

08. Explain Internal conditioning methods of softening hard water.

To remove hardness producing salts, chemicals were added to the boiler water in the boiler itself and that treatment is called internal conditioning.

(i). Colloidal Conditioning (ii).

Phosphate Conditioning (iii). Carbonate Conditioning (iv). Calgon Conditioning.

(i) Colloidal Conditioning:

In low-pressure boilers, scale formation can be avoided by adding organic substances like kerosene ,tannin, agar-agar (a gel), etc., which get coated over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.

(ii). Phosphate conditioning:

Three types of phosphates- mono, di and trisodium phosphates are employed in phosphate conditioning. The advantages of phosphate conditioning over carbonateconditioning are (i).It can be applied to high pressure boilers and (ii) It can be used for softening/ conditioning acidic, neutral or alkaline water sample.



If acidic water is to be conditioned, trisodium phosphate can be used. For neutral and alkaline water samples disodium phosphate and monosodium phosphate can be used respectively.

(iii) Carbonate conditioning:

In low pressure boilers, calcium ions are converted into soft and loose sludge by adding sodium carbonate solution. It forms soft CaCO_3 which can be removed by blow-down operation.



(iv). Calgon conditioning:

Calgon interacts with calcium ions forming a highly soluble complex and it

prevents the precipitation of scale forming salt. The complex $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ is soluble in water and no problem for its sludge disposal.



v) Sodium Aluminate Conditioning

1. Sodium Aluminate reacts with boiler water to give NaOH and gelatinous precipitate of coagulant Aluminium hydroxide.



2. Sodium hydroxide reacts with Mg^{2+} ions to give Magnesium hydroxide.



3. Finally it forms sludge which can be removed by blow down operation.

11. What is Desalination? Describe desalination of by Reverse Osmosis method with neat diagram.

Or

Explain the reverse osmosis process for desalination of brackish water in detail.

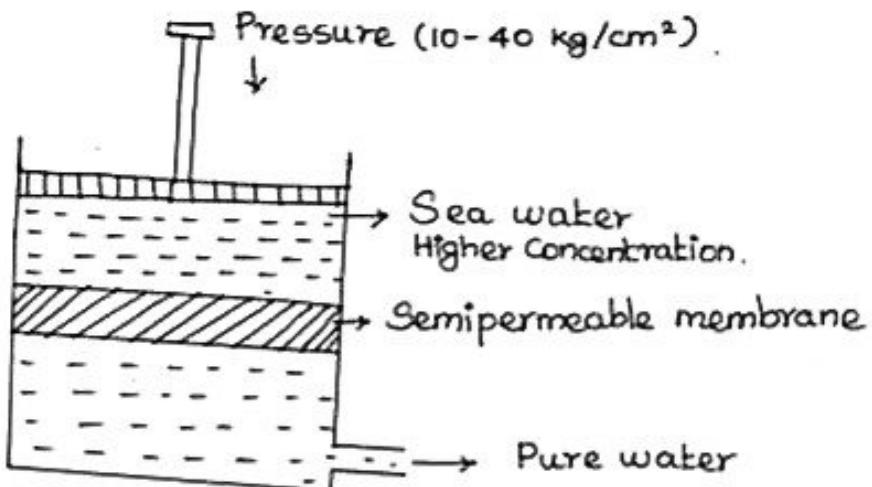
Desalination = Removal of common salt-NaCl from water.

Brackish water = Water containing dissolved salts with a peculiar salty taste. Ex: sea water

Reverse Osmosis(RO):

When a pressure greater than osmotic pressure applied on the concentrated side, the solvent flow takes place from higher concentration to lower concentration is known as reverse osmosis.

Diagram:



Process:

- 1) In this RO process, Pure water is separated from salt water.
- 2) This RO process is also known as Super filtration or Hyper filtration
- 3) When the pressure is applied from the higher concentration side, the solvent flow takes place to lower side and these two concentrations are separated by semipermeable membrane, the salt water is converted into pure water.
- 4) The membranes used as cellulose acetate, polyamide and some polymers.

Advantages & RO method:

1. Low capital cost, easy operating.
 2. It is used for converting sea water into drinking water
 3. It removes all types of impurities like non-ionic and colloidal
 4. The life time of membrane is high and it can be replaced within few minutes.

12. Explain demineralization process in detail.

Demineralisation - The process of removing all ions both cations and anions from hard water is known as demineralisation.

It is known as Ion- Exchange process.

D.M. Process - Removal of all cations like Na^+ , K^+ and all anions like SO_4^{2-} , Cl^- etc.

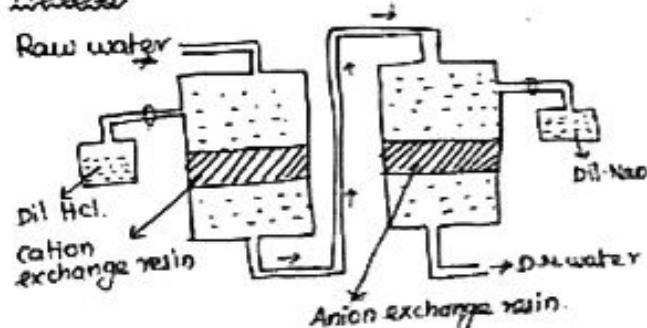
D.M. Process is done by Ion- Exchange resins method.

Ion-Exchange method: The process of releasing the ion and adsorbing another ion is known as ion-exchange adsorption.

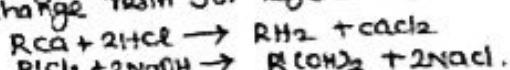
Types of Ion-Exchangers: 1. Cation Exchanger. 2. Anion Exchanger.

1. Cation Exchanger.	2. Anion Exchanger.
(i) They are exchanging only H^+ ions.	Only OH^- ions.
(ii) Represented by RH_2	$R'(OH)_2$
(iii) Contains acidic functional groups. -COOH, -SO ₃ H	Basic functional groups. -NH ₂ , -OH
(iv) Ex: Sulphonated coals, styrene	Ex: Urea-formaldehyde resin. Cross-linked Quaternary NHa Salts.

Index:



(iv) Regeneration: - dil HCl for cation exchange resin and dil NaOH for anion exchange resin for regeneration.



(iv) The hard water is first passed through a cation exchange resin column, which absorbs all the cations like Ca^{2+} , Mg^{2+} , Na^+ , K^+ etc.

$$\text{RH}_2 + \text{CaCl}_2 \rightarrow \text{RCA} + 2\text{HCl}$$

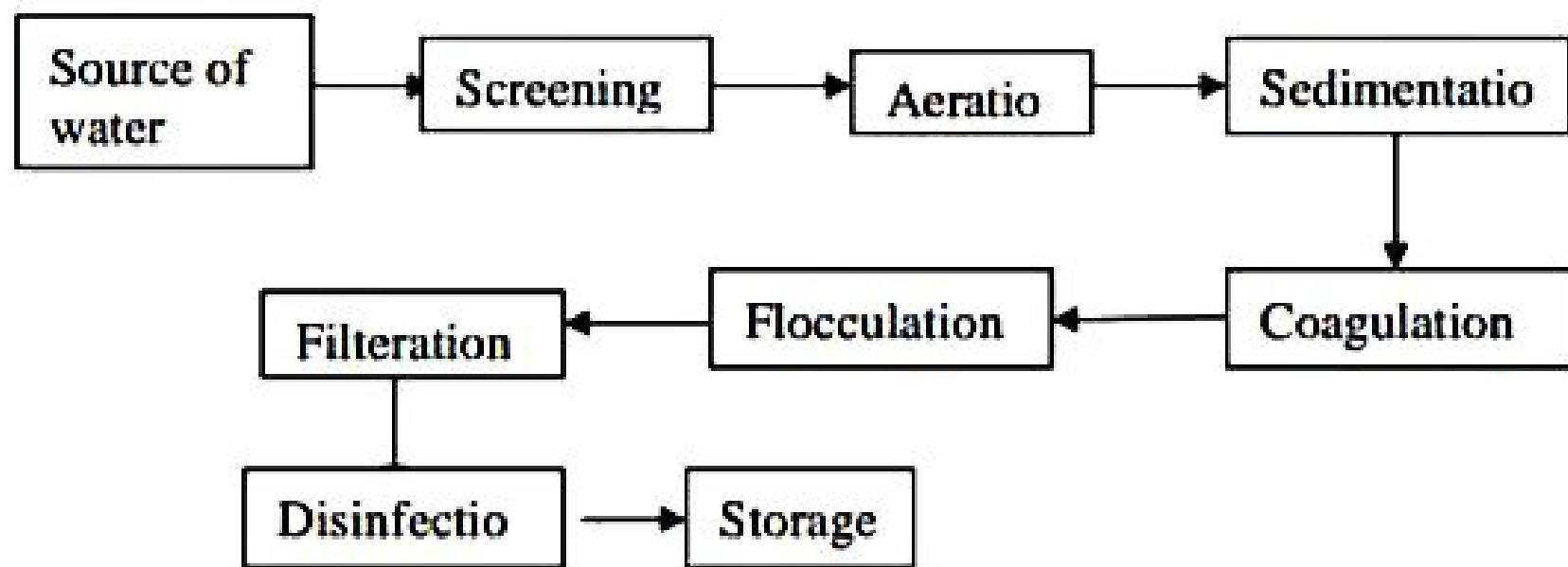
Then the cation free water is passed through an anion exchange column, which adsorbs all the anions like, Cl^- , SO_4^{2-} , HCO_3^- , etc.

(ii) The water coming out from anion exchanger is completely free from anions and cations. This water is known as D.M. water or Deionised water.

uses: used to remove acidity from basic substances and basic from acidic substances.

14. Discuss the domestic waste water treatment with neat diagram,

Raw water has to be treated safely to make it safe to drink. In water treatment various stages are present that can be indicated by following flow chart.



Screening :

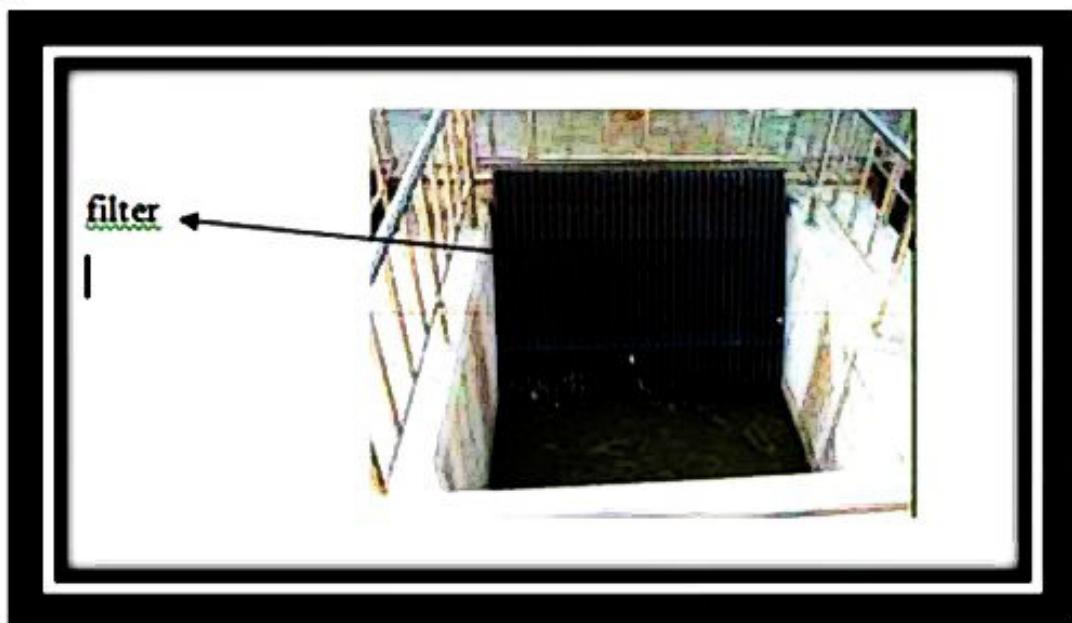
By this process the floating materials like paper, plastics, twigs, leaves, logs, cloth, fish, plants and trash etc from the water are removed. The purpose of screening process is to avoid the entry of garbage into the water treatment plant and to prevent the clogging or damage of the pipe. The screening process has two filters

- 1) Coarse filter
- 2) Fine filter

Coarse filter is to remove the large floating garbage and twigs

Fine filter is to remove the smaller floating water plants leaves and so forth.

Thus the raw water is allowed to pass through both the filters to eliminate the floating particles.



Sedimentation:

It is a process of removing the suspended impurities by allowing the water to stand undisturbed for 2-6 hr in a tank to settle the suspended materials due to the force of gravity.. Thus the suspended materials settled down and the suspended impurities are removed from the bottom. It removes 75% of the impurities.

Aeration:

After the sedimentation process the water is mixed with air which is called as aeration. This process is used to add oxygen for oxidation of undesirable substances like oils,algae, etc. It is mostly used for ground water not for surface water. It is also used to remove volatile liquids like phenols and humic acid. It increases the acidity of water. The process of aeration can be done by spray nozzle, cascade aerators, diffused air aerators and

trickling bed air aerators.

Advantages :

Aeration processes promote the taste and odour of water.

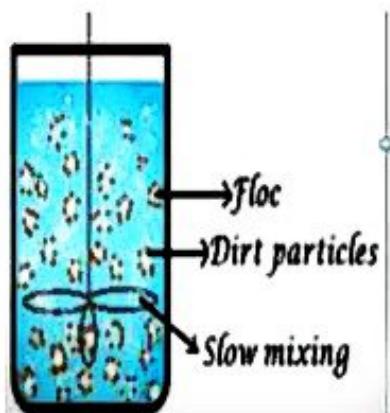
It removes CO_2 , H_2S and some volatile impurities which cause bad taste and odour to the water.

It removes Fe and Mn salts as their precipitate

Coagulation:

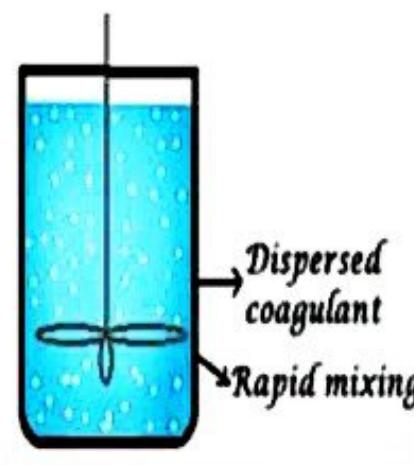
Some impurities like finely divided clay, silica not removed by sedimentation. Such type of impurities are removed by coagulation.. In this method certain chemicals called as coagulants (alum, sodium aluminate, FeCl_3 , FeSO_4 etc) are added. Rapid mixing uniformly disperses coagulant.

When the coagulant is added it reacts with water to form a gelatinous precipitate which entraps the impurities



Flocculation

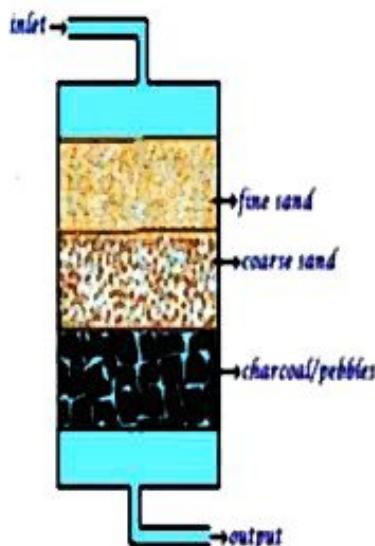
The slow mixing of coagulant will form a floc with dirt particles. The fine colloidal particles will combine with the impurities to form a bigger floc . The floc is heavier in size and settled down by sedimentation process.



Filtration:

It is the process of removal of colloidal and suspended matter, bacteria, odour, colour and taste etc. By passing the water through filter beds containing fine sand, coarse sand and charcoal/pebbles. When the water passes through the filter it removes the left out particles residual turbidity and few microorganisms. It also removes bad taste and odour.

After continuous usage the rate of filtration decreases slowly due to the clogging of pores by impurities. Hence the top layer of the sand can be scrapped and replaced with new sand to avoid the decrease in efficiency



Disinfection:

The process by which harmful bacteria are destroyed to make the water safe for drinking is called disinfection. The chemicals or radiations used for this purpose are called disinfectants.

Disinfection methods includes

Physical methods- boiling, UV irradiations

And chemical methods- ozonation and chlorination.

Physical methods

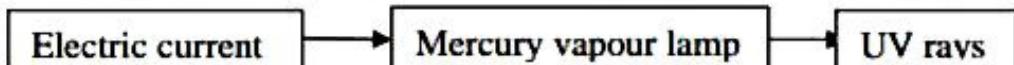
1)Boiling:

When water is boiled for 10-15 min all the harmful bacteria's are killed and water becomes safe for use

Disadvantages

- 1.The water taste is changed.
 - 2.It is impossible for large treatment plants.
- 2) Ultraviolet light

UV rays are produced by passing electric current through mercury vapour lamp.



This treatment is used particularly in Swimming pools. UV light alters the DNA of the bacterial cells that are exposed.

Merits:

- (i) The disinfection is highly effective compared to chlorination and ozonation.
- (ii) Disinfection by this process is a "clean" process, since no chemical additives are used.

Demerits

- (i) The unit is costly.
- (ii) The method is not applicable to turbid water.

Chemical methods

3) Ozonation:

Ozone (O_3) is a powerful disinfectant and is readily adsorbed by water . As a powerful oxidant, it reduces the contents of iron, manganese, and lead, and eliminates most of the objectionable taste and odor present in water. Since ozone is relatively unstable, it is generated almost invariably at the point of use.

Ozone is highly unstable and readily decomposes to give nascent oxygen. This nascent oxygen is a powerful oxidizing agent and kills the germs in water.



Merits:

- (i)Ozone removes color, odor and taste of water.
- (ii) It does not leave any residue.

Demerits:

- (i) It is not economical.
- (ii) At high doses, ozone imparts a fishy odor to water.
- (iii) It is unstable cannot be stored for long time.

4) Chlorination:

The process of adding Chlorine to water is known as chlorination.

Chlorination can be done by the following methods.

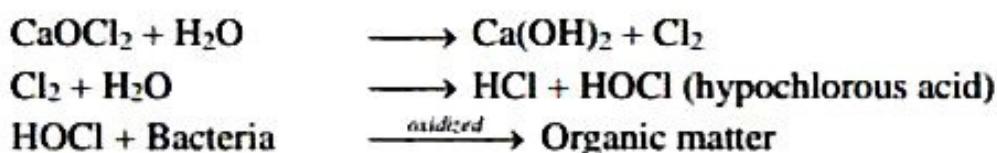
i) By adding Chlorine gas

Chlorine gas can be bubbled in to the water



ii) Bleaching powder. As a substitute for chlorine gas, bleaching powder can be used as disinfectant. Bleaching powder is nothing but calcium hypochlorite powder

with the formula CaOCl_2 . When bleaching powder is added to water, it dissolves in water and liberates the chlorine gas. This chlorine gas which in turn dissolves in water to form hypochlorous acid (HOCl) is produced. HOCl is a powerful disinfectant.



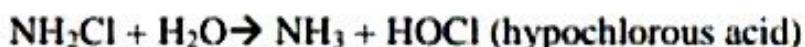
Merits:

- (i) It is economical.
- (ii) It can be applied even for small communities and small water supply schemes.

Demerits:

- (i) It is highly unstable and hygroscopic. When exposed to air or moisture, it loses its strength. Hence it should be stored only in tight containers.
- (ii) The disinfection effect is effective for certain period of time (about 30 minutes) only.

- iii) **Chloramines:** Chlorine is unstable in water. Hence, it is mixed with ammonia to form chloramine. This chloramine which in turn dissolves in water to form hypochlorous acid (HOCl) is produced. HOCl is a powerful disinfectant.



Merits:

- (i) Chloramines impart good taste and do not give irritating odor.
- (ii) Chloramines help to maintain the disinfection effect up to the consumer end.

Demerit:

- (i) May be carcinogenic.
- iv) **Break point chlorination : refer answer 13**

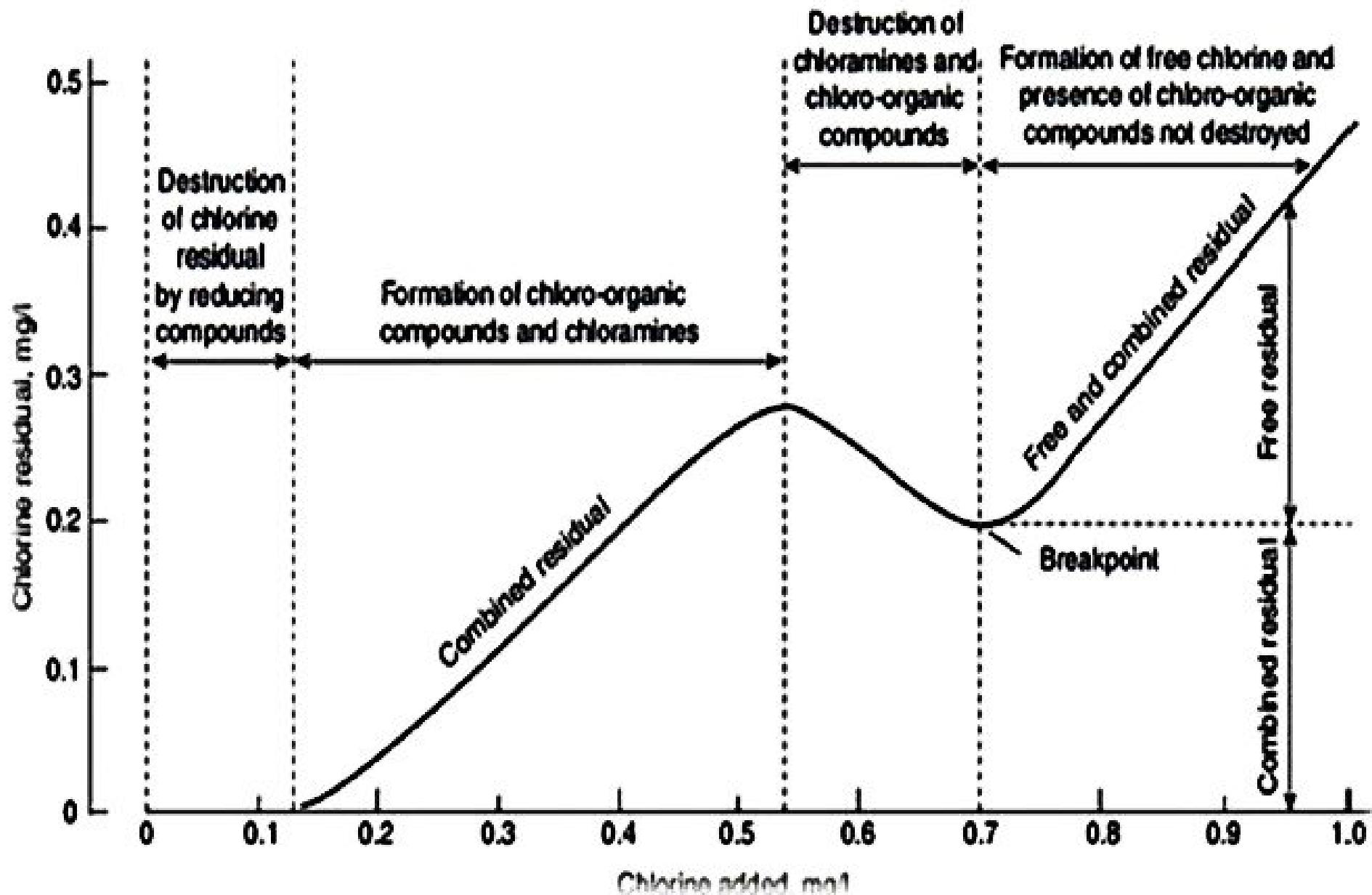
Break Point Chlorination (Break Point Chlorination Curve) : It may be defined as the chlorination of water to such an extent that not only living organism but also other organic impurities in water are destroyed.

When chlorine is added to water, it is used for different reactions like oxidation of oxidizable substance, chlorination of organic substance, destructive oxidation of organic substances and disinfection of pathogens.

Initially all the chlorine added is consumed and there is no free chlorine. This is due to complete oxidation of oxidizable substances. As the applied chlorine increases, there is steady increase in amount of residual chlorine. This stage corresponds to formation of chloro-organic compounds and chloramines when the dose of chlorine increase, destruction of chloro organic and chloramines take place.

Addition of chlorine in such dosages is known as break point or free residual chlorination. The breakpoint chlorination ensure complete destruction of organic compounds, which gives color, unpleasant odour and bad taste. In addition to it a complete destruction of disease producing micro-organisms is also ensured.

Break Point Chlorination Curve



Advantages

- (1) It oxidizes complete organic matters, dissolved ammonia and other reducing particles.**
- (2) It removes color (which is due to the presence of organic compounds).**
- (3) It destroys (~ 100%) all the bacterias.**
- (4) It removes bad odour and bad taste.**

3. Discuss the applications of Nanomaterials in energy, medicine, sensor and catalysis.

Nano-technology finds significant impact on all most all the industries and all areas of society. Since nano-materials possess unique beneficial chemical, physical and mechanical properties, they can be used for a wide variety of applications.

(i) In Energy

Nanomaterials are used in several applications to improve the efficiency of energy generation (or) develop new methods to generate energy.

- Power generation**

Sun light, concentrated on nanoparticles, can produce steam with high energy efficiency, which can even be used in running power plants.

- Generating hydrogen sea water**

The use of a nanostructured thin film of nickel selenide as a catalyst for the electrolysis of hydrogen from sea water.

- Producing high efficiency light bulbs**

Nano-engineered polymer matrix is used for the production of high efficiency light bulbs.

- Increasing the electricity generated by wind mills**

Stronger and lower weight blades, made from nanotubes-filled epoxy, in wind mills increases the amount electricity.

- Generating electricity from waste heat**

Sheets of nanotubes have been used to build thermocells that generates electricity, when the sides of the are at different temperature

- Storing hydrogen for fuel cell powered cars**

Graphene layers are used in fuel tank, resulting higher amount of hydrogen storage and therefore lighter weight fuel tank.

- Reducing power loss in electric transmission wires**

The wires containing carbon nanotubes lowers resistance than the wires currently used in the electric transmission grid.

- **Reducing the cost of solar cell**

Nanotech solar cells are manufactured at significantly lower cost than the conventional solar cells.

- **Nano battery and fuel cell**

Nanomaterials, used in batteries and fuel cell, increases their efficiency.

(ii) Medicine

- **Nano drugs**

Nano materials are used as nano drugs for the cancer and TB therapy.

- **Laboratories on a chip**

Nano technology is used in the production of laboratories on a chip.

- **Nano-medibots**

Nano particles function as nano-medibots that release anti-cancer drug and treat cancer.

- **Gold-coated nanoshells**

It converts light into heat, enabling the destruction of tumours. Gold nano particles as sensors
Gold nano particles undergo colour change during the transition of nano particles.

- **Protein analysis**

Protein analysis can also be done using nanomaterials.

- **Gold nanoshells for blood immuno assay**

Gold nano shells are used for blood immuno assay.

- **Gold nano shells in imaging**

Optical properties of the gold nano shells are utilized for both imaging and therapy.

- **Targeted drug delivery using gold nano particles**

It involves slow and selective release of drugs to the targeted organs.

- **Repairing work**

Nano technology is used to partially repair neurological damage.

(iii) Electronics

- Quantum wires are found to have high electrical conductivity. 2. The integrated memory circuits have been found to be effective devices.

- A called NOMFET, (Nanoparticle Organic Memory Field Effect Transistor) is created by combining gold nanoparticles with organic molecules.
- Nano wires are used to build transistors without p-n junctions.
- Nano radios are the other important devices, using carbon nanotubes.
- MOSFET (Metal Oxide Semi-conductor Field Effect Transistor), performs both as switches and as amplifiers.

(iv) In Catalysis.

Nanoparticle catalysts are highly effective because of the following two reasons

- huge surface area
- enhanced reactivity
- **Water purification**

Nano silver catalyst is highly efficient in controlling microbes in water.

- **Bio-diesel production**
- Solid base nano catalyst KF/CaO can be used for biodiesel production with yield more than 96%.
- **Fuel cell application.**

Carbon supported electro-catalysts play an important role in fuel cell.

- **In drug delivery Lives**
- Carbon nanomaterials find more applications in biological fields.
- CNTS may be suitable for bio-applications in bio recognition and drug delivery systems.
- **Gold nanoparticles**

It is an important catalyst in co-oxidation, epoxidation of propylene, hydrogenation of unsaturated hydrocarbons.

- Nanopowder silica catalyst (or) platinum nanoparticles exhibit very strong catalytic activity for hydrolysis reactions.
- Titania-based nanocatalysts are being increasingly used in photocatalysis.
- Nanocrystalline MgO particles act as an effective catalyst for dehydrogenation.

In Agriculture

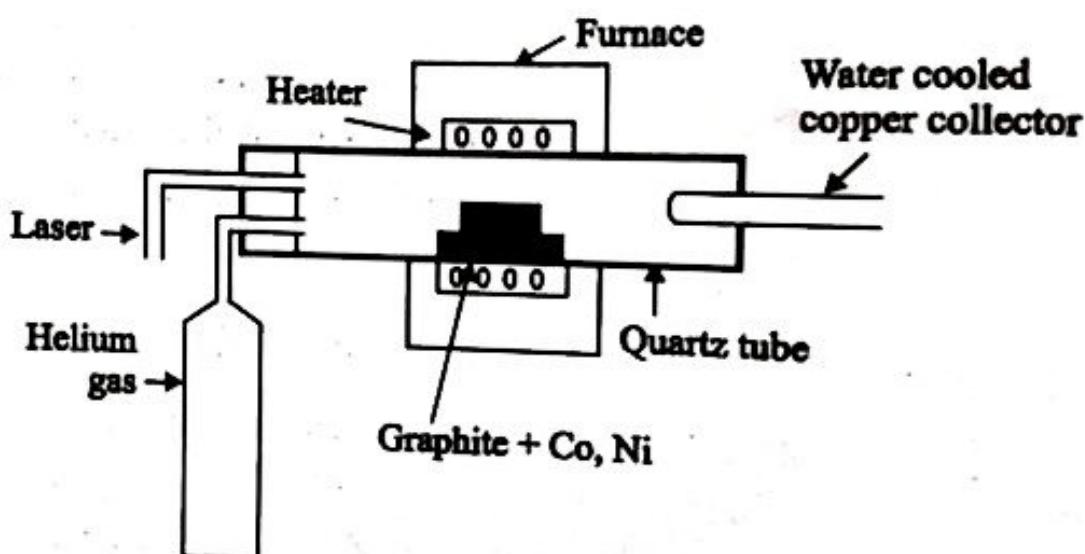
- Nanomaterials prepared by eco-friendly and green method with plant extracts (Nano formulations) could increase agriculture potential for improving fertilization process, plant growth regulators.
- They also minimize the amount of harmful chemicals that pollute the environment.
- Nano sensors are used in crop protection for the identification of diseases and residues of agrochemicals

- Nanodevices are used for the genetic engineering of plants.
- Nanomaterials are used in plant disease diagnostics. It is also used in postharvest management.
- Precision farming techniques might be used to further improve the crop yields but not damage soil and water.
- Some nanomaterials are used as antimicrobial agents in food packing especially silver nanoparticles are in great interest.
- Nano particle-based pesticides and herbicides are being explored for the application of antimicrobial agents to protect crops from various diseases.

4. Explain laser ablation process for producing nanomaterials with a neat diagram.

In laser ablation technique, high-power laser pulse is used to evaporate the material from the target. The stoichiometry of the material is protected in the interaction. The total mass ablated from the target per laser pulse is referred to as the ablation rate.

This method involves vaporization of target material containing small amount of catalyst (nickel or cobalt) by passing an intense pulsed laser beam at a higher temperature to about 120°C in a quartz tube reactor. Simultaneously, an inert gas such as argon, helium is allowed to pass into the reactor to sweep the evaporated particles from the furnace to the colder collector.



Uses

1. Nanotubes having a diameter of 10 to 20 nm and 100 nm can be produced by this method.
2. Ceramic particles and coating can be produced.

2.6

PREPARATION OF NANOMATERIALS

The following two approaches are used for the synthesis of nanomaterials.

1. Top-down process (or) Physical (or) Hard methods.
2. Bottom-up process (or) Chemical (or) Soft methods.

2.6.1 *Top-down process*

Top-down process involves the conversion of bulk materials into smaller particles of nano-scale structure.

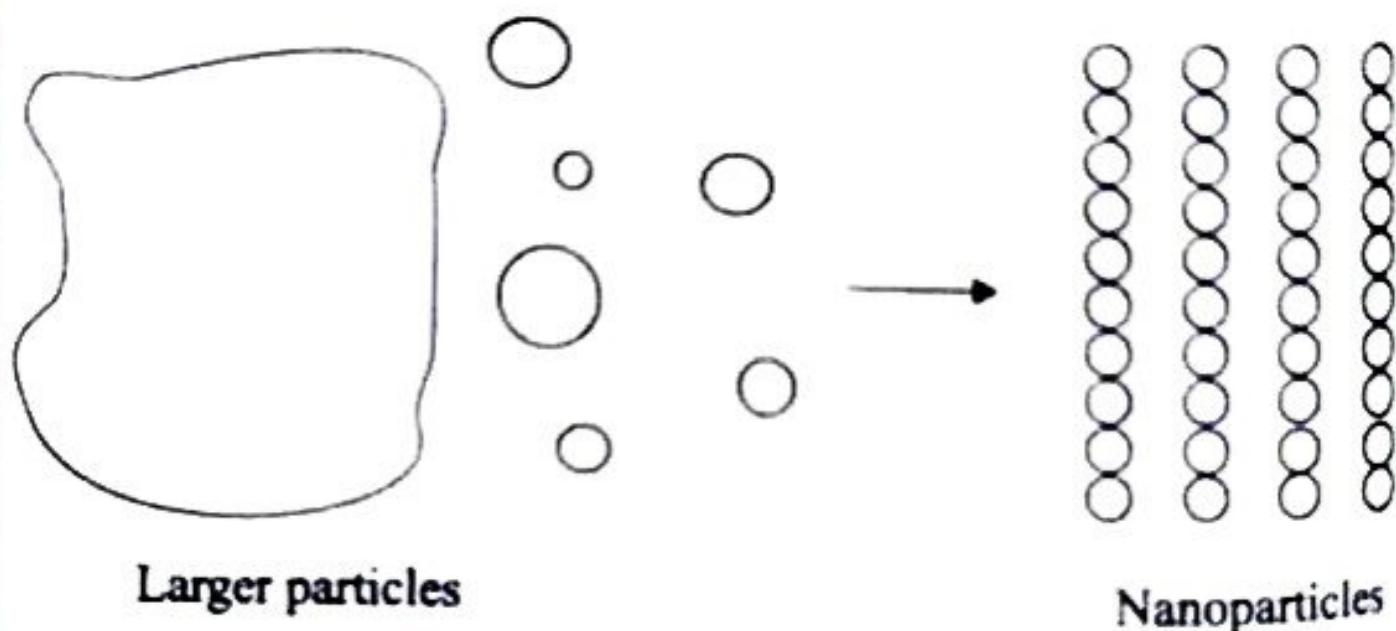


Fig. 2.6 Top-down process

2.6.2 *Bottom-up process*

Bottom-up process involves building-up of materials from the bottom by atom by atoms, molecule by molecule (or) cluster to the nanomaterials.

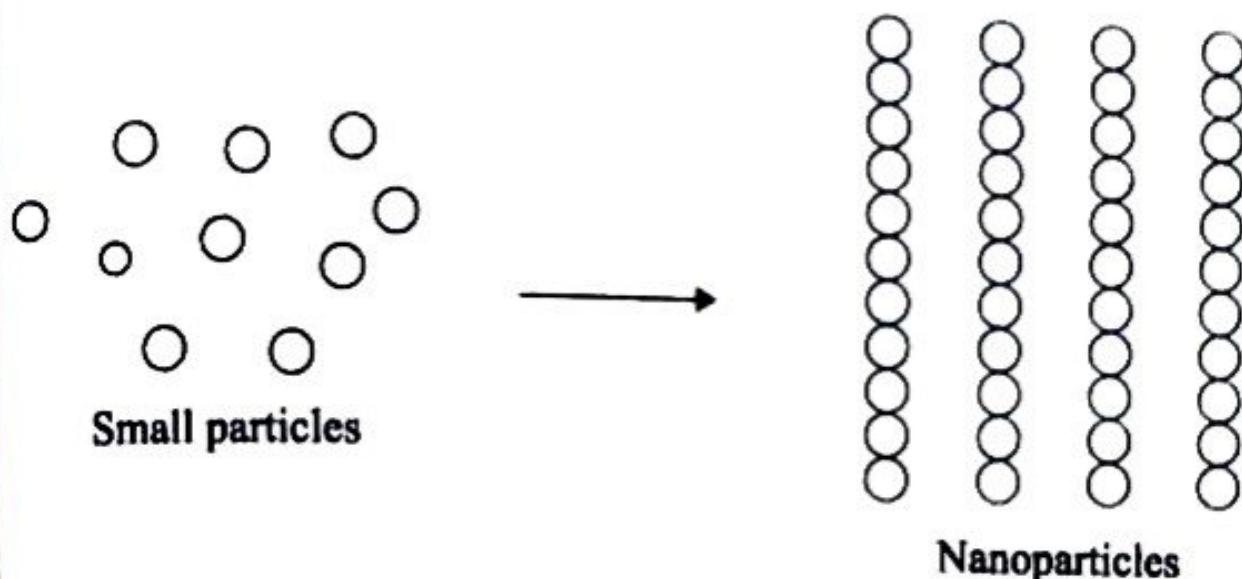


Fig. 2.7 Bottom up process

2.6.3 *Important Preparations*

1. Sol-Gel process

Definition

Sol-gel process is the conversion of colloidal solution (sol) to “gel” like structure.

Principles of Sol-gel process

It is a method of producing solid materials from small molecules. In this method, the precursor is dissolved in water (or) alcohol to form “sol” and then converted to gel like structure by heating.

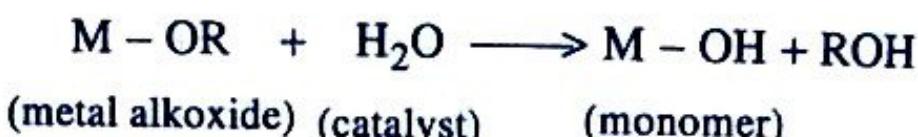
Sol-gel process is a wet chemical technique. Generally, it is used to produce metal oxides.

Preparation: Preparation of metal oxide sol-gel

Preparation of sol-gel involves the following steps.

Step I: Preparation of monomers (precursor)

Metal alkoxide is dissolved in alcohol and then diluted with water. Metal alkoxide gets hydrolysed to form reactive monomers.



Step II: Formation of “Sol”

Condensation of these monomers to form colloid like solution (sol).



Step III: Formation of “Gel”

“Sol” gets converted to “gel” via polycondensation.

Step IV: Aging process

It is the process, where condensation occurs with the gel network that can cause expulsion of solvent.

Step V: Drying

It removes liquid phases and M-OH groups

Step VI: Tempering

It is the process of densification of the gel to remove the pores of the gel network.

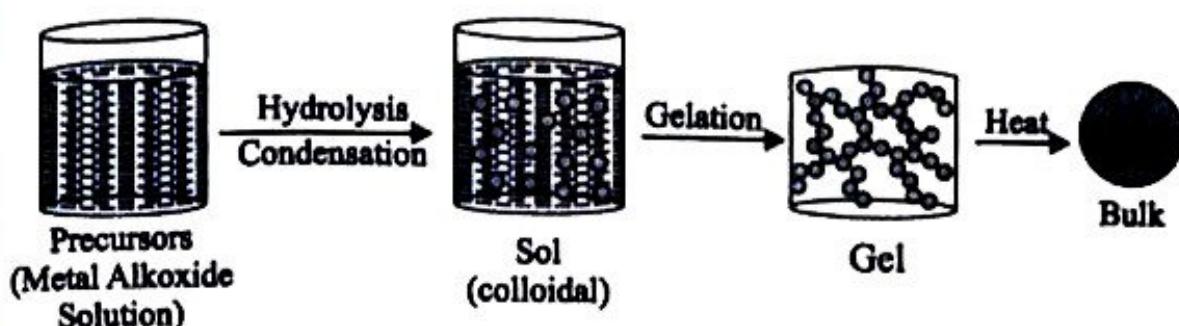


Fig. 2.8 Sol-Gel Process

2. Solvothermal Synthesis

Solvothermal synthesis involves the use of solvent under high temperature (between 100°C to 1000°C) and moderate to high pressure (1 atm to 10,000 atm) that facilitate the interaction of precursors during synthesis.

Method

A solvent like ethanol, methanol, 2-propanol is mixed with certain metal precursors and the solution mixture is placed in an autoclave kept at relatively high temperature and pressure in an oven to carry out the crystal growth. The pressure generated in the vessel, due to the solvent vapour, elevates the boiling point of the solvent.

Example Solvothermal synthesis of zinc oxide

Solvothermal synthesis of zinc oxide

Zinc acetate dihydrate is dissolved in 2-propanol at 50°C . Subsequently, the solution is cooled to 0°C and NaOH is added to precipitate ZnO. The solution is then heated to 65°C to allow ZnO growth for some period of time. Then a capping agent (1-dodecanethiol) is

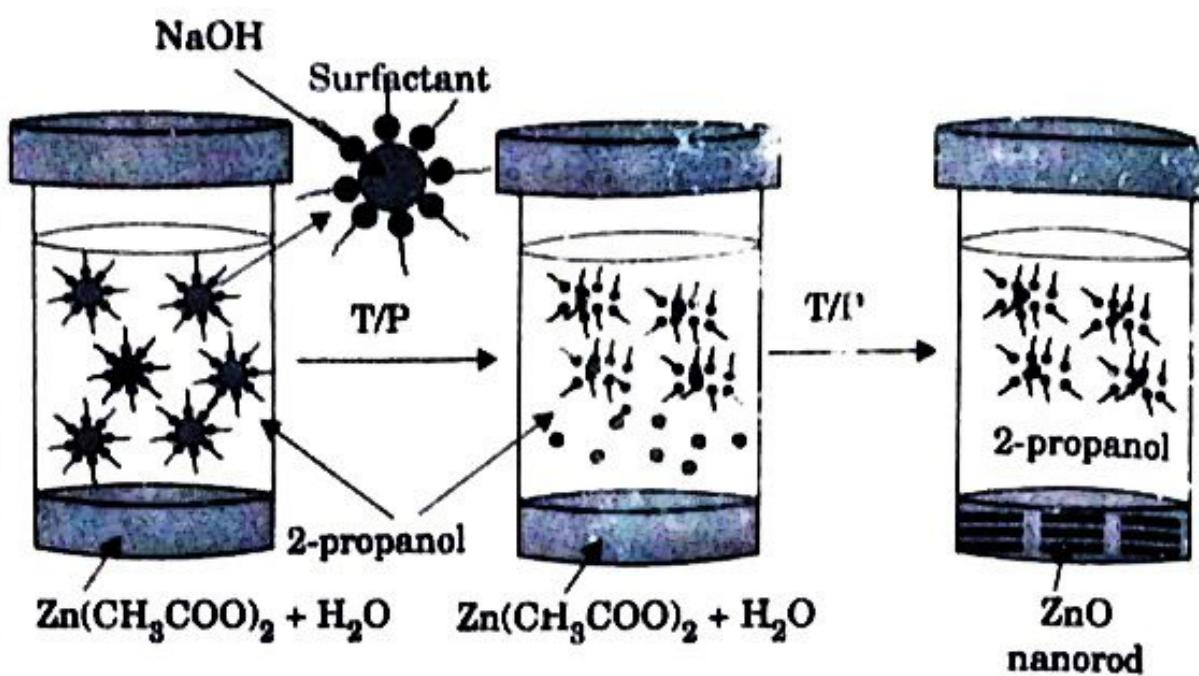


Fig. 2.9 Solvothermal synthesis

injected into the suspension to arrest the growth. The rod shaped ZnO nano-crystal is obtained.

3. Laser ablation

In laser ablation technique, high-power laser pulse is used to evaporate the material from the target. The stoichiometry of the material is protected in the interaction.

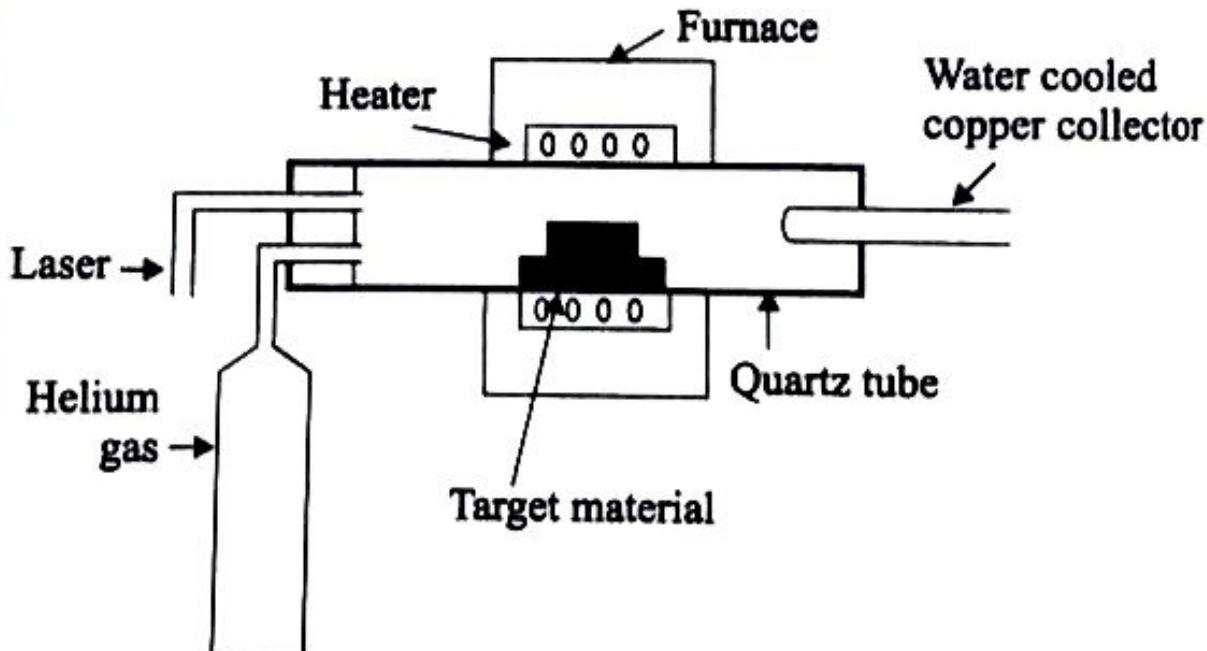


Fig. 2.10 Laser ablation chamber

The total mass ablated from the target per laser pulse is referred to as the **ablation rate**.

This method involves vapourisation of target material containing small amount of catalyst (nickel (or) cobalt) by passing an intense pulsed laser beam at a higher temperature to about 120°C in a quartz tube reactor. Simultaneously, an inert gas such as argon, helium is allowed to pass into the reactor to sweep the evaporated particles from the furnace to the colder collector.

Uses

1. Nanotubes having a diameter of 10 to 20 nm and 100 μm can be produced by this method.
2. Ceramic particles and coating can be produced.
3. Other materials like silicon, carbon can also be converted into nanoparticles by this method.

Advantages of laser ablation.

1. It is very easy to operate.
 2. The amount of heat required is less.
 3. It is eco-friendly method because no solvent is used.
 4. The product, obtained by this method, is stable.
 5. This process is economical.
- 4. Chemical Vapour Deposition (CVD)**

This process involves conversion of gaseous molecules into solid nanomaterials in the form of tubes, wires (or) thin films. First the solid materials are

converted into gaseous molecules and then deposited as nanomaterials.

Example *CNT preparation.*

The CVD reactor consists of a higher temperature vacuum furnace maintained at inert atmosphere. The solid substrate containing catalyst like nickel, cobalt, iron supported on a substrate material like, silica, quarts is kept inside the furnace. The hydrocarbons such as ethylene, acetylene and nitrogen cylinders are connected to the furnace. Carbon atoms, produced by the decomposition at 1000°C , condense on the cooler surface of the catalyst.

As this process is continuous, CNT is produced continuously.

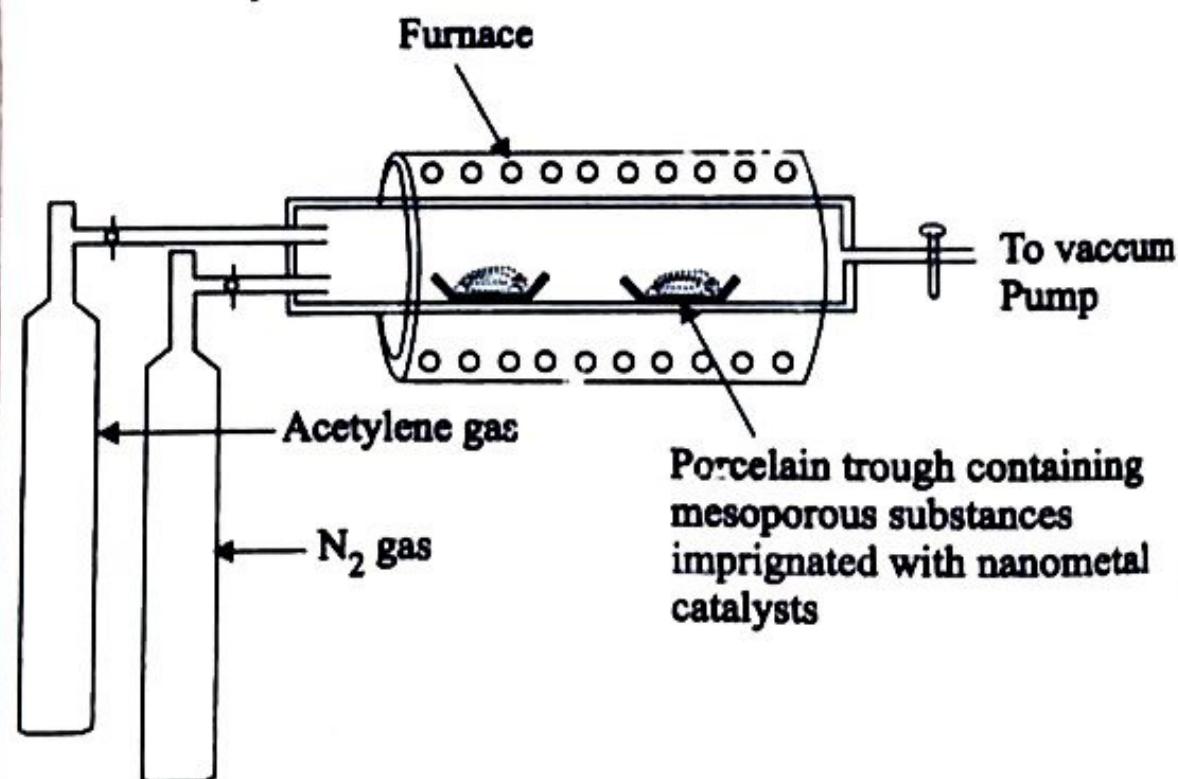
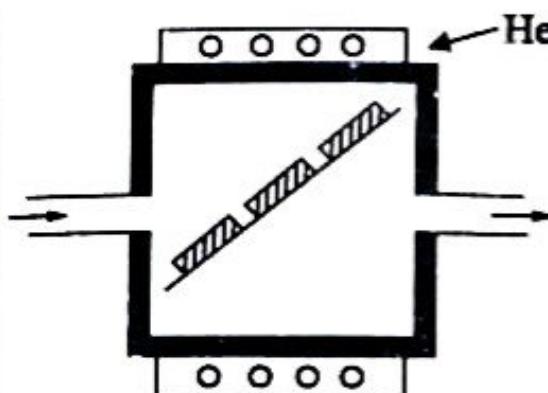


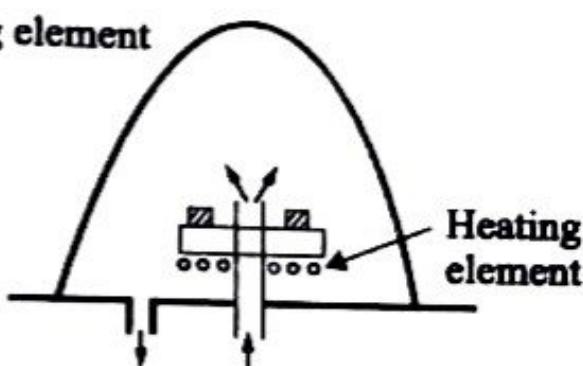
Fig. 2.11. Chemical vapour deposition

Types of CVD Reactor

Generally the CVD reactors are of two types



(a) Hot-wall CVD



(b) Cold wall CVD

Fig. 2.12 Types of CVD Reactors

1. Hot-wall CVD

Hot wall CVD reactors are usually tubular in form. Heating is done by surrounding the reactor with resistance elements.

2. Cold-wall CVD

In cold-wall CVD reactors, substrates are directly heated inductively while chamber walls are air (or) water cooled.

Advantages of CVD

1. Nanomaterials, produced by this method, are highly pure.
2. It is economical.
3. Nanomaterials, produced by this method, are defect free.
4. As it is simple experiment, mass production in industry can be done without major difficulties.

5. Electro-deposition (or) Electrochemical deposition

Electro-deposition is an electrochemical method in which ions from the solution are deposited at the surface of cathode. Template assisted electro-deposition is an important technique for synthesizing metallic nanomaterials with controlled shape and size. Array of nano-structured materials with specific arrangements can be prepared by this method using an active template as a cathode.

Process of electro-deposition

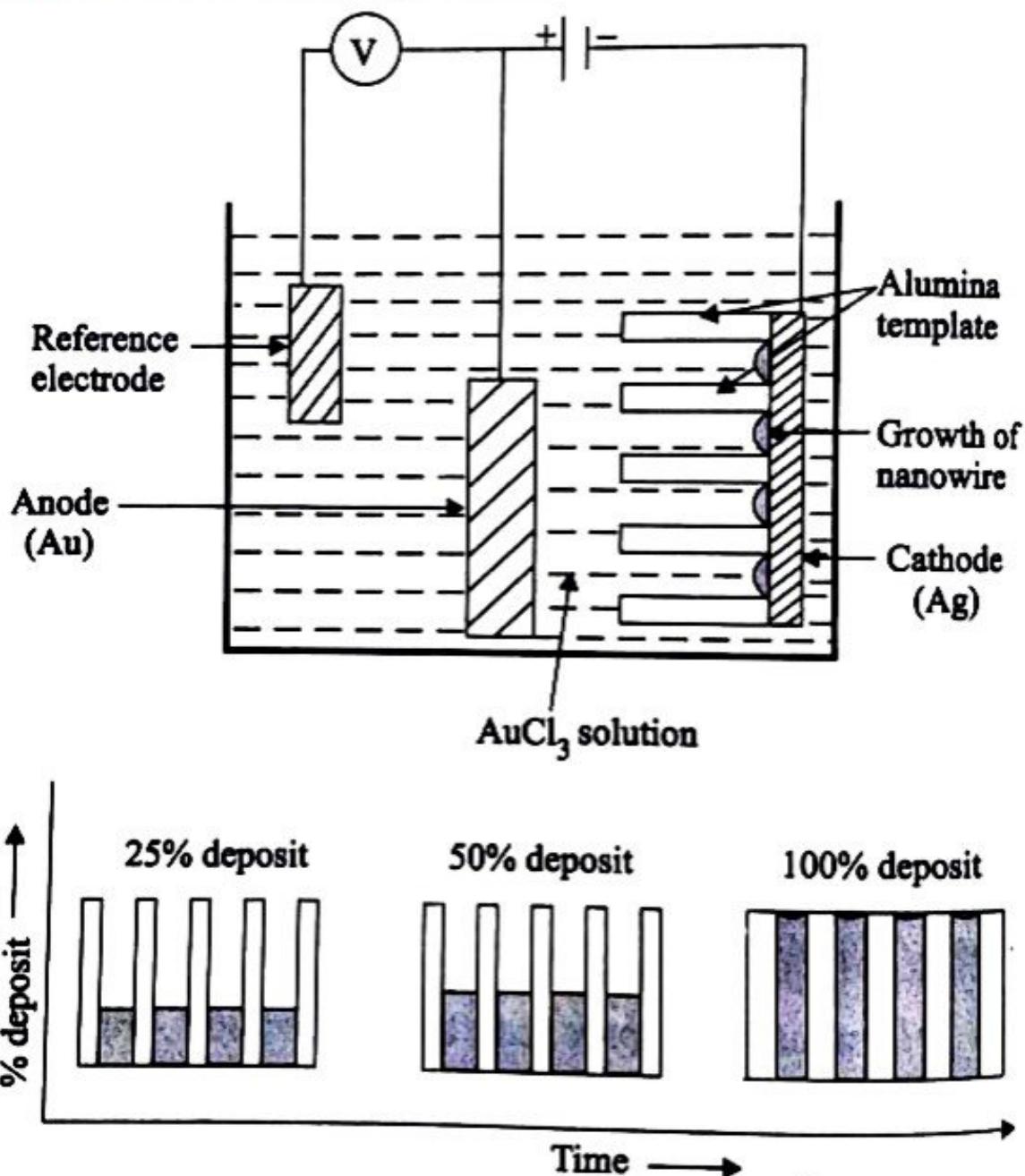


Fig. 2.13 Electrodeposition method

The cell consists of a reference electrode, specially designed cathode and anode. All these electrodes are connected with the battery through an voltmeter and dipped in an electrolytic solution of a soluble metal as shown in figure. When the current is passed through the electrodes of template, the metal ions from the solution enter into the pores and gets reduced at the cathode, resulting in the growth of nanowire inside the pores of the template.

Example *Electrodeposition of Gold on Silver*

Nanostructured gold can be prepared by the electrodeposition technique using gold sheets as an anode and silver plate as a cathode. An array of alumina template is kept over the cathode as shown in the figure 2.13 and AuCl_3 is used as an electrolyte.

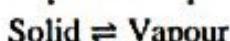
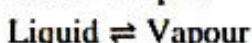
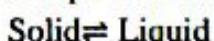
When the current of required strength is applied through the electrodes, Au^+ ions diffuse into the pores of alumina templates and gets reduced at the cathode resulting in the growth of nanowires (or) nanorods inside the pores of the alumina templates.

Advantages of Electro-deposition

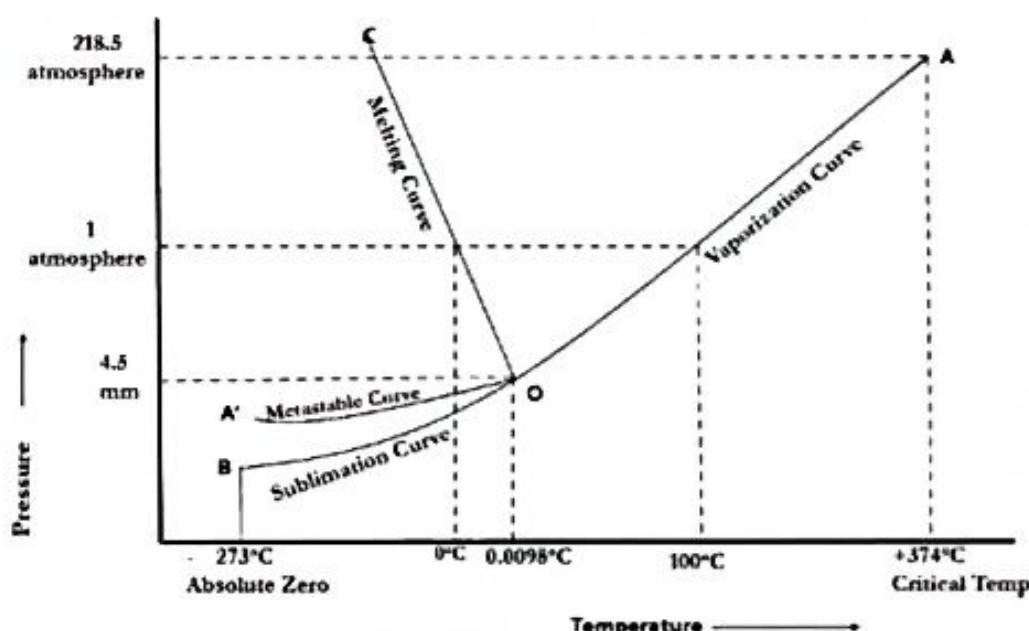
1. This method is relatively cheap and fast.
2. Complex shaped objects can be coated.
3. The film (or) wire obtained is uniform.
4. Metal nanowires including Ni, Co, Cu and Au can be fabricated by this method.

L DRAW A NEAT ONE COMPONENT WITH SYSTEM AND EXPLAIN ONE COMPONENT SYSTEM.

Water exists in three phases namely solid, liquid and vapor. Hence, there can be 3 forms in equilibria.



Each of the above equilibrium involves two phases. The phase diagram for the water systems is

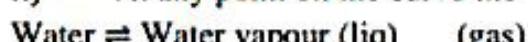


1. Curve OA : [Vapourisation curve]

i) The curve OA is called Vapourisation curve

The equilibrium exist between water and vapour.

ii) At any point on the curve the following equilibrium will exist



$$P=2; C=1$$

$$= C \cdot P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

a) The degree of freedom is one [univariant]

b) The equilibrium (line OA which extend upto the critical temperature (373°C).

c) Beyond critical temperature the equilibrium will disappear only vapor exist.

2. Curve OB : [Sublimation curve]

The curve OB is called Sublimation curve of ice, it represents the equilibrium between solid (ice) and vapour



a) The degree of freedom is one [univariant]

b) The equilibrium (line OB) will extend upto the absolute zero (-273°C).

c) Where no vapour can be present and only ice will exist.

$$P=2; C=1$$

$$F = C \cdot P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

3. Curve OC [Melting point curve] :

The curve OC is Melting point curve.

It represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

Ice \rightleftharpoons water

- a) The degree of freedom is one [univariant]
- b) The curve Oc is slightly inclined towards y-axis (pressure). This, Shows that melting point of ice decreases with increase of pressure.

$$P=2 ; C=1$$

$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

4. Point 'Q' (Triple Point)

The three curves OA , OB, OC meet at point 'O', where three phases namely solid, liquid and vapour are simultaneously at equilibrium.

Ice \rightleftharpoons Water \rightleftharpoons Vapour

- a) The degree of freedom is zero [non varient]
- b) Temperature = 0.0075°C
- c) Pressure = 4.58 mm at the point O.

$$P=2; C=1.$$

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

5. Curve OB' (Metastable equilibrium)

The curve OB' is vapour pressure curve of the super-cool or Metastable equilibrium

Where the following equilibrium will exist

super – cooled water \rightleftharpoons Vapour

- a) The degree of freedom is one [univariant]
- b) water cooled below 0°C without formation of ice that water is called super cooled water
- c) Super cooled water is unstable and can be converted to solid by seeding.

6. Areas (AOC , BOC , AOB)

AOC represents water ;

BOC represents Solid Ice;

AOC represents Vapour respectively.

$$P=2; C=1.$$

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

- a) Only one phase exist at each area,
- b) So the degree of freedom is 2 . [Bivalent].

IV . DRAW THE PHASE - DIAGRAM OF LEAD - SILVER SYSTEM TWO COMPONENT SYSTEM AND EXPLAIN BRIEFLY WRITE ABOUT PATTISON'S PROCESS :

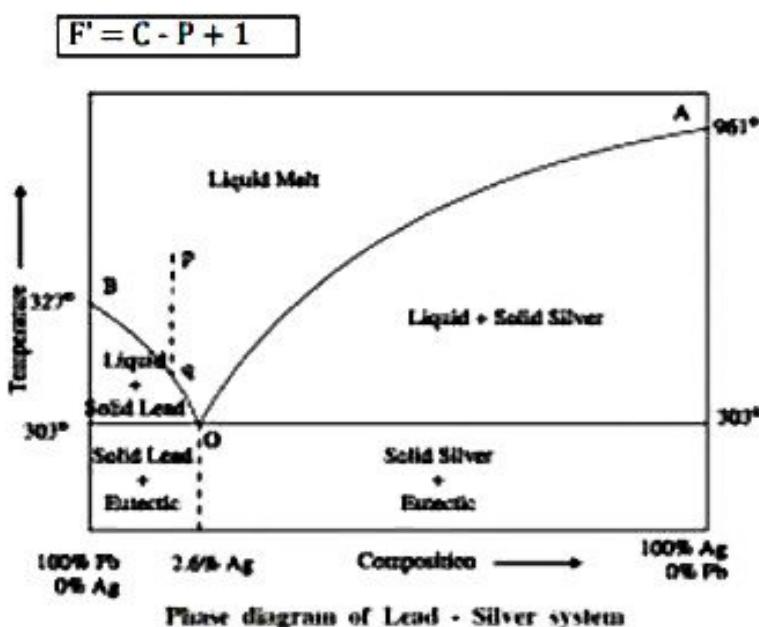
LEAD SILVER SYSTEM (Pb -Ag alloy):

This system has two components and four phases.

The phases are

- (i) Solid silver
- (ii) Solid lead
- iii) Solution of molten Ag & Pb and
- (iv) vapour.

The boiling points of Ag & Pb being considerably high, the vapour phase is practically absent. Thus Pb/Ag is a condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need only two variables, namely temperature (T) and composition (C).



1. Curve AO [Freezing Point curve of silver]

- A'' represents the melting point of pure Ag (961°C).
- The curve AC is the freezing point curve of Ag.
- Addition of Pb lowers the melting point of Ag along the curve AC.
- Along AC, solid Ag and liquid melt (solution of Ag & Pb) are in equilibrium.
- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant along the curve AC.
- **Solid Ag \rightleftharpoons Melt**

(S) (I)

The degree of freedom is univariant [i.e. one]

2. Curve BO [Freezing Point curve of lead]

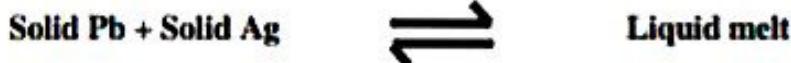
- B'' represents the melting point of pure lead ($\gamma\beta70^{\circ}\text{C}$).
- The curve BC is the freezing point curve of Pb.
- Addition of Ag lowers the melting point of Pb along the curve BC.
- Along BC, the solid Pb and liquid melt (solution of Ag & Pb) are in equilibrium.
- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant along the curve BC.
- **Solid Pb \rightleftharpoons Melt**
- The degree of freedom is univariant [i.e. one]

3. Eutectic Point „C”:

- The curve AC and BC intersect at „C” which is called eutectic point.

- Below the point „C” both Pb & Ag exist in the solid state.

- At this point three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.



- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 3 + 1 = 0$. Hence the system is nonvariant at point „C”.

- Eutectic point is the lowest possible temperature (303°C) in the system that corresponds to fixed composition (97.4% Pb & 2.6 % Ag), below which a liquid phase cannot exist and above which the solid phases disappear.

- The temperature and composition corresponding to the eutectic point „C” are called eutectic Temperature and eutectic composition.

- A liquid mixture of two components – Ag & Pb, which has the lowest freezing point compared to all other liquid mixtures, is called eutectic mixture.

4. Areas:

- The area above ACB represents a single phase (solution of molten Pb & Ag).

- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 1 + 1 = 2$. The system is bivariant.

- Area below AC represent the phases solid Ag + liquid melt, area below BC represents the phases solid Pb + liquid melt and area below .

DCE'' represents solid Pb + solid Ag.

All the three areas have two phases and hence the system is univariant.

$$(F'' = C - P + 1 = 2 - 2 + 1 = 1)$$

12. Discuss the Polymer matrix composites (PMC) or Fibre reinforced plastics (FRP)

About 90% (by weight) of composites used in the industries are fibre reinforced plastics. When polymers are used as structural composites even complex structural shapes can be easily fabricated and

manufactured.

Preparation:

Fibre reinforced plastics are produced by suitably bonding a fibre material with a resin matrix and curing them under pressure and heat. The main reinforcing agents used in FRP composites are glass, boron, carbon, aramid, alumina etc. The reinforcement material can be in the form of short fibres, continuous filaments or woven fabrics.

The resin matrixes commonly used in FRP are polyesters or epoxy, phenolic, silicone and polyamide polymer resins.

Properties:

- (i) They possess superior properties like higher yield strength, fracture strength and fatigue life.
- (ii) They possess good mechanical properties as the fibre prevents slip and crack propagation.
- (iii) They possess high corrosion and heat resistance properties.

The properties of FRP depend mainly on the resin matrix used.

SINo.	Resin matrix	Specific properties
1.	Polyester resin	Provides very good strength and mechanical properties.
2.	Epoxy resin	Imparts good mechanical properties.
3.	Silicone resin	Imparts excellent thermal and electrical properties.
4.	Phenolic resin	Withstands high temperature
5.	Polyamide polymer resin	Shows repeatability and repairability.

The types of FRP composites available are tabulated below:

TYPES OF FRP COMPOSITES

SINo.	Reinforcing agent	Properties	Uses
1.	Glass	<ul style="list-style-type: none">(i) lower densities, dielectric constants(ii) higher tensile strength and impact resistance(iii) excellent corrosion and chemical resistance, non-flammability	Automobile parts, storage tanks, plastic pipes, floorings and in transportation industries
2.	Boron	<ul style="list-style-type: none">(i) excellent stiffness and compressive strength	Horizontal and vertical tails in aero plane, stiffening spares, nibs etc.
3.	Carbon	<ul style="list-style-type: none">(i) lighter density(ii) high resistance to	Structural components of air craft and

		<p>corrosion</p> <p>(iii) retention of properties even at high temperature</p>	<p>helicopters;</p> <p>recreational equipment,</p> <p>sports material,</p> <p>antenna disc,</p> <p>solar panel etc.</p>
4.	Aramid	<p>(i) ductile</p> <p>(ii) respond non-catastrophically to compressive stresses (since they can absorb energy)</p>	<p>Structural components in air craft,</p> <p>helicopter parts.</p>
5.	Alumina	<p>(i) good abrasion resistance</p> <p>(ii) good creep resistance</p> <p>(iii) good dimensional stability</p>	<p>Components of engine parts in automobile industry;</p> <p>components of turbine engine.</p>

METAL MATRIX COMPOSITES

- A metal matrix composite (MMC) is composite material with at least two constituent parts, one being a metal.
 - The other material may be a different metal or another material, such as a ceramic or organic compound.
 - When at least three materials are present, it is called a hybrid composite
-

MMC- REINFORCEMENT

- Composition: MMCs are made by dispersing a reinforcing material into a metal matrix. The reinforcement surface can be coated to prevent a chemical reaction with the matrix.
 - For example, carbon fibers are commonly used in aluminum matrix to synthesize composites
 - **Reinforcement:** The reinforcement material is embedded into the matrix.
 - It is used to change physical properties such as wear resistance, friction coefficient, or thermal conductivity. The reinforcement can be either continuous, • or discontinuous.
-

MMC- MATRIX

- Matrix: The matrix is the monolithic material into which the reinforcement is embedded, and is completely continuous.
- This means that there is a path through the matrix to any point in the material, unlike two materials sandwiched together.
- The matrix is usually a lighter metal such as aluminum, magnesium, or titanium, and provides a compliant support for the reinforcement.

MMC- PROPERTIES

(i)They exhibit extremely good thermal stability, high strength, good stiffness and low specific weight.

Specific weight The specific weight, also known as the unit weight (symbol γ , the Greek letter gamma) is a volume-specific quantity defined as the weight per unit volume of a material.

(ii)They show fracture toughness, ductility and enhanced performance at high temperature

(iii)They withstand corrosive environment even at high temperature.

• •

MMC's USES

(i)They are used in engine parts (here Al, Ti and Ni alloys are used as one of the matrix materials and Al₂O₃, B, C and SiC are used as one of the reinforcements)

(ii)They are used in engine blades, combustion chambers etc.

(iii)They are used in automotive industry (Al, Mg – MMCs).

(iv)They are used in biomedical and sports industry.

• •

MMC

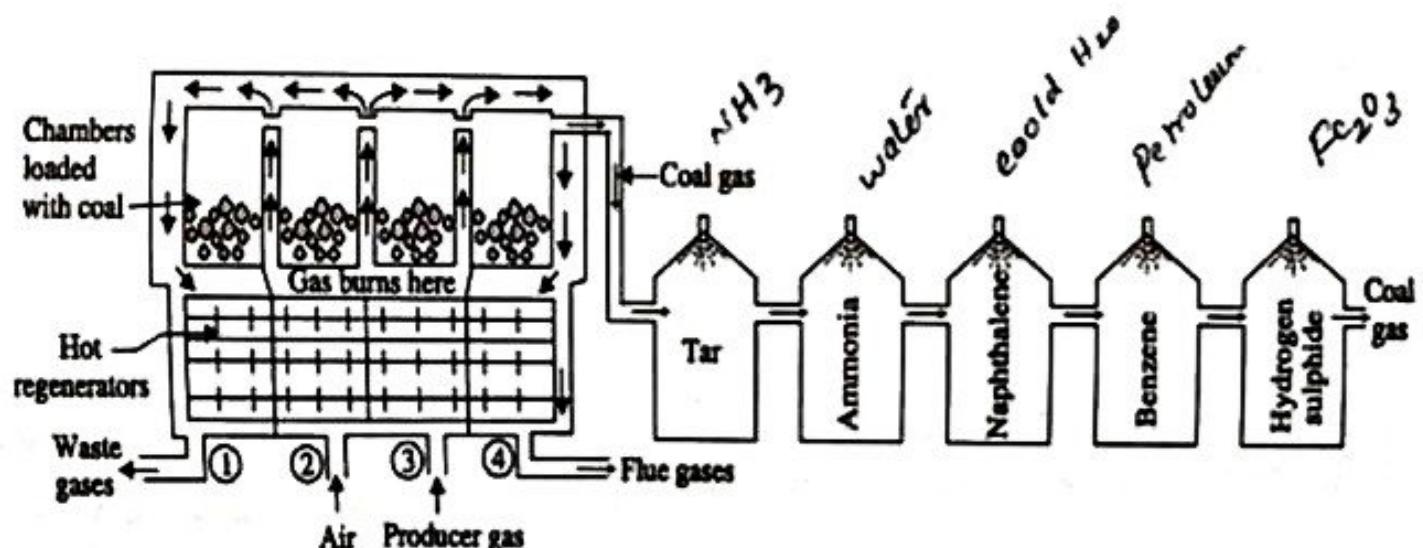
- Advantages
 - Higher temperature capability
 - Fire resistance
 - Higher transverse stiffness and strength
 - No moisture absorption
 - Higher electrical and thermal conductivities
 - Better radiation resistance
- Disadvantages
 - Higher cost of some material systems .
 - Relatively immature technology .
 - Complex fabrication methods for fiber-reinforced systems (except for casting).

3. DESCRIBE THE OTTO HOFFMAN PROCESS FOR THE MANUFACTURE OF METALLURGICAL COKE.

There are so many types of ovens used for the manufacture of metallurgical coke. But the important one is Otto-Hoffman's by product oven.

Objectives & Advantages

- Increase the thermal efficiency of the carbonization process and
- Recover the valuable by products like Tar, Ammonia, Naphthalene, Benzene, H_2S and coal gas



Time taken for complete combustion=12-20 hours

Yield of coke=70

DESCRIPTION OF OTTO HOFFMAN'S BY PRODUCT OVEN:

The oven consists of a number of silica chambers each chamber is about 10 -12m long, 3-4m in height and 0.4-0.45m wide. Each chamber is provided with a charging hole, gas off take valve and iron door for discharging coke.

Working:

1. Coal is introduced into the silica chamber and the chambers are closed. The chambers are heated to 1200°C by burning the preheated air and the producer gas mixture in the interspaces between the chambers.
2. The air and gas are preheated by sending them through 2nd and 3rd regenerators. Hot flue gases produced during carbonisation are allowed to pass through 1st and 4th hot regenerators until the temperature has been raised to 1000°C. While the 1st and 4th regenerators are heated by hot flue gases, 2nd and 3rd regenerators are used for heating the incoming air and gas mixture.
3. For economical heating, the direction of inlet gases and flue gases are changed frequently. The above system of recycling the flue gases to produce heat energy is known as the regenerative system of heat economy. When the process is complete the coke is removed and quenched with water.
4. Time taken for complete carbonisation is about 12 -20 hours. The yield of coke is about 70%.The valuable by products like coal gas, tar, ammonia, H₂S and benzol, etc. can be recovered from flue gas.

Recovery of by- products:

BY PRODUCTS	CHEMICALS USED FOR RECOVERY
Tar	Tar is recovered by spraying liquid ammonia
Ammonia	Ammonia is recovered by spraying water and forming NH ₄ OH
Naphthalene	Naphthalene is recovered by spraying cool water
Benzene	Benzene is recovered by spraying petroleum
Hydrogen sulphide.	H ₂ S is recovered by passing through moist Fe ₂ O ₃ .
Gaseous fuel	The final gas left out is called coal gas which is used as a gaseous fuel.

ADVANTAGES:

- valuable by-products are recovered
- carbonization time is less
- Heating is done extremely by producer gas.

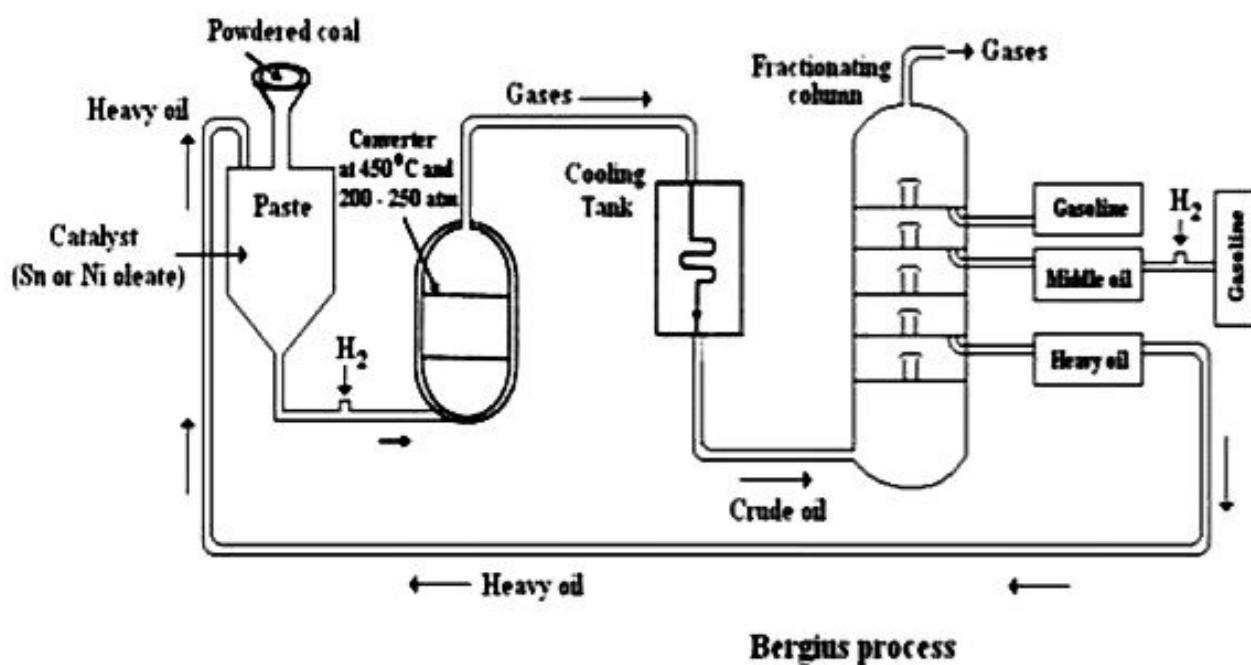
5. WHAT IS SYNTHETIC PETROL? HOW IS IT MANUFACTURED BY BERGIUS PROCESS?

The gasoline, obtained from the fractional distillation of crude petroleum oil, is called straight run petrol. As the use of gasoline is increased, the amount of straight run gasoline is not enough to meet the requirement of the present community. Hence, we are in need of finding out a method of Synthesizing petrol

Hydrogenation of coal (or) Synthetic petrol

Coal contains about 4.5% hydrogen compared to about 18% in petroleum. So coal is a Hydrogen deficient compound. If coal is heated with hydrogen to high temperature under high pressure, it is converted to gasoline. The preparation of liquid fuels from solid coal is called **Hydrogenation of coal (or) synthetic petrol**.

Bergius process:



Bergius process (or) direct method

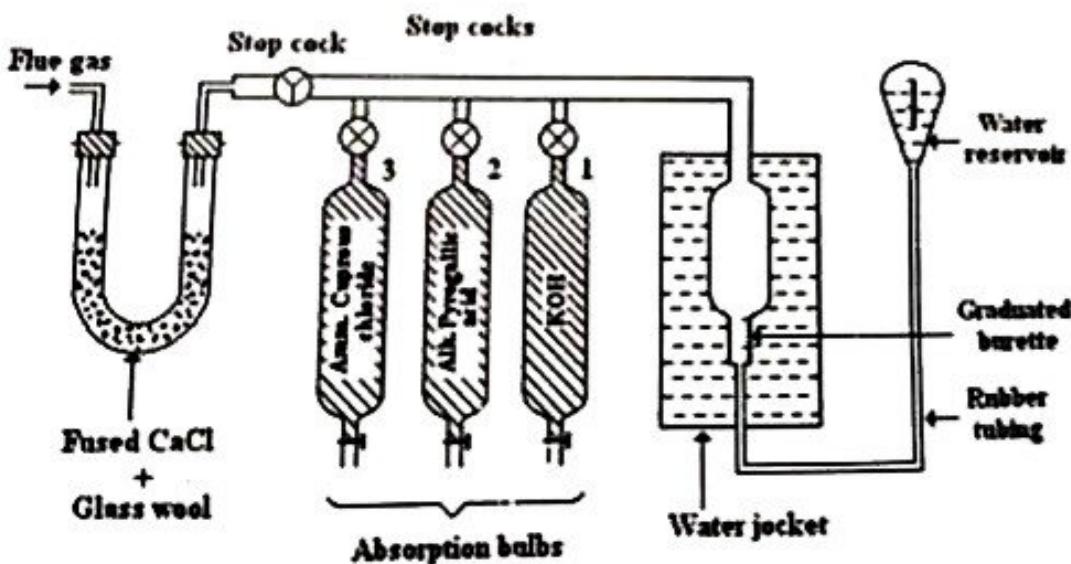
1. In this process, the finely powdered coal is made into a paste with heavy oil and a catalyst powder (tin or nickel oleate) is mixed with it.
2. The paste is pumped along with hydrogen gas into the converter, where the paste is heated to 400 – 450°C under a pressure of 200 – 250 atm.
3. During this process hydrogen combines with coal to form saturated higher hydrocarbons, which undergo further decomposition at higher temperature to yield mixture of lower hydrocarbons.
4. The mixture is led to a condenser, where the crude oil is obtained.
5. The crude oil is then fractionated to yield (i) Gasoline (ii) Middle oil (iii) Heavy oil.
6. The middle oil is further hydrogenated in vapour phase to yield more gasoline. The heavy oil is recycled for making paste with fresh coal dust.
7. The yield of gasoline is about 60% of the coal used.

11. WHAT IS FLUE GAS? EXPLAIN IN DETAIL

Flue gas:

The mixture of gases (i.e. CO_2 , O_2 and CO) coming out from the combustion chamber is called 'flue gases'.

The flue gas is analyzed using orsat apparatus



CONSTRUCTION OF ORSAT APPARATUS:

- Orsat's apparatus consists of a horizontal tube.
- One end of horizontal tube is connected to a U- tube containing fused CaCl_2 through a 3-way stopcock.
- The other end of the horizontal tube is connected to a burette which is surrounded by a water jacket to maintain constant temperature.
- The lower end of the burette is connected to a water reservoir by means of a rubber tube for level maintenance
- The horizontal tub is connected to three different adsorption bulbs each one having solution of KOH, alkaline pyrogallal and ammoniacal cuprous chloride.

ABSORBING SOLUTIONS:

- ✓ KOH
- ✓ ALKALINE PYROGALLAL
- ✓ AMMONIACAL CUPROUS CHLORIDE.

ORDER OF ABSORBANCE:

- ✓ 1st - CO_2 (with KOH)
- ✓ 2nd - O_2 (with alkaline pyrogallal)
- ✓ 3rd - CO (with ammoniacal cuprous chloride)

EXPERIMENT:

I. Absorbance of CO₂:

- The stopper of the adsorption bulb-1, containing KOH solution is opened.
- All the flue gas in the burette is passed into bulb-1 by raising the water level in the burette.
- As the gas enters into the bulb -1, CO₂ present is absorbed. The gas is now withdrawn into the burette. This process is repeated several times to ensure complete adsorption of CO₂.
- The decrease in volume of flue gas in the burette indicates the volume of CO₂ present in the 100cc of the flue gas.

II.ABSORBANCE OF O₂:

- The stopcock of bulb-1 is closed and stopcock of bulb-2 is opened
- The gas is now sent into absorption bulb-2, where O₂ in the flue gas is absorbed.
- The process of sending the gas into the bulb and then withdrawing into the burette is repeated till all O₂ in the flue gas is absorbed.
- The decrease in volume of the flue gas in the burette indicates the volume of O₂ presents in 100cc of the flue gas.

III.ABSORBANCE OF CO:

- The stopcock of bulb-2 is closed and stopcock of bulb-3 is opened.
- The gas is now sent absorption bulb-3, where CO in the flue gas is adsorbed
- The process of sending the gas into the bulb and then withdrawing into the burette is repeated till it is repeated till all CO in the flue gas is adsorbed.
- The decrease in volume of the flue gas in the burette indicates the volume of CO present in 100cc of the flue gas.

SIGNIFICANCE OF FLUE GAS ANALYSIS:

- ❖ Flue gas analysis gives an idea about the complete or incomplete combustion process.
- ❖ If the flue gases contain considerable amount CO, it indicates incomplete combustion and supply of O₂.
- ❖ If the flue gases contain considerable amount of O₂, it indicates complete combustion and excess supply of O₂.

12. WRIT DETAILED NOTES ON CARBON EMISSION AND CARBON FOOTPRINT.

CARBON EMISSION

Definition:

It is defined as the release of carbon into the atmosphere. Since greenhouse gas emissions are often calculated as carbon dioxide equivalents, they are often referred to as "carbon emissions".

Source:

Burning of fossil fuels like coal, oil and natural gas are the primary sources due to the following activates.

- (i) Transportation
- (ii) Electricity production
- (iii) Industry
- (iv) Agriculture
- (v) Land use and forestry
- (vi) Commercial and residential

Reduction of carbon emission

Carbon emission can be reduced by reducing greenhouse gas emission. It can be done by the following ways.

1. In industry, green house gases can be reduced by many ways.

- (i) Including energy efficiency
- (ii) Fuel switching
- (iii) Combined heat and power
- (iv) Use of renewable energy

2. Avoid of using HFC's in refrigeration, air conditioning and foam blowing.

3. In oil and gas production, the leakage of green house gases can be controlled by reducing pressure from pipelines.

CARBON FOOTPRINT:

Definition:

It is the total amount of green house gases (including CO₂ and CH₄) that generated (emitted) by our direct and indirect activities.

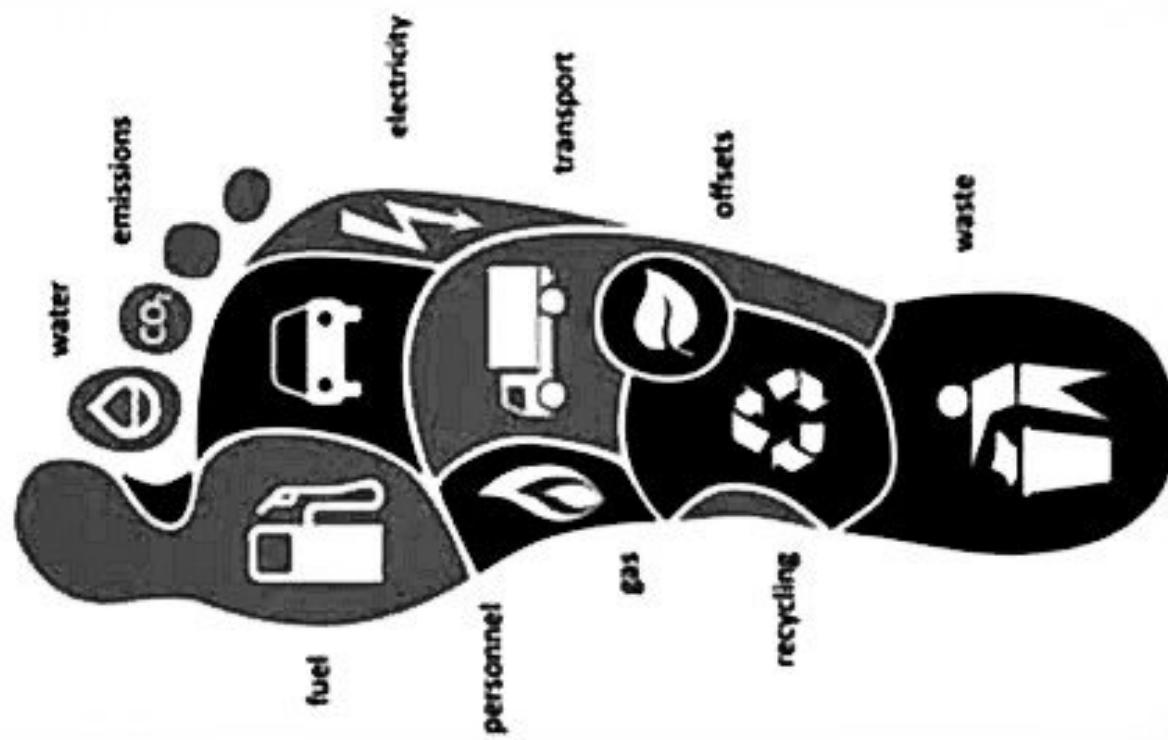
Individual carbon footprint:

It is the sum total of their direct and indirect carbon emissions over the course of a year.

i.e., Smaller your carbon footprint : better for the future

Bigger your carbon footprint: Have bigger negative impact in environment

The average carbon footprint for a person in united states is 16 tons. Globally, the average is closer to 4 tones. To avoid 2°C rise in global temperatures, the average global carbon footprint per year needs to drop under 2 tons by 2050.



2. What are lead accumulators? Explain the constructions and functioning of a lead accumulator.

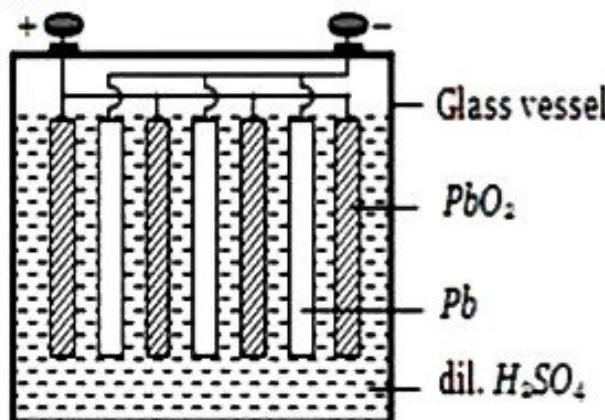
- Lead-acid batteries are secondary batteries. The cell **Construction** operates both as a voltaic cell and as an electrolyte cell. They are also called Lead storage cell

Anode: Lead plates

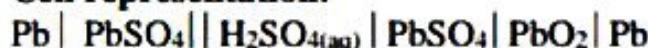
Cathode: PbO_2 plates

Electrolyte: dil. H_2SO_4 (38% by mass) having a density of 1.30 gm/mL

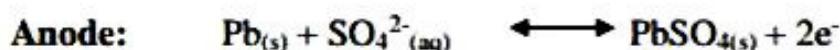
The Pb and PbO_2 plates are arranged alternately. Adjacent plates are separated by insulators like rubber or glass fiber. There will be 3 to 6 cells connected in series to get 6 to 12V.



Cell representation:



Working and Discharging



$PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is used up. The concentration of H_2SO_4 decreases and when its density falls below 1.2 gm/ML. So the battery requires recharging.

Recharging of Battery

The cell is recharged by passing electric current in the opposite direction. The electrode reaction gets reversed. As a result, Pb is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 increases.



Advantages

1. Produces very high current
2. Self discharging is low
3. Functions effectively at low temperature

Uses:

1. It is used to supply current in automobiles
2. It is used along with inverters
3. It is used in telephone, mines, laboratories, hospitals, power plants, etc.

6. Explain the construction and working process of Microbial fuel cells (MFCs)

Microbial fuel cell is a device that converts chemical energy to electrical energy by the action of micro-organisms under anaerobic conditions.

Bioelectricity is generated by the oxidation of organic waste and renewable biomass using bacteria.

Construction (or) Principle

- MFCs are type of electrochemical cells, constructed using either bioanode and (or) a biocathode.
- A membrane separates the compartments of the anode (where oxidation occurs) and the cathode (where reduction occurs).
- The electrons produced during oxidation are transferred directly to the cathode. The charge balance of the system is maintained by the ionic movement inside the cell.
- Organic electron donors, that is oxidized to produce CO_2 , protons and electrons, are used in most MFCs.
- The cathode reaction uses a variety of electron acceptors, mostly oxygen (O_2).

Components

A typical MFC consists of the following two compartments.

- (i) Anodic compartment
- (ii) Cathodic compartment

(i) Anodic compartment

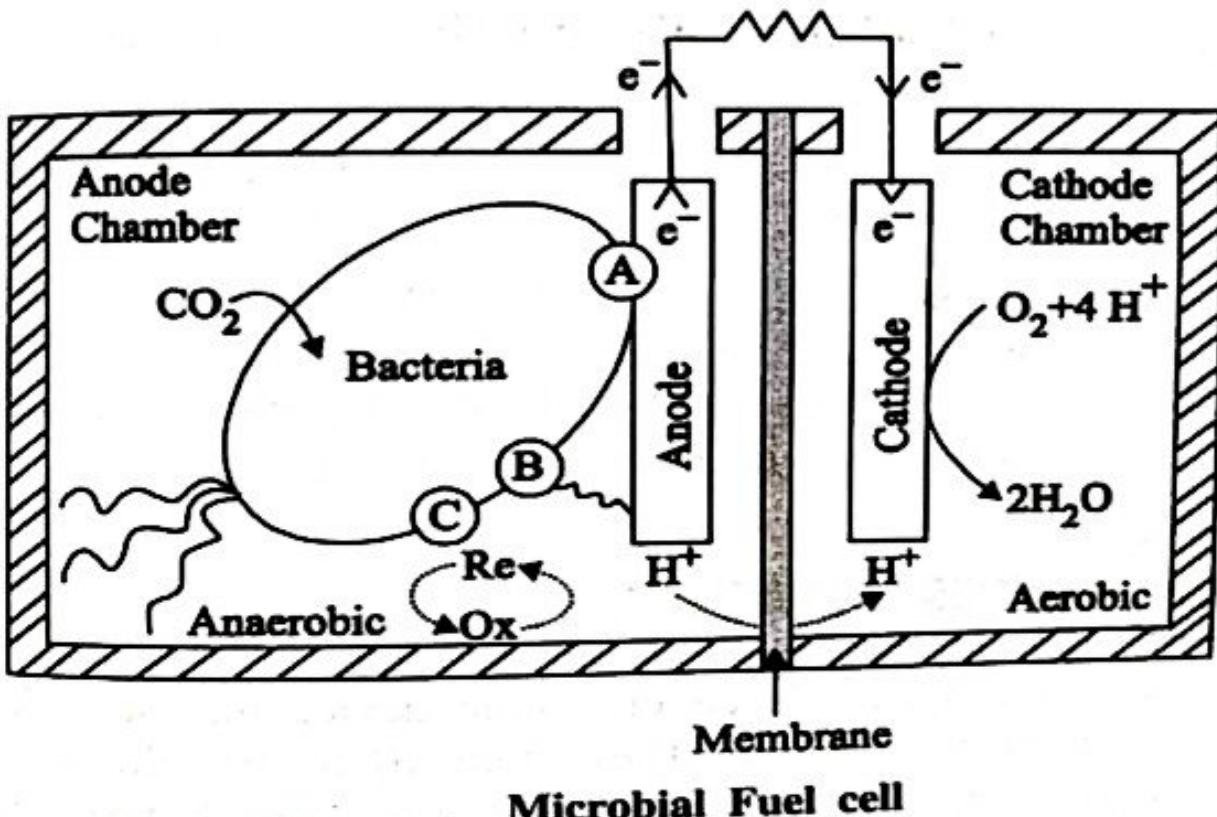
It consists of microbes suspended under anaerobic conditions in the anolyte.

(ii) Cathodic compartment

It consists of electron acceptor (oxygen)

Permeable membrane

Anionic and cationic compartments are separated by selectively permeable, cation-specific membrane.



Working

When both the electrodes are connected, anode oxidation occurs on organic waste (biomass) and electrons released from the process are transferred to the anode. The electrons, transferred to the anode, can be accomplished by the electron mediators.

From the anode these electrons are directed to the cathode across external circuit. For every electron, a proton is transported across the membrane to the cathode. Finally oxygen present at the cathode recombines with hydrogen and electron to produce water.

Applications

1. In waste water treatment, MFCs, generate less excess sludge as compared to the aerobic treatment process.
2. MFCs can be used in river and deep-water environments, where it is difficult to use batteries.
3. MFCs are used to convert carbon rich wastewater into methane gas.
4. MFCs are used as convenient biosensor for waste water streams.
5. MFCs are used in space, especially to operate remotely operated vehicles.
6. MFCs play an important role in the field of microbiology, soil chemistry and electrical engineering.
7. Many commercial soil based MFC kits are available for the purchase on the web and in toy stores.

5. Write a note on Photo conversion

Photo conversion involves conversion of light energy directly into electrical energy. Photovoltaic cell (or) Solar cell is used for photo conversion.

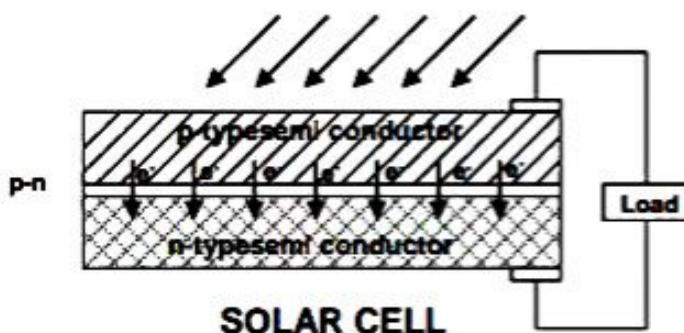
SOLAR CELL

Solar cells are also known as photovoltaic cells or simply PV cells.

Solar cells consist of an n-type semiconductor (such as Si doped with As) and a p-type semiconductor (such as Si doped with B). They are in close contact with each other.

When the solar rays fall on the top layer of p-type semi conductor, the electrons from the valence band are promoted to the conduction band by absorbing light energy and cross the p-n junction into n-type semiconductor.

A potential difference is created between the two layers. This potential difference causes flow of electrons (i.e. an electric current). When this p- and n- layers are connected to an external circuit, electrons flow from n-layer to p-layer externally, thereby generating current. As more and more solar rays fall on the surface of the outer layer, the potential difference increases, and hence the flow of current also increase



Applications of Solar Cell

- 1) Used in calculators, electronic watches, street lights, radios and TVs.
- 2) Used in boilers to produce hot water.
- 3) Used to drive vehicles.
- 4) Used as source of power in space crafts and satellites.
- 5) Used to produce H₂ by electrolysis of water. This hydrogen can be used in H₂-O₂ fuel cells.

- 6) Energy from solar cells can be stored by charging Ni-Cd batteries or Pb-acid batteries.
- 7) Solar cells are useful in use in remote areas.

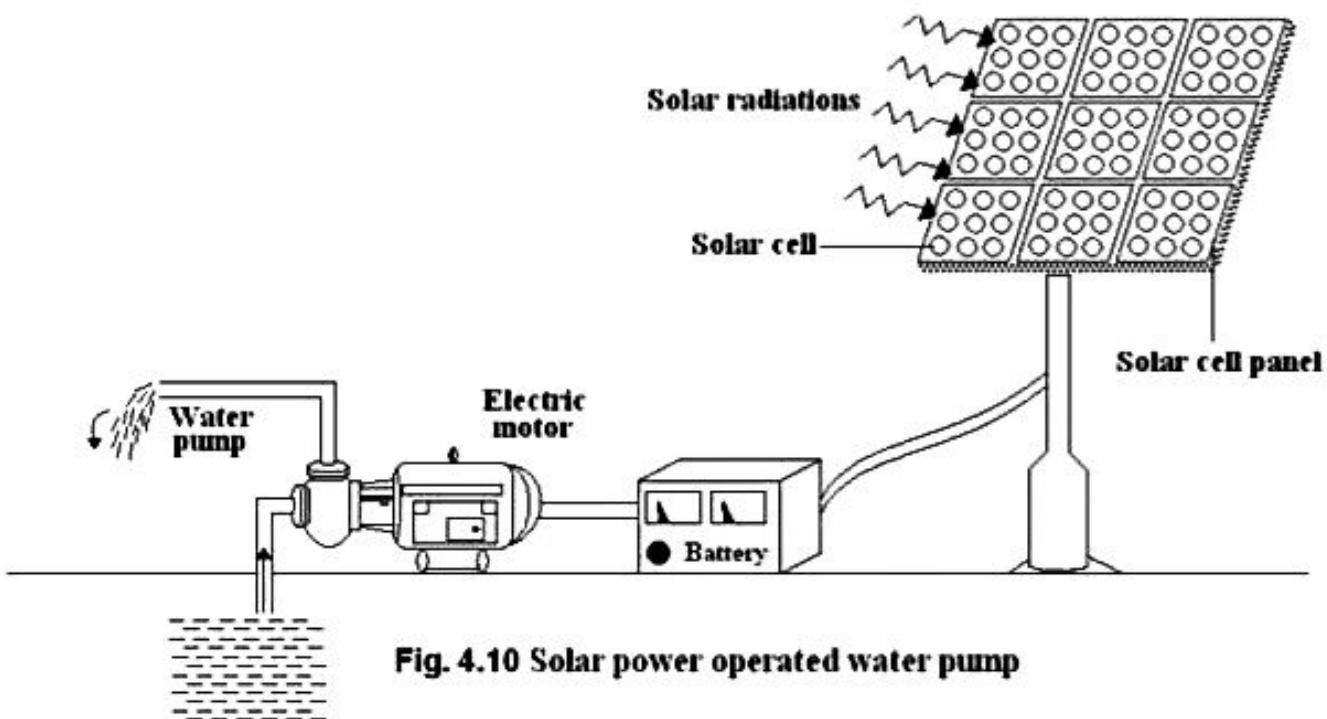


Fig. 4.10 Solar power operated water pump

Advantages:

- (1) 0.7W electricity is produced
- (2) No maintenance is required; it has long life
- (3) Can be used in remote areas
- (4) No pollution and eco-friendly
- (5) Renewable

Disadvantages:

- (1) Initial cost is high
- (2) It requires sunshine; cannot be used during night time
- (3) Does not produce much current in winter