28/7

Nano chemistry

Nanochemistry
- Synthesis of nanomaterials.
- characterisation of Nanomaterials.
- Properties and Applications of Nanomaterials.

→ If the particles sizes are in the range of 1-100 nm then they are generally called as Nano particles (or) Nanomaterials.

→ They may have one dimensional structure (eg: nanorods, nanowires)

→ Can have two dimensional structure. (eg: surface films)

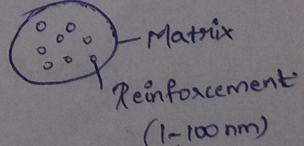
→ They may have 3D structure. (eg: Particles)

→ Nanomaterials posses large surface atoms per unit volume

$$\left[\frac{\text{Surface Area of sphere}}{\text{volume}} = \frac{3}{r}\right]$$

Different Nano materials include :

- Nanowire, nanorods.
- carbon nano-tubes., Graphene
- Mesoporous materials. eg: Zeolites, Aerogel, Xerogel.
- Organic - Inorganic Hybrids.
- Core shell structures
- metal polymer core-shell structure. eg: Ag - polystrene.
- Metal oxide polymer core shell structure
- Nanocomposites.



Synthesis of Nanoparticles

Synthesis of Nanoparticles

Top-down Approach | Bottom up Approach

Top-down Approach

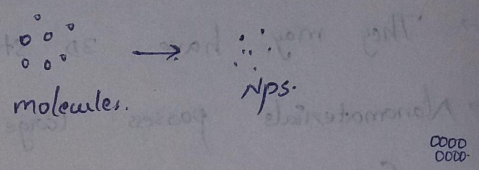
→ Nano particles are generated from size reduction of Bulk materials using physical methods

→ This is done by mechanical grinding / milling.

→ Gives broad size distribution

Bottom up Approach

Nano particles are generated from atomic (or) molecular level using physical (or) chemical methods



→ Homogeneous - chemical composition.

→ This is done by pyrolysis

1. Gas phase synthesis
2. liquid phase synthesis.

1, Gas phase eg:

Spray pyrolysis

chemical vapour deposition method (CVD)

2, liquid phase synthesis.

eg. - Precipitation method

- sol gel method
- solvothermal synthesis
- Hydrothermal synthesis
- Microwave Assisted syn.,
- Microemulsion.

Biomolecule syn.,

Arginine + $CuCl_2$ → CuO.

Cystene. ↓ CuS.

Advantages of Bottom-up Approach over Top-down Approach.

→ Bottom-up Approach helps to produce homogenous chemical composition, better ordering (short and long range), with less surface defects.
This is because the B-U approach is mainly given by reduction of Gibbs free energy.
→ less internal stress

(This is due to reduction of its free energy) so that nanostructures or nanomaterials produced are in a state closer to thermodynamic equilibrium state, whereas the top down approach introduces internal stress and contaminations.

4/8 Nano Material Synthesis

Precipitation Method: Fe_3O_4 Nano Particles (Iron Ferrite)

- $FeCl_2$ solution + $FeCl_3$ solution. (1:2 Molar ratio) in water.

$\downarrow$ NaOH or NH_4OH, 80-90°C

$Fe(OH)_2 \cdot Fe(OH)_3$ Precipitate.

$\downarrow$ wash, dry.

$FeO \cdot Fe_2O_3$ (or Fe_3O_4 NPs) — Nano Particles

- Ethylene glycol + $FeCl_2$ solution + $FeCl_3$ solution

B.P - 192°C — solvent with high BP

$\downarrow$ 160°C, 6hr, Urea NH_2CONH_2 (90-100°C degradation)

$Fe(OH)_2 \cdot Fe(OH)_3$ Precipate.

$\downarrow$ wash, dry.

$FeO \cdot Fe_2O_3$ (or Fe_3O_4 Nano Particles)

- Ethylene glycol + $CoCl_2$ + $FeCl_3$ solution $\xrightarrow[160°C]{Urea}$ $Co(OH)_2 \cdot Fe(OH)_3$ $\xrightarrow{wash, dry}$

$\downarrow$ same process as above

$(CoFe_2O_4)$ NPs. ← $CoO \cdot Fe_2O_3$

Ethylene glycol + $NiCl_2$ + $FeCl_3$ solution

$\downarrow$ same process

$NiFe_2O_4$

Ethylene glycol + $CaCl_2$ + $FeCl_3$ solu

$\downarrow$ same process

$CaFe_2O_4$

Sol gel Method :

Sol : Colladial solution.

Gel : Porous ~~Pa~~ Material.

Reactive metal Precursor

Metal Alkoxide ($Ti(OBut)_4$
$Si(OC_2H_5)_4$) + H_2O (or) any organic solvent

↓

ppt (gel)

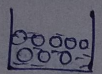
↓

washed & dried

↓

Calcined at elevated temp.

Sol:



A sol is ~~a~~ A colloid that has continuous liquid phase in which solid are suspended in liquid

Gel: Gel is a Porous, three dimensional solid network enclosing a continuous liquid ~~at~~ ~~des~~ phase.

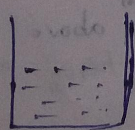
→ Solgel method is one of the most popular solution processing maker method for preparing nanoparticle materials.

→ In this method reactive metal ~~precu~~ alkoxide such as Titanium Butanoxide, ($Si(OC_2H_5)_4$) is hydrolysed with water and the hydrolysed species is allowed to condense with each other to form precipitate of metal oxide particles.

→ The obtained ppt is washed dried and then calcined at elevated temp, to form metal oxide Nanoparticles

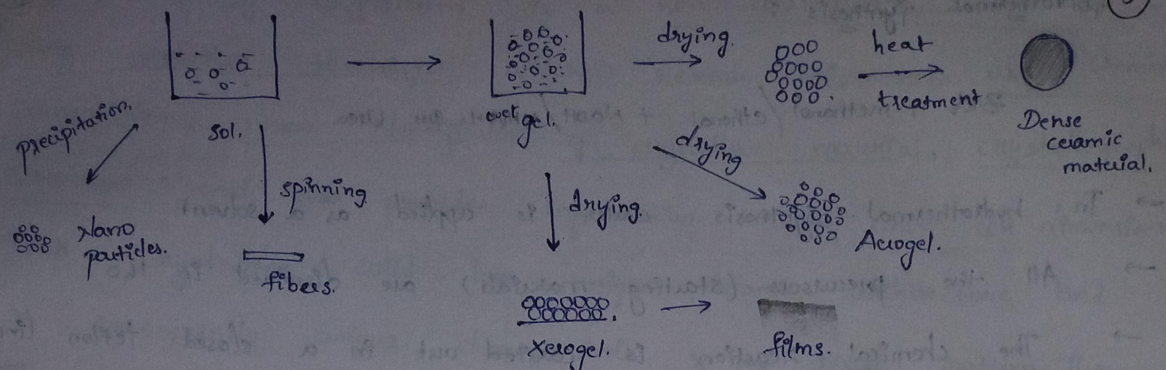
→ By using this method we can have the Nanoparticles as Glasy fibers.

Various Steps involved in sol. gel process :



solution of precussor

↓ H_2O hydrolysis & Condensation



→ In the first step, the hydrolysis and condensation reaction takes place resulting in formation of Inorganic polymer.

→ Hydrolysis leads to a sol and further condensation results in gel.

→ Upon the removal of pore liquid the network gets shrinked and yield Xerogel.

→ On drying, the network doesn't collapse and results in Aerogel.

→ By using this method, the material can be shaped into films, fibers, particles and dense ceramic materials by heat treatment

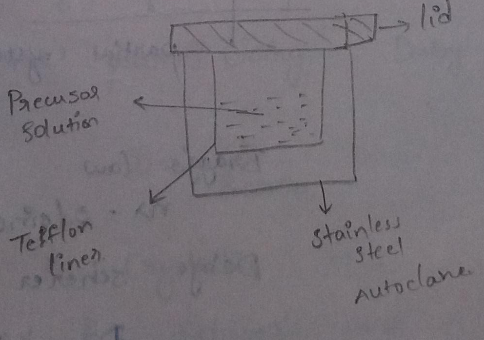
Reactions involved in sol-gel process :

$$\equiv M-OR + H_2O \longrightarrow \equiv M-OH + R-OH$$

$$\equiv M-OH + \equiv M-OH \longrightarrow \equiv M-O-M\equiv + H_2O \quad \text{(Oxolation)}$$

$$\equiv M-OH + \equiv M-OR \longrightarrow \equiv M-O-M\equiv + R-OH \quad \text{(Alkoxolation)}$$

Hydrothermal Synthesis :



$ZnCl_2 + NaOH / NH_4OH$ (or) Urea $+ H_2O$

~~Solvothermal Synthesis~~ :

ZnCl₂ + methanol / ethanol + NaOH / NH_4OH or Urea

→ In hydrothermal synthesis water is applied as a solvent

→ All the precursors (starting materials) are dissolved in H_2O

→ The chemical reaction is carried out in a closed teflon lined, stainless steel autoclave above the b.p of water

Solvothermal synthesis :

→ In solvothermal synthesis, Organic solvents like methol, ethanol are employed.

→ All the precursors are dissolved in organic solvent

→ The chemical reactions are performed in a closed teflon lined, stainless steel autoclave above the b.p of ~~H_2O~~. solvent

11/8

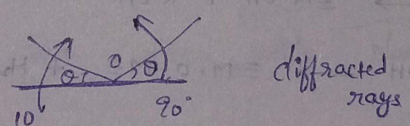
Characterization of Nanomaterials :

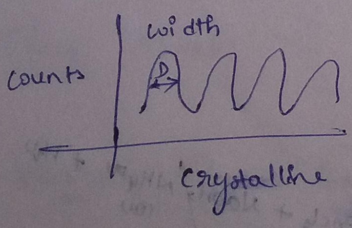
1, X-ray diffraction (XRD)

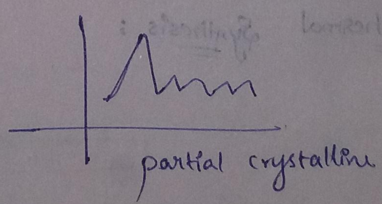
2, Scanning Electron Microscopy (SEM)

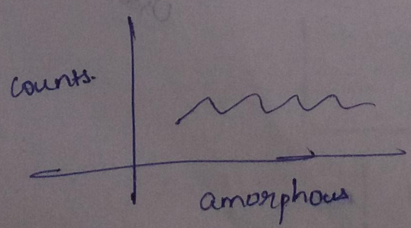
3, Transmission Electron microscopy (TEM)

Principle of XRD :









Bragg's law

$$n\lambda = 2d\sin\theta$$

Debye scherer Equation

$$D = \frac{K\lambda}{B\cos\theta_B}$$

XRD : X-ray diffraction is a non constructive rapid ~~any~~ analytical tenchinque which reveals information about chemical composition, phase identification of crystalline material, crystallographic structure and also provide information about unit cell dimensions. Each crystalline solid has unique atomic architecture and as consequently unique characteristic x-ray powder pattern. These These patterns can be used as finger prints for identification of solid phases. In XRD, x-ray beom is incident on the specimen or sample and is diffracted by a crystalline phase present in the sample. Acc to Braggs law. $n\lambda = 2d\sin\theta$

where n = integer.

λ = incident wavelength.

d = spacing b/w two ~~atom~~ atomic planes or layers

$\sin\theta$ = sine of angle b/w incoming x-rays and the atomic layer.

These diffracted rays are then detected possesed and proceesed and obtained. By scanning the sample through a range of 2θ angles.

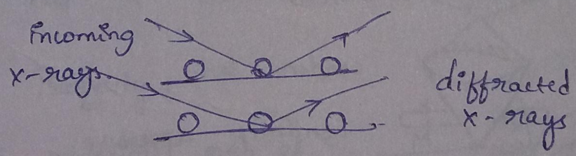


Fig: showing incident x-rays and the diffracted x-rays from a pair of the ~~peak. Using~~ atom in a lattice plane

Crystalline size of Nanoparticles can be estimated from the width of the peak. Using Deby Scherer Equation

$$D = \frac{K\lambda}{B\cos\theta_B}$$

D = Crystalline size

K = Scherer's const.

λ = wavelength of X-ray

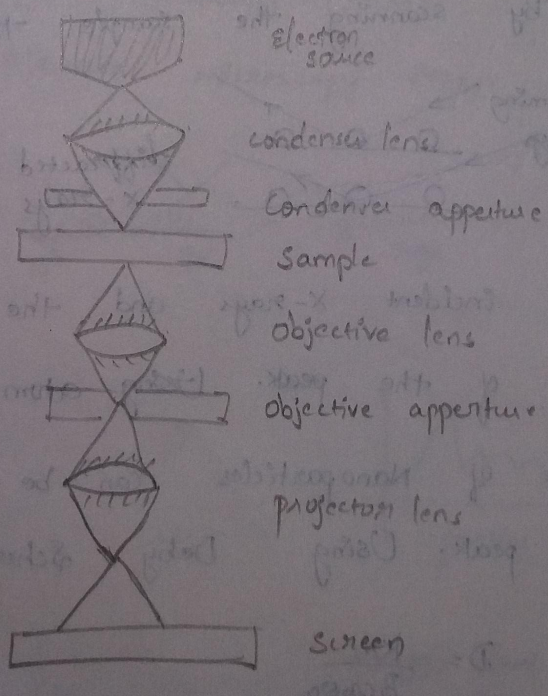
B = Full width of ht. maximum of a diffracted peak.

θ_B = angle of diffraction

2, Scanning Electron Microscopy (SEM):

3, TEM: Transmission Electron Microscopy: It is a technique where by a beam of electrons is transmitted through an ultra beam specimen and interacts as it passes through the sample. An image is formed from the electrons transmitted through the specimen which is then magnified and focussed by an objective lens and the image appears on the screen

Application: Both biological and chemical science, it reveals info about dispersion of Nano particles in polymer matrices of Nano-Composites, fibres, nano coatings etc.



Properties of Nanomaterials and Their Applications

→ Materials in the micrometre scale have the same physical properties as that of bulk.

However, the materials in the Nanometer scale have physical properties distintively diff. from that of data bulk materials.

1, Surface Area
2, Melting Point
3, Crystal structure
4, Magnetic Property
5, Band Gap.
6, Catalytic Property.
7, Electrical property.

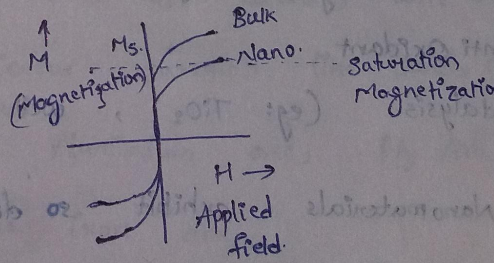
1, Surface Area : The nanoparticles have large surface area compared to the bulk materials.

2, Melting Point : They require low temp. to melt. M.P ↓ dramatically as the particle size get reduced.

3, Crystal structure : The crystal structure of Nanomaterial is same as that of bulk structure with diff. latice Parameters.

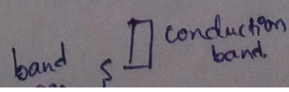
4, Magnetic Property :

For Magnetic materials such as Iron (Fe), cobalt (CO), nickel (Ni), Fe_3O_4, $CoFe_2O_4$ etc.



The magnetic Properties are size dependent. Magnetic moments of Nanoparticles is found to be very less when compared them with bulk size.

5, Band Gap : It is the Energy needed to promote an $\bar{e}$ from valence band to conduction band. The band gap ↑ with reducing size of particles.



For semiconductors, such as, ZnO, CdS, Si etc band gap changes with size.

6, Catalytic Property : The large surface area to volume ratio, the variations in Geometry and electronic structure of nanomaterials have strong effect on catalytic properties.

7, Electrical Property : The electrical Properties of Nanomaterials vary between metallic to semi conducting materials. It depends on diameter of Nanomaterials.

Applications of Nano ~~Particles~~ Materials :

→ Nanomaterials have applications in ~~energy~~ -

→ Energy storage devices : eg: Solar cells, batteries, fuel cells, super capacitors.

→ Memory storage devices : eg Hard disk.

→ Electromagnetic sheilding :

→ Microwave absorption :

→ Anti corrosive coatings.

→ ~~Anti~~ Drug delivery.

→ Anti Oxidant

→ Catalysis. (eg: TiO_2, well known as Photocatayst)

Why Nanomaterials exhibit so different physical properties from that of Bulk ?

Ans: There are two reasons.

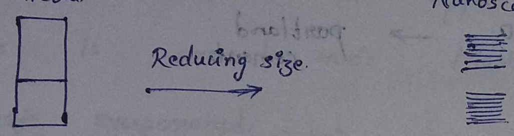
1, Surface effects.

2, Quantum Confinement or Quantum size effect.

1, Nano materials have relatively large surface area when compared to same volume or mass ~~mass~~ of the material produced in a larger form.

2, In Nanocrystals the electronic energy levels are not continuous as in the bulk. but are ~~descreate~~ discret. (separate). because of the confinement of electronic wave function. to the physical dimensions of the particles. This phenomenon is called Quantum Confinement. and therefore nanocrystals are also refered to as Quantum dots. (QDs)

Bulk metal. Nanoscale metal.



close lying bonds

Unbounde electron have motion that is not confined

separation between valence band and Conduction band

Electron motion becomes confined and quantization sets in.

1/9

CEMENT

Manufacturing process of Portland Cement :

Raw Materials :

1, CaO (lime) component (Calcareous) such as calcite, lime stone.

2, Silica component i.e., siliceous materials like sand, clay (i.e. Argillaceous)

3, Al_2O_3 component, such as Aluminium ore, Fly Ash, clay.

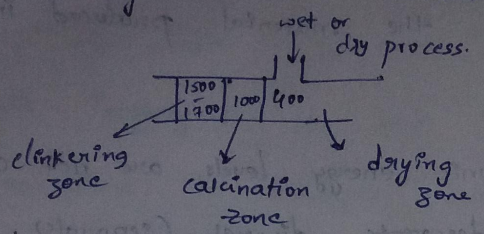
4, Fe_2O_3 component such as iron ore

Operations which are involved.

1, Crushing. — Primary Crushing / Secondary Crushing

2, Mixing — dry process → fine ground powder / wet process. → slurry.

3, Burning : Done in Rotatory kiln.



$CaCO_3 \rightarrow \underset{\text{quick lime}}{CaO} + CO_2$ (takes place in calcination zone)

4, Grinding. :

$\text{clinkers} + \underbrace{CaSO_4 \cdot 2H_2O}_{\substack{\text{gypsum} \\ 2\text{-}3\%}} \rightarrow \text{portland cement}$

67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3

Manufacturing process of Portland Cement :

Raw materials required are : limestone, clay and sand

Operations :

Crushing :

It is done by primary crusher which reduces the size of lime stone to 5 inch. followed by secondary crusher which further reduces the size to 3/4 inch.

Mixing :

Raw materials such as lime stone, clay and sand are mixed together in a grinding mill. It is done by either dry process or wet process.

The dry process is fine ground powder and wet process gives slurry in presence of water.

Burning :

Burning is usually done in rotory kiln., which is steel tube about 2.5 - 3 meter in diameter and 90-120 m. in length, lined with refractory bricks.

Both dry and wet process are ~~filled~~ fed in rotory kiln where burning results in actual chemical changes.

There are different zones in rotary kiln.

1, Dry zone 2, Calcination zone 3, Clinkering zone.

1, Dry zone : It is the upper part of kiln where the temperature is around 400°c. Most of the water present in slurry gets evaporated.

2 Calcination Zone : It is the central part of kiln where the temperature is around 1000°c. Lime stone of dry mixture or slurry undergoes decomposition to form quick lime

$$CaCO_3 \rightarrow \underset{\text{quick lime}}{CaO} + CO_2$$

3, Clinkering Zone : It is the lower part of kiln where the temperature is between 1500°c - 1700°c. Here, lime and clay undergoes chemical fission yeilding calcium silicates and aluminates

C - CaO
S - SiO_2
A - Al_2O_3
F - Fe_2O_3

Yielding :

$$2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2 \cdot C_2S$$

$$3CaO + SiO_2 \rightarrow 3CaO \cdot SiO_2, \; C_3S$$

$$3CaO + Al_2O_3 \rightarrow 3CaO \cdot Al_2O_3 \; C_3A$$

$$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3, \; C_4AF$$

Grinding :

From clinker storage, the material is transported to final grinding where it is ground to requisite fineness.

To control setting time of portland cement 2-3 % gypsum is added. The mixture of clinker and gypsum powder is called Portland cement.

Flow diagram for manufacturing Portland cement

Raw Materials

limestone → Crushing

clay → Washing

Crushing, Washing → Proportioning

↓

Grinding (Mixing)

Dry process → Dry powder

Wet Process → Slurry

Dry powder, Slurry → Rotatory kiln ← Pulverised Coal ← Coal

↓

Clinkers

↓

Grinding

↓

Fine clinkers

↓ ← Gypsum

Portland cement

↓

Packaging

↓

Shipment

Flow diagram for manufacturing Portland Cement

8/9

Cement

Cement have the property of setting and hardening under water by virtue of chemical reaction with water. Therefore called hydrolic cement.

Cement

- Natural cement → Argillaceous (Al+Si) limestone 20-40% clay containing lime stone.
- Puzzolana cement → Natural puzzolrum (deposites of volcanic ash + slaked lime) $Ca(OH)_2$
- slag cement → Blast furnace slag + Hydrated lime.
- Portland cement → 1500-1700°c Argillaceous + Calcareous

→ Cement may be broadly described as the material possesing adhesive and cohesive ~~particles.~~ properties and capable of ~~barn~~ bonding —

- Materials like stones, bricks and building blocks.

→ The main constituent of cement are compounds of calcium (Calcaroeus) and Al + Si (Argillaceous)

→ Cement have property of setting and hardening under water by virtue of chemical reaction with water.

Therefore called hydrolic cement.

It is classified into four catogeries.

1. Natural cement
2. Puzzolana cement
3. Slag cement
4. Portland cement

1. Natural Cement :

It is made by naturally occuring Argillaceous limestone (20-40% clay containing lime stone) at high temp.

and subsequently pulvarizing (grinding) calcined mass

During calcination, silica and alumina present in sufficient quantites combines with calcium oxide to form Calcium silicates and aluminium silicates.

Natural cement contains hydrolic properties. ~~It~~ which sets quickly and

3 Puzzolana cement

It is the oldest cementing material invented by . and used by them for preparing concrete or construction of walls.

It consists of silicates of aluminium, iron and calcium

It is made by mixing and grinding of natural puzzolana and slaked lime. It consists hydrolic properties.

3 Slag cement :

It is made from blast furnace slag and lime. It sets more slowly and have lower strength.

4 Portland cement :

It is obtained by calcining together an intimate and properly proportion mixture of Argillaceous (clay containing) and Calcareous (lime containing) raw materials. at about 1500°c.

It is the most important cementic material

Chemical composition of portland cement

Compound	Chemical formula	Abbrivation
Tricalcium silicate	$3 \cdot CaO \cdot SiO_2$	C_3S
Dicalcium silicate	$2\, CaO \cdot SiO_2$	C_2S
Tri calcium Aluminate	$3\, CaO \cdot Al_2O_3$	C_3A
Tetracalcium Aluminoferrite	$4 \cdot CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF
Calcium sulphate	$CaSO_4$	
Calcium oxide	CaO	
Magnesium oxide	MgO	

Characteristics

Tri calcium silicate

→ It ~~cohtch~~ has medium rate of ~~aggration~~ hydration. It develops high - ultimate strength rapidly. The ~~rate~~ heat of ~~aggration~~ hydration is about 880 kJ/kg.

Dicalcium silicate

→ It has ~~gai~~ low early strength. but develops ultimate strength slightly less than C_3S. It hydrates very slowly. Heat of ~~aggresion~~ hydration is 420 kJ/kg.

Tricalcium Aluminium.

→ It hydrates very slowly and doesnot contribute much to the strength of cement. Ultimate strength is poorest among all the constituent of cement. The heat of ~~aggresion~~ hydration is about 250 kJ/kg

→ Tetracalcium Aluminofersite

→ Acts as a flux in the cement kiln, but its ~~aggresion~~ hydration products play ~~different~~ little part in the setting and hardening process.

contributes colour to the cement

15/9 Setting of cement :

The process of solidification of cement comprises of setting and hardening. When water is mixed with cement it forms 'fluid paste' and hydration of cement takes place. The mixture ultimately becomes stiff and then hard. This process is called 'Setting'

Hardening :

It is the development of strength due to crystallization. It depends on amount of Gel formed and the extent of crystallization. In the Initial setting of cement paste hydration of C_3S , C_2S , C_4AF, C_3A takes place and the reactions are.

$$3\,CaO\,Al_2O_3 + 6\,H_2O \longrightarrow 3\,CaO \cdot Al_2O_3 \cdot 6H_2O$$ (Hydrated Tricalcium Aluminate)

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

$$2(2\,CaO \cdot SiO_2) + 4\,H_2O \longrightarrow 3\,CaO \cdot 2SiO_2 \cdot 6H_2O + Ca(OH)_2$$

Tobermonite gel.

The final setting and hardening of cement paste occurs due to the formation of Tobermonite gel and crystallization of calcium hydroxide and hydrated tricalcium Aluminate

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

Tobermonite gel. Crystalline

(or)

$$2C_3S + 6H_2O \longrightarrow C_3S_2 \cdot 3H_2O + 3 \cdot Ca(OH)_2$$

Decay of cement :

The cement constituents are attacked by water, salty solutions and acidic solutions. Although cement concrete i.e., mixture of cement, sand and course aggregates is quite strong. But due to the presence of free lime (CaO) on long exposure, severe deterioration occurs and structure weakens.

Acidic water can attack the cement structure. With decrease in pH, the rate of attack increases. Dissolved CO_2 and other organic and inorganic acids. are responsible for acidity of water.

The decay of cement is due to leaching out of free lime from it due to chemical action of CO_2 present in acidic water. and the reactions are

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{insoluble}}{CaCO_3 \downarrow} + H_2O$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$$

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

The insoluble $CaCO_3$ futher reacts with CO_2 and water, to form soluble $Ca(HCO_3)_2$. This process continues till the depletion of CO_2 occurs.

The decay of cement is due to hydrolysis of silicates and aluminates by water. and dissolves the liberated calcium hydroxide. ~~CaO~~. $Ca(OH)_2$

Prevention :

The decay of cement can be minimised by putting the surface with 'epoxy resin paint' or 'linseed oil.'

This coating makes inpermeable to acidic water

Types of Portland Cement :

1, Rapid Hardening Cement

2, low Heat Cement

3, Oil well cement

4, Hydrophobic or water proof cement

5, White cement

6, Sulphate Resisting cement

7, Expansive Cement

8, Moderate Heat Cement