* Common Impurities :-

water is a good solvent due to its ability to acquire acidity or alkalinity. Contamination of water takes place when it comes in contact with ground, rocks or soil and also from sewage or industrial wastes.

Impurities in natural water may be classified as -

Impurities of water

Dissolved

(1) Inorganic : Carbohydrates, bicarbonates, nitrate, sulphates and chloride of calcium, Mg, Na, K, Fe, Mn, Al, Zn & Cu.

(2) Organic

3) Gaseous : CO_2, SO_2, H_2S, NH_3, O_2, N_2 and oxides of nitrogen

Suspended

(1) Organic : vegetables, animal matter, oil globules.

(2) Inorganic : clay and sand

(3) Colloidal Impurities : Finely divided silica, clay, Aluminium Hydroxide [$Al(OH)_3$], Ferric hydroxide, organic waste products, colouring matter.

(4) Microscopic : E Coli & Pathogenic

* Hardness of Waters :-

Hardness of water means water which makes cleaning action of soap difficult. The water which does not form lather with soap and is hard to wash.

Causes of Hardness :-

Hard water is defined as the water which contains bicarbonates, chlorides and sulphates, nitrates of calcium and magnesium which does not produce lather readily with soap.

This can be explained as follows :-

When hard water containing Ca^{+2} & Mg^{+2} ions are treated with a soap, does not produce lather but produce a white precipitate of the Ca^{+2} & Mg^{+2} salts of the corresponding fatty acid.

$$2\,C_{17}H_{35}COONa + CaSO_4 \rightarrow (C_{17}H_{35}COO)_2Ca + Na_2SO_4$$

(Sodium Sterate) (Calcium Sterate)

$$2\,C_{17}H_{35}COONa + MgCl_2 \rightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$$

Thus, no lather is formed until all the Ca^{+2} & Mg^{+2} ions get precipitated completely.

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Hardness of water termed as the soap consuming capicity of a water.

* Types of Hardness :-

Temporary Hardness (Carbonate Hardness)
↓
→ due to bicarbonate ions of calcium and magnesium.
→ It is removed by simple boiling of water which converts the bicarbonates into insoluble carbonate or hydroxides.
→ Insoluble carbonates or hydroxides can be removed by filteration. It is called alkaline Hardness.

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

→ Can also be removed by adding calculated amount of lime -

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

Permanent Hardness (non Carbonate or non alkaline Hardness)
↓
It is due to dissolved chloride sulphates & nitrates of calcium and magnesium.
→ Cannot be removed by simple boiling process

Total Hardness − temporary Hardness = Permanent Hardness

Hardness due to $CaSO_4$ is more than $MgSO_4$.

* Degree of Hardness :-

The hardness of water depends upon the amount of Calcium and magnesium salts present in it.

If a sample of water contains n parts of $CaCO_3$ equivalent 10,00,000 (10^6) parts, by defination it posses n degree of hardness

→ One degree of hardness is therefore, the hardness caused by one part of $CaCO_3$ or its equivalent in one million (10^6) parts of water

~~Soft~~ Hardness of water	Degree of hardness (PPM)
Soft Water	0 – 10
Medium hard Water	10 – 20
hard water	20 – 30
Very hard water	above 30

The degree of hardness of water is usually expressed in term of equivalent amount of $CaCO_3$. Moreover $CaCO_3$ has been adopted as standard for expressing hardness since its molecular mass is 100 (easy for calculation) and it is the most insoluble salt that can be precipitated in water treatment operations.

Thus equivalent of $CaCO_3$ for hardness producing substance can be calculated by formula..

$$\text{Equivalent of } CaCO_3 = \frac{\left[\text{mass of hardness producing substance (mg/l)}\right] \times \left[\text{Chemical equivalent of } CaCO_3 = 50\right]}{\left[\text{chemical equivalent of hardness producing substance}\right]}$$

$$= \left[\text{mass of hardness producing sub. (mg/l)}\right] \times \frac{100}{2 \times \left[\text{chemical equivalent of hardness producing substance}\right]}$$

$$= \left[\text{Mass of hardness producing substance (mg/l)}\right] \times \left[\text{Multiplication factor}\right]$$

Ex $Mg(HCO_3)_2$

Molar mass of $Mg(HCO_3)_2 = 146$

chemical equivalent of $Mg(HCO_3)_2 = \frac{146}{2} = 73.$

$Mg^{+2} + HCO_3^{-2}$ $\quad n = 2$

Molar mass of $CaCO_3 = 100$

Multiplication factor $= \frac{100}{2 \times 73} = \frac{100}{146}$

* Units of Hardness :- four types of units

(i) Parts Per Million (PPM) :- is the parts of calcium carbonate equivalent hardness per 10^6 parts of water.

(ii) Milligrams per liter (mg/l) is the no. of milligram of $CaCO_3$ equivalent hardness present in 1 Liter of water.

1 mg/l = 1 mg of $CaCO_3$ eq. hardness per L of water (1 L water = 1 kg)

= 1 mg of $CaCO_3$ eq. hardness per kg of water

= 1 mg of $CaCO_3$ eq hardness per 10^6 mg of water.

= 1 part of $CaCO_3$ eq. hardness per 10^6 parts of water.

1 mg/l = 1 PPM.

* ~~Degree Hardness of Hardness~~ :-

(iii) Clark's degree (°Cl) → is no. of grains (1/7000 lb) of $CaCO_3$ eq. hardness per gallon (10 lb) of water

7000 grains

(1/7000)

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1 °Clark = 1 grain of $CaCO_3$ equivalent hardness per gallon of water

1 °Clark = 1 part of $CaCO_3$ equivalent hardness per 70,000 (7X10⁴) parts of water.

(iv) Degree French (°Fr) → it's one parts of $CaCO_3$ eq. hardness per 10^5 parts of water.

1 °Fr = 1 part of $CaCO_3$ eq hardness per 10^5 parts of water.

1 mg/l = 1 PPM = 0.1°F = 0.07°Cl

14 mg/l = 14.3 PPM = 1.43°Fr = 1°Cl

10 mg/l = 10 PPM = 1°Fr = 0.7°Cl

1 ppm = 1 mg/l = 0.1°Fr = 0.07°Cl

* **Determination of Hardness of water :-**
two methods are used to determine Hardness of water.
(a) Clark's Method
(b) EDTA method

(a) **Clark's Method (Soap titration Method) :-**
This method is based on the principle that soluble soap (Na or K salts of fatty acids) when added to hard water (having hardness causing metal ions) firstly form insoluble compounds with the metal ions and doesn't produce any lathes.
But as soon as all such metal ions are precipitated out, addition of further drop of soap solution will produce lathes.

$$2C_{17}H_{35}COONa + MgCl_2 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + 2NaCl$$

$$2C_{17}H_{35}COONa + CaSO_4 \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + Na_2SO_4$$

Soluble Soap Hardness Stearate (insoluble)

So we can determine total hardness of water by means of its titration against a standard soap solution. The appearance of lathes indicates the end point of titration.

Procedure

(1) Preparation of standard Hard Water :-

Dissolve 1.0 gm of pure, dry $CaCO_3$ in minimum quantity of dil HCl.

Boil to dryness to ~~repel~~ expel excess of acid and CO_2. Dissolve the residue in distilled water and make upto 1 lt sol?

Thus standard hard water contains 1 gm/l or 1 mg/ml $CaCO_3$ hardness.

(2) Preparation and standardization of Soap solution :-

Firstly fill up the burette with soap solution [Prepared by dissolving 10 gm. pure, dry soap in 1 lt ~~mix~~ mixture of alcohol (800 ml) and water (200 ml).

Take 50 ml of standard hard water and add soap to it from the burette with continuous shaking till a parmanent lather (stable atleast for 2 minutes) is formed.

Let the volume of soap so consumed be V_1 ml.

(3) Lather factor of distilled water :-

Titrate 50 ml of distilled water against the standard soap solution till permanent lather is formed. Let the volume of soap

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solution used is noted as V1 ml.
" It is minimum quantity of standard soap solution, required to produce lather with distilled water (zero hardness) the factor is substracted from the actual volume of soap solution used.

(4) Determination of total Hardness :-
50 ml of hard water sample is titrated against soap solution. Let the reading of burette is V2 ml.

(5) Determination of permanent Hardness :-
Take 250 ml of sample hard water is boiled till the volume is reduced to 50 ml All the temporary hardness causing salts (Bicarbonates) are converted into insoluble carbonates and hydroxides. These precipitates are filtered off and the volume is again made 250 ml by adding distilled water. Now this sample water contains only permanent hardness 50 ml of this water is titrated against soap solution and volume of soap solution is noted as V3 ml.

Calculations :-

1) Strength of soap soln :-

1 ml of standard hard water contains 1 mg of hardness causing substances in terms of $CaCO_3$.

50 ml of standard hard water = 50 mg of $CaCO_3$

50 ml of standard hard water = $(V_1 - V)$ ml of soap soln

or

$(V_1 - V)$ ml of soap solution = 50 mg of $CaCO_3$

1 ml of soap solution = $\left(\frac{50}{V_1 - V}\right)$ mg of $CaCO_3$

2) Calculation of total Hardness :-

1 ml soap = $\frac{50}{V_1 - V}$ mg of $CaCO_3$

$(V_2 - V)$ ml of soap solution = $(V_2 - V) \times \frac{50}{V_1 - V}$ mg of $CaCO_3$.

50 ml of sample water contains = $\frac{(V_2 - V) \times 50}{V_1 - V}$ mg/l

1 ml of sample water = $\frac{(V_2 - V) \times 1000}{(V_1 - V)}$ mg/l.

Total hardness of water = $\frac{(V_2 - V)}{(V_1 - V)} \times 1000$ mg/l

$= \frac{(V_2 - V)}{(V_1 - V)} \times 1000$ PPM.

(1 mg/l = 1 PPM)

~~1000 mg/l =~~

(c) Calculation of permanent hardness:-

1 ml of soap solution contains $= \left(\frac{50}{V_1 - V}\right)$ mg of $CaCO_3$

$(V_3 - V)$ ml of soap solution $= \frac{(V_3 - V)}{(V_1 - V)} \times 50$ mg of $CaCO_3$

1000 ml of boiled water contains $= \frac{(V_3 - V)}{(V_1 - V)} \times 1000$ mg of $CaCO_3$

Permanent Hardness $= (V_3 - V) \times 5$

50 ml of given water contains $= \frac{V_3 - V}{V_1 - V} \times \frac{50}{50}$ mg of $CaCO_3$

1000 ml of boiled water contains $= \frac{V_3 - V}{V_1 - V} \times 1000$ mg of $CaCO_3$

Permanent Hardness	$= \frac{V_3 - V}{(V_1 - V)} \times 1000$	mg/l or ppm.

(d) Temporary Hardness:-

Temporary Hardness	=	Total Hardness	−	Permanent Hardness.

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$$= \left(\frac{V_2 - V}{V_1 - V}\right) \times 1000 - \left(\frac{V_3 - V}{V_1 - V}\right) \times 1000$$

$$= \frac{1000}{V_1 - V}\left[(V_2 - V) - (V_3 - V)\right] \text{ PPM}$$

$$= \frac{1000 \times (V_2 - V_3)}{(V_1 - V)} \text{ PPM}$$

Temporary Hardness $= 1000 \times \frac{x (V_2 - V_3)}{(V_1 - V)}$ PPM

Total Hardness $= \frac{x \times (V_2 - V)}{(V_1 - V)} \times 1000$ PPM

Permanent Hardness $= \frac{x (V_3 - V)}{V_1 - V} \times 1000$ PPM

Temporary Hardness = Total Hardness − Permanent Hardness

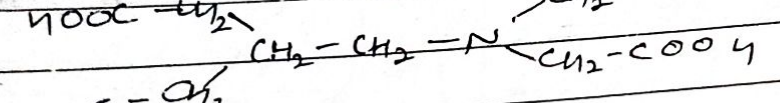
x = Amount of $CaCO_3$ in gm/l
V = Volume of soap solution used by 50 ml
V_1 = Volume of soap solution used by 50 ml of standard Hard water.
V_2 = Volume of soap solution used by 50 ml of given hard water
V_3 = Volume of soap solution used by 50 ml boiled water.

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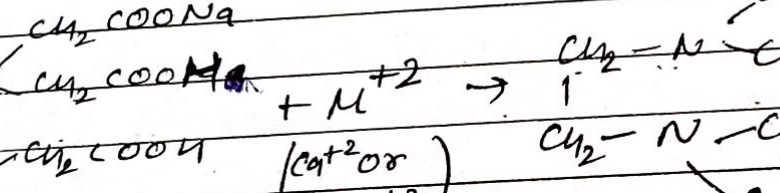
EDTA Method :-

(Ethylene di amine tetra acetic acid)



This method is complexometric titration of water sample with EDTA using Eriochrome Black T as the indicator. EDTA (Ethylene diamine tetra acetic acid) is strong complexing agent.

Since EDTA has limited solubility in waters. The disodium salt of EDTA which is soluble in water is used. In these titrations known as complexometric titrations.

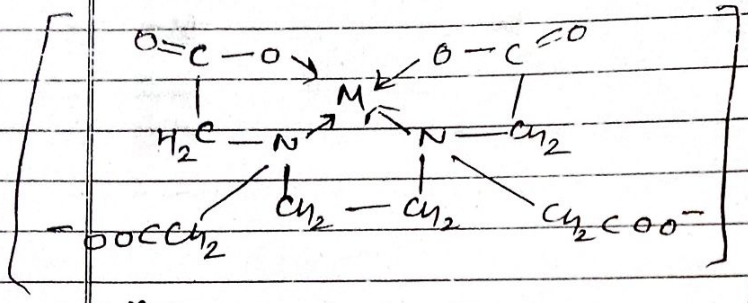


Disodium salt of EDTA

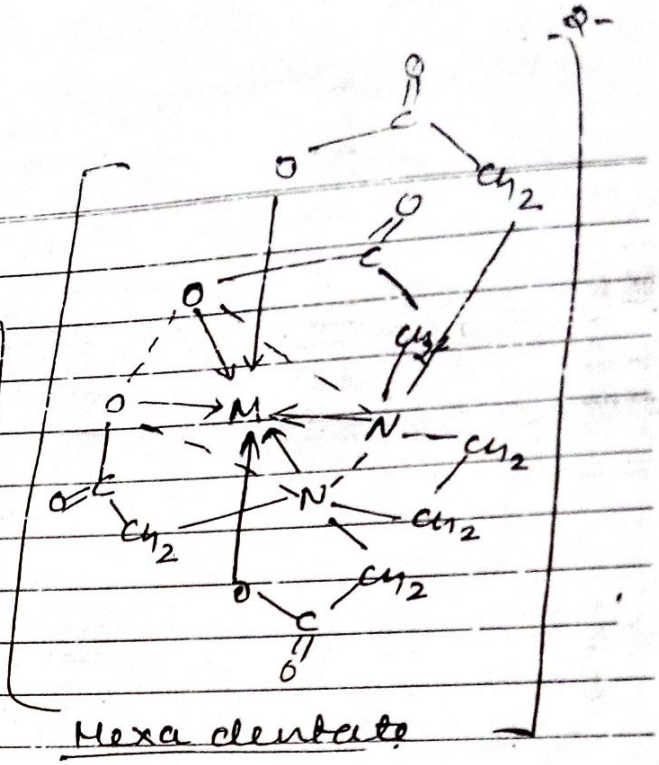
Complex of EDTA with metal ion.

EDTA acts as a tetra / hexa dentate ligand and attaches itself with metal ion (through O or N atoms) to give very stable, soluble and colourless complexes (chelates) (1:1)

EDTA Complexes :-

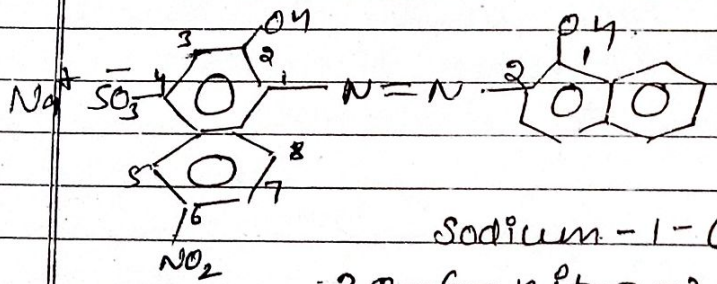


Tetra dentate form
where M = Ca^{+2} or Mg^{2+}



Hexa dentate form

Eriochrome Black T. (EBT) :- (Indicator)



Sodium - 1 - (1-hydroxy-2-nephthylo-
-3o-6-nitro-2-naphthol-4-sulphonate)

(Blue in colour)

Principle :-

The water sample is buffered using (NH_4OH - NH_4Cl sol^n) to a P^H value nearly about 10 and few drops of indicator solution are added.

A weak complex of wine red colour is formed. and hence whole

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rexn mixture becomes wine red.

Co^{2+} or Mg^{2+} ions + EBT $\xrightarrow{pH=10}$ M-Eriochrom Black T complex

from water — Blue — ↓ unstable complex, wine red colour.

⇒ In the course of rexn of water against EDTA disodium salt [Na_2H_2Y] it combines with the metal ions to give very stable and colourless metal EDTA complex.

M + EDTA → [M-EDTA] Complex
colourless and stable

and when the excess drop of EDTA solution added to rexn solution it displaces the indicator from [M-EBT] complex. Since the stability of [M-EDTA] complex is very high in comparison of former one.

[M-EBT] complex + EDTA → [M EDTA] complex + EBT
Blue.

So at the end point there is change in colour from wine red (free to MEBT complex) to blue (free EBT indicator)

* Procedure :-

i] Preparation of standard Water Sample :- Exact 1 gm of pure and dry $CaCO_3$ is dissolved in a minimum quantity of HCl and the solution is evaporated to dryness over a hot water bath. The residue left behind is dissolved in distilled water and the solution is made up to one lt. Now each ml of this solution has 1 mg of $CaCO_3$ equivalent hardness (1 PPM). This sol^n is 0.01 M solution of Ca^{+2} ions

(ii) Preparation of EDTA solution :- 3.72 gm of disodium salt of EDTA is dissolved in distilled water and made upto 1 lt. (0.01 M sol^n)

(iii) Preparation Of Eriochrome Black T solution :- 0.5 gm of Eriochrome Black T indicator is dissolved in 100 ml of ~~ethanol~~.

(iv) Preparation of Buffer solution (pH = 10) :- Mix 67.5 gm of NH_4Cl to 570 ml of conc.

ammonia. Solution is dissolved and made up to 1 lt with distilled water.

* Steps involved in EDTA method :-

[i] Standardization of EDTA solution :-
Fill the burette with EDTA soln. Pipette out 50 ml of standard water (0.01 M solution) into a conical flask.
Add 10 ml buffer solution (pH 10) and 3-4 drops of EBT. Titrate the solution of conical flask against EDTA until the wine red colour change to blue. Let the volume of EDTA used be V_1 ml.

[ii] Determination of total Hardness of water :- Take 50 ml of water sample (tap water) and titrate it against EDTA as per procedure discussed above Let the volume of EDTA consumed be V_2 ml.

[iii] Determination of Permanent Hardness of water :-
Take 250 ml of water sample and boil it till the volume is reduced to about 50 ml. Any bicarbonate of Ca^{+2} & Mg^{2+} present

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would be decompose to insoluble $CaCO_3$ & $Mg(OH)_2$. Filter and wash the precipitate with distilled water, Collecting filterate and washing in a 250 ml volumetric flask and make it up to 250 ml with distilled water. Titrate 50 ml of boiled water sample. Just as in step I. Let volume of EDTA used be V_3 ml.

* Calculation :-

Step I Standardization of EDTA Solution :-

50 ml of standard hard water
= V_1 ml of EDTA is used.

V_1 ml of EDTA = 50 mg of $CaCO_3$
(Since 1 ml of standard water solution gives 1 mg of $CaCO_3$)

1 ml of EDTA = $\frac{50}{V_1}$ mg of $CaCO_3$ equivalent hardness.

Step II Determination of total hardness of water :-

50 ml of hard water = V_2 ml of EDTA (before boiling)

V_2 ml of EDTA = $\frac{50}{V_1} \times V_2$ mg of $CaCO_3$ equivalent

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one lt of hard water (1000 ml) $= \frac{50}{V_1} \times V_2 \times \frac{1000}{50}$ mg of $CaCO_3$ equi

$= \left(\frac{V_2}{V_1} \times 1000\right)$ mg of $CaCO_3$ equivalent

→ Total Hardness $= \left(\frac{V_2}{V_1} \times 1000\right)$ PPM or mg/l

Step II Determination of permanent Hardness of water :-

50 ml of hard water = V_3 ml of EDTA (After boiling)

$= \frac{V_3}{V_1} \times 50$ mg of $CaCO_3$ equivalent.

1 lt of boiled water $= \frac{50}{V_1} \times V_3 \times \frac{1000}{50}$ mg of $CaCO_3$ equivalent

→ Permanent Hardness $= \frac{V_3}{V_1} \times 1000$ PPM

Since

Temporary Hardness = Total Hardness − Permanent Hardness

$= 1000\left(\frac{V_2}{V_1} - \frac{V_3}{V_1}\right)$ PPM.

Temporary Hardness $= \left(\frac{V_2 - V_3}{V_1} \right) \times 1000$ PPM.

This method is more accurate, convenient and rapid. So it is advisable to prefer over other methods.

Municipal water supply :-

As 80% of sickness in the world is attributed due to lack of safe drinking water. It is unfortunate that a large portion of world's population has a problem for safe scepply of water for drinking, washing and other purpose.

Water flows over the earth surface and it picks up a number of impurities in the form of dissolved particles of soil, garbage, sewage, pesticides and other human, animal or chemical waste.

Useful in small quantity :- Iron, Calcium, Magnesium, flosine etc. ~~may be use~~ But when these are present in large amount water is unfit for human to drink.

Water may contain toxic substances arsenic, barium, Cadmium, lead etc. low amount of these substances is also harmful.

Hence water has to be treated for drinking purpose.

Municipal Water requisites :-

1) Clear, colourless, odourless, pleasant in taste.
2) Turbidity 10 PPM
3) Free from harmful gases as H_2S,
4) Free from poisonous metals and its salts as Pb, As, Cr, Na.
5) pH b/w 7.0 - 8.5
6) TDS and total Hardness < 500 PPM.
7) Cl^- and SO_4^{2-} < 250 PPM
8) Fluoride content < 1.5 PPM.
9) NO E. Coli organisms should be present.
10) Free from all disease producing bacterias and germs.

Purification of drinking water :-

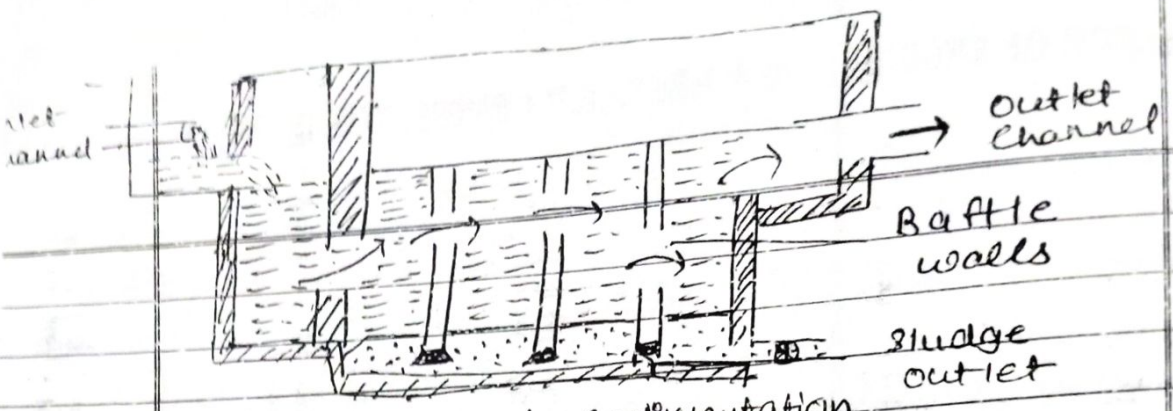
The natural water from river, lakes or wells does not confirm to all the requirements of drinking water. Surface water, which is generally used for domestic supply is contaminated with large no of impurities.

→ To make water suitable for drinking the following treatment methods are used :-

1) Screening
2) Sedimentation
3) Sedimentation with coagulation
4) Filteration
5) sterlization or disinfection

1) Screening :- Screening is the process of removal of floating materials like leaves, wood pieces etc. from water. Water is allowed to pass through screens having holes. The floating material of large number of these holes.
is retained by

2) Sedimentation :- Sedimentation is the process of allowing water to stand undisturbed in big tanks for some time so that the suspended impurities settle down at the bottom. In this process flow of water is slowed down so that the suspended impurities can settle at bottom due to



Process of sedimentation

The basin in which flow of water is retarded is called sedimentation tank. It is provided with baffle walls to reduce the velocity of water. The sattled sludge is taken out through the outlet at the bottom.

This process removes 75% of suspended matter.

3) Sedimentation with coagulation :-

The fine particles of silica, clay and organic matter can not be removed by sedimentation. As they do not settle down easily. These particles are removed by addition of certain chemicals known as Coagulents. Common Coagulants are -

i) Alum $[K_2SO_4 . Al_2(SO_4)_3 . 24H_2O]$
ii) Sodium Aluminate $[NaAlO_2]$
iii) Mohr's salt $[FeSO_4 . 7H_2O]$

Mech The fine particles of silica and clay act as colloidal particles and carry negative charge. These negatively charged particles repel each other and do not combi

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to form bigger particles. So they cannot settle easily.

When a coagulent is added in water, it forms bulky gelatinuous precipitate called flock.

Coagulent + Water → Gelatinous Precipitate (Flock)

For example when alum is added in water a bulky precipitate of $Al(OH)_3$ is formed.

$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 6CO_2$

From coagulent (Flock)

When heavier insoluble flocks of $Al(OH)_3$ descend through water, they absorb and neutralize fine suspended particles. These flocks grow bigger and ultimately settle down.

Flock + fine Particles → Bigger flock (settle down)

A slow and gentle stirring of water results in formation of thick flocks. The precipitate settled at the bottom of tank is removed from time to time.

4) Filtration :- This is the process of removing insoluble, colloidal and bacterial impurities from water by means of filters.

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The commonly used filters are -

(a) Gravity Sand Filter
(b) Pressure Filter

a) Gravity Sand Filter :- It consist of large rectangular tank made up of concrete The tank is provided with an inlet for raw water and a channel at bottom throughout which filtered water goes out. Over this channel, the layers of gravels, coarse sand & fine sand are placed

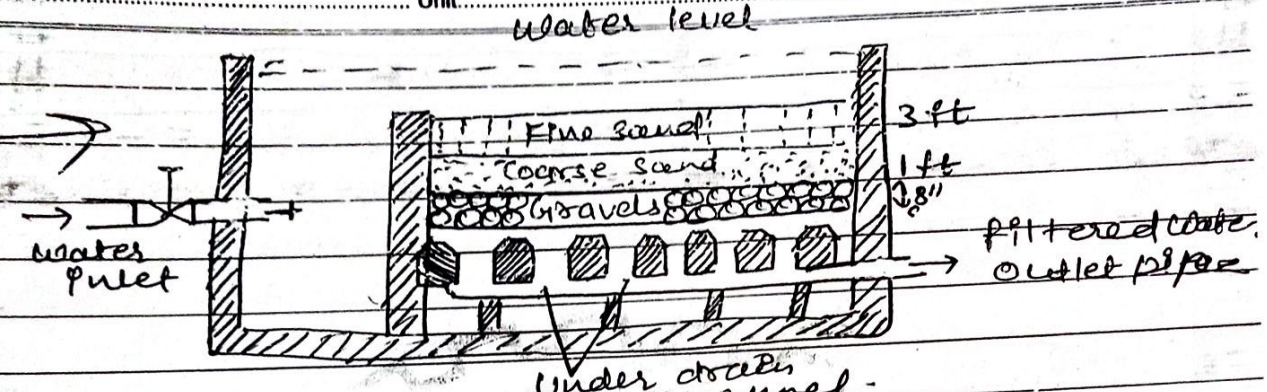
Water enters sand filter from top. As water percolates through these layers, fine suspended particles, germs and bacteria are retained in these layers. The filtered water is collected in the under drain channel.

After some time, rate of filteration becomes slow due to retention of impurities in top layer of fine sand. The impurities block the pores in the top layer of fine sand. Then portion of top layer is scrapped (खरच) off and replace by new sand layer leading to increase in rate of filteration.

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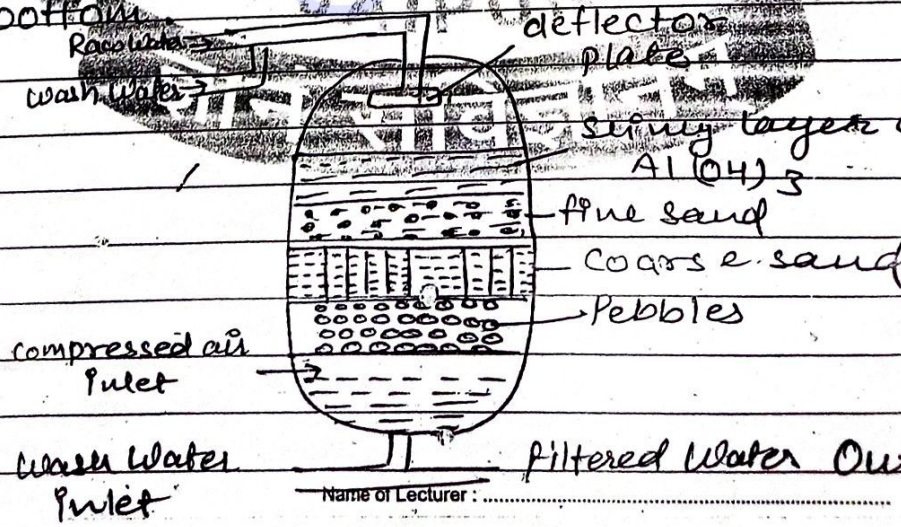
gravity sand filter



b) Pressure Filter :- It consists of a cylindrical vertical steel tank containing three layers of filtering media one above the other i.e. Pebbles, coarse sand, fine sand.

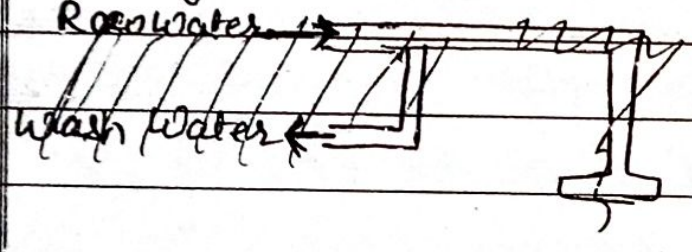
Raw water is mixed with a small amount of alum solution and pumped into steel tank at high pressure by means of pumps. Alum forms a thin layer on filter bed and this helps in removal of colloidal and bacteriological impurities. The function of deflector plate is to distribute the alum layer uniformly. Filtered water comes out from the bottom.

Vertical Pressure filter



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After some time, pressure filter gets blocked due to impurities. Then it is cleaned by back washing. The water under pressure is forced up the tank which removes the impurities that has blocked sand pores. The back wash water is allowed to go to drain.



5) **Sterlization Of Disinfection :-**

Sterlization or disinfection is the process of removal of microorganism and pathogenic bacteria present in water. The chemicals used for this purpose are called disinfectants or sterilizers.

→ The disinfection of water can be carried out by following methods.

a) Boiling b) Ultra-violet radiation c) aeration d) Ozonization e) Chlorination

a) **Boiling** → Boiling of water is an excellent and rapid method for sterilization. Boiling kills all the disease causing microorganisms and bacteria present in water. However, this method is useful for household purpose only. It cannot be employed in municipal town supply of water as it kills bacteria at the time of boiling but does not provide any protection against future contamination.

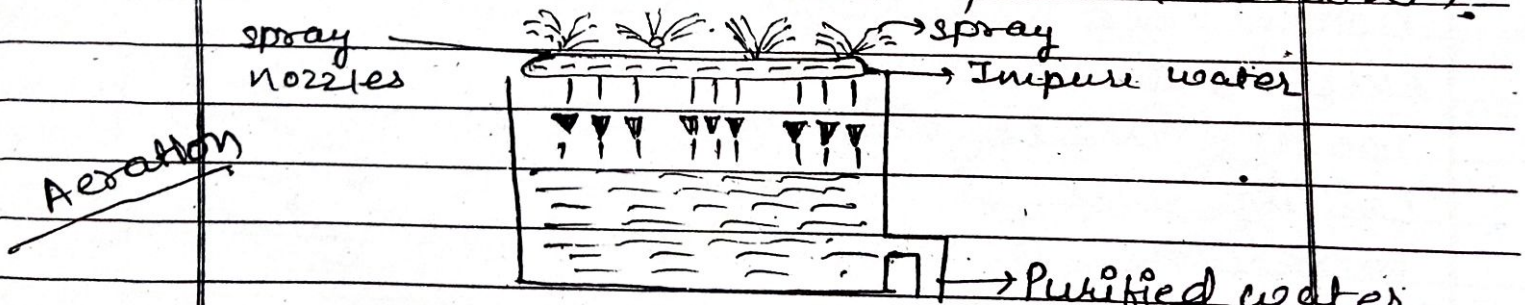
b) **Ultra Violet Radiation** → UV radiation is very effective to destroy microorganism present in water. Mercury vapour lamps enclosed in quartz bulbs are used as source of UV radiation. Disinfection with UV radiation does not impart any additional taste or odour to water as no chemicals are

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used. But this method is very costly and unsuitable for treating large water supplies.

c) Aeration → This is the process of spraying water in the form of fine droplets into atmosphere. Aeration of water is carried out with the help of spray nozzles.

Here water is sprinkled in air or atmosphere through special nozzles which produce water droplets. As water is sprinkled in air it comes in contact with oxygen and is exposed to UV rays of sun. This kills bacteria and oxidises organic matter present in water. The pure water is collected in the tank placed below.



d) Ozonization → Ozone (O_3) is a powerful disinfectant used for water purification. Ozone, being energy rich triatomic molecule is very reactive and unstable.

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When ozone is passed through raw water, ozone decomposes to produce nascent oxygen which oxidises and kills the germs

$$O_3 \rightarrow O_2 + O$$

Nascent Oxygen



Germs + O → Germs are oxidised

The nascent oxygen is capable of destroying harmful micro organism. Ozone being very powerful and rapidly acting oxidizer, oxidises all bacteria, moulds and viruses.

e) Chlorination → Chlorination is the process of addition of chlorine for deriding water for disinfection. Chlorination is universally used for disinfecting domestic water supplies.

Chlorination can be carried out by following methods :-

i) By using chlorine gas
ii) By using Bleaching powder
iii) By using Chlorine dioxide

i) By using chlorine gas → low pH

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

(Chlorine gas) (Hypochlorous acid)

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$HOCl \longrightarrow HCl + O$

Nascent oxygen

Germs + O $\longrightarrow$ Germs are oxidised

* Chlorine can be added directly as a gas or in the form of concentrated solution in water. The effectiveness of chlorine disinfection depends on chlorine concentration, contact time, temperature, pH of water and concentration of microorganism & organic matter in water.

Excess of chlorine cannot be used as it produces unpleasant odour and taste and irritant to eyes.

(ii) By using bleaching Powder → Bleaching powder, $CaOCl_2$ is a very useful disinfectant for water purification. On treatment with water, bleaching powder produces nascent oxygen

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$HOCl \longrightarrow HCl + O$$

Nascent oxygen

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Germ + O → Germs are oxidised

Only calculated quantities of bleaching powder should be used as its excess produces bad taste and odour. It introduces calcium in water and thus increases hardness.

(iii) By using Chloramine → Chloramine, $ClNH_2$ is also used for disinfection of water. Chloramine is prepared by mixing chlorine and ammonia.

$$Cl_2 + NH_3 \longrightarrow \underset{\text{Chloramine}}{ClNH_2} + HCl$$

Chloramine reacts with water to produce nascent oxygen. This process is called Chloramination

$$ClNH_2 + H_2O \longrightarrow HOCl + NH_3$$

$$HOCl \longrightarrow HCl + \underset{\text{nascent oxygen}}{O}$$

Germs + O → Germs are oxidised

The advantage of Chloramine over chlorine as disinfectant is that it does not impart any bad odour or taste to water. Chloramine tablets are also used for sterilization of water.

* **Break Point Chlorination :-**

Break Point chlorination refers to the addition of sufficient amount of chlorine in water to oxidise organic matter, reducing substances and free ammonia present in water, leaving behind mainly free chlorine which possesses dis-infecting action against disease producing micro-organisms.

When chlorine is added in water for sterlization, the process of chlorination takes place in four distinct stages,

Stage I In 1st stage, all the chlorine added is used in the oxidation of reducing agents present in water such as NH_3, H_2S, Fe^{+2} etc. So, there is no free residual chlorine present as shown by line AB.

Stage II More addition of chlorine results in the formation of chloramines and chloro organic compounds leading to increase in residual chlorine along curve BC.

$$Cl_2 + NH_3 \longrightarrow \underset{\text{Chloramine}}{NH_2Cl} + HCl$$

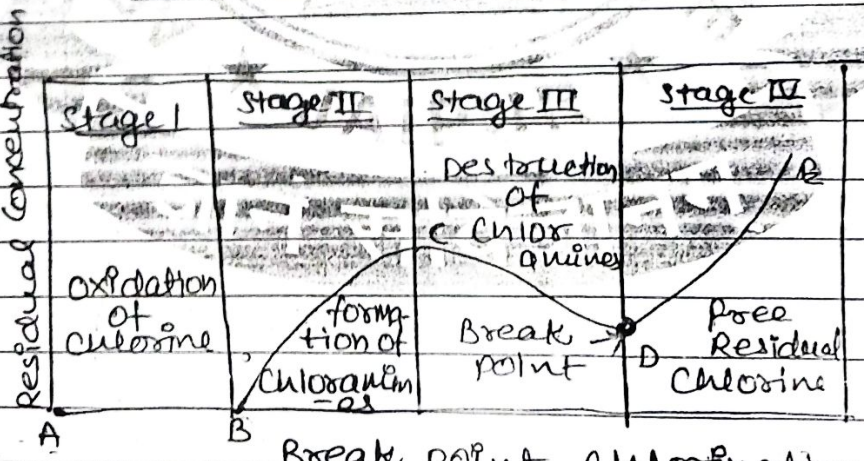
$$2Cl_2 + NH_3 \longrightarrow \underset{\text{Dichloramine}}{NHCl_2} + 2HCl$$

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Stage III - At this stage oxidation of micro organisms present in water takes place by the decomposition of chloramines. It leads to decrease in residual chlorine along line CD. When oxidative destruction of micro organism is complete the minima point D is obtained.

Stage IV After minima point D, the added chlorine is not used in any reaction. Hence the concentration of residual chlorine in water keeps on increasing with the added chlorine.

Thus for effective killing of micro-organisms, sufficient chlorine corresponding to minima has to be added. Addition of chlorine in such amount is called break point chlorination.



Boiler Troubles :-

Water is efficiently used as an engineering material for generation of steam. The water used for steam making should be free from impurities, otherwise it can give certain troubles or problems in the boiler may causes explosion of in the boiler.

Boiler Troubles

(I)
- (a) Priming
- (b) Foaming
- (c) Carry over

(II)
- Boiler corrosion

(III)
- Caustic Embrittlement

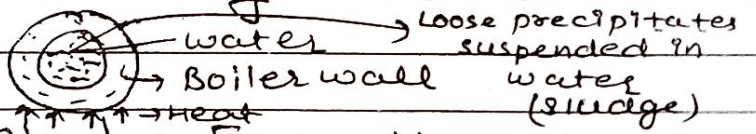
(IV)
- (a) Scale
- (b) Sludge

Boiler Troubles :-

Various types of problem occures if the quality of water is not suitable for the boiler. These problem are called boiler troubles which include:

2.3.1 **Sludge:**

Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solublities in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc. They are formed at comparatively colder portions of the boiler and get collected at places where the flow rate is slow, they can be easily removed with a wire brush.



Disadvantage of Sludge Formation:-

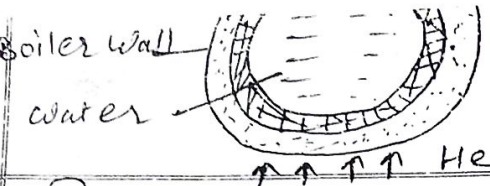
→ Fuel wastage:- As the sludges are poor conductor of heat they result in loss of heat.

→ Working efficiency:- Sludge formation decreases the efficiency of the boilers.

→ Chocking of pipes:- Formation of sludge may choke the pipelines and plug openings.

Scales:

Scales are hard deposits firmly sticking to the inner surfaces of the boiler

v) 

coating on inner walls of boiler scale.

Prevention of scale Formation:-

(a) External Treatment:-

Treatment of water before feeding to the boiler is called external treatment.

~~This will be dis~~

(b) Internal Treatment:-

Treating the raw water inside the boiler is called 'internal treatment' or 'internal conditioning'.

* Important Internal Treatment Methods are:

(1) Carbonate conditioning:-

When sodium carbonate is added to boiler water it converts $CaSO_4$ into $CaCO_3$, which is a loose sludge and can be removed by blow-down operation. { cold water moves downward & hot water moves upwards }

$$CaSO_4 + Na_2CO_3 \rightarrow \underset{\text{loose sludge}}{CaCO_3} + Na_2SO_4 \rightarrow \text{removed by blow down process.}$$

(2) Phosphate conditioning:-

When sodium phosphate is added in boilers it forms soft sludge of calcium and magnesium phosphate.

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

$$3MgCl_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2\downarrow + 6NaCl$$

(3) Colloidal Conditioning :- Addition of organic substances as kerosine, tannin, agar-agar etc. which get coat over scale forming ppt giving non stick loose deposites which can be removed by blow down operations.

(4) Electrical Conditioning :- Sealed glass bulb containing mercury connected to a battery is get rotating in the boiler. When water boils, mercury bulbs emits electrical discharge which prevents scale forming particles and joining together to form scale.

(5) Radioactive Conditioning :- Radioactive salts in form tablets are placed inside the boiler at a few points. The energy radiations emmitted by these salts prevent scale formation.

(6) Complexometric Method :- 1.5% alkaline (pH-8.5) solution of EDTA is added to feed water. EDTA binds the scale forming cations to form stable and soluble complex. As a result the sludge and scale formation in boiler is prevented.

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Moreover this treatment is -

(i) Prevents deposition of iron oxides in boiler.

(ii) Reduces carry over of oxides with steam.

(iii) Protects the boiler units from corrosion by wet steam (steam coating liquid water)

(7) Treatment with Sodium Aluminate :- (Na_4AlO_2) :-

When sodium Aluminate is added to the boiler water, it get hydrolysed.

$$Na_4AlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$

(Gelatinous precipitate)

The sodium hydroxide formed as per the above reaction precipitates any Mg salts presents.

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

Both $Al(OH)_3$ and $Mg(OH)_2$ are flocculent precipitates and they easily trap any finely suspended and colloidal impurities such as silica and oil. These loose precipitates can then be removed by blow operation.

(8) Calgon conditioning

If calgon (sodium hexametaphosphate) is added to boiler feed water, it forms soluble complex with $CaSO_4$ which remains in dissolved form in water.

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

$$2CaSO_4 + [Na_4(PO_3)_6]^{-2} \rightarrow [Ca_2(PO_3)_6]^{-2} + 2Na_2SO_4$$

Soluble complexion

Difference between Sludges and Scales

S.No	Sludges	Scales
1.	Sludges are soft, loose and slimy precipitate.	→ Scales are hard deposits
2.	They are non-adherent deposits and can be easily removed	→ They stick very firmly to the inner surface of boiler and are very difficult to remove
3.	Formed by substances like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$ etc.	→ Formed by substances like $CaSO_4$, $Mg(OH)_2$ etc
4.	Formed at comparatively colder portions of the boiler	→ Formed generally at heated portions of the boiler

x)

	Sludges	Scales
5.	They decrease the efficiency of boiler but are less dangerous.	→ Decrease the efficiency of boiler and chances of explosions are also there
6.	Can be removed by blow-down operation	→ Cannot be removed by blow-down operation

2.3.2 Boiler Corrosion

It is disintegration or decay of boiler material either due to chemical or electrochemical reaction with its environment.

Causes of Boiler Corrosion

(i) Due to presence of dissolved gases in water such as O_2, CO_2, H_2S etc.

(ii) Due to acidic salts

Chemical Treatment

The dissolved oxygen is removed through addition of Na_2SO_3 or Na_2S or hydrazine

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

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

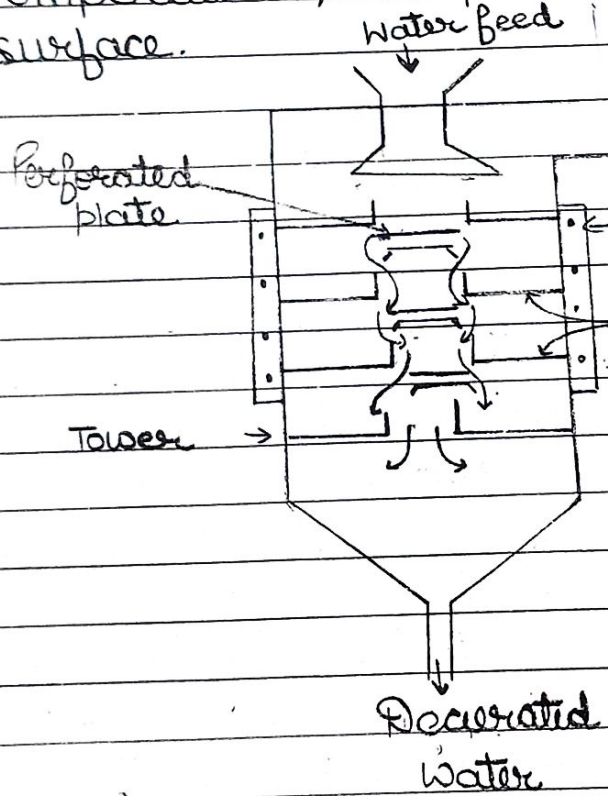
$$H_2N\text{-}NH_2 + O_2 \rightarrow N_2\uparrow + 2H_2O$$

Hydrazine is found to be an ideal compound for removing dissolved oxygen since the products are water and N_2 gas, which does not form hard

Mechanical Deaeration:-

This deaeration involves spraying of raw water through a perforated plate - fitted tower heated from sides by steam jacket. Low pressure is maintained in the tower with the help of vaccum pump connected to it.

Since the solubility of a gas is directly proportional to pressure and inversely proportional to temperature, so the oxygen concentration in water, can be reduced by maintaining high temperature, low pressure and large exposed surface.



Mechanical deaeration of water

Solubility ∝ pressure / temp.

y

c. Dissolved Carbon-Dioxide (CO_2)

The source of CO_2 in water either dissolved CO_2 gas or bicarbonates

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2\uparrow$$

The CO_2 forms a weak acid H_2CO_3, which has a corrosive effect on iron plates of boiler.

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + Fe \rightarrow FeCO_3 + H_2\uparrow$$

2.3.8 (a) Carry Over:-

The process of carrying of water along with impurities by steam is called carry over.

This is mainly due to priming and Foaming

(a) Priming:

When steam is produced rapidly in the boilers, some very small droplets of water are carried along with the steam which is known as 'wet steam' or priming. it contains dissolved salts in it.

Minimization of Priming

(a) By ensuring efficient softening of boiler feed water
(b) By controlling rapid change in steam velocities
(c) By fitting mechanical steam purifier.
(d) By proper designing of boiler.
(e) By maintaining low level of water.

(b) Foaming

Foaming is the formation of continous foams or bubbles in the boiler due to presence of an oil and alkalies in boiler feed water. Oily substances and alkalies react to form soaps which reduced the surface tension of water and thus increases the foaming tendency of water.

Minimization of Foaming:

(a) By removing oil from boiler water by adding coagulants like sodium aluminate ($NaAlO_2$).

(b) By adding anti-foaming agents like castor oil etc.

Disadvantages:

Priming and Foaming which usually, occure together, are objectionable because

(i) Dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. These deposits reduce their efficiency

(ii) Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinary.

2.3.4 Caustic Embrittlement:

Caustic Embrittlement is the phenomenon during which boiler material becomes brittle due

to accumulation of caustic substances.

It is a type of boiler corrosion, which is caused by high alkaline water in boilers, particularly at those places which are under stress, such as rivets, joints and bends with the result that boiler material become brittle.

When water is softened by lime soda process, some free soda (Na_2CO_3) may still be present in soft water which undergoes decomposition in high pressure boiler and NaOH and CO_2 are produced.

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

NaOH makes boiler water caustic or alkaline. This caustic water penetrates into minute cracks present in the inner walls of boilers. On evaporation of water the concentration of dissolved NaOH progressively increases which attacks the iron converting it to sodium ferrate (Na_2FeO_2) and cause embrittlement of boiler parts.

Another source of formation of NaOH in boiler water is presence of natural alkalinity in water.

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

The iron surrounded by concentrate NaOH becomes anodic side, which is corroded whereas the iron surrounded by dilute NaOH becomes cathodic side.

(+)			(-)
Iron at bends joint, rivets	Concentrated NaOH solutions	Dilute NaOH solutions	Iron at plane surface
(Anodic area)			(Cathodic area)

The concentrate alkali dissolves the iron as sodium ferrate (Na_2FeO_2). Na_2FeO_2 decomposes a short distance away from its place of formation according to the following reaction.

$$3Na_2FeO_2 + 4H_2O \longrightarrow 6NaOH + Fe_3O_4 + H_2$$

Further dissolution of iron takes place because of the regeneration of NaOH and precipitate of Fe_3O_4 according to the above reaction.

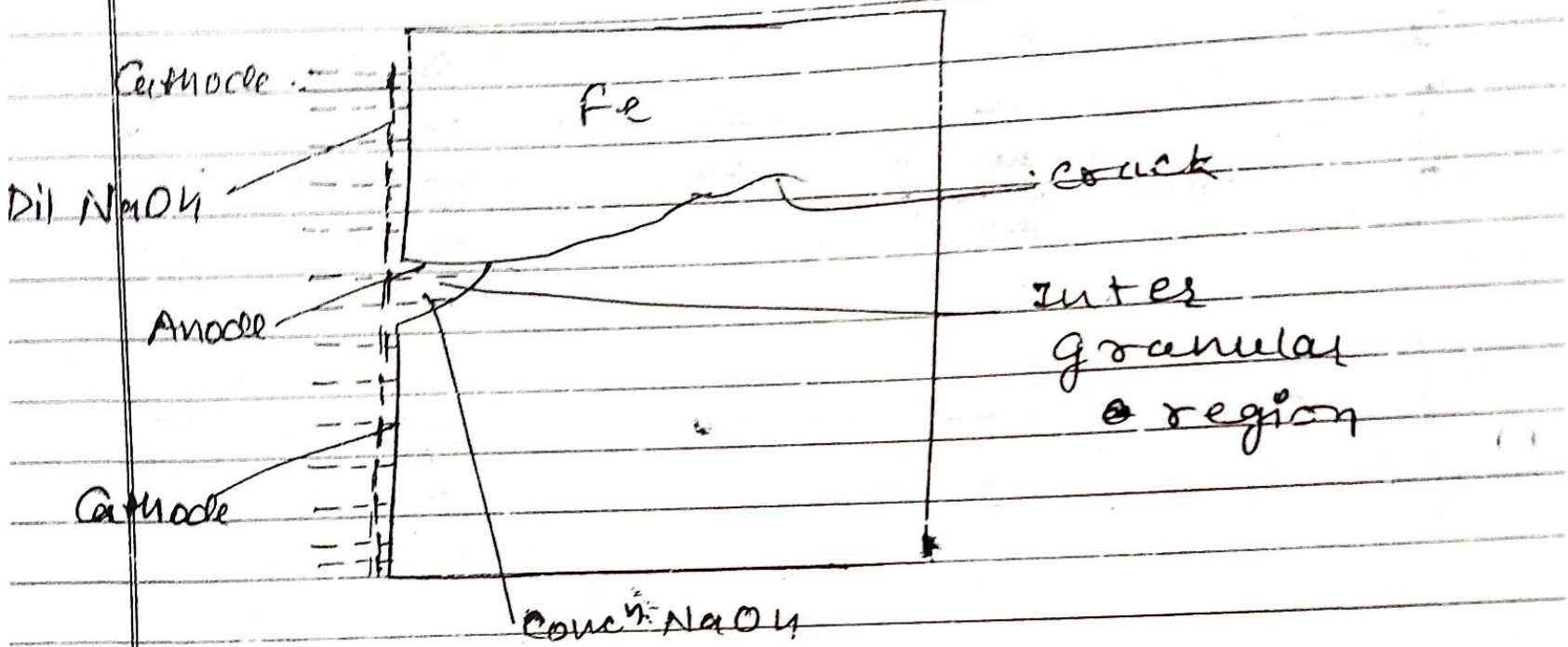
Prevention of Caustic Embrittlement

(a) The pH of the boiler feed water should be carefully adjusted to 8-9.

(b) By using sodium phosphate (Na_3PO_4) as softening reagent instead of Na_2CO_3 in water treatment

(c) excess use of Na_2CO_3 should be avoided in lime soda process.

(d) By adding Na_2SO_4, tannis, lignin to the boiler water which blocks the minute cracks & thus preventing the infiltration of NaOH.



Caustic Embrittlement at the Cracks

UNIT-II

Introduction:

Water is a unique material. It is abundant on the earth. It is essential for the life of man, animals and plants. The water possesses unique physical and chemical properties due to the presence of highly electropositive hydrogen and highly electronegative oxygen. The high boiling point and melting point of water are attributed to the formation of associated molecule through hydrogen bonding.

The high b.P, high m.p., ionic nature, low electrical conductivity, low thermal conductivity high m.p. latent heat of vaporisation and fusion are the unique physical properties that have made water a unique engineering material. Water is also a universal solvent. i.e. almost all materials are soluble in water. NaCl is highly soluble whereas gold, uranium, calcium, carbonate, calcium sulphate have very low to low solubility. The water can exist in all the three phase i.e. ice, liquid & vapour at ordinary temperature and pressure conditions, therefore sometimes it is reffered as nature's most wonderful compound.

Topic: Treatment Unit: II Lecture No.

2.1 Treatment of water (Softening of water)

The term treatment of water is known as Softening of water.

The process of removing the hardness causing salts from water is called Softening of water.

2 Methods For Softening of water

- Lime - Soda Process
- Zeolite Process or Permutit Process
- Ion-Exchange Process

2.2.1 Lime Soda Process

Theory of Lime-Soda Process

The lime soda process is based on the principle that all the soluble, hardness causing salts are chemically converted into insoluble precipitates, which are then removed by setting and filtration.

In this process calculated amount of Lime [$Ca(OH)_2$] and Soda [Na_2CO_3] are added to raw water which react with Ca & Mg salt so as to form insoluble precipitates of calcium Carbonate and magnesium hydroxide. The Chemical reactions involved are -

Reaction With Lime

1. Removal of temporary hardness

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

Calcium bicarbonate — Lime — Calcium Carbonate (insoluble)

$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 + CaCO_3 \downarrow + H_2O$

Temporary — Lime — Magnesium Carbonate

$Ca^{+2} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$

(2L)

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

Magnesium hydroxide (insoluble)

2. Removal of Permanent magnesium hardness

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

Magnesium chloride — Calcium Chloride (L+S)

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

permanent

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

Magnesium sulphate — Calcium Sulphate.

3. Removal of dissolved H_2S & CO_2

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

Calcium Sulphide

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

4. Removal of free mineral acids.

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

Calcium Chloride

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

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6. Removal of dissolved iron and aluminium salts

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

Ferric hydroxide (unstable)

$Ca^{+2} + Na_2CO_3 \longrightarrow CaCO_3 + H_2O + 2Na^+$

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

Aluminium hydroxide (L+S)

$CaSO_4 + 3Na_2CO_3 \longrightarrow 3Na_2SO_4 + 3CaCO_3$

(5) 8. Reaction with $NaHCO_3$

$2NaHCO_3 + Ca(OH)_2 \longrightarrow \underset{\text{Soda}}{Na_2CO_3} + CaCO_3\downarrow + 2H_2O$ (L)

Calculation of the amount of lime required

100 parts of $CaCO_3$ equivalent hardness requires

= 74 parts of $Ca(OH)_2$

Total lime requirment = (for 1 Ltrs of water)

$\frac{74}{100}$ [2 × Temp. Mg hardness + Temp. Ca hardness + Perm. Mg hardness + CO_2 + HCl + H_2SO_4 + (Salts of Fe + Al) + HCO_3^- + $NaAlO_2$]

all in terms of $CaCO_3$ equivalents.

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Reactions with Soda (Na_2CO_3)

1. $CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3 \downarrow$

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

Calculations of amount of Soda required.

100 parts of $CaCO_3$ equivalent hardness requires = 106 parts of Na_2CO_3.

Total Soda requirement (for 1 ltrs of water)

$$\frac{106}{100}\left[\text{Perm. Ca hardness} + \text{Perm. Mg hardness} + \text{salts of } (Al+Fe) + HCl + H_2SO_4 - H_2CO_3^-\right]$$

all in terms of $CaCO_3$ equivalents.

Purity Factor

If a lime and Soda used are 95% and 85% pure respectively therfore, the values obtained in each case are multiplied by purity factor (100/95 for lime and 100/85 for soda.

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Advantage:—

(1) Coagulents ↓

(2.) Economical

(3.) Extra salts were also removed by this process.

The softener consist of a big steel tank with two chambers. The inner chamber is provided with a stirrer and outer chamber has two wood fibre filters to remove the last particles of sludge.

Raw water and calculated amount of lime, soda and coagulant amount of lime are fed through two opposite inlets into the inner chamber at room temperature and stirring is started. Softening of water taken place in a inner chamber slude (ppt.) settle down at the bottom in the outer chamber and the softened water goes upward in the outer chamber where it passes through the wood fibre filters to ensure complete removal of the sludge.

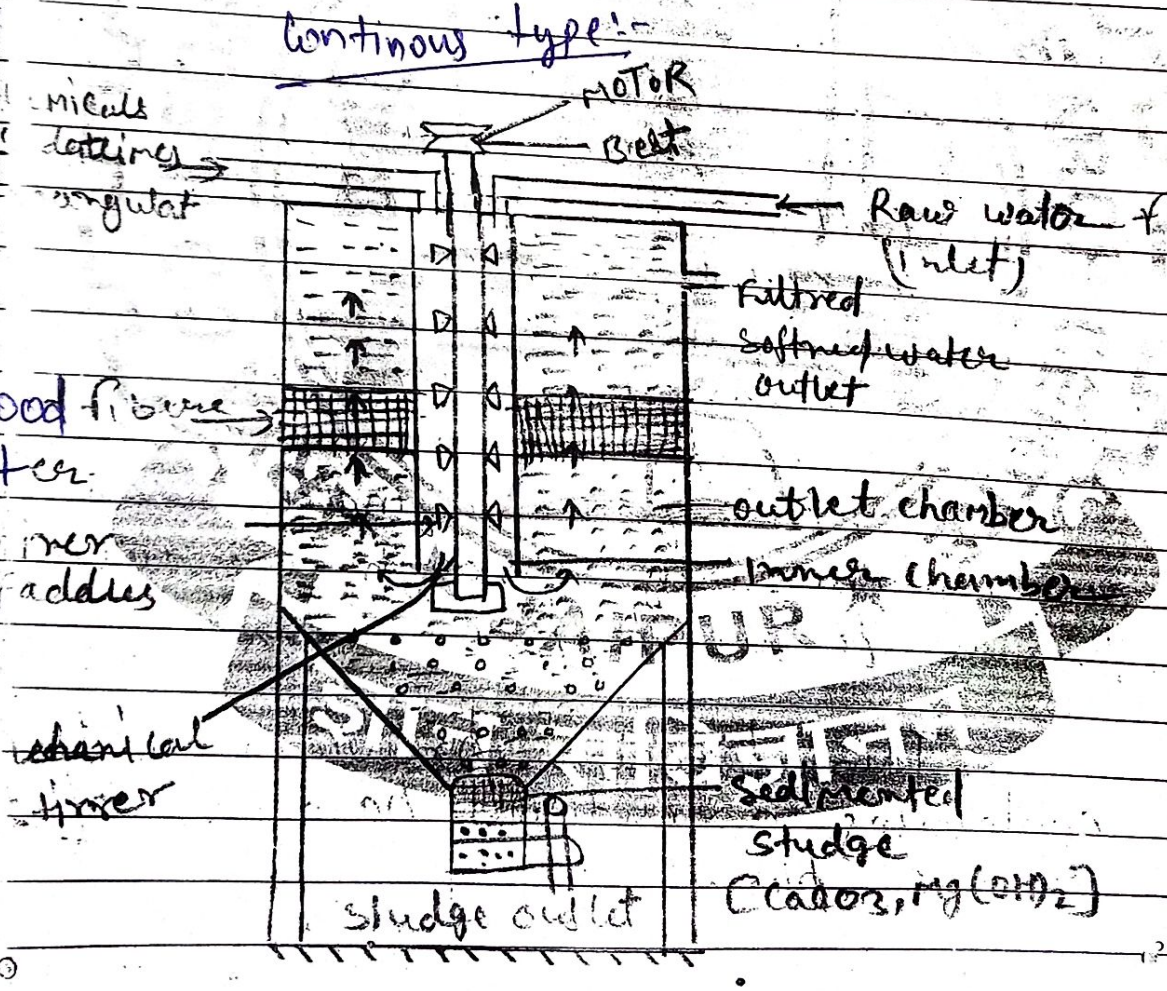
Filtered soft water finally comes out continuously through the outlet provided for the purpose.

This process provides water containing a residual hardness of 50-60 ppm.

Lime-Soda process may be carried out in either cold or hot conditions.

Cold lime-Soda Process

In the continuous process, there is a continuous feed of raw water, chemicals and uninterrupted outflow of soft water is obtained.



Continuous Cold lime-Soda Softener

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2. Hot Lime Soda Process

In this process, water is treated at temperature of 80-150°C. The softeners used may be of intermittent type and continuous type.

(1) Intermittent Type :- The heating coils are installed in it.

(2) Continuous Soft :-

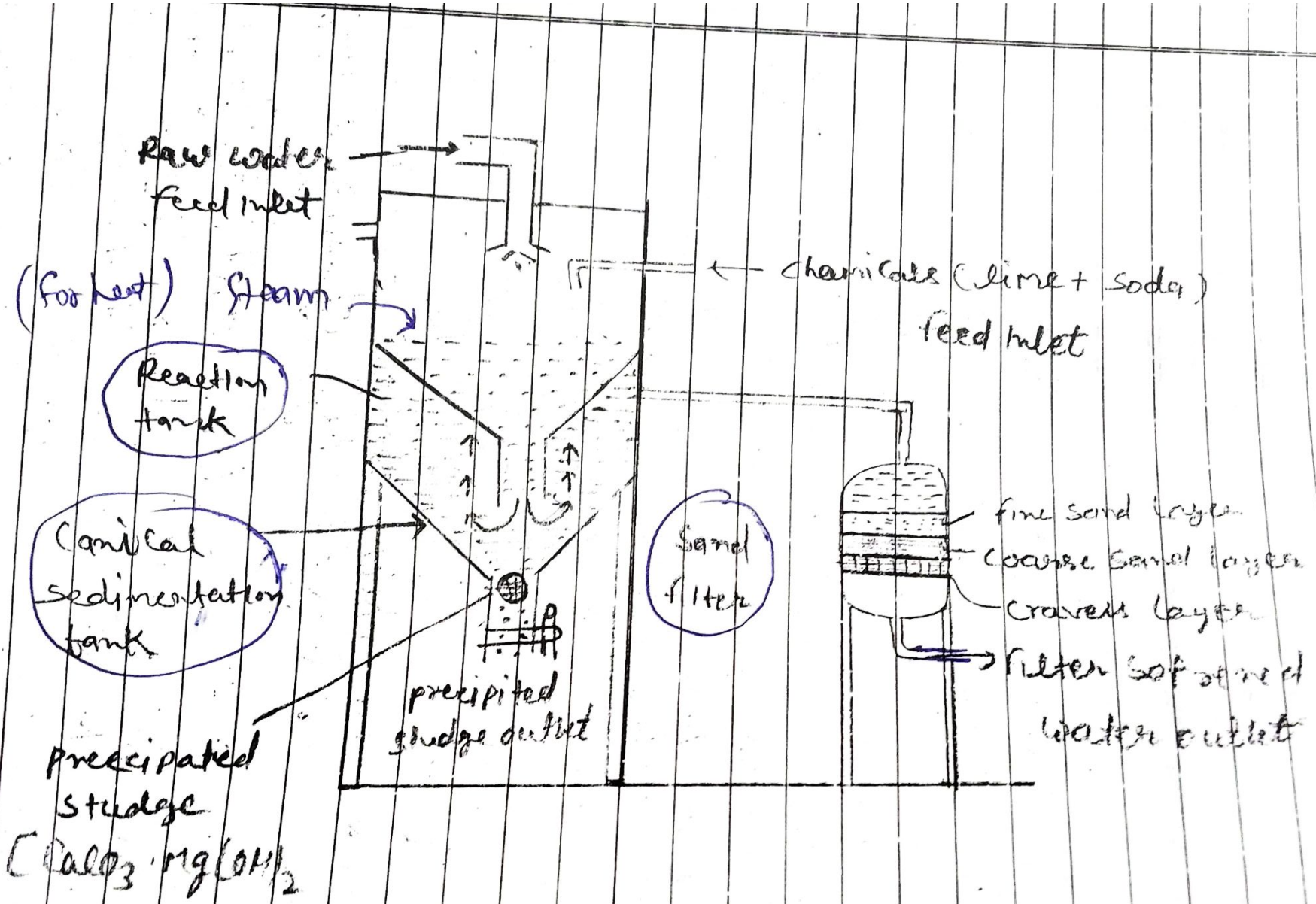
It consists of following three parts

(a) Reaction tank :- Raw water and chemicals are fed from two different inlets. The tank is also having a separate inlet for steam. The reaction starts and also gets completed in this tank.

(b) Settling tank :- From the reaction tank the contents go to the conical settling tank in which sludge settles down and removed by opening sludge valve.

(c) Sand filter :- Clear and soften water from the settling tank passes to filter vessel having layers of fine sand and coarse sand. The sand layers act as filters and remove any suspended particles.

This process provides water containing a residual hardness of 15-30 ppm.



Continous Hot Lime-Soda Softener

Advantage of Continous hot lime-Soda Process :-

1) Due to high temperature, precipitation takes place rapidly, thus the reaction completes in less time (15 min.)

2) Residual hardness is much less than the cold process.

3) Due to rapid settling of prepitate. no coagulant is required.

4) Most of dissolved gases like CO_2 and O_2 are also removed.

→ Rexn time ↓
→ Hot 5 min cold → hours
→ No coagulants
→ Gas removes
→ Less chemical

Disadvantage :— Sludge ↑ → disposed difficult.

2.2.2 Zeolite process or Permutit process :-

Permutit or zeolite is sodium aluminium orthosilicate having general formula.

$$Na_2Al_2Si_2O_8 \times H_2O$$

$$Na_2Ze.$$

where $Ze = Al_2Si_2O_8 \times H_2O$

It occurs naturally or can be manufactured synthetically.

The use of zeolite as softener is based on the fact that it exchanges its sodium ions easily with the heavy metal ions (such as Ca^{+2} & Mg^{+2}) present in hardwater

e.g.

$$Na_2Al_2Si_2O_8 + CaCl_2 \rightarrow CaAl_2Si_2O_8$$

zeolite. $+$

$2NaCl$

Process :-

Zeolite softener consists of a steel tank packed with a thick layer of permutit. Hard water percolated through the permutit when Ca and Mg salts present in it are removed in the form of insoluble zeolites and the resulting soft water is collected from the tap T.

Removal of Temporary and Permanent Hardness :-

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

(ii) $CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$

(iii) $CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$

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

(v) $MgCl_2 + Na_2Ze \longrightarrow MgZe + 2NaCl$

(vi) $MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$

Thus both temporary and permanent hardness can be removed by this method.

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Regeneration of Zeolite / Permutit

Activation of exhausted permutit is called Regeneration. Permutit can work about 12 hours after that it is completely converted Ca and Mg Zeolites and water softening is caused ultimately. It can be made active (regenerate) again by passing 10% solution of NaCl (brine)

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

exhausted zeolite — Regenerate zeolite

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

Soluble Ca and Mg chlorides are washed away through tap T_2.

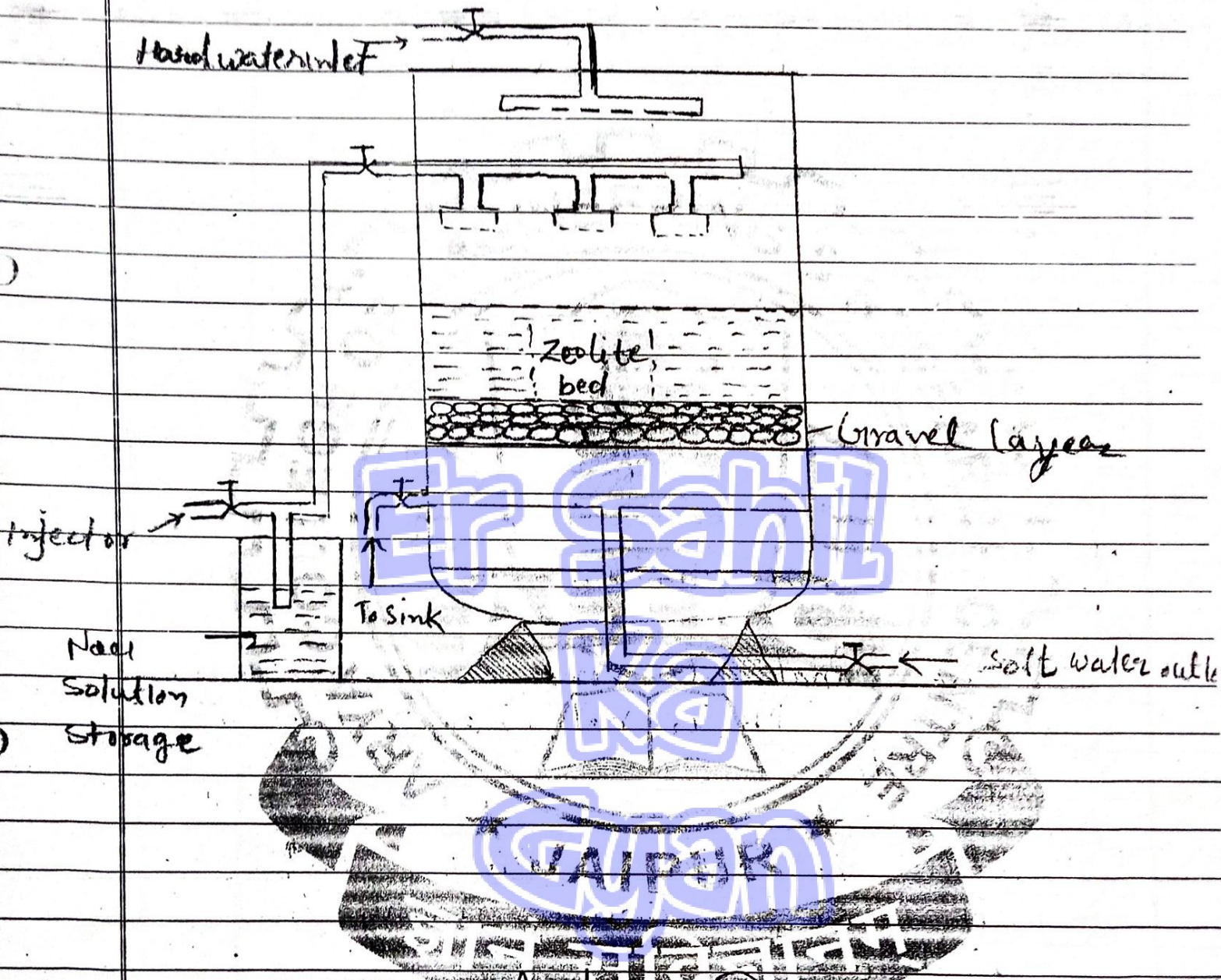
Hardness of water can be calculated by following formula :-

here W = Amount of NaCl in per litre water.

$$\text{Hardness (mg/l)} = \frac{50 \times W \times V_2 \times 10^3}{58.5 \times V_1}$$

V_2 = Total volume of NaCl used, V_1 = Total Volume of water softened

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Zeolite Process

For Water Softening

Advantages of Zeolite Process :

1. This method can produce water having zero hardness.
2. Softening plant occupies small area.
3. This method is very cheap.

Disadvantages of Zeolite Process.

1. This process is not used in case of turbid water.
2. Pb cannot be removed by this method because Pb is not changed to lead zeolite.
3. All the anions remains in soft water. HCO_3^{-2}, OH^-, SO_4^{-2} cause many problems in boilers.

223 Demineralization or Ion-Exchange Process

Demineralization is the process of complete removal of all the ions present in water.

This Process make use of ion exchange resins for the complete removal of ion.

Ion exchange resins are organic, cross linked, insoluble polymers having acidic or basic functional groups and are capable to exchange reversibly there H^+/OH^- ion with hardness producing ions.

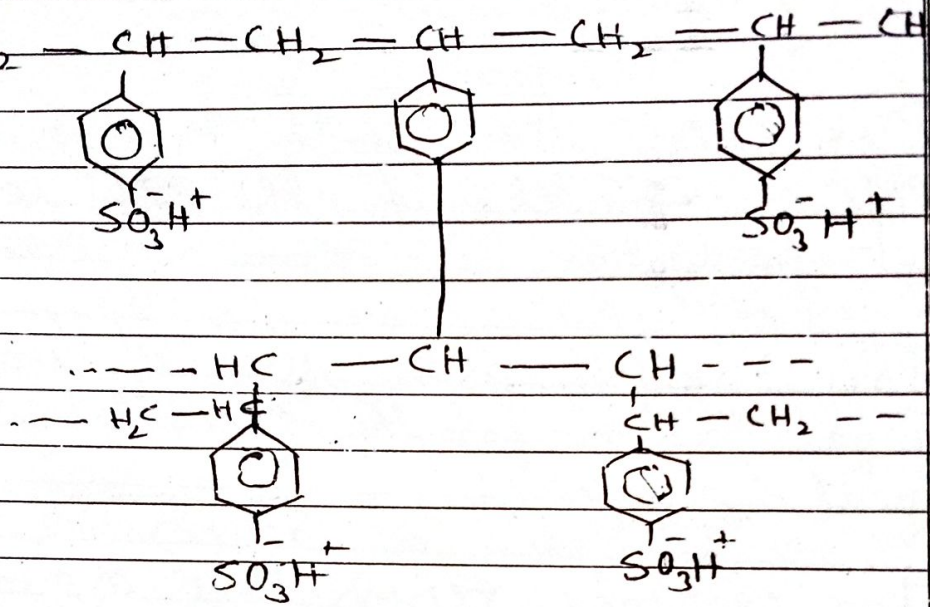
1. Cation Exchange Resin or Cation Exchanger (RH):

These resins contain acidic groups like $-SO_3H$, $-COOH$ or $-OH$ groups as the ionizable group. Since these resins exchange the cationic portion of minerals by their hydrogen atom. They are known as Cation exchanger eg- Styrene and Divinyl benzene copolymers having $COOH$ or SO_3 group.

Name of Lecturer : .....

$2R-COOH + Ca^{+2} \rightarrow (R(OO))_2 Ca + 2H^+$

R = Rest part of the cation exchanger.



Cation Exchange Resin.

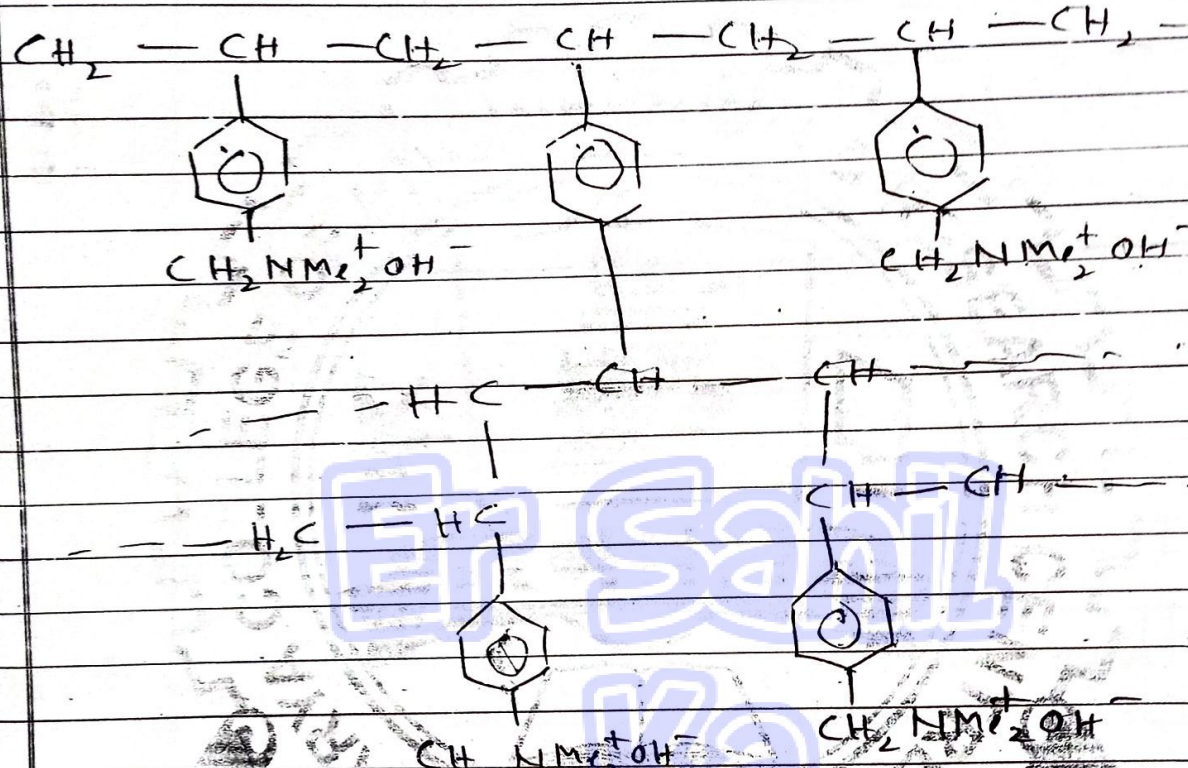
2. Anion Exchange Resin or Anion Exchanger (R-OH) :-

The resins containing basic functional group like $-NH_2$, $-NHCH_3$, $-N(CH_3)_2$ or -OH group as the ionizable group are termed as anion exchanger. According to their name, they exchange the anionic portion of the minerals e.g. styrene-divinyl benzene or amino-formaldehyde copolymers having quaternary ammonium groups.

Name of Lecturer : .....

$R'(OH)_2 + SO_4^{-2} \longrightarrow R'SO_4 + 2OH^-$

R' = Rest part of the anion exchanger



Anion Exchange Resin

Process

The ion exchange softener consists of two tanks. The first tank contains cation exchanger and the second one containing

anion exchanger.

The hard water is first passed through cation exchanger its H^+ ions for Ca^+ and Mg^{+2} ions in water.

Ions for At cation exchanger

$$2R'H + CaCO_3 \longrightarrow R'_2Ca + H_2CO_3$$
$$2R'H + CaSO_4 \longrightarrow R'_2Ca + H_2SO_4$$
$$2R'H + CaCl_2 \longrightarrow R'_2Ca + 2HCl$$
$$2R'H + MgSO_4 \longrightarrow R'_2Mg + H_2SO_4$$

$R' = RCOO^-, RSO_3^-, RO^-$
R = Rest part of resin.

Thus, water passing through cation exchanger is free of Ca^{+2} and Mg^{+2} ions and containing HCl H_2SO_4, H_2CO_3 in equivalent amounts to the anions present in raw water

Now, this water is then passed through anion exchanger tank. Hence the anions like SO_4^{-2}, Cl^- etc present in water are exchanged for OH^- ions of the resin.

At anion exchanger

$$ROH + Cl^- \longrightarrow RCl + OH^-$$
$$2ROH + SO_4^{-2} \longrightarrow R_2SO_4 + 2OH^-$$

Thus the water coming out of the anion exchanger is completely free from cations and anions which are responsible for hardness. It is known as demineralize or deionized water (or pure as distilled water)

H^+ ions released from cation exchanger and OH^- ions released from anion exchange combine to form ionized water.

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

Regeneration :-

It is the process by which exhausted resin is again converted into its original form.

When the resins are used for some period, they get exhausted and stop working. They can be regenerated as follows.

Cation exchangers are regenerated by

passing Through it a moderately Conc. H_2SO_4 or HCl. solution.

$$R'_2Ca + H_2SO_4 \longrightarrow 2\text{-}R'H + CaSO_4$$

Exhausted Resin — Regenerated Resin

The washings Contains $CaSO_4$ and $MgSO_4$ or $CaCl_2$/$MgCl_2$ are passed to sink.

Similarly, the exhausted anion exchangers are regenerated by passing through it an excess of dilute alkali solution like NaOH.

$$R'SO_4 + 2NaOH \longrightarrow R'(OH)_2 + Na_2SO_4$$

$$R'Cl_2 + 2NaOH \longrightarrow R'(OH)_2 + 2NaCl$$

Exhausted anion exchanger — Regenerated anion exchanger.

The washing Containing Na_2SO_4 and NaCl are led to sink.

Name of Lecturer : .....

Merits of Ion-Exchange Process:

(4.) Anion & cations are removed.

1. By this process, water of very low hardness can be produced (= 2ppm)
2. This process can be used to soften highly acidic or alkaline water.
3. Problems like corrosion and caustic embrittlement are reduced because process also removes anions.

Demerits of Ion-Exchange Process:-

1. The equipment and chemicals used for regeneration of Ion-exchange softener are costly.
2. Turbid water can not treated in this process because it may clog pores of resin and hence decreases the efficiency.

Turbid water (↓) efficiency.

1.9.8 Numarical Problems :-

→ Based on Hardness of water.

Q-1 A sample of water on analysis has been found to contain following impurities :-

$Mg(HCO_3)_2$ = 14.6 mg/l , $MgCl_2$ = 19 mg/l .

$Mg(NO_3)_2$ = 29.6 mg/l , $CaCO_3$ = 10 mg/l .

$MgSO_4$ = 36 mg/l , NaCl = 29 mg/l .

Calculate temporary, permanent and total hardness of water sample in ppm and °Clark

Solution - Conversion into $CaCO_3$ equivalents

S.No.	Substance	Amt (mg/l)	Multiplication factor	$CaCO_3$ equivalent (mg/l)
1	$Mg(HCO_3)_2$	14.6	100/146	$14.6 \times 100/146 = 10$
2	$MgCl_2$	19	100/95	$19 \times 100/95 = 20$
3	$Mg(NO_3)_2$	29.6	100/148	$29.6 \times 100/148 = 20$
4	$CaCO_3$	10	100/100	$10 \times 100/100 = 10$
5	$MgSO_4$	36	100/120	$36 \times \frac{100}{120} = 30$

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Temporary hardness = hardness due to [$(Mg(HCO_3)_2$ + $CaCO_3$]

= 10 + 10 = 20 mg/l of $CaCO_3$ eq.

Temporary hardness = 20 ppm

(in °C) = 20 × .07°C = 1.4°C.

Permanent Hardness = hardness due to [$MgCl_2$ + $Mg(NO_3)_2$ + $MgSO_4$]

= 20 + 20 + 30 = 70 mg/l of $CaCO_3$ eq.

(in ppm) = 70 × 1ppm = 70 ppm

(in °C) = 70 × .07°C = 4.9°C

Total hardness = Temporary hardness + Permanent hardness

= 20 + 70 = 90 mg/l.

= 90 × 1ppm = 90ppm.

= 90 × .07°C = 6.30°C.

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Q.2 Calculate the degree of permanent and temporary hardness in ppm of a water the following data :-

(i) 50 ml of the standard distilled water = 0.5 of soap solution.
(ii) 50 ml of $CaCl_2$ solution = 40.5 of soap solution.
(iii) 50 ml of the given water = 15.5 ml of soap solution.
(iv) 50 ml of the boiled water = 12.5 ml of soap solution.
(1 ml of $CaCO_3$ solution = 1.0 mg of $CaCO_3$)

Sol. Since 1 ml of $CaCl_2$ solution (standard water) = 1 mg of $CaCO_3$.
1 litre of $CaCl_2$ solution (standard water) = 1 gm of $CaCO_3$.
Hence $x = 1$ gm, $V = 0.5$ ml, $V_1 = 40.5$ ml, $V_2 = 15.5$ ml
$V_3 = 12.5$ ml.

$$\text{Total Hardness of } x = \frac{(V_2 - V) \times 1000}{(V_1 - V)} \text{ ppm}$$

$$= \frac{1 \times 15 \times 1000}{40} \text{ ppm}$$

$$= 375 \text{ ppm}$$

$$\text{Permanent Hardness} = x \frac{(V_3 - V) \times 1000}{(V_1 - V)} \text{ ppm}$$

$$= \frac{1 \times 12 \times 1000}{40} \text{ ppm}$$

$$= 300 \text{ ppm}.$$

Hence,

Temporary hardness = Total hardness - Permanent hardness.

$= 375 - 300 = 75$ ppm.

Q-3. 1 gm of $CaCO_3$ was dissolved in diluted HCl and the solution diluted to 1 litre. 50 ml of this solution required 45 ml of EDTA solution. While 50 ml. of hard water sample required 18 ml of EDTA solution. On the other hand, 50 ml of boiled water consumed 9 ml of the EDTA solution. Find out temporary, permanent & total hardness of this water sample in ppm of $CaCO_3$ equivalents.

Sol.

Step 1 : Determination of Strength of EDTA.

1 L of standard hard water = 1 g of $CaCO_3$

so 1 ml of standard hard water = 1 mg of $CaCO_3$

As 45 ml of EDTA solution = 50 ml of standard hard water.

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$= 50 \times 1$ mg of $CaCO_3$ equivalent

$\therefore$ 1 ml of EDTA solution $= \frac{50}{45}$ mg of $CaCO_3$ equ.

$= 1.11$ mg of $CaCO_3$

Step II :- Total Hardness

As 50 ml of sample water = 18 ml of EDTA solution

$= 18 \times 1.11$ mg of $CaCO_3$

1 ml of sample water $= \frac{18 \times 1.11}{50}$ mg of $CaCO_3$

1000 ml of sample water $= \frac{18 \times 1.11}{50} \times 1000$ mg of $CaCO_3$

$= 399.6 = 400$ mg of $CaCO_3$

so Total Hardness $= 399.6 = 400$ ppm

Step III : Permanent Hardness

As 50 ml of boiled water sample = 9 ml of EDTA solution

$= 9 \times 1.11$ mg of $CaCO_3$ equivalent

1 ml of boiled water $= \frac{9 \times 1.11}{50}$ mg of $CaCO_3$ eq.

1000 ml of boiled water $= \frac{9 \times 1.11}{50} \times 100$ mg of $CaCO_3$ eq.

So Permanent hardness = 199.8 mg/l

= 200 mg/l

= 200 ppm.

Temporary Hardness = Total Hardness − Permanent Hardness

= 400 − 200 = 200 ppm.

Solved Numerical Problems Based On Hardness :-

Q-1 A water sample contains :-

$Mg(HCO_3)_2 = 80$ mg/l, $Ca(HCO_3)_2 = 135$ mg/l, $CaSO_4 = 124$ mg/l, $MgCl_2 = 80$ mg/l, $CaCl_2 = 90$ mg/l, NaCl = 50 mg

Calculate the temporary and permanent hardness in degree clark.

Solution : Calculation of $CaCO_3$ Equivalents :-

Compound	Quantity (mg/l)	Multi factor	$CaCO_3$ equivalent (mg/l)
$Mg(HCO_3)_2$	80	100/146	54.79
$Ca(HCO_3)_2$	135	100/162	83.33
$CaSO_4$	124	100/136	91.17
$MgCl_2$	80	100/95	84.21
$CaCl_2$	90	100/111	81.08
NaCl	50	—	—

Temporary Hardness = Hardness due to $Mg(HCO_3)_2 + Ca(HCO_3)_2$

= 54.78 + 83.33

= 138.12 mg/l or ppm.

= 138.12 X 0.07°cl = 9.61°Cl

Permanent Hardness = Hardness due to $[CaSO_4 + MgCl_2 + CaCl_2$

= 91.17 + 84.21 + 81.08

= 256.46 mg/l or 256.46 ppm

= 256.46 X 0.07°cl = 17.95°cl

...ge of Engg. & ...

Solved Numerical Problems Based on EDTA Method's

Q-2 One gram of $CaCO_3$ was dissolved in dil HCl and the solution diluted to one litre. 100 ml of this solution required 90 ml of EDTA solution, while 100 ml of the sample water required 40 ml of EDTA. On the other hand, 100 ml of the boiled sample water when titrated against EDTA consumed 30 ml of solution. Calculate each type of hardness in ppm.

Solution: Strength of standard hard water = 1 mg/ml.
= 1 g/l.

Strength of EDTA →
90 ml of EDTA is required for = 100 ml of standard hard water
= 100 mg $CaCO_3$.

∴ 1 ml of EDTA is required for = $\frac{100}{90}$ mg of $CaCO_3$
= $\frac{10}{9}$ mg of $CaCO_3$

Total Hardness
100 ml of sample required = 40 ml of EDTA.
Since 1 ml of EDTA is required for = $\frac{10}{9}$ mg of $CaCO_3$
40 ml of " " = $\frac{10}{9} \times 40$ mg of $CaCO_3$
Hence 100 ml of sample water contains = $\frac{400}{9}$ mg of $CaCO_3$
1000 ml " " = $\frac{400}{90} \times \frac{1000}{100}$ mg of $CaCO_3$
= 444.4 mg/l

Total Hardness = 444.4 mg/l or ppm

Permanent Hardness :-

After boiling 100ml of sample water requires = 20ml of EDTA

100 ml of sample water contains = $20 \times \frac{10}{9}$ mg of CaCO3

$= \frac{200}{9}$ mg of $CaCO_3$

1000 ml of sample water contains = $\frac{200}{9} \times \frac{1000}{100}$ mg of $CaCO_3$

= 222.2 mg/l or ppm.

Permanent Hardness = 222.2 mg/l or ppm.

Temporary Hardness = Total Hardness - Permanent Hardness

= 444.4 - 222.2 = 222.2 ppm.

Temporary Hardness = 222.2 PPm.

Name of Lecturer : Rajan

Q-3

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

Solution:-

Standardization of EDTA solution:-

Given - 1 L of standard hard water contains 0.28gm $CaCO_3$. Hence each ml of standard hard water contains 0.28 mg $CaCO_3$.

As, 28 ml of EDTA = 100 ml of standard hardwater

$= 100 \times 0.28 = 28$ mg $CaCO_3$

1 ml of EDTA $= \frac{28}{28} = 1$ mg of $CaCO_3$

Determination of total hardness of water.

100 ml of unknown hard-water sample = 35 ml of EDTA

= 35 mg of EDTA

∴ 1000 ml of unknown hard water sample.

$= \frac{35}{100} \times 1000 = 350$ mg of $CaCO_3$ equi. or mg/l.

Hence Total hardness = 350 ppm.



Determination of Permanent Hardness

100 ml of boiled water = 10 ml of EDTA

$= 10 \times 1 = 10$ mg of $CaCO_3$ eq. of hardness

1,000 ml of boiled water

$= \frac{10}{100} \times 1000 = 100$ mg of $CaCO_3$ eq.

Hence, Permanent Hardness of water = 100 ppm.

Determination of Temporary Hardness -

Temporary = Total hardness - Permanent Hardness

$= 350 - 100 = 250$ ppm

Temporary = 250 ppm

Numerical Problems Based On Clark's Method

Q-4 Calculate the degree of permanent and temporary hardness in ppm of a water with the following data

(i) 50 ml of the distilled water = 0.5 ml of soap Sol.
(ii) 50 ml of $CaCl_2$ solution = 40.5 ml of soap Sol.
(iii) 50 ml of the given water = 15.5 ml of soap Sol.
(iv) 50 ml of the boiled water = 12.5 ml of soap Sol.

Solution :-

Since 1 ml of $CaCl_2$ solution (Std water) = 1 mg of $CaCO_3$

1 litre of $CaCl_2$ solution (Std water) = 1 gm of $CaCO_3$

Hence if $x = 1$ gm, $V = 0.5$ ml, $V_1 = 40.5$ ml, $V_2 = 15.5$ ml, $V_3 = 12.5$ ml.

Hence

Now Total Hardness $= x \times \frac{(V_2 - V)}{(V_1 - V)} \times 1000$ ppm.

$= \frac{1 \times 15}{40} \times 1000$ ppm $= 375$ ppm.

Permanent hardness $= x \times \frac{(V_3 - V)}{(V_1 - V)} \times 1000$ ppm.

$= 1 \times \frac{12}{40} \times 1000$ ppm $= 300$ ppm.

Hence Temporary hardness = Total hardness - Permanent hardness

$= 375 - 300$ ppm. $= 75$ ppm.

Numericals based on Lime - Soda

Method -

(1) A sample of water was analyzed and found to contain the following:-

$Mg(HCO_3)_2$ = 20 mg/l

$MgCl_2$ = 10 mg/l.

$CaCl_2$ = 12 mg/l.

NaCl = 1 mg/l.

$CaSO_4$ = 25 mg/l.

$CaCO_3$ = 5 mg/l.

SiO_2 = 2 mg/l.

Calculate Lime and Soda required for softening 20,000 litres of hard water

Solution :-

Conversion into $CaCO_3$ equivalents

Constituents	Amount (mg/l)	Multiplication factor	$CaCO_3$ equivalent mg/l
$Mg(HCO_3)_2$	20	100/146	$20 \times \frac{100}{146} = 13.6$
$CaSO_4$	25	100/136	$25 \times \frac{100}{136} = 18.3$
$MgCl_2$	10	100/95	$10 \times \frac{100}{95} = 10.52$
$CaCO_3$	5	100/100	$5 \times \frac{100}{100} = 5$
$CaCl_2$	12	100/111	$12 \times \frac{100}{111} = 10.81$
SiO_2	2	Do not impart hardness.	—
NaCl	1	Do not impart hardness.	—

formula used :-

Total hardness = $\frac{74}{100}$ (Temp Ca^{+2} + 2 temp Mg^{+2} + perm ($Mg^{+2} + Al^{+3} + Fe^{+2} + H^+ + CO_2 + HCO_3^- - NaAlO_2$ all in $CaCO_3$ eq.

Lime requirement $= \frac{74}{100}[CaCO_3 + 2 \times Mg(HCO_3)_2 + MgCl_2] \times$ Val. of water.

$= \frac{74}{100}[5 + 2 \times 13.69 \times 10.52] \times 20000$ mg

$= \frac{74}{100}(42.9) \times 20000$ mg.

$= 634920$ mg.

Soda requirement $= \frac{106}{100}[CaSO_4 + CaCl_2 + MgCl_2]$

$\times$ Volume of water.

$= \frac{106}{100}[18.38 + 10.81 + 16.52]$

$\times 20000$ mg.

$\Rightarrow 841852$ mg $= .84$ kg.



Date
12/9/18

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Unit-2 (Corrosion).

(S.N)

1. Defination of Corrosion
2. Theories of Corrosion → Chemical Attack Theory (Dry corrosion) (Detail/Ques.)
   → Electrochemical Theory (Wet Corrosion.)
3. Type of Corrosion → Galvenic Corrosion.
   → Concentration Cell Corrosion. } (Sh. Note)
   → Pitting Corrosion.
4. Corrosion Protection Methods. (Detail/Ques.).

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1. Defination of Corrosion :→ Decay or destruction of metals by the electrochemical reaction of metal with its environment or the conversion of metal into metallic compound (like oxides, carbonates, chlorides, Bromides etc).

Metal (High energy state) —Corrosion→ Metallic compounds + Energy ↑ (low energy state)

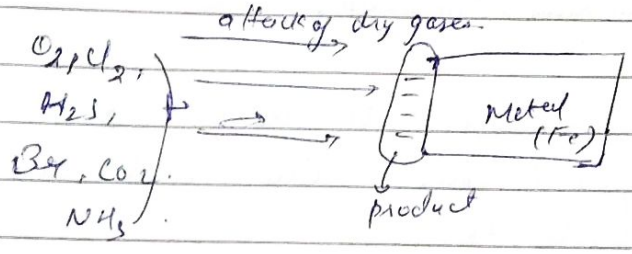
2. Theories of Corrosion :→

(1) Chemical Attack Theory (Dry Corrosion) :—

The chemical attack theory deals with the attack of dry gases like (oxides, chlorides, Sulphide, Carbonate on the metal surface at high temperature

forming a product layer on metal surface.

→ This type of corrosion occurs in absence of moisture so that known as dry corrosion.

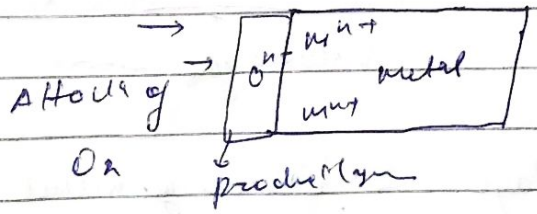


Dry corrosion is of three types. :-

Dry corrosion

Oxidation corrosion (attack of O_2)	Corrosion by other gases. ($Cl_2, NH_3, H_2S, Br_2, CO_2$)	By Liquid Metal on the solid metal.

1. Oxidation Corrosion → In this type of corrosion dry oxygen gas attacks on the metal surface forming a oxide layer on the metal at high temperature.



$$2M \rightarrow 2M^{n+} + 2ne^-$$

$$\frac{n}{2} O_2 + 2ne^- \rightarrow nO^{-2}$$

metal oxide

Generaly four types of product layers are formed on the metal.

(1) Stable → A fine stable layer is formed on the metal which is protective in nature.
ex- Aluminium, Tin, lead.

(2) Unstable layer → Oxide layer is formed and further decomposed back into metal and oxides.
Ex → Ag, Au, Pt.

(3) Volatile → As soon as the oxide layer is formed and volatise immediately leaving metal exposed for further attack.
ex → MoO_3 (Molebidm trioxide)

(4) Porous → In this type of layer containing pours through which, oxygen attacks on the metal till all the metal is converted into oxide.
Ex → Li, Na, K.

★→ Pilling Bedworth Rule :→ (PBR)

P.B.R. = $\frac{\text{Volume of metal oxide layer.}}{\text{Volume of metal consumed.}}$

Situation → (1.) Volume of layer < Volume of metal, then corrosion

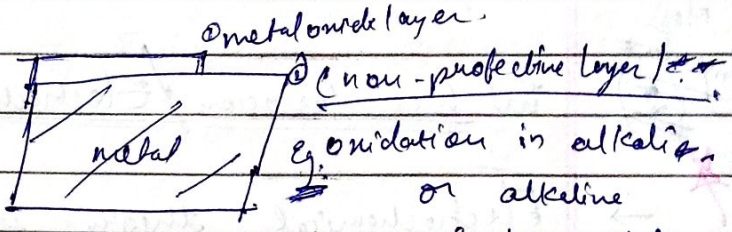
(2.) P.B.R less than Unity.

(3.) Non-protective film is formed.

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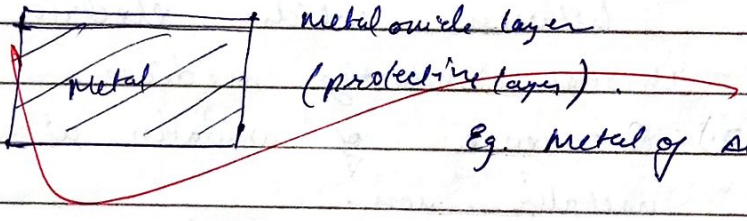
Eg. oxidation in alkali or alkaline earth metal.

→ Situation 1 → If the volume of oxide film < Volm of metal consumed then the ratio is less than Unity.



Points are ⇒

→ Situation 2 → If the volm of metal oxide layer is equal or greater than metal than protective film is formed on the metal.



Eg. metal of Al.

① Volume of layer ≥ volm. of metal, then rate of corrosion decreases.

② P.B.R. greater than unity.

③ Protective film is formed.

2. Oxidation by other gases :- Chemical corrosion also occurs due to the attack of other gases like SO_2, CO_2, Cl_2, H_2S, Br, NH_3, etc on the metal surface.

The extent of corrosion (limit) depends upon the formation of non-protective or protective film on the metal.

Eg. :- ① attack of Cl_2 on the Ag. (protective)

② attack of Cl_2 on the Sn. (non-protective).

DATE :

3. Corrosion by liquid :- This type of corrosion occurs due to the attack of liquid metal on the solid metal either by (i) it dissolution or by (ii) liquid metal penetrate into solid

Eg.- devices used in nuclear power plant.

Most Important

Wet Corrosion / Electrochemical theory of Corrosion :-

→ Electrochemical theory is a most accepted theory and takes place under moist conditions.

→ The essential features for this theory is are

1. presence of a conducting medium.
2. The formation of anodic and cathodic areas between which electric current flows through conducting medium.
3. Occurence of oxidation at anode which generate metallic ion.
4. Occurence of reduction at cathode which produces non-metallic ion.
5. Diffusion of metallic and non-metallic ions towards each other through medium and formation of corrosion product b/w anode and cathode

* Mechanism :-

1) At Anodic Area → Metal oxidises and gives electrons

$Fe \longrightarrow Fe^{+2} + 2e^-$ (At Anode)

CT = Cathod to anode

simple] = An to Cath

2) At Cathodic Area → The cathodic reaction consume electrons either by →

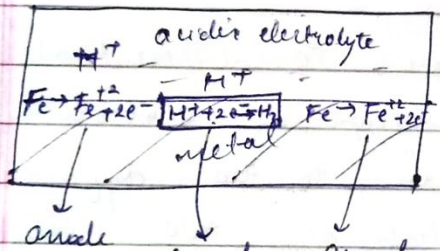
(1.) Evolution of H_2 gas (in presence of Acidic electrolyte).

(2.) Absorption of oxygen gas (in presence of Neutral or alkaline electrolyte).

Cathodic Rxn..

(I.) By H_2 gas evolutions

→ H_2 gas liberated when acidic electrolyte present.



large anode, small Cthode (Uniform Corrosion)

$Fe \rightarrow Fe^{+2} + 2e^-$

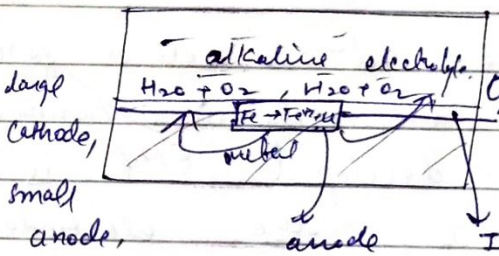
$2H^+ + 2e^- \rightarrow H_2 \uparrow$

→ At anode iron oxidise and converted into Fe^{+2} ion.

→ Liberated e^- flows throw conducting medium and excepted by H^+ ion and releases H_2 gas at cathode.

By O_2 gas absorption.

O_2 gas absorbed when alkaline or metal electrolyte present.



(localized corrosion / non-uniform)

$Fe^{+2} + 2H^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3$ (Rust)

→ The surface of iron usually covered by iron oxide layer if any crack/scratch developed in the layer then small anode is formed while the rest part of metal act as cathode.

→ At anode iron oxide and converted into Fe^{+2} ion; at cathode liberated e^- are excepted by H^+ ion &

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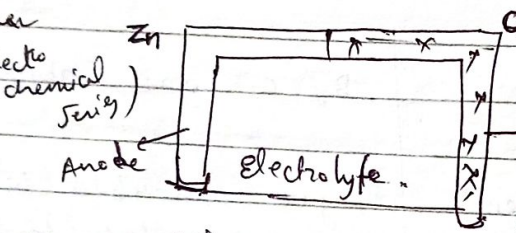
(Cu) reduces (Easily)

finally rust is formed b/w anode & cathode.

Types of Corrosion :-

1. Galvenic Corrosion →

(i) Zn-Cu coupling



$Zn \longrightarrow Zn^{2+} + 2e^-$ $\quad Cu^{2+} + 2e^- \rightarrow Cu(s)$

→ The galvenic cell is formed when to different metals are electricaly connected through an electrolyte.

→ The developed EMf is equal to the difference to the electrode potentials of two different metal.

$$\Delta E = E_A - E_B$$

$$(emf) = E_{cathode} - E_{anode}$$

→ The metal higher in electro chemical series always acts as anode. and corroded in zinc copper coupling. Zinc act as anode oxidises and releases 2e-

Anodic Reaction $\quad Zn \longrightarrow Zn^{2+} + 2e^-$

→ The metal lower in electrochemical series always act as cathode and protected.

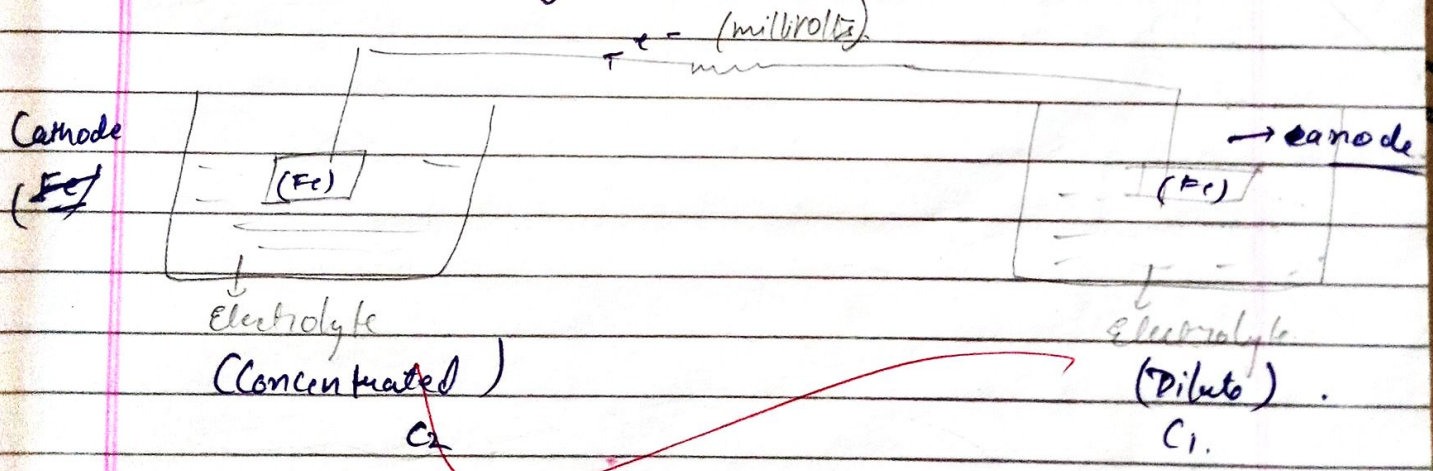
In Zn-Cu coupling, Cu get as cathode reduces & accept 2e⁻.

$Cu^{2+} + 2e^- \rightarrow Cu(s)$

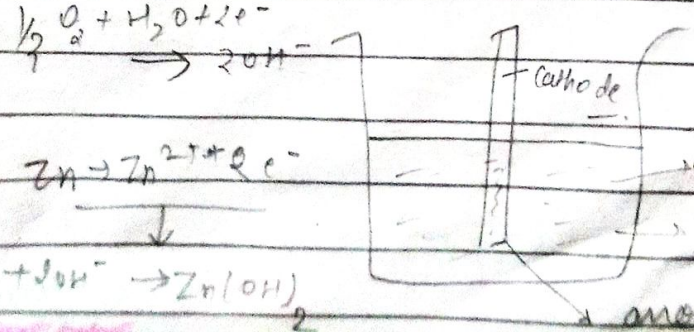
→ If acid electrolyte is present then hydrogen is also liberated and if the medium is alkaline then cathodic reaction is also occured by oxygen absorption.

② Concentration Cell Corrosion :-

Ex → small emf is generated



② Differential aeration



solutions.

Sol. (c) Pitting Corrosion : Pitting corrosion is a *localized accelerated attack* at some place on the metal surface, pitting corrosion thus results in the formation of pinholes, pits as well as cavities in the metal, and these irregularities may penetrate deep into the metal causing destruction of pipes and tubes.

Pitting corrosion may be due to the following important reasons–

(a) External environment is not homogeneous.

(b) Metal surfaces are not homogeneous.

(c) Films are not perfectly uniform.

(d) Environment is not uniform with respect to concentration.

(e) Crystallography directions are not equal in the reactivity.

(f) Scratches or cut edges sliding under load.

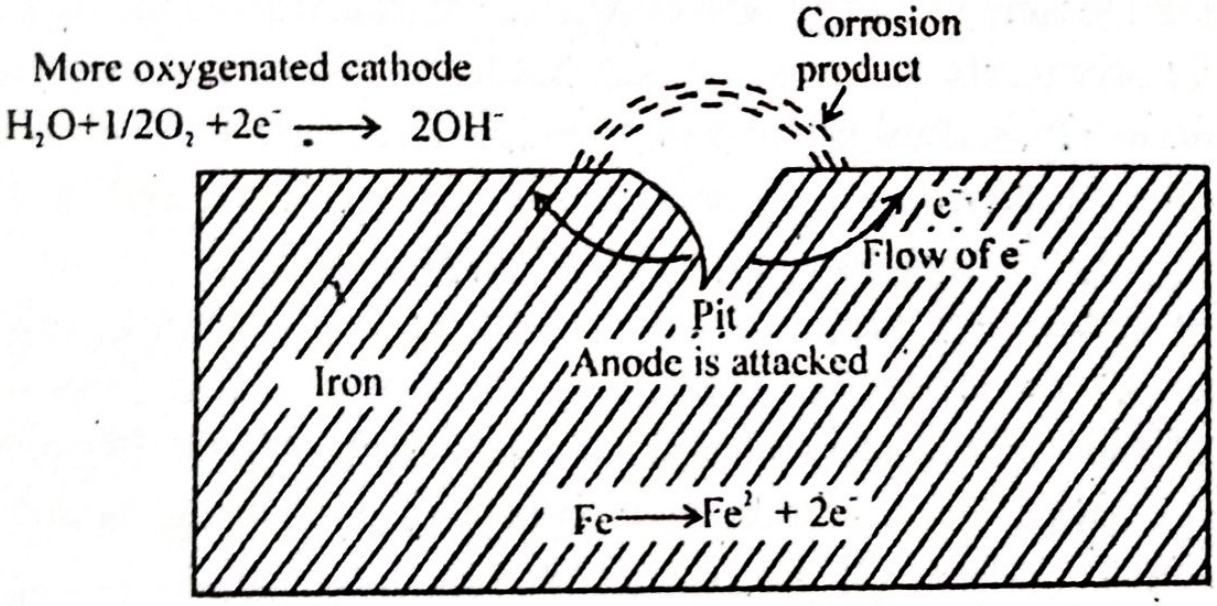


Fig. : Pitting Corrosion at the Surface of Iron

Pitting is generally caused as a result of breakdown or cracking of the protective film on a metal at specific point and pitting is neither uniform nor has a constant rate. As a result of pitting, small anodic and large cathodic areas are developed and once a pit is formed, the rate of corrosion will be increased. Pitting occurs mostly in chloride solution containing a depolarizer (oxygen or oxidizing salt).

Sol.(b) Corrosion Control (Protection against Corrosion) :

1. Using Pure Metal

The corrosion-resistance of a given metal may be improved by increasing its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces, when exposed to environment. However, corrosion-resistance of a purified metal depends on the nature of corrosive environment. For example, the corrosion resistance of Al depends on its oxide film formation, which is highly protective only on the high purity metal. So, impurities in a metal cause heterogeneity, which decreases corrosion resistance of the metal.

2. Proper Designing

The design of the material should be such that "corrosion even if it occurs is uniform and does not result in intense and localized corrosion". Some important design principles are :

(i) If two dissimilar metals in contact have to be used, they should be as close as possible to each other in the electrochemical series.

(ii) The anodic metal should not be painted or coated, when in contact with a dissimilar cathodic metal, because any break in coating would lead to rapid localized corrosion.

(iii) When two dissimilar metals are to be in contact, the anodic material should have as large area as possible; whereas the cathodic metal should have as much smaller area as possible.

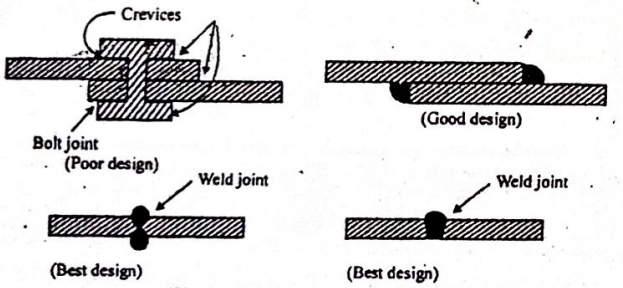


Fig.1 : Different types of joints

(iv) Prevent the occurrence of hetrogeneties, both in the metal and in the corrosive environment. Thus, a proper design should avoid the presence of crevices between adjacent parts of the structure, even in the case of the same metal, since crevices permit concentration differences. Bolts and rivets are, therefore undesirable for this reason and these should preferably be replaced by a butt-weld.

(v) Avoid the contact of dissimilar metals in the presence of a corroding solution.

If this principle is not followed, then corrosion is localized on the more active metal (in the immediate vicinity of contact). While the less active metal remains protected.

(vi) Whenever the direct joining of dissimilar metals, is unavoidable, an insulting fitting may be applied in-between them to avoid direct metal-metal electrical contact.

(vii) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.

(viii) It is desirable that the design allows for adequate cleaning and flushing of the critical parts (i.e., susceptible to dirt, deposition etc.) of the equipment.

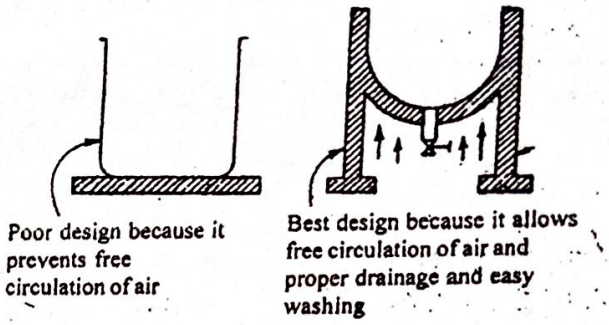


Fig. 2 : Prevention of corrosion by design

Sharp corners and recesses should be avoided because they favour the formation of stagnant areas and accumulation of solids, etc.

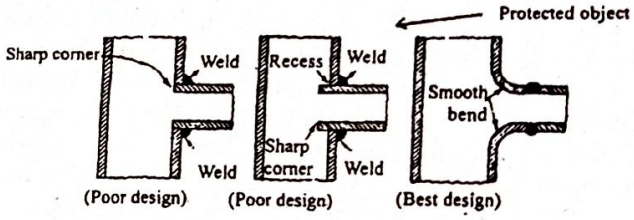


Fig. 3 : Prevention of corrosion by design

3. Cathodic Protection : The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protections

(i) Impressed Current Cathodic Protection : In this method, an impressed current is applied in opposite direction to nullify the corrosion current and concert the corroding metal from anode to cathode.

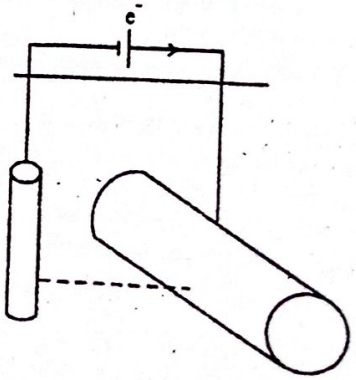


Fig. 1 : Electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized

The object to be protected is made cathode by connecting it to negative terminal of DC source. This type of cathodic protection has been applied to open water- box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine pipes, laid-up ships, etc. This kind of protection technique is, particularly, useful for large structures for long-term operations.

(ii) Sacrificial Anodic Protection Method: In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, water-tanks, etc.

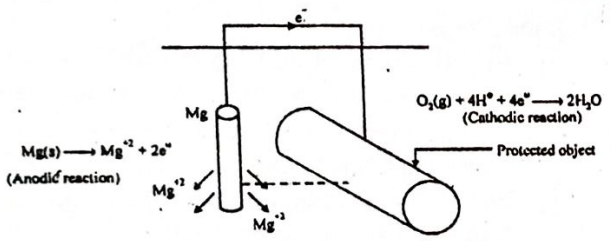


Fig. 2 : An anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object

4. Application of Metallic Coatings

The coating of one metal over the other is the most important method of protection from corrosion. Such protective layers may be produced on the surface by more corrosion resistant metal (such as Ni, Cr, Zn and Sn) by the process of electroplating, hot dipping, vapourising etc.

(i) Metals such as Au, Ag, W, Pt etc. (noble metals) are used for electroplating on the desired metal. When a noble metal is electroplated, it projects the base metal by virtue of its noble character. Tin plating and nickel plating are the most common examples. The electroplating of zinc is known as cold galvanizing. In electroplating, the object to be plated is made the cathode. The electrolyte is a salt of the metal to be deposited. The anode may be of the metal to be deposited or it may be an inert electrode (such as graphite). The anode (that of the metal to be deposited) dissolves to coat the metal in the solution. Au, Ag, Cr, Ni, Cu, Zn, Sn etc. can be electroplated.

(ii) Vapourising: Some metals can also be used as surface layers (deposition) by allowing their vapours to strike metallic surfaces with which they undergo alloying. Zn and Al are examples of this category. The deposition of Zn by this process is known as dry galvanizing and deposition of aluminium is called calourising.

(iii) Hot Dipping: It involves coating metals with films of metals having low melting points like Zn, Sn, Pb etc. This process involves dipping the cleaned metal in the both of molten metals. The liquid metal forms an alloy with the solid metal and as a result, a coating is formed on the surface. Tin plated iron and zinc plated iron (galvanizing) are the examples of 'Hot dipping process'.

The tin coating of iron does not allow iron to have a direct interaction with moisture and air and hence no rusting takes place. In Zn coating of iron, even when the protective coating is broken, iron is still resistant to corrosion (or rusting) because Zn is above iron in electrochemical series (so, Zn is more reactive than Fe).

A cheaper coating called 'terneplate' is produced by dipping iron in a molten alloy containing 20% Sn (tin) and 80% Pb (lead).

(iv) Metal Spraying: It is only used when hot dipping is not possible. This method is also utilized for huge structures such as bridges or industrial plants etc.

In scoop process, molten metal (Zn, Al, Cu etc.) are sprayed on the cold surface to be coated from spraying pistol and this adheres strongly but does not actually penetrate.

(v) Cementation : In this method, the metal to be deposited forms an alloy with the surface of the metal on which deposition occurs. The articles to be coated are packed in powdered coating metal in a drum which can be rotated and heated at a temperature slightly below the melting point of the more fusible metal.

Prob.4 ***What is corrosion? Discuss the mechanism of electrochemical corrosion.*** ***[R.T.U. 2016]***

Sol. Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. One of the most widely accepted definition is that **"Corrosion is the slow but spontaneous deterioration of metals (except gold and platinum) by chemical or electrochemical reaction with its environment".**

Examples

(1) Formation of a layer of reddish brown scale of $Fe_2O_3.2H_2O$ on the surface of iron, also known as *"rusting of iron"*.

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$$

(2) Formation of green layer of basic carbonate, $CuCO + Cu(OH)_2$ on the surface of copper when exposed to moist air containing CO_2.

(3) Reaction of Cl_2 gas with Mg or Sn.

Wet or Electrochemical Theory : *Refer to Long Answer Prob.3(a).*

Date 9/10/18

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Important

Unit-3 = Fuels.

(1) Definition of fuel :- A fuel can be defined as a combustible substance containing carbon as a major constituents which is capable to releases large amount of heat or energy on burning that can be used in domestic as well as industrial purposes.

Combustion reaction :-

$$\text{Fuel} + O_2 \xrightarrow[\text{Combustion}]{\text{air}} CO_2 + H_2O + \text{ash} + \text{Energy}$$

Ex → wood, coal, coke, charcoal, diesel, petrol, kerosine, LPG etc.

(2) Classification of Fuels :- Fuels may be classified on the basis of.

1) there occurence 2) there state of aggregation (Physical form)

(1) On the Basis of there Occurence.

- Primary / Natural fuel (These are available in nature)
- Secondary / derived fuel. (these are obtained from primary fuel)
  - → Liquid - Petrol, diesel
  - → Solid - charcoal, coke
  - → Gas - LPG, CNG, Biogas

(2) State of Aggregation :-

- Solid (wood, coal)
- Liquid (crude oil)
- Gaseous - Natural gases

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(3.) Important Characteristics of a good fuel :-

~~(1)~~ Calorific value of fuel :- Calorific value means amount of heat liberated by the complete combustion of unit mass of fuel.

Units → Calorie/gm or Kilo Calorie/Kg.

→ A good fuel should have high calorific value that means amount of heat liberated by the combustion of fuel, should be high.

→ A good fuel should have low moisture content contained because moisture reduces the calorific value of fuel.

→ A good fuel should have moderate ignition temperature because low ignition temperature is harmful for storage while high ignition temperature causes difficulty to ignitiate the fuel.

→ It should burn in air with more efficiency with producing smoke.

→ It should not give harmful gases on burning.

→ It should be easy to handle, store and transport.

→ It should be available in bulk at low cost.

→ A good fuel should have low volatile matter and non combustible matter (Ash) because volatile matter & non combustible matter reduces the Calorific value of fuel.

→ The fuel should involved in burning in a controled manner & should be easy to stop when required.

→ A good fuel should not undergo spontaneous combustion.

Teacher's Signature

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Solid Fuel

(I) Classification of Coal :-

Wood → Coal → Peat (45-60)% (I) → Lignite (60-75)% (II) → Bituminous (75-90)% (III) → Anthracite (90-97)% (IV)

C, H, O, N, ash, S.

Coal transformation stages.

(I) **Wood :-** wood is the primary solid fuel available in abundence in forests.

→ About 25 to 50% moisture in green wood, and it become 10 to 15% after drying.

→ Calorific value of wood is 3500 - 4500 Kcal/kg.

→ Elemental composition is carbon 40-50%, oxygen 43%, Hydrogen 6%, ~~N2~~ 1%, ash 1%.

→ It burns rapidly with producing long smoky flame and leaves behind small amount of ash.

→ **Peat →** It is the first stage of coal transformation.

→ Peat is produced by the gradual decomposition of vegetable matter under high temperature and pressure in moist places.

→ The upper layer of peat is brown in colour.

→ It is not a economical fuel because its drying cost is very high.

→ **Lignite →** It is the second stage of coal transformation upper layer of lignite is dark brown in colour due to high percentage of carbon.

→ Lignite involved in burning with producing long smooky flame.
→ It is used in the manufacturing of producer gas.

→ Bituminous → It is the most widely used fuel because the high amount of carbon & high calorific value.
→ It is the denser and harder than Lignite.
→ It burn with smooky yellow flame.
→ bituminous is used in gas industry coaltar distillation and gas furnaces etc.
→ Bituminous is further divided on the basis of carbon percentage in three category.
(1.) Sub-bituminous (70-80%)
(2.) Bituminous (78-90%)
(3.) Semi-Bituminous (90-95%).

→ Anthracite → It is the final stage of coal transformation
→ Anthracite is black in colour, hard & very dense.
→ It ignition with very difficulty but burns slowly which producing non smooky blue flame.
→ Anthracite has low volatile matter but high percentage of carbon.
→ Anthracite is used in domestic purposes and in metallurgical operations also.

Type of fuel	C	H	O	Ash	C.f.V. kcal/kg
Wood	40-50 %	50-60 %	20-40 %	1-5	3500 - 4500
Peat	45-60 %	35-65	20-45	4-0	4000 - 5000
Lignite	60-75 %	45-55	17.35	6-3	4000 - 7000
Bituminous	80-85 %	40-55	20-30	7-0	6000 - 8500
Anthracite	90-95 %	3-25	2-3.	4-0	8500 - 8700

* very very important ⇒ **Carbonization Process** :- when coal is subjected to distructive distillation leaves behind white, dense, porus, coherent mass which is known as coke.

$$\text{Coal} \xrightarrow[\text{distillation}]{\text{distructive}} \text{Coke} + \text{Coalgas} + \text{Coke oven gases.}$$

It is the conversion of coal into coke.

Low Temp. Carbonization	High temp. Carbonization
① 500° - 700° c	1000° - 1200° c.
② Soft coke (Poor Mechanical strength)	Hard coke (good mechanical strength)
③ Domestic purposes	Metallurgical purposes.
④ C.f.V. 6500 - 9000 Kcal/kg.	5500 - 6000 kcal/kg.
yield 75-80 %.	65-70 %.

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Most Important

Manufacturing Methods for metallurgical coke :-

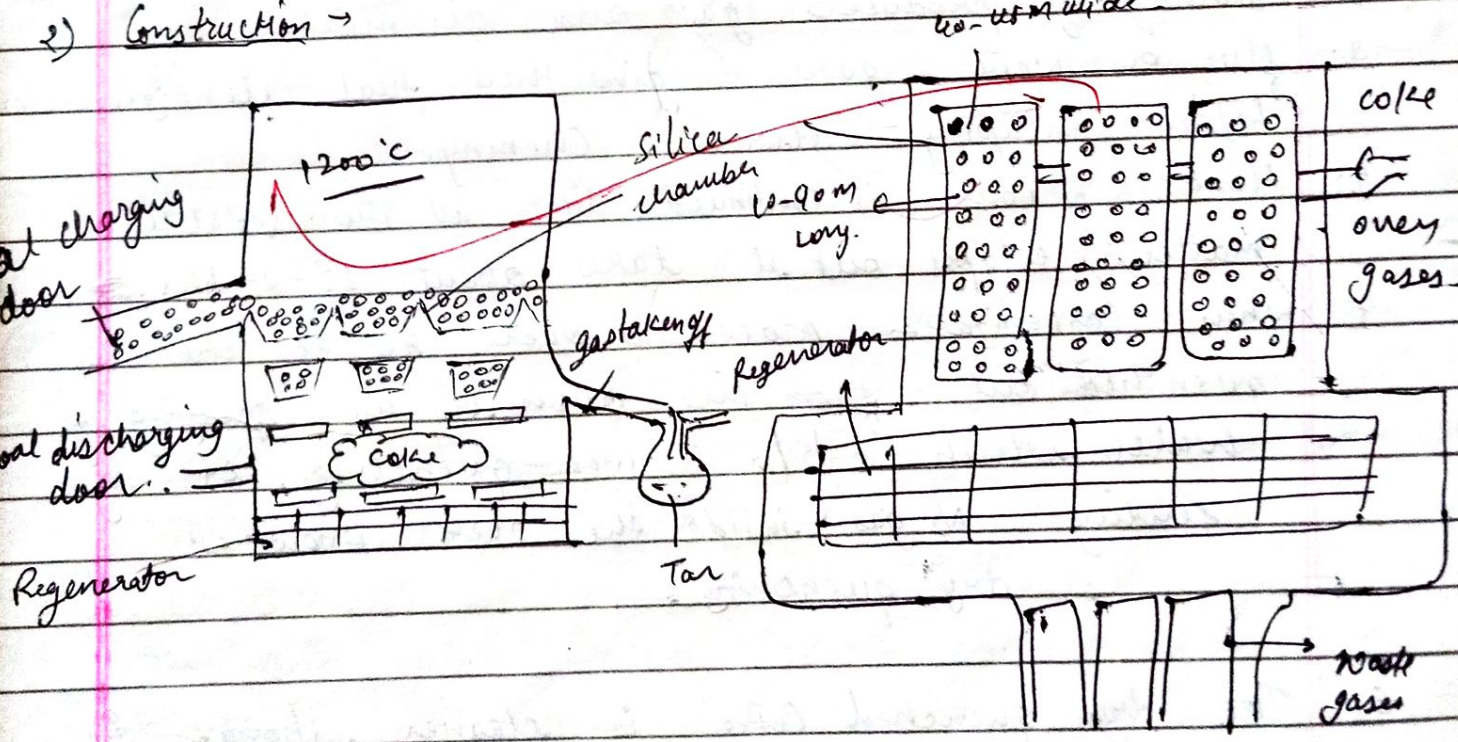
(1) Otto's Hoffmann by-product coke oven method :-

most important

1) Principle → The method is based on regenerative principle of heat economy that means utilization of heat from waste hot flue gases before escaping throw chimneys.

This method has the advantage that by product like ammonia, tar, benzene, nepthalene & H_2S can be recovered and heating is also done by coal gas which is the one of the by product of this ~~product~~ method.

2) Construction →



→ This oven consist of number of silica chambers (10-90) are seperated by interspace which is provided for the path of hot burnt gases.

→ Each silica chamber is about 10-12 m long and 40-45 m wide

- This oven is provided with a coal charging door for charging the coal, a gas take off for the removal of coke oven gases and a coke discharging door.

→ A single oven can hold 15-25 tons of coal.

Working :-

1. Powdered coal is introduced through coal charging door at the top of chambers and the chambers are closed.
2. Then the ovens are heated at 1200°C temperature by burning of producer gas and air mixture.
3. flue or waste gases gives there heat to regenerator before escaping through Chemnye.
4. Heating of coal is continued till all the volatile matter escapes out it takes about 18-24 hrs.
5. When carbonization process is over red hot coke is quenched out from the oven by the spraying of water which is k/a wet quenching. or by sending N_2 gas inside the oven known as dry quenching.
6. The dry quenched coke is cleaner, stronger & contain less dust then wet quenched ~~then~~ coke yields of coke is 75%.

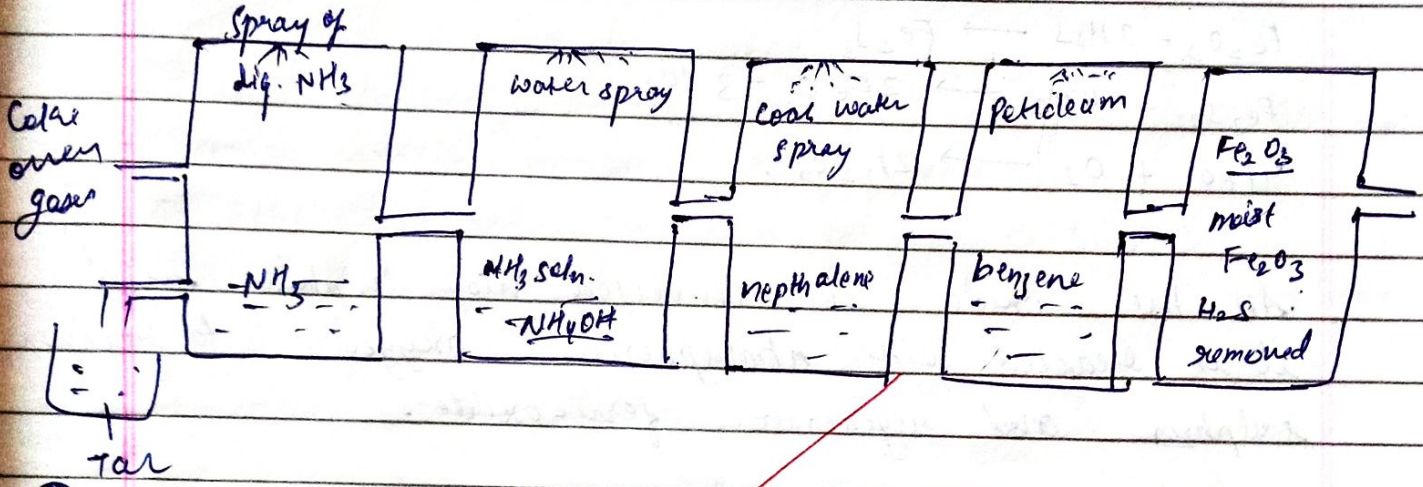
Coke oven gas

To

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Recovery of by product from coke oven gases :-

The gases evolving out from the coke oven is called coke oven gases. Containing large number of valueable fractions like (Tar, NH_3, benzene, nephthalene, H_2S) can be recovered.



(1.) → Removing of Tar / Recovery of Tar :→ The coke oven gases passed throw a tower in which liquid amonia is ~~spread~~ sprayed. Then tar and just get collected in a trank and ammonia and tar recovered.

(2.) Recovery of NH_3 :- The gases is passed throw another chamber in which water is sprayed then NH_3 goes into the solution as amonium hydroxide foam.

(3.) The gases passed throw 3rd chamber in which water is sprayed at extremely low temperature in this ~~tower water is sprayed at extremly~~ napthelene is recovered.

(4.) Then the coke oven gases passed throw next chamber in which petroleum is sprayed.

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then benzene is condensed.

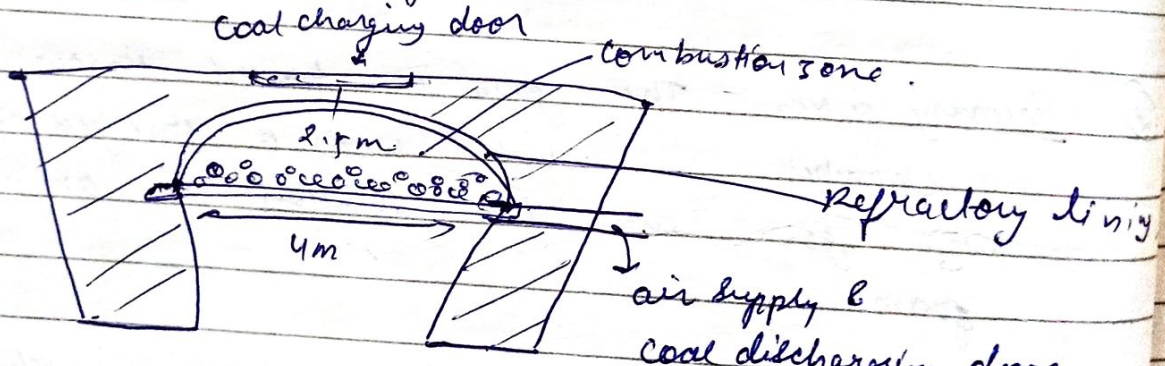
(3.) In the last step coke oven gases passed through another chamber in which moist Fe_2O_3 is placed.

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3$$
$$Fe_2S_3 + 4O_2 \longrightarrow 2FeO + 3SO_2.$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3.$$

All the oxide is converted into sulphide and it is reacted with atmospheric oxygen to recover sulphur and regenerate ferric oxide.

(2.) Beehiene's Oven Method :-

1) It is the earliest & cheapest method for Carbonization of coal.



(1.) In this method Carbonization is carried out in dome shaped bricked structured oven about 4m wide & 2.5 m high.

(2.) It has two openings, one for coal charging at the top & other for air supply & coke discharging

at the side.

(3) A uniform layers of coal (about 0.6m) is introduced through coal charging door.

(4) Then heating is done by the supply of air through side door.

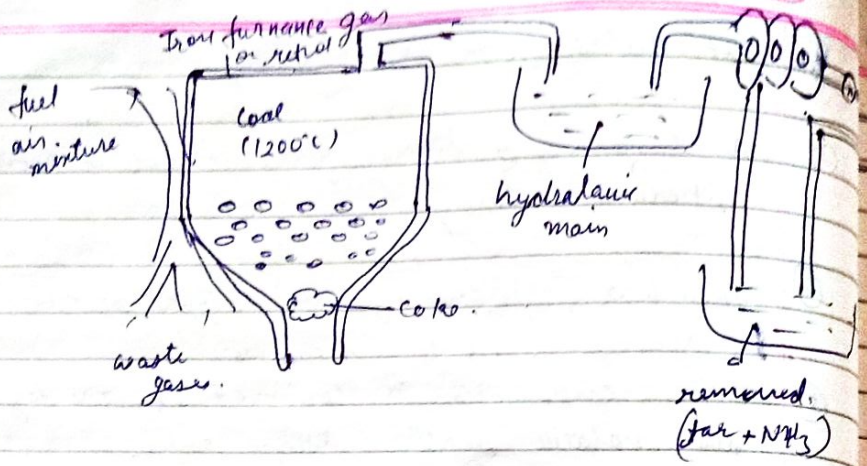
(5) Then carbonization is continued for 3-4 days till all the volatile matter escape out.

(6) At the last 70 %. coke is obtained which is quenched by spray of water.

⇒ Gaseous Fuel :-

⇒ Manufacturing of coal gas :-

→ It is a colourless gas having a characteristic ~~order~~ odour.
→ It is lighter then air & slightly soluble in water.
→ It burns with long smoky flame.
→ C.f.v → 4900 K cal / m^3.
→ Average
Composition → CH_4 - 32 %., H_2 = 48 %., N_2 = 8 %., CO_2 1
C_2H_2 = 2 %., C_2H_4 = 3 %.,
CO = 7 %., other hydrocarbon 4 %.



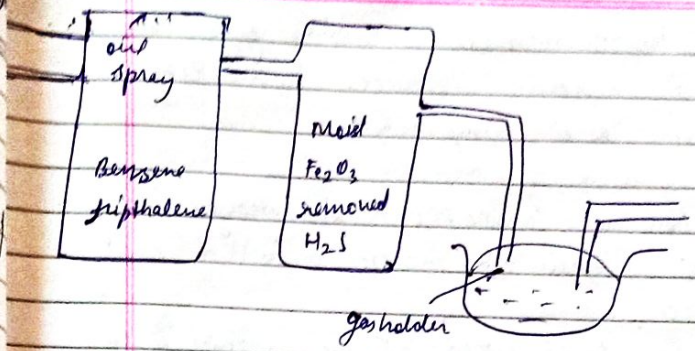
→ The coal gas is obtained by the distructive distillation of coal at 1200°C Temperature.
Carbonization process is carried out in iron furnance which is externaly heated by fuel air mixture.
→ The coal gas coming out from iron furnance, it first scrabbed by water in hydrolaric main which is heat exchanger and remove tarr from coal gas.
→ Ammonia and remaining tarr present in coal gas can also again removed by scrabbing with water.
+ with the help of condenser.
→ Benzene & Naphthalene etc are removed by scrabbing with petroleum. H_2S can be removed by reaction with moist Fe_2O_3.

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

$$Fe_2S_3 + 4O_2 \longrightarrow 2FeO + 3SO_2$$

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

→ All the oxide is converted into sulphide & sulphide again reacted atmospheric oxygen to regenerate Fe_2O_3.



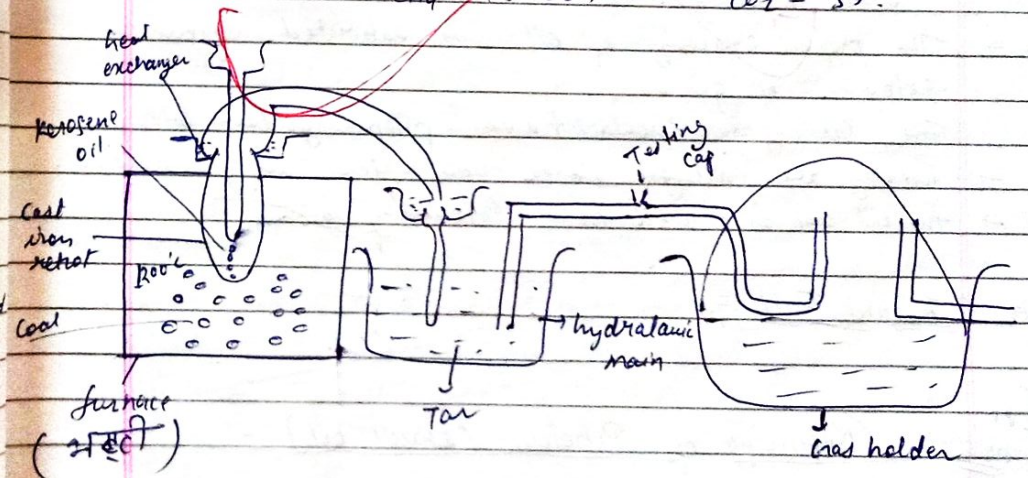
Manufacturing of Oil Gas :-

→ Oil gas burns with a long smoky flame having characteristic golden colour.

Calorific value = 4500 - 5400 K cal/m³.

Composition – H_2 - 50-55 %. CO - 10-12 %.

CH_4 - 25-30 %. CO_2 - 3 %.



$$C_{12}H_{26} \xrightarrow[1200°C]{\text{Thermal decomposition}} H_2 + CH_4 + C_2H_6 + C_2H_4 + C_3H_6 + C_3H_8 + \text{Tar}$$

→ Oil gas is prepared by thermal decomposition of kerosene. Oil gas is a mixture lower hydrocarbon containing tarr as a impurity.

→ Thermal decomposition is carried out in strong iron ~~furnace~~ retort which is inclosed in a coal fired furnace.

→ ~~The retort~~ A bonnet is fitted at the mouth of the iron retort.

→ The retort is heated to Red hot. and a stream of oil is allowed to fall on the bottom of retort.

→ Kerosene oil decomposis into lower hydrocarbon the gaseous mixture coming out from iron retort through bonnet first passed throw hydraulic main to remove the tarr impurity.

→ The proper cracking of oil is estimated from the colour of gas.
The Oil gas should have proper golden colour.

→ Finally the oil gas stored over water in gas holder.

→ The oil gas is used as a laboratory gas.

* Liquid Fuels :-

Next
Next VV. Improved

Refining of Petroleum (crude oil) :-

→ Crude oil is a dark greenish brown mucus oil which is found deep in earth crust. At some places it is associated with natural gas.

→ Chemically it is a mixture of various hydrocarbon (aliphatic, cyclic, aromatic along with oxygen, nitrogen & Sulphur containing compound.

→ Crude oil is an emulsion of oil and water. The average composition of crude oil is carbon - 80-87%, H = 11-15%, S - 0.1 to 4%, O_2 & N_2 = 0.1-0.5%.

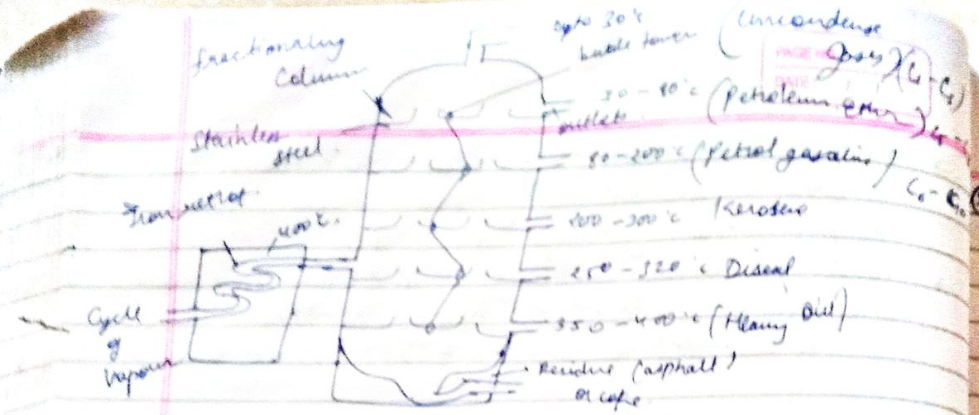
Definition

→ The Process of seperation of crude oil into various fractions by fractional distillation and desired Specific product can be obtained from these fractions with the removal of impurity is known as refining of petroleum. The plant set-up for this proces is known as refineries.

(1) Removal of water (brine by Cottrell's process →
In this method crude oil which is basically emulsion of oil and water is passed in b/w two highly charged electrode when electric current flows throw mixture and small water droplets get combined to form large droplets and water seperates from oil, at the opposite charged electrode.

(2) Removal of Sulphur :-
In this method oil is allowed to be treated with Copper oxide then Sulphur is converted into Copper Sulphide ppt. which is seperated by the filteration of oil.

(3) Fractional Distillation - In this method crude oil is heated in iron retort at 400°c palmost. oil is evaporated except asphalt as coke then Oil vapour are passed throw fractionating columns.



→ Fractionating Column is a long steel cylinder containing a series of stainless steel trays are provided with chimneys which are covered by bubble towers.

→ As the vapours go high as they become cooler and condense the higher boiling fraction condensed first at the bottom and lower b boiling fraction condenses later at the top of the tower.

→ The outlet in tower are provided in the side of the column to to withdraw withdraw a number of fractions.

Composition and Uses of the main petroleum fraction →

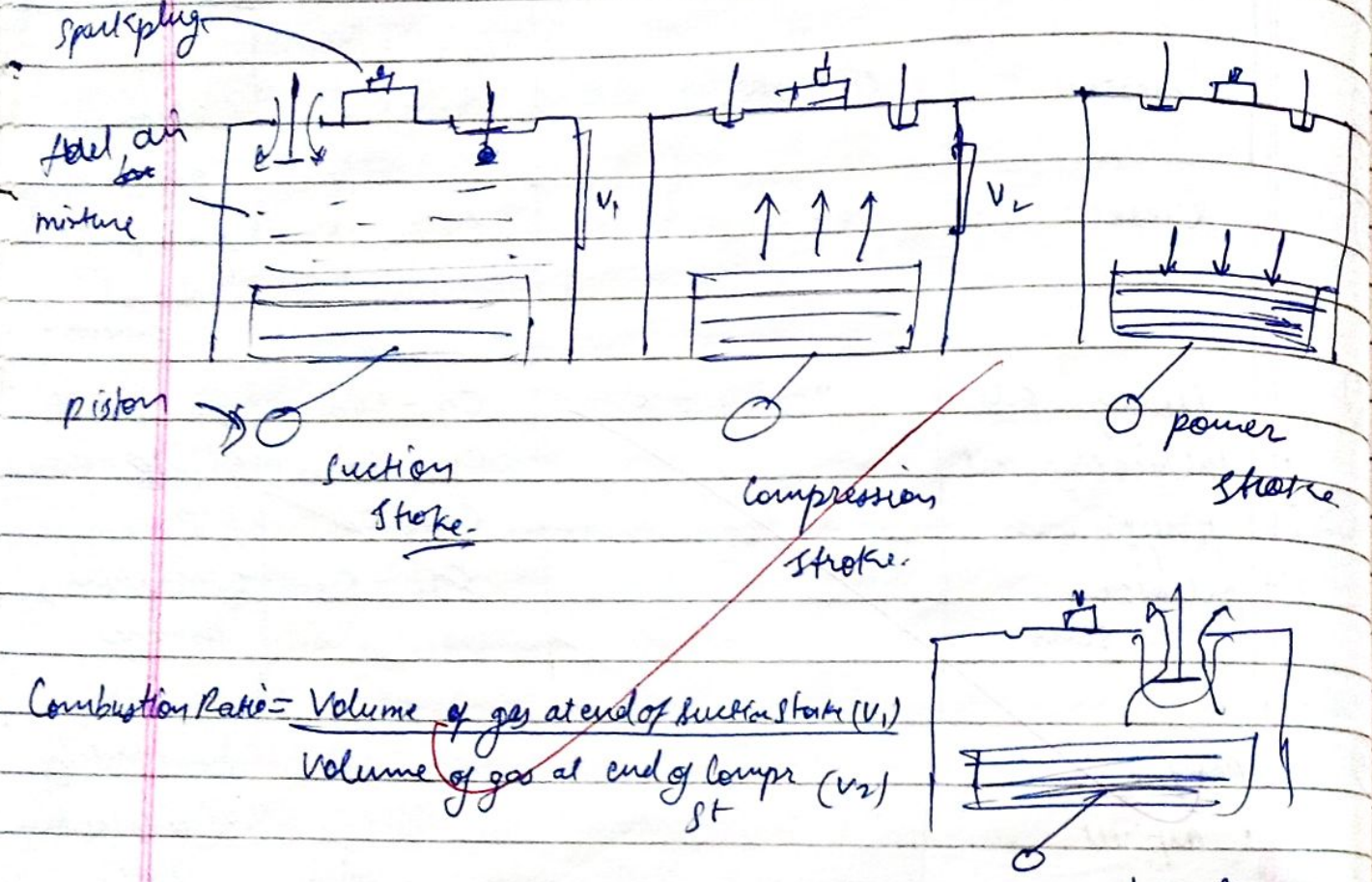
Name of Fraction	Temp.	Approx. Composition	Uses
① Uncondense gases	upto 30°c	$C_1 - C_5$	Domestic fuel.
② Petroleum ether	30 - 80°c	$C_5 - C_6$	As a solvent
③ Petrol or Gasoline	80 - 200°c	$C_6 - C_{10}$	fuel for I.C. engine
④ Kerosene	200 - 300	$C_{10} - C_{16}$	fuel for oil gas
⑤ Diesel	250 - 320°c	$C_{10} - C_{18}$	fuel for diesel purpose
⑥ Heavy oils	350 - 400°c	$C_{18} - C_{40}$	for lubricant
1) lubricating oil		$C_{18} - C_{20}$	Wax paper
2) paraffin wax		$C_{20} - C_{30}$	
3) petroleum jelly.		$C_{20} - C_{40}$	In medicine, cosmetics
⑦ Residue			road making as a secondary fuel.
1. asphalt			
2. coke			

Important Knocking :- When low quality fuel used in internal combustion engine which does not burn smoothly and rate of combustion in I.C. engine become so great. so that last portion of the fuel air mixture get ignitiate rapidly with producing explosive sound which is known as knocking.

→ Petrol air mixture is used as a fuel in the internal combustion engines of automobile.

DATE: / /

Working Cycle (Four stroke cycle) in I.C. engine :-



Combustion Ratio = $\frac{\text{Volume of gas at end of Suction Stroke } (V_1)}{\text{Volume of gas at end of Compr St } (V_2)}$

(1) Suction Stroke → A fuel air mixture is drawn into the I.C. engine during the suction stroke of cycle. It is the initiation of working cycle of a fuel.

(2) Compression Stroke → The piston compresses the mixture in the compression stroke of cycle. compression ratio is directly proportional to the efficiency of I.C engine.

(3) Power Stroke → The mixture is ignited by supply of electric spark through spark plug. the hot combustion product increase the

pressure inside the engine and pushes the piston and providing the output of power to the vehicle

(4) Exhaust Stroke → In the last part of cycle the piston ascends and expels exhaust gases from the engine.

Higher the compression ratio, higher the efficiency of engine. If the compression ratio exceed a certain limit (critical compression ratio.) it increased the temp of fuel air mixture greater that its ignition temp. ~~fuel ignited~~ of fuel air mix & fuel ignited before sparking with producing sound.

Order of knocking :- anti knocking property increase with compactness of molecule. straight chain hydrocarbon > Branched chain > alkenes > cyclic paraffin/aromatics.

very very important short note

Octane Number :- The major measure of a gasoline (petrol) ability to burn without producing sound ~~to burn~~ (knocking) is known as Octane number

→ It is measured by two standard hydrocarbon. Two standard hydrocarbon are n-heptane & Iso-octane.

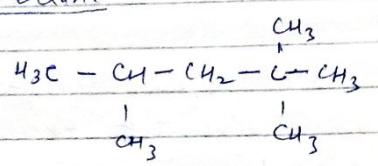
$H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

(n-heptane) (O.N. = 0)

n-heptane is a straight chain hydrocarbon which

produces maximum sound during burning. that means the anti-knocking value of n-heptane is very less assigned an octane number is equal to zero.

② Iso-Octane →



(2,2,4-trimethyl pentane) (O.N = 100)

The second standard is iso octane which involved in burning without producing sound that means it has high anti knocking properties. assigned an octane number 100.

→ The Octane number of a gasoline is defined as percentage of iso-octane present in a mixture of n-heptane & iso-octane.

For example → A sample of fuel as octane no. = 80 that means fuel containing 80% iso-octane & 20% n-heptane.

This sample gives as much knocking as a mixture of 80% iso octane and 20% n-heptane.

→ The petrol having large amount of branched paraffin has high octane number, and less knocking property.

→ Knocking can be minimized by adding certain anti knocking compound to the fuel.

Generally, Tetra ethyl lead $(CH_3CH_2)_4Pb$, Tetramethyl Lead $(CH_3)_4Pb$, Tertiary butyle acetate, diethyl telluride and iron carbonyl are used as anti knocking compound.

* Cracking :- cracking may be defined as the decomposition of high molecular weight hydrocarbon into low molecular weight hydrocarbon.

$C_{10}H_{22}$ —(Cracking, high temp. high pressure, Catalyst)→ C_5H_{12} + C_5H_{10}

n-decane — n-pentane + n-pentene.

BP = 174°C — (BP-36°C)

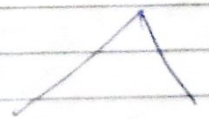
(Low O.N.) — (High O.N.)

→ Cracking needs high temperature, high pressure, Catalyst.

→ Cracking process increase the octane number and anti knocking properties of a fuel.

Types of Cracking :- Cracking process are of 2 types.

① Thermal Cracking (high temp. & press.)



② Catalytic cracking. (high temp. & (catalyst))



DATE: / /

(1) Thermal Cracking → when cracking is carried out by applying high temperature and pressure is known as thermal cracking.

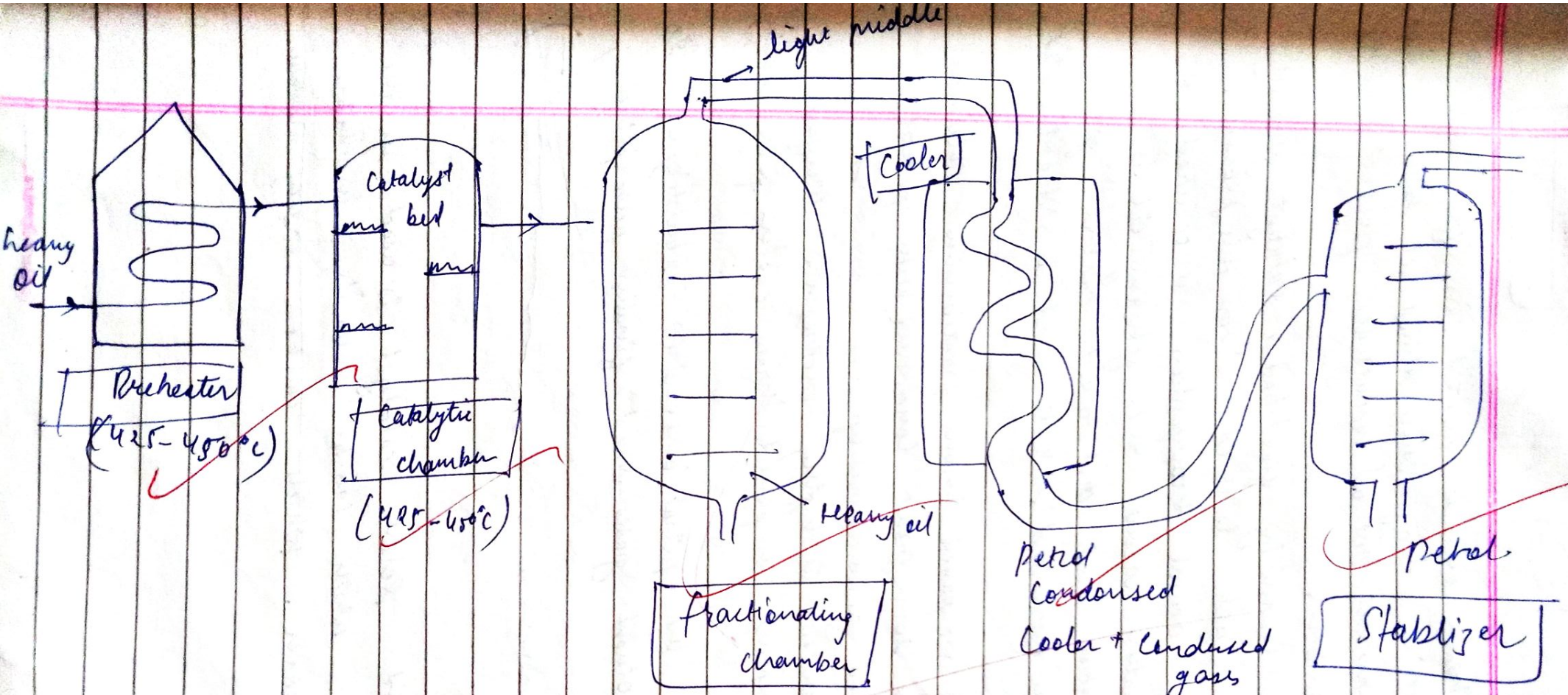
→ Liquid phase thermal cracking → In this method the heavy oil is cracked at 475 to 530°C temperature & upto 7 to 10 atmospheric pressure to keep reaction product in liquid phase.

→ Vapour phase → In this method heavy oil is cracked at 670 to 730°C temperature & atmospheric to keep the reaction products in vapour phase.

Most important (1) Catalytic cracking → Catalytic cracking, in this process the cracking take place in presence of catalyst. Usually silica alumina gel and aluminium silicate is used as a catalyst is known as Catalytic cracking.

→ Catalytic cracking is superior in comparision to thermal cracking because it does not require high pressure. and yield of Gasoline is very high with more branching that means Catalytic cracking increases the Octane Number and anti knoking properties of fuel.

(a) → Fixed bed Catalytic cracking →


light middle
Heavy oil
Catalyst bed
Cooler
Preheater
(425-450°C)
Catalytic chamber
(425-450°C)
Heavy oil
Petrol
Condensed
Cooler + Condensed gas
Petrol
Fractionating chamber
Stablizer

→ first of all, the heavy oil is heated in free heater at 425 to 450°C temperature, almost oil is evaporated then the hot oil vapours are passed throu catalytic chamber.

→ Catalytic Chamber Containing fixed bed of Catalyst generally silica alumina gel is used for this process. In this chamber actual decomposition is occured at 425 - 450°C temperature about 40% of heavy oil is converted into petrol and 2 to 4% carbon get deposited on the Catalytic bed so that bed is deactivated.

→ The cracked oil vapours are passed throw fractionating columns where some gases condensed with petrol and uncondensed gases moves up.

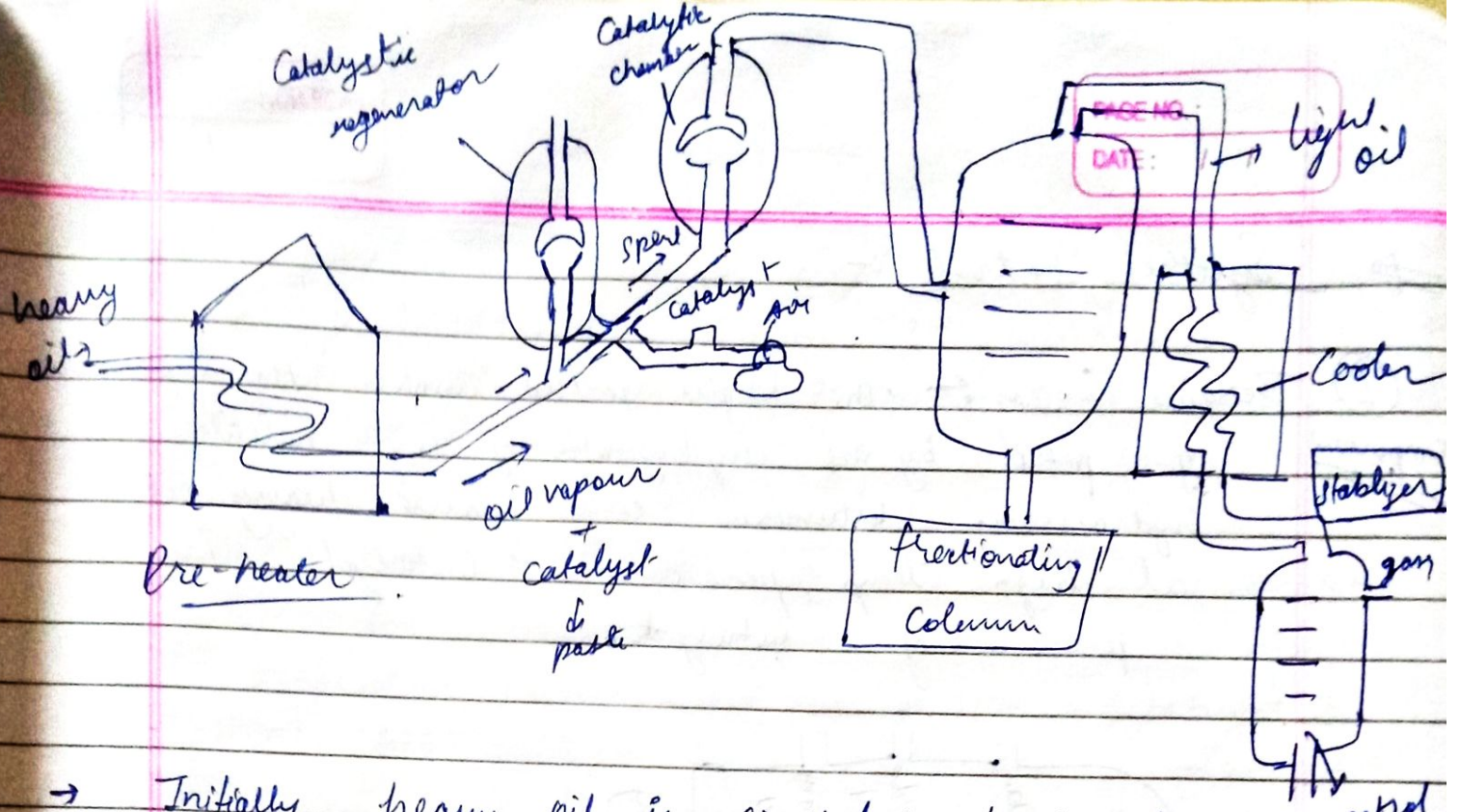
→ The fixed bed process is highly exothermic therfore the hot product vapours are passed throw cooler for cool.

→ In the last step the petrol is send to stabilizer to remove the dessolved gases and finally pure petrol is obtained.

same as

⇒ Moving bed :—

In this method Solid catalyst is used in the powder foam which can be easily movable in gas stream.



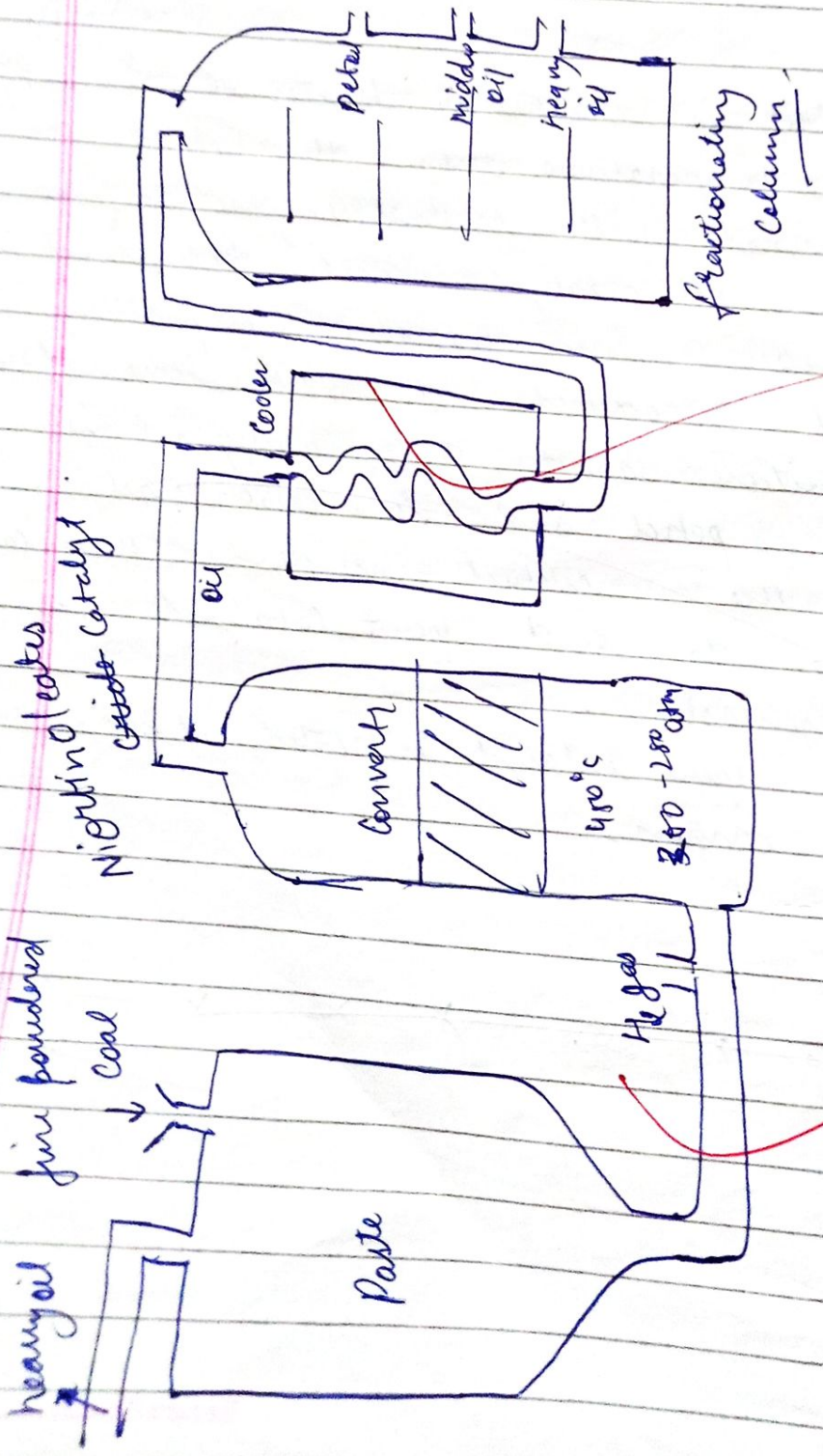
→ Initially heavy oil is cracked in heater at 425 to 450 °c temperature then the hot oil vapours are mixed with catalyst powder to form the paste then oil-catalyst paste is forced to Catalytic chamber where actual decomposition of heavy oil is occured at 500°c temperature. After decomposition about 50 % heavy oil is converted into petrol and some carbon get deposited on the catalyst powder which can be regenerate to send spent catalyst to the regenerator.

→ In regenerator spent catalyst is heated at 600°c temp. to burn off the carbon.

Synthetic Petrol :-

(1) **Bergius Process** :- The bergius process involves the formation of petrol by the hydrogenation of high volatile hydrocarbon bituminous coal and heavy oil at high temp., pressure & Catalyst. In presence of catalysts.

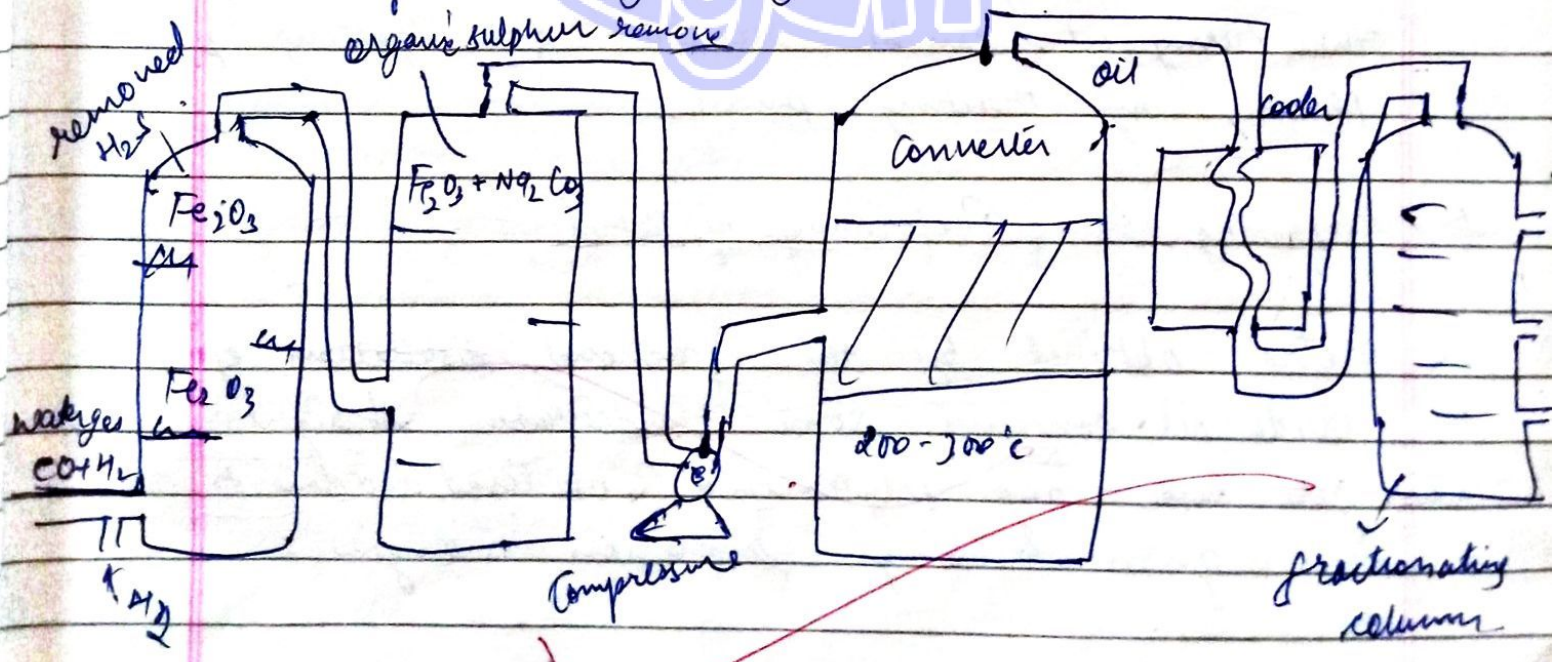
Important



→ The fine powdered coal is mixed with heavy oil to form a paste. The paste is heated with hydrogen in converter at 450°C, 200 atm pres & in presence of Ni or Sn oleates catalyst for about 2 hours.

→ Where hydrogen combine with coal to form saturated hydrocarbon, these hydrocarbons decompose at high temperature pressure and in presence of catalyst to give low boiling liquid hydrocarbons. About 60% of coal is converted into crude oil, which
→ is refined by fractional distillation
After fractional distillation petrol, middle oil & heavy oil are obtained.
⇒ Heavy oil is recycled for forming paste.
and middle oil is cracked to get more petrol.

(2) Fischer Tropsch Method ⇒ In this method petrol is obtained by the formation of water gas.



→ A mixture of water gas and hydrogen is passed over Fe_2O_3 to remove H_2S and then passed over a mixture of $Fe_2O_3 + Na_2CO_3$ to remove organic sulphur.

→ The purified gas is compressed to 5 to 25 atm pressure with the help of compressure. Then the purified gas is passed throw converter which is maintained at 200 - 300°C temp.

The converter containing a mixture of Catalyst, cobalt + thorea (5 parts) + magnesium (8 parts) + Kieselguter (100 parts) (360 parts)

where actual decomposition of purified gas is occured at high temp. Then after decomposition a mixture of Saturated & unsaturated hydrocarbons is obtained.

→ This process is highly exothermic so that hot oil vapours are passed throw condenser for cooling. In the last step crude oil vapours are refined by fractional distillation to get pure petrol and heavy oil.

The heavy oil can be reused for getting more petrol by cracking process.

Refineing & Reforming of Petrol :-

→ Petrol obtained by the fractional distillation of crude oil contains some undesirable straight chain which gets oxidised and polymerised leading to gum & sludge formation in engine.

Removal of unsaturated hydrocarbons :- 80% cold sulphuric acid is mixed in petrol which reacted with these hydrocarbons forming esters

alcohol.

→ Petrol contains sulphur and mercaptans leading to corrosion on inner metallic parts of engine.

→ Petrol contain mercaptan is K/a Sour petrol. and the removal proof mercaptans is K/a Sweetning of petrol.

→ In the sweeting process Sodium plumbite is mixed in petrol.

$$Na_2PbO_2 + 2RSH \rightarrow Pb(SR)_2 + 2NaOH$$

$$Pb(SR)_2 + S \rightarrow PbS + R-S-S-R$$

(disulphide) (removed by filtration).

Removal of Olefins & Culring

It is remove by fuller's earth which absorb colour & olefins.

→ Removal of Dissolved gases →

Dissolved gases like methane & ethane removed from pure gasoline by using fractionating column. is called stabilisation process.

In the last step after refining of petrol some anti-oxidants are mixed. in petrol like aromatic amine & phenyl to prevent oxidative degradation of petrol during storage.

Teacher's Signature

★ Reforming :- Reforming is the process by which structural modification is carried out in petrol at high temperature, pressure & in presence of catalyst to improve it octane number and anti knocking property.

This is carried out to convert straight chain hydrocarbon (with low O.N) into branched chain/hydrocarbon (or cyclic) with high octane number.

So that this process is also known as upgradation of petrol.

Type of Reforming :-

(1) Thermal Reforming

(2) Catalytic Reforming

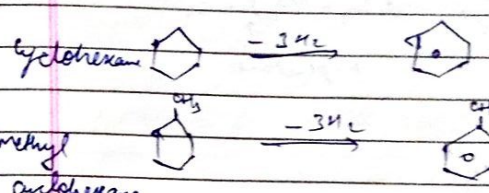
(1) Thermal → It is carried out at 500 - 600°C temp and 65 atm pressure in absence of catalyst.
Thermal reforming is controled by the quenching of product vapour by spray of cold oil.

The reformed product are then fractionate to remove dissolved gases ~~to removed gases~~ from petrol

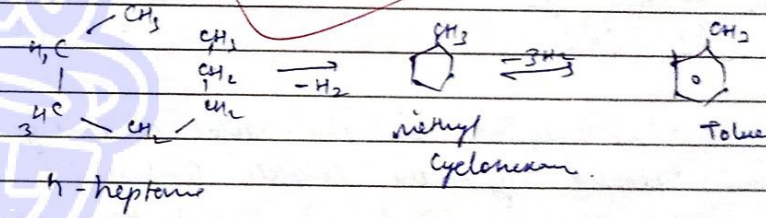
(2) Catalytic Reforming → It is carried out at 450 - 460°C 35 - 50 atm pressure by using either a fixed bed or moving bed Catalyst.

★ few type of reforming reactions are giving below —

(1) Dehydrogenation → Cyclic alkanes undergo dehydrogenation to form aromatic compound.

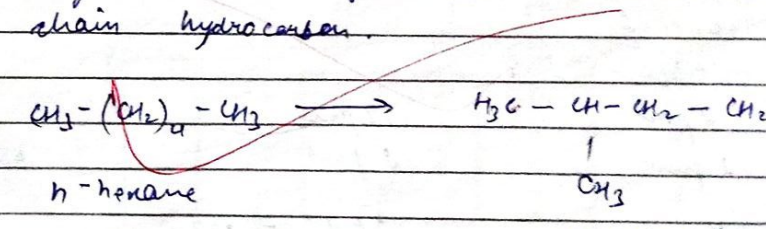


(2) Dehydrocyclization → Normal alkane become cyclic alkane which undergo dehydrogenation and cyclization to form aromatic compound.



n-heptane
methyl Cyclohexane
Toluene.

(3) Isomerisation :- This is used for conversion of straight chain hydrocarbon into branch chain hydrocarbon.



n-hexane
2 methyl pentane

(4) Hydrocracking → An alkane are mixed with ~~Catalyst~~ hydrogen and passed over hot Catalyst. Hydrocracking takes place resulting in higher

molecular weight hydrocarbons

Ex- $CH_3-(CH_2)_6-CH_3 \xrightarrow[Pt]{H_2}$ $2\,CH_3-(CH_2)_3-CH_3$

n-Decane. n-pentane

Calorific Value of fuel :-

→ Calorific Value means total amount of heat liberated by the complete combustion of unit mass of fuel.

Type of C.f.V. :-

1. High or Gross C.f.V. (H.C.V)
2. Low or Net C.f.V (L.C.V.)

most important

1. H.C.V → It is defined as the total amount of heat is liberated by the complete combustion of unit mass of fuel and the combustion products are cooled at room temperature.

short view

fuel

$C_xH_yO_zN_zS$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

2 part 18 part

1 part 9 part.

H Kg gm $9 \times \frac{H}{100} = 0.09H$.

2. L.C.V → It is defined as amount of heat is liberated by the complete combustion of unit mass of fuel and the combustion products are allowed to escape at room temp.

$$L.C.V. = H.C.V. - 0.09H \times 587$$

most important

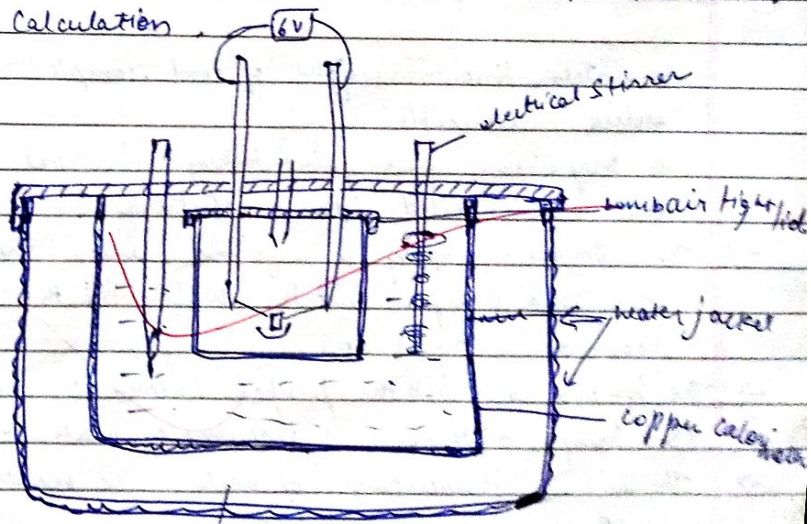
P-T-V

Calorific value determination by Bomb calorimeter :-

1. Principle
2. Apparatus Diagram
3. construction
4. working.
5. Calculation.

1. Principle :- A known mass or volume of fuel sample is burnt completely and the amount of heat generated is absorbed by the non volume of water. and then liberated heat is measured by Calculation.

2.



(3) Construction :-

→ Bomb Calorimeter consist of a stainless steel vessel which is called bomb.

→ The bomb is provided with a stainless steel electrodes and a oxygen intake wall and bomb is covered by air tight lid. These electrodes are attached with coal sample by magnisium fused wire which act as a support for the ~~pan~~ Crucible.

These electrodes are also connected by 6V battery.

The placed is placed in a copper calorimeter having a known volume of water.

→ Copper calorimeter is provided with an electrical stirrer and a Backmann's thermometer.

→ The copper calorimeter is also surrounded by an air Jacket and water Jacket. to prevent heat loss due to radiation.

(4) Working :-

Accurately known weight of coal sample is taken in silica crucible.

A magnisium fuse wire toching the coal sample and then connected to a electrodes.

→ The oxygen supply is forced into the bomb. through oxygen intake wall. till the pressure is reached 5-25 atm.

→ The bomb is placed into the proper calorimeter which is containing a known volume of water.

→ The initial temperature of water is noted by Beckmann's thermometer.

→ The electrodes are then connected to 6 V battery & circuit is completed.

→ The sample burns & heat is liberated which is transfered to water.

→ Uniform stirring is continued throw out the experiment by electrical stirrer.

The maximum temperature of water is recorded by thermometer.

(5) Calculation

(1) Weight of fuel sample taken = x gm

(2) weight of water taken = W.

(3) Water eq. of apparatus = Wt. of apparatus × Specific heat (w).

(4) Initial temp. of water = t_1 °C

(5) final temp. of water = t_2 °C.

Heat liberated by fuel sample = xL

Heat absorbed by water & apparatus = $(W+w)(t_2-t_1)$

Heat liberated = Heat absorbed.

$$xL = (W+w)(t_2-t_1)$$

$$\frac{L}{(H.C.V)} = \frac{(W+w)(t_2-t_1)}{x}$$ Cal/gm

$$L.C.V = H.C.V - 0.09\,H \times 587 \text{ Cal/gm.}$$

Corrections :-

① Fuse wire Correction → Heat is also produced by the fusion of magnesium wire hence it must be substracted from the total value of heat.

② Acid Correction → During the combustion of fuel Nitric acid & sulphuric is formed. If formation is a exothermic proces. so that liberated heat must be substracted from total value.

③ Cooling Correction : Rate of cooling must be added in temperature difference.

$$HCV = \frac{(W+w)(t_2 - t_1 + \text{Cooling correction}) - (\text{Acid} + \text{Base wise (correction)})}{\text{mass}}$$

$$CCV = HCV - 0.09H \times 587 \text{ Cal/gm}$$

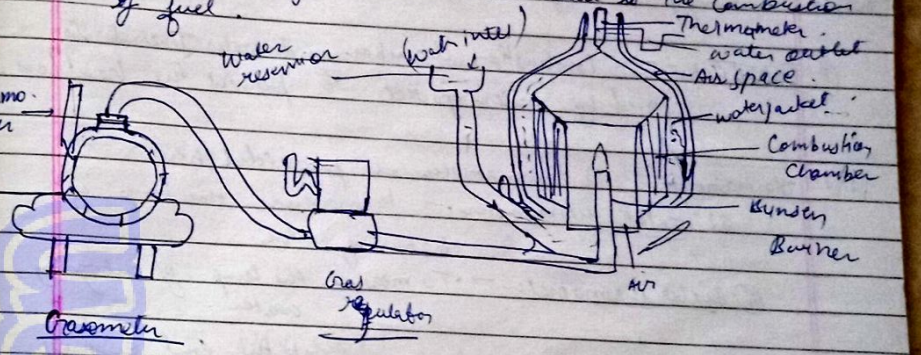
Important ⇨

Calorific value Determination of Gaseous fuel by Junkers Calorimeter :-

① Principle → The Calorimeter works on water flow principle. A known volm. of gas is burned at constant known rate in the inclosed combustion chamber.

Under such condition total amount of liberated heat is absorbed by water which is flowing at constant rate through water jacket out side the combustion chamber.

→ By the volm. of gas, volm. of water and temp. rise of water. we can calculate the total amount of liberated heat due to the combustion of fuel.



② Construction :- The Junker's Calorimeter consist of following parts ① gaso meter.
① gas regulator.
② Gas Calorimeter.
③ Bunsen Burner.

① Gasometer → Gaso meter measure the volume of gas per unit time. A thermometer and a manometer are also attached to it to measure the initial temp. of burning gas and starting pressure of gas.

② Pressure regulator → It regulate the supply the of gas at a constant pressure.

③ Gas calorimeter → ① Combustion Chamber → This a is vertical cylinder in which gaseous fuel burn

at constant rate whose Calorific value is to be determined. Combustion Chamber is surrounded by water jacket containing a large no. of water tubes.

(ii) Outer Jacket → Combustion chamber and water jacket is covered by outer jacket to prevent the heat loss.

(iii) Thermometer → 3 thermometer are provided here.

(i) Inlet thermometer → to measure the temp. of incoming water.

(ii) Outlet thermometer → To measure the temp. of outgoing water.

(iii) third thermometer is present at the exit end of combustion gases to measure the temp. of exit gases.

(iv) Bunsen Burner → A bunsen burner is present at the bottom of gas calorimeter which performing the burning of gaseous fuel.

Working :—

(1) A known volm. of gas is burned at constant rate in combustion chamber the heat liberated by the combustion of fuel increases the temperature of water jacket.

(2) Circulation of water & burning of fuel are performed continuously about 15-20 minutes at uniform rate

(3) The total amount of circulated water is measured and final rise in temp. noted.

(4) water formed by steam condensation is collected in measuring cylinder which is placed at the bottom of gas calorimeter.

* Calculation → Volume of gas burnt at S.T.P in combustion chamber at constant rate = V

amount of water circulated through water jacket = W

Initial temp. of water = t_1 °C.

Final " " = t_2 °C

$$H.C.V = \frac{W(t_2 - t_1)}{V}$$ for Calorimetric ton, kcal m³

$$L.C.V = H.C.V - \text{latent heat}$$

$$= H.C.V - \frac{m}{V} 587$$

$\left(\frac{m}{V}\right)$ = Amount of water produced by condensation of steam.

m = amount of water, V = volume of gas

Analysis of Coal :—

Proximate

* % moisture
% of V.M
ash
% of fixed carbon

ultimate analysis

A % C, H, N, O, S

(elemental analysis)

(1) Proximate Analysis (Quantitative) :-

→ It is a Quantitative analysis.
→ It involves the determination of moisture, volatile matter, ash and fixed carbon in coal sample.

⇒ Determination of percentage of moisture content in coal sample

→ A known amount of powdered coal sample is taken in empty silica crucible which is already weighed.
→ It is heated for 1 hour in electric oven at 110°C temp.
→ Cool the crucible in desiccator and weigh again.

(1) wt. of empty silica crucible = W_1 gm
(2) wt. of silica crucible + coal sample = W_2 gm (placed electric oven 110°C)
(3) wt. of dried crucible = W_3.

$$\% \text{ of moisture} = \frac{\text{loss in wt.}}{\text{wt. of sample}} \times 100$$

$$\% = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

⇒ Determination of percentage of volatile matter in coal sample

A known amount of dried coal sample is taken in empty silica crucible which is already weighed.

→ The crucible is placed in electric oven at 950°C temp for seven minutes. Then crucible is cooled in desiccator & again ~~weight~~ weighed.

(1) wt. of empty silica crucible = W_4 gm.
(2) wt. of silica crucible + coal sample = W_5 gm.
(3) wt. of dried crucible = W_6 gm.

$$\% \text{ of V.M} = \frac{\text{loss in wt.}}{\text{wt. of sample}} \times 100$$

$$= \frac{W_5 - W_6}{W_5 - W_4} \times 100$$

⇒ Determination of percentage of Ash ~~matter~~ :-

→ A known weight of dried coal sample is burnt in muffle furnace at 950°C, until a constant weight of residue is obtained.

$$\text{percentage of Ash} = \frac{\text{wt. of Ash}}{\text{wt. of sample}} \times 100$$

(4) Determination of fixed carbon :-

Higher the percentage of fixed carbon greater is the Calorific value.

$$\% \text{ of fixed Carbon} = 100 - [\% \text{ of moisture} + \% \text{ of volatile} + \% \text{ of ash}]$$

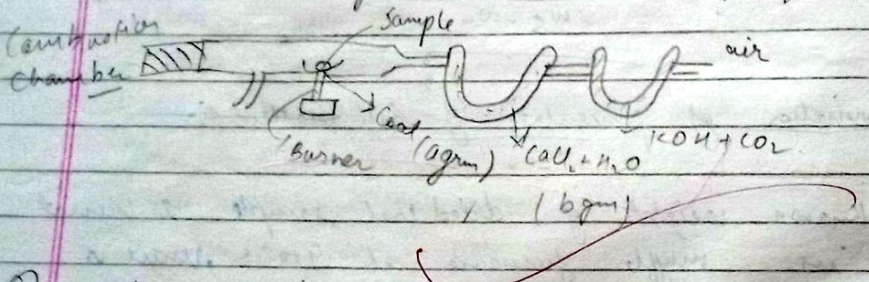
Importance of Proximate Analysis :-

→ Moisture, Volatile matter and Ash reduces the calorific value of fuel. hence lesser the moisture, V.M., & Ash better is the quality of coal as a fuel.

→ Greater fixed carbon is required for high calorific value.

Ultimate Analysis of Coal :-

* Determination of Carbon and hydrogen in Coal sample



① A known weight of coal sample is taken in silica crucible then it is burnt in combustion chamber in presence of oxygen.

After combustion Carbon & hydrogen ~~Carbon & hyd~~ present in coal sample are converted into CO_2 & H_2O.

H_2O & CO_2 are absorbed in already weighed $CaCl_2$ tube and KOH tube.

The increase in weight of KOH tube & $CaCl_2$ tube gives the amount of CO_2 & water formed.

wt of coal = a gm

Increase in wt. of $CaCl_2$ tube = b gm

Increase in wt of KOH tube = c gm

$C + O_2 \rightarrow CO_2$

12 gm 44 gm

44 gm of CO_2 contain — 12 gm C

1 gm — $\frac{12}{44}$

C gm — $\frac{12}{44} \times C$

% C gm = $\frac{12}{44} \times \frac{C}{a} \times 100$ → coal gm.

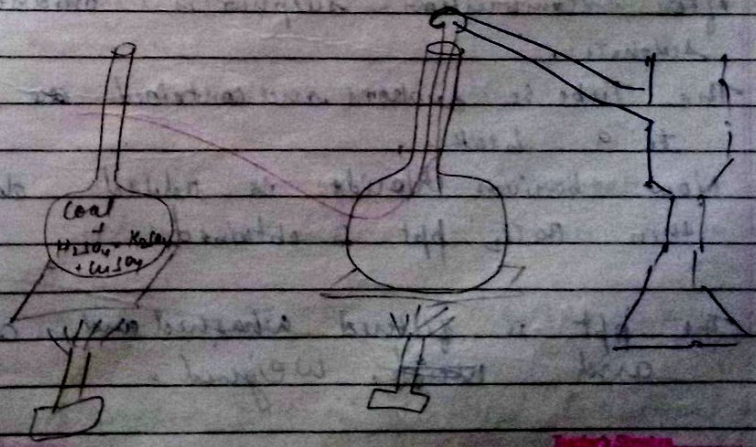
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

2 gm 18 gm

18 gm H_2O — 2 gm

b gm — $\frac{2}{18} \times \frac{b}{a} \times 100$.

→ Determination of nitrogen in Coal Sample :-



wt. of coal sample = w gm
Total volume of $\frac{N}{10}$ acid = V ml
Volume of std. alkali = V ml
Volume of used acid = $V - V = x$ ml.
x ml of acid = x ml NH_3 solution,

100 ml of (1N) NH_3 —— N_2 (14 gm)
1 ml —— $14/1000$
x ml of 1N —— $\frac{14}{1000} \times \frac{x \cdot N}{w} \times 100$

% of $N_2 = \frac{14}{1000} * \frac{x \times N}{w} \times 100$

③ Determination of percentage of Sulphur :-

A known weight of coal sample is taken in combustion tube and concentrate H_2SO_4 in presence of nitric acid is added. The combustion tube is maintained at 300° temp. for 5 hours.
After combustion sulphur is oxidised into sulphate.
The Tube is broken and contained are transfered to a beaker,
Now barium chloride is added drop wise then $BaCl_2$ ppt is obtained.

The ppt is filtered ashashed and dried and weight, weighed.

Coal sample (a gm) + H_2SO_4 / HNO_3 (at 300°c) → S_{32} → SO_4^{2-} → $BaSO_4$ ppt in Beaker

$BaCl_2$ ↓ $BaSO_4$ ppt (x gm).

$BaSO_4$ (233 gm) contain Sulphur = 32 gm.
1 —— 32/233.
x gm —— $\frac{32}{233} \times \frac{x}{a}$

% of S —— $\frac{32}{233} \times \frac{x}{a} \times 100$.

⇒ Nitrogen Procedure

To estimate the percentage of nitrogen a known wt of coal sample is taken in round bottom flask.

And then heated with H_2SO_4, K_2SO_4 & $CuSO_4$. here K_2SO_4 & $CuSO_4$ are worked as a Catalyst.
After heating nitrogen is converted into ammonium sulphate

$$N_2 + 2H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

In the second step ammonium sulphate is heated with sodium hydroxide to liberate amonia.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O.$$

then liberated amonia distilled & observed own

Stand. H_2SO_4 solution of N/10 (total volume of acid is V ml.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

④ Determine Percentage of Oxygen & Coal sample :-

Percentage of oxygen = 100 − (% of H + % of C + % of N + % of S)

★ Importance of Ultimate Analysis :-

→ Greater the percentage of Carbon better is the quality of fuel and higher Calorific value.

→ The percentage of nitrogen in coal sample is undesirable. because it has no Calrofic value. Hence a good quality coal must have low nitrogen.

→ The Combustion product of sulphur are sulphur dioxide (SO_2 & SO_3) & has harmful effects of corrosion on machinary and pollute the environment.

→ Oxygen contain is associated with moisture hence lesser amount of oxygen better is the quality of coal.

Date 10/18

Unit-4

⇒ Cement

PAGE NO.:
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Cement:- It is an extremely fine grey powder prepared by calcining together (at about 1200°C) an intimate mixture of Argillaceous (Al_2O_3, SiO_2, silicate) and calcereous (CaO, $CaCO_3$, lime stone, chalk marbles, raw material with gypsum ($CaSO_4 \cdot 2H_2O$) (2% of wt.)

→ Composition

(i) Lime (CaO) → 60-68% :- To provide strength & hardness to cement.

(ii) Silica (SiO_2) → 17-25% :- " "

(iii) Alumina (Al_2O_3) → (3-8%) Presence of alumina makes to cement quick setting

(iv) Iron oxide (2-4%) :- It imparts grey colour to cement.

(v) MgO - (1-5%) :- To provide strength & hardness.

(vi) SO_3 → (1-3%) :- It imparts soundness to cement.

(vii) $Na_2O + K_2O$ (0.3-0.5%) Makes the cement effor- extent cement.

(viii) Gypsum ($CaSO_4 \cdot 2H_2O$) (2% by wt) :- It is work as a retarder.

That means it enhance the initial setting time period of cement.

Manufacturing of cement:-

By Rotary/Luton Technology

Teacher's Signature

There are 3 steps (i) Mixture (mixing of R.M.)
(ii) Burning (mixture at 1200°C in Rotary kilen → clinkers)
(iii) Grinding (Grinding of clinkers + addition of gypsum)

① Annealing of glass
② Safety glass
③ Setting & hardening of cement
④ Borosilicate glass
⑤ Viscosity index
⑥ Steam emulsion lubricant

① Cement & Cement Manufacturing by rotary kiln technology

② Glass & its properties & Manufacturing of glass

③ Cloud & pour point & its significance

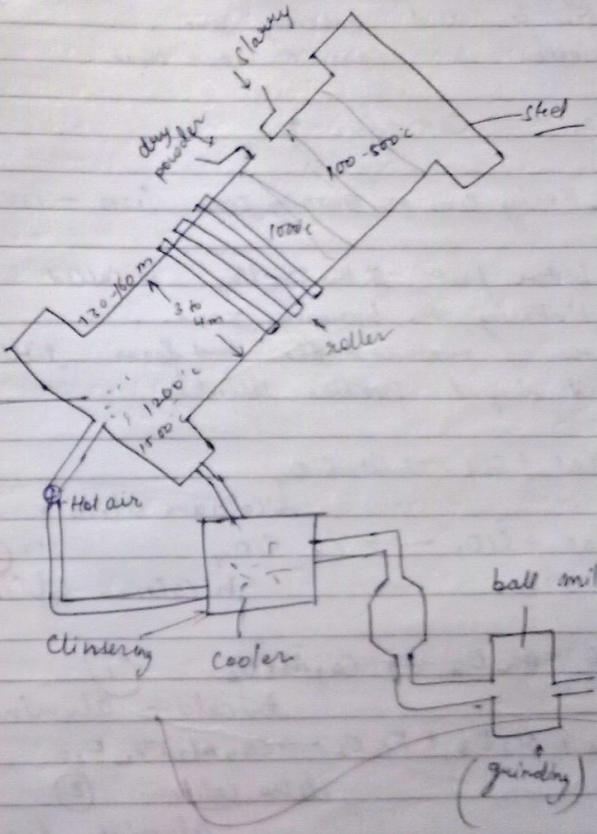
④ Thick film lubrication
⑤ Solid lubricant
⑥ Boundary lubrication its Mechanism

(i) Mixing :— It this step raw materials are mixed either by dry process or wet process.

(a) Dry process :— In which raw materials are crushed, dried & ground in ball mills to get fine powder.

(b) Wet process :— In wet process raw materials are crushed & ground in wash mill in presence of water to get slurry of R.M.

(2.) Burning :— In which fine power of R.M. or slurry is pumped into rotary kiln for burning. Burning is carried out in rotary kiln at 1200°C



The rotary clinker is a long steel cylinder (length about 30-150 m) & diameter (3-4 m.).

→ It is slightly inclined towards the exit end.

① Drying Zone :- (Temp. 100-500°C) :- The upper one fourth part is called drying zone, The moisture driven out here.

② Calcining zone → (900 - 1000°C) → The middle zone of the clin is called calcining zone. Calcination is carried out here.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

③ Clinkering zone or Burning zone :- (1200° - 1500°C)

The bottom part of the clin is called clinkering or burning zone. Where the mixture melts and form little round shaped pea-like Klinker.

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4$$ dicalcium silicate (4)

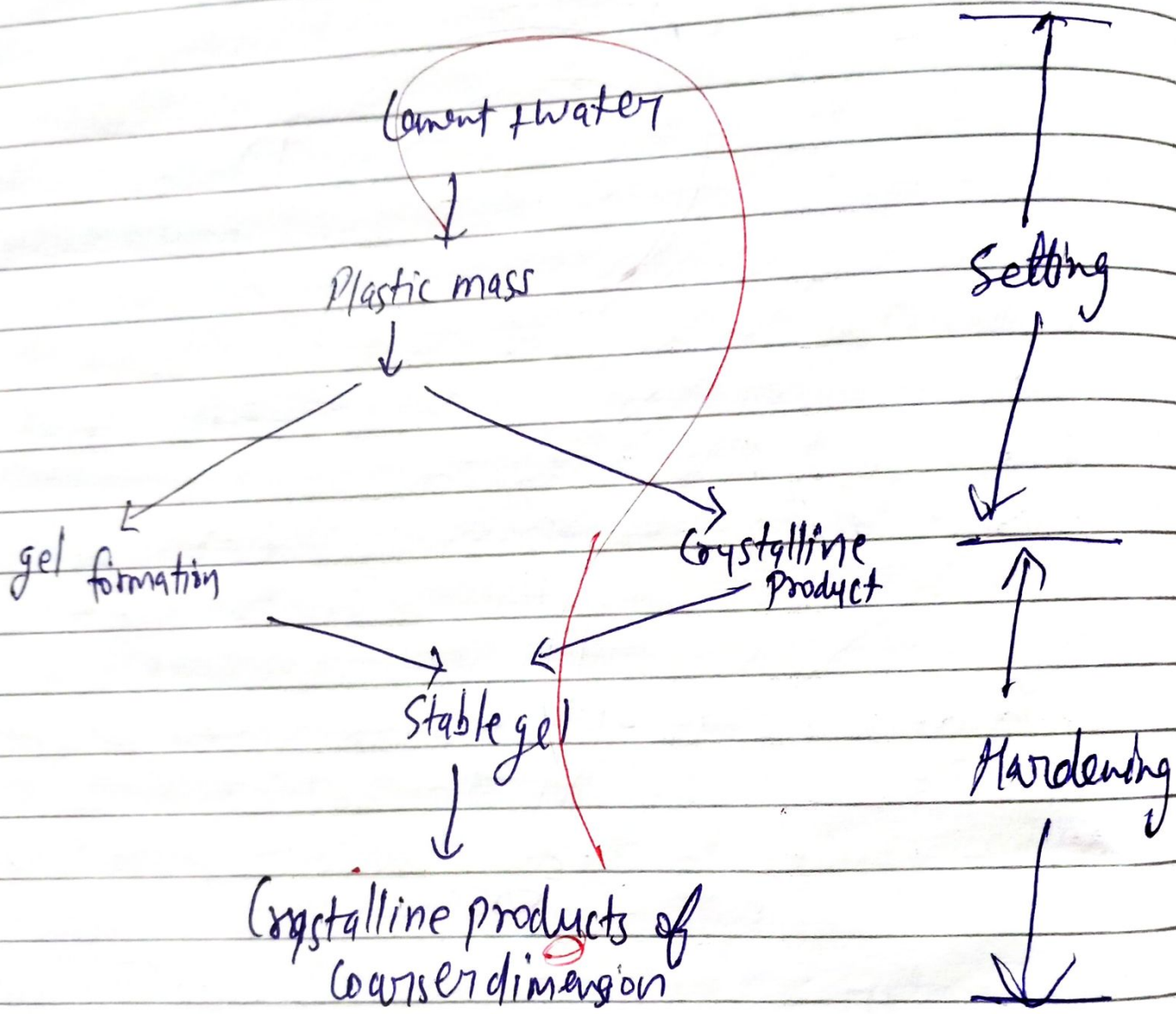
$$3CaO + SiO_2 \longrightarrow Ca_2SiO_4$$ tricalcium silicate (3)

$$3CaO + Al_2O_3 \rightarrow Ca_3Al_2O_6$$ tricalcium aluminate (1)

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$$ tetra calcium alumino ferrate (2)

The hot Klinkers fall out from lower end into cooler for cooling.

* Grinding step :- In this step the cooled clinkers are ground to find powder in ball mill.


Cement + water
Plastic mass
gel formation
Crystalline Product
Stable gel
Crystalline products of coarser dimension
Setting
Hardening

* Final setting :- In this step tetra calcium alumino ferrate and tri calcium silicate is involved in rxn with water.

These constituents get hydrates. and contribute in final setting by gel formation on hydrolysis.

$4CaO\,Al_2O_3\,Fe_2O_3 + 7H_2O \rightarrow 3CaO\,Al_2O_3 \cdot 6H_2O + CaO\,Fe_2O_3\,H_2O$

$3(CaO\,SiO_2) + 6H_2O \rightarrow 3CaO\,2SiO_2\,3H_2O + 3\,Ca(OH)_2$

Tobermonide gel

In the final setting hydration is started also with in a 24 hours & completed in 7 days.

The cement strength in early days due to the formation of tobermonide gel.

→ Hardenning of Cement :- After final setting the plastic mass begin to gain strength due to crystallization and finally all the stable gel is converted into crystalline product. is K/a Hardenning of Cement.

Rxn : $2(2CaO\,SiO_2) + 4H_2O \rightarrow (3CaO\,2SiO_2 \cdot 3H_2O) + Ca(OH)_2 + 250\ KJ.$

Tobermonide gel.

→ The dicalcium silicate also react with water but at a slower rate (7-28) days.

→ It is responsible for progressive development of strength in cement.

→ The second time depends on the composition of cement, temperature and quantity of water.

Glass :- (Short Note - 4)

(1) General Properties of glass.
(2) Manufacturing of glass ← Longe
(3) Types of glass. ← S.N.

(1.) General Properties :-

what is glass:
→ Glass is hard, brittle, amorphous, transparent, supercooled liquid with infinite viscosity.
→ Glass is silicate, it is not a true solid, it has no sharp melting point.
→ It is represented by general formula $xM_2O \cdot yNO \cdot 6SiO_2$.
M = alkali metal (Na, K)
N = alkaline earth metal (Ca, Ba).
→ Glass is highly viscous, and insulator of heat and electricity.
→ Glass is not attacked by air and oxidising agent
→ Glass is easily attacked by alkalies but resistant to acid (except H.F.).
→ It can ~~Eco~~ incorporate colouring material preserving transperancy.
→ Glass exhibits viterification property (Conversion of molten glass into amorphous solid on cooling. instead of crystalline solid.

opalescent glass → Ca

Manufacturing of Glass :-

⇒ General composition of glass (2017).
- (1) Melting of R.M.
(2) Shaping
(3) Annealing of glass (2010)
(4) finishing.

(1.) General Composition of Glass :-

Raw material.

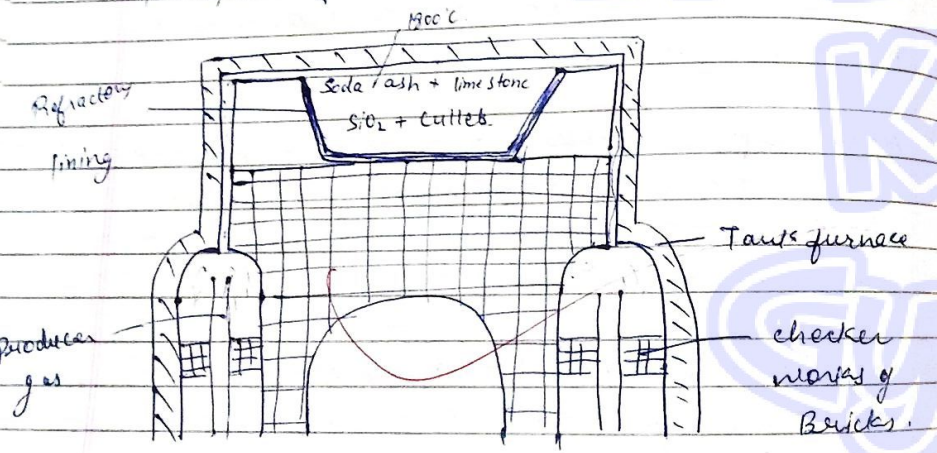
(1) Silica → Silica is used as fine sand particle should be free from impurity.
(2) Alkali metal Oxide → It are used like NaCl, Na_2SO_4, $NaNO_2$, Na_2SO_3, K_2O, K_2CO_3, KNO_2, potash, felsphor etc. to prepare hard glass.
(3) Alkaline earth metal oxide → They are used like $CaCO_3$, CaO, Dolamite (CaO, MgO) Hard glass, $BaCO_3$ to make glass resistant to heat, chemicals & whether change.
(4) Borax ($Na_2B_4O_7 \cdot 10H_2O$) → Source of B_2O_3 used, in making heat & electrical resistant glass. also increases glass durability.
(5) Heavy metal Oxide → PbO, Pb_3O_4, to increase the refractive index of glass.
(6) Zinc oxide → It is used to lower the thermal expansion coefficient of glass.

④ Refining agents → NaCl, $NaNO_2$, Na_2SO_4 to remove air bubble.

⑤ Colouring agent → To provide colour.
Cr_2O_3 - green, CuO - red
CaO - Blue, CdS - Yellow

⑥ Cullets → Broken glass pieces are used to facilate the melting.

① Melting of R.M. → A common rectangular tanks used for melting raw material.
It is heated by producer gas and works on regenerative principle of heat economy.



→ Raw materials are crushed ground and mixed with cullet to get homogeneous mixture which is known as batch.
→ Batch is heated in tank furnace by producer gas at 1800°C temp.
Heating is continued till all the CO_2 & SO_2 air & bubbles are removed and finally transpa...

viscous molten fused mass is obtained. which is known as plane.
→ Now heating is stoped and plane is allowed to cool.
Some sulphides and sulphates of alkali metals are mains undecomposed. which is (known) K/a glass scum and can be easily seperate out from the molten glass.

→ Now the molten glass is ready for shaping.

④ Shaping → Molten glass is shaped into desired artical either by blowing or by molding.

Most Important ③ Annealing :- The glass article are allowed to cool gradualy at room temp. by passing throw a series of different chamber with decending temp. order is K/a Annealing process.

The manufactured glass is a bad conductor of heat is allowed to cool rapidly the upper layer of glass will cool down first. but inner layer are in stress and strain due to which unequal expansion of glass is occured. and finally glass broken into small pieces so that annealing is very important for manufacturing of glass.

⑤ Finishing :- After Annealing process all the types of annealed glass are required to finishing.
Finishing is carried out by cleaning, washing, grinding and by polishing of glass article.

chemical Rxn :-

(1) $Na_2CO_3 + SiO_2 \xrightarrow{700-800^\circ C} Na_2SiO_3 + CO_2 \uparrow$

(2) $CaCO_3 \xrightarrow{900-1000^\circ C} CaO + CO_2 \uparrow$

(3) $CaO + SiO_2 \xrightarrow{1000-1100^\circ C} CaSiO_3$

(4) $Na_2CO_3 + CaCO_3 + 6SiO_2 \longrightarrow Na_2O\,CaO \cdot 6SiO_2$.

Type of Glasses :-

(1) Soda-lime glass (Soft glass) → It is prepared by fusing Na_2CO_3, $CaCO_3$, SiO_2.
→ represented by $Na_2O\,CaO\,6SiO_2$

Properties → 1) Low m.p easily melts 2) cheap glass
3) less resistant to heat & chemicals.

Uses → Used in manufacturing of window glass.
cheap lab glass wares, cheap kitchen wares etc.

(2) Potash-lime glass (Hard glass) → It is prepared by fusing K_2CO_3, $CaCO_3$, SiO_2.
represented by $K_2O\,CaO \cdot 6SiO_2$.

Properties → 1) High melting point with difficulty 2) expansive
3) More resistant to heat & chemical.

Uses → Used in manufactories of lab glass wares, combustion tubes, etc

(3) Lead glass (flint glass) (Lead potash glass) → It is prepared by fusing K_2CO_3, Pb_3O_4, SiO_2.
represented by $K_2O \cdot PbO \cdot 6SiO_2$.

Properties → low m.p. 2) Expansive.
3) more resistant to heat & chemical.
4) Bright lustrous with high refractive index.

Uses → used in manufacturing of optical devices, lenses, prism, neon tubes, mercury tubes.

(4) Optical glass :- It is prepared by phosphorus, Cerium oxide, lead silicate which make the glass capable to absorbing U.V. lights.

Property → 1) low m.p, low durability 2) expansive.

Uses → Used in manufacturing of lab glass wares, combustion tubes etc.

Most Important

(5) Boro Silicate → (Pyrex, Jena glass) :- It contains B_2O_3 & Al_2O_3 → alumina, with Silica. $Na_2O + K_2O$.
2.1 %. 80.5 %. 1.1 %. 13 %.

Pro → high m.p., more durability, 3) Expansive glass.
3) more resistant to heat & chemical.
4) low thermal expansion coefficient.

Uses → 1) Used in manufacturing of T.V. tubes, insulators, industrial pipe lines, lab apperatus, lab glass wares etc.

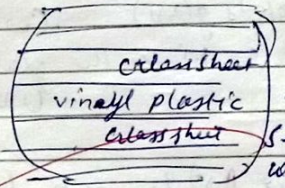
→ (1) Alumino Silicate glass → It contain B_2O_3 and alumina with silica.

SiO_2 , B_2O_3 . Al_2O_3 , $Na_2O + K_2O_3$, MgO , CaO,
85% 3.5% 23% 11% 9% 5%

Property → Same as previous.

→ Uses → Used in manufacturing TV.
Combustion & ~~Happrossing.~~ High pressure, lab apparatus & domestic ~~fa~~ equipments.

Most important (6) Safety laminated or layered glass Bullet proff glass →



→ edges are sealed by water resistant compound.

→ A glass which when break does not allow it broken pieces fly apart.

Preparation :- A safety glass is prepared by placing a thin layer of vinyl plastic in between 2 glass sheet those sheets are pressed together under heat so that vinyl plastic is sandwitched in b/w glass sheet.

The edges are sealed by water resistant compound to make longer glass.

Uses → Three layer glass is used as a wind shield in automobile and aeroplane industry
5 layered is used in building construction

Teacher's Signature

and 7 layer laminated are used in for making bullet proof jacket. and in automobile wind screen.

Most important (8) Glass wool → It is a fibrus wool like glass.

Preparation → It is prepared by forcing molten glass through small holes (.0005 - .0005 mm) diameter continuously to get thread like glass.
The glass thread are thrown over rapidly revolving drums to get material like glass.

Properties → (1) This glass is resistant toward heat fire and chemical.

(2) It density is very low but tensile strength is very high.

Uses → (1) Used in manufacturing for making fire men costume,
(2) in domestic appliances like vacuum cleaner, oven & motors.
(3) Used in making for electrical insulator wires.

Fuel Numerical :-

(1) Dulong's formula (Q1) A coal sample contain 60% carbon, 39% O_2, 4% H_2, 0.5% Sulphur, 0.2% nitrogen, & 0.28% Ash.

Q: Calculate H.C.V. & L.C.V of Sample. :-

$$H.C.V = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240 \times S\right] \text{ cal/gm}$$

$$= \frac{1}{100}\left[8080 \times 60 + 34500\left(6 - \frac{33}{8}\right) + 2240 \times 0.5\right] = 5514.70 \text{ cal/gm}$$

Teacher's Signature

$LCV = HCV - 0.09H \times 587$

$= 5514.70 - 0.09 \times 6 \times 587$

$= 5197.72$ cal/gm.

Q2 → A Sample of Coal contains 93% C, 5% H & 6% ash. when this sample of coal is heated in bomb calorimeter, the following results are obtained

wt. of coal (x) = 0.95 gm

wt of water w = 2000 gm

wt. eq. of apparatus : w = 700 gm.

$t_2 - t_1 = 2.48°C$; Cooling Correction = 0.02°C

Acid correction = 60 cal. fuse wire = 10 cal.

$$H.C.V = \frac{(w+w)(t_2 - t_1 + \text{cooling correction}) - (\text{Acid correction} + \text{fuse wire})}{x}$$

$$= \frac{(2000+700)(2.48 + 0.02 - (60+10))}{0.95}$$

$= 7031.6$ Cal/gm.

$LCV = H.CV - 0.09H \times 587$.

$= 7031.6 - 0.09 \times 587$

$= 6767.42$ Cal/gm.

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Lubricants :- ① Defination & function of Lubricants
② classification of Lubricants ← Liq, semi, Solid
③ Type of Lubrication.
→ SEN (Steam emulsion number) —

① Defination :- The metal to metal fractional resistance can be minimized by using certain substances which forms a thin layer in between surfaces which keep them apart such substances are called lubricant.

Function of lubricant —

① Reduces the fractional resistance in between moving metallic surfaces of machinary.
② Lubricant reduces ~~reas~~ wear & tear and surface deformation in machinary.
③ It reduces runing and maintenance cost of machinary.
④ It improves the efficiency of machinary.
⑤ The Lubricant cover the metallic surface hence attack of corrosive environment on metal is prevented thus the lubricant provides the ~~protection~~ against corrosion.

Classification of lubricant :- Lubricants are classified into 3 catg..
① Liquid lubricant ② Semi solid ③ Solid.

① Liquid Lubricant → Liquid lubricants are k/a lubricating oil can be capable to providing continues film in b/w moving metallic surfaces of machinary.

→ Animal / Vegitable oil ⇒ Animals & vegitable oil are obtained from animals & plants. These lubricating oil having good oiliness These oil are very expensive and stable upto extreme condition (High temperature & pressure) but can undergo oxidation to form gummy products.
These oil cannot be used in pure form always used as additive.

→ Mineral Oil → These oils are obtained from fractional distillation of petroleum.
→ They are low molecular weight hydrocarbon with about 12-250 carbon atom
→ They are cheap and available in abundance.
→ They are quite stable under service condition
→ These oil having poor oiliness so that animal and Vegetables oil are mixed into these type of oil to improve their oiliness

→ Blended oil (Additives) ⇒ Blended oils are capable of giving desired quality of lubricant and which is required for specific machinary.

Antioxident ⇒ Aromatic phenol or Aromatic Amine are used as a antioxidant in oil.

Anti foaming → Glycerols & glycols as anti foaming gent in oil.

Corrosion inhibitors → Organic phosphorus & organic sulphur are used as a corrosion inhibitor :-

Oiliness Carrier → Animal & vegetable oil & fatty acid are used as a oiliness carrier compound.

→ Viscosity Index improver → Relationship b/w temperature & viscosity both are inversly proportional to each other as the temperature increases viscosity will decreases.
→ Viscosity means internal resistance which is offered by the liquid or oil against its own flow.

Low VI	High VI
→ Rapid change in viscosity with respect to temp.	Slow change in viscosity w.r.t. temp

→ A lubricating oil should have high viscosity index.

→ Emulsifiers → alkali metal salt of Carbonylic & sulphonic acids.

→ Synthetic Oil :- Lubricant which will not only work under extreme conditions but also bear wide range of variable operational conditions.
→ They are synthesised by the help of inorganic & organic chemical in laboratory.

Semi-Solid Lubricants → They are prepared by combining liquid lubricant with thickening agent (soap based).
→ The thickeners are higher molecular weight fatty acids of lithium sodium & potassium.
→ Semi solid lubricant are used when lubricating oil cannot remain in placed due to high pressure temperature and high speed.
→ Grease are used at high temp. in gears & ball bearing

DATE: / /

Type of semi solid lubricant

Lithium based - 17°C - 130°C lab use.
Na based - 170°C - gear & ball bearing
K based - 90°C - water pumps

Solid lubricant → When Operational temp. pressure & load is extremely high such that condition lubricating oil or greases cannot remain in film. So that solid lubricants are used.

Gr → Graphite used in food stuff industries and air compressures.

MoS_2 → Stable up to 400°C temp. used in extreme temp, pressure, condition

Types of Lubrication:-

Thick film. (Hydrodynamic) | Thin film. Boundary | extreme. pressure.

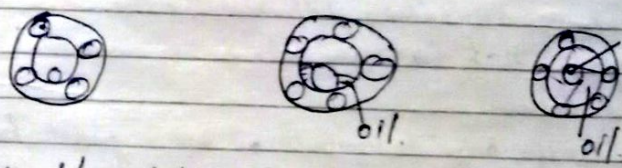
* (1) Thick film → In this type the metal surfaces are separated from each other by thick film of lubricant so that the direct contact of metal surfaces is avoided to reduces friction and to wear.

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Thick film lubricant → moving metalic surfaces (friction coefficient)

→ The resistance to movement of metallic surfaces is only due to the internal resistance between the lubricating particles moving over each other. So, that lubricant should have minimum viscosity under service condition.

→ It should remain in place and seperate the metallic surfaces. Hydrodynamic lubrication occurs in a case of a shaft moving at a fare speed in ball bearing.



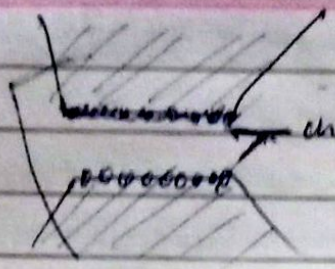
→ Thick film lubricantin occurs in delicate machinary watches clocks, scientific instrument, sewing machine etc.

→ Thick film lubrication is effectively done by hydrocarbon oil. blended with long chain polymer with antioxidants

(2) Thin film/lubrication → Under heavy load and a very low (boundary/lubric) viscosity of oil. a thick film cannot be maintained in between moving metallic surfaces. and direct metale to metal contact is posible than thin film lubrication is done.

→ when the speed is very low.
→ The load is very high.
→ low viscosity of oil.
→ The shaft that moving from rest.

cloud & four
Red wood



moving metallic surfaces

chemically absorbed thin film

Friction coefficient = 0.05 - 0.15.

→ Thin film lubrication is achieved by chemical absorption of lubricant on the metal surface.

→ For good boundary lubrication the lubricant should have
(i) long hydrocarbon chain.
(ii) active functional group.
(iii) Can capable to form bond with surface.
(iv) Lateral attraction between the chain.
(v) high V.I. (Viscosity Index)
(vi) Good oiliness.

→ Graphite, MoS_2, animal & vegetable oil are good boundary lubricant.

(3.) Extreme Pressure Lubrication :-

Under heavy load and high speed of operational condition of high temp. develops at the metal surface. In that situation liquid lubricant fail to stick the metal surface and get decomposed or vaporised. under such condition a special type of lubricants are used these are known as extreme pressure additives.
These are stable and capable of with standing at very high load and pressure & high temp. Metallic Compounds of phosphate, chloride and Sulphides. (mp. 650 - 1200°C) are used as

2. A high pour point leads to the solidification of lubricant that may cause jamming of the machines.
3. Pour point also gives an idea of the lowest temperature at which an oil can be transferred by pouring.
4. Pour point determines suitability of the lubricant for low temperature installations which may be required to start and operate at sub-zero temperature.

Prob.19 *Write short notes on Neutralization Number.* *[R.T.U. Jan. 2016, 2011]*

Sol. Neutralization Number : The neutralization number of an oil is described as the number of milligrams of KOH required to produce a pink colour in 1 g of oil during titration using phenolphthalein as an indicator. The neutralization number indicates all the acidic constituents present in the oil. A rise of neutralization number does not always indicate that the lubricating oil should be changed. The more important consideration is that how much time it takes to reach the neutralization number to that level. In general, rise in neutralization number with increase in viscosity of the oil suggests that a series condition has been reached and the lubricating oil needs to be examined.

Prob.20 *Discuss the significance of viscosity in lubricating oils. How is viscosity of lubricating oil determined using redwood viscometer?* *[R.T.U. Jan. 2016]*

OR

Explain Viscosity and its measurement. *[R.T.U. 2014]*

OR

Write notes on the following:
(i) Viscosity and Viscosity index
(ii) Redwood viscometer *[R.T.U. 2015]*

OR

Write short note on 'Viscosity and Viscosity Index'.

OR

Discuss the significance of viscosity in lubricating oil. How the viscosity is determined by Redwood viscometer? *[R.T.U. 2011, 2007, Raj. Univ. 2008, 2006]*

Sol.(i) Viscosity : Viscosity is most important and representative property of lubricants. Viscosity is the property of lubricant or fluid by virtue of which it offers resistance to its own flow. It is mainly due to forces of cohesion between the fluid molecules.

Significance : *Refer to Short Answer Prob.2.*

Determination of Viscosity Index

The Viscosity index represent the average decrease in viscosity of an oil per degree rise in temperature between 100° F (38° C) and 210° F (99°C).

(1) The viscosities of the lubricating oil (under test) are first determined at 100° F (38°C) and 210° (99°C).

(2) This difference is compared with two standard oils one paraffinic base Pennsylvania oils with Viscosity Index (V.I.) of 100 and another naphthalenic base Gulf oils with Viscosity Index (V.I.) zero (0).

(3) Viscosities of standard oils at 100° F (38° C) and 210° F (99° C) (fig.) are marked.

The Viscosity Index (V.I.) of oil under test is given by formula:

$$V.I. = \frac{L-U}{L-H} \times 100$$

where, U = Viscosity at 100° F (38° C) of an oil whose V.I is to be determined.

L = Viscosity at 100° F (38° C) of an oil of zero V.I having the same viscosity at 210° F. (99° C) as the oil whose V.I. is to be determined.

H = Viscosity at 100° F (38° C) of an oil of 100 V.I having the same viscosity at 210 ° F as the oil whose V.I. is to be determined.

The standard oils having V.I. = 100 are known as H oils (High Viscosity Index Standard) and those having V.I. = 0 are called as L oils (Low Viscosity Index Standards).

In case of a good lubricating oil under test, the difference between the two values of viscosity should be minimum. If the difference will be large, the oil is of poor quality.

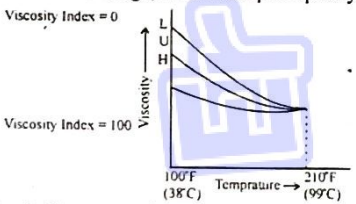


Fig. : Viscosity Temperature Curve for the Standards (L & H) and the Oil under Test (U).

An oil whose viscosity changes rapidly with change in temperature has a low V.I. (the slope of V.I. curve is high while the one whose viscosity changes only slightly has a high V.I. (the V.I. curve is flatter).

Viscosity Index of lubricating oils can be increased by adding certain polymers, which are only partially soluble in the oil.

(ii) Measuremnt by Redwood Viscometer : It consist of the following parts:

(a) Oil Cup : It is silver plated brass cup, which is

is fitted with an agate jet that can be kept closed or open by a valve rod fitted with a ball made of brass. The lid of the cup is fitted with a thermometer, which indicates the oil temperature.

(b) Heating bath : Oil cup is surrounded by a cylindrical copper bath containing copper with containing water having an outlet for taking out water, a stirrer with four blades and a thermometer.

(c) Kohlrausch flask : It is a special type of receiver for receiving the oil. Its capacity is 50 ml to the mark in its neck.

Working : Water is filled in the bath and the brass ball is kept in position to seal the orifice. Test oil is filled in the oil cup upto the tip of the indicator. An empty Kohlrausch flask is kept just below the jet. The desired temperature at which the viscosity is to be measured, maintained by stirring the water and oil in the heating bath and the oil cup respectively. The ball value is lifted and the time is noted for 50 ml of the oil to collect in the flask and the value is immediately closed to stop the overflow of the oil.

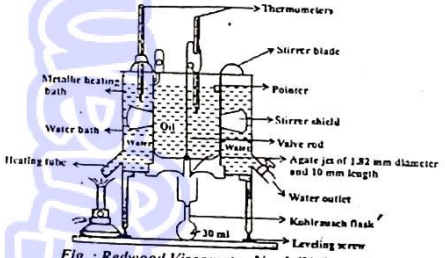


Fig. : Redwood Viscometer No. 1 (Universal)

Prob.21 *Write short note on Silica Refractories.* *[R.T.U. Jan. 2016]*

OR

Explain Silica Refractory. *[R.T.U. 2014, 12, 11]*

Sol. Silica Refractories : It contains 90 to 95% silica and about 2% lime is added during grinding to furnish the **bond preparation**. The raw material used for the manufacturing of silica bricks are quartz, quartzite, ganister, sand, sandstone etc. The silicious rock is first crushed and grounded with 2% lime and water and results the thick paste.

It is converted into bricks either by hand moulding or by machine pressing. The bricks are dried in air and heated. After drying, bricks are burnt in kilns. In about 24 hours, the temperature is slowly raised to about 1500°C. This high temperature is maintained for about 12 hours. This step is very important. Since it allows quartzite to be converted into cristobalite (allotropic transformation). Then, cooling is done carefully and it takes about 7 days to 14 days.

Crystobalite is slowly changed into tridymite during cooling. So that a mixture of tridymite and cristobalite results in the final bricks. In final silica bricks mixture of tridymite and crystobalite is present.

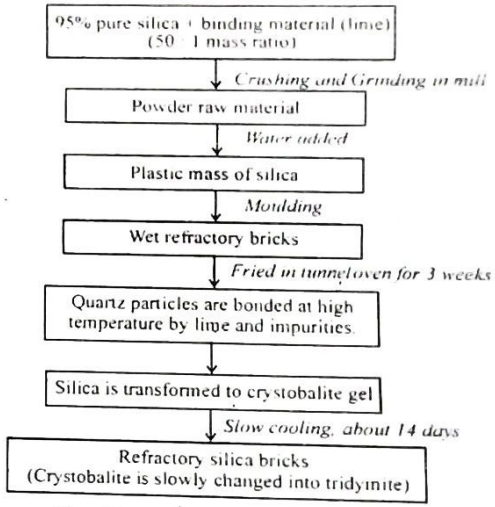


Fig. : Flow chart of manufacturing of Silica Bricks

Properties

1. **Silica Bricks** are yellowish in colour with brown specks (buff coloured). It depends upon the raw materials used for making them.
2. **Composition :** SiO_2 = 95%, Al_2O_3 = 0.75%, Fe_2O_3 = 0.5% CaO = 2%, and MgO = 0.05%
3. **Hardness :** Silica bricks are quite hard and abrasion resistant.
4. **Texture :** Silica bricks have homogenous texture free from air-voids and other moulding defects.
5. **Thermal Conductivity :** It is greater than that of fire clay bricks and is 0.0013 gm cal. per second at 200°C.
6. **Porosity :** 20-30% porosity which imparts low spalling and good thermal characteristics to silica bricks.
7. **Refractoriness :** The fusion temperature of silica refractory is about 1700° C, thus, the refractoriness is high, therefore, it can be used at an operating temperature of 1690°C.

Prob.33 *What is Refractory? Describe properties of refractories.* *[R.T.U. 2014]*

OR

What are Refractories? Give essential requirements of a good refractory material.

[R.T.U. 2013, 12, 2011, (II Sem.) 2009, Raj. Univ. 2005]

OR

What are refractories? Discuss essential properties of good refractory material.

Sol. Refractories : *Refer to Long Answer Prob.6(a).*

Properties of Good Refractory Material : *Refer to Prob.6(a).*

Prob.34 *Explain Requisites of good refractory.* *[R.T.U. 2014]*

OR

What are refractories? How are they classified? Give the essential requirements of good refractories.

[R.T.U. 2012, 2010, Raj. Univ. 2003]

OR

Discuss classes of refractories. *[R.T.U. (II Sem.) 2008]*

OR

Classify the refractories with suitable example. Explain in detail silica refractories. *[R.T.U. (I Sem.) 2009]*

Sol. Refractory : *Refer to Long Answer Prob.6(a).*

Requisites of Refractory Material or Essential Requirement of Good Refractory : *Refer to Long Answer Prob.25.*

Classification : Refractories are of 3 types :

(A) Acid refractories

(B) Basic refractories

(C) Neutral refractories

(A) Acid Refractories : These are acidic in nature, thus they are resistant to acidic materials but are attacked by basic materials. They include :

(1) Silica refractories,

(2) Siliceous or Semi-silica refractories,

(3) Fireclay refractories.

(1) Silica Refractories : Silica (Quartz or ganister) is mainly used for making refractories. The content of basic oxides should be minimum as they decrease the m.p. of silica. Silica bricks tend to undergo slight permanent expansion upon prolonged exposure to high temperature. Tendency of silica bricks to expand is useful in producing a good furnace arched Silica refractories are used as the lining material for acid open hearth and acid bessemer convertors and for roofs of furnaces

(2) Siliceous or Semi-silica Refractories : These ar clay bonded silica bricks. They may be made from naturall occurring sand clay mixtures or from batches prepared fron ground ganister bonded with a refractory clay. These are use for constructing steel furnace plants.

(3) Fire Clay Refractories : Main ingredient in Kaolinit *i.e.*, hydrated aluminium silicate ($Al_2O_3.2SiO_2.2H_2O$ containing 18 – 45% Al_2O_3. During firing, the product shrink due to expulsion of water and fluxing effect of impurities They are used as casting pit refractories and high for th bricks used for blast furnace hearths and the roofs of ope hearth checkers.

(B) Basic Refractories : They are composed of basi materials such as magnesia (MgO), dolomite etc. Example of such refractories are magnesite, dolomite and chrome magnesite. These are attacked by acidic slags but are resistan towards basic slags.

(1) Magnesite : It is basic refractory. Basic slags hav little or no corrosive effect. It has good chemical resistanc Mechanical strength is much more than ordinary bricks. has low thermal spalling. The resistance to abrasion is lo They can be used up to 2000° C without load and under loa ($3.5\ kg/cm^2$) upto 1500° C.

(2) Dolomite Refractories : Dolomite refractori (CaO.MgO) are highly basic in nature and have proved good and cheap substitute for magnesite bricks. They ca withstand high temperature load and also a very goo mechanical load.

(3) Chrome-magnesite Refractories : Chrom magnesite bricks containing about 70%, chrome and 30 magnesite are much superior to the magnesite or chromi bricks because these refractories are also quite resistant thermal shocks. The main defect of these refractories swelling and bursting in the presence of slags containing ir oxide.

(C) Neutral Refractories : This group includes a wi range of materials such as chromite, silicon carbide, zircon carbon etc.

(1) Chrome Refractories : The chromite bricks a neutral in character. Chromite bricks are resistant to ba

and acid slags. They are not resistant to thermal shock. These chromite refractories can be used up to 1800° C and their refractoriness under load is 3.5 kg/cm^2 at 1430° C. They have moderate thermal conductivity and good mechanical strength.

(2) Silicon carbide : Silicon carbide decomposes in the temperature range of 2200 – 2700° C before its melting and does not react with hydrogen, nitrogen or carbonmonoxide. A small proportion of clay or bentonite is added as binder, and the bricks are fired to a high temperature say 1500° C.

Silica Refractory : *Refer to Long Answer Prob.21.*

I. Short Answer Type Questions

Prob.1 ***What do you mean by organic reaction?***

Sol. An organic reaction is a change in structure or functional group leading to formation of a new substance. The compound undergoing a change in structure or functional group is called a reactant or substrate. The knowledge of organic reactions helps in the synthesis of useful chemical compounds such as polymers, dyes, drugs, perfumes, cosmetrics, fertilizers, food preservatives.

Prob.2 ***What are the types of organic reactions?***

Sol. The organic reactions can be generally classified as substitution, addition, elimination, rearrangement, oxidation and reduction reactions.

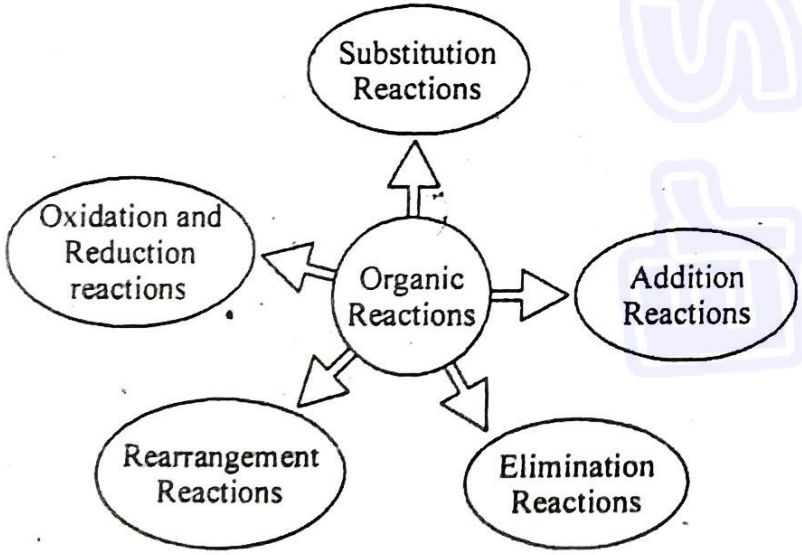


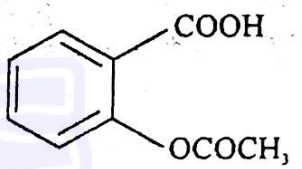
Fig. : Types of Organic Reactions

Prob.3 ***What do you mean by drugs?***

Sol. Drugs are a way of modifying the chemistry of the body. They can be used to treat diseases and infections, correct imbalances in electrolytes and fluids, or alter mental status (such as inducing amnesia or stopping hallucination). Drugs are used both for medical purposes and for recreation. In both cases, no drug is perfect. A perfect drug would be 100% effective while causing no side effects. Drugs offer many benefits, but there are always trade-offs and risks to consider.

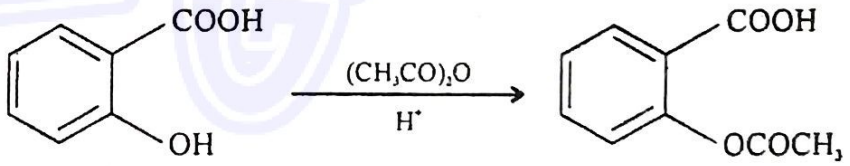
Prob.4 ***Write down the properties and uses of aspirin.***

Sol.



2-Aceloxytenzoic acid (or) Acetyl anlicytain

Synthesis



Salieylic acid — Aspirin

Properties and Uses : Aspirin is a white crystalline powder, slightly soluble in water and soluble in alcohol, indicated for the relief of minor aches and mild-to-moderate pain in the conditions such as arthritis and related arthritic condition. Also used in myocardial infarction prophylaxis.

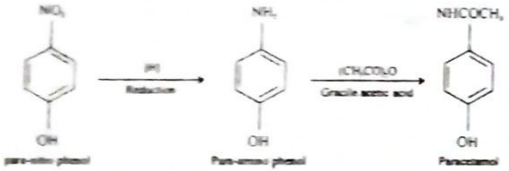
Prob.5 ***Write down the properties and uses of paracetamol.***

Sol.



Para-acetamino phenol

Synthesis



Properties and uses : Paracetamols exist as white crystalline powder, sparingly soluble in water, soluble in alcohol, and very slightly soluble in methylene chloride. Paracetamols produce antipyresis by acting on the death have been observed following over dosage; hepatic damage is likely in an adult who takes more than 10g in a single dose or if a 2-year old child takes more than 3g.

II. Long Answer Type Questions

Prob.1 ***Explain substitution reaction with the help of example.***

Sol. Substitution Reactions : These reactions involve the displacement of an atom or a group by another atom or group.



It takes place at

1. sp^3 hybridised carbon (alkane, haloalkane, alcohol)
2. sp^2 hybridised carbon (benzene)

A substitution reaction can be uncleophilic, electrophilic or free radical substitution reaciton.

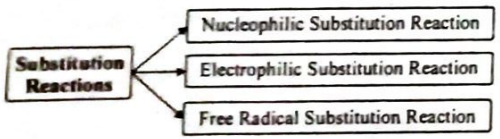


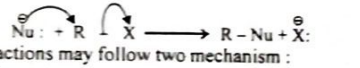
Fig. 1 : Types of Substitution Reaction

1. Nucleophilic Substitution (SN) Reactions

These reactions involves the attack of a nucleophile and are more common in aliphatic compounds. For example, hydrolysis of alkyl halides by aqueous KOH.

$$R - X + K - OH \rightarrow R - OH + KX$$

In general it may be represented as :



These reactions may follow two mechanism :

(i) Unimolecular Mechanism (S_N 1)

The rate or such reactions depends only on the concentration of alkyl halide (susbstrate) and is independent of nucleophile.

$$\text{Rate} \propto [RX] \qquad \ldots (1)$$

Such reactions are belived to be completed in two steps. The first step is the rate determining step (slow) in which they alkyl halide ionizeds to give carbonium ion. In the second step, the carbonium ion combines with the nucleophile to give the substituted product. This can be explained by the hydrolysis of ter-butyl bromide.

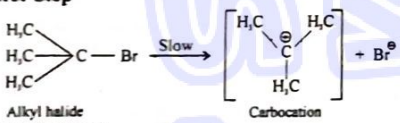


The rate of above reaction depends only on the concentration of t-butyl bromide

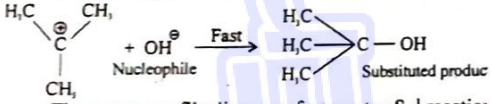
$$\text{Rate} = k[(CH_3)_3\,C - Br] \qquad \ldots(2)$$

Based on the kinetics, the reaction takes place in following two steps:

First Step



Second step :



The energy profile diagram of a two step S_N1 reaction is shown in fig. (2)

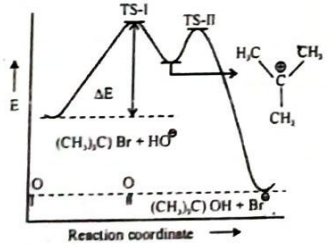


Fig. 2 : Energy Profile for an S_N1 Reaction

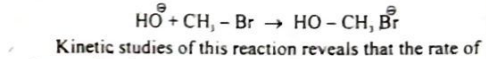
Solvents play very important role in S_N1 reactions as the ionization is facilitated by solvation of carbocation.

(ii) Bimolecular (S_N 2) Mechanism

The rate of such reactions depends on the concentration of alkyl halide (substrate) as well as the base (nucleophile).

$$\text{Rate} \propto [RX]\,[OH^-] \qquad \ldots(3)$$

Such reactions are completed in one step. Consider the hydrolysis of methyl bromide by aqueous NaOH.

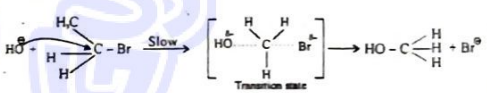


Kinetic studies of this reaction reveals that the rate of such a reaction depends upon the concentration of alkyl halide as well as the hydroxide ion.

$$\text{Rate} \propto [CH_3Br]\,[OH^-] \qquad \ldots(4)$$

If the concentration of any of them is doubled then the rate of reaction is also doubled and when the rate or reaction of any one of them is halved, the rate of reaction is also halved.

In such a process the hydroxide ion (nucleophile) attacks the carbon atom from the side opposite to that of the bromine (leaving group). This is because of the fact that both hydroxide ion and the bromine are electron rich. So, the bond breaking and bond making are simultaneous processes and such a reaction, therefore, involve a transition state in which the carbon atom appears to be pentavalent. In transition state, carbon atom is joined to three substituents by full covalent bonds and to the nucleophile and leaving group by partial bonds. The three substituents acquire a coplanar geometry.



The energy profile of such a reaction is shown in Fig. (3).

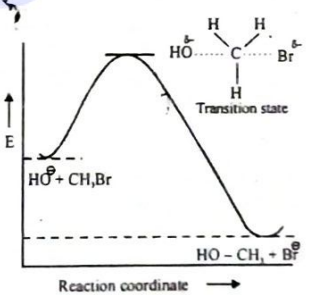


Fig. 3 : Energy Profile for an S_N2 Reaction

Prob.2 ***Give the difference between S_N1 and S_N2 reaction.***

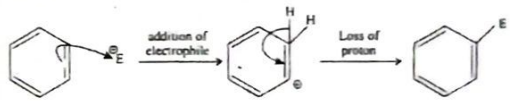
Sol.

S. No.	S_N1	S_N2
1.	These are first order reactions.	These are second order reactions.
2.	The nucleophile can attack from both back side as well as front side.	The nucleophile can attack only from the back side.
3.	Reaction rate is influenced by electronic factors.	Reactions is influenced by steric factors.
4.	The order of reactivities of alkyl halides is : Benzyl > allyl > 3° > 2° > 1° halides.	The order of reactivities is : Methyl > 1° > 2° > 3° halides.
5.	Favoured by low concentration of nucleophiles	Favoured by high concentration of nucleophiles.
6.	Favoured by polar solvents	Favoured by non-or low polar solvents

Prob.3 ***Write short notes on***
(i) Electrophilic Substitution Reactions
(ii) Free Radical Substitution Reaction

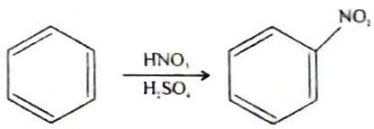
Sol.(i) Electrophilic Substitution Reactions

It involves substitution in the aromatic ring by an electrophile. In the first step the electrophile is attacked by the π-electrons of the aromatic ring leading to the formation of a new carbonelectrophile bond. It is followed by loss of a proton. In these reaction, electrophile first attack to give an intermediate with positive charge, known as arenium ion and in the second step leaving group departs. This is known as arenium ion mechanism.

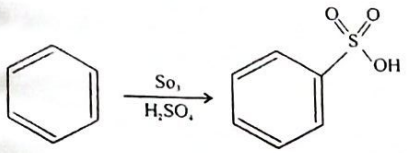


Examples of electrophilic substitution reactions are :

(a) Nitration : It involves a nitronium ion (NO2) as an electrophile.



(b) Sulphonation : In this reaction sulphur trioxide (SO_3) acts as an electrophile.



benzenesulfonic acid

(ii) Free Radical Substitution Reactions

Such reactions begin with the formation of a free radical which substitutes a group or atom present in the reactant molecule. The reaction of methane with chlorine in the presence of light is a free redical substitutiion reaction.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

The first step is initiation i.e free radical formation by homolytic cleavage of bonds. Second step is chain propagation and finally chain termination step

Initiation

Initiation step may happen spontaneously or may be induced by heat or light depending on the type of bond.

$$Cl_2 \rightarrow 2Cl^{\bullet}$$

Chain Propagation

In this step, a molecule reacts with a free radical to generate a new radical.

$$CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl$$
$$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$$

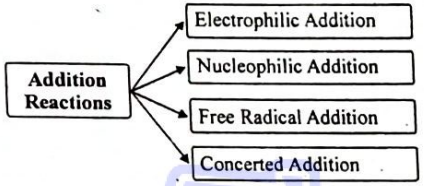
Chain Termination

This step is also known as destruction of free radicals. This step involves a combination of two like or unlike radicals to form a new bond.

$$2Cl^{\bullet} \rightarrow Cl_2$$
$$CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$$
$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3CH_3$$

Prob.4 ***Explain addition reaction with the help of example.***

Sol. These reactions are characteristic of compounds containing multiple bonds. The alkene (=), alkynes (≡), C = O, C ≡ N react by addition to multiple bond. Thus in addition reaction there is increase in the number of groups attached to the substrate and decrease in its unsaturation. Addition reactions are of four type namely electrophilic, nucleophilic, free radical and concerted. The first three are the two-step processes, with initial attack by electrophile, nucleophile or a free radical. The second step consists of a combination of the resulting intermediate with a negative species, a positive species or a neutral entity. In addition, attack at the two carbon atoms of the double or triple bond is simultaneous.



1. Electrophilic addition reaction

These reactions are brought about by the attack of electrophiles and are generally given by compounds containing carbon-carbon double and triple bonds. For example addition of HBr to propene. This reaction takes place in following steps :

Step 1 : H^+ from HBr is added to propene to form a π-complex, which then forms isopropyl carbocation (2°-carbocation, which is more stable than 1°-carbocation).

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \rightarrow CH_3-CH=CH_2 \rightarrow CH_3-\overset{\oplus}{C}H-CH_3 + Br^{\ominus}$$

π-Complex: $\overset{\delta+}{H}-\overset{\delta-}{Br}$; Isopropyl carbocation: $CH_3-\underset{H}{\overset{\oplus}{C}}H-CH_3$

Step 2 : The bromide ion (nucleophile) combines with the carbocation to give isopropyl bromide.

$$\underset{\text{Propene}}{CH_3-\overset{\oplus}{C}H-CH_3} + Br^{\ominus} \rightarrow \underset{\text{Isopropyl bromide}}{CH_3-\underset{Br}{CH}-CH_3}$$

The product formed in above reaction follows Marknownikoff's Rule, according to which the negative part of the addendum is added to that doubly bonded carbon atom which bears the minimum number of hydrogens.

In the above case during first step : two carbocations may be formed giving two different products in following manner.

$$CH_3-CH=CH_2 + H^{\oplus} \longrightarrow \underset{\text{2°-Carbocation}}{CH_3-\overset{\oplus}{C}H-CH_3} \xrightarrow{Br^{\ominus}} \underset{\text{2-Bromopropane}}{CH_3-\underset{Br}{CH}-CH_3}$$

$$CH_3-CH_2-\overset{\oplus}{C}H_2 \xrightarrow{Br^{\ominus}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2Br}$$

(1° Carbocation)

The major product of the reaction is 2-bromopropane as the secondary carbocation formed is more stable than primary carbocation forming 1-bromopropane. Thus, Markownikoff's rule is obeyed.

Anti-Markownikoff's Addition or Peroxide Effect : According to this effect, the addition of HBr to propene in presence of peroxides gives 1-bromopropane as major product rather than 2-bromopropane.

$$\underset{\substack{Br\\ \text{(Not formed)}}}{CH_3-CH-CH_3} \xleftarrow[\text{Peroxide}]{HBr} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Peroxide}]{HBr} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

This is because in the presence of peroxides the addition involves free radical mechanism. This effect was put forth by Kharasch and Mayo, so it is also called Kharasch effect.

2. Radical Addition Reactions

The addition reactions of alkenes catalyzed by small amount of peroxides or irradiated by ultraviolet light are nearly always free radical chain reactions and often lead to the formation of polymetric products. These reactions are illustrated by some examples.

Addition of HBr to Olefins : This is most famous 'abnormal' addition to alkenes and the entire mechanism consists of chain initiation, propagation and finally termination.

Chain Initiation : It starts with light or by thermal decomposition of initiators such as peroxides. The peroxides present in most olefin samples due to autoxidation, are sufficient to initiate the chain. In fact, olefins must be carefully purified to suppress the radical processes.

$$\underset{\text{Dibenzoyl peroxide}}{C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5} \xrightarrow{\Delta,\ 60-80°C} \underset{\text{Dibenzoyl oxy radical}}{2C_6H_5CO_2^{\bullet}}$$

$$C_6H_5CO_2^{\bullet} + HBr \longrightarrow C_6H_5COOH + Br^{\bullet}$$

Chain Propagation : With propylene the chain propagating steps are as follows :

$$Br^{\bullet} + CH_2=CH-CH_3 \longrightarrow Br-CH_2-\dot{C}H-CH_3 + 9\ \text{kcal/mol (exothermic)}$$

$$Br-CH_2-\dot{C}H-CH_3 + HBr \longrightarrow BrCH_2-CH_2-CH_3 + Br^{\bullet} + 7\ \text{kcal/mol (exothermic)}$$

Thus, the overall result is 'anti-Markownikoff, addition, i.e. reverse of the normal addition to the olefin. The bromine adds to the less hindered end of the bond and forms a more stable radical. Therefore, we find that with the decomposition of a single initiator molecule, a large number of molecules of the product are formed.

This abnormal addition of bromine is a good method of preparing primary bromides from terminal olefins.

Chain Termination : Chain termination occurs by combination with bromine atoms, or with alkyl radicals or by coupling or disproportionation of alkyl radicals.

$$2Br^{\bullet} \longrightarrow Br_2$$

$$Br-CH_2-\dot{C}H-CH_3 + Br^{\bullet} \longrightarrow Br-CH_2-\underset{Br}{CH}-CH_3$$

$$2Br-CH_2-\dot{C}H-CH_3 \longrightarrow Br-CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-Br$$

It is interesting to note that in presence of polar solvents or in presence of inhibitors like thiophenol or hydroquinone the above addition becomes a heterolytic process. It is homolytic in conditions in which it is described. So we can say that homolytic addition is the result of peroxide effect and distinguishes it from ionic reactions.

We can explain the anology in orientation in the same manner as we explain orientation in heterolytic addition. In heterolytic addition, just as the secondary carbocation $CH_3-\overset{\oplus}{C}HR$ is more stable than primary $\overset{\oplus}{C}H_2-CH_2R$, so is the secondary radical CH_2Br-CR is assumed to be more stable than the primary radical $\bullet CH_2-CHR-Br$. Therefore, the basic difference is not that in one, the process is heterolytic and in the other it is homolytic, but in one case the addition begins with the formation of a new C–H bond whereas in the other it is the C–Br bond, which is formed first. However, if somehow the reaction conditions could be so altered that the initial attack at the double bond were by a H radical, than Markownikoff's type of addition would be expected.

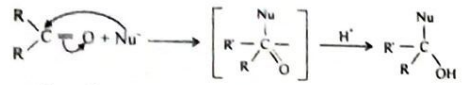
Having read the mechanism of addition of HBr to olefins in presence of peroxides, it is pertinent to ask if HCl of HI also combine by radical addition? In this connection it has to be noted that HCl or HI do not undergo abnormal addition to olefins under normal conditions. The reasons for failure are different for the two compounds. The H-Cl bond is too strong to be broken readily in the atom abstraction reaction. The hydrogen iodide bond breaks up easily to give atoms but these do not add rapidly to double bonds.

$$R^{\bullet} + HI \xrightarrow{Fast} RH + I^{\bullet}$$

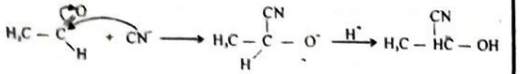
$$I^{\bullet} + >C=C< \xrightarrow{Slow} I-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\bullet}$$

3. Nucleophilic Additions

The carbonyl group of aldehydes and ketones facilitates addition reactions by both nucleophilic as well as electrophilic pathways. The electron deficient carbonyl carbon atom can react with nucleophiles while the electron rich carbonyl oxygen can react with electrophiles. The typical reaction of aldehydes and ketones is nucleophilic addition involving a base can be represented in general as



One of the simplest addition reactions to the carbonyl group is the cyanohydrin reaction. Cyanide ion adds to the carbonyl carbon atom to give an unstable intermediate oxyanion (alkoxide). The alkoxide being a strong base then abstracts a proton from the solvent or another molecule of the weak acid HCN to form the cyanohydrin.

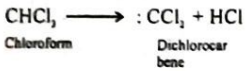


Other examples of nucleophilic additions include the addition of acids (HCl), alcohols to hemiacetals or hemiketals, addition of Grignard reagents, addition of organozinc compounds (Reformatsky reaction), etc. An interesting example is the aldol condensation.

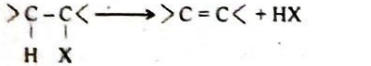
Prob.5 ***What is Elimination Reaction? Explain its reaction mechanism with an example.***

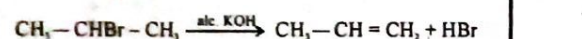
Sol. These reactions are reverse of addition reaction and involve the loss of atoms or groups from the same molecule to form multiple linkage. On the basis of mechanism, elimination reactions may be of two types.

1. α-Elimination : This type of elimination is very rare and involves elimination of two groups or atoms from the same carbon atom. For example,



2. β-Elimination : It involves the removal of two groups or atoms from the two adjacent (α and β) carbon atoms of the molecule. For example,

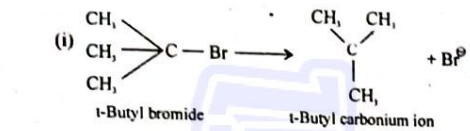




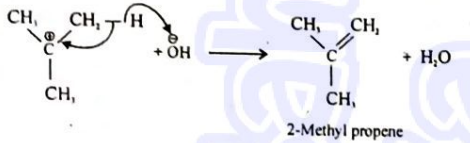
These reactions proceed via unimolecular (E_1) or bimolecular (E_2) mechanism.

1. Unimolecular (E_1) mechanism

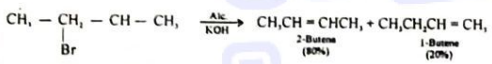
When the rate of an elimination reaction depends only on the concentration of the substrate. Like S_N1 reactions these also occur in two steps. For example, dehydrohalogenation of T-alkyl halides. The first step involves the ionisation of alkyl halide to give carbonium ion (slow) and the second step involves that fast abstraction of a proton by the base adjacent to β-carbon leading to the formation of alkene.



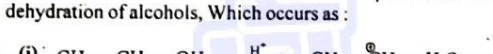
(ii)

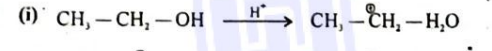


When there is a possibility of formation of two types of alkenes, then the main product is most highly substituted alkene as per Saytzeff rule. For example



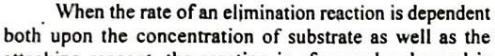
The other common example of E_1 reaction is dehydration of alcohols, Which occurs as :





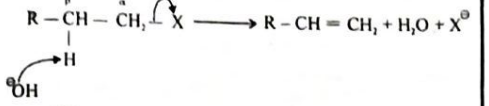
2. Bimolecular (E_2) Mechanism

When the rate of an elimination reaction is dependent both upon the concentration of substrate as well as the attacking reagent, the reaction is of second order and is represented by E_2. For example, reaction of alkyl halide with alc. KOH.



$$\text{Rate} = k\,[CH_3CH_2Br]\,[KOH] \qquad \ldots(1)$$

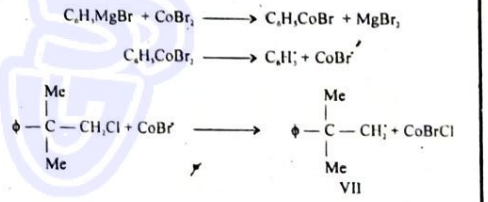
The mechanism is a one step process in which the abstraction of the proton from the β-carbon and the expulsion of the leaving group, i.e., halide ion from the α-carbon atom occur simultaneously.

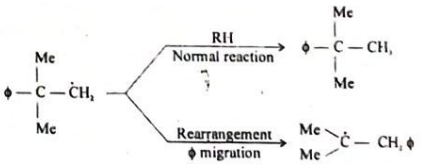


This is also known as dehydro halogenation reaction.

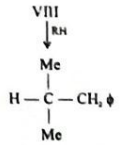
Prob.6 ***What is free radicals? How they are formed.***

Sol. Free radicals, compared to many other electron deficient species, show less tendency to undergo rearrangements. The largest number of radical rearrangements known are those in which an aryl group migrates to an adjacent position. However, no example of a hydrogen or alkyl shift in a monoradical has been reported. The first case of a phenyl migration scheme was observed in 1944 by Urry and Kharasch. Treatment of 1-chloro-2-methyl-2-phenylpropane with phenylmagnesium bromide, in the presence of cabaltous bromide, afforded a mixture of products. The following radical mechanism was proposed to rationalize the products. The neopentyl radical (VII) may abstract a hydrogen atom to give the normal product:

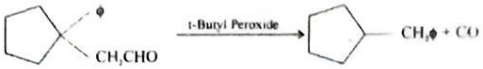




(VII)

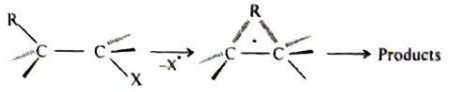


t-butylbenzene, or it may also rearrange to a more stable tertiary radical (VIII) which then forms isobutylbenzene. Both the radicals, (VII) and (VIII), dimerize and are disproportionate in their yields. This sequence of steps was confirmed by sub sequent workers who generated the radicals by different methods and observed exclusive migration of the phenyl group. In cycle compounds, equation (1)

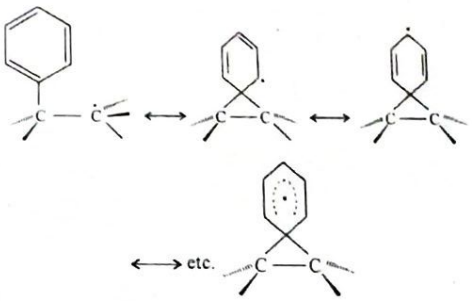


...(1)

of the migration of a phenyl group was reported by Wild and Philip. The mechanism of radical rearrangements has not been investigated in detail but the intramolecular 1, 2-shift, in general, may be described. This assumes the formation of a triangular non-classical radical (IX) which presumably provides a path of lower activation energy compared to the dissociation and coupling processes. Moreover, for aryl migration additional resonance structures are available for the delocalization of the odd electron, as shown, and thus stabilization is possible an in (X).



(IX)



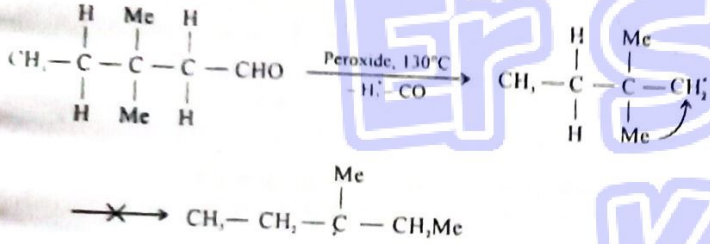
Based on the molecular orbital treatment of Huckelx, it has been argued that the transition state (IX) is less stable than either the initial or the rearranged product when R is hydrogen or an alkyl group. This implies that there is no reason to expect 1,2-alkyl or hydrogen shifts in radical reactions though they are well known in the corresponding carbocations. No unambiguous case of an alkyl or hydrogen migration is yet known in simple radicals. Kornblum and coworkers pyrolyzed optically active 2-octyl nitrite and obtained an optically active octanol. They concluded that the radical (XI) does not undergo a 1, 2 hydrogen shift to carbon to give XI (a) but, rather, abstracts a hydrogen atom from the solvent to yield actanol. Brown and Russel found similar negative



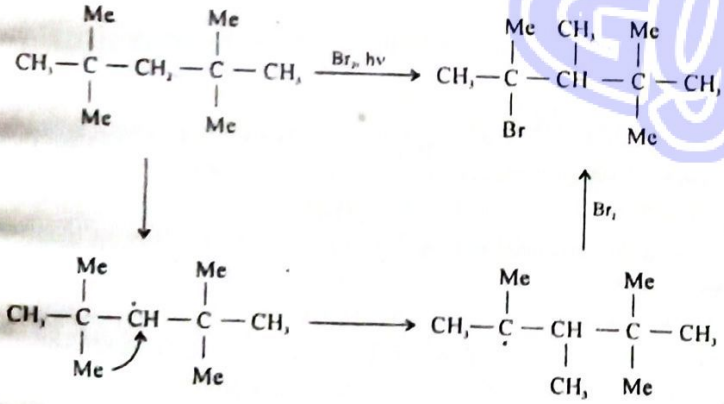
(XI)

evidence of hydrogen migration in the photochlorination of isobutane because the isobutyl radical did not rearrange to the t-butyl radical. Similar results by other workers have demonstrated that such rearrangements are unlikely. Considerations of orbital symmetry do not apply to reactions proceeding through bridged intermediates. Thus intermediates of the above type are possible.

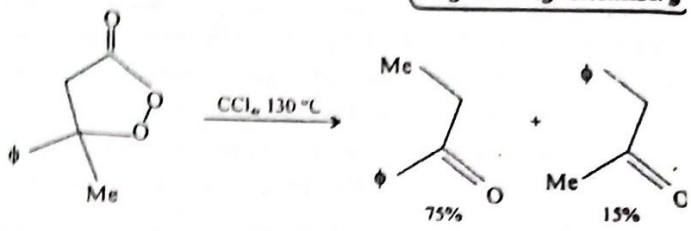
The migration of an alkyl group in carbocations is frequencly observed, but the free radicals show no tendency to rearrange. Seubald observed no rearrangement of 2,2-dimethylpentanal to t-amyl radical on decarbonylation in the liquid phase.



Kharasch and cowrkers brominated 2,2,4,4-tetramethylpentane under u.v. light in the gaseous phase and obtained a rearranged product, 2-bromo 2,3,4,4-tetramethylpentane. The bromo derivative was identified by treatment with silver nitrate which yielded 2,3,4,4-tetramethylpentane.



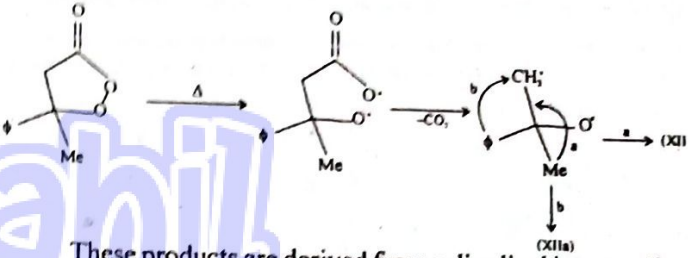
These authors postulated the formation of the original product as the result of the initially formed secondary to the rearranged tertiary radical by a 1, 2-shift. The validity of this interpretation was questioned later and it was suggested that the rearrangement actually took place on reaction of the rearranged bromide with silver nitrate. Nevertheless, recently, several reactions have been reported in which the alkyl group



(XII) (XIIa)

migration has been observed to be even faster than that of the phenyl group. Green and coworkers, for instance, among others, isolated two major products (XII) and XIIa) in the decarbonylation of β-methyl-β-phenyl-β-peroxypropiolactone.

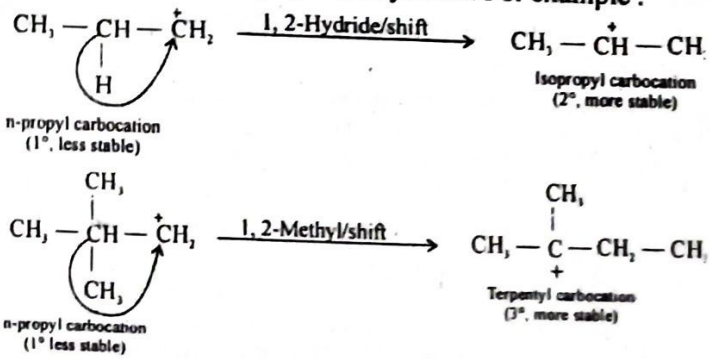
A possible mechanism for this may be postulated as follows :



These products are derived from a diradical intermediate and the yield of (XII) via methyl migration (path a) is almost five times more than that obtained from phenyl migration (path b). The formation of these products can, however, be explained alternatively by a two-step rather than an intramolecular rearrangement. According to the latter pathway, the migrating group may fragment and then recombine in the cage to form the product. Though alkyl migrations have been suggested to take place at high temperatures, the complexity and low yields of the products obtained in such cases a re still ambiguous.

Prob.7 ***Write short note on Rearrangement of Carbocations.***

Sol. Carbocations are prone to rearrangements. During these rearrangements, less stable (1° or 2°) carbocations are converted into more stable (2° or 3°) carbocations either by 1, 2-hydride shift or by 1, 2-methyl shift. For example :



Er Sahil Gyan