3.1 TECHNOLOGY OF WATER

INTRODUCTION

Water is the most essential compound for all living matter on the earth. It plays an important role in human living, industrial and agricultural purposes. So there is no life in the earth without water.

Sources of water

The two important sources of water are (1) surface water and (2) underground water.

Surface water

The water available on the earth’s surface is called as surface water. Surface water includes rainwater, river water, lake water and seawater.

Underground water

Underground water includes water present between the rocks in the earth crust, spring water, well water etc.

Reason for Depletion of underground water

The decrease in the quantum of underground water is depletion of water. Depletion of water is mainly caused by,

1. Modernization, industrialization and population growth
2. Global warming causing excess evaporation of surface water
3. Deforestation
4. Decrease in rainfall caused by seasonal changes and
5. Effluents from the industries spoiling the ground water source.

To meet out this depletion of ground water sources, it is essential to find alternate plans using water management techniques to recharge the ground water sources. One of the techniques adopted is rainwater harvesting.

Rainwater Harvesting

Rainwater harvesting (RWH) is a technique of capturing and storing of rainwater (tanks, slums, lake) for useful purposes and recharging the excess water into the ground.

The methods employed are

1. Roof top harvesting
2. Open space harvesting

Roof top harvesting

Rainwater is directly used for recharging open wells and bore wells by directing them into it. It can also be stored in sumps or overhead tanks and used directly.
Open space Harvesting
Open spaces around the buildings are used for rainwater harvesting as follows
1. With percolation/recharge pits
2. Recharge trenches
3. Recharge wells

The recharge method used depends on the soil condition.

Advantages of rain water harvesting
1. RHW increases the ground water level.
2. It avoids the depletion of underground water.
3. Soil erosion is prevented.
4. It also prevents flooding in urban areas during rainy season.
5. It ensures the availability of water for our future generation.

Types of impurities present in water
There are three types of impurities present in water. They are
(i) Suspended and colloidal impurities.
(ii) Dissolved salts.
(iii) Microorganisms.

Types of water
There are two types of water.
They are (i) soft water and (ii) hard water.
I. Soft water readily gives lather with soap.
II. Hard water does not give lather with soap.

Hardness of water
There are two types of hardness in water. They are:
(i) Temporary Hardness: (Carbonate hardness)
   It is due to the presence of calcium bicarbonate \([\text{Ca(HCO}_3\text{)}_2]\) and magnesium bicarbonate \([\text{Mg(HCO}_3\text{)}_2]\).
   Temporary Hardness can be removed by boiling.
(ii) Permanent Hardness: (Non-Carbonate hardness)
   It is due to the presence of chloride and sulphate salts of calcium and Magnesium. \((\text{CaCl}_2, \text{CaSO}_4, \text{MgCl}_2, \text{MgSO}_4)\). Hence it is called as permanent hard water.
Methods of expressing the Hardness.
The hardness of water can be expressed by any one of the following two methods.

Units for measuring hardness
1. **mg/litre of CaCO$_3$**
   
   It is the number of mg CaCO$_3$ of present in one litre of water or mg/lit

2. **part per million of CaCO$_3$**
   
   It is the number of parts by weight of CaCO$_3$ present in million parts of water or ppm.
   
   1 mg / litre = 1 ppm
   
   Usually, the hardness of water is expressed in terms of calcium carbonate equivalents.

   The formula used to convert the mass of hardness producing salt to the mass of CaCO$_3$ equivalent is given below.

   \[
   \text{Calcium Carbonate Equivalents} = \frac{\text{Mass of salt x Molecular mass of CaCO}_3}{\text{Molecular mass of salt}}
   \]

To prove the relation between mg/litre and ppm

Let us consider a water sample whose hardness is ‘x’ mg/litre of CaCO$_3$.

Therefore, Mass of CaCO$_3$ present in 1000ml of water = Y mg  

\[\text{i.e. Mass of CaCO}_3 \text{ present in 1000g of water } = Y \times 10^{-3}g\]

Therefore,

\[\text{Mass of CaCO}_3 \text{ present in } 10^6\text{g of water } = Y \times 10^{-3}g \times 10^6\]

\[= Y \times 1000g.\]

Hence hardness of water is \[= Y \text{ ppm.}\]

Therefore, 1 mg / litre = 1 ppm. Hence it is proved.

Even though CaCO$_3$ is not a hardness producing salt and is insoluble in water, it is used as the standard to express the hardness of water. Since the hardness producing salts are present in traces, mass of CaCO$_3$ equivalent to hardness producing salt is calculated to express the hardness of a water sample.

The formula used to convert the mass of hardness producing salt to mass of CaCO$_3$ is given as follows.

One molecular mass of \[\equiv\] one molecular mass of

Hardness producing salt \[\quad\text{CaCO}_3\]

Note: Molecular masses of hardness producing salts are given below.
<table>
<thead>
<tr>
<th>Hardness producing salt</th>
<th>Molecular Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄</td>
<td>136</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>120</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>111</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>95</td>
</tr>
<tr>
<td>Ca (HCO₃)₂</td>
<td>162</td>
</tr>
<tr>
<td>Mg (HCO₃)₂</td>
<td>146</td>
</tr>
</tbody>
</table>

1. A water sample contains 48 mg of MgSO₄ per 200 ml of water. Calculate the hardness in terms of CaCO₃ equivalent in mg/litre of CaCO₃.

One molecular mass of MgSO₄ = one molecular mass of CaCO₃

i.e. 120 mass of MgSO₄ = 100 mass of CaCO₃

Therefore mass of 48 mg of MgSO₄ = \( \frac{48 \times 100}{120} = 40 \text{ mg of CaCO}_3 \)

Mass of CaCO₃ present in 200 ml of water = 40 mg
Therefore,
Mass of CaCO₃ present in 1000 ml of water = 200 mg

Hardness of water = 200 mg/litre of CaCO₃

**Disadvantages of a hard water sample**
- Hard water cannot be used for drinking, as it does not quench thirst.
- It cannot be used for cooking purposes.
- It cannot be used for bathing and washing purposes as it does not give lather with soap.
- Hard water cannot be used in laboratories as it gives unwanted chemical reactions.
- Hard water cannot be used in boilers in steam raising.
- It cannot be used in sugar and paper industries.
- Hard water cannot be used in textile and leather industries.

**ESTIMATION OF HARDNESS OF WATER – EDTA METHOD**

EDTA method is used to determine the hardness of a sample of water. EDTA refers to Ethylene-diamine tetra acetic acid. This method is also called Modern method.
**PRINCIPLE:**

This is a volumetric method based on the principle of formation of complexes. Ethylene diamine tetra acetic acid (E.D.T.A.) forms colorless complexes with Ca$^{2+}$ and Mg$^{2+}$ ions present in water. Similarly Eriochrome Black-T, another dye, also forms wine red coloured complexes with Ca$^{2+}$ and Mg$^{2+}$ ions. Pure Eriochrome Black-T is blue in colour. At the pH range of 9 to 10, the Eriochrome complexes are less stable when compared to E.D.T.A. complexes. Thus when E.D.T.A. solution is added to Eriochrome-Ca$^{2+}$ or Mg$^{2+}$ complexes it displaces pure Eriochrome to form E.D.T.A-Ca$^{2+}$ or Mg$^{2+}$ complexes. Thus at the end point E.D.T.A. frees the total Eriochrome Black-T to change the colour of the solution from wine red to steel blue.

\[
\text{Eriochrome-Ca}^{2+} + \text{E.D.T.A} \rightarrow \text{E.D.T.A-Ca}^{2+} + \text{Eriochrome Black-T}
\]

**PROCEDURE:**

The burette is filled with the standard E.D.T.A. solution. A 50-ml pipette is washed with distilled water and rinsed with the sample of hard-water. Exactly 50 ml of hard-water is pipetted out into a conical flask and 5 ml of NH$_4$Cl - NH$_4$OH buffer solution is added. A pinch of Eriochrome Black-T indicator is added. The colour of the conical flask solution changes into wine red. The water sample is titrated against the E.D.T.A.Solution taken in the burette. The colour changes from wine red to steel blue. This is the end point of the titration. The burette reading is noted. Titrations are repeated until two consecutive values agree. From the volume of E.D.T.A. the hardness of the sample of water is calculated.

**Note:** In the estimation of hardness of water, a standard already established formula is used. This gives a standard data relating the mass of CaCO$_3$ and volume of 0.01M EDTA solution. The formula is

\[
1 \text{ml of 0.01M EDTA solution} \equiv 1 \text{mg of CaCO}_3
\]

**HARD WATER Vs EDTA**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Volume of Hard water</th>
<th>Burette Reading</th>
<th>Volume of EDTA (ml)</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial/Final</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>0/0</td>
<td>0</td>
<td>Eriochrome Black-T</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0/0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0/0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

**CALCULATION:**

Let \( V \) ml be the volume of E.D.T.A. Hard water.

\[
1 \text{ml of 0.01 M E.D.T.A.} \equiv 1 \text{mg of CaCO}_3
\]

Therefore \( V \text{ ml of 0.01 M E.D.T.A.} = V \text{ mg of CaCO}_3 \)

50 ml of Hard water contains \( V \text{ mg of CaCO}_3 \)
Therefore Weight of CaCO₃ present in 1000 ml of Hard water

\[
\frac{V \times 1000}{50} = 20V \text{ mg}
\]

**HARDNESS OF WATER = 20V mg /litre of CaCO₃**

(Note: In the estimation of hardness, 0.01M EDTA solution is prepared by dissolving 3.72 g of Disodium salt of EDTA in 1000 ml of distilled water.

NH₃ - NH₄Cl buffer solution is prepared by dissolving 67.5 g of ammonium chloride (AR) in 200ml of water and by adding 570ml of Liquor ammonia (AR) with specific gravity 0.92 and the total volume is made up to one litre.)

**Worked out Example**

1. A sample of 100 ml of hard water consumes 25 ml of 0.01M EDTA solution. Calculate the hardness of the sample of water.

Formula

1ml of 0.01M EDTA solution ≡ 1mg of CaCO₃

Therefore, 25ml of 0.01M EDTA solution ≡ 25 mg of CaCO₃

By titration, 25ml of 0.01M EDTA solution ≡100 ml of hard water

Therefore

Mass of CaCO₃ present in 100 ml of hard water = 25 mg

Therefore

Mass of CaCO₃ present in 1000ml of hard water = 250mg

Hence hardness of water = 250mg/litre of CaCO₃

To give in ppm

Mass of CaCO₃ present in 100 ml of hard water = 25 mg

Mass of CaCO₃ present in 100g of hard water = 25×10⁻³ g

Therefore

Mass of CaCO₃ present in 10⁶g of hard water = \(\frac{25\times10^{-3}g\times10^6}{100}\)

= 250g

Hence hardness of water = 250 ppm of CaCO₃

2. A sample of 100 ml of water consumed 12.5 ml of 0.01 M EDTA solution. In another titration 100 ml of the same sample, after boiling for half an hour consumed 8.2 ml of the same EDTA solution. Calculate the carbonate and non-carbonate hardness of the sample of water.

(Note: In the given problem, volume of EDTA consumed in the first titration is equivalent to total hardness of water which includes both carbonate and
non-carbonate hardness. But the volume of EDTA consumed by the water after boiling is equivalent to non-carbonate hardness as carbonate hardness in water can be removed by boiling water.)

**Total hardness**

1ml of 0.01M EDTA solution ≡ 1mg of CaCO$_3$

Therefore,

12.5ml of 0.01M EDTA solution ≡ 12.5 mg of CaCO$_3$

By titration,

12.5ml of 0.01M EDTA solution ≡100 ml of hard water

Therefore

Mass of CaCO$_3$ present in 100 ml of hard water = 12.5 mg

Therefore mass of CaCO$_3$ present in 1000ml of Hard water =

125mg

Hence Total hardness of water = 125 mg/litre of CaCO$_3$

**Non-carbonate Hardness**

1ml of 0.01M EDTA solution ≡ 1mg of CaCO$_3$

Therefore,

8.2ml of 0.01M EDTA solution ≡ 8.2 mg of CaCO$_3$

By titration,

8.2ml of 0.01M EDTA solution =100 ml of hard water

Therefore

Mass of CaCO$_3$ present in 100 ml of hard water = 8.2 mg

Therefore

Mass of CaCO$_3$ present in 1000ml of hard water = 82 mg

Hence

Non-carbonate hardness of water =82 mg/litre of CaCO$_3$

Therefore

Carbonate Hardness = Total hardness – Non-carbonate hardness

= (125 – 82) = 43 mg/litre of CaCO$_3$

**SOFTENING OF HARD WATER**

The method of converting the hard water into soft water is called softening of hard water. Two important methods of softening the hard water are 1. Ion-Exchange method 2.Reverse Osmosis method.
Ion Exchange method
(Demineralization Method or de-ionization method)

In this method the hard water is first passed through an acidic resin having replaceable hydrogen ion (RH₂) to remove the cations [Ca²⁺, Mg²⁺] and then it is passed through a basic resin [R’(OH)₂] having replaceable hydroxyl ion to remove the anion. Thus both types of ions are totally removed.

Acid resin is represented by RH₂.
Base resin is represented by R’(OH)₂.

Softening Process:
When the hard water sample is passed through the acid resin, calcium and magnesium ions are removed.

\[
\begin{align*}
2RH + Ca^{2+} &\rightarrow R_2Ca + 2H^+ \\
& \text{Acidic resin}
\end{align*}
\]

\[
\begin{align*}
2RH + Mg^{2+} &\rightarrow R_2Mg + 2H^+ \\
& \text{Acidic resin}
\end{align*}
\]

When this water is passed through the base resin, chloride, bicarbonate and sulphate ions are removed.

\[
\begin{align*}
R’OH + Cl^- &\rightarrow R’Cl + OH^- \\
& \text{Basic resin}
\end{align*}
\]

\[
\begin{align*}
2R’OH + SO_4^{2-} &\rightarrow R’_2SO_4 + 2 OH^- \\
& \text{Basic resin}
\end{align*}
\]

Acid for Regeneration

Base for Regeneration

HCl

NaOH

Hard water

Acidic resin

Cation Exchanger

Anion Exchanger

Basic resin

Soft water

ION-EXCHANGE METHOD
Thus both types of ions are removed from water. The $H^+$ and $OH^-$ ions combine together to form water.

$$H^+ + OH^- \rightarrow H_2O$$

The quality of water obtained by this method is equivalent to distilled water.

**Regeneration of Acidic Resin and Basic Resin:**

After a long use, the acidic resin can be regenerated by washing it with strong solution of Hydrochloric acid.

$$R_2Ca + 2HCl \rightarrow 2RH + CaCl_2$$

The basic resin after a long use can be regenerated by washing it with a strong solution of NaOH.

$$R'Cl + NaOH \rightarrow R'OH + NaCl$$
$$R'SO_4 + 2NaOH \rightarrow 2R'OH + Na_2SO_4$$

**Advantages**

1) In this method, both types of hardness are removed.
2) The quality of water obtained is equivalent to distilled water.
3) There is no wastage of water.

**Reverse Osmosis Method**

**Osmosis**

When two solutions of different concentrations are separated by a semi-permeable membrane, solvent molecules move from the region of low concentrated side to the region of high concentrated side until the two concentrations become equal. This process is called osmosis. The pressure gradient produced due to osmosis is called osmotic pressure.

**Reverse Osmosis**

When a hydrostatic pressure greater than the osmotic pressure is applied on the high concentration region, solvent molecules move from high concentration region to the low concentration region across the semi permeable membrane. This is called reverse osmosis. This principle is used in Reverse Osmosis plants to soften hard water.

**Method**

- In this method hard water and soft water are taken in two different chambers separated by semi permeable membrane.
- When a hydrostatic pressure greater than the osmotic pressure is applied on the hard waterside, the water molecules move from hard waterside to soft waterside leaving the impurities on the membrane due to reverse osmosis.

Thus hard water is converted to soft water by Super filtration or hyper filtration.
The semi permeable membrane is made of polysulphone or cellulose acetate or polyamide.

**Advantages**

1) In this method ionic, non-ionic, colloidal, and organic particles are removed from water.
2) The semipermeable membrane can be replaced and reused.
3) There is no wastage of water.

**MUNICIPAL WATER SUPPLY**

**WATER FOR DRINKING PURPOSE (Potable water)**

Water used for drinking should be
1. Colourless and odourless
2. Free from colloidal and suspended impurities and
3. Free from microorganisms and bacteria.

The three stages involved in purifying a water sample for drinking purpose are
1. **SEDIMENTATION**
2. **FILTRATION**
3. **STERILISATION**

**SEDIMENTATION**

Water from river or lake is taken in the big tank called sedimentation tank. Here the insoluble matter settles down at the bottom of the tank as sediments. In this tank, the colloidal impurities are converted into precipitate by adding Alum. The clear water from the top layer is sent to the next tank called Filtration tank.
FILTRATION TANK

In filtration tank, the suspended impurities and the microorganisms are removed. In all types of filtration, the filter bed used is constructed as follows.

The filter bed consists of a layer of fine sand followed by the layer of coarse sand, which is then followed, by a layer of gravel. There is a drain at the bottom to remove the filtered water. The layer of fine sand acts as the filtering unit and the other two beds support the fine sand layer. Generally filtration is done due to the gravitational force. The filtered water is then taken to the sterilization tank.

Sterilization is the process of killing the bacteria. It is done by Chlorination.

Chlorination

Chlorination is addition of chlorine. Chlorine is added to water in the acidic pH range of 6.5 to 7. When chlorine is added to water, it forms HCl and HOCl. The hypochlorous acid molecule enters into the living cells of bacteria and kills them.

\[ \text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{HCl} + \text{HOCl (Hypochlorous acid)} \]

Other sterilizing agents used apart from chlorine are chloramines, bleaching powder etc. The advantage of using chloramines is that it does not evaporate out easily and can be carried over to a longer distance along with the water.

Ultra-violet rays can also be used for sterilizing purpose.
BOILER FEED WATER

Water is used in boilers, steam engines etc., to raise steam. When a sample of hard water is used in boiler to prepare steam, the following problems will occur.

1. Scale formation
2. Corrosion of boiler metal
3. Caustic Embrittlement and
4. Priming and foaming.

Boiler Scale Formation:
When hard water is used in boilers to get steam, the impurities that are present in the hard water will settle down on the sides of the boiler. This residue in due course will adhere to the boiler vessel surface in the form of a sludge or scale. This is called as boiler scale. The following calcium salts are responsible for the formation of boiler scale \( \text{CaSO}_4, \text{CaCO}_3, \text{Ca (OH)}_2, \text{Mg (OH)}_2 \) etc.

Disadvantages of using hard water Boilers
1. The salt deposit formed is a poor conductor of heat. Therefore fuel is wasted in raising the temperature of the boiler.
2. Due to the increase in the temperature, the plates may melt. This may lead to explosion of boiler.
3. At higher temperature, more oxygen may be absorbed by the boiler metal, which causes corrosion of boiler metal.
4. The sudden spalling of the boiler scale exposes the hot metal suddenly to super-heated steam, which causes corrosion of boiler.

Methods employed to prevent scale formation are,
1. Internal conditioning method
2. External conditioning method.

1. Internal conditioning methods involve addition of complexing agents like Calgon to boiler feed water. Another method of internal conditioning is Phosphate conditioning. In this method, sodium phosphate is added to boiler feed water which forms non-sticky Calcium and Magnesium Phosphate Which can be removed by blow down operation.

2. In External conditioning methods water is purified either by Zeolite process or by ion-exchange method before being fed into boilers.

Corrosion of Boiler metal:

Water containing the following impurities is responsible for the corrosion of boiler metal. The impurities such as dissolved oxygen, dissolved Carbon dioxide, mineral acids, dissolved salts of calcium and magnesium, organic matter etc. are responsible for the corrosion of the boilers.

The dissolved matter undergoes hydrolysis and forms acids. The acid slowly attacks the inner part of the boiler.

The dissolved oxygen attacks iron at high temperature. The \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) form carbonic acid \( (\text{H}_2\text{CO}_3) \), which slowly attacks the metal.
Prevention of Boiler Corrosion:
1. By using proper water treatment procedures.
2. By degasification to remove the dissolved gases like oxygen, CO₂ etc.,
3. The dissolved CO₂ can be removed by the addition of limewater.
4. Adding calculated amount of base could neutralize the mineral acids.

Caustic Embrittlement:
Sometimes cracks appear inside the boiler parts, particularly at the places, which are under stress. Metal becomes brittle at these places. It is due to the high concentration of caustic soda (NaOH) and a little amount of silica in water. This is called as caustic embrittlement.

Caustic soda is formed by the hydrolysis of Na₂CO₃.

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2 \]

Removal of Na₂CO₃ present in water can prevent caustic embrittlement.
This can be done by the following methods.
1. By adding sulphuric acid.
2. By adding CaSO₄ and CaCl₂ to boiler water
3. By adding Na₂SO₄.
4. By adding trisodium phosphate. etc.

Foaming and Priming

Foaming
Foaming is nothing but the formation of foam. Bubbles of water will enter the surface of water inside the boilers and results in the formation of foam. Foam comes out of the boiler along with the steam. Hence the steam becomes wet and the heat content of the steam is reduced considerably. This type of wet steam spoils the machine parts where it is used.

The main cause for foaming is the presence of dissolved salts in water. Hence soft water should be used in boilers to avoid foaming.

Priming
Priming is violent and rapid boiling of water inside the boiler. Due to priming, the water particles mix up with the steam when it comes out of the boiler. Like foaming, priming also reduces the heat content of the steam and reduces the efficiency of the steam.
Main reasons for Priming:
a) Defective design of the boiler.
b) Presence of large quantities of dissolved salts, oily matter, alkaline and suspended matter.

Control
1. Priming can be controlled by proper design of the boiler
2. By uniformly heating the water in the boiler.
3. By using a better sample of water.
Summary

Students have learnt about rain water harvesting, estimation of hardness, methods of softening and bad effects of hard water in boilers.

QUESTIONS

PART – A

1. Define hard and soft waters.
2. List the salts that cause Carbonate and non-carbonate hardness in a water sample.
3. What is rain water harvesting?
4. Mention any two problems caused by using hard water sample.
5. List any two methods of softening of hard water.
6. What is osmosis?
7. What is osmotic pressure?
8. Explain reverse osmosis.
9. Name the membranes used in R.O.method of softening of hard water
10. What is ppm?
11. What is sedimentation?
12. What is sterilization of water?
13. Explain the reaction that takes place when chlorine is added to water.
14. What are boiler scales?
15. What is caustic embrittlement?
16. What is priming?
17. What is foaming?
18. Give any one problem caused by boiler scale.

PART – B

1. List the problems caused by hard water?
2. What is rainwater harvesting? What are its goals?

PART-C

2. What is regeneration of Ion-exchange plant? How is it carried out?
3. Explain Reverse Osmosis method of softening a hard water sample.
4. Explain EDTA method of estimating hardness of a sample of water.
5. Describe the method used in water supply schemes to get potable water.
6. What are boiler scales? List the problems caused by boiler scale. How to overcome this problem.
7. Explain caustic embrittlement, priming and foaming in boilers during the production of steam.
UNIT II
FUELS

INTRODUCTION

In this present age of rapid industrial development, the power requirement is increasing day-by-day. Heat energy is the main source of power. Burning of carbon, an exothermic reaction produces heat energy. Hence, the carbon compounds have been used as the main source of heat energy.

Fuel

A fuel is a substance, which on proper burning gives large amount of heat energy on combustion. It is used for domestic and industrial purposes. They contain carbon as a main constituent.

Fossil fuel

The main sources of fuels are coal and petroleum oils available in earth’s crust and they are called fossil fuels.

The other sources of fuels are
(i) Radioactive elements and
(ii) Sunlight

Calorific value of a fuel

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

Unit of heat

Heat energy is measured in terms of calorie or kilocalorie.

Calorie is the quantity of heat required to raise the temperature of 1 gram of water through 1° Centigrade (1 kcal = 1000 calories)

Gross calorific value

Gross calorific value of a fuel is defined as the total quantity of heat liberated when a unit mass of the fuel is completely burnt and the combustion products are cooled to room temperature

Gross calorific value = Heat of reaction + Latent heat of steam produced + Sensible heat obtained by cooling the combustion Products to room temperature

Net calorific value

The net calorific value of a fuel is the actual amount of heat available when unit mass of the fuel is completely burnt and combustion products are permitted to escape.

Net Calorific Value = Gross calorific value – Latent heat of water vapour formed.
Classification of fuels

Fuels are classified into natural or primary fuels and artificial or secondary fuels. Each type is further subdivided into solid, liquid and gaseous fuels.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>State of fuel</th>
<th>Natural</th>
<th>Artificial</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solid</td>
<td>Wood, peat, lignite, coal</td>
<td>Wood charcoal, coke</td>
</tr>
<tr>
<td>2</td>
<td>Liquid</td>
<td>Crude petroleum</td>
<td>Kerosene, petrol, diesel, alcohol</td>
</tr>
<tr>
<td>3</td>
<td>Gaseous</td>
<td>Natural gas</td>
<td>Water gas, producer gas, biogas, coal gas, LPG</td>
</tr>
</tbody>
</table>

Solid fuels

Wood

It is a low-grade fuel. Freshly cut wood contains 25-50% moisture. Moisture may be reduced to 25% on air-drying. The composition of moisture free wood is C = 55%; H₂ = 6%; O₂ = 43% and ash = 1%. The calorific value of dried wood is 3500 to 4500 kcal/kg. It burns with a long and non-smoky flame. It is used as a domestic fuel.

Coal

Coal is a natural fuel formed by the slow carbonization of vegetable matter buried under the earth some thousands of years ago. It is classified into four kinds based on the carbon content and the calorific value.

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

1. Peat

It is the first stage of formation of coal from wood. It is brown, fibrous jelly-like mass. It contains 80-90% moisture. The composition of peat is C = 57%; H₂ = 6%; O₂ = 35% and ash = 2.5%. The calorific value of peat is 5400 kcal/kg. It is a low-grade fuel due to high water content.

Uses
1. It is used as fertilizer.
2. It is used as packing material.

2. Lignite

Lignite is immature form of coal. It contains 20-60% moisture. Air-dried lignite contains C = 60-70% and O₂ = 20%. It burns with a long smoky flame. The calorific value of lignite is 6500-7100 kcal/kg.

Uses
1. It is used as a domestic fuel.
2. It is used as a boiler fuel for steam production.
3. It is used in the manufacture of producer gas.

3. **Bituminous coal**
   - It is a high quality fuel. Its moisture content is 4%. Its composition is C = 83%; O₂ = 10%; H₂ = 5% and N₂ = 2%. Its calorific value is 8500 kcal/kg.

   **Uses**
   1. It is used in metallurgy.
   2. It is used in steam production.
   3. It is used for making coal gas.
   4. It is also used for domestic heating.

4. **Anthracite coal**
   - It is the superior form of coal. It contains C = 92-98%; O₂ = 3%; H₂ = 3% and N₂ = 0.7%. It burns without smoke. Its calorific value is 8700 kcal/kg.

   **Uses**:
   1. It is used for steam production and household purposes.
   2. It is used for direct burning in boilers and in metallurgy.
   3. It is used in thermal power plant.
   4. It is used in coal tar distillation.
   5. It is used in glass furnaces.

**Liquid fuels**

a. **Petroleum**
   - Petroleum (Crude oil) is a naturally available liquid fuel. It is a dark greenish-brown viscous oil found deep in earth’s crust. It is composed of various hydrocarbons with small amount of other organic compounds as impurities.

**Refining of petroleum**
   - The process of purification and separation of various fractions present in petroleum by fractional distillation is called refining of petroleum. Refining is carried out in oil refineries.

**Fractional distillation**
   - It is the process of separation of various components of a liquid mixture based on the difference in their boiling points by repeated evaporation and condensation.

**Refining of petroleum – Process**
   - The crude oil is treated with copper oxide to remove sulphur impurities. Then it is repeatedly washed with sulphuric acid to remove basic impurities. It is then washed with sodium hydroxide to remove acidic impurities. Then it is
subjected to fractional distillation and various fractions are collected. The various fractions obtained and their uses are given in the table below.

**Products of fractional distillation of petroleum and their uses:**

<table>
<thead>
<tr>
<th>SL. No.</th>
<th>Fractions</th>
<th>Temperature</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gases</td>
<td>Below 30°C</td>
<td>Used as industrial and domestic fuel</td>
</tr>
<tr>
<td>2</td>
<td>Petroleum ether</td>
<td>30°C to 80°C</td>
<td>Used as a solvent</td>
</tr>
<tr>
<td>3</td>
<td>Gasoline or petrol</td>
<td>40°C to 180°C</td>
<td>Used as a solvent, fuel and in dry cleaning</td>
</tr>
<tr>
<td>4</td>
<td>Kerosene oil</td>
<td>180°C to 250°C</td>
<td>Used as illuminant and fuel</td>
</tr>
<tr>
<td>5</td>
<td>Diesel oil or gas oil</td>
<td>250°C to 320°C</td>
<td>Used as fuel for diesel engine</td>
</tr>
<tr>
<td>6</td>
<td>Heavy oil or lubricating oil</td>
<td>320°C to 400°C</td>
<td>Used for lubrication, cosmetics and in medicines</td>
</tr>
<tr>
<td>7</td>
<td>Residue or asphalt or pitch</td>
<td>Above 400°C</td>
<td>Used for road making and water proofing of roofs</td>
</tr>
</tbody>
</table>

**Cracking**

Cracking is a process by which the hydrocarbons of high molecular mass are decomposed into hydrocarbons of low molecular mass by heating in the presence or absence of a catalyst. Generally aluminum silicates are used as catalyst.

\[ \text{Cracking} \quad \begin{array}{c} \text{C}_{10}\text{H}_{22} \rightarrow \text{C}_{5}\text{H}_{12} + \text{C}_{5}\text{H}_{10} \\ \text{n-Decane} \rightarrow \text{n-Pentane} + \text{Pentene} \end{array} \]

**b. Liquid hydrogen as a fuel**

Hydrogen is a colourless and odourless gas composed of diatomic molecules. It holds greater role as fuel in future.

Liquid hydrogen is a favourable rocket fuel. On combustion, it produces more heat per gram than any other fuel. Further, it produces only water on combustion whereas the fossil fuels produce gases like SO₂, NO₂ and CO₂ causing environmental pollution. Hence, hydrogen as a fuel has more advantages than any other fossil fuels.

\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]

Hydrogen is not a primary fuel. It is obtained from other sources of energy. It can be obtained directly from water by decomposing with some energy source. Solar photovoltaic collectors are used to decompose water by electrolysis.

Hydrogen can be liquefied below its temperature of 33.1K. It is a colourless, odourless liquid below 20.2 K. When allowed to expand, it gets heated up above 22 K.
Gaseous fuels
Examples: Producer gas, water gas, CNG and LPG

Producer gas
Producer gas is a mixture of carbon monoxide and nitrogen. It also contains traces of hydrogen and carbon dioxide.

The average composition of producer gas is CO = 22-30%; H₂ = 8-12%; N₂ = 52-55% and CO₂ = 3%. Its calorific value is about 1300 kcal/m³.

Preparation
Producer gas is prepared by passing air over a red hot coke at about 1100°C in a reactor called gas producer.

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]
\[ \text{CO}_2 + \text{C} \rightarrow 2 \text{CO} \]

The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it is provided with cup and cone arrangement and an exit for producer gas. At the bottom, it has an inlet for passing air. There is an exit for the ash at the base.

Uses
1. It is used as a fuel in the extraction of metal.
2. It is used in the manufacture of glass.
3. It is used as a reducing agent in metallurgy.

Water gas
Water gas is a mixture of carbon monoxide and hydrogen. It also contains traces of carbon dioxide and nitrogen.
The average composition of water gas is CO = 41%; H₂ = 51%; N₂ = 4% and CO₂ = 4%. Its calorific value is 2800 kcal/m³.

**Preparation**

Water gas is prepared by passing steam and little air alternatively over a red hot coke at about 1000°C in a reactor. It is an endothermic reaction. So the temperature of the system decreases.

\[
C + H_2O \rightarrow CO + H_2 \text{ (Endothermic reaction)}
\]

But, the reaction between carbon and air is exothermic and raises the temperature to about 1000°C

\[
C + O_2 \rightarrow CO_2 \text{ (Exothermic reaction)}
\]

Thus, the steam and air are sent in alternatively to maintain the temperature at about 1000°C.

The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it has cup and cone feeder and an exit for water gas. At the base, inlet pipes for steam and air are provided. At the bottom, outlet for ash is also available.

**Uses**

1. It is used as a source of hydrogen gas.
2. It is used as an illuminating gas.
3. It is used as a fuel in ceramic industries.
CNG (Compressed natural gas)

CNG is a good alternative fossil fuel. It mainly contains methane. CNG is made by compressing natural gas which is found in oil deposits, landfills and waste water treatment plants to less than 1% of its volume, it occupies at standard atmospheric pressure. It is stored and distributed in hard containers at a pressure of 2900-3600 psi.

Advantages
1. It is cheaper than petrol or diesel.
2. It emits fewer pollutants like CO₂, CO, etc. In New Delhi, it is used as a fuel for entire city bus fleet, taxis and three wheelers.
3. It is safer than other fuels. In the event of a spill, it disperses quickly in air because, it lighter than air.

LPG (Liquefied petroleum gas)

1. It is a mixture of propane and butane.
2. It is stored in steel cylinder under high pressure.
3. When the cylinder is opened, it comes out in the form of gas.
4. Commercially, it is supplied under various trade names.
5. Its calorific value is 27,800 kcal/m³.

Uses
1. It is mainly used as a domestic fuel.
2. It is used as a fuel in diesel engines.
3. It is used as a motor fuel.

Relative advantages of solid, liquid and gaseous fuels

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Property</th>
<th>Solid fuel</th>
<th>Liquid fuel</th>
<th>Gaseous fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Calorific value</td>
<td>Low</td>
<td>Greater than solid fuel and less than gaseous fuel</td>
<td>Very high</td>
</tr>
<tr>
<td>2</td>
<td>Smoke production</td>
<td>High</td>
<td>Low</td>
<td>Nil</td>
</tr>
<tr>
<td>3</td>
<td>Ash formation</td>
<td>Ash produced</td>
<td>Very low</td>
<td>Nil</td>
</tr>
<tr>
<td>4</td>
<td>Storage</td>
<td>Large space needed</td>
<td>Less space needed</td>
<td>Minimum space needed</td>
</tr>
<tr>
<td>5</td>
<td>Transportation</td>
<td>More labour involved</td>
<td>Much less labour involved</td>
<td>Transported easily through pipelines</td>
</tr>
<tr>
<td>6</td>
<td>Ignition</td>
<td>Difficult</td>
<td>Easy</td>
<td>Very easy</td>
</tr>
<tr>
<td>7</td>
<td>Flame control</td>
<td>Difficult</td>
<td>Easy</td>
<td>Very easy</td>
</tr>
</tbody>
</table>
Summary
In this lesson, different types of fuels, their composition and uses are discussed. The manufacture, composition and uses of producer gas, water gas and some details about CNG and LPG are also discussed.

QUESTIONS
PART – A
1. Define fuel.
2. Define fossil fuel.
3. Define calorific value of a fuel.
4. How are fuels classified?
5. Give two examples for solid fuels.
6. Give two examples for liquid fuels.
7. Give two examples for gaseous fuels.
8. What are the varieties of coal?
9. What is petroleum?
10. What is meant by cracking?
11. What is producer gas?
13. What is water gas?
15. What are the components present in CNG?
16. Mention the uses of CNG.
17. What are the components present in LPG?
18. Mention the uses of LPG.

PART – B
1. What is refining of petroleum?
2. Write a note on liquid hydrogen as fuel.
3. Give the composition and uses of producer gas.
4. Give the composition and uses of water gas.
5. Give the composition and uses of CNG.
6. Give the composition and uses of LPG.

PART – C
1. Write a note on solid fuels.
2. Explain the fractional distillation of petroleum.
3. Describe the manufacture of producer gas. List its uses.
4. Describe the manufacture of water gas. List its uses.
5. Write a note on CNG.
6. Write a note on LPG.
7. Compare the relative advantages of solid, liquid and gaseous fuels.

TEST YOUR UNDERSTANDING
Think of how household waste can be utilized to produce gaseous fuel.
2.2 COMBUSTION

INTRODUCTION

Combustion is an exothermic chemical reaction accompanied by heat and light. To ensure complete combustion, substance should be brought to its ignition temperature. Most of the combustible substances are enriched with carbon, hydrogen and sulphur. During combustion they undergo thermal decomposition and oxidation to give products like CO₂, H₂O and SO₂ etc.

Hence for an efficient combustion it is essential that the fuel must contact with sufficient quantity of air. The air contains oxygen which is used for combustion. But the non-combustible constituents like N₂, CO₂, and H₂O do not take any oxygen from air.

Incomplete combustion occurs only when there is too little air or oxygen is supplied. During incomplete combustion the carbon monoxide is formed instead of CO₂.

Ignition temperature:

The minimum temperature at which a fuel catches fire and burns is called ignition temperature.

Definition:

The chemical reaction of a fuel with oxygen (oxidising agent) which produces heat and light energy is called combustion of a fuel.

Example: Combustion of carbon

\[
C + O₂ \rightarrow CO₂(g) + 97 \text{ kcal}
\]

The gaseous products of combustion are mainly CO, CO₂, N₂, SO₂, O₂ and H₂O which are known as flue gases. The main elements present in most of the fuels are carbon (C), hydrogen (H), oxygen (O) and sulphur (S).

Air contains 23% by mass of oxygen and 21% by volume of oxygen.

Combustion calculation by mass (for solids and liquids):

Stochiometric or minimum quantity of air required for the complete combustion of solid and liquid fuels

Substances always combine in definite proportions which are determined by the molecular masses of the substances involved and the products formed.

1. Combustion of Carbon

\[
C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}
\]

12 32 44

12 kg of carbon requires 32 kg of oxygen for complete combustion
2. Combustion of Hydrogen

\[ 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \]

4 kg of hydrogen requires 32 kg of oxygen for complete combustion.

\[ \therefore \text{For C Kg of carbon in the fuel requires} \]
\[ \frac{32}{12} \times C \text{ kg oxygen for complete combustion} \]

\[ = \frac{8}{3} \times C \text{ kg} \quad (1) \]

3. Combustion of Sulphur

\[ \text{S}_\text{(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \]

32 kg of sulphur requires 32 kg of oxygen for complete combustion.

\[ \therefore \text{For H Kg of hydrogen in the fuel requires} \]
\[ \frac{32}{4} \times H \text{ kg oxygen for complete combustion} \]

\[ = 8 \times H \text{ kg} \]

Combined hydrogen in fuel present as moisture (H\text{O}) does not undergo combustion. The rest of hydrogen only takes part in the combustion reaction.

3. Combustion of Sulphur

\[ \text{S}_\text{(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \]

32 kg of sulphur requires 32 kg of oxygen for complete combustion.

\[ \therefore \text{For C Kg of carbon in the fuel requires} \]
\[ \frac{32}{32} \times C \text{ kg oxygen for complete combustion} \]

\[ = C \text{ kg} \quad (3) \]

On combining the above three equations,

Let us assume that 1 Kg of fuel contains' C' Kg of carbon, H Kg of hydrogen and S Kg of sulphur. Then the total mass of oxygen required for the complete combustion of 1 Kg of fuel is given below:

\[ \text{The theoretical oxygen required for combustion of 1 Kg of fuel} \]
\[ = \frac{8}{3} \times C + 8H + S \text{ Kg} \]

'C' = Wt. of carbon; H = Wt. of hydrogen; S = Wt. of sulphur
Minimum mass of oxygen is calculated on the basis of complete combustion. Note. If the fuel already has some amount of oxygen, then that amount of oxygen has to be deducted from the total mass.

Minimum mass of oxygen required = Theoretical O₂ required – O₂ present in fuel

\[
\text{Total mass of oxygen required per Kg of fuel} = \left[ \frac{8}{3} \times (\text{C} + 8\text{H} + \text{S}) \right] - \frac{\text{O}_2}{M\text{o}}
\]

Where \( \frac{\text{O}_2}{M\text{o}} \) is the Mass of oxygen.

**Mass percentage of oxygen**

The mass percentage of oxygen in air = 23%

23% of Oxygen is supplied by 100% Mass of air supply.

That is, to supply 23 kg of oxygen = 100 kg of air required.

Hence, one kg of oxygen is supplied by \( \frac{100}{23} \) kg of air.

Hence the mass of air that is required for combustion of 1 kg of fuel is

\[
\text{Minimum mass of air required for combustion of 1 kg of fuel} = \left[ \frac{8}{3} \times (\text{C} + 8\text{H} + \text{S}) \right] - \frac{\text{O}_2}{M\text{o}} \times \frac{100}{23} \text{ Kg}
\]

Where C, H, O and S are the respective masses of carbon, hydrogen, oxygen and sulphur present in 1 kg of the fuel.

**Examples:**

**Example 1**

A fuel contains 90% carbon, 3.5% hydrogen, 3% oxygen and 0.5% sulphur.

Determine the stoichiometric mass of air required to completely burn 1 kg of this fuel.

\[
\begin{align*}
\text{C} &= 90\% = 0.9 \text{ kg} \\
\text{H} &= 3.5\% = 0.035 \text{ kg} \\
\text{O} &= 0.3\% = 0.03 \text{ kg} \\
\text{S} &= 0.5\% = 0.005 \text{ kg}
\end{align*}
\]

1. Combustion of carbon
For 0.9 kg of C requires oxygen for complete combustion

\[ \frac{8}{3} \times 0.9 \]

= 2.4 kg

2. Combustion of hydrogen

\[ \text{For } H \text{ kg of hydrogen in the fuel requires} \]

\[ 8 \times H \text{ kg} \]

\[ \text{0.035 kg of hydrogen requires oxygen for complete combustion} \]

\[ 8 \times 0.35 = 0.28 \text{ kg} \]

3. Combustion of Sulphur

\[ \text{The given sulphur in the fuel requires} \]

\[ \frac{32}{32} \times S \text{ kg} \]

\[ S \text{ kg} \]

\[ \text{0.005 kg of sulphur requires oxygen for complete combustion} \]

\[ \frac{32}{32} \times 0.005 \]

= 0.005 kg

Minimum mass of oxygen required for complete combustion of 1 kg of the fuel

\[ 2.4 + 0.28 + 0.005 \]

(Theoretical \( O_2 \) required)

\[ 2.685 \text{ kg} \]

Minimum mass of oxygen required = Theoretical \( O_2 \) required – \( O_2 \) present in fuel

\[ 2.685 – 0.03 \]

\[ 2.655 \text{ kg} \]

Minimum mass of air required for complete combustion of 1 kg of the fuel

\[ \frac{100}{23} \times 2.655 \]

= 11.54 kg

Example 2:
Calculate the minimum mass of air required for complete combustion of 1 kg of a fuel having the composition \( C = 92\% \), \( H_2 = 4\% \), \( O_2 = 2\% \) and ash = 2\% by weight.
C = 92% = 0.92 kg
H₂ = 04% = 0.04 kg
O₂ = 02% = 0.02 kg

1. Combustion of carbon

\[ \text{For } C \text{ Kg of carbon in the fuel requires oxygen for complete combustion} \]
\[ = \frac{8}{3} \times C \text{ kg} \]

\[ \therefore 0.92 \text{ kg of C requires oxygen for complete combustion } = \frac{8}{3} \times 0.92 \text{ kg} \]
\[ = 2.45 \text{ kg} \]

2. Combustion of hydrogen

\[ \text{For } H \text{ Kg of hydrogen in the fuel requires oxygen for complete combustion} \]
\[ = 8 \times H \text{ kg} \]

For 0.04 kg of hydrogen requires oxygen for complete combustion
\[ = 8 \times 0.04 \]
\[ = 0.32 \]

Minimum mass of oxygen required for complete combustion of 1 kg of the fuel
\[ = 2.45 + 0.32 \]
\[ = 2.77 \text{ kg} \]

Minimum mass of oxygen required = Theoretical O₂ required – O₂ present in fuel
\[ = 2.77 - 0.02 \]
\[ = 2.75 \text{ kg} \]

Minimum mass of air required for complete combustion of 1 kg of the fuel
\[ = \frac{100}{23} \times 2.75 \]
\[ = 11.96 \text{ kg} \]

Example 3:
Calculate the minimum amount of air by mass required for complete combustion of 2 kg of coke assuming 100% carbon.

\[ \text{For } C \text{ Kg of carbon in the fuel requires oxygen for complete combustion} \]
\[ = \frac{8}{3} \times C \text{ kg} \]

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Mass of O₂ required for combustion of 2 kg of coke = \( \frac{8}{3} \times 2 \) kg

= 5.33 kg

Minimum mass of air required for combustion of 2 kg of coke

\[ \text{Minimum mass of air} = \frac{100}{23} \times 5.33 \]

= 23.17 kg

**Excess air**

During combustion, there is an incomplete combustion, when stoichiometric air is supplied. In practice, excess amount of air is supplied to get complete combustion. To avoid cooling effect, about 25% to 50% preheated air is supplied.

Total mass of air/kg of fuel = Stoichiometric mass of air + Excess mass of air

Let the theoretical minimum air supplied = \( Y \) Kg

Let the Air supplied in excess is = 50%

Excess air supplied = \( \frac{150}{100} \)

Then the actual amount of air supplied per Kg of the fuel including the excess air

\[ \text{Minimum mass of air required for complete combustion of 1 kg of the fuel} = \frac{100 + 50}{100} \times Y = Y \times \frac{150}{100} = Y \times 1.5 \text{ Kg of air} \]

**Example 4**

Calculate the mass of air to be supplied for the combustion of 1 kg of a fuel containing 75% carbon, 8% hydrogen and 3% oxygen, if 40% excess air is supplied.

\[ C = 75\% = 0.75 \text{ kg} \]
\[ H = 8\% = 0.08 \text{ kg} \]
\[ O = 3\% = 0.03 \text{ kg} \]

1. Combustion of carbon

\[ \therefore \text{For } C \text{ Kg carbon in the fuel requires} \frac{8}{3} C \text{ kg oxygen for complete combustion} \]

\[ \therefore 0.75 \text{ kg of C requires oxygen for complete combustion} = \frac{8}{3} \times 0.75 \text{ kg} \]
2. Combustion of hydrogen

\[ \text{For } H \text{ kg of hydrogen in the fuel requires} \]  
\[ \text{oxygen for complete combustion} = 8 \times H \text{ kg} \]

0.08 kg of hydrogen requires oxygen for complete combustion

\[ = 8 \times 0.08 \]

\[ = 0.64 \text{ kg} \]

Minimum mass of oxygen required for complete combustion of 1 kg of the fuel

\[ = 2 \times 0.64 \]

\[ = 2.64 \text{ kg} \]

Minimum mass of oxygen required = Theoretical O₂ required – O₂ present in fuel

\[ = 2.64 - 0.03 \]

\[ = 2.61 \text{ kg} \]

Minimum mass of air required for complete combustion of 1 kg of the fuel

\[ = \frac{100}{23} \times 2.61 \]

\[ = 11.35 \text{ kg} \]

Excess air supplied = 40%

Minimum mass of air required for complete combustion of 1 kg of the fuel

\[ = 11.35 \times \frac{140}{100} \]

\[ = 15.89 \text{ kg} \]

Combustion calculation by volume (for gaseous fuels):

Stochiometric or minimum volume of air required for the complete combustion of 1 m³ gaseous fuels

The volume of air required for the combustion of gaseous fuels is calculated mainly based on the balanced combustion equation.

1. Combustion of carbon monoxide

\[ 2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2 \]

\[ 2\text{ vol} \quad 1\text{ vol} \quad 1\text{vol} \]

2 m³ of CO needs 1 m³ of oxygen

Therefore;

**1 m³ of CO needs 0.5 m³ of O₂ for combustion**
2. Combustion of hydrogen

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]

2 vol 1 vol 1 vol

2 m³ of Hydrogen needs 1 m³ of oxygen

Hence;

1 m³ of H₂ needs 0.5 m³ of O₂ for combustion

3. Combustion of methane

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

1 vol 2 vol 1 vol 2 vol

1 m³ of CH₄ needs 2 m³ of O₂ for combustion

4. Combustion of ethane

\[ 2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O} \]

2 vol 7 vol 4 vol 6 vol

2 m³ of ethane needs 7 m³ of oxygen

Hence;

1 m³ of C₂H₆ needs 3.5 m³ of O₂ for combustion

5. Combustion of ethylene

\[ \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \]

1 m³ of C₂H₄ needs 3 m³ of O₂ for combustion

Calculation of minimum volume of air required:

The minimum volume of air required is calculated by multiplying the oxygen required by 100/21 since the percentage volume of air is 21%.

Example 1

Determine the volume of air needed for complete combustion of one cubic meter of producer gas having the following composition by volume.

\[ \begin{align*}
\text{H}_2 &= 30\% \quad \Rightarrow \quad 0.3 \text{ m}^3 \\
\text{CO} &= 12\% \quad \Rightarrow \quad 0.12 \text{ m}^3 \\
\text{CH}_4 &= 5\% \quad \Rightarrow \quad 0.05 \text{ m}^3 \\
\end{align*} \]
1. Combustion of hydrogen

\[
1 \text{ m}^3 \text{ of H}_2 \text{ needs } 0.5 \text{ m}^3 \text{ of O}_2 \text{ for combustion}
\]

\[
\therefore 0.3 \text{ m}^3 \text{ of H}_2 \text{ requires oxygen for complete combustion } = \frac{0.5}{1} \times 0.3
\]

\[
= 0.15 \text{ m}^3
\]

2. Combustion of carbon monoxide

\[
1 \text{ m}^3 \text{ of CO needs } 0.5 \text{ m}^3 \text{ of O}_2 \text{ for combustion}
\]

\[
\therefore 0.12 \text{ m}^3 \text{ of CO requires oxygen for complete combustion } = \frac{0.5}{1} \times 0.12
\]

\[
= 0.06 \text{ m}^3
\]

3. Combustion of methane

\[
1 \text{ m}^3 \text{ of CH}_4 \text{ needs } 2 \text{ m}^3 \text{ of O}_2 \text{ for combustion}
\]

\[
0.05 \text{ m}^3 \text{ of CH}_4 \text{ requires oxygen for complete combustion } = \frac{2}{1} \times 0.05
\]

\[
= 0.1 \text{ m}^3
\]

Volume of oxygen needed for complete combustion of 1 m\(^3\) of gas

\[
= 0.15 + 0.06 + 0.1
\]

\[
= 0.31 \text{ m}^3
\]

Minimum volume of air required for combustion of 1 m\(^3\) of gas

\[
= \frac{100}{21} \times 0.31
\]

\[
= 1.48 \text{ m}^3
\]

Example 2
A fuel contains 45% of H\(_2\), 40% CO, 12% CH\(_4\) and 3% O\(_2\) by volume. Determine volume of air required to burn 1 m\(^3\) of this fuel.

\[
\text{H}_2 = 45\% = 0.45 \text{ m}^3
\]

\[
\text{CO} = 40\% = 0.4 \text{ m}^3
\]

\[
\text{CH}_4 = 12\% = 0.12 \text{ m}^3
\]
1 m³ of H₂ needs 0.5 m³ of O₂ for combustion

Hence;

\[ \therefore 0.45 \text{ m}^3 \text{ of H}_2 \text{ requires oxygen for complete combustion} = \frac{0.5}{1} \times 0.45 \]

\[ = 0.225 \text{ m}^3 \]

2. Combustion of carbon monoxide

1 m³ of CO needs 0.5 m³ of O₂ for combustion

\[ \therefore 0.4 \text{ m}^3 \text{ of CO requires oxygen for complete combustion} = \frac{0.5}{1} \times 0.4 \]

\[ = 0.20 \text{ m}^3 \]

3. Combustion of methane

1 m³ of CH₄ needs 2 m³ of O₂ for combustion

\[ \therefore 0.12 \text{ m}^3 \text{ of CH}_4 \text{ requires oxygen for complete combustion} = \frac{2}{1} \times 0.12 \]

\[ = 0.24 \text{ m}^3 \]

\[ \text{Volume of oxygen needed for complete combustion of 1 m}^3 \text{ of gas} = 0.225 + 0.20 + 0.24 \]

\[ (\text{Theoretical O}_2 \text{ required}) \]

\[ = 0.665 \text{ m}^3 \text{ O}_2 \]

Minimum volume of oxygen required = Theoretical O₂ required - O₂ present in fuel.

\[ = 0.665 - 0.03 \]

\[ = 0.635 \text{ m}^3 \]

Minimum volume of air required for combustion of 1 m² of gas

\[ = \frac{100}{21} \times 0.635 \]

\[ = 3.023 \text{ m}^3 \text{ of air} \]
Example 3

Volumetric analysis of producer gas supplied to an engine is,
H₂ = 20%, CO = 22%, CH₄ = 3%, CO₂ = 8% and N₂ = 47%

Excess air supplied is 50%. Estimate the volume of air required for combustion of 1 m³ of gas.

H₂ = 20% = 0.2 m³
CO = 22% = 0.22 m³
CH₄ = 3% = 0.03 m³

1. Combustion of hydrogen

\[
\text{1 m}^3 \text{ of H}_2 \text{ needs } 0.5 \text{ m}^3 \text{ of O}_2 \text{ for combustion}
\]

\[
\therefore 0.2 \text{ m}^3 \text{ of H}_2 \text{ requires oxygen for complete combustion } = \frac{0.5}{1} \times 0.2
\]

\[
= 0.1 \text{ m}^3
\]

2. Combustion of carbon monoxide

\[
\text{1 m}^3 \text{ of CO needs } 0.5 \text{ m}^3 \text{ of O}_2 \text{ for combustion}
\]

\[
\therefore 0.22 \text{ m}^3 \text{ of CO requires oxygen for complete combustion } = \frac{0.5}{1} \times 0.22
\]

\[
= 0.11 \text{ m}^3
\]

3. Combustion of methane

\[
\text{1 m}^3 \text{ of CH}_4 \text{ needs } 2 \text{ m}^3 \text{ of O}_2 \text{ for combustion}
\]

\[
\therefore 0.03 \text{ m}^3 \text{ of CH}_4 \text{ requires oxygen for complete combustion } = \frac{2}{1} \times 0.03
\]

\[
= 0.06 \text{ m}^3
\]

\[
\text{Volume of oxygen needed for complete combustion of } 1 \text{ m}^3 \text{ of gas } = 0.1 + 0.11 + 0.06
\]

\[
= 0.27 \text{ m}^3
\]

\[
\text{Minimum volume of air required for combustion of } 1 \text{ m}^3 \text{ of gas } = \frac{100}{21} \times 0.27
\]

\[
= 1.26 \text{ m}^3
\]
Excess air supplied = 50%

\[
\text{Minimum volume of air required for combustion of 1 m}^3\text{ of gas} = 1.28 \times \frac{150}{100}
\]

\[
= 1.92 \text{ m}^3
\]

**Problem: 4**

A gas has the following % composition by volume \( \text{CH}_4=4\% \), \( \text{CO}=22\% \), \( \text{H}_2=14\% \), \( \text{CO}_2=6\% \), \( \text{N}_2=52\% \) and \( \text{O}_2=3\% \).

\[
\begin{align*}
\text{H}_2 & = 14\% = 0.14 \text{ m}^3 \\
\text{CO} & = 22\% = 0.22 \text{ m}^3 \\
\text{CH}_4 & = 4\% = 0.04 \text{ m}^3 \\
1. \text{ Combustion of hydrogen} & \\
\text{1 m}^3 \text{ of H}_2 \text{ needs 0.5 m}^3 \text{ of O}_2 \text{ for combustion} \\
\therefore 0.2 \text{ m}^3 \text{ of H}_2 \text{ requires oxygen for complete combustion} &= \frac{0.5}{1} \times 0.14 \\
&= 0.700 \text{ m}^3 \\
2. \text{ Combustion of carbon monoxide} & \\
\text{1 m}^3 \text{ of CO needs 0.5 m}^3 \text{ of O}_2 \text{ for combustion} \\
\therefore 0.22 \text{ m}^3 \text{ of CO requires oxygen for complete combustion} &= \frac{0.5}{1} \times 0.22 \\
&= 0.11 \text{ m}^3 \\
3. \text{ Combustion of methane} & \\
\text{1 m}^3 \text{ of CH}_4 \text{ needs 2 m}^3 \text{ of O}_2 \text{ for combustion} \\
\therefore 0.03 \text{ m}^3 \text{ of CH}_4 \text{ requires oxygen for complete combustion} &= \frac{2}{1} \times 0.04 \\
&= 0.08
Volume of oxygen needed for complete combustion of 1 m$^3$ of gas 

\[ = 0.07 + 0.11 + 0.08 \]

\[ = 0.26 \text{ m}^3 \]

Oxygen already in the fuel \( = 0.24 \)

Total volume of oxygen required for the complete combustion is \( = 0.26 - 0.02 \)

\[ = 0.24 \text{ m}^3 \]

\[
\text{Minimum volume of air required for combustion of 1 m}^3 \text{ of gas} \]

\[ = 0.24 \times \frac{100}{21} \]

\[ = 1.148 \text{ m}^3 \text{ AIR} \]

**Flue gas**

Flue gas is a mixture of gases produced from the products of combustion of a fuel. Its major constituents are CO, CO$_2$, O$_2$ and N$_2$.

The efficiency of combustion can be understood by quantitative analysis of flue gas. Usually, excess oxygen in the flue gas suggests that excess of air is supplied for combustion. More carbon monoxide content suggests, incomplete combustion process. Based on flue gas analysis, improvement in the design of internal combustion engines, combustion chamber, furnace, etc., can be done.

**Flue gas analysis by Orsat's apparatus**

Mainly, the flue gases CO, CO$_2$ and O$_2$ are quantitatively analysed by Orsat's apparatus.

The apparatus consists of a graduated burette (100 ml) surrounded by water, for maintaining constant temperature. One end of burette is connected to a levelling bottle through a rubber tube. The levelling bottles contain saturated NaCl solution which does not absorb any flue gases. By raising and lowering the levelling bottle, the volume of gases present in it are made to overflow and have close contact with three absorption pipette solutions.

The absorption pipettes have solution for absorption of CO$_2$, O$_2$ and CO respectively. The first pipette is filled upto the mark with standard KOH solution to absorb CO$_2$. The second pipette is filled with standard alkaline pyrogallol solution. This solution absorbs CO$_2$ and O$_2$. The third pipette is filled with standard ammoniacal cuprous chloride. This solution absorbs CO$_2$, O$_2$ and CO. Hence, it is necessary to pass the flue gas first through standard KOH solution and then through standard alkaline pyrogallol solution and finally through standard ammoniacal CuCl$_2$ solution.

To flush out the air in the apparatus, the three way stop clock is opened to the flue gas supply after closing the entries of absorption pipettes. By lowering the levelling bottle, the flue gas is admitted in the burette and the three way stop clock is opened to the flue gas supply after closing the absorption pipettes. Now, the levelling bottle is raised and the gas-air mixture
is pushed out into the atmosphere. The procedure is repeated until the pure flue gas occupies the apparatus.

Then adjust the levelling bottle and exactly permit 100 ml of the flue gas as noted in the burette and close the three way stop clock completely. First, the stopper of the first absorption pipette having KOH solution is opened and the flue gas in the burette is forced into pipette solution by raising the levelling bottle. By repeatedly raising and lowering the levelling bottle, the gas is brought into intimate contact with the pipette KOH solution which absorbs the CO₂ gas completely. Then, the residual gases are taken into the burette and the levels of the KOH solution is made to stand in fixed mark. By adjusting the levelling bottle, the volume of residual gases after the removal of CO₂ by the absorption pipette is measured in the burette. The decrease in volume gives the volume of CO₂ in 100 ml.of the sample flue gas.

The same procedure is then repeated with the alkaline pyrogallol solution. After the absorption of O₂ in the absorption pipette, the pipette level is fixed and entry closed. After that the burette reading is noted by levelling with the levelling bottle. The further decrease in volume gives the volume of O₂ in 100 ml.of the flue gas.

Finally, the third absorption pipette is opened and by adjusting the levelling bottle up and down, the remaining flue gas is forced to pass through the ammoniacal cuprous chloride solution of the absorption pipette. This is done to have complete absorption of the remaining CO gas in the absorption pipette.
After this, the level of pipette is made fixed and entry closed. The residual gas finally present in the burette is then measured by using the levelling bottle. The decrease in value from the last noted value gives the volume of CO present in 100 ml. of the flue gas.

The percentage of nitrogen is obtained by the difference.

**Summary**

In this lesson, combustion, combustion calculations and flue gas analysis are discussed.

**QUESTIONS**

**PART – A**

1. Define combustion.
2. Write the complete equation for the combustion of methane present in a fuel.
3. What is flue gas?

**PART – B**

1. Mention the use of flue gas analysis.
2. Name the reagents used for the absorption of CO₂, O₂ and CO in flue gas analysis.

**PART – C**

1. Explain flue gas analysis by Orsat apparatus.
2. Calculate the mass of oxygen required for the combustion of 1 kg of a carbon, hydrogen and sulphur.
3. A sample of hydrocarbon contains 18.18% hydrogen and 81.82% of carbon by weight. Find the mass of air required for the complete combustion of 1 kg of the fuel.
4. A sample of coal was found to have the following composition.
   - C = 75%, H₂ = 5.2%, O₂ = 12.1%, N₂ = 3.2% and ash = 4.5% by mass.
   - Calculate the amount of air required for complete combustion of 1 kg of coal.
5. A fuel is found to contain C = 90%, H = 6%, S = 2.5%, O₂ = 1% and ash = 0.2% by mass.
   - Calculate the amount of air required for complete combustion of 1 kg of fuel.
ii. Calculate the amount of air required for complete combustion of 1 kg of fuel if 25% excess air is used.

6. A gaseous fuel has the following composition by volume. \( H_2 = 15\% \), \( CO = 30\% \), \( CH_4 = 3\% \), \( CO_2 = 5\% \), \( O_2 = 2\% \) and remaining \( N_2 \). Calculate the volume of air needed for complete combustion of 1 m\(^3\) of fuel.

7. The composition of gaseous fuel is Carbon monoxide = 22\%, Hydrogen = 14\%, Methane = 4\%, Carbon dioxide = 6\%, Nitrogen = 52\% and Oxygen = 2\% by volume. Calculate the volume of air required for the combustion of 1 m\(^3\) of the fuel.

8. A gaseous fuel has following composition by volume. Methane = 5\%, Hydrogen = 20\%, \( CO = 25\% \), \( CO_2 = 6\% \) and the rest nitrogen. If 20\% excess air is used for combustion, calculate the volume of air supplied per m\(^3\) of fuel.

9. A fuel contains 45\% \( H_2 \), 40\% \( CO \), 12\% \( CH_4 \) and 3\% \( O_2 \) by volume. Excess air supplied is 50\%. Determine the volume of air required to burn 1 m\(^3\) of the fuel.

TEST YOUR UNDERSTANDING

1. How to distinguish between complete and incomplete combustion of coal.
2. How can you analyse the masses of \( CO_2 \) and \( H_2O \) produced during combustion of a fuel?
3. Why a good fuel must have low ash content?
UNIT III
LUBRICANTS

INTRODUCTION
Whenever a machine works, its moving, sliding or rolling parts rub against each other with the result of that a friction is developed. This friction causes a lot of wear and tear of the concerned surfaces. Further due to friction, large amount of energy is dissipated in the form of heat and thus causes loss in the efficiency of a machine. Moreover, the heat produced due to friction causes damage to the moving parts.

The above ill effects can be minimized by applying a thin layer of certain substances known as lubricant in between the moving parts.

The process of applying the lubricant in between the two moving or sliding surfaces is called as lubrication.

Lubricant

Lubricant may be defined as the substance which reduces the friction between the two moving surfaces or parts of a machine.

Characteristics of a lubricant
1. It should have enough viscosity and oiliness.
2. It should have flash and fire points higher than the operating temperature of the machine.
3. It should be chemically inert.
4. It should not come out of the surface under pressure.
5. It should not evaporate easily.
6. It should stick on the surface.
7. It should leave low carbon residue.
8. It should not form emulsion with water.
9. It should have cloud and pour points lower than the operating temperature of the machine.
10. The volatility of the lubricating oil should be low.
11. It should possess a higher resistance towards oxidation and corrosion.

Classification of lubricants
Lubricants may be broadly classified as follows.
1. Solid lubricants
2. Semi-solid lubricants
3. Liquid lubricants
Solid lubricants

The most widely used solid lubricants are graphite and molybdenum sulphide.

Solid lubricants are used in the following areas.
(a) For heavy machinery working as a crude job at very high loads.
(b) When the operating temperature or load is very high.
(c) Where a liquid or semi-solid lubricant film cannot be maintained.

1. Graphite

Graphite is an allotrope of carbon. Graphite has a layered structure of carbon atoms. The carbon atoms are joined together by strong covalent bonds. The adjacent layers are held together by the weak Vanderwall’s force. Thus, they form a network of hexagons. Graphite is soapy to touch, non-inflammable and not oxidized in air below 375°C. It is used as a lubricant in the form of powder or as suspension in oil or water. It fills the cavities and prevents the friction. It is used for lubricating the joints or railways tracks.

Graphite can be used as a dry powder or as a colloidal dispersion.

A dispersion of graphite in water is called aqua dag and that in oil is called oil dag.

Uses

It is used as a lubricant in IC engines, air compressors, lathes, food-stuff industry, railway track joints, general machine job works, etc.

2. Molybdenum sulphide

Fine powder of molybdenum sulphide is used as lubricant. It has the capacity to withstand very high temperature. It is stable in air upto 500°C.

Uses

It is used as lubricant in high-speed machines.

Semi-solid lubricant

Example: Grease and Vaseline

Grease

It is a mixture of mineral oil and soap. It is used for heavy load and low speed machines. It is mainly used in bearing and gears. Grease is a semi-solid lubricant obtained by thickening of lubricating oil by the addition of a metallic soap. The thickener is usually sodium, calcium, and lithium or aluminium soap.

Greases are manufactured by saponification of fats with alkali followed by adding hot lubricant oil under severe agitation. Their properties depend on both the base used for saponification and the fatty acid present in the oil.
Liquid lubricants

Vegetable oils
They are commonly used liquid lubricants.
Examples: Castor oil, coconut oil, etc.
They are classified as drying and semi-drying oils. They are easily oxidized by atmosphere.

Animal oils
They are oils of animal origin. They are mainly animal fats.
Examples: Tallow oil, whale oil, lards oil, coconut oil and olive oil etc.,
They are very costly. Hence, they find little use as lubricants. They are also easily oxidized by atmosphere.

Mineral oil
Hydrocarbons with higher molecular mass obtained by the fractional distillation of petroleum are used as lubricants. They are obtained from the paraffin residue.
Examples: Paraffin oil, lubricating oil, etc.

Blended oils
They are mixture of vegetable oils and petroleum products. They show improved properties. Different oils are suitably mixed depending on the requirement. They are synthetic lubricants.

Summary
In this lesson, lubricant, purpose of lubrication, properties and types of lubricants are discussed.

QUESTIONS

PART – A
1. What is a lubricant?
2. How are lubricants classified?
3. Mention the uses of graphite.
4. Mention the uses of molybdenum sulphide.

PART – B
1. How are lubricants classified? Give examples.
2. Write a note on semi-solid lubricant.

PART – C
1. List the essential characteristics of lubricants.
2. Write a note on solid lubricants.
3. Write a note on liquid lubricants.

TEST YOUR UNDERSTANDING
1. What types of lubricants are used for transformers?
2. Why does graphite act as a good lubricant on the surface of the motion?
INTRODUCTION

Corrosion is a ‘billion’ dollar thief’. Even though it is a natural phenomenon in which the gases, moisture and other chemicals present in the atmosphere react chemically with metals to convert them into their salts, it results in loss of material and money. We know very well that metals have a strong crystalline structure and when they are converted into their salts they lose the metallic strength resulting in the damage to machineries in which they are used. Thus corrosion causes damage to metals and thereby to the society. The estimate of loss due to corrosion is approximately 2.5 billion dollars per annum all over the world. Hence it is necessary to understand the mechanism of corrosion.

In this lesson we are going to study about the causes and the mechanism of corrosion so that we can find ways to prevent this social enemy.

Corrosion is defined as the slow and continuous destruction of metal or alloy by the environment.

Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost.

The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions.

Another example is the formation of green film or basic Carbonate \([\text{CuCO}_3+\text{Cu(OH)}_2]\) on the surface of copper when exposed to moist air containing \(\text{CO}_2\) and oxygen.

Definition

Corrosion is defined as the slow and continuous destruction of metal or alloy due to the chemical or electrochemical reaction with its environment. It may be due to chemical or electrochemical reaction of the metals with the environment.

Example: Rusting of iron.

Causes of corrosion:

Metal occur in nature in two different forms. They are

1. Native state
2. Combined state.
1. Native state:

The metals occur in native, free, uncombined states or **pure metal are highly stable and non-reactive with the environment.** They do not combine with other elements. They are noble metals exist as such in the earth crust. They have very good corrosion resistance.

Ex. Au, Pt, Ag, Pd, Cu etc,

2. Combined state

Except noble metal, all other metals are reactive and form stable compounds as their oxides, sulphides, chloride and carbonates. They exist in the form of stable compounds called ores or mineral.

Ex. FeO₂, ZnO, PbS, CaCO₃ etc.,

Except noble metal, the other metals in the pure state are thermodynamically **unstable** as they are considered in excited state i.e., higher energy state. Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form stable **metallic compounds**, which are thermodynamically stable, i.e., lower energy state.

\[
\begin{align*}
\text{Corrosion(oxidation)} & \\
\text{Metal (unstable)} & \xrightarrow{\text{Metallurgy(Reduction)}} \text{Metallic Compound (stable)}
\end{align*}
\]

Higher energy  lower energy state

The properties such as electrical conductivity, ductility, malleability etc., are lost due to corrosion.

**Types of Corrosion:**

Corrosion is of two types.

1. Chemical Corrosion or Dry Corrosion
2. Electrochemical Corrosion or Wet Corrosion

1. Chemical Corrosion or Dry Corrosion

The direct chemical action of atmospheric gases like oxygen, halogens, H₂S etc., in a dry environment on metals is known as chemical Corrosion. Due to this, a dry layer of the Corrosion product is formed on the surface of the metal.

Example:

When magnesium is exposed to atmosphere, magnesium oxide is formed over the surface.

\[
2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}
\]
A solid film of the corrosion product is formed on the surface of the metal which protects the metal from further corrosion. If a soluble or volatile corrosion product is formed, then the metal is exposed to further attack. For example, chlorine attack silver generating a protective film of silver halide on the surface which prevents the further corrosion.

\[ 2Ag+Cl_2 \rightarrow 2AgCl \]

On the other hand, stannic chloride formed on tin is volatile and so corrosion is not prevented.

2. Electro Chemical Corrosion or wet corrosion

Wet corrosion

Wet corrosion occurs due to the electrochemical action of moisture and oxygen on metals. Corrosion of iron takes place due to electrochemical attack.

There are two theories to explain the rusting of iron.
1. Galvanic cell formation theory
2. Differential aeration theory.

1. Galvanic cell formation theory

Definition

“When a metal with impurities (or two dissimilar metals (Fe and Cu) are in contact with each other) is exposed to atmosphere in presence of an electrolyte or moisture, a mini galvanic cell is formed. The more anodic metal undergoes corrosion. This type of corrosion is known as galvanic corrosion”.

Example: Rusting of iron

Corrosion is an oxidation process. Oxidation is a process which involves loss of electron. Oxidation takes place at anode.

When iron metal with small amount impurities (Cu) is placed in the environment is exposed to the environment (moisture), it undergoes corrosion. Hence it acts as anode and undergoes Oxidation. Iron metal loses its two electrons and becomes Fe\(^{2+}\) ion. Hence the iron metal undergoes oxidation when it is corroded.

The impurities present in the metal act as cathode and undergo reduction. The electron released at anode is absorbed at cathode to form either Hydrogen or water or hydroxide ion depending on the environment. The moisture in the environment behaves like electrolyte. Hence a galvanic cell is formed.

Rusting of iron is explained as below.

Anodic reaction (oxidation)

The metal at the anode is oxidised into ferrous ions.

\[ Fe \rightarrow Fe^{2+} + 2e^- \] (oxidation-loss of electron)
Fe^{2+} + 2OH^- → Fe(OH)_2 → Fe(OH)_3 → Fe_2O_3

Fe^{2+} ions combine with OH^- in the environment forming ferrous hydroxide Fe(OH)_2, which undergoes further oxidation to give ferric hydroxide Fe(OH)_3. The ferric hydroxide undergoes decomposition to give ferric oxide Fe_2O_3 (Rust).

Thus rust formed is explained based on the theory of Galvanic cell formation.

**Electrolyte**

The moisture (H_2O) in the environment acts as electrolyte. It dissociates to give H^+ and OH^- ions.

\[ H_2O \rightarrow H^+ + OH^- \]

**Cathodic reaction (Reduction)**

The electrons released at the anode are taken up by the H^+ ion in the environment.

(i) In acidic medium (reduction-gain of electron)

\[ 2H^+ + 2e^- \rightarrow H_2 \text{(gas)} \]

(ii) In neutral solution with oxygen

\[ \frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \]

The ferric oxide formed (Fe_2O_3) over iron is called as Rusting of iron.

Examples:

1. Corrosion of soldered metal around copper wire.
2. Corrosion of steel shaft in bronze bearing.
3. Corrosion of steel pipe connected to copper plumbing.

**Control**

Galvanic corrosion can be avoided by selecting two dissimilar metals which are very close in the electrochemical series.

It can also be avoided by connecting two dissimilar metals through insulating material.

By making cathodic area smaller and anodic area larger.
Differential aeration theory or concentration cell formation theory

According to this theory, when a metal is exposed to varying concentrations of air (oxygen) or an electrolyte, concentration cell is formed. The metallic area which is exposed to less amount of oxygen act as anode undergoes corrosion.

The metallic area which is exposed to greater amount of oxygen act as cathode. Corrosion of metal occurs due to difference in concentration of air or electrolyte. **Hence this theory is called as Differential aeration theory or concentration cell formation theory.**

Example:

1. Corrosion on wire fence

In an iron fence the point where wires cross is less exposed to oxygen and becomes anode. Therefore corrosion takes place at the point of contact where the wire crosses.

2. Metal partially immersed in water, the immersed portion is less exposed to oxygen and becomes anode. Therefore corrosion takes place.

3. Metal area covered by drop of water, sand or dust.

   The less oxygenated area acts as Anode (gets corroded)
   The more oxygenated area acts as the Cathode (Protected from Corrosion).

Reaction

At anode- (less oxygenated area)-oxidation-loss of electron-corrosion takes place.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(oxidation or corrosion)}
\]

At cathode (more oxygenated area)

\[
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \quad \text{(Reduction)}
\]

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2.
\]

Which is further oxidized to Fe (OH)_3. Since the anodic area is small and the cathodic area is large, corrosion is more concentrated at the anode. Thus, a small hole is formed on the surface of the metal. This type of intense localized corrosion is called pitting.
Factors influencing the rate of corrosion:
The factors that affect the rate of corrosion are

1) Nature of the metal and its surface

2) Nature of the atmosphere

3) Nature of the corrosion product.

Factors connected with the metal:

1) The position of the metal in the Electrochemical Series

   The type of impurity present in it and its electropositive nature decides the corrosion of a metal. For example, when iron has impurities like copper, tin, etc., iron corrodes since iron is more electropositive than metals like copper and tin. On the other hand, when iron is coupled with zinc, zinc corrodes since zinc is more electropositive than iron.

2) Purity of the metal.

   Generally pure metal does not corrode, as there is no cathode spot available to induce corrosion.

3) Surface of the metal.

   A rough surface corrodes readily as it collects more dirt and provides more cathode spot for corrosion. A polished surface does not corrode easily.

4) Stress corrosion.

   Stress in a metal surface is produced by mechanical workings such as quenching, pressing, bending, and riveting improper heat treatment etc. The portion subjected to more stress acts as anode and other portion act as cathode. This leads to the formation of stress corrosion. Stress corrosion is noted in fabricated articles of certain alloys like high zinc brasses and nickel brasses. Caustic embrittlement noted in boilers is a typical example for stress corrosion, which is due to the attack of alkali present in water on stressed boiler metal.

5) Anode to cathode area ratio.

   When a bigger cathode area covers a smaller anode area, severe corrosion is noted in the anodes pot. This is called erosion. It is frequently encountered in piping agitators, condenser tubes etc. where turbulent flow of gases and vapors remove the coated surfaces resulting in differential cells. Removal of surface coatings can also be caused by rubbing or striking activities of solids on the coated surfaces.

6) Physical state of a metal.

   The rate of corrosion is influenced by grain size, orientation of crystals, stress etc. The smaller the grains size of the metal greater the rate of corrosion.
Factors connected with the Nature of the atmosphere

1. Temperature of the atmosphere:
   The rate of corrosion increases with increase of temperature.

2. PH of the atmosphere:
   Lower the $P^H$, greater is the corrosion.

3. Amount of moisture in the atmosphere:
   Increase of moisture in the environment increases the rate of corrosion.

4. Amount of oxygen in the atmosphere:
   In some cases oxygen enhances the corrosion, and in another it passivates the metal.

5. Amount of chemical fumes in the atmosphere:
   Industrial fumes like HCl, H$_2$SO$_4$ produces electrolytes which are acidic in nature and increases the rate of corrosion.

Examples

1. Buried pipelines and cables passing from one type of soil to another suffer corrosion due to differential aeration.

2. Lead pipeline passing through clay get corroded because it is less aerated than sand.

Factors connected with the corrosion product

In some cases the corroded product sticks to the surface and absorbs more moisture. This induces further corrosion. Examples:

a). In rusting of iron, as rust formed over iron absorbs more moisture, rate of rusting of iron increases.

b). In some cases the corroded product acts as the protective coating which prevents further corrosion.

c). Aluminium oxide formed over the surface of aluminium prevents further corrosion and act as a protective coating. This is the basic principle of Anodization.

d). In some other cases the corroded product falls out of position exposing the fresh metal surface for further corrosion.
E.g. Magnesium Oxide formed over the surface of Magnesium falls out of position exposing a fresh surface for further corrosion.

**SUMMARY**

In this lesson various types of corrosion, theories explaining corrosion and factors influencing corrosion are explained.

**Questions:**

**Part A**

1. What is corrosion?
2. What is dry corrosion?
3. What is wet corrosion?
4. What type of corrosion takes place in a metal when anode is small and cathode is large? Why.

**Part B**

1. Write a note on galvanic cell formation theory.
2. Write a note on differential aeration theory.
3. What are the factors influencing the rate of corrosion?

**PART-C**

1. Explain the mechanism of Galvanic corrosion.
2. Explain the differential aeration theory with suitable examples.

**TEST YOUR UNDERSTANDING**

1. Why corrosion often takes place under metal washers.
2. Welded joints are better than riveted joints. Why?
5.2 METHODS OF PREVENTION OF CORROSION

INTRODUCTION
Corrosion can be prevented by the following methods:
1. Control of environment
2. Alloying
3. Surface coating
4. Cathodic protection

Control of environment:
The corrosion rate can be reduced by modifying the environment. The environment can be modified by the following:

1. Deaeration: Removal of dissolved oxygen and other gases in water by mechanical agitation is called deaeration. The presence of increased amounts of oxygen is harmful since it increases the corrosion rate. Deaeration aims at the removal of dissolved oxygen. Dissolved oxygen can be removed by deaeration or by adding some chemical substance like Na$_2$SO$_3$.

2. Dehumidification: Removal of moisture content present in air is called as dehumidification. This can be achieved by adding silica gel which can absorb moisture preferentially on its surface.

3. Inhibitors: In this method, some chemical substance known as inhibitors are added to the corrosive environment in small quantities. These inhibitors substantially reduce the rate of corrosion.

Alloying:
Both corrosion resistance and strength of many metals can be improved by alloying. eg. Stainless steels containing chromium produce a coherent oxide film which protects the steel from further attack.

Surface Coating:
Surface coating the method of coating of one metal over the other metal (metal to be protected from corrosion). Corrosion of metal surfaces is a common phenomenon. To protect a metal surface from corrosion, the contact between the metal and the corrosive environment (air, moisture, corrosive gases, etc.) is to be cut off. This is done by coating the surface of the metal with a continuous, non-porous material. Such a coating is referred to as surface coating or protective coating. In addition to protective action, such coatings also give a decorative effect and reduces wear and tear.

Objectives of Coating Surfaces
1. To prevent corrosion
2. To enhance wear and scratch resistance
3. To increase hardness
4. To insulate electrically
5. To insulate thermally
6. To impart decorative colour.

**Metallic Coating:**
Surfacing coatings made up of metals are known as metallic coatings. These coatings separate the base metal from the corrosive environment and also function as an effective barrier for the protection of base metals.

The metal which is coated upon is known as the base metal.

The metal applied as coating is referred to as coat metal.

The different methods used for metal coating are.

1. Hot dipping
   (a) Galvanization
   (b) Tinning

2. Metal spraying.

3. Cladding.

4. Cementation
   (a) Sheardizing – Cementation with Zinc powder is called Shearding.
   (b) Chromizing - Cementation with 55% Chromium powder & 45% Alumina is called Chromizing.
   (c) Calorizing – Cementaion with Aluminium and Alumina powder is called Calorizing

5. Electroplating or electrodeposition.

**Hot dipping.**

In the process of hot dipping, the metal to be coated is dipped in the molten bath of the coating metal. Such hot dip coatings are generally non-uniform. The common examples of hot dip coatings are galvanizing and tinning.

1. **Galvanization:** The process of coating a layer of zinc over iron is called galvanization. The steel article is first pickled with dilute sulphuric acid to remove traces of rust, dust, etc. at 60-90°C for about 15-20 minutes. Then this metal is dipped in a molten zinc bath maintained at 430°C.

When zinc is coated over iron, zinc and iron forms a galvanic cell. The electropositive zinc forms the anode and undergoes corrosion. Hence iron is protected from corrosion by sacrificial protection method.

The surface of the bath is covered with ammonium chloride flux to prevent oxide formation on the surface of molten zinc. The coated base metal is then passed through rollers to correct the thickness of the film.

It is used to protect roofing sheets, wires, pipes, tanks, nails, screws, etc.
2. Tinning:

The coating of tin over iron is called tin plating or tinning.

Tinning is done to protect iron, steel and copper from corrosion. It is also called tinplating. Since tin is non-toxic, it is mainly used in food industry for coating food containers. Tin-coated utensils are used for storing foodstuffs, pickles, oils, etc.

Tin is nobler metal (more cathodic) than iron. It is more resistant to atmospheric corrosion. Thus, uniform layer of tin protects iron from corrosion.

Tinning the base metal is first pickled with dilute sulphuric acid to remove surface impurities. Then it is passed through molten tin covered with zinc chloride flux. The tin coated article is passed through a series of rollers immersed in a palm oil bath to remove the excess tin. Galvanizing is preferred to tinning because tin is Cathodic to iron, whereas zinc is anodic to iron. So, if the protective layer of the tin coating has any cracks, iron will corrode. If the protective layer of the zinc coating has any cracks, iron being Cathodic and is not corroded. The corrosion products fill up the cracks, thus preventing corrosion.

**Differences between Galvanizing and Tinning.**

<table>
<thead>
<tr>
<th>Galvanizing</th>
<th>Tinning</th>
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<tbody>
<tr>
<td>1. A process of covering iron or steel with a thin coat of ‘Zinc’ to prevent it from rusting.</td>
<td>A process of covering iron or steel with a thin coat of ‘Tin’ to prevent it from corrosion.</td>
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<tr>
<td>2. Zinc protects the iron sacrificially. (Zinc undergo corrosion)</td>
<td>Tin protects the base metal without undergo any corrosion (non sacrificially)</td>
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<td>3. Zinc continuously protects the base metal even if broken at some places.</td>
<td>If any break, in coating causes rapid corrosion of base metal.</td>
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<tr>
<td>4. Galvanized containers cannot be used for storing acidic food stuffs as Zinc becomes toxic in acidic medium.</td>
<td>Tin is non-toxic in nature of any medium.</td>
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**Electroplating (Refer Electrochemistry)**

Electroplating is process in which the coat metal is deposited on the base metal by passing a direct current through an electrolytic solution by means of electrolysis.

**Objectives of Electroplating:**

1. To increase corrosion resistance.
2. To get better appearance.
3. To increase the hardness.
4. To change the surface properties of metals and non metals.
Process

In electroplating, the cleaned base metal is made as the cathode and the coat metal is taken as the anode. A solution of the coat metal salt is taken as the electrolyte. The electrodes are connected to the battery and DC current is passed. Now electrolysis takes place and the coat metal is deposited over the base metal.

The nature of coating depends on 1) the current density 2) time 3) temperature and 4) the concentration of the electrolyte.

For example, to electroplate a spoon made of copper with silver, the copper spoon is taken as the cathode. A silver plate is taken as the anode. Silver thiocyanate solution is the electrolyte. When the electrodes are connected to a DC source of electricity, silver is deposited over the copper spoon.

Electroplating Diagram

The following electrolytes are used for coating other metals.

- Copper sulphate – Copper
- Nickel sulphate – Nickel
- Chromic acid – Chromium

Factors affecting electroplating

The following are the factors affecting electroplating:

1. Cleaning of the article is essential for a strong adherent electroplating.
2. Concentration of the electrolyte is a major factor in electroplating.
3. Low concentration of metal ions will produce uniform coherent metal deposition.
4. Thickness of the deposit should be minimized in order to get a strong adherent coating.
5. Additives such as glue and boric acid should be added to the electrolytic bath to get a strong adherent and smooth coating.

6. The electrolyte selected should be highly soluble and should not undergo any chemical reaction.

7. The pH of the electrolytic bath must be properly maintained to get the deposition effectively.

INORGANIC COATING

Anodizing:

Anodizing is the process of coating aluminium oxide on the surface of aluminium or its alloy.

![Diagram of anodizing process]

This type of coating is produced on non ferrous metals like Al, Zn, Mg and their alloys, by anodic oxidation process, by passing direct electric current though a bath in which the metal is suspended from anode. Here the base metal behaves as an anode. For anodizing 8% sulphuric acid is used as the electrolyte. Since it is a good oxidising agent, it oxides aluminium (at the anode) into aluminium oxide. The electrolytes are sulphonic, chromic, phosphoric, oxalic or boric acid.

Anodized coatings have more corrosion resistance due to thicker coating.

‘Aluminium oxide coatings’ are formed by the oxidation taking place on the aluminium surface at moderate temperatures (35 to 40°C) and moderate current densities. The formed oxide film is initially thin and gain thickness by the continuous oxidation of aluminium anode. The surface of oxide film contains pores, which may cause corrosion. The pores can be sealed by exposing to boiling water, when the oxide is converted into monohydrate (Al₂O₃.H₂O). This process is called sealing process.

The anodized aluminium and its alloy are used in: 1.aircrafts 2.window frames 3.machine parts 4.fancy article and 5.Refrigerator, etc.
Cathodic Protection:

The principle involved in cathodic protection is to force the metal behave like a cathode. Since there will not be any anodic area on the metal, corrosion does not occur. There are two types of cathodic protection.

(a) Sacrificial anodic protection.
(b) Impressed current cathodic protection.

(a) Sacrificial Anodic Protection:

In this technique, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal and thus saving the metal structure from corrosion. This method is used for the protection of sea going vessels such as ships and boats. Sheets of zinc or magnesium are hung around the hull of the ship. Zinc and magnesium being anodic to iron get corroded. Since they are sacrificed in the process of saving iron (anode), they are called sacrificial anodes. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

Important applications of sacrificial anodic protection are as follows:
(i) Protection from soil corrosion of underground cables and pipelines.
(ii) Magnesium sheets are inserted into domestic water boilers to prevent the formation of rust.

(b) Impressed current cathodic protection:

In this method, an impresses current is applied in an opposite direction to nullify the corrosion current and converting the corroding metal from anode to cathode. This can be accomplished by applying sufficient amount of direct current from a battery to an anode buried in the soil and connected to the corroding metal structure which is to be protected.

![Impressed Cathodic Protection Diagram](image-url)
The anode is in a backfill (composed of gypsum) so as to increase the electrical contact with the soil. Since in this method current from an external source is impressed on the system, this is called impressed current method. This type of protection is given in the case of buried structures such as tanks and pipelines.

**SUMMARY:**
In this lesson, prevention of corrosion, Control of environment, Alloying, Surface coatings, Metal coatings, Electroplating, Galvanization and Tinning, Inorganic coating, Anodizing, Cathodic Protection, Sacrificial Anode Method and Impressed Voltage Method are discussed.

**Question:**

**PART -A**
1. What is Galvanization?
2. What is anoding?
3. What is base metal?
4. What is coat metal?
5. Galvanizing is preferred to tinning. Why?
6. What is Sherardizing?

**PART -B**
1. What is a sacrificial anode? How does it function?
2. Differentiate between galvanizing and tinning.
3. What is anodizing? How it is carried out? what are its applications?.
4. What is tinning? What are its merits & demerits?

**PART-C**
1. Explain the various methods of prevention of corrosion.
2. Explain briefly about cathodic protection.
3. Explain briefly about electroplating.

**TEST YOUR UNDERSTANDING**
1. Why is moderate current density employed during electroplating?
2. Chromium anode is not used in chromium plating. Give Reason.