MODULE 5 WATER CHEMISTRY

Water Technology: Introduction, boiler troubles with disadvantages & prevention methods-scale and sludge formation, priming and foaming, boiler corrosion (due to dissolved O2, CO2 and MgCl2). Determination of DO, BOD and COD, numerical problems on COD. Sewage treatment: Primary, secondary (activated sludge method) and tertiary methods. Softening of water by ion exchange process. Desalination of sea water by reverse osmosis & electro dialysis (ion selective).

<u>COURSE OUTCOME:</u> Boiler troubles; sewage treatment and desalination of sea water. INTRODUCTION:

Water is one of the most basic and essential component of all life. It cove s nea ly 72% of the earth's surface. It is the second most important substance required to sustain human, animal, and plant lives. Water is essential resource for living system, indust ial p ocesses, ag icultural production, and domestic use.

Pure water is a clear, colorless, and odorless liquid that is m de up of one oxygen and two hydrogen atoms. The chemical formula of the water molecule, H₂0, w s defined in 1860 by the Italian scientist **Stanislao Cannizzarro**. Water is a ve y powe ful subst nce that acts as a medium for many reactions, which is why it is often efe ed to s the "universal solvent." Although pure water is a poor conductor of electricity, impu ities that occur naturally in water transform it into a relatively good conductor. Water has unusually high boiling (100° C/212° F) and freezing (0° C/32° F) points. It also shows unusual volume changes with temperature. As water cools, it contracts to a maximum dens ty of 1 grain per cubic centimeter at 4° C (39° F). Further cooling actually causes it to expand, espec ally when it reaches the freezing point. The fact that water is denser in the liquid form than the solid form explains why an ice cube floats in a beverage, or why a body of water freezes from the top down. While the density property of water is of little importance to the beverage example, it has a tremendous impact on the survival of aquatic life inhabiting a body of water. Water exists in many forms in the nature. i.e. in the form of clouds, rain, snow, ice and fog. The distribution of water on the earth is as follows.

Boiler feed water

The boilers are used in industries to generate steam. This steam is used in power production, sterilization etc. The water used to generate steam in boiler s called boiler feed water.

Boiler Troubles:

Water used to generate steam is contaminated; it brings problem to boiler and reduces its efficiency, he major boiler troubles are

- 1. Scale and sludge formation
- 2. Priming and foaming
- 3. Boiler corrosion

1. Scale formation:

During the production of steam, water evaporates continuously leaving behind the dissolved salts in the boiler. Concentration of the salt increases and reaches saturation level to get precipitated. If the precipitate is hard and strongly adhering on the inner walls of the boiler is known as scale.

Causes for scale formation:

The various dissolved salts of water are responsible for scale formation

1. Decomposition of bicarbonates: bicarbonates undergo decomposition and forms insoluble carbonates. i.e.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3+CO_2+H_2O$$

- 2. Presence of silica: Impurities like calcium silicates, magnesium silicates are highly insoluble in hot water, they precipitate and deposit as scale
- 3. Hydrolysis of salts of magnesium: Magnesium salts are precipitated as their hydroxides at high temperature.i.e

$$MgCl_2+2H_2O \longrightarrow Mg(OH)_2+2HCl$$

Prevention of scale formation:

The scale formation in boilers can be controlled by two methods.

- 1. By feeding soft water (external treatment): Water used in boile s is pu ified by emoving suspended and hardness impurities. Suspended impurities are removed by sedimentation and filtration process and hardness is removed by lime soda or ion exch nge methods. Prevention of sludge formation:
- 2. By internal treatment: Process of adding chemicals di ectly to w ter in boilers to remove the scale forming impurities which were not removed during exte n l t e tment methods is known as internal treatment. In this process, an ion is prohibited to exhibit its original character by complexing or by converting into more soluble salt by adding app op iate reagent.

Example: colloidal conditioning, phosphate conditioning, ca onate conditioning.

Disadvantages of Scale:

- 1. Wastage of fuel: Scales have a poor conductor of heat, so the rate of heat transfer from boiler to water is greatly reduced.
- 2. Reduces boiler efficiency: Decompos t on of scales in the valves and condensers of the boiler, choke them partially.
- 3. Increase in cleaning expenses: Scales must be removed regularly and this cleaning process is very expensive.
- 4. Lowering of boiler safety: The overheating of the boiler tube makes the boiler material softer and weaker.
- 5. Danger of explosion: The scale formation also leads to uneven expansion of boiler material.

Sludge formation:

During the production of steam, water evaporates continuously leaving behind the dissolved salts in the boiler. Concentration of the salt increases and reaches saturation level to get precipitated. If the precipitate is soft, loose and suspended in boiler feed water is called as sludge.

Causes for sludge formation:

he impurities of water which causes sludge formation are MgCO₃, MgSO₄, and MgCl₂ etc. If the sludge is not removed periodically, then it will form scale.

Prevention of sludge formation:

Sludge formation can be prevented by using softened water, more over sludge can be removed by flowing off technique ie. by drawing off some of the concentrated water from the bottom of the boiler through a tap.

Disadvantages of scale and sludge formation:

- 1. The sludge is bad conductor of heat. So it requires more heating of boiler to produce steam which results in wastage of fuel.
- 2. Because of more and more heating of boiler, there is a chance of explosion of the boiler

- 3. It reduces the efficiency of boiler.
- 4. Sludge's need to be removed regularly and this cleaning process is expensive.
 - 2. **Priming:** The process of carrying water droplets along with steam is called priming.
- 1. Formation of steam of high velocity
- 2. Sudden boiling
- 3. Maintaining very high water levels in boiler
- 4. Presence of dissolved impurities in boiler feed water

Prevention of priming:

- 1. Filtration of the boiler feed water by fitting mechanical purifiers.
- 2. By supplying soft water by changing boiler water from time to time.
- 3. By avoiding rapid change in steaming velocity.
- 4. Maintain low water level.

Disadvantages of priming

- 1. Due to priming, it reduces the heating ability of steam
- 2. Priming causes corrosion of blades and pipelines
- 3. It reduces the life of engine.
- 4. A sudden boiling
- 5. An improper design of boiler

Foaming: The process of formation of pers stent ou les on the surface of boiler water is called foaming.

Causes for Foaming:

- 1. The difference in the concentration of d ssolved salts between surface layer and bulk of the water in boiler.
- 2. Due to the presence of impurities like oils, fats etc.forms foaming

Prevention of foaming:

- 1. The addition of anti foaming agents like caster oil.
- 2. The removal of foaming from boiler water by adding aluminium compounds like sodium aluminates and aluminium sulphate.

Disadvantages of foaming:

- 1. It is difficult to maintain boiler pressure
- 2. Decreases the boiler efficiency

3. Boiler corrosion

he decay of boiler material due to the presence of impurities in boiler feed water is called boiler corrosion.

Causes for Boiler corrosion:

1. Corrosion due to dissolved Oxygen:

When water containing dissolved oxygen is heated in the boiler, the free gas is evolved under high pressure of the boiler and attacks the boiler material and forms the rust.

2. Corrosion due to dissolved carbon dioxide:

The CO₂ is obtained from the decomposition of bicarbonates. So formed CO₂ is react with H₂O and produce carbonic acid. This carbonic acid is slightly acid and corrosive in nature.

3. Corrosion due to MgCl₂:

The salts like MgCl₂ in boiler feed water forms hydroxides and acid. The acid so formed will attack the boiler parts and causes corrosion.

$$MgCl_2+2H_2O \longrightarrow Mg (OH)_2+2HCl$$
 $Fe+2HCl \longrightarrow FeCl_2+H2$
 $FeCl_2+2H_2O \longrightarrow Fe (OH)_2+2HCl$

Prevention of boiler corrosion:

Boiler corrosion can be controlled by reducing the quantities of O₂, CO₂ and any acid from the feed water.

- 1. By removing oxygen: Dissolved oxygen can be removed by tre ting boiler feed water with sodium sulphite or hydrazine.
- 2. By removing carbon dioxide: Lime stone easily emoves c bondioxide or by adding ammonium hydroxide.
- 3. Finally acidic impurities if there any can be removed by t eating with alkaline agents like ammonium hydroxide.

DETERMINATION OF DISSOLVED OXYGEN (DO): (WINKLER'S METHOD)

The dissolved oxygen can be determ ned e ther y the Winkler (iodometric) method or by the use of dissolved oxygen electrodes. The results are either expressed as a simple concentration (mg/l) or as a percentage of full saturat on.

Principle: The dissolved oxygen is not capable of oxidizing KI. Therefore oxygen carrier like Mn (OH)₂ is produced in water to liberate I₂ from KI. The liberated Iodine is titrated against Na₂S₂O₃ by using starch as indicator.

$$MnSO4+2KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

The Mn(OH)₂ is reacted with DO to form oxygen carrier ie manganic oxide.

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

The manganic oxide is treated with H₂SO₄ to liberate nascent oxygen.

$$\underline{MnO(OH)_2 + H_2SO_4} \longrightarrow \underline{MnSO_4 + 2H_2O + [O]}$$

The nascent oxygen in presence of acid react with KI to liberate equivalent amount of iodine.

he liberated iodine is titrated against Na₂S₂O₃ using starch indicator

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Procedure:

- 1. Pipette out 300 ml of water sample into a clean glass stoppered bottle.
- 2. Add 3 ml MnSO₄ solution and 3 ml alkaline KI solution. The bottle is closed immediately and shakes well to get brown precipitate. Allow the precipitate to settle down at the bottom.
- 3. Add 1 ml of concentrated H₂SO₄ slowly and mix well. Precipitate dissolves completely liberating iodine.
- 4. Pipette out 100 ml of this solution into a clean conical flask.
- 5. Titrate against 0.02N Na₂S₂O₃ using freshly prepared starch as indicator.
- 6. Record the volume of the Na₂S₂O₃ solution used.

Calculations:

Normality
$$\times$$
 Volume of exygen = Normality \times Volume of $Na_2S_2O_3$

Therefore Hormality of exygen = $\frac{\text{Normality} \times \text{Volume of Na}_2S_2O_3}{\text{Volume of exygen solution}}$

$$= \frac{\text{NNV}}{100}$$

$$= a$$
Mass of dissolved exygen/am² = $\text{Normality} \times \text{Volume of Na}_2S_2O_3$

$$= \frac{\text{Normality} \times \text{Volume of Na}_2S_2O_3}{\text{Volume of exygen solution}}$$

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DETERMINATION OF BOD BY WINKLER'S METHOD:

Definition of BOD: Biological Oxygen Demand is an important measu e of water quality. BOD is defined as "The amount of oxygen required by microorganism to oxidize the o ganic matter in a water sample over a period of 5 days under aerobic condition t 20° C".

Characteristics of BOD:

- 1) The unit of BOD is mg/dm³ or ppm.
- 2) Determination is slow and time consuming method.
- 3) It represents only biodegradable organic matter under ae obic condition.

Principle: The dissolved oxygen is not capable of oxidizing KI. The efore oxygen carrier like Mn (OH)₂ is produced in water to liberate I₂ from KI. The li e ated Iodine is titrated against Na₂S₂O₃ by using starch as indicator.

The oxygen carrier is produced by the react on of MnSO₄ and KOH.

$$\underline{MnSO4+2KOH} \longrightarrow \underline{Mn(OH)_2 + K_2SO_4}$$

The Mn(OH)₂ is reacted with DO to form oxygen carr er ie manganic oxide.

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

The manganic oxide is treated with H₂SO₄ to liberate nascent oxygen.

$$\underline{MnO(OH)_2 + H_2SO_4} \longrightarrow \underline{MnSO_4 + 2H_2O + [O]}$$

The nascent oxygen in presence of acid reacts with KI to liberate equivalent amount of iodine.

The liberated iodine is titrated against Na₂S₂O₃ using starch indicator

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Procedure: A known volume of sewage sample is diluted to definite volume with water which contains nutrients for bacterial growth and sufficient oxygen. The diluted sample is separated in two bottle of equal volume.

DO at zero time (D1): DO content in one of the BOD bottle is determined immediately. **Procedure:**

- 1. Pipette out 300 ml of water sample into a clean glass stoppered bottle.
- 2. Add 3 ml MnSO₄ solution and 3 ml alkaline KI solution. The bottle is closed immediately and shakes well to get brown precipitate. Allow the precipitate to settle down at the bottom.
- 3. Add 1 ml of concentrated H₂SO₄ slowly and mix well. Precipitate dissolves completely liberating iodine.
- 4. Pipette out 100 ml of this solution into a clean conical flask.
- 5. Titrate against 0.02N Na₂S₂O₃ using freshly prepared starch as indicator until blue colour disappears.
- 6. Record the volume of the Na₂S₂O₃ solution used.

Do after 5 days (D2): The second bottle is incubated for 5 days at 20 0 C. After 5 days DO is measured as described above. (D2). Then BOD is calculated from the formula Calculation:

Normality
$$\times$$
 Volume of oxygen = Normality \times Volume of $Na_2S_2O_3$

Therefore Normality of oxygen = $\frac{Normality \times Volume \text{ of } Na_2S_2O_3}{Volume \text{ of oxygen solution}}$

$$= \frac{N\times V}{100}$$

$$= a$$

Mass of dissolved oxygen/dm $^{\Xi}$ = N × Equivalent mass oxygen = $a \times 8.0 \times 1000 \text{ mg/L}$

Mass of dissolved oxygen is D₁ similarly calculate for second bottle ie D₂.

$$BOD = \frac{D_1 - D_2}{A} \times B \, m_{\mathcal{G}} / dm^3$$

Where D₁ is the DO in the solution at start, D₂ is the DO in the solution fter 5 days, 'A' is the volume of the sample before dilution and 'B' is the volume of the s mple fter dilution.

DETERMINATION OF COD OF WASTE WATER:

Definition of COD: It is defined as "The amount of oxygen equi ed for the complete oxidation of both organic & inorganic matter present in 1 lit e of waste water using strong oxidizing agent".

Characteristics of COD:

- 1) The unit of COD is mg/dm^3 or ppm.
- 2) In general COD > BOD since both odegrada le and non biodegradable organic load are completely oxidized.

Principle: In this method, the given samples of water containing organic and inorganic impurities are oxidized by K₂ Cr₂ O₇ in acidic media in the presence of catalyst Ag₂SO₄ and HgSO₄.(Added to prevent the interference the chloride and silver ions). The unreacted K₂Cr₂O₇ is titrated against FAS solution in the presence of a redox indicator, ferroin which shows its color change in the oxidized (bluish green) and reduced states (reddish brown).

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + 3(O)$$

3(O) + 2CHO \longrightarrow 2CO₂ + H₂O

Procedure: **Preparation of standard solution**: Standard FAS solution is prepared by adding dilute H₂SO₄ (Added to prevent hydrolysis of FAS) to a known weight of FAS salt.

- 1. Pipette out known amount of the waste water into a clean conical flask.
- 2. Add 10 ml of K₂Cr₂O₇ and 10 ml 1:1 H₂SO₄ into a conical flask.
- 3. Add 1 g of Ag₂SO₄ followed by 1 g of HgSO₄ and warm if necessary.
- 4. Titrate with standard FAS using ferroin as indicator till color changes from bluish green to reddish brown.
- 5. Note down the volume of FAS consumed as 'V₁' ml.

Perform the blank titration without waste water sample. Note down the volume as 'V2' ml.



Normality of FAS = 'A' N

Volume of FAS consumed during blank titration = B cm³

Volume of FAS consumed during Back titration = C cm³

Volume of FAS consumed for the titration = (B - C) cm³

Volume of water sample = V cm³

1 ml of 1N FAS = 8 mg of oxygen

(B-C) cm³ of 'A'N FAS = A*(B-C)*8 mg of oxygen

Vcm³ of water sample = <u>A*(B-C)*8</u> mg of oxygen

Therefore 1000cm3 of water sample = $A*(B-C)*8*1000 \text{ mg/dm}^3$ of oxygen

SEWAGE: Water containing any one of the waste is called s **effluent or sew ge**.

SEWAGE TREATMENT: The water containing heavy lo d of BOD, p thogenic bacteria, colour and annoying smell can't be directly discharged into the rivers s they mainly affect the aquatic life and causes many water borne diseases. The domestic sew ge therefore needs proper treatment which is carried out in 3 stages

Primary treatment
Secondary treatmen
Tertiary treatment

Primary treatment: It involves

Screening: Removal of large suspended or float ng matter in sewage using mesh screens.

Silt and Grit removal: Removal of heavy part cles like sand, glass pieces etc. using grit chambers.

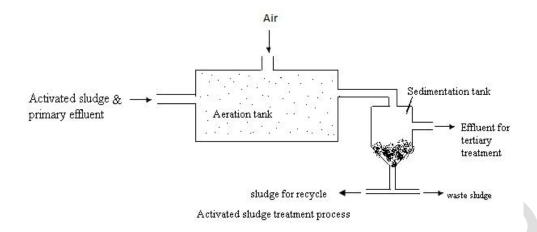
Removal of oil and grease: is mainly done using skimming tanks by blowing air through the sewage and oils are lifted to the surface as foams (soapy mixture)which is then skimmed off. **Sedimentation process**: involves addition of coagulants like alum, ferrous salts etc. and there by ppt. out the suspended particles by sedimentation process.

Secondary treatment:

It involves aerobic biological oxidation of sewage water. The sewage water after sedimentation is subjected to aerobic oxidation during which the organic matter is converted into H₂O and CO₂ and N₂ to NH₃ and finally to nitrates and nitrites.

<u>Activated Sludge Method (Biological treatment)</u>: Activated sludge is a thick greasy mud containing aerobic bacteria.

his method involves extensive aeration of the sewage water after primary treatment is mixed with activated sludge and allowed to enter in a large aeration tank for biological treatment. Air is continuously passed into tank to maintain the aerobic condition. Under these condition microorganisms present in activated sludge attack on organic matter of sewage and decomposes them into CO₂ and H₂O. The effluent after this treatment is passed to sedimentation tank where sludge will settle down. The clear effluent is sent to tertiary treatment. A part of sludge is used for further treatment and rest is disposed off and used as manure.



Tertiary treatment: It involves

Removal of phosphate using lime

$$PO_4$$
 + $Ca(OH)_2$ \longrightarrow $Ca_3(PO_4)_2$

Removal of heavy metals by sulphides.

Degasification of NH₃, H₂S, and CO₂ by stripping hot water.

Disinfection of microorganisms by chlorine. Acid kills microorganisms.

Softening of water by Ion exchange process:

In this method all the ions present in water are removed. In this insoluble ion exchange resins are used. Resins means it is a long chain organic polymer with functional groups. Depending upon the functional groups attached to resins they are classified into

1. Cation Exchange Resin:

These resins exchange its H⁺ ions with cations of water sample. Generally it is expressed as RH⁺

2. Anion Exchange Resin:

These resins exchange its OH⁻ ions with anions of water sample. Generally it is expressed as ROH⁻

Working:

The ion exchange resin contains two compartments. One is cation exchange resin and another is anion exchange resin. For the regeneration of respective resins, acid and alkali regeneration units are connected to compartments. The schematic diagram of ion exchange unit as shown in fig.

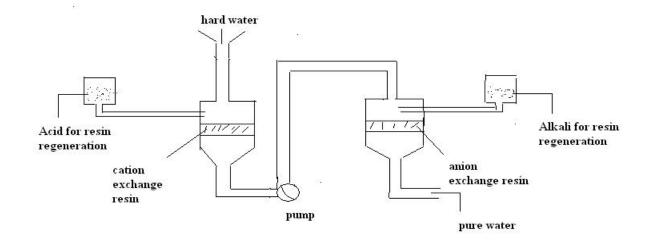
he water sample containing high minerals are first allowed to pass through cation exchange resins, which exchanges its H^+ ions with Ca^{2+} ions of water .i.e

Now the water sample is free from cations.

The same water is further allowed to pass through anion exchange resin, which exchanges its OH- ions with Cl- of water. i.e.

Now the water is totally free from all the ions.

Now H⁺ ions formed at cation exchange resin and OH⁻ ions formed at anion exchange resin will combine to form pure water.



Advantages:

- 1. The ion exchange apparatus, once set up, is easy to ope ate and cont ol.
- 2. Both acidic and alkaline water can be softened.
- 3. Water of very low hardness is produced.
- 4. Water produced by this method is used as o ler feed water.

Disadvantages:

- 1. Equipment and process is costly.
- 2. Turbid water needs to be filtered first before softening.

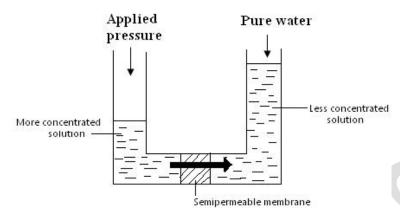
POTABLE WATER-Water that is fit for human consumption and free from pathogenic bacteria and toxic chemicals is called potable water.

<u>DESALINATION</u>-The process of removal of dissolved salts from sea water to the extent that water becomes usable is described as desalination. The important methods of desalination are a) Reverse Osmosis. B) Electrodialysis.

REVERSE OSMOSIS:

Principle: - he principle of osmosis is that water flows from lower concentration to higher concentration side through semi permeable membrane. If the pressure is applied on solution side, the solvent will flow in the reverse direction. This is called reverse osmosis.

It is studied that sea water exerts an osmotic pressure of about 4500-5500 KPa. In reverse osmosis, hydrostatic pressure which is greater than osmotic pressure is applied on the salt solution side then water flows from salt solution to fresh water side. This water can be used for human consumption.



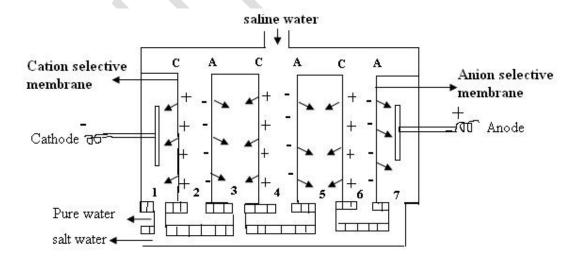
Reverse Osmosis

Application:

- 1. It is economical, simple and continuous.
- 2. The process needs extremely low energy.
- 3. It has long life and membrane is easily replaceable.

ELECTRODIALYSIS: The process of migration of ions p esent in the solution towards the oppositely charged electrodes under the influence of applied emf is known as electrodialysis.

It consists of two electrodes and ion selective mem ranes which are permeable to either cation or anion. The anode is placed near an on selective mem rane, while the cathode is placed near to the cation selective membrane. The an on selective membrane has positively charged functional groups and allows negatively charged ons to pass through them similarly cation allows only negatively charged ions. When emf s applied between the two electrodes, the cation of salt move towards cathode ie Na⁺ and anion move towards anode ie Cl⁻ through selective membrane. As a result the concentration of the ions in alternate compartment decreases ie 2, 4, 6 etc., and on other compartment increases ie 1, 3, 5, 7 etc., of ions. Thus water in even compartment becomes pure and is collected from the bottom. The water in odd compartment becomes rich in the salts and it is rejected.



NANO MATERIALS

Nano Materials: Introduction, properties (size dependent). Synthesis-bottom up approach (solgel, precipitation, gas condensation & chemical vapour condensation processes). Nano scale materials- carbon nano tubes, nano wires, fullerenes, dendrimers, nano rods, & nano composites.

<u>COURSE OUTCOME:</u> Over viewing of synthesis, properties and applications of nanomaterials Program.

INTRODUCTION: Nanotechnology is a multidisciplinary science and technology and encompasses physical, chemical, biological, engineering and electronic p ocesses. It is the study deals with various structures of matter having dimensions of the order of billionth of a meter. These materials or particles are called as nano particle. Nano technology is the making of usage and technique, in order to solve a problem to perform specific functions. The p ticles which are smaller than about 100nm give rise to enhance properties of n no structures built from them. Matter arranged by exercising control over length of one to hundred n nometers and the formulating structures exhibit characteristics that are specific to their size nd dimensions, the resulting materials are called nano materials.

SIZE DEPENDENT PROPERTIES

- a) **Surface area**: Nanomaterials have a s gn f cant proportion of atoms existing at the surface. Properties like catalytic activity, gas adsorpt on and chemical reactivity depend on the surface area. Therefore nanomaterials can show spec f c related properties that are not observed in bulk materials.
- b) **Electrical properties:** the electronic bands in bulk materials are continuous due to overlapping of orbitals of billion of atoms. But in the nanomaterials, very few atoms or molecules are present so the electric band becomes separate and the separation between different electric stated varies with the size of the nanomaterials. Hence, some metals which are good conductors in bulk semiconductors and insulator as their size is decreased to nano level.
- c) **Optical properties:** Nanomaterials have particular optical properties as a result of the way light intersects with their fine nanostructures. The discrete electronic states of nanomaterials allow absorption and emission of light at specific wavelength. Hence, nanomaterials exhibit unique color different from bulk materials.
- d) **Magnetic properties:** Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. The large surface area to volume ration results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to different magnetic properties. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles. Gold nano particles become ferromagnetic when they are capped with appropriate molecules such as thiol.
- e) **Mechanical properties:** Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of the bulk materials. For

example, the bending of bulk solution(wire, ribbon etc...) occurs readily with the movement of copper atoms/clusters at about 50nm scale. Copper nanoparticles smaller than 50nm are considered super hard materials that do to exhibit the same malleability and ductility as bulk copper.

SYNTHESIS OF NANOMATERIALS

There are two methods of preparing nanomaterials. One is top-down approach & the other is bottom-up approach.



☐ In top-down approach, the mater all s reduced from ulk size to nano scale. Examples for top-down approach are ball m ll ng method & nanolithography.

 \Box In bottom-up approach, matter n atom c or molecular level gets assembled to form tiny clusters which grow to reach nano -size.

Examples for bottom-up approach are arc discharge method, chemical vapor deposition, physical vapor deposition & sol gel method.

SOL - GEL PROCESSES

Sol gel processes principle is conversion of precursor solution into gel via hydrolysis and condensation reactions.

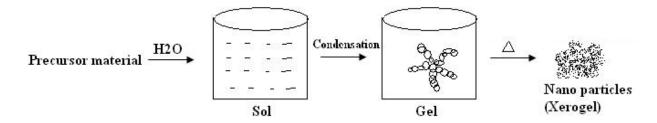
Sol gel processes allow to synthesis of nano materials of high purity.

This process involves five steps

1. Preparation of sol: sol is prepared by suspended particles in water during suspension hydrolysis reaction takes place.

$$M-OR + H2O \longrightarrow M-OH + R-OH$$

- 2. Conversion of sol into gel: sol is converted into gel by condensation reaction forming network between oxides. When networking takes place, the viscosity of the solution increases. $\mathbb{M} 0H + \mathbb{M} 0H \rightarrow \mathbb{M} 0 \mathbb{M} + H_{+}0$
- 3. Aging of gel: during which poly condensation reaction continue until the gel is transformed into solid mass.
- 4. Removal of solvent: Further the solid mass is isolated from the solvent by thermal evaporation. The product formed is xerogel.
- 5. Heat treatment: solid mass (xerogel) obtained is dried at nearly to 800C to get fine nano particle powder.



Advantages:

Nano materials of high purity with good homogeneity can be obtained.

Samples can be prepared at low temperature.

Easy to control the synthesis parameters like shape and size of esulting mate ial

PRECIPITATION METHOD

Principle: The principle involved in the precipitation of precursor m te i ls t constant pH via condensation.

Processes: In this method inorganic metal salt such as chlo ide, sulph te, nitr te ions etc.., are used as precursor. Precursor materials is dissolved in water nd unde go hydrolysis where metal ions exist in metal hydrates form. On adding base like NaOH/NH4OH, pH of the solution changes and reaches super saturation level leading to condensation of precursor to form metal hydroxide precipitate. The precipitate is washed with water, filtered and finally calcinated at higher temperature to convert metal hydroxide into metal oxide y dehydrogenation takes place.

$$MLx + xH2O \longrightarrow M(H_2O)_x + xL-$$

$$M(H_2O)_x \stackrel{NaOH}{\longrightarrow} M(OH)x$$

$$M(OH)x \longrightarrow MOx + H_2O$$

$$Metal Insoluble salt \stackrel{H_2O}{\longrightarrow} MaOH \stackrel{Metal oxide}{\longrightarrow} Metal oxide (nano particle)$$

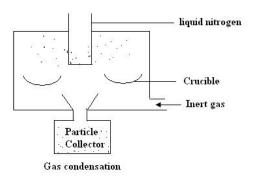
Advantages: The process is relatively economical.

The wide range of single and multi components to oxide nano powders can be synthesized.

GAS CONDENSA ION

Principle: the principle of this method is to heat the bulk material to vaporize. Vapours are carried by inert gas and allow collecting in cold surface.

Process: The precursor material taken in crucible and heated to high temperature, precursor material vaporizes and that mean time inert gas is passed from bottom. Condensation reaction takes place between them.



The product formed is passed onto cold surface (cool area is created on passing liquid nitrogen on to the rod). The vapors condenses on cold surface and grow, later the particles are collected in receiver plate and removed by scraping.

Advantages:

Used to control the particle size and uniform size.

Better suited for larger scale synthesis of nano powders.

The products formed are free from impurities.

CHEMICAL VAPOUR CONDENSATION

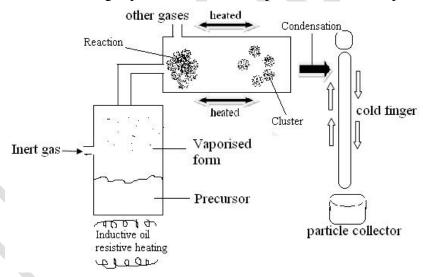
Principle: the process involved is conversion of precursor (metal organic compound) into vapors in reduced pressure atmosphere.

Processes: the precursor (starting material) is vaporized in a bubble and mixed with inert gas like helium to carry vapors into heating furnace. Condens tion re ction t kes place in heating furnace at a particular temperature. The product formed after the condens tion process is in the form of clusters. The clusters are then condensed into nano p rticles in cold finger which are removed by scraping.

Advantages:

Simple technique and does not require high vacuum

It is possible to deposit nano materials with almost any shape and size. The byproducts are removed to gas phase. Therefore the product obtained is pure.



NANO SCALE MATERIAL

Nano scale materials are defined as a set of substances where atleast one dimension is less than approximately 100nm. A nanometer is one millionth of a millimeter. Nano materials are of interest because of this scale unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine and other fields.

FULLERENES: Fullerenes are class of molecules made of only carbon atoms having closed cage like structure. Many number of fullerene molecules with different carbon atoms like C_{60} , C_{70} , C_{74} , C_{76} etc.., have been prepared but C_{60} is more stable. The C_{60} molecule had spherical

shape resembling a soccer ball (foot ball). It is also commonly called as Bucky ball. The C_{60} molecule consist of 12 pentagons and 20 hexagons and each pentagon is surrounded by five hexagons and each hexagon is surrounded by three hexagons and three pentagons placed next to each other alternately fold in the form of ball. Each carbon atom on the cage surface is bonded to three carbon neighbors therefore is sp2 hybridized. The chemical formula for fullerene is C_{20+2n} .



Fullerene

In fullerenes, 12 pentagonal rings are necessary and sufficient to form the cage closure. It is quite stable, breaking the balls requires temperature of about 1000C. Fullerene has high tensile strength and high packing density.

Applications:

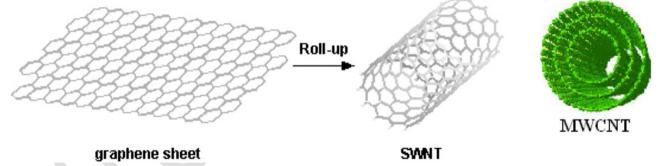
It is used in electrographic imaging, solar cells, non linear optical thin films etc...

Used to make carbon films, diodes, double layer cap citor nd sto ge devices. Used for the conversion of diamond

Used as gas sensors, temperature sensors, particle sensors nd detection of organic vapors.

<u>CARBON NANO TUBES:</u> Carbon nanotubes are allot opes of carbon with a cylindrical nanostructure having diameter of 1nm and longer than a mic ometer. It is one dimensional material like nano wires. CNT is made up of graphite sheet. When the graphite sheet is rolled up hexagonally, it forms a tube like structure s called as CNT. Types of CNT:

1. Single walled nanotubes (SWCNT): These are formed y rolling up of single graphite layer. Diameter is 1.4nm and length upto few m crometers.



2. Multi walled nanotubes (MWCNT): These are formed by rolling up of two or more graphite layers. Diameter is from 30 to 50nm and length upto few micrometers. Properties:

CN s have High Electrical Conductivity, Tensile Strength, Thermal Conductivity And flexibility and elasticity.

Applications: It can be used in

Conductive plastics ,Structural composite materials, Flat-panel displays, Gas storage Micro- and nano-electronics, Radar-absorbing coating, Batteries with improved lifetime, Biosensors for harmful gases

NANO WIRES: Nanowires are one dimensional structure because one dimension is in micro scale and the rest two are in nano scale. The width of the nanowire is in the range of 1-100nm

whereas length can be more than nanoscale. Nano wires will be able to reduce the size of electronic devices in order to increase the efficiency. Applications:

- 1. Used in bio molecular nano sensors
- 2. Used for metallic interconnections in nano quantum devices
- 3. Used as additives for nano composites
- 4. Used as photocatalysis to decompose organic molecules in polluted water

Nano rods are one dimensional nano structured. The aspect ratio of nano rods is less than 10. The aspect ratio is defined as the ratio of length of a particle to width of a particle. The length and width usually vary from 10 to 100nm. Nano rods are very useful to study about the effect of size and shape on the magnetic, electronic, optical and chemical properties of materials at nano scale range.



Nano rod

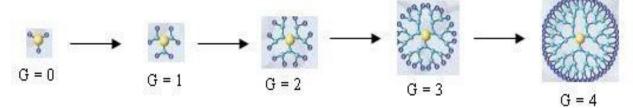
Applications:

- 1. Nano rods of metal oxides like TiO₂, V₂O₅, CuO and MnO₂ e used in c talysis.
- 2. They are used in gas sensors, video displays, and computer components.
- 3. Nano rods absorb in the near IR and gene ate heat when excited with IR light. This property is used as cancer treatment to selectively kill cancer cells without affecting nearby healthy tissues.
- 4. It is used as light emitting dev ces ased on semi conducting material used.
- 5. In display technologies, the reflect v ty of the rods can be changed by changing their orientation with an applied electric field.

<u>DENDRIMERS</u>: Dendrimers are repetitively branched molecules. They have a central core with more than two functional groups to which branched molecules are added repeatedly step by step. Each addition of branches to a dendrimers is called as generation. A dendrimers can grow upto 10 -15 generations with size ranging from 1 to 25nm.

Dendrimers of lower generation posses more open structures as compared to higher generation dendrimers. The repetitive addition of branches leads to globular structure and becomes densely packed. Further growth is restricted due to lack of space.

Dendrimer generations



Applications:

1. Dendrimers have less dense central core and large number of functional groups or outer surface. Both these sites can be used to accommodate drug of any size and for any type of delivery. Their surface can be further modified with addition of other bio responsive elements like lipids and fatty acids.

- 2. They have nano scale spherical shape, which can move and diffuse easily through the human body. They are very quickly cleared by kidneys after the drug delivery.
- 3. It is used as medical imaging agents in magnetic resonance imaging (MPI scan) of human body.
- 4. Dendrimers themselves are biologically active and used as antiviral and anti microbial agents.
- 5. It is used as coating agent to protect drug deliver it to specific sites in the body.

NANO COMPOSITE: Composite is a combination of two or more different materials that are mixed in an effort to blend the best properties of both. Nano composite material is obtained by inserting nano material into the matrix layer. Such material will have the properties of both nano particle and matrix. This allows the combination of properties in one material that would never exist together in nature. In nano composite particles are distributed in such a way that they do not touch each other. Nano composite materials are of three types, depending on the dimension and distribution of nano materials on to matrix

- 1. Zero dimensions: In which isolated nano particles are distributed in mat ix. Interaction between different particles is minimized by maintaining sufficient dist nee between particles.
- 2. One dimension composites: In which nano tubes nd n no rods re distributed in a matrix.
- 3. Two dimension composites: In which thin nano films e pl ced between the two matrix layers.

