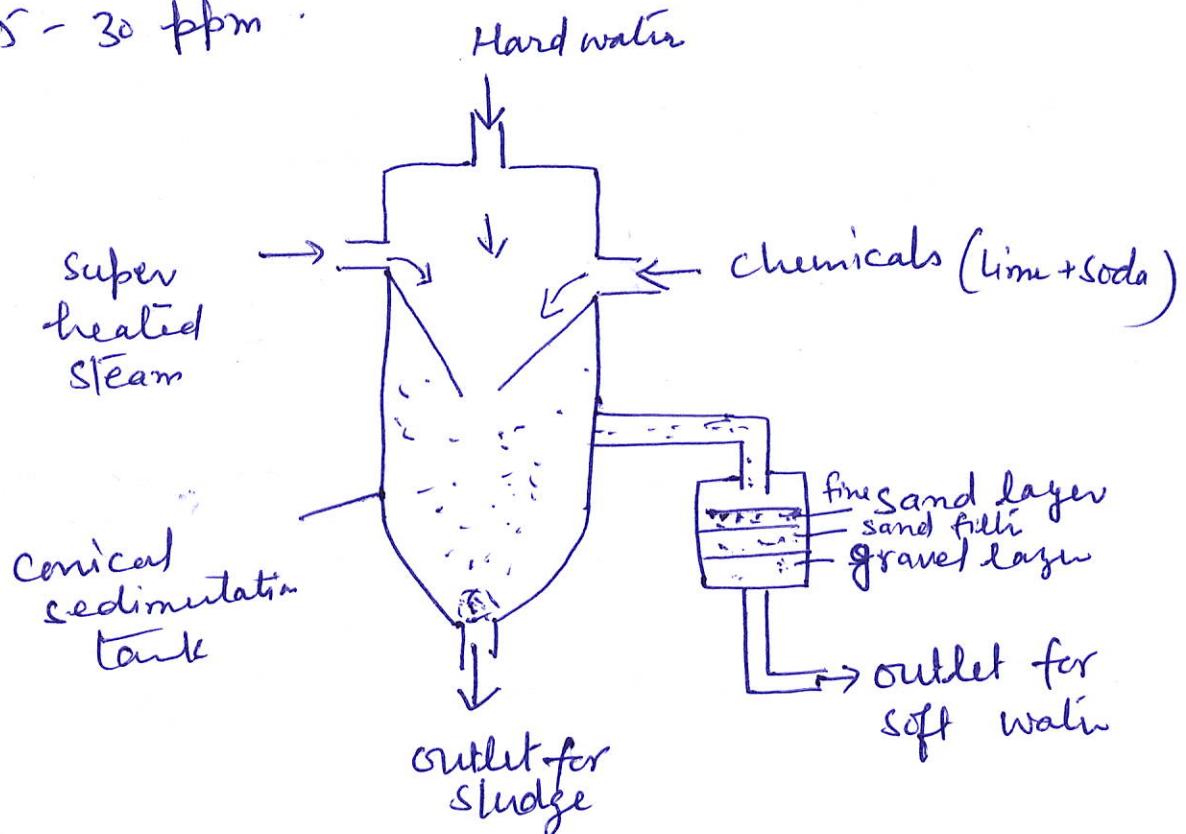
② Continuous type hot-soda process: This softener consists of the following three parts:-

a) Reaction tank    b) Sedimentation tank    c) Sand filter

a) Reaction tank: - Raw water and chemicals are added in this tank through two different inlets. Tank is also provided with an additional inlet for steam.

b) Sedimentation tank: - The sedimentation of sludge takes place in a conical sedimentation tank.

c) Sand filter: - Sand filter ensure the complete removal of sludge from the clear and softened water from the sedimentation tank. Water thus obtained has the residual hardness 15 - 30 ppm.



## Advantage of Lime-soda process:-

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- ① Lime-soda process is very economical
- ② lesser amount of coagulant are required
- ③ The alkaline nature of treated water reduces the amount of pathogenic bacteria in water to a considerable extent

## Disadvantages of lime-soda process:

- ① Disposal of large amount of sludge is a problem
- ② Treated water removes hardness only upto 15 ppm which are not ideal for boilers

## Difference b/w Cold & Hot lime-soda process

### Cold-lime soda process

1. calculated amount of lime and soda is mixed at room temperature
2. it is slow process
3. The ppt formed are finely divided and can't settle easily and hence filtration is not easy
4. use of coagulant is must
5. Dissolved gases are not removed
6. softening water has residual hardness around 60 ppm

### Hot lime-soda process

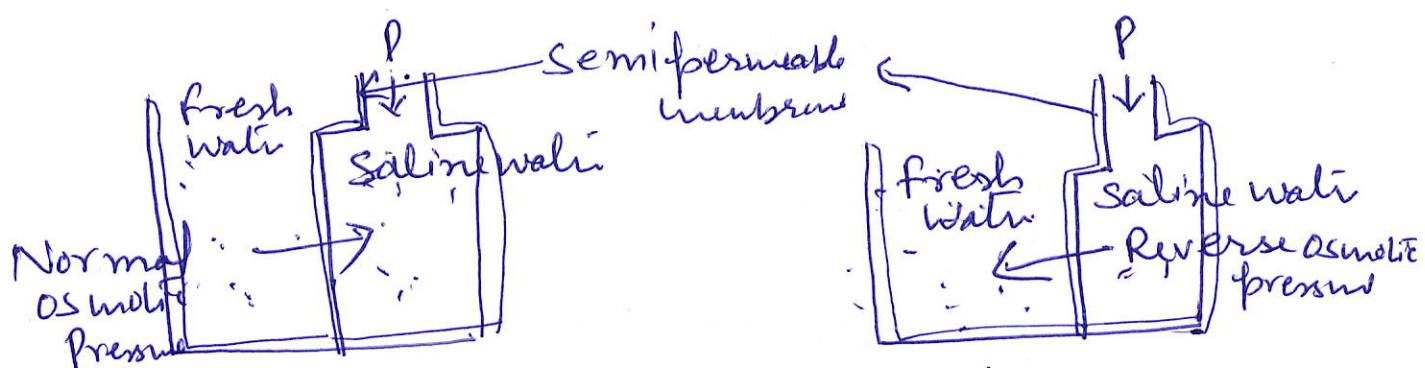
This is done at elevated temp.  
(80° - 150°)

fast process

ppt formed like sludge settle down easily & hence filtration is easy

Coagulants are not required  
Dissolved gases are removed  
Residual hardness is about 15 - 30 ppm

Reverse Osmosis :- The flow of solvent but not the solute from a region of low concentration to high concentration when the two solutions of different concentration are separated by a semi permeable membrane is known as Osmosis.



If a hydrostatic pressure in excess of osmotic pressure is applied to the higher concentration side the flow of solvent gets reversed and this process is known as reverse osmosis.

Therefore in reverse osmosis the solvent is forced to move from concentrated soln. to dilute soln. across the semi permeable membrane.

Advantage of reverse osmosis :-

- ① Semi permeable membrane is durable & can be easily replaced within few minutes
- ② No phase change takes place during the process
- ③ The process is promising for the future it requires extremely low energy for consumption.

## water softening Techniques :- Internal Treatment of Boiler feed water

The treatment of raw water inside the boiler is known as Internal Treatment.

Internal treatment methods are -

i) colloidal Conditioning :- Scale formation can be reduced by adding colloidal substances like Kerosene tanin, glue, agar etc. to the boiler water. These substances act as Protective Coatings. They surround the minute particles of scale forming salts and prevent their coalescence & coagulation. Hence, the salt remains as loose, non sticky deposits in the form of sludges which can be removed by simple blow-down operation. This process is suitable for low-pressure boilers.

ii) Carbonate Conditioning :- In this process  $\text{Na}_2\text{CO}_3$  is added to boiler water due to which the main scale forming salt  $\text{CaSO}_4$  gets converted into  $\text{CaCO}_3$  and falls out in the form of loose sludge which can be removed by blowdown operation

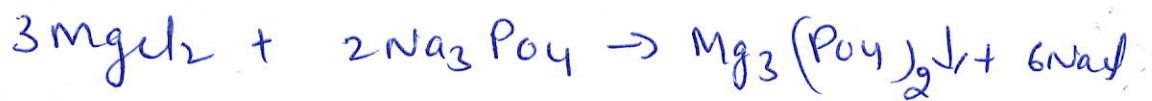
$$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$$

Carbonate conditioning is not suitable for high pressure boiler because  $\text{CO}_3^{2-}$  ions undergo hydrolysis to form  $\text{OH}^-$  ions.

$$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-$$

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{OH}^-$$

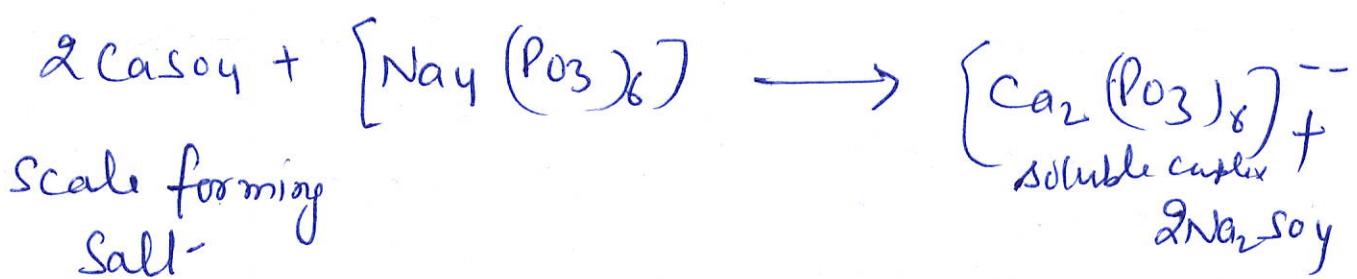
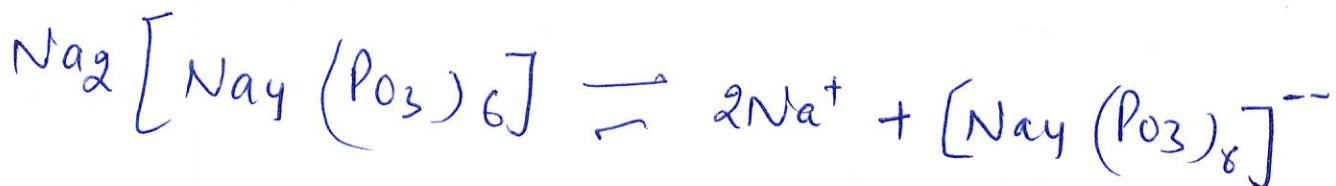
iii) Phosphate Conditioning :- Scale formation is prevented by addition of sodium phosphate which react with calcium and magnesium salts giving non-adherent and soft sludge of calcium & magnesium phosphate respectively. (low pressure boilers)



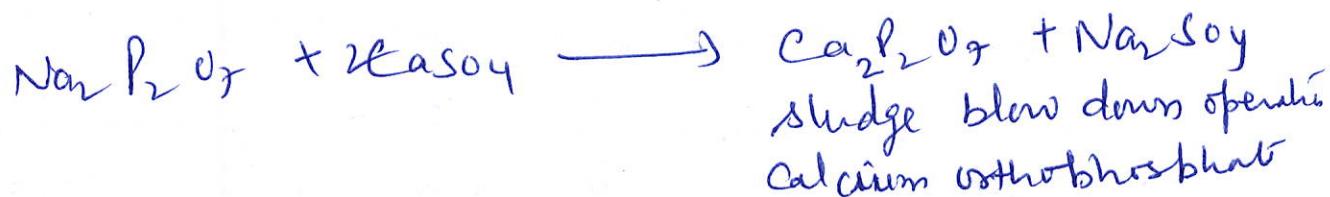
(4) Calgon conditioning :- Calgon is sodium

hexameta phosphate  $\text{Na}_2[\text{Na}_5(\text{PO}_3)_6]$

It is extensively used in Internal treatment and prevent the ~~scale~~ scale and sludge formation by converting scale forming turbidity like  $\text{CaSO}_4$  to highly soluble complex



At high temp. and pressure



# Topics

- Classification of fuels
- Analysis of coal
- Determination of calorific value (Bomb calorimeter and Dulong's methods).

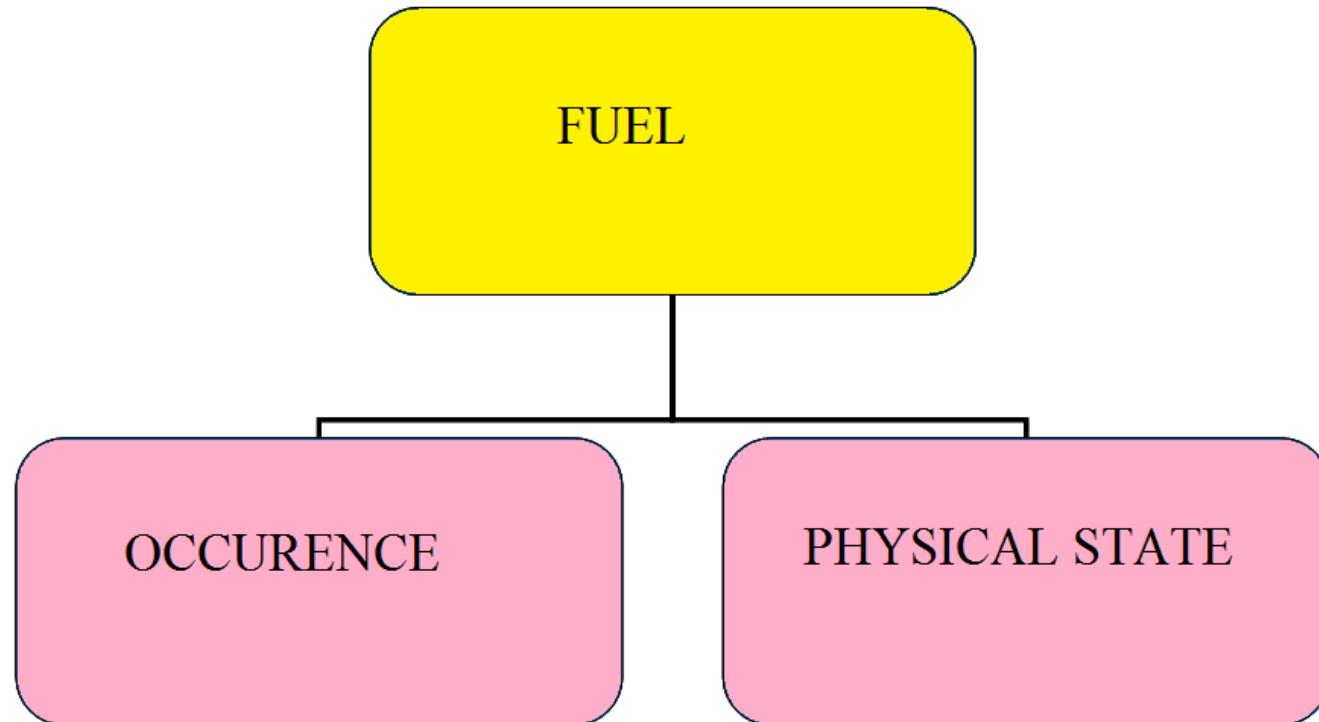
# Fuels

**The combustible substances which on burning in air produces large amount of heat that can be used economically for domestic and industrial purposes are called fuels.**

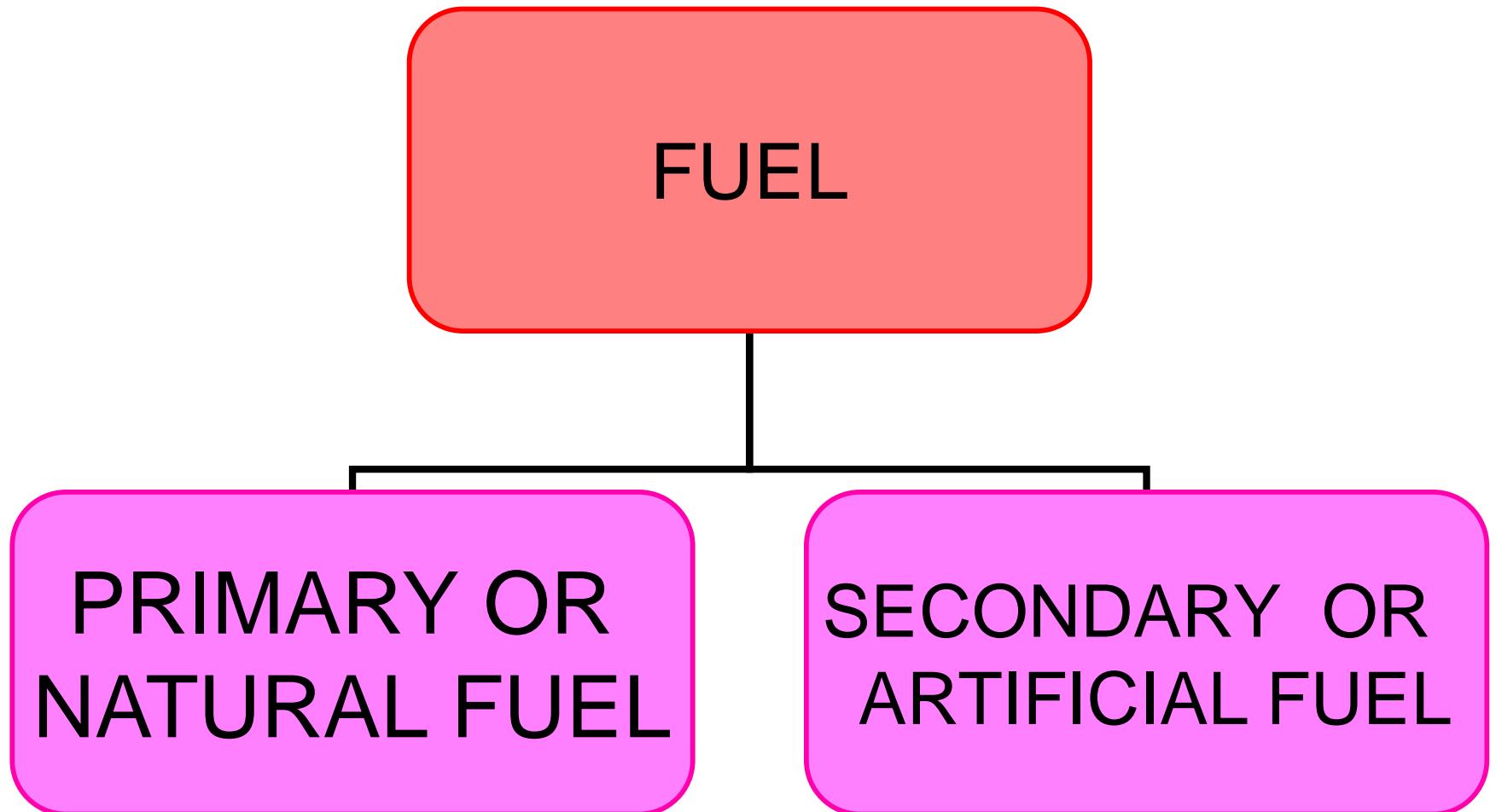
**Eg. Wood ,Coal etc**

There are chemical fuels, nuclear fuels and fossil fuels.

# CLASSIFICATION OF FUEL



## On the basis of occurrence

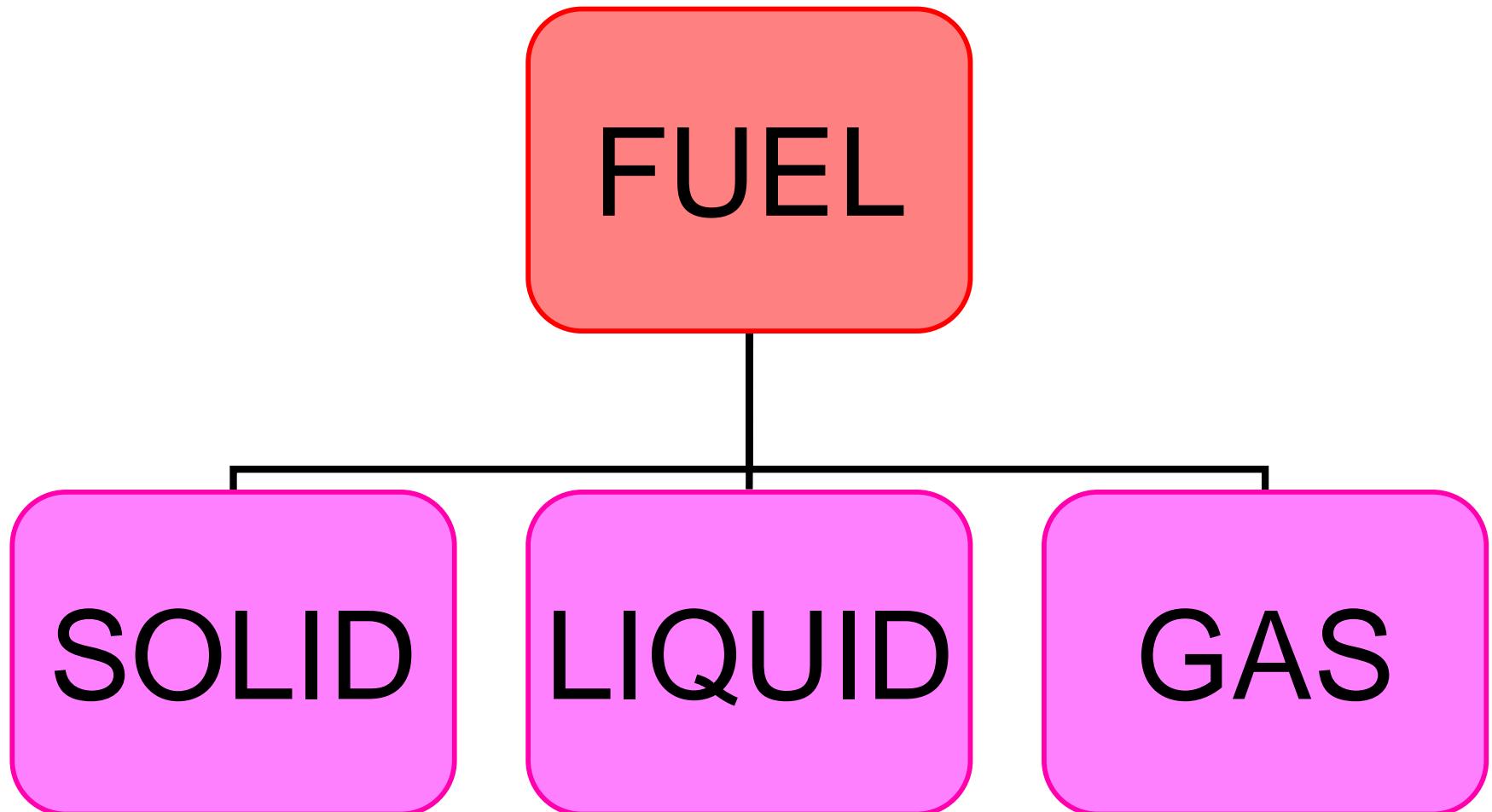


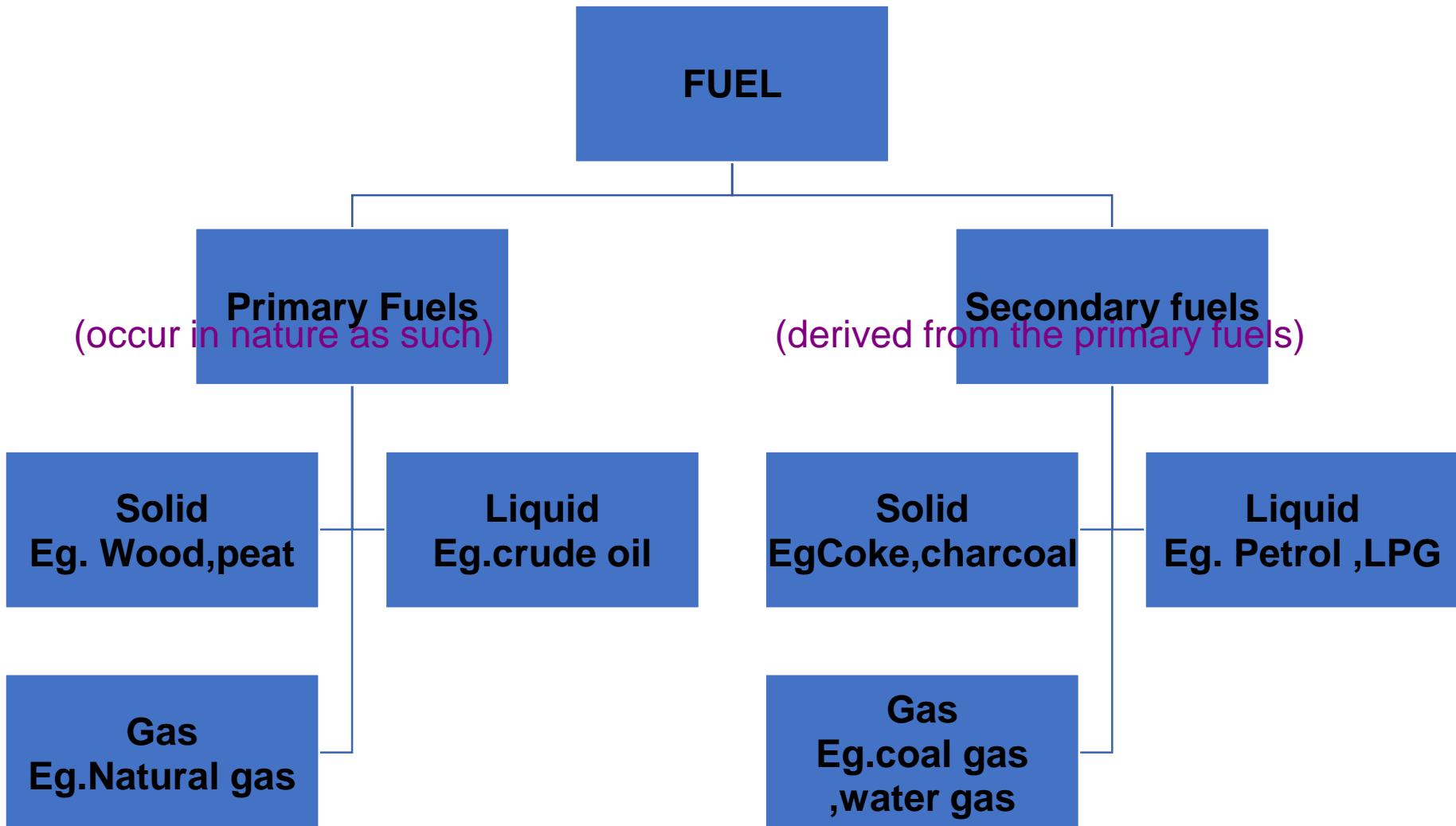
These can be classified on the basis of their occurrence and physical state

On the basis of occurrence they are of two types:

- **Primary Fuels:** Fuels which occur in nature as such are called primary fuels. E.g., wood, peat, coal, petroleum, and natural gas.
- **Secondary Fuels:** The fuels which are derived from the primary fuels by further chemical processing are called secondary fuels. E.g., coke, charcoal, kerosene, coal gas, producer gas etc.

## On basis of physical state





# Characteristics of Good Fuel:

- (i) High Calorific value
- (ii) **Ignition Temperature:** A good fuel should have moderate ignition temperature.
- (iii) **Moisture content:** Should be low
- (iv) **Non combustible matter content:** Should be low
- (v) **Velocity of combustion:** It should be moderate
- (vi) **Nature of the products:** Non polluted
- (viii) **Cost of fuel:** Should be Cheap
- (ix) Should be Smokeless
- (x) Control of the process

# Calorific value:

It is defined as the total quantity of heat liberated when a unit mass of a fuel is burnt completely.

A good fuel should have high calorific value i.e. it should produce large amount of heat on burning.

# Types of Calorific Value

## (i) Higher or Gross Calorific Value (HCV or GCV) :-

It is total quantity of heat generated when a unit quantity of fuel is completely burnt in excess supply of oxygen and **the products of combustion are cooled down at room temperature.**

## (ii) Lower or Net Calorific Value (LCV or NCV) :-

It is defined as the amount of heat liberated when one unit of fuel is burnt completely in excess supply of oxygen and **the combustion products are allowed to escape.**

## RELATIONSHIP BETWEEN NCV and HCV:

**Net calorific value = Gross calorific value - Latent heat of water vapours**

**NCV= GCV- weight of hydrogen x 9 x Latent heat of water vapours**

**Latent heat of water vapours is 587 kcal/kg**



2 gm hydrogen gives 18 gm water on combustion.

Therefore, 1 gm hydrogen gives 9 gm water on combustion.

Since 1 part by mass of hydrogen gives 9 parts by mass of water.

Let H is the percentage of hydrogen in the fuel.

Amount of water produced by burning unit mass of fuel= $9H/100$  g

Latent heat of steam=587cal/g

$$\text{NCV} = \text{GCV} - 9H/100 \times 587$$

$$\text{NCV} = \text{GCV} - 0.09H \times 587 \text{ cal/g}$$

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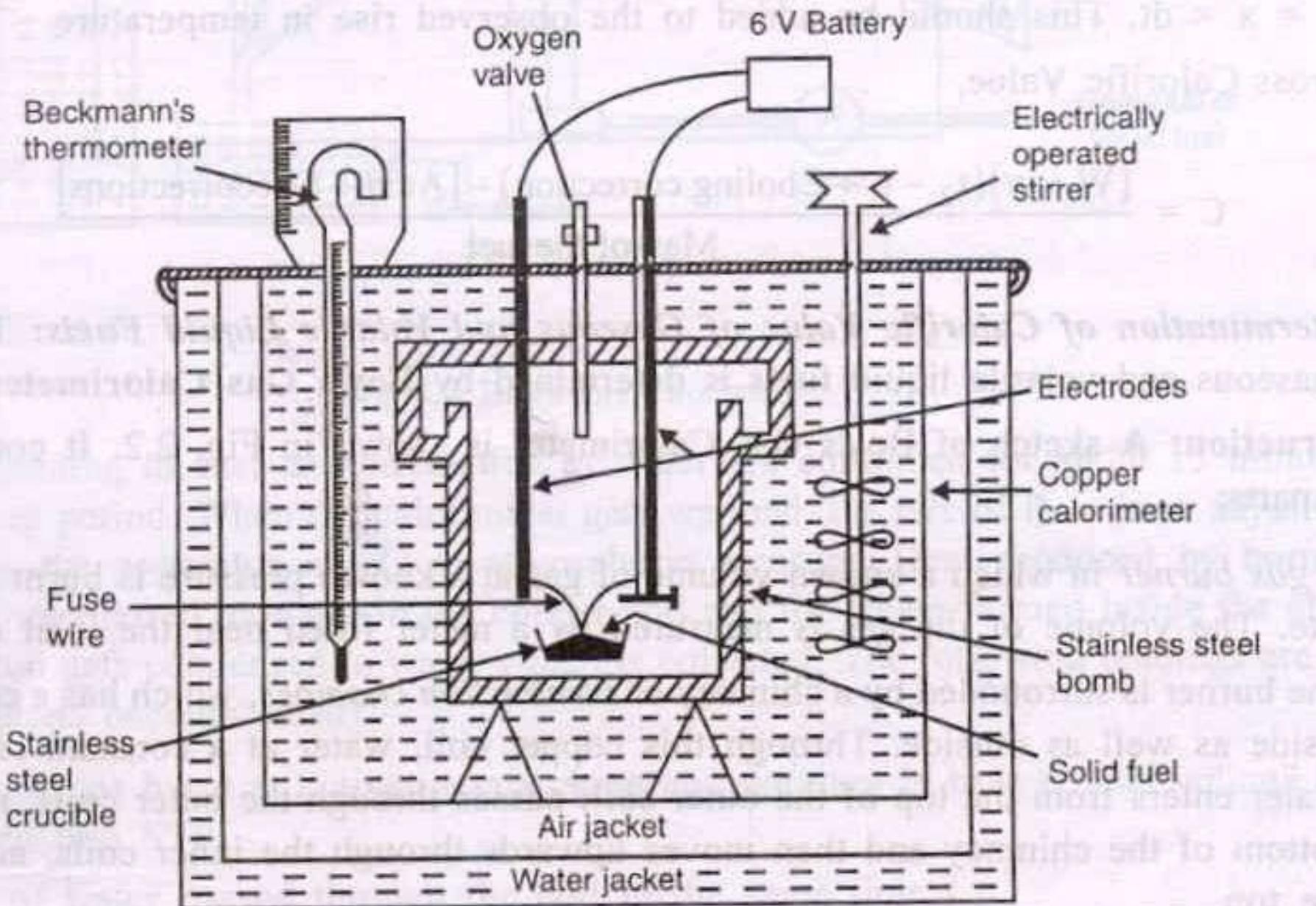
$$\text{NCV} = \text{GCV} - 0.09H \times 587 \text{ cal/g}$$

$$\text{NCV} = \text{GCV} - 9H \times 587 \text{ cal/g}$$

## Determination of Calorific value

### Determination of calorific value of solid and non volatile liquid fuels by **bomb calorimeter**

**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 calorimetry i.e. Heat gained = Heat lost



## 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 =  $t_1$  °C

Final temperature of water =  $t_2$  °C

Higher or gross calorific value =  $L$  cal/g

Heat gained by water =  $W \times \Delta t$

$$= W \times (t_2 - t_1) \text{ cal}$$

Heat gained by Calorimeter =  $w (t_2 - t_1)$  cal

Heat gained by water and calorimeter =  $(W+w) (t_2 - t_1)$  cal

Heat liberated by the fuel =  $x L$  cal

Total heat liberated by the fuel = Total heat gained by water and calorimeter

$x L = (W+w) (t_2 - t_1)$  cal

$$L = \frac{(W+w)(t_2 - t_1)}{x} \text{ cal/g}$$

# If Corrections are given

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

Where,

$t_c$  = Cooling Correction

$C_A$  = Acid Correction

$C_T$  = Cotton thread Correction

$C_F$  = Fuse wire Correction

Q. Describe how the calorific value of coal or liquid fuel is determined by Bomb Calorimeter. The following data is obtained in a Bomb Calorimeter experiment :

Weight of crucible = 3.649 gm

Weight of crucible + fuel = 4.678 gm

Water equivalent of calorimeter = 570 gm

Water taken in the calorimeter = 2200 gm

Observed rise the temperature = 2.3 °C

Cooling correction = 0.047°C

Acid correction = 62.6 calories

Fuse wire correction = 3.8 calories

Cotton thread correction = 1.6 calories

Calculate the gross calorific value of the fuel sample. If the fuel contains 6.5% H, determine the net calorific value.

Ans.

$$L(HCV) = \frac{(W + w)(t_2 - t_1 + t_c) - (C_A + C_F + C_T)}{x}$$

$$\begin{aligned} HCV &= \frac{(2200 + 570)(2.3 + 0.047) - (62.6 + 3.8 + 1.6)}{(4.687 - 3.649)} \\ &= 6197.67 \text{ cal/gm} \end{aligned}$$

Since the fuel contains 6.5% hydrogen,

$$\begin{aligned} LCV &= HCV - 0.09H \times 587 \text{ cal/g} \\ &= 6197 - 0.09 \times 6.5 \times 587 \text{ cal/g} \\ &= 5854.28 \text{ cal/g} \end{aligned}$$

## DULONG'S FORMULA:

$$\text{HCV} = \frac{1}{100} [8080 \text{ C} + 34500 (\text{H} - \text{O}/8) + 2240 \text{ S}] \quad \text{Kcal/Kg or cal/g}$$

# DULONG'S FORMULA

Q.1. Calculate the GCV and NCV of coal having the following compositions:

Carbon = 85%, Hydrogen = 8%, Sulphur = 1%, Nitrogen = 2% and Ash = 4% The latent heat of combustion of steam = 587 cal/g.

# DULONG'S FORMULA

Solution:

We know,

$$\text{HCV} = \frac{1}{100} [8080 \text{ C} + 34500 (\text{H} - \text{O}/8) + 2240 \text{ S}] \text{ Kcal/Kg or cal/g}$$

$$\begin{aligned}\text{HCV} &= \frac{1}{100} [8080 \times 85 + 34500 (8 - 0/8) + 2240 \times 1] \text{ cal/g} \\ &= \frac{1}{100} [6,86,800 + 2,76,000 + 2,240] \text{ cal/g} \\ &= 9,65 \frac{1}{100} \text{ cal/g}\end{aligned}$$

# DULONG'S FORMULA

Solution:

$$\begin{aligned} \text{LCV} &= \text{HCV} - 0.09 \text{ H} \times 587 \\ &= 9,650.4 - 0.09 \times 8 \times 587 \text{ cal/g} \\ &= 9,650.4 - 422.64 \text{ cal/g} \\ &= 9227.76 \text{ cal/g} \end{aligned}$$

# Analysis of Coal

**Coal:** coal is regarded as a fossil fuel produced from the vegetable debris under conditions of high temperature and pressure over million of years.

The peat gets enriched in carbon whereas its oxygen content decreases.

Classification of coal : Different varieties of coal are given below:

1. Peat
2. Lignite
3. Bituminous coal
4. Anthracite coal

## **Analysis of Coal**

Coal is analysed in two ways:

1. Proximate analysis
2. Ultimate analysis

# Proximate Analysis

Proximate analysis of coal determines the moisture, ash, volatile matter and fixed carbon of coal.

## 1. Moisture Content:

Air dried moisture is determined by heating a known amount of coal to 105-110 °C in an electric hot air oven for about one hour. After one hour, it is taken out from the oven and cooled in a dessicator and weighed.

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

**2. Volatile Matter:** It is determined by heating a known weight of moisture free coal sample in a covered platinum crucible at  $950 \pm 20^{\circ}\text{C}$  for 7 minutes.

$$\text{Percentage of volatile matter} = \frac{\text{Loss of weight due to volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

**3. Ash:** Coal contains inorganic mineral substances which are converted into ash by chemical reactions during the combustion of coal.

Ash content is determined by heating the residue left after the removal of volatile matter at  $700 \pm 50^{\circ}\text{C}$  for  $\frac{1}{2}$  an hour without covering

Percentage of ash =

$$\frac{\text{Weight of the residue left}}{\text{Weight of the coal}} \times 100$$

**4. Fixed Carbon:** Fixed carbon content increases from lignite to anthracite. Higher the percentage of fixed carbon greater is its calorific value and better is the quality of coal.

The percentage of fixed carbon is given by:

Percentage of fixed carbon =

100-[% of moisture+volatile matter+ash]

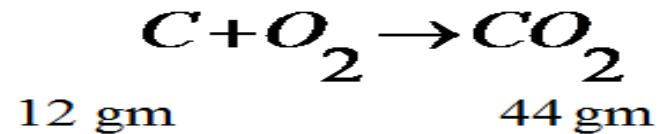
## **Ultimate analysis:**

Ultimate analysis includes the estimation of carbon, hydrogen, sulphur, nitrogen and oxygen.

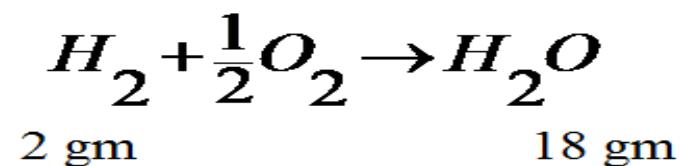
**1. Carbon and Hydrogen:** A known amount of coal is taken in a combustion tube and is burnt in excess of pure oxygen.

The carbon and hydrogen present in the coal sample are converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively.

Combustion of carbon



Combustion of hydrogen



The gaseous products of combustion  $CO_2$  and  $H_2O$  are absorbed in  $KOH$  and  $CaCl_2$  of known weights. The increase in weight of these are then determined.

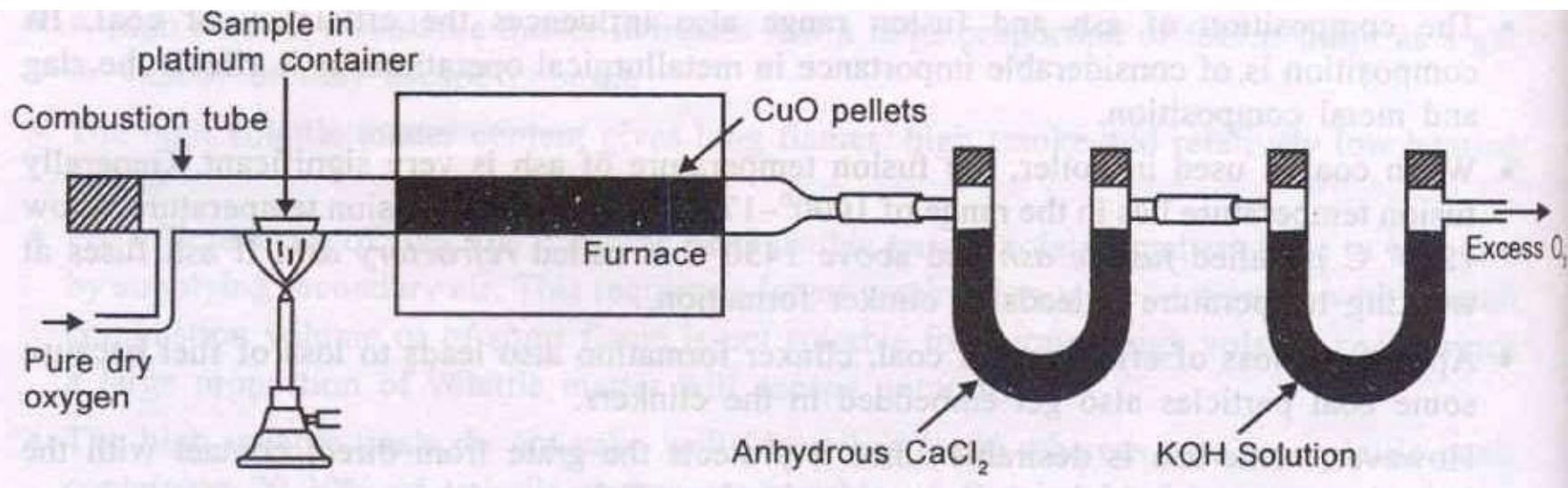
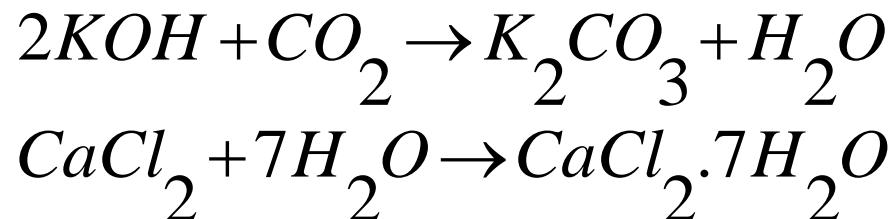


Fig . Estimation of carbon and hydrogen



$$\% \text{ of Carbon} = \frac{\text{Increase in wt. of KOH tube} \times 12}{\text{Wt. of coal sample taken} \times 44} \times 100$$

$$\% \text{ of Hydrogen} = \frac{\text{Increase in wt. of CaCl}_2\text{ tube} \times 2}{\text{Wt. of coal sample taken} \times 18} \times 100$$

**2. Nitrogen:** Nitrogen present in coal sample can be estimated by Kjeldahl's method.

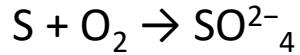
To determine the % of  $N_2$ , coal is heated with conc.  $H_2SO_4$  along with  $K_2SO_4$  (catalyst). From the volume of acid used by ammonia liberated, the % of  $N_2$  in coal can be calculated as,

$$\% \text{ of } N_2 = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Wt. of coal sample taken}}$$

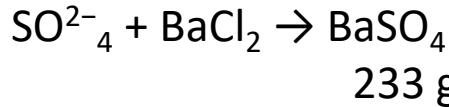
### 3 . Sulphur :

It is determined from the washing obtained from the known mass of coal, used in a bomb calorimeter for determination of calorific value. During this, sulphur is converted into sulphate.

The washings are treated with  $\text{BaCl}_2$ , when  $\text{BaSO}_4$  is precipitated.



32 g



$$\% \text{ of Sulphur in coal} = \frac{\text{Weight of precipitate} \times 32 \times 100}{\text{Weight of coal sample taken} \times 233}$$

**4. Ash:** Ash is determined by Proximate analysis .

**5. Oxygen:**

$$\% \text{ of Oxygen} = 100 - \% \text{ of } [C + H + N + S + \text{ash}]$$

Q. Calculate the minimum weight of air required for complete combustion of 1 kg of fuel containing C = 90%, H = 3.5% O = 3%, S = 0.5%,  $H_2O$  = 1%, N = 0.5% & ash = rest.

Q. Calculate the minimum weight of air required for complete combustion of 1 kg of fuel containing C = 90%, H = 3.5% O = 3%, S = 0.5%, H<sub>2</sub>O = 1%, N = 0.5% & ash = rest.

Ans. 1 kg of fuel contains:

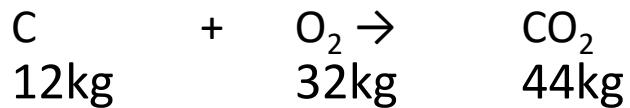
C = 900 g, H = 35 g, S = 5 g, O = 30 g, N = 5 g,  
H<sub>2</sub>O = 10 g & ash = rest

Minimum weight of oxygen required for complete combustion of 1 kg of fuel

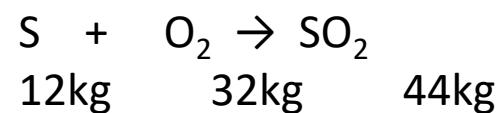
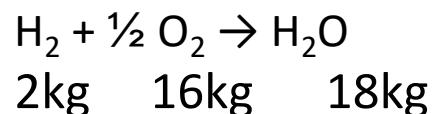
$$= [32/12 \times (\text{wt. of C}) + 16/2 \times (\text{wt. of H}) + 32/32 \times (\text{wt. of S})] - (\text{wt. of O})$$

## Hint

For the carbon:



Similarly



Q. Calculate the minimum weight of air required for complete combustion of 1 kg of fuel containing C = 90%, H = 3.5% O = 3%, S = 0.5%, H<sub>2</sub>O = 1%, N = 0.5% & ash = rest.

Ans. 1 kg of fuel contains:

C = 900 g, H = 35 g, S = 5 g, O = 30 g, N = 5 g,  
H<sub>2</sub>O = 10 g & ash = rest

Minimum weight of oxygen required for complete combustion of 1 kg of fuel

$$\begin{aligned} &= [32/12 \times (\text{wt. of C}) + 16/2 \times (\text{wt. of H}) + \\ &\quad 32/32 \times (\text{wt. of S})] - (\text{wt. of O}) \\ &= [32/12 \times 900 + 16/2 \times 35 + 32/32 \times 5] - 30 \\ &= 2655 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Minimum quantity of air required} &= 2655 \times 100/23 \\ &= 11543.48 \text{ g} = 11.5 \text{ kg} \end{aligned}$$

# BIOGAS / Biogasfication

- Biogas is an important renewable energy resource for rural areas in India.
- Biogas is also known as Gobar gas.
- It is produced by anaerobic digestion of biological wastes .
- It was known that methane gas ( $\text{CH}_4$ ) is produced by the decay of vegetable matter.

- Biogas (or gobar gas) is obtained by the anaerobic fermentation of animal dung, plant wastes in the presence of water but absence of oxygen.
- Micro organism like anaerobic bacteria is used in the fermentation of the waste.
- On decomposition methane, carbon dioxide, hydrogen, nitrogen etc. are obtained.
- The average composition of biogas :

$\text{CH}_4$  = 55%,

$\text{CO}_2$  = 35%,

$\text{H}_2$  = 7.5%,

$\text{N}_2$  = 2.5%

$\text{H}_2\text{O}$  in traces.

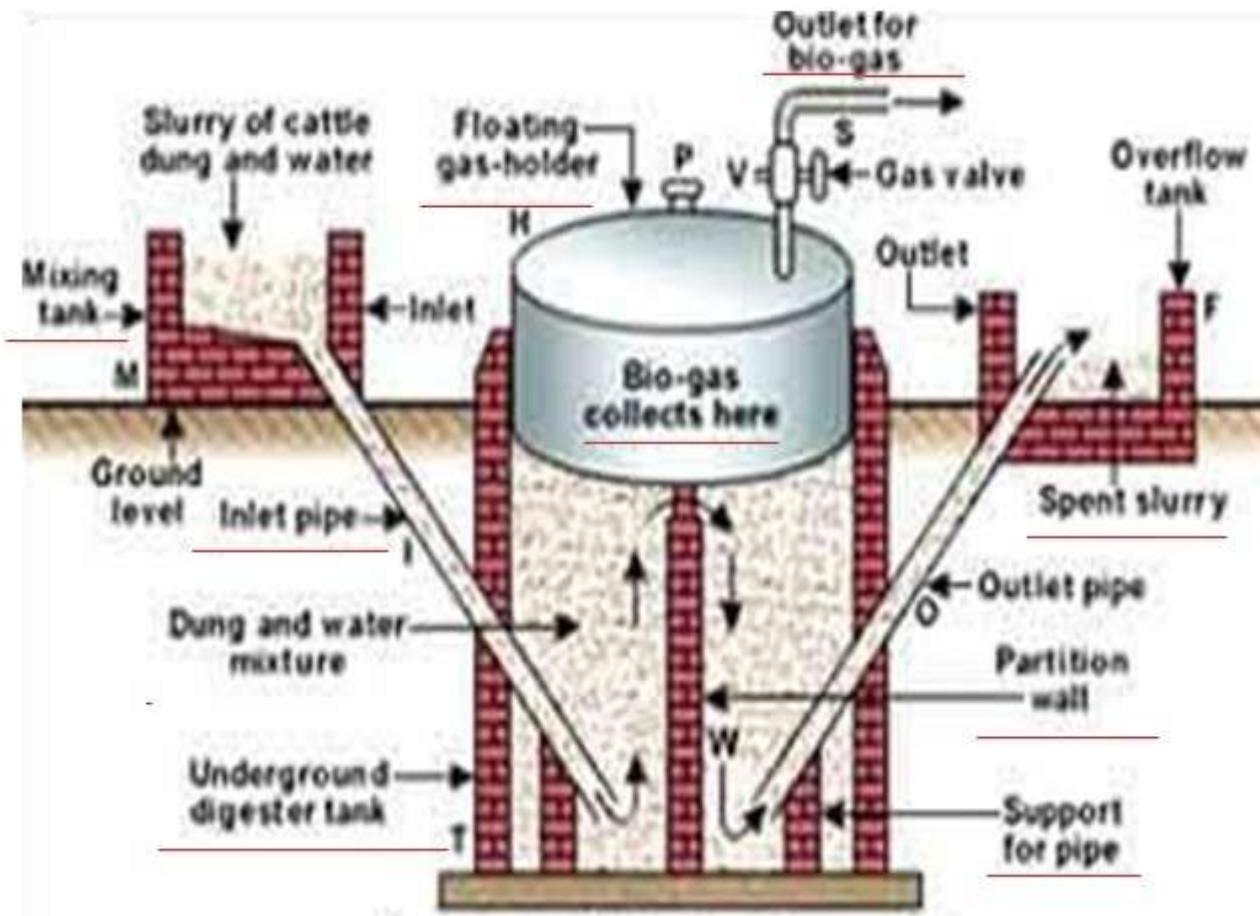
## **Advantages of Biogas :**

- It burns with non-smoky flame and does not pollute environment.
- Its calorific value is high.
- It can be used directly thus there is no storage problem.
- It is most common and cheapest gas.
- It does not contain any poisonous gas.
- It is used as renewable fertilizers, reduction in commercial herbicides and pesticides.

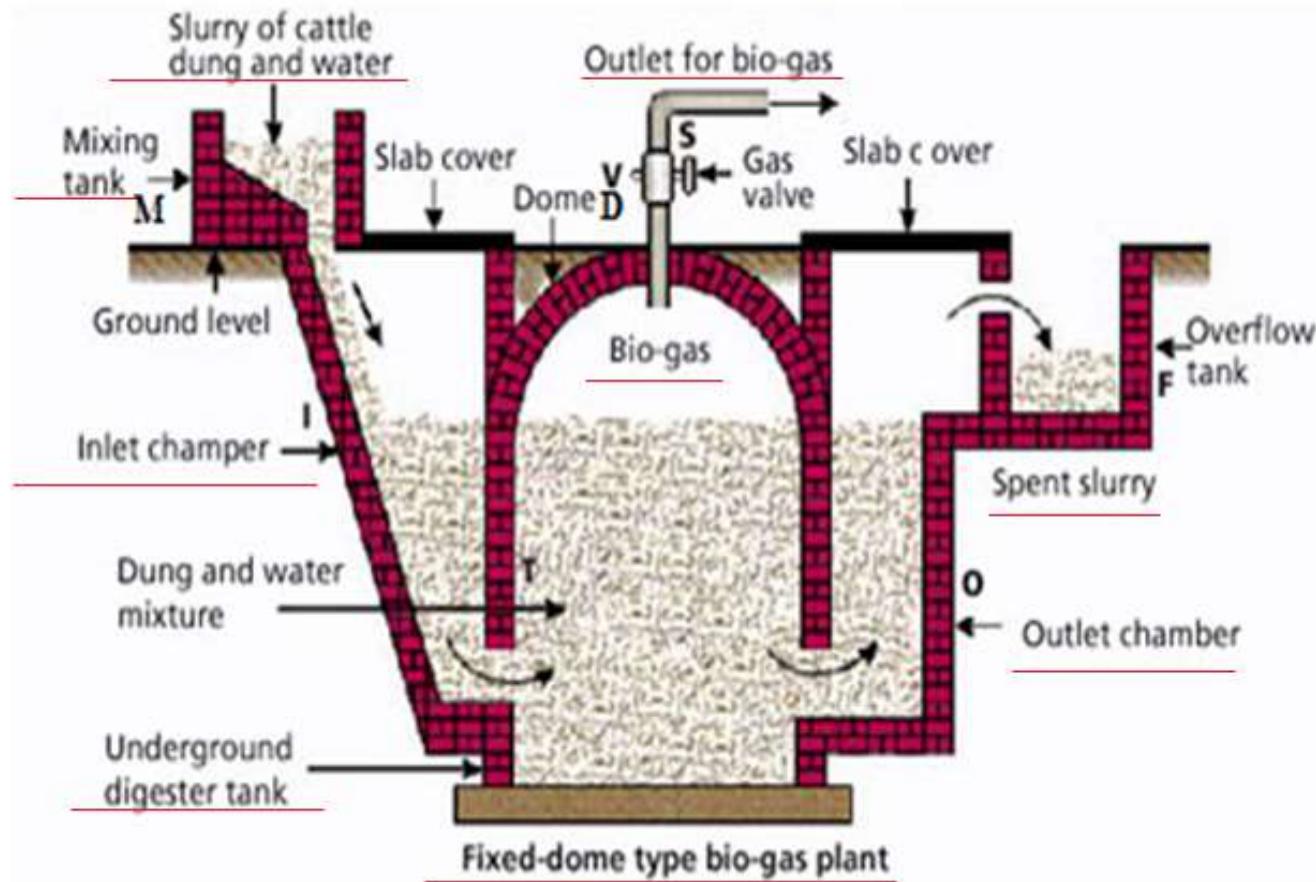
## Biogas Plant :

In India generally following two types of biogas plants are established :

- (i) Floating gas holder type biogas plant
- (ii) Fixed dome type biogas plant.



Floating gas-holder type biogas plant



Fixed dome type biogas plant.

# **BIO-MASS**

The term bio-mass is used for the waste material of living organism and the dead plants of living object i.e. plants, trees and animals.

It includes cattle dung, wood, sewage, agricultural wastes or crop residue such as biogases or rice husk.

There are following two ways of using bio-mass as a fuel :

(i) Generally bio-mass (like wood, cattle dung, agricultural waste) is used directly in chulhas

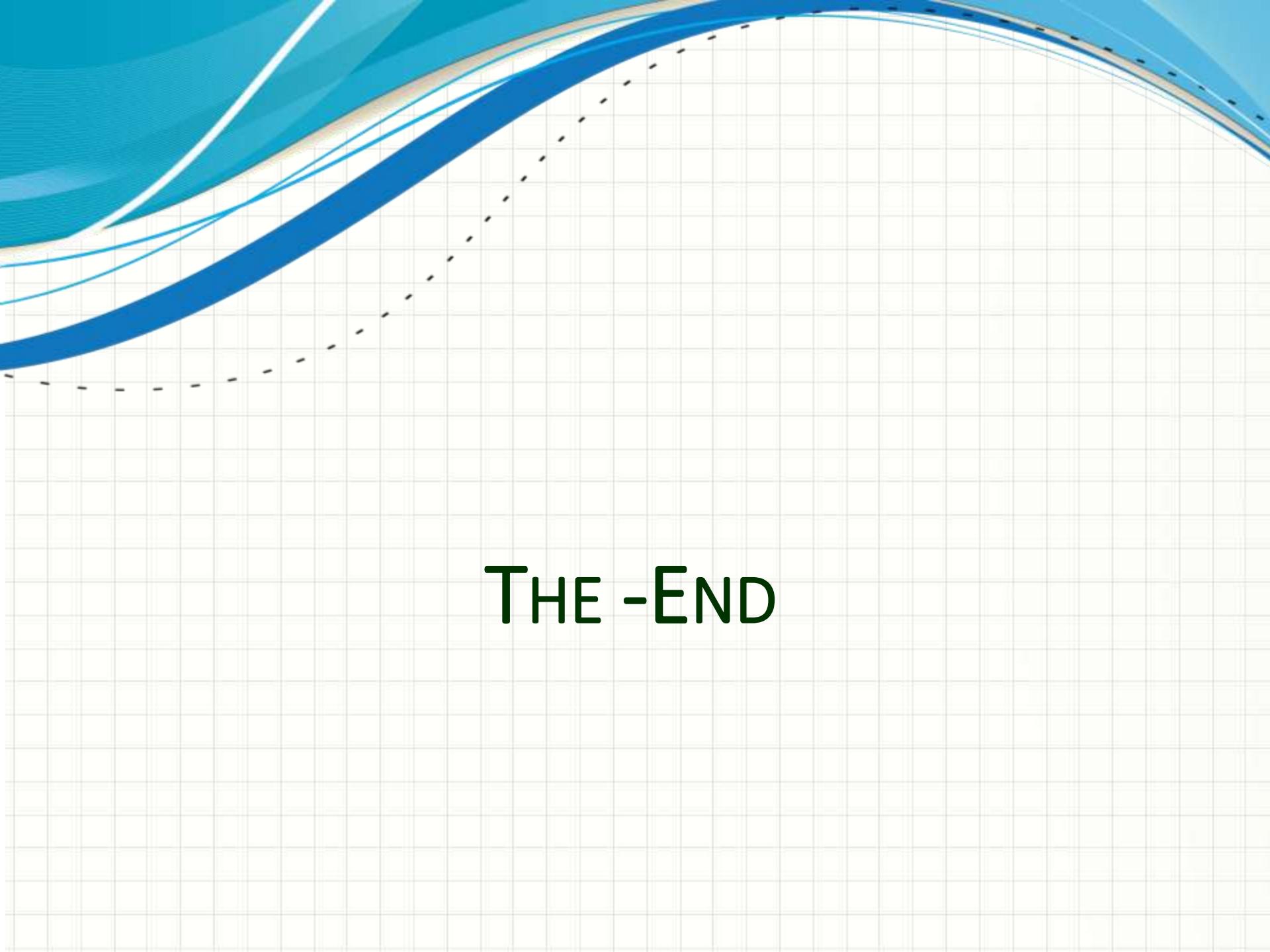
(ii) The bio-mass is converted into a fuel by a certain process and the fuel is used for heating purposes.

For example,

- wood is converted into charcoal,
- cattle dung is converted into bio-gas,
- paddy husk (obtained during milling of paddy) is converted into smokeless solid fuel,
- rice bran (obtained during polishing of rice) is converted into methyl ester for use as fuel etc.

# References

- <https://www.slideshare.net/pradyumnagujar7/fuels-33032404>
- <https://www.slideshare.net/rayvarun/introduction-of-fuel>
- <https://www.slideshare.net/srikanthlaxmanvinjam/fuels-42744960>



THE -END