IMPORTANT ENGINEERING MATERIALS

Q.1) Define Cement?

Ans. It is defined as a material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc.

They have the property of setting and hardening under water by virtue of certain chemical reactions with it and are therefore called as "Hydraulic Cement". Eg Compounds of

Ca (Calcarious)and Al+Si (Argillaceous)

Q.2) Explain the classification of Cement.

Ans. Cement can be classified as follows:

a)**Natural cement:** It is made by calcining lime stone which contains impurities of silica, alumina and iron oxide(extent of 20-40%).During calcination, silica and alumina combine with lime to form calcium silicates and aluminates.

b)**Puzzolano cement**: It was invented by Romans and used by them in making concrete for construction of walls and domes. They are materials which when mixed with lime in the absence of heat form hydraulic cementing materials. It essentially consists of silicates of aluminium , iron and calcium. It is made by mixing and grinding natural puzzolano and slaked lime.

c)**Slag cement**: It is made from blast furnace slag and hydrated lime The blast furnace slag is granulated by pouring it into a stream of cold water, dried and mixed with hydrated lime. The mixture is then finely pulverized . Slag cements are slow to harden and hence accelerated by adding clay, salt or caustic soda.

d**) Portland cement**: An extremely finely ground product obtained by calcining together, at about 1500°C, an intimate and properly proportioned mixture of argillaceous (containing clay)and calcareous (contain lime)raw materials ,without the addition of anything subsequent to calcination, excepting the retarder gypsum.

Q.3)What are the raw materials required for the manufacture of Portland cement and give its functions?

Ans: **Raw Materials:** i**)** Calcerous materials :CaO(lime Stone, Chalk etc)

ii) Argillaceous materials:Al_2O_3 and SiO_2(Shale, Slate, Clay)

iii) Powdered Coal or Fuel Oil iv)Gypsum ($CaSO_4.2H_2O$)

Functions: a **)Lime:** It is the principal constituent of cement .It proportion must be properly regulated because excess of lime reduces the strength of cement and therefore expands and disintegrate . Lesser amount of lime reduces the strength of cement and makes it quick setting.

b)**Silica:** It imparts strength to cement.

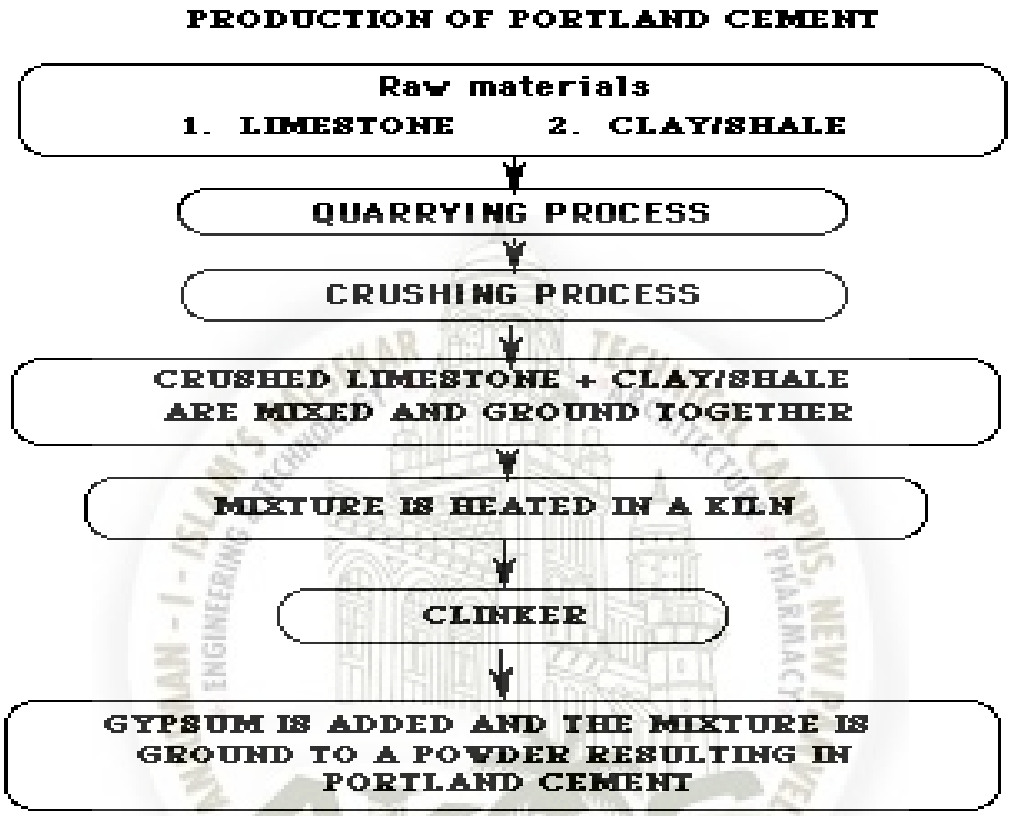
c)**Alumina**: It makes the quick setting of cement and if used in excess weakness the cement.

d)**Calcium Sulphate (Gypsum)**: It helps to retard the setting action of cement and enhances the initial setting time of cement.

e)**Iron Oxide**: It provides color, strength and hardness to the cement.

f**) Sulphur Trioxide:** It is desirable in small proportion as it imparts soundness to cement.

Q.4) Explain the various steps involved in the manufacture of Portland cement.?



Ans.: The manufacture of Portland cement involves the following steps :

1)**Mixing of raw materials** : Can be done either by i) Dry process or ii)Wet process

a**) Dry process**: The raw materials ie limestone and clay are crushed into roughly 2-5 cm size pieces and then further ground to fine power in the ball mills. Each powdered ingredient is stored separately in a separate hopper. The powdered materials are mixed in the requited proportions to get dry 'Raw mix', which is stored in storage bins called as 'Silos' and kept ready to be fed in rotary kiln.

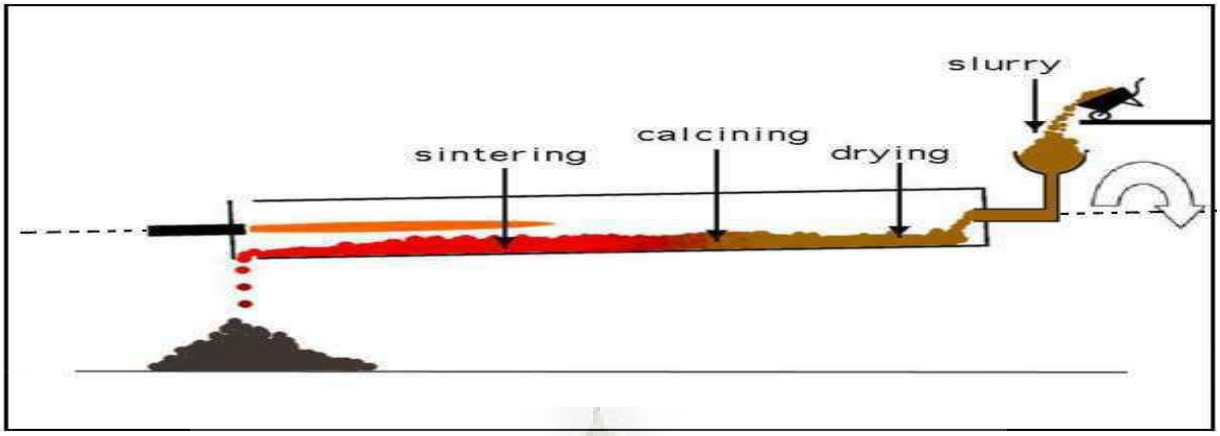
b)**Wet process** :The calcareous raw materials are crushed , powdered and stored in silos.

The argillaceous material (ie clay) is mixed with water in wash mills and stored in basins.

Powered limestone (from silos) and washed wet clay(from basins)are allowed to flow in a channel in right proportions. Further they are grind in 'grinding mills' where they are mixed to form a paste called as **Slurry.** The composition of slurry is adjusted in '**correcting basins'.**

This slurry contains about 38 to 40% water which is stored in storage tanks and kept ready for feeding in a rotary kiln.

2**) Burning**:



It is carried out in rotary kiln which is a steel tube of about 2.5 to 3.0 m in diameter. and 90 to120 m in length, lined inside with refractory bricks.

It is capable of rotating at 1r.p.m (revolution per minute) along its longitudinal axis which is placed in slightly inclined position,

Burning fuel and air is injected at the lower end which provides a hot flame and heats the interior of the kiln upto a max temp. of 1750°C

Process: The 'raw mix '*or* 'corrected slurry' is injected into the kiln at its upper end.

Due to slope and slow rotation of the kiln ,the materials fed in move continuously towards the hottest end at a speed of about 15 m per hour.

Reactions: i)Drying Zone: It is the upper part of the kiln where the temp is about 400°C and in this zone most of the water in the slurry gets evaporated.

ii) Calcination zone: It is the central part of the kiln where the temperature is around 1000°C. Here the dried slurry undergoes decomposition to form quick lime and carbon dioxide .

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

Limestone Quicklime

iii)Clinkering Zone : It is the lower part of the kiln where the temperature is between 1500 to 1700°C. Hence lime and clay combines to yield calcium aluminates and silicates.

$2CaO+SiO_2 \rightarrow Ca_2SiO_4$ (Dicalcium silicate) C_2S

$3CaO+SiO_2 \rightarrow Ca_3SiO_5$ (Tricalcium silicate) C_3S

$3CaO+Al_2O_3 \rightarrow Ca_3Al_2O_6$ (Tricalcium Aluminate) C_3A

$4CaO+Al_2O_3+Fe_2O_3 \rightarrow Ca_4Al_2Fe_2O_{10}$(Tetra calcium aluminoferrite) C_4AF

The aluminates and silicates of calcium then fuse together to form **'clinkers'**. The rotary kiln at the base is provided with another small rotary kiln. In this, hot clinkers fall and cool air is admitted from opposite direction. Air counter blast cools the clinkers. Hot air so produced is used for burning powdered coal or oil. The cooled clinkers are cooled in small trolleys.

iv) Grinding : The cooled clinkers are ground to a fine power in ball mills along with 2-3% Gypsum , so that the resulting cement does not set very quickly when it comes in the contact with water .Thus the Gypsum act as retarding agent for early setting of cement.

$$3CaO.Al_2O_3 + x\ CaSO_4.7H_2O \rightarrow 3CaO.Al_2O_3.xCaSO_4.7H_2O$$

After initial setting — Gypsum — Tricalcium Sulphoaluminate (Insoluble)

Formation of insoluble Tricalcium Sulphoaluminate prevents early reactions of setting and hardening.

iv**)Packing** : The ground cement is stored in silos from which it is fed to automatic packing machines.

Q.**5)<u>What is the chemical composition of cement?</u>**

Ans: As Per I.S.269-1975The composition of Portland cement shall satisfy the following conditions

Constituents	**Percentage**
Ratio of percentage of lime to that of silica, alumina and iron oxide is calculated by the formula $\frac{CaO-0.7SO3}{2.8SiO2+1.2Al2O3+0.065Fe2O3}$	Not less than 0.66% and more than 1.02%
Ratio of percentage of alumina to that of iron oxide	Not less than 0.66%
Weight of insoluble residue	Not more than 2%
Weight of magnesia	Not more than 6%
Total sulphur Contents	Not more than 2.75%
Total loss on ignition	Not more than 4%
Initial setting time	Not less than 30 min
Final setting time	Not more than 600 min
Compression strength	3 days Not Less Than 1.6Kg/mm^2 ,7 days Not Less Than 2.2Kg/mm^2 and 215m^2/kg

Q6) What is the chemical constitution of Portland cement? Give the characteristics of constituents.

Ans:The average composition of Portland cement is as follows:

Name of the Compound	Chemical Formula	Abbreviation uses	Average%	Setting time
Tricalcium Silicate	$3CaO.\ SiO_2$	C_3S	45	7days
Dicalcium silicate	$2CaO.SiO_2$	C_2S	25	28days
Tricalcium Aluminate	$3CaO.Al_2O_3.$	C_3A	1	1day
Tetracalcium Aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	9	1day
Calcium Sulphate	$CaSO_4$	------	5	----
Calcium oxide	CaO	------	2	-----
Magnesium Oxide	MgO	-----	4	----

Characteristics of constituents:

A)Tricalcium Silicate:C_3S

It has medium rate of hydration. It develops high ultimate strength quite rapidly and is also the highest among all the constituents. The heat of hydration is about 880KJ/Kg

B)Dicalcium Silicate:C_2S

It has quite low early strength, but develops ultimate strength of slightly less than that of C_3S

It hydrates very slowly. The heat of hydration is 420KJ/Kg

C)Tricalcium Aluminates:C_3A

It hydrates slowly and does not contribute to the strength of cement. It has the poorest early strength and ultimate strength. The heat of hydration is 250KJ/Kg.

Q7)Explain the setting and hardening of Portland cement.

Ans: When the cement is mixed with water, hydration reaction takes place resulting in the formation of gel and crystalline products by the process of setting followed by hardening of cement.

Setting: It is defined as stiffening of the original plastic mass due to initial gel formation

Hardening: It is development of strength due to crystallization.

The following reactions takes place during setting and hardening of cement.

a) Initial Setting is due to the hydration of tricalcium aluminate (C_3A)and gel formation of tetracalcium aluminoferrite. C_4AF)

1)$3CaO.Al_2O_3+6H_2O \rightarrow 3CaO.Al_2O_3+6H_2O+880KJ/Kg$

Tricalcium Aluminate Hydrated TriCalcium aluminate

Or $C_3A+6H_2O \rightarrow C_3A.6H_2O+880KJ/Kg$

2) $4CaO.Al_2O_3.Fe_2O_3+ 7H_2O \rightarrow 3CaO\ Al_2O_3+6H_2O+CaO.Fe_2O_3.H_2O+420KJ/Kg$

Tetracalcium aluminoferrite Gel

Or $C_4AF + 7H_2O \rightarrow C_3A.6H_2O+ CF.H_2O + 420KJ/Kg$

3) Dicalcium silicate starts hydrolysing to tobermonite gel ,which also contributes to initial setting

$2(2CaO.SiO_2) +4H_2O \rightarrow 3CaO.2SiO_2.6H_2O+Ca(OH)_2+250KJ/Kg$

Or $2C_2S +4H2O \rightarrow C_3S_2.6H_2O + Ca(OH)_2+250\ KJ/Kg$

4) Final setting and hardening of cement is due to the formation of tobermonite gel

crystallization of calcium hydroxide and tricalcium aluminate

$2\ (2CaO.SiO_2) +6H_2O \rightarrow 3\ CaO.2SiO_2.3H_2O+3Ca(OH)_2+500KJ/Kg$

Thus the sequence of changes during setting and hardening of cement is as follows :

Cement + water paste

↓1day

Hydration of C_3A andC_4AF

↓ 7days

Gelation of C_3S

↓28 days

Gelation of C_3S &
Gelation of C_2S

Q8) Distinguish between Dry Process and wet process.

Sr No	Dry Process	Wet Process
1)	It is used when the raw materials are quite hard	It can be used for any type of raw material
2)	Fuel consumption is low	Fuel consumption is high
3)	Process is slow.	Process is comparatively faster
4)	Cement produce is of inferior quality	Cement produce is superior quality
5)	Lower cost of production	Higher cost of Production.

NANOMATERIALS

Q1)Write a short note on Carbon-nanotubes.

Ans) Carbon nanotubes are seamless cylinders composed of carbon atoms in a regular hexagonal arrangement, closed on both ends by hemispherical end caps. They are allotropes of carbon. A single wall carbon nanotube is a one atom thick graphene sheet of graphite rolled up into a seamless cylinder.

There are two main types of nano-tubes:

a) **Single walled carbon nanotubes(SWNT):** These are formed by rolling of a single grapheme layer into a seamless cylinder

b) **Multiwalled carbon nanotubes(MWNTs) :**These are nothing but a coaxial assembly of a cylinders of SWNTs.

The nature of the bonding of a nanotube is described by applied quantum chemistry specially orbital hybridization .The chemical bonding of nanotubes are composed entirely of sp2 bonds, similar to those of graphite .

This bonding structure which is stronger than sp3bonds found in diamond provides the molecules with their unique strength . Nanotubes naturally align themselves into “ropes” held together by Vander Waal’s forces .

Under high pressure nano tubes can merge together trading some sp2bonds for sp3 bonds giving great possibility for producing strong unlimited length wires through high pressure nano tubes linking.

These tubes are extremely strong and stiff and relatively ductile. For single walled nano tubes tensile strengths range between 50& 200Gpa ,this is the strongest known ,material .

Elastic modulus values are on the order of one tetrapascal {TPa(1TPa=10^3GPa)}with fracture strains between about 5% &20%.Furthmore nano tubes have relatively low densities. On the basis of these properties the carbon nano tube has been termed the 'ultimate fiber" & is extremely promising as reinforcement in composite material.

Q2) What are the properties of carbon Nanotube.

Ans) Properties of Caron Nano Tubes(CNTs)

There are many useful and unique properties of this.

i)Electrical Conductivity-: Electrical properties of CNTs vary between semiconducting to metallic. Synthesis of CNTs gives a mixture of about two third of semiconducting tubes and 1/3 of metallic tubes .

Tubes with arm chair structure have been shown to be metallic while all other types of semiconductor, their conductivity has shown to be a function of their chirality, the degree of twist as well as their diameter..

SWNTs are metallic, where as conductivity in MWNTs is quite complex .Some type of arm chair structured CNTs appear to conduct better than other metallic CNTs.

The conductivity and resistivity of ropes of single walled nano tubes has been measured by placing electrodes at different parts of the CNTs. The resistivity of the SWNT ropes is of the order of 10^{-4} ohm.cm at 27°c .This means that single walled nano tube ropes are the most conductive carbon fibers known.

The SWNT ropes should be able to sustain much higher stable current densities as high as 10^{13} A/Cm^2. Individual SWNTs may contain defects which allow them to act as transistors. Therefore joining CNTs together may form transistor like devices.

A nano tube with a natural junction behaves as a rectifying diode-that is a half transistor in a single molecule .It is also found that single walled nano tubes can route electrical signals at speeds up to 10GHz when used as interconnects on semi-conducing devices.

ii)Strength and Elasticity-: The carbon atoms of a single sheet of graphite form a planar honeycomb lattice, in which each atom is connected via strong chemical bond to 3 neighbouring atoms.

Because of these strong bonds, the basal plane elastic modulus of elasticity of graphite is one of the largest of any known material .

For this reason, CNTs are expected to be the ultimate high strength fibers. SWNTs are stiffer than steel & are very resistant to damage from physical forces .

Pressing on the tip of a nano tube will cause it to bend ,but without damage to the tip .When force is removed ,the nanotube returns to its original state .This property makes CNTs very useful as probe tips for very high resolution scanning probe microscopy .

The current Young's modulus value of SWNTs is about 1 Tetra Pascal .This value is being widely debated and valued of 1.8 TPa and significantly higher than that have also been reported .The difference probably arise through different experimental measurement technique .

Theoretically is has been established that the young's modulus of SWNTs depend on the size and chirality ,ranging from 1.22Tpa to 1.26Tpa.A value of 1.09 Tpa has been calculated for generic nano tube.

iii)Thermal Conductivity and Expansion-:

Ultra small SWNTs have even been shown to exhibit superconductivity below temperature 20°K.

It has been found that these exotic strands already heralded for their unparalleled strength and unique ability to adopt the electrical properties of either semiconductors or perfect metals may someday also find applications as miniature heat conduits in a host of devices and materials .

The almost zero in plane thermal expansion but large inter plane expansion of single walled nano tubes implies strong in plane coupling and high flexibility against non axial strains.

CNTs find their applications in nanoscale molecular electronic sensing and actuating devices or as reinforcing additive fibers in functional composite materials .

CNTs show very high thermal conductivity .Therefore nanotube reinforcements in polymeric materials & thermo mechanical properties of the composites.

iv) Field Emission-:

Results from the tunneling of electrons from a metal tip into vacuum under application of a strong electric field .

The small diameter and high aspect ratio of CNTs is very favorable for field emission .Even for moderate voltage a strong electric field develops at the free end of supported CNTs because of their sharpness.

It is establishes that these field emitters are superior to conventional electrons source and may find their way into all kind of application particularly flat panel displays.

It has also been observed that together with electrons light is emitted as well. Thus luminescence is induced by the electrons field emission. The light emission occurs in the

visible part of the spectrum and can sometimes be seen with the naked eye.

v)High Aspect Ratio-: CNTs represent high aspects ratio conductive additive for plastics of all types. Their high aspect ratio means that a lower loading of NTs is needed compared to other conductive additive to achieve the same electrical conductivity .

This low loading preserves more of the polymer resins toughness especially at low temperatures as well as maintaining other key performances properties of the matrix resin.

CNTs have proven to be an excellent additive to impart electrical conductivity in plastics.

Their high aspect ratio, about 1000:1 imparts electrical conductivity at lower loading compared to conventional additive materials such as carbon black, chopped carbon fiber or stainless steel fiber.

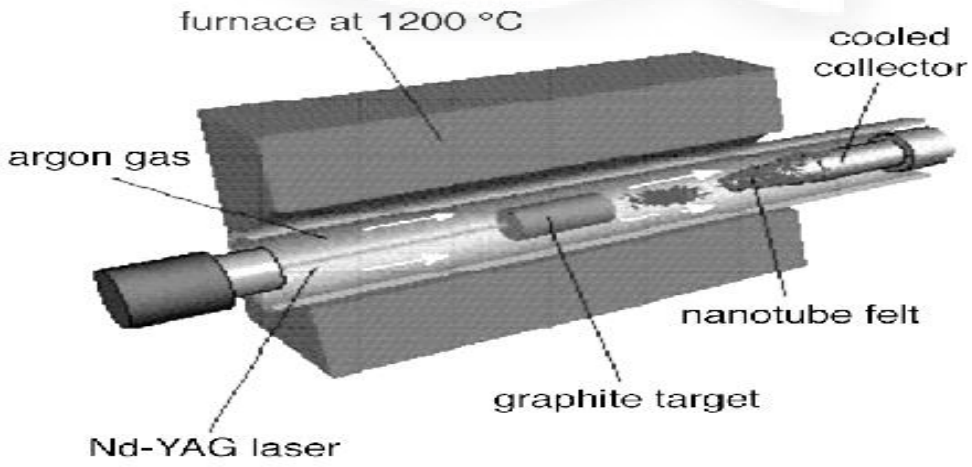
vi) Highly Absorbent: The large surface area and high absorbency of CNTs make them ideal candidates for use in air ,gas, water filtration .A lot of research is being done in replacing activated charcoal with CNTs in certain ultra high purity application

Applications of carbon Nano Tubes-:

- The utility of carbon nano tubes is found mainly in molecular electronics or computers.
- They are used in field emission based flat panel displays .
- They can be used as chemical sensor and ultra sensitive electromechanical sensors .
- They find application in novel semi-conducting devices .
- It is used in batteries and fuel cells .
- It is used as filling material in polymer composites.
- IT is anticipated that future application of carbon nano tube will include diodes and transistors.

Q3) Explain the production of carbon nanotubes using Laser Furnace method and gives its application.

Ans:



Process:

The apparatus consists of a furnace , a quartz tube with a window, a target carbon composite doped with catalytic metals , water cooled tray and flow systems for the buffer gas to maintain constant pressure and flow rates. A laser beam is introduced through the window and focused on the target located in the center of furnace. A target is vaporized at high temperature. Inert gas (He or Ar) is passed through the tube during the process, which helps in transfer of soot to copper collector being cooled by water. SWCNTS condense as ropes or bundles of SWCNTS.

ADVANTAGES:

1) High quality SWNT production, diameter control , investigation of growth dynamics and the production of new materials.

2) High quality SWNT with minimal defects and contaminants, such as amorphous carbon and catalytic metals have been produced.

3) High crystallinity has been known to originate in high power laser vaporization , homogeneous annealing conditions and target materials without hydrogen .

APPLICATIONS:

1) It is used as electrodes in batteries and capacitors

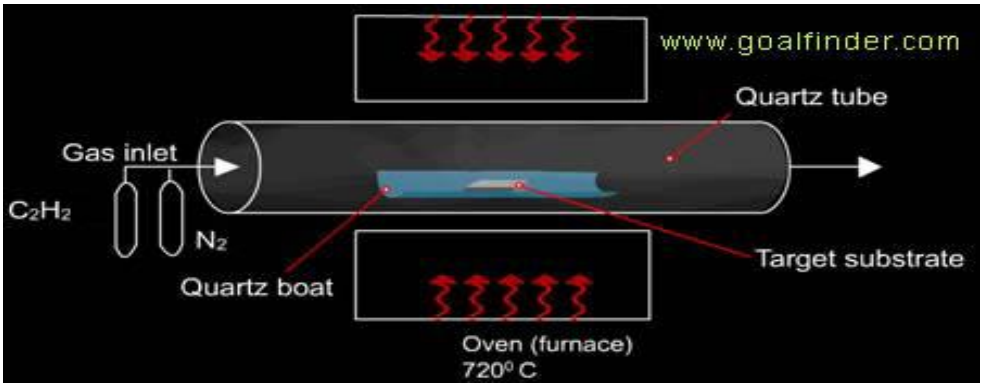
2) A ceramic materials reinforced with carbon nanotubes is far tougher than conventional ceramics.

3) CNT based air and water filtration are already developed and these filters cannot only look the smallest particle but also kill most bacteria.

4) CNTS intrinsically have an enormously high surface area and hence can be exploited in the search of new catalysts and catalytic behavior.

5) CNTS represent a very small ,high aspect ratio conductive additive for plastics of all types.

Q4) Explain the production of CNTS using chemical vapour deposition method.



In this process a mixture of hydrocarbon gas (ethylene ,methane or acetylene)and a process gas (ammonia ,Nitrogen, hydrogen) is made to react in a reaction chamber on heated metal substrate to a temperature of around 700°c-900°c at atmospheric pressure.

CNTS are formed as a result of decomposition of hydrocarbon gas deposits and grow on metal catalyst (substrate)

- The catalysts particle can stay at the bottom or tap of growing carbon nanotube.
- The use of the catalyst and preparation of the substrates is one of the most important factors in CVD ,this substrate will define the nature and type of carbon nanotubes formed. Silicon is generally used as a substrate material.
- This process is able grow a significant amount of SWCNT in a couple of hours. Keeping selectivity towards SWCNT better than 80%
- Catalyst is most effective when both metals CO, Mo are present at a time on silica substrate with low CO-MO ratio.
- **ADVANTAGE-:**
- A)Reaction process and reactor design is simple reaction is easy to control.
- B)Raw material are abundant and available readily in the form of gases.
- C)Process is unique for the production of vertically aligned nanotubes . No other process can produce aligned nanotubes.

Q5) Write a short note on Fullerene or Give the preparation, properties and uses of Fullerene.

Ans)

Defination : Fullerenes are hollow, pure carbon molecules in which the carbon atoms lie at the vertices of a polyhedron with 12 pentagons faces and any number of hexagonal faces.

Structure: It is the most stable cage cluster in which 12 pentagons are present and all the pentagons are separated by hexagons.

In the C60 molecule, carbon atoms are bonded in an isosahedral structure which is made up of 20 hexagons and 12 pentagons.

After the first discovery of Buckminister Fullerene C60,other types of fullerenes C70,C76,C78,C80 etc have also been discovered.

Preparation: An arc was caused between two graphite rods to burn them in a helium atmosphere. This resulted in producing the carbon condensate .ie .C 60 fullerene.

C60 was isolated by using an organic solvent. This method gave considerable quantity of fullerene C60.Later fullerene C50,C70,C76,C78,C80 and C90 were also produced.

Properties of C60 Fullerene:

- It is a mustard coloured solid, which appears brown to black with increasing thickness of its film.
- On sublimation , it forms translucent magenta face-centered cubic crystals.
- It is moderately soluble in aromatic hydrocarbons giving magenta solution.
- As a pure solid, it is electrically insulating. With proper impurity addition, it can be made highly conductive and super conductive.
- With alkali metals, they form alkali fullerides, which are superconducting.

Uses of Fullerene:

- It is used in synthetic , pharmaceutical and industrial applications, as inhibitor of the HIV protease, to make new drugs or proteins.
- It is used in cosmetics preparation applicable in halting the ageing process.
- It is used as light emitting diodes(LED),molecular electronics and computing, as lubricants, rocket fuel etc.
- It shows odd magnetic and electronic properties due to its shape being intermediate between a sphere and a disk.
- In diverse areas as superconductivity and materials chemistry/physics, fullerenes have been useful.
