#### **UNIT-4: WATER AND IT'S TREATMENT**

**WATER:** Water is one of the most abundent compound present on earth. It is necessary for living beings. The molecular formula of water is **H<sub>2</sub>O.** When hydrogen and oxygen combined in 2:1 by volume or 1:8 by mass, water is formed. 70% of earth is covered with water. 90% of plant body and 75% of animal body is made up of water.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

**SOFT WATER:** Water which produces lather easily on shaking with soap solution is called soft water.

**HARD WATER:** Water which does not produces lather on shaking with soap solution is called hard water. Hard water form white precipitate (Scum) with soap solution.

HARDNESS OF WATER: Soap consuming capacity of water is called hardness of water.

**CAUSES OF HARDNESS OF WATER:** Hardness of water is due to presence of soluble salts of  $Ca^{2+} \& Mg^{2+}$  ions.

**UNITS OF HARDNESS OF WATER:** Different units of hardness of water are ppm, mg/L, °F & °Cl.

## RELATIONSHIP BETWEEN DIFFERENT UNITS OF HARDNESS OF WATER: 1 ppm = 1 mg/L = 0.1 °F = 0.07 °Cl

Hardness of water is measured in terms of calcium carbonate equivalent because it is almost insoluble in water and its molar mass is 100 which makes calculation easy.

**TYPES OF HARDNESS OF WATER:** Generally their are two types of hardness of water.

1. Temporary Hardness or Carbonated Hardness: Hardness of water which can be removed by boiling of water is called temporary hardness of water. It is also called carbonated hardness of water.

**Causes of Temporary Hardness:** Temporary hardness of water is due to presence of soluble bicarbonates of calcium and magnesium.

Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>.

The temporary hardness of water is removed by boiling of water beacause on boiling of water soluble bicarbonates of calcium and magnesium are converted into their insoluble carbonates.

$$\begin{array}{cccc} Ca(HCO_3)_2 & \xrightarrow{Boil} & CaCO_3 \downarrow & + H_2O + CO_2 \\ Mg(HCO_3)_2 & \xrightarrow{Boil} & MgCO_3 & \downarrow + H_2O + CO_2 \end{array}$$

2. Permanent Hardness or Non-Carbonated Hardness: Hardness of water which can not be removed by boiling of water is called permanent hardness of water. It is also called non-carbonated hardness of water.

**Causes of Permanent Hardness:** Permanent hardness of water is due to presence of soluble chlorides, sulphates of calcium and magnesium ions.

CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub> & MgSO<sub>4</sub>

**METHODS FOR REMOVING TEMPORARY HARDNESS:** Temporary hardness can be removed by boiling of water. It is due to decomposition of calcium and magnesium bicarbonates into insoluble carbonates and hydroxides on boiling.

$$\begin{array}{c|cccc} Ca(HCO_3)_2 & \underline{boil} & CaCO_3 + H_2O + CO_2 \\ Mg(HCO_3)_2 & \underline{boil} & MgCO_3 + H_2O + CO_2 \\ Mg(HCO_3)_2 & \underline{boil} & Mg(OH)_2 + 2CO_2 \end{array}$$

**METHODS FOR REMOVING PERMANENT HARDNESS:** Permanent hardness of water can be removed by following methods.

- 1. Zeolite method or Permutit method
- 2. Soda-Lime or Lime-Soda method
- 3. Ion-Exchange Resins
- 4. R.O. (Reverse Osmosis)
- 5. Calgons process
- 6. Clarks method.

**ZEOLITE METHOD OR PERMUTIT METHOD:** Zeolite method is one of the most important method for the purification of water. It can remove temporary as well as permanent hardness of water. It is also called Permutit method.

The word Zeolite is taken from **Greek** words **Zein & Lithos** which means **boiling stones**. Zeolites are **hydrated sodium aluminium silicates**. The molecular formula of zeolites is Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.xSiO<sub>2</sub>.yH<sub>2</sub>O

where 
$$x = 2$$
 to 10  
  $y = 2$  to 6

**Types of Zeolites:** Zeolites can be classified into two parts.

- A) Natural Zeolite: The zeolite which is obtained from nature is called natural zeolite. It is non-porous green sand. It is more durable. The molecular formula of natural zeolites is Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.3H<sub>2</sub>O
- B) **Synthetic Zeolite:** The zeolite which is synthesized in laboratory is called synthetic zeolite. It is prepared by mixing sodium meta aluminate (**NaAlO**<sub>2</sub>), aluminium hydroxide **Al(OH)**<sub>3</sub> & silica (**SiO**<sub>2</sub>). Synthetic zeolite is highly porous in nature so it have higher exchange capacity per unit weight.

**Process:** In this process hard water passes at a specific rate through a bed of active granular sodium zeolite present in a zeolite softner. All the Ca<sup>2+</sup> & Mg<sup>2+</sup> ions are taken up by zeolite and converted into insoluble CaZ and MgZ, while outgoing water contains equivalent amount of sodium salts.

In general sodium zeolite is represented by Na<sub>2</sub>Z.

The chemical reactions taking place are as follows.

It can remove temporary hardness of water.

$$Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ_{\psi} + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Z \longrightarrow MgZ_{\psi} + 2NaHCO_3$$
It can remove permanent hardness of water.
$$CaCl_2 + Na_2Z \longrightarrow CaZ_{\psi} + 2NaCl$$

$$MgCl_2 + Na_2Z \longrightarrow MgZ_{\psi} + 2NaCl$$

$$CaSO_4 + Na_2Z \longrightarrow CaZ_{\psi} + Na_2SO_4$$

$$MgSO_4 + Na_2Z \longrightarrow MgZ_{\psi} + Na_2SO_4$$

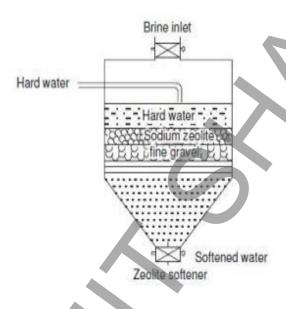
Small quantity of ferrous and manganese bicarbonates may also get removed.

$$Fe(HCO_3)_2 + Na_2Z \longrightarrow FeZ \downarrow + 2NaHCO_3$$

$$Mn(HCO_3)_2 + Na_2Z \longrightarrow MnZ \downarrow + 2NaHCO_3$$

**Regeneration of Zeolite:** When the zeolite is completely changed into CaZ and MgZ, then it can be regenerated and reused by treating it with a 10% NaCl solution (Brine solution).

The washing containing CaCl<sub>2</sub> and MgCl<sub>2</sub> are led to drain and the regenerated zeolite bed is again used for water softening.



#### **Advantages of Zeolite Process:**

- 1. It removes the temporary and permanent hardness almost completely.
- 2. The equipment used is compact, occupying less space and easy to operate.
- 3. It requires less time for softening.
- 4. It starts automatically and not need electricity.
- 5. The plant can be installed in the water supply line itself, decreasing the cost of pumping.

#### **Disadvantages of Zeolite Process:**

- 1. The outgoing water contains more sodium salts.
- 2. This method only replaces Ca<sup>2+</sup> & Mg<sup>2+</sup> ions.
- 3. It can not remove acidic ions.
- 4. High turbidity water can not be softened by zeolite method.

## **Limitations of Zeolite Process:**

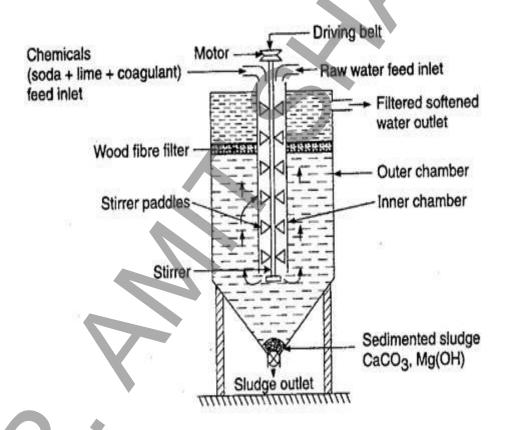
- 1. The water must be free from turbidity and suspended matter.
- 2. Hot water can not be used as the zeolite tend to dissolve in it.
- 3. Coloured ions can not be removed by zeolite process.
- 4. Water containing excess of acidity or alkalinity should not be used as mineral acids may destroy the zeolite bed.

**SODA-LIME METHOD OR LIME-SODA PROCESS:** Soda lime process is used to remove temporary as well as permanent hardness of water. It can also remove acidic impurities and coloured ions.

**PROCESS:** In this method a suspension of lime milk is added to water, together with calculated amount of soda solution.

The process can be classified into two parts

- 1. **Cold Soda-Lime Process:** The process which takes place at room temperature is called cold soda-lime process. It involves the mixing of calculated quantity of mixture of soda -lime with water at room temperature.
- 2. **Hot Soda-Lime Process:** The process which takes place at temperature 80-150 °C is called hot soda-lime process. It involves the mixing of calculated quantity of mixture of soda -lime with water at 80-150 °C temperature.



The chemical reactions takes places are as follows: It can remove temporary hardness of water.

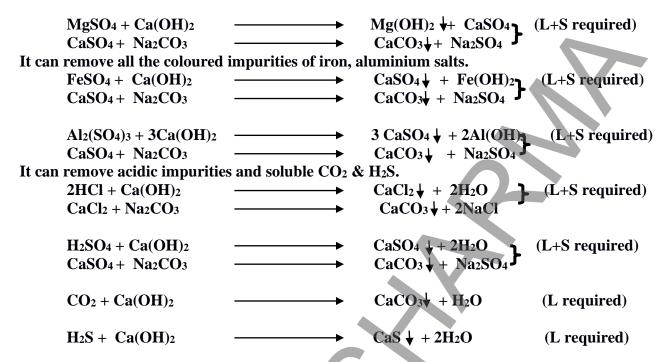
$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O \qquad (L \ required)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O \qquad (2L \ required)$$
It can remove permanent hardness of water
$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl \qquad (S \ required)$$

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl \qquad (L+S \ required)$$

$$CaCO_3 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl \qquad (S \ required)$$

$$CaCO_3 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4 \qquad (S \ required)$$



#### **Advantages of Soda-Lime Process:**

- 1. It is very cheap and economical.
- 2. It can remove temporary and permanent hardness
- 3. It can also remove acidic impurities and iron & manganese ions.
- 4. Less amounts of coagulants will required.

## **Disadvantages of Soda-Lime Process:**

- 1. Careful operation and skilled supervision is required in this process.
- 2. Formation of large amount of sludge.
- 3. Softened water from this process can not be used in boilers.

**ION- EXCHANGE PROCESS OR DEIONIZATION OR DEMINERALIZATION:** It is one of the most important methods for purification of water. It can remove temporary, permanent, acidic and ionic hardness of water. It is also called deionization or demineralization process. Ion-Exchange resins are cross linked, long chain organic polymers with a microporous structure. These polymers are attached with a number of functional groups such as -SO<sub>3</sub>H, -COOH, -NH<sub>2</sub>, -NH(R)OH, -N=NH, which are responsible for ion exchange properties. There are two types of ion-exchange resins.

- 1. **Cation Exchange Resins:** Those ion-exchange resins which contains -COOH, -SO<sub>3</sub>H as a functional group, which are capable to exchange Ca<sup>2+</sup> & Mg<sup>2+</sup> ions. For Ex. Styrene divinyl benzene sulphonic acid & Styrene divinyl benzoic acid.
- 2. **Anion Exchange Resins:** Those ion-exchange resins which contain -NH<sub>2</sub>, quaternary ammonium hydroxide as a functional group, which are capable to exchange anion such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> are called anion exchange resins. For Ex. Styrene divinyl benzene quarternary ammonium hydroxide.

A strongly acidic sulphonated polystyrene cation exchange resin

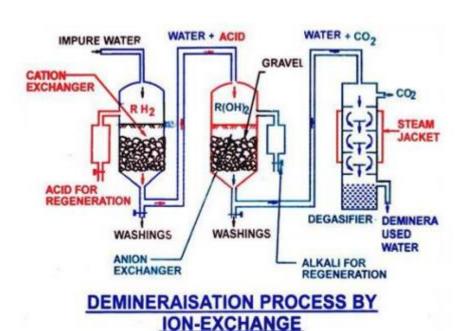
A strongly basic quaternary ammonion anion exchange resin

**Process:** In this process hard water is passed first from the cation exchangecolumn which removes  $Ca^{2+}$  &  $Mg^{2+}$  ions.

$$2RH^{+} + Ca^{2+}$$
  $\longrightarrow$   $R_{2}Ca^{2+} + 2H^{+}$   
 $2RH^{+} + Mg^{2+}$   $\longrightarrow$   $R_{2}Mg^{2+} + 2H^{+}$ 

After this water is passed through anion exchange column which removes all the anions.

ROH<sup>-</sup> + Cl<sup>-</sup> 
$$\rightarrow$$
 RCl<sup>-</sup> + OH<sup>-</sup>  $2ROH^{-} + SO_{4}^{2-}$   $\rightarrow$  R<sub>2</sub>SO<sub>4</sub><sup>2-</sup> + 2OH<sup>-</sup>  $2ROH^{-} + CO_{3}^{2-}$   $\rightarrow$  R<sub>2</sub>CO<sub>3</sub><sup>2-</sup> + 2OH<sup>-</sup>



**Regeneration:** When capacities of cation and anion exchange resins are lost, they can be regenerated.

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil.  $H_2SO_4$ .

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

Both the columns are washed with deionised water and washing is passed to sink or drain and regenerated ion-exchange resins are used again.

## **Advantages:**

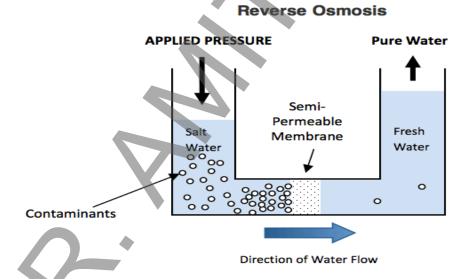
- 1. The process can be used to soften highly acidic or alkaline water.
- 2. It can remove all temporary and permanent hardness upto 2 ppm.

## **Disadvantages:**

- 1. The ion-exchange equipment is very costly.
- 2. Eexpensive chemicals are needed for regeneration.
- 3. If water contains high turbidity, then the output of the process is reduced.
- 4. It requires electricity.

**REVERSE OSMOSIS OR DESALINATION OF SALINE WATER:** t is one of the most important methods for purification of water. It can remove temporary, permanent, acidic and ionic hardness of water. It is based on the principal of reverse osmosis.

"When external or hydraulic pressure or applied pressure is greator than osmotic pressure, then osmosis takes place in reverse direction i.e. water molecules moves from high concentration medium to low concentration medium, this process is called reverse osmosis.



**Process:** In R.O. process two different concentration solution are seperated by semipermiable membrane. A hydraulic or external pressure is applied from the side of high concentrated solution. If external pressure is greator than osmotic pressure, then water molecules moves from high concentration solution to low concentration solution and water becomes pure or desalinized.

#### **Advantages:**

- 1. It can remove temporary, permanent and ionic impurities or hardness of water.
- 2. It is applicable for all kinds of water i.e. turbid water, colloidal particles and suspended impurities can be removed by this method.
- 3. The life-line of good quality membrane is quite high.

### **Disadvantages:**

- 1. The membrane is costly.
- 2. Electricity is required for some times.

**BOILER FEED WATER:** The water which is used in industries for steam generation is called boiler feed water.

**PROBLEMS ASSOCIATED WITH BOILER FEED WATER:** If water feed into the boiler contains hardness then it causes some problems. These problems are called problems associated with boiler feed water.

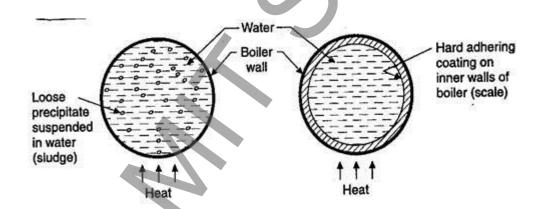
These are as follows:

- 1. Scale and Sludge
- 2. Priming and Foaming
- 3. Caustic embrittlement
- 4. Boiler corrosion
- 5. Desalination of brackish water

**SCALE & SLUDGE:** In boilers water evaporates continuously and the concentration of the dissolved salts increases progressively. When their concentration reach saturation point, they are precipitated on the inner walls of boiler.

"The loose and slimy precipitate suspended in the boiler is called sludge"

"The precipitate which forms a hard adhering layer or coating on the inner walls of boiler is called scale"



**Disadvantages of Scale and Sludge:** Scale and sludge are the poor conductor of heat and electricity, So they have various disadvantages.

- 1. It causes wastage of heat.
- 2. Consumption of electricity increases.
- 3. Scale and sludge have low thermal conductivity, So the rate of heat transfer from boiler to inner water decreases, hence we need more fuel or electricity for boiling the water.
- 4. Due to scale and sludge formation boiler metal corrodes which increase the risk of boiler explosion.
- 5. Efficiency of boiler decreases.

#### **Prevention of Scale and Sludge Formation:**

- 1. By using well softened water.
- 2. By using frequently blow down operations.
- 3. By coating boiler metal with paints or redoxide.
- 4. By using chemical treatments or internal treatment of boiler feed water.
- 5. **By Colloidal Conditioning:** In low pressure boilers scale formation can be avoided by adding organic sustances like kerosene, tanin, agar-agar gel, which get coated over the scale forming precipitates and can be removed by blow down operations.
- 6. **By Calgon Conditioning:** It involves the adding of calgon (sodium hexa meta phosphate) to the boiler water. It prevents the scale and sludge formation by forming soluble complex compounds with CaSO<sub>4</sub>.

$$Na_{2}[Na_{4}(PO_{3})_{6}]$$
  $\longrightarrow$   $2Na^{+} + [Na_{4}P_{6}O_{18}]^{2-}$   $[Na_{4}P_{6}O_{18}]^{2-} + CaSO_{4}$   $\longrightarrow$   $[Ca_{2}P_{6}O_{18}]^{2-} + 2Na_{2}SO_{4}$ 

7. **By Phosphate Coditioning:** In high pressure boilers scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming soft sludge of calcium and magnesium phosphate, which can be removed by blow down operations.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$$

8. **By Carbonate Conditioning:** In low pressure boilers scale formation can be avoided by adding sodium carbonate to boiler water, then hardness is precipitated which can be removed by blow down operations.

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

**PRIMING AND FOAMING:** When a boiler producing steam rapidly then some of the liquid water is carried along with steam. "The process of wet steam formation is called priming". Causes of Priming:

- It is due to presence of large amount of dissolved solids.
- Due to high steam velocity.
- Due to sudden boiling of water.
- Due to sudden increase in the rate of steam formation.
- Due to high level of water in boilers.

**Prevention of Priming:** It can be prevented by

- Fitting mechanical steam purifires.
- Avoiding rapid change in steam formation.
- Maintaining low level of water in boilers.
- By efficient softening and filtration of boiler feed water.

**FOAMING:** The process of formation of bubbles or foam in boiler which do not break easily is called foaming.

**Causes of Foaming:** It is due to presence of some foam producing substances such as organic substances and oils.

Prevention of Foaming: It can be prevented by

- Adding anti-foaming chemicals such as cator oil.
- By removing foam producing substances by adding some chemicals such as NaAlO<sub>2</sub> (sodium meta aluminate).

**CAUSTIC EMBRITTLEMENT:** The process of corrosion or decaying of boiler metal by caustic is called caustic embrittlement.

Caustic embrittlement is a type of boiler corrosion. It is caused by using highly alkaline water in the boiler during soda-lime water softening process, free Na<sub>2</sub>CO<sub>3</sub> decomposes into NaOH (alkali) and CO<sub>2</sub>.

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

This alkali NaOH makes boiler water caustic (basic) which decompose the inner walls of boiler metal.

#### **Prevention of Caustic Embrittlement:**

- 1. By using sodium phosphate as softening reagent, instead of sodium carbonate.
- 2. By adding tanin or lignin to boiler water, these blocks the hair-cracks.
- 3. By adding sodium sulphate to boiler water, it blocks the hair-cracks.

**BOILER CORROSION:** The process of decaying of boiler material by chemical or

electrochemical attack is called boiler corrosion.

Causes of Boiler Corrosion: The main causes of boiler corrosion are dissolved oxygen and dissolved CO<sub>2</sub>.

**Dissolved Oxygen:** Water usually contains dissolved oxygen (8 mL/L) at room temperature. This dissolved oxygen present in water at high temperature attack boiler material and corrodes the boiler.

$$2Fe + 2H2O + O2 \longrightarrow 2Fe(OH)2$$

$$4Fe(OH)2 + O2 \longrightarrow 2[Fe2O3.2H2O] or Rust$$

**Dissolved Carbondioxide:** Dissolved CO<sub>2</sub> is also responsible for boiler corrosion, because it forms carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

#### **Prevention of Boiler Corrosion:**

1. Boiler corrosion can be prevented by adding calculated quantity of sodium sulphite which absorbs dissolved oxygen.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

2. Boiler corrosion can be prevented by adding calculated quantity of ammonium hydroxide which absorbs dissolved CO<sub>2</sub>.

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

**DESALINATION OF BRACKISH WATER:** The process of removing common salts from the water is known as desalination of brackish water.

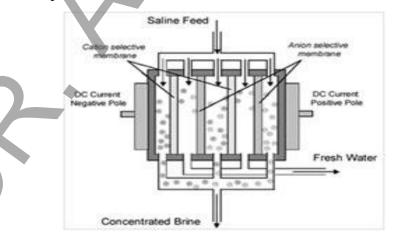
Generally, there are two methods used for desalination of brackish water.

- 1. Reverse osmosis
- 2. **Electrodialysis:** The process of removing ions from the brackish water by using a membrane in the presence of electrical field is called electrodialysis.

**Process:** In this process we use sea water or brackish water. It is taken in electrodialyser which contains two semipermeable membranes. In the presence of electric field cations present in brackish water moves towards cathode and anions moves towards anode & finally we get the pure water.

#### **Advantages:**

- 1. It is one of the most important method for the purification of water.
- 2. The cost of installation of plant is minimum.
- 3. The unit is compact.



#### NUMERICALS ON HARDNESS OF WATER IN TERMS OF CALCIUM CARBONATE

**EQUIVALENT:** The hardness of water is expressed in terms of calcium carbonate equivalent because the molecular weight of calcium carbonate is 100g/mol. It is easy to calculate. Also calcium carbonate is insoluble in water therefore it is easy to calculate its amount in water.

## Hardness of water = mass of hardness producing salt X multiplication factor

Molecular formula of	Molar mass of	Multiplication factor for	Lime and
hardness producing salt	hardness	converting hardness in	Soda
	producing salt	CaCO <sub>3</sub> equivalent or ppm	Required
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	100/162	L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	100/146	2L
CaCl <sub>2</sub>	111	100/111	S
MgCl <sub>2</sub>	95	100/95	L,S
CaSO <sub>4</sub>	136	100/136	S
CaCO <sub>3</sub>	100	100/100	L
MgCO <sub>3</sub>	84	100/84	2L
MgSO <sub>4</sub>	120	100/120	L,S
HCO <sub>3</sub> - ion	61	100/(2*61) = 100/122	L, -S
CO <sub>2</sub>	44	100/44	L
MgCO <sub>3</sub>	84	100/84	2L
Ca(NO <sub>3</sub> ) <sub>2</sub>	164	100/164	S
Mg(NO <sub>3</sub> ) <sub>2</sub>	148	100/148	L, S
OH <sup>-</sup> ion	17	100/(2*17) = 100/34	L,S
CO <sub>3</sub> ··ion	60	100/60	S
H <sup>+</sup> ion	1	100/(2*1) = 100/2	L,S
HCl	36.5	100/(2*36.5) = 100/73	L,S
NaAlO <sub>2</sub>	82	100/(2*82) = 100/164	-L
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	342	(3*100)/342 = 300/342	L,S
FeSO <sub>4</sub> .7H <sub>2</sub> O	278	100/278	L,S
Ca <sup>++</sup>	40	100/40	S
Mg <sup>++</sup>	24	100/24	L,S
Al <sup>3+</sup>	27	(3*100)/(2*27) = 300/54	L,S

## **PROBLEMS BASED ON HARDNESS OF WATER:**

1. A sample of ground water contains 150 mg/L of calcium ion and 60 mg/L of magnesium ions. Calculate the toatal hardness of water in terms of calcium carbonate. Solution:

S.No.	Costituents of hardness	Quantity in mg/L or ppm	Multiplication factor	Hardness in terms of calcium carbonate equivalent = quantity * multiplication factor
1	Ca++	150	100/40	150 * 100/40 = 375
2	Mg <sup>++</sup>	60	100/24	60 * 100/24 = 250

Total hardness of water = 375 + 250 = 625 ppm.

2. Calculate the temporary (carbonated), permanent (non-carbonated) and total harness of water sample containing following impurities.

Ca(HCO <sub>3</sub> ) <sub>2</sub>	16.2 mg/L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	7.3 mg/L
CaSO <sub>4</sub>	13.6 mg/L

MgCl <sub>2</sub>	9.5 mg/L

#### **Solution:**

S.No.	<b>Costituents of</b>	Quantity in	Multiplication	Hardness in terms of calcium
	hardness	mg/L or ppm	factor	carbonate equivalent =
				quantity * multiplication factor
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	16.2 mg/L	100/162	16.2*100/162 = 10
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	7.3 mg/L	100/146	7.3 *100/146 = 5
3	CaSO <sub>4</sub>	13.6 mg/L	100/136	13.6*100/136 = 10
4	MgCl <sub>2</sub>	9.5 mg/L	100/95	9.5 *100/95 = 10

Temporary hardness( Carbonated Hardness) =  $Ca(HCO_3)_2 + Mg(HCO_3)_2 = 10 + 5 = 15$  ppm Permanent hardness(Non-Carbonated Hardness) =  $CaSO_4 + MgCl_2 = 10 + 10 = 20$  ppm Total hardness = Temporary hardness + Permanent hardness = 15 + 20 = 35 ppm

3. Calculate the carbonated, non-carbonated and total hardness of a sample of water that is analysed as: Mg(HCO<sub>3</sub>)<sub>2</sub>= 6 mg/l, Ca(HCO<sub>3</sub>)<sub>2</sub>=8 mg/l, MgCl<sub>2</sub>= 10 mg/l and CaSO<sub>4</sub>= 12 mg/l.

## **Solution:**

S.No.	<b>Costituents of</b>	Quantity in	Multiplication	Hardness in terms of calcium
	hardness	mg/L or	factor	carbonate equivalent =
		ppm		quantity * multiplication
				factor
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	8 mg/L	100/162	<b>8*100/162 = 4.9</b>
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	6 mg/L	100/146	6*100/146 = 4.1
3	CaSO <sub>4</sub>	12 mg/L	100/136	<b>12*100/136 = 8.8</b>
4	MgCl <sub>2</sub>	10 mg/L	100/95	10*100/95 = 10.5

Temporary hardness (Carbonated Hardness) =  $Ca(HCO_3)_2 + Mg(HCO_3)_2 = 4.9 + 4.1 = 9$  ppm Permanent hardness (Non-Carbonated Hardness) =  $CaSO_4 + MgCl_2 = 8.8 + 10.5 = 19.3$  ppm Total hardness = Temporary hardness + Permanent hardness = 9 + 19.3 = 28.3 ppm

4. Calculate the temporary, permanent and total harness of water sample containing following impurities.

Ca(HCO <sub>3</sub> ) <sub>2</sub>	10 mg/L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	8.5 mg/L
CaSO <sub>4</sub>	12 mg/L
Mg SO <sub>4</sub>	14 mg/L

## **Solution:**

1	S.No.	<b>Costituents of</b>	Quantity in	Multiplication	Hardness in terms of calcium
	X	hardness	mg/L or ppm	factor	carbonate equivalent =
					quantity * multiplication factor
	1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	10 mg/L	100/162	10 * 100/162 = 6.17
	2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	8.5 mg/L	100/146	8.5* 100/146 = 5.82
	3	CaSO <sub>4</sub>	12 mg/L	100/136	12 * 100/136 = 8.82
	4	Mg SO <sub>4</sub>	14 mg/L	100/120	14 *100/120 = 11.66

Temporary hardness =  $Ca(HCO_3)_2 + Mg(HCO_3)_2 = 6.17 + 5.82 = 11.99$  ppm Permanent hardness =  $CaSO_4 + MgSO_4 = 8.82 + 11.66 = 20.48$  ppm Total hardness = Temporary hardness + Permanent hardness = 11.99 + 20.48 = 32.47 ppm 5. Calculate the temporary, permanent and total harness of water sample containing following impurities.

Ca(HCO <sub>3</sub> ) <sub>2</sub>	40.5 mg/L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	36.5 mg/L
CaSO <sub>4</sub>	34 mg/L
Mg SO <sub>4</sub>	30 mg/L
CaCl <sub>2</sub>	27.75 mg/L

#### **Solution:**

S.No.	<b>Costituents of</b>	Quantity in	Multiplication	Hardness in terms of calcium
	hardness	mg/L or ppm	factor	carbonate equivalent =
				quantity * multiplication factor
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	40.5 mg/L	100/162	40.5*100/162 = 25 ppm
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	36.5 mg/L	100/146	36.5*100/146 = 25 ppm
3	CaSO <sub>4</sub>	34 mg/L	100/136	34 * 100/136 = 25 ppm
4	Mg SO <sub>4</sub>	30 mg/L	100/120	30 * 100/120 = 25 ppm
5	CaCl <sub>2</sub>	27.75 mg/L	100/111	27.75*100/111= 25 ppm

Temporary hardness =  $Ca(HCO_3)_2 + Mg(HCO_3)_2 = 25 + 25 = 50$  ppm Permanent hardness =  $CaSO_4 + MgSO_4 + CaCl_2 = 25 + 25 + 25 = 75$  ppm Total hardness = Temporary hardness + Permanent hardness = 50 + 75 = 125 ppm

6. Calculate the temporary (carbonated), permanent (non-carbonated) and total harness of water sample containing following impurities.

$CO_2$	22 mg/L
HCO <sub>3</sub> -	305 mg/L
Ca++	80 mg/L
$Mg^{++}$	48 mg/L

#### **Solution:**

S.No.	Costituents	Quantity in	Multiplication	Hardness in terms of calcium
	of hardness	mg/L or	factor	carbonate equivalent =
		ppm		quantity * multiplication factor
1	CO <sub>2</sub>	22 mg/L	100/44	22 * 100/44 = 50
2	HCO <sub>3</sub> -	305 mg/L	100/(2*61) = 100/122	305 * 100/122 = 250
3	Ca++	80 mg/L	100/40	80* 100/40 = 200
4	$Mg^{++}$	48 mg/L	100/24	48 * 100/24 = 200

 $Temporary\ hardness(\ Carbonated\ Hardness) = HCO_3^- = 250\ ppm$   $Permanent\ hardness(\ Non-Carbonated\ Hardness) = Ca^{++} + Mg^{++} - HCO_3^- = 200 + 200 - 250 = 150\ ppm$   $Total\ hardness = Temporary\ hardness + Permanent\ hardness = 250 + 150\ = 400\ ppm$ 

7. A water sample has the following analysis: Mg(HCO3)2 = 83 mg/L, Ca(HCO3)2 = 134 mg/L, CaSO4 = 124 mg/L, MgCl2 = 84 mg/L, CaCl2 = 94 mg/L and NaCl = 50 mg/L. Calculate temporary, total and permanent hardness of water.

#### **Solution:**

S.No.	<b>Costituents of</b>	Quantity in	Multiplication	Hardness in terms of calcium
	hardness	mg/L or	factor	carbonate equivalent =
		ppm		quantity * multiplication
				factor

1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	134 mg/L	100/162	134 *100/162 = 82.7 ppm
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	83 mg/L	100/146	83*100/146 = 56.8 ppm
3	CaSO <sub>4</sub>	124 mg/L	100/136	124 * 100/136 = 91.2 ppm
4	MgCl <sub>2</sub>	84 mg/L	100/95	84 * 100/95 = 88.4 ppm
5	CaCl <sub>2</sub>	94 mg/L	100/111	94*100/111= 84.7 ppm
6	NaCl	50 mg/L	X	X

Temporary hardness =  $Ca(HCO_3)_2 + Mg(HCO_3)_2 = 82.7 + 56.8 = 139.5$  ppm Permanent hardness =  $CaSO_4 + MgCl_2 + CaCl_2 = 91.2 + 88.4 + 84.7 = 264.3$  ppm Total hardness = Temporary hardness + Permanent hardness = 139.5 + 264.3 = 403.8 ppm

#### PROBLEMS BASED ON SODA-LIME METHOD:

1. Calculate the amount of lime and soda required for softening 50000 litres of water containing the following impurities.

A  $Ca(HCO_3)_2 = 9.2 \text{ mg/L}$ ,  $Mg(HCO_3)_2 = 7.9 \text{ mg/L}$ ,  $CaSO_4 = 15.3 \text{ mg/L}$ ,  $MgSO_4 = 15.0 \text{ mg/L}$ ,

 $MgCl_2 = 3.0 \text{ mg/L} \& NaCl = 4.3 \text{ mg/L}.$ 

#### **Solution:**

S.No.	Costituents	Quantity	Multiplication	Hardness in terms of	Requirement
	of hardness	in mg/L or	factor	calcium carbonate	of Soda &
		ppm		equivalent = quantity	Lime
				* multiplication	
				factor	
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	9.2 mg/L	100/162	9.2*100/162 = 5.68	L
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	7.9 mg/L	100/146	<b>7.9</b> *100/146 = 5.41	2L
3	CaSO <sub>4</sub>	15.3 mg/L	100/136	15.3*100/136 = 11.25	S
4	MgSO <sub>4</sub>	15.0 mg/L	100/120	15.0* 100/120 = 12.5	L & S
5	MgCl <sub>2</sub>	3.0 mg/L	100/95	3.0 *100/95 = 3.16	L & S
6	NaCl	4.3 mg/L	neglected	neglected	X

$$\label{eq:limits} \begin{aligned} \text{Lime required} &= 74/100 \ [\text{Ca}(HCO_3)_2 + 2 \ Mg(HCO_3)_2 + MgSO_4 + MgCl_2] \ x \ volume \ of \ water \\ &= 74/100 \ [5.68 + (2x \ 5.41) + 12.5 + 3.16] \ x \ 50000 \\ &= 23.40 \ x \ 50000 = 1170000 \ mg = \frac{1.17 \ Kg}{1.17 \ Kg}. \\ \text{Soda required} &= 106/100 \ [\text{CaSO}_4 + MgSO_4 + MgCl_2] \ x \ volume \ of \ water \\ &= 106/100 \ [11.25 + 12.5 + 3.16] \ x \ 50000 \\ &= 28.52 \ x \ 50000 \ mg = 1426000 \ mg = \frac{1.426 \ Kg}{1.426 \ Kg}. \end{aligned}$$

2. Calculate the amount of lime (92% pure) and soda (98% pure) required for softening 30000 L of water containing the following impurities:  $Ca(HCO_3)_2 = 40.5 \text{ mg/L}$ ,  $Mg(HCO_3)_2 = 36.5 \text{ mg/L}$ ,  $CaSO_4 = 34 \text{ mg/L}$ ,  $MgSO_4 = 30 \text{ mg/L}$ ,  $CaCl_2 = 27.75 \text{ mg/L}$  Solution:

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	S.No.	Costituents	Quantity	Multiplication	Hardness in terms of	Soda & Lime
		of hardness	in mg/L	factor	calcium carbonate	Required
			or ppm		equivalent = quantity *	
					multiplication factor	
	1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	40.5 mg/L	100/162	40.5*100/162 = 25	L
	2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	36.5	100/146	<b>36.5</b> * <b>100/146</b> = <b>25</b>	2L
			mg/L			
	3	CaSO <sub>4</sub>	34 mg/L	100/136	<b>34*100/136 = 25</b>	S
	4	MgSO <sub>4</sub>	30 mg/L	100/120	<b>30* 100/120 = 25</b>	L & S
	5	CaCl <sub>2</sub>	27.75	100/111	27.75 *100/111 = 25	S

	/ <b>T</b>		
	mg/L		

Lime required = 74/100 [Ca(HCO<sub>3</sub>)<sub>2</sub> + 2 Mg(HCO<sub>3</sub>)<sub>2</sub> + MgSO<sub>4</sub>] x (100/purity) x volume of water

$$= 74/100 [25 + (2x 25) + 25] x (100/92) x 30000$$

$$= 2413043.48 \text{ mg} = 2.41 \text{ kg}$$

$$= 106/100[25 + 25 + 25] \times (100/98) \times 30000$$

$$= 2433676.47 \text{ mg} = 2.43 \text{ kg}$$

3. Calculate the amount of lime and soda required for softening 30000 liters of water, using 20 ppm of sodium aluminate as a coagulant. Impurities in water are as follows:  $Ca^{2+}=160$  ppm,  $Mg^{2+}=96$  ppm, dissolved  $CO_2=34$  ppm and  $HCO_3^-=403$  ppm.

## **Solution:**

S.No.	Costituents	Quantity	Multiplication	Hardness in terms of	Soda & Lime
	of hardness	in mg/L	factor	calcium carbonate	Required
		or ppm		equivalent = quantity	
				* multiplication	
				factor	
1	Ca <sup>2+</sup>	160	100/40	160*100/40 = 400	S
2	$Mg^{2+}$	96	100/24	96 *100/24 = 400	L & S
3	CO <sub>2</sub>	34	100/44	<b>34*100/44</b> = <b>77.27</b>	L
4	HCO <sub>3</sub> -	403	100/122	403* 100/122 = 330.33	L & -S
5	NaAlO <sub>2</sub>	20	100/164	20 *100/ 164 = 12.20	-L

Lime required =  $74/100 [Mg^{2+} + CO_2 + HCO_3 - NaAlO_2] x$  volume of water

Lime required = 74/100 [400 + 77.27 + 330.33 - 12.20] X 30000 = 17657880 mg = 17.66 kg

Soda required = 106/100 [Ca<sup>2+</sup> + Mg<sup>2+</sup> - HCO<sub>3</sub>] x volume of water

Soda required =  $106/100 [400 + 400 - 330.33] \times 30000 = 14935506 \text{ mg} = 14.94 \text{ kg}$ 

4. A sample of water contains following impurities  $Ca(HCO_3)_2 = 4.86$  mg/l;  $Mg(HCO_3)_2 = 7.3$  mg/l,  $Ca SO_4 = 6.8$  mg/l,  $MgSO_4 = 9$  mg/l,  $MgCl_2 = 5.7$  mg/l,  $SiO_2 = 3.5$  ppm, NaCl = 5.85 ppm. Calculate the quantity of lime and soda needed for softening 25000 L of water. Also write the chemical reactions takes place for above impurities.

#### **Solution:**

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	S.No.	Costituents	Quantity	Multiplication	Hardness in terms of	Soda & Lime
		of hardness	in mg/L	factor	calcium carbonate	Required
			or ppm		equivalent = quantity *	
					multiplication factor	
	1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	4.86 mg/L	100/162	4.86 * (100/162) = 3	L
	2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	7.3 mg/L	100/146	7.3 * (100/146) = 5	<b>2</b> L
1	3	CaSO <sub>4</sub>	6.8 mg/L	100/136	6.8 * (100/136) = 5	S
	4	MgSO <sub>4</sub>	9 mg/L	100/120	9 * (100/120) = 7.5	L & S
	5	MgCl <sub>2</sub>	5.7 mg/L	100/95	<b>5.7</b> * (100/95) = 6	L & S
	6	SiO <sub>2</sub>	3.5 mg/L	neglected	neglected	neglected
	7	NaCl	5.85 mg/L	neglected	neglected	neglected

Lime required = 74/100 [Ca(HCO<sub>3</sub>)<sub>2</sub> + 2 Mg(HCO<sub>3</sub>)<sub>2</sub> + MgSO<sub>4</sub> + MgCl<sub>2</sub>] x volume of water

= 74/100 [3 + (2x 5) + 7.5 + 6] x 25000

= 490250 mg = 0.49 kg

Soda required = 106/100 [CaSO<sub>4</sub> + MgSO<sub>4</sub> + MgCl<sub>2</sub>] x volume of water

5. A sample of water contains following impurities  $MgCO_3=84$  mg/l,  $CaCO_3=40$  mg/l,  $MgCl_2=95$  mg/l,  $CaCl_2=111$  mg/l,  $Mg(NO_3)_2=37$ mg/l & KCl=5.0 mg/l. Calculate the quantity of lime(74%) pure and soda(92%) pure needed for softening 20000 L of water. Solution:

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S.No.	Costituents of hardness	Quantity in mg/L or ppm	Multiplication factor	Hardness in terms of calcium carbonate equivalent = quantity * multiplication factor	Soda & Lime Required
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	4.86 mg/L	100/162	4.86 * (100/162) = 3	L
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	7.3 mg/L	100/146	7.3 * (100/146) = 5	2L
3	CaSO <sub>4</sub>	6.8 mg/L	100/136	6.8 * (100/136) = 5	S
4	MgSO <sub>4</sub>	9 mg/L	100/120	9 * (100/120) = 7.5	L & S
5	MgCl <sub>2</sub>	5.7 mg/L	100/95	5.7 * (100/95) = 6	L & S
6	SiO <sub>2</sub>	3.5 mg/L	neglected	neglected	neglected
7	NaCl	5.85 mg/L	neglected	neglected	neglected

Lime required = 74/100 [Ca(HCO<sub>3</sub>)<sub>2</sub> + 2 Mg(HCO<sub>3</sub>)<sub>2</sub> + MgSO<sub>4</sub> + MgCl<sub>2</sub>] x (100/purity) x vol. of water

Soda required = 
$$106/100$$
 [CaSO<sub>4</sub> + MgSO<sub>4</sub> + MgCl<sub>2</sub>] x (100/purity) x volume of water =  $106/100[5 + 7.5 + 6]$  x (100/92)x 25000 =  $532880.4$  mg =  $0.53$  kg

## PROBLEMS BASED ON ZEOLITE METHOD:

1. An exhausted Zeolite softener was regenerated by passing 150 litres of NaCl, having a strength of 150 g/l of NaCl. How many litres of hard water sample, having hardness of 600 ppm, can be softened, using this softener?

**Solution: Given Volume of NaCl = 150 L** 

**Total volume of NaCl solution required for treatment = 150 L** 

So total NaCl required =  $150 \times 150 = 22500g = 22500 \times 10^3 mg$ .

Or in terms of equivalent =  $22500 \times 10^3 \times (100/117) = 1.923 \times 10^7 \text{ mg}$ 

Let the volume of water is = V L

So,  $600 \text{ mg/L} \times V = 1.923 \times 10^7 \text{ mg}$ 

 $V = 1.923 \times 10^7 \text{ mg} / 600 \text{ mg/L} = 32050 \text{ Ltrs.}$ 

2. 10000 L of hard water can be softened using Zeolite softener. The softner then required 200 L of NaCl solution(containing 5.86 % NaCl) for regeneration. Calculate the hardness of water sample.

Solution: Given %oNaCl = 5.86,

So Strength of NaCl =  $5.86 \times 10 = 58.6 \text{ g/L}$ 

Total volume of NaCl solution required for treatment = 200 L

Vol. NaCl solution x Strength of NaCl x 1000 x 100

**Hardness of Water =** 

Vol. of Hard water x 2 x 58.5

Hardness of Water = 
$$\frac{200 \times 58.6 \times 1000 \times 100}{10000 \times 2 \times 58.5} = 1001.7 \text{ ppm}$$

3. The hardness of 1000 L of a sample of water was removed by passing it through a zeolite softener. The zeolite softner then required 30 litres of NaCl solution, having strength of 1.50 g/l of NaCl for regeneration. Calculate the hardness of water sample.

**Solution: Given** 

Strength of NaCl = 1.50 g/L

Total volume of NaCl solution required for treatment = 30 L

Vol. NaCl solution x Strength of NaCl x 1000 x 100

**Hardness of Water =** 

Vol. of Hard water x 2 x 58.5

Hardness of Water = 
$$\frac{30 \times 1.50 \times 1000 \times 100}{1000 \times 2 \times 58.5} = 38.46 \text{ ppm}$$

4. The hardness of 10000 L of a sample of water was removed by passing it through a zeolite softener. The zeolite softner then required 58.5 litres of NaCl solution, having strength of 25 g/l of NaCl for regeneration. Calculate the hardness of water sample.

**Solution: Given** 

Strength of NaCl = 25 g/L

**Total volume of NaCl solution required for treatment = 58.5 L** 

Vol. NaCl solution x Strength of NaCl x 1000 x 100

**Hardness of Water =** 

Vol. of Hard water x 2 x 58.5

Hardness of Water = 
$$\frac{58.5 \times 25 \times 1000 \times 100}{10000 \times 2 \times 58.5} = 125 \text{ ppm}$$

## PROBLEMS BASED ON ALKALINITY OF WATER:

1. 20 ml of std water containing 1 g of pure CaCO<sub>3</sub> per lit consumed 25 ml of EDTA. 100 ml of water sample consumed 18 ml of EDTA using EBT as indicator. While same water sample requires 12 ml of EDTA solution Calculate carbonate and non-carbonate hardness of water 20 ml of std water containing 1 g of pure CaCO<sub>3</sub> per lit consumed 25 ml of EDTA. 100 ml of water sample consumed 18 ml of EDTA using EBT as indicator. While same water sample requires 12 ml of EDTA solution Calculate carbonate and non-carbonate hardness of water?

**Solution:** 1ml of std water = 1mg of KOH

20 ml of std water = 20 mg of CaCO<sub>3</sub> 25 ml of std water = 20 mg of CaCO<sub>3</sub>

1 mi of EDTA = 20/25 mg of CaCO<sub>3</sub> = 0.8 mg of CaCO<sub>3</sub>

 $1000 \text{ ml of H}_2\text{O} = 1000/100 \text{ X } 18\text{X } 0.8$ 

Total hardness = 144 ppm

 $1000 \text{ ml of H}_2\text{O} = 1000/100 \text{ X } 12\text{X } 0.8$ 

Permanent hardness = 96 ppm

**Temporary harness = Total hardness – permanent hardness** 

Temporary harness = 144 - 96

Temporary harness = 48 ppm

2. 100 ml of a water sample requires 20 ml of EDTA solution for titration. 1 ml of EDTA solution is equivalent to 1.1 mgs of CaCO<sub>3</sub>. Calculate hardness in ppm.

**Solution:** Given 1 ml of EDTA solution = 1.1 mgs of CaCO<sub>3</sub>

∴ 20 ml of EDTA solution = 20 × 1.1 mgs of CaCO<sub>3</sub> = 22 mgs of CaCO<sub>3</sub>

100 ml of water sample requires = 20 ml of EDTA = 22 mgs of CaCO<sub>3</sub>

∴ 1000 ml of water sample =  $22 \times 1000 \ 100 \ \text{mgs}$  of CaCO<sub>3</sub>

Hardness = 220 mgs/lit or ppm.

3. 100 ml of a sample of water requires 18 ml of an EDTA solution for titration. 22 ml of thesame EDTA solution was required for the titration of 100 ml of standard hard water containing 1 gm CaCO<sub>3</sub> per litre. Calculate hardness of water sample in ppm.

Solution: Given 1 litre of std. hard water contains 1 gm of CaCO3 i.e.

1000 ml of std. hard water contains 1000 mgs of CaCO<sub>3</sub>

∴ 1 ml of std. hard water = 1 mg of CaCO<sub>3</sub>

22 ml of EDTA = 100 ml of std. hard water =  $100 \times 1$  mg of CaCO<sub>3</sub>

 $\therefore$  1 ml of EDTA = 100/22mgs of CaCO<sub>3</sub>

100 ml of sample of water = 18 ml of EDTA =  $18 \times 100 / 22$  mgs of CaCO<sub>3</sub>

: for 1000 ml of sample of water =  $18 \times 100 / 22 \times 1000 \times 100$ 

Hardness = 818.18 mgs/lit or ppm

4. 0.28 gm of CaCO<sub>3</sub> was dissolved in HCl and the solution was made up 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 33 ml of same EDTA solution on titration. 100 ml of this water, after boilingcooling and filtering required 10 ml of EDTA solution on titration. Calculate the temporary and permanent harness of water.

**Solution:** Given 1000 ml of std. hard water contains = 0.28 gm of CaCO3 ie.,

1000 ml of std. hard water contains =  $0.28 \times 1000$  mgs of CaCO3 = 280 mgs of CaCO3

∴ 1 ml of std. hard water = 0.28 mg of CaCO3

28 ml of EDTA = 100 ml of the std. hard water =  $100 \times 0.28$  mgs of CaCO3 =  $100 \times 0.28$  x28 1 ml of EDTA = 1 mgs of CaCO3.

**Total hardness** 100 ml of hard water = 33 ml of EDTA = 33 × 1 mgs of CaCO3 = 33 mgs of CaCO3

: 1000 ml of hard water =  $33 \times 1000/100$ 

Total hardness = 330 mgs/lit (or) ppm.

**Permanent hardness (NCH)** 100 ml of the same water, after boiling, cooling and filtering required = 10 ml of EDTA =  $10 \times 1 \text{ mgs}$  of CaCO3 = 10 mgs of CaCO3

 $\therefore$  1000 ml of the water =  $10 \times 1000 \ 100 \ \text{mgs}$  of CaCO3

Permanent hardness = 100 mgs/lit (or) ppm.

Temporary hardness (CH)

Temporary hardness = Total hardness = permanent hardness = 330 - 100 Temporary hardness = 230 mgs/lit (or) ppm.

5. 100 ml of a sample of water required 25.0 ml of 0.01 M EDTA for the titration using Eriochrome-Black-T indicator. Calculate the total hardness.

**Solution:** We know that, 1 ml of 0.01 M EDTA = 1 mg of CaCO3

25 ml of 0.01 M EDTA = 25 mgs of CaCO3

100 ml of sample of water required = 25.0 ml of 0.01 M EDTA = 25.0 mgs of CaCO3 equivalent

 $\therefore$  1000 ml of water is equal to = 25.0 × 1000 100 mgs of CaCO3 equivalent

Total hardness = 250 mgs/lit or ppm.

6. Calculate permanent hardness from the following. 500 ml of a water sample is boiled for 1 hr. It isthen cooled and filtered. The filtrate is made up to 500 ml again with distilled water. 50 ml of this solution requires 10 ml of N/50 EDTA with EBT-indicator and NH4Cl – NH4OH buffer.

**Solution:** Given 50 ml of water sample after boiling, filtering requires 10 ml of N / 50 EDTA

We know that, 1 ml of N /50 EDTA  $\equiv$  1 mg of CaCO3 equivalent hardness

 $\therefore$  10 ml of N /50 EDTA = 10 mgs of CaCO3

50 ml of the boiled water sample requires = 10 ml of N/50 EDTA = 10 mgs of CaCO3

 $\therefore$  1000 ml of the water sample =  $10 \times 1000 / 50$ 

Permanent hardness = 200 mgs/lit or ppm.

7. 100 ml of a sample of water required 15.0 ml of 0.01 M EDTA for titration using Eriochrome Black-T indicator. In another experiment, 100 ml of the same sample was boiled to remove the CH, the precipitate was removed and the cold solution required 8.0 ml of 0.01 M EDTA using Erio-chrome Black-T indicator. Calculate (i) the total hardness, (ii) permanent hardness or NCH, (iii) carbonate hardness (CH), in terms of mg/lit of CaCO3.

**Solution:** We know that, 1 ml of 1 M EDTA  $\equiv$  100 mgs of CaCO3

1 ml of 0.01 M EDTA  $\equiv$  1 mg of CaCO3

**Total Hardness** 100 ml of a sample of water required = 15 ml of 0.01 M EDTA =  $15 \times 1$  mgs = 15 mgs of CaCO3

 $\therefore$  1000 ml of sample of water is equivalent to =  $15 \times 1000/100$  mgs of CaCO3 = 150 mgs of CaCO3 equivalents

Total hardness = 150 mgs/lit or ppm.

**Permanent Hardness (NCH)** 100 ml of the same water sample after boiling, filtering consumes = 8.0 ml of 0.01 M EDTA =  $8.0 \times 1 \text{ mgs} = 8.0 \text{ mgs}$  of CaCO3

 $\therefore$  1000 ml of sample of water is equal to =  $8.0 \times 1000/100$  mgs = 80 mgs of CaCO3 equivalents Permanent hardness of the water sample = 80 ppm.

**Temporary Hardness (CH)** Temporary hardness = Total hardness - Permanent hardness = 150 - 80 = 70 ppm

Temporary hardness = 70 ppm.

8. 100 ml of a water sample required 20 ml of 0.01 M EDTA for the titration with Eriochrome Black- T indicator 100 ml of the same water sample after boiling and filtering required 10 ml of 0.01 M EDTA. Calculate the total, carbonate and non-carbonate hardness of the sample.

**Solution:** We know that , 1 ml of 1 M EDTA  $\equiv$  100 mgs of CaCO3

1 ml of 0.01 M EDTA  $\equiv$  1 mg of CaCO3

**Total Hardness** 100 ml of a sample of water required = 20 ml of 0.01 M EDTA =  $20 \times 1$  mgs = 20 mgs of CaCO3

 $\therefore$  1000 ml of sample of water is equivalent to =  $20 \times 1000/100$  mgs of CaCO3 = 200 mgs of CaCO3 equivalent

Total hardness = 200 mgs/lit or ppm.

**Non-carbonate Hardness (NCH)** 100 ml of the same water sample after boiling, filtering consumes = 10 ml of  $0.01 \text{ M EDTA} = 10 \times 1 \text{ mgs} = 10 \text{ mgs}$  of CaCO3

 $\therefore$  1000 ml of sample of water is equal to =  $10 \times 1000 / 100$  mgs = 100 mgs of CaCO3 equivalent Permanent hardness of the water sample = 100 ppm.

**Carbonate Hardness** (CH) Carbonate hardness = Total hardness - Non-carbonate hardness = 200 - 100 = 100 ppm

Carbonate hardness = 100 ppm.

9. In an estimation of hardness of water by EDTA titration, 250 ml of a sample of water required 15ml of 0.025 M EDTA solution to get the end point. Calculate the hardness of water.

**Solution:** We know that 1 ml of 1 M EDTA  $\equiv$  100 mgs of CaCO3 1 ml of 0.01 M EDTA  $\equiv$  1

mg of CaCO3

∴ 1 ml of  $0.0\beta5$  M EDTA = 2.5 mgs of CaCO3 equivalent

**Total Hardness**: 250 ml of a sample of water required = 15 ml of 0.025 M EDTA =  $15 \times 2.5$  mgs = 37.5 mgs of CaCO3 equivalent

 $\div$  1000 ml of a sample of water required = 37.5  $\times$  1000 250 mgs = 150 mgs of CaCO3 equivalent

Total hardness = 150 ppm.

#### **UNIT-4 FUELS AND COMBUTION**

**FUELS:** Fuels are the main energy sources for industry and domestic purposes.

"A fuel is a substance containing carbon as the major constituent which provides energy on combustion for industry and domestic purposes". **OR** 

"The chemical substance which on combution produce energy, that can be used for producing power is called fuel". **OR** 

"Fuel is a combustible substance which may be burnt to supply energy and heat without production of exclusively objectionable biproducts".

For Example: Coal, Charcoal, Wood, fossil fuel, Petrol etc.

### Characteristics of a good fuel:

- The fuel should be easily available.
- It should be cheap.
- It shoulld be easily transportable.
- It should has high calorific value.
- It must have moderate ignition temperature.
- It should leave less ash after combustion.
- It should be dry and should have less moisture content. Dry fuel increases its calorific value.
- The combustion speed of a good fuel should be moderate.
- It should not burn spontaneously to avoid fire hazards.
- Its handling should be easy and should not give poisonous gases after combustion.
- The combustion of a good fuel should not be explosive.

**FLASH POINT:** The flash point is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material.

**FIRE POINT:** The fire point of a fuel is the lowest temperature at which the vapour of that fuel will continue to burn for at least 5 seconds after ignition by an open flame.

**IGNITION POINT:** The ignition temperature or kindling point of a substance is the lowest temperature at which it spontaneously ignites in normal atmosphere without an external source of ignition, such as a flame or spark.

**CALORIFIC VALUE:** The minimum amount of energy librated when unit mass or unit volume of a fuel is burnt completely in excess of air is called calorific value.

**UNITS OF CALORIFIC VALUE:** Calorie, Kilo calorie, Joules, Kilo Joules, Ergs & British Thermal Unit (B.Th.U.)

 $1 \text{ Cal} = 4.2 \text{ J} = 4.2 \text{ x } 10^7 \text{ ergs}$ 

1 kcal = 1000 cal. 1 kJ = 1000 J

1 B.Th.U. = 252 cal = 0.252 kcal

**GROSS CALORIFIC VALUE (GCV OR HCV):** The toatal amount of energy librated when unit mass or unit volume of a fuel is burnt completely in excess of air and the product of combution are cooled at room temperature is called gross calorific value or high calorific value. It is represented by GCV or HCV.

**NET CALORIFIC VALUE (NCV OR LCV):** The net amount of energy librated when unit mass or unit volume of a fuel is burnt completely in excess of air and the product of combution are allowed to escape is called net calorific value or low calorific value. It is represented by NCV or LCV.

#### **CLASSIFICATION OF FUELS:** Fuels can be classified as follows

- 1. On the basis of origin or occurrence:
  - **A.** Natural Fuel Or Primary Fuel: The fuel which is obtained from the nature is called natural fuel or primary fuel.
    - For Example: wood, coal, fossil fuel, natural gas, petroleum etc.
  - **B.** Man-made Or Secondary Fuel: The fuel which is formed from natural fuel is called manmade or secondary fuel.
    - For Example: Petrol, diesel, kerosene oil, biogas, coke etc.
- 2. On the basis of Physical State:
  - **A. Solid Fuel:** The fuel (primary or secondary) which exist in solid state is called solid fuel. **For Example:** Wood, peat, lignite, dung, bituminous coal, anthracite coal, coke and charcoal.
  - **B.** Liquid Fuel: The fuel (primary or secondary) which exist in liquid state is called liquid fuel. For Example: Crude oil, Petrol, diesel and kerosene oil etc.
  - **C. Gaseous Fuel:** The fuel (primary or secondary) which exist in gaseous state is called gaseous fuel.

For Example: Natural gas, Coal gas, oil gas, bio gas, water gas etc.

## Characteristics of Solid, Liquid and Gaseous Fuel:

S.No.	Characteristic	Solid Fuel	Liquid Fuel	Gaseous Fuel
	<b>Property of A Fuel</b>			
1	Cost	Cheap	Costlier than solid fuels	Costly
2	Storage	Easy to store	Closed containers should be used for storing	Storage space required is huge and should be leak proof.
3	Risk towards fire hazards	Less	More	Very high, since these fuels are highly inflammable
A	Combustion rate	It is a slow process	Fast process	Very rapid and efficient
5	Combustion control	Cannotbe controlled	Cannot be controlled or stopped when necessary	Controlled by Regulating the supply of air
6	Example	Coal, Wood	Crude Oil, Petrol	Coal gas, CNG

**COAL:** Coal is a fossil fuel which occurs in layers in the earths crust. It is formed by the partial decay of plant materials accumulated millions of years of ago and further altered by action of heat and pressure. The process of conversion of wood into coal can be represented as

#### Wood → Peat → Lignite → Bituminous Coal → Anthracite

**Types of Coal:** Generally coal can be divided into 4 parts.

- 1. Vast Peat Coal: It occurs in the temperate climate of the world. It is formed by the partial decomposition of vegetable & woody material under marshy conditions. Its calorific value range is 4000 to 5000 Kcal/Kg.
- **2. Lignite Coal or Brown Coal:** It is brown in colour and it is the intermediate stage between peat and bituminius coal. Its calorific value range is 4000 to 6000 Kcal/Kg.
- **3. Bituminious Coal or Soft Coal or Black Coal:** It is compact black substance and it is most widely used form of coal. It is used for steam generation and manufacturing of electricity.
- **4. Antracite Coal:** It is much less abundent form of coal. It contains volatile matter. It has very high calorific value. It is used in industries.

	: Fuel part, is	Percentage carbon	Calorific value (kcal/kg)	Main opplications
1.	Wood	50	4000 to 4500	Domestic fuel
2.	Peat	57	4125 to 5400	Used when there is deficiency of high rank coals.
3.	Lignite	67	6500 to 7100	Used for steam generation in thermal power plants and for the production of producer gas.
4.	Bituminous	83	8000 to 8500	Used for steam generation in thermal plants and for domestic heating. It is also used for making coal gas and metallurgical coke.
5.	Anthracite	93	8650 to 8700	Used in metallurgical purposes where no smoke and high local heat is desired. It is also used in household purposes and steam raising.

**ANALYSIS OF COAL:** To determine the composition of coal or fuel quantitatively as well as qualitatively is called analysis of coal or fuel. It involves two steps.

- 1. Proximate Analysis of Coal: To determine the percentage of moisture content, volatile matter content, fixed carbon content and ash content is called proximate analysis of coal. Method or Process:
  - **A. Moisture Content:** About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110 °C for one hour. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed. Loss in weight is reported as moisture.

Weight of moisture x 100	Loss in weight due to moisture removal x 100	
=	·	
Mass of Fuel or coal	Mass of Fuel or coal	

**B.** Volatile Matter: The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at  $925 \pm 20C$ . The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

	Wt. of Volatile Matter x 100	Loss in wt. due to Volatile Matter removal x 100
% Volatile Matter Content =	=	
	Mass of Fuel or coal	Mass of Fuel or coal

**C.** Ash Content: The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at  $700 \pm 50$  °C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

```
Weight of Ash x 100

% Ash Content =

Mass of Fuel or coal
```

% Moisture Content =

- D. Fixed carbon Content: Percentage of fixed carbon = 100 % of (Moisture + Volatile matter + ash)
- 2. Ultimate analysis of coal: This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of percentage of carbon, hydrogen, nitrogen, suphur and oxygen.
  - **A. Carbon and Hydrogen:** About 1 to 2 gram of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO<sub>2</sub> and H<sub>2</sub>O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl<sub>2</sub> tubes of known weights. The increase in weights of these are then determined.

 $C + O_2 \rightarrow CO_2$   $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$   $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$  $CaCl_2 + 7 H_2O \rightarrow CaCl_2.7H_2O$ 

Percentage of C = <u>Increase in weight of KOH tube X 12 X 100</u>

Weight of Coal sample taken X 44

OR

Percentage of  $C = W_{\underline{eight}} \text{ of } CO_2 \times 12 \times 100$ 

Weight of Coal sample taken X 44

Percentage of H = <u>Increase in weight of CaCl<sub>2</sub> tube X 2 X 100</u> Weight of Coal sample taken X 18

OR

Percentage of  $H = Weight of H_2O X 2 X 100$ 

Weight of Coal sample taken X 18

**B. Nitrogen:** About 1 gram of accurately weighed powdered coal is heated with concentrated H<sub>2</sub>SO<sub>4</sub> along with K<sub>2</sub>SO<sub>4</sub> (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

#### Percentage of $N = Volume acid X Normality of acid X_1.4$

### Weight of coal taken

C. Sulphur: Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted in to Sulphate. The washings are treated with Barium chloride solution, when Barium-sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

# Percentage of Sulphur = Weight of BaSO<sub>4</sub> obtained X 32 X 100 Weight of coal sample taken in bomb X 233

**D. Percentage of Halogens:** In this process known mass of coal is acidified with nitric acid thn treated with silver nitrate solution. Colour of precipitate determine the presence of

chloride ( white curdy ppt), bromide (pale yellow ppt) and iodide ( dark yellow ppt). The percentage of halogens can be determined as:

Percentage of Chloride = Weight of AgCl obtained X 35.5 X 100 Weight of coal sample X 143.5

Percentage of Bromide = Weight of AgBr obtained X 80 X 100
Weight of coal sample X 188

Percentage of Iodide = Weight of AgI obtained X 127 X 100
Weight of coal sample X 235

E. Percentage of Oxygen:

Percentage of Oxygen = 100 - % of (%C + %H + %N + %X + %S + %Ash)

## Solved Numerical Examples based on Proximate and Ultimate Analysis

**Example 10** A sample of coal was analysed as follows:

Exactly 1.5 gm of coal was weighed into a silica crucible. After heating for one hour at  $100^{\circ}$ C, the residue weighed 1.415 gm. The crucible was then covered with a vented lid and strongly heated for exactly seven minutes at  $950 \pm 20^{\circ}$ C. The residue weighed 0.528 gm. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weight 0.254 gm. Calculate

- (i) The percentage results of the above analysis,
- (ii) To which type of analysis does the above description below? Why is the analysis so-named?

  [UPTU, 2nd Sem., 2010-11]

Solution. (i) (a)

% of moisture = 
$$\frac{\text{Loss in weight due to removal of moisture}}{\text{weight of coal sample taken}} \times 100 = \left[\frac{A - B}{A}\right] \times 100$$
  
=  $\frac{1.5 - 1.415}{1.5} \times 100 = 5.67\%$ 

(b)

% of volatile matter = 
$$\frac{\text{Loss in weight due to removal of volatile matter}}{\text{weight of coal sample taken}} \times 100 = \left[\frac{B-C}{A}\right] \times 100$$
  
=  $\frac{1.415 - 0.528}{1.5} \times 100 = 59\%$ 

(c) % of ash = 
$$\frac{\text{weight of ash formed}}{\text{weight of dry coal taken}} \times 100 = \left[\frac{D}{A}\right] \times 100 = \frac{0.254}{1.5} \times 100 = 16.93\%$$

(d) Fixed Carbon (%) = 
$$100 - \%$$
 of (moisture + volatile matter + ash)  
=  $100 - (5.67 + 59 + 16.93) = 18.4\%$ 

(ii) This type of analysis is known as proximate analysis because the data collected vary with the procedures adopted.

Example 11 3.25 gm of the coal was Kjeldahlized and  $NH_3$  gas thus evolved was absorbed in 45 mL of 0.1 N  $H_2SO_4$ . After absorption, the excess (residual) acid required 11.5 mL of 0.1 N NaOH for exact neutralization. Determine the percentage of nitrogen in the sample of coal.

[UPTU, 2009]

Solution. Amount of sulphuric acid used to neutralize the ammonia evolved

$$= (0.1 \times 45 - 0.1 \times 11.5) \text{ milli equivalents}$$
$$= \frac{0.1 (45 - 11.5)}{1000} \text{ equivalents}$$

:. Weight of Nitrogen = 
$$\frac{0.1(45-11.5)}{1000} \times 14 = 0.0469$$

$$=\frac{0.0469}{3.25}\times100=1.44\%$$

**Example 12** 0.1 gm of a sample of coal was used in a bomb calorimeter for the determination of calorific value. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium chloride solution and a precipitate of barium sulphate was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.01 gm. Calculate the percentage of sulphur in the coal sample.

Solution. Percentage of sulphur = 
$$\frac{\text{Weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$
$$= \frac{0.01 \times 32 \times 100}{0.1 \times 233} = 1.3734\%$$

**BOMB CALORIMETER:** Bomb calorimeter is a device which is used to determine the calorific value of a solid and liquid fuel.

#### **Construction:**

Bomb calorimeter consists of a stainless steel bomb. The bomb is covered with a stainless steel lid which can be screwed over it. It contains two stainless steel electrodes and one oxygen inlet valve. One electrode is attached with a steel ring which holds the steel crucible.

Both the electrodes are attached with a magnesium fuse wire and both the electrodes are joined to the 6 volt battery.

This bomb is placed inside a copper calorimeter which consist of known amount of water.

Copper calorimeter consists of one Beckmann's thermometer and one electrical stirrer.

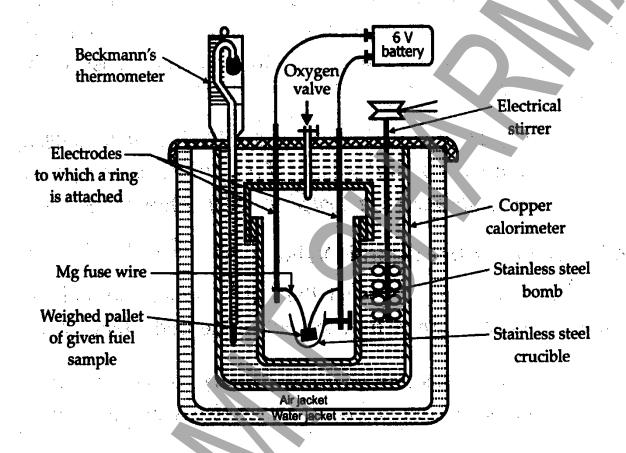
The copper calorimeter is placed inside an air jacket and water jacket to make it perfectly insulated.

#### **Working Principle:**

A known mass of fuel is burnt in crucible and the heat produced is absorbed in water and measured with the help of Beckmann's thermometer.

A weighted amount of fuel is taken in crucible and placed on the ring. It is attached with magnesium fuse wire and place inside the bomb. The bomb is now covered with a lid and screwed. The bomb is placed inside a copper calorimeter which contains W gram of water. The bomb is filled with sufficient amount of oxygen (25-30 atm pressure). The temperature of the chamber is measured through Beckmann's thermometer. Both the electrodes are then connected with 6 volt

battery. As the current pass the magnesium fuse wire start to burn and it will ignite the fuel, as a result the combustion of fuel takes place and it will generate heat, due to which the temperature of calorimeter rises which can be measured with the help of Beckmann's thermometer.



#### **Calculation:**

H. C. V. or (G. C. V.) = 
$$\frac{(W+w)(\Delta T + C_c) - (C_F + C_A + C_T)}{m}$$
 cal/g or Kcal/Kg

Where: W = mass of water taken in calorimeter in g.

w = water equivalent of copper calorimeter. = (weight of apparatus x specific heat of water)

 $\Delta T = (T_2 - T_1) = \text{observed rise in temperature}$ 

Cc = cooling correction

 $C_F$  = fuse wire correction

 $C_A$  = acid correction

 $C_T$  = Cotton thread correction

m = mass of fuel

L.C.V. or N.C.V. = G.C.V.  $-[0.09 \times \%H \times L]$  cal/g or Kcal/Kg

Where L = latent heat of condensation of water = 587 cal/g

**Example 1** A 0.80 g sample of solid fuel was completely combusted in the excess of oxygen using bomb calorimeter. The rise in temperature of water in calorimeter was 2.5°C. Calculate the High calorific value of the fuel, if water taken in calorimeter is 2000 g and water equivalent of calorimeter is 2200 g. Also calculate Low Calorific Value.

(Given: % Hydrogen in fuel = 2.2)

[UPTU, Ist Sem., 2008-09]

Solution. Given,

Weight of water taken in calorimeter = W = 2000 g,

Water equivalent of calorimeter =  $\omega$  = 2200 g

Rise in temperature =  $T_2 - T_1 = 2.5$  °C,

Weight of solid fuel combusted in the excess of oxygen using bomb calorimeter = x = 0.8 g.

Let, The high calorific value of the fuel = HCV

As 
$$HCV = \frac{(W + \omega)(T_2 - T_1)}{x}$$

$$\Rightarrow$$
 HCV =  $\frac{(2000 + 2200)(2.5)}{0.8}$  = 13125 cal/gm.

Let.

The low calorific value of the fuel = LCV

As 
$$LCV = HCV - 0.09 H \times 587$$

$$\therefore$$
 LCV = 13125 - 0.09 × 2.2 × 587 = **13008.0** cal/g.

**Example 2** 0.72 gm of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3 °C to 29.1 °C. If the calorimeter contains 250 grams of water and if its water equivalent is 150 grams, calculate the HCV of fuel.

[UPTU, Ist Sem., 2009-10; 2nd Sem., 2010-11]

Solution. Given,

Weight of water taken in calorimeter = W = 250 g,

Water equivalent of calorimeter =  $\omega$  = 150 g

Rise in temperature =  $T_2 - T_1 = 29.1 - 27.3 = 1.8$ °C,

Weight of solid fuel combusted in the excess of oxygen using bomb calorimeter = x = 0.72g. Let, The high calorific value of the fuel = HCV

As 
$$HCV = \frac{(W + \omega)(T_2 + T_1)}{x}$$

$$\Rightarrow$$
 HCV =  $\frac{(250 + 150) (1.8)}{0.72}$  = 1000 cal/gm.

**Example 3** Write the relationship between high and low calorific values. If HCV of a coal sample is 7500 cal/g and %H = 5. Calculate its LCV. Given; latent heat of condensation of steam = 580 cal/g.

[UPTU, 2nd Sem., 2009-10]

**Solution.** The relationship between high calorific value (HCV) and low calorific value (LCV) is given below:

$$LCV = HCV - 0.09(\% H) \times 580$$

Given HCV = 7500 cal/g

%H=5

$$LCV = 7500 - 0.09(5) \times 580 = 7239 \text{ cal/g}$$

**Example 4** The following data is obtained in a bomb calorimeter experiment:

Weight of crucible = 3. 649 gms.

Weight of (crucible + fuel) = 4.678 gms.

Water equivalent of calorimeter = 570 gms.

Water taken in the calorimeter = 2200 gms.

Observed rise in the temperature = 2.3 °C

Cooling correction = 0.047 °C

Acid correction = 62.6 °C

Fuse wire correction = 3.8 °C

Cotton thread correction = 1.6 calories.

Calculate the gross calorific value of the fuel sample. If the fuel contain 6.5% H, determine the net calorific value. [UPTU, 2003, 2011]

**Solution.** Weight of fuel = 4.678 - 3.649 = 1.029 gms.

Gross calorific value (GCV) =

Weight of water + equivalent of calorimeter 
$$\left(\frac{\text{Rise in temperature}}{\text{temperature}} + \frac{\text{Cooling correction}}{\text{correction}}\right) = \left(\frac{\text{Acid}}{\text{correction}} + \frac{\text{Fuse wire}}{\text{correction}} + \frac{\text{Cotton thread}}{\text{correction}}\right)$$

Weight of fuel

$$\frac{\text{Weight of fuel}}{1.029}$$

$$= \frac{2770 \times 2.347 - 68}{1.029}$$

$$= \frac{6433.19}{1.029} = 6251.88 \text{ cal/gm}$$

Net calorific value (NCV) =  $\left[\text{GCV} - (0.09 \times \% + 587)\right] \text{ cal/gm}$ 

$$= \left[6251.88 - 0.09 \times 6.5 \times 587\right] \text{ cal/gm}$$

$$= \left[6251.88 - 343.395\right] \text{ cal/gm}$$

= 5908.48 cal/gm.

Example 5 A sample of coal containing 89% C:8% H; 3% ash. When this coal was tested in the laboratory for its calorific value in the bomb calorimeter, the following data were obtained:

> Weight of coal Burnt =  $0.85 \, \text{gm}$ ; Weight of water taken =  $650 \, \text{gm}$ ; Water equivalent of bomb and calorimeter = 2500 gm; Rise in temperature =  $2.5 \,^{\circ}\text{C}$ ; Cooling correction = 0.03 °C; Fuse wire correction = 10 cal;  $Acid\ correction = 50\ Cal;$

Assuming that the latent heat of condensation of steam as 580 cal / gm, calculate the (i) gross and (ii) net calorific values of the coal in cal / gm.

## **Solution.** (i) GCV (or HCV)

$$= \frac{(W+w) (T_2 - T_1 + \text{cooling correction}) - (\text{Acid + fuse correction})}{x}$$

$$= \frac{(650 + 2500) (2.5 + 0.03) - (50 + 10)}{0.85} = 9205.2 \text{ cal / gm}$$

(ii) NCV (or LCV) = HCV - 
$$0.09 \,\text{H} \times 580$$
  
=  $9205.2 - 0.09 \times 8 \times 580$   
=  $8787.6 \,\text{cal/gm}$ 

A sample of coal contains C=93%, H=6% and ash=1%. The following data were Example 6 obtained when the above coal was tested in bomb calorimeter:

(a) Weight of coal burnt = 0.92 g

- (b) Weight of water taken = 2200 g
- (c) Water equivalent of bomb calorimeter = 550 g (d) Rise in temperature = 2.42 °C
- (e) Fuse wire correction = 10.0 cal
- (f) Acid correction = 50.0 cal

Calculate gross and net calorific values of the coal, assuming the latent heat of condensation of steam as 580 cal/g. [UPTU, 2003-04]

```
Solution. Gross calorific value (GCV), 1, pr.
                  \{(W+w)(T_2-T_1)\} - {Acid correction + Fuse wire correction}
```

Weight of coal burnt  $= x = 0.92 \,\mathrm{gm}$ ; Weight of water taken = W = 2200 gmWater equivalent of bomb calorimeter =  $w = 550 \,\mathrm{gm}$ ; Rise in temperature  $=T_2 - T_1 = 2.42$ °C Fuse wire correction =10.0 cal; and Acid correction = 50.0 cal.

$$GCV = \frac{\{(2200 + 550)(2.42)\} - \{50.0 + 10.0\}}{0.92}$$

= 7168.478 cal / gm

 $\approx$  7,168.5 cal / gm

Now, net calorific value

$$(NCV) = GCV = 0.09 H \times 580$$
  
 $NCV = 7168.5 - 0.09 \times 6 \times 580$ 

= 6,855.3 cal / gm.

## **Dulongs Formula:**

Theoretical Calculations of Gross Calorific Value (GCV) and Net Calorific Value (NCV) by Dulong's formula (using Ultimate Analysis Data for Coal).

Formulae used

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

$$NCV = [GCV - 0.09 \text{ %H} \times 587] \text{ cal/gm}$$
 ...(2)

where,

- (a) GCV  $\equiv$  HCV and NCV  $\equiv$  LCV
- (b) %C = Percentage of carbon in coal sample,

%H = Percentage of hydrogen in coal sample,

%O = Percentage of oxygen in coal sample,

%S = Percentage of sulphur in coal sample.

(c) % 
$$[C + H + N + S + Ash] = 100$$
 ...(3)

Example 7 A sample of coal contains 60% Carbon, 33% Oxygen, 6.0% Hydrogen, 0.5% Sulphur, 0.2% Nitrogen and 0.3% Ash. Calculate GCV and NCV of coal.

Solution. GCV = 
$$\frac{1}{100} \left[ 8080 \% C + 34500 \left( \% H - \frac{\% O}{8} \right) + 2240 \% S \right]_{cal}^{b} / gm$$

Given 
$$%C = 60$$
,  $%H = 6$ ,  $%O = 33$  and  $%S = 0.5$ 

$$\Rightarrow GCV = \frac{1}{100} \left[ 8080 \times 60 + 34500 \left( 6 - \frac{33}{8} \right) + 2240 \times 0.5 \right] \text{ cal/gm}$$

 $\Rightarrow$  GCV = 5506.1 cal/gm

$$NCV = (GCV - 0.09\%H \times 587) \text{ cal/gm}$$

$$\Rightarrow$$
 NCV = (5506.1 - 0.09 × 6 × 587) cal/gm

$$\Rightarrow$$
 NCV = 5189.1 cal/gm

**Example 8** The ultimate analysis of a coal gave the following results: C = 84%, S = 1.5%, N = 0.6%, H = 5.5% and O = 8%. Calculate the gross and net calorific value of the coal using Dulong's formula.

#### Solution. Given

Percentage of carbon in coal sample = %C = 84

Percentage of hydrogen in coal sample = %H = 5.5

Percentage of oxygen in coal sample = %O = 8

Percentage of sulphur in coal sample = %S = 1.5

According to Dulong's formula,

Gross calorific value (GCV) = 
$$\frac{1}{100} \left[ 8080 \times \% \text{ C} + 34500 \left( \% \text{H} - \frac{\% \text{O}}{8} \right) + 2240 \times \% \text{S} \right] \text{Cal/gm}$$
...(1)

$$\Rightarrow \qquad \text{GCV} = \frac{1}{100} \left[ 8080 \times 84 + 34500 \left( 5.5 - \frac{8}{8} \right) + 2240 \times 1.5 \right]$$

Net calorific value (NCV) = 
$$[GCV - 0.09\% H \times 587]$$
 Cal/gm ...(3)

$$\Rightarrow$$
 NCV = 48175.95 - 0.09  $\times$  5.5  $\times$  587

$$NCV = 48175.95 - 290.565$$

Example 9 Calculate LCV of a fuel which has 8% hydrogen and HCV as 6500 cal/g. Given that the latent heat of steam = 580 cal/g.

**Solution.** Given %H = 8.

$$HCV = 6500 \text{ Cal/gm}$$

$$LCV = [HCV - 0.09\% H \times 580] Cal/gm$$

$$\Rightarrow$$
 LCV = 6500 - 0.09 × 8 × 580 = 6500 - 417.6 = 6082.4 Cal/gm.