COMPOSITE MATERIALS

Definition: Composites are materials made up of two or more physically and/or chemically different phases with an interface separating them.

Constituents of Composites: Two essential constituents of composites are

Matrix phase: It is the continuous body constituent (Dispersion phase) which encloses the composite and gives its bulk form. It may be polymer, metal or ceramic material.

Dispersed phase: It is the Structural constituent (Dispersed phase) which determines internal structure of the composite and gives its bulk form. It may be Fiber, Particulate, Flakes or Whiskers

CLASSIFICATION OF COMPOSITES

Composites are classified into several types as following

1. **Based on matrix phase**

- Metal matrix composites: a metal matrix composite (MMC) is a composite material with fibers or particles dispersed in a metallic matrix, such as copper, aluminum, or steel
- Polymer matrix composites: a polymer matrix composite (PMC) is a composite material composed of a variety of short or continuous fibers bound together by a matrix of organic polymers.
- Ceramic matrix composites: ceramic matrix composites (CMCs) are a subgroup of composite materials and a subgroup of ceramics. They consist of ceramic fibers embedded in a ceramic matrix. The fibers and the matrix both can consist of any ceramic material, including carbon and carbon fibers.

2. **Based on fibre reinforcement composites**

- **Glass fibre reinforced composites:** Fiber glass reinforced composites can be produced by properly incorporating the continuous or discontinuous glass fibers with in a plastic matrix. Polyesters are most commonly used matrix material.
- **Carbon fibre reinforced composites:** Carbon fibers like (graphite, Graphenes or carbon nano tubes) dispersed in the polymer matrix. They provide excellent resistance to corrosion, lighter density, retention of desired properties even at elevated temperatures.
- **Aramid fibre reinforced composites:** Aramid fibers, short for aromatic polyamide, are a class of heat-resistant and strong synthetic fibers. They are used in aerospace and military

applications, for ballistic-rated body armor fabric.

- **Alumina fibre reinforced composites:** Fibers of alumina or carbon dispersed in metal or metal alloy matrix which possesses improved specific strength, stiffness, wear resistance, creep resistance and resistance to thermal distortion etc.

3. Based on particle reinforcement composites

- **Large particles:** The most common large-particle composite is concrete, made of a cement matrix that bonds particles of different size (gravel and sand).
- **Dispersion strengthened**: Very small particles of the range 10-100nm size are used in this which improves strength and hardness.

4. Based on layers

- **Layered composite:** A Laminar composite consists of two-dimensional sheets or panels that have preferred high strength direction, successive oriented fiber reinforced layers of these are stacked and then cemented together in such a way that the orientation of the high strength varies with each successive layer.

  Example: Plywood, Copper bottom steel articles
- **Sandwich composite:** These usually consist of two strong outer sheets called faces, separated by a layer of less dense material called core which is of lower strength and lower stiffness. Face materials: ply wood, titanium, steel, and aluminum alloy and Core materials: Synthetic rubber, Foamed polymer

PROPERTIES OF COMPOSITES

- Possibility for electrical or thermal conductivity.
- Enhanced resistance to abrasion.
- Reduced weight and density.
- Potential for magnetic properties.
- Adjustable optical characteristics.
- Resilience to shock.
- Resistance to fatigue and creep
- High-strength, high-modulus fibres are incorporated into a matrix to create a composite material (polymer, metal, or ceramic).

APPLICATIONS OF COMPOSITES

- automobiles industries: Automobile parts like components of engine, spray nozzle, mud guards, tires etc
- Aeronautical applications: structural components like wings, body & stabilizer and fuel of aircraft, rocket army missiles in military etc
- Marine applications: shaft, hulls, spars and other part of ships
- Safety equipment like helmets
- Sport equipment like tennis rockets, golf sticks, other safety equipment
- Communication Industry like preparation of antennae and electronic circuit boards

REFRACTORIES

Definition: Refractories are the inorganic substances which can withstand very high temperatures without softening deformation. The main function of refractories varies depending on the purpose. They are used for the construction of kilns, ovens, crucibles, retorts, furnaces etc.

CHARACTERISTICS OF A REFRACTORY MATERIAL

Good refractory material should possess the following characteristics

- High temperature resistance under working conditions.
- Good abrasion resistance by dusty gases and molten metals
- High mechanical strength, structural strength and crack resistance to withstand overlying load.
- Thermal strength to withstand thermal shock due to rapid and repeated temperature fluctuations.
- They should posses low thermal coefficient of expansion

CLASSIFICATION OF REFRACTORIES

a) Refractories are classified into three types based on their chemical nature as following

1. **Acidic refractories:** They are made of acidic materials such as alumina, silica. These are resistant to acidic slags, but attacked by basic materials. **Ex.** Silica, alumina, fireclay refractories
2. **Basic refractories:** Basic refractories are those which consist of basic materials, but attacked by acidic materials. **Ex.** Lime brick and Dolomite
3. **Neutral refractories**: They are not completely neutral in chemical sense. They consist of weakly basic/acidic materials. **Ex.** Graphite and Chromite

b) Refractories are classified into three types based on the temperature range of fusion as following

Refractory type	Fusion range
Low refractory	1580-1780 ^oC
High refractory	1780-2000 ^oC
Super refractory	> 2000 ^oC

PROPERTIES OF REFRACTORIES

1. **Refractoriness:** The ability a refractory material to withstand high temperatures without melting or softening is known as Refractoriness. A good refractory material should have softening temperatures much higher than the operating temperatures of furnaces.
2. **Refractory Under Load (RUL):** The refractories used for lining high temperature furnaces should with stand heavy loads of the charge. Hence refractories should possess high mechanical strengths to bear the maximum possible load without breaking. A good refractory must have high RUL value.
3. **Porosity:** Porosity of a refractory material is a ratio of its pores volume to the bulk volume. Refractory material with high porosity is not performed for furnace lining etc. because the molten charge gases etc. may either passes through the pores and this may create problem. A good refractory material should have lower porosity.
4. **Thermal Spalling:** The fracturing (or) flaking off the refractory material due to sudden change in temperature is known as thermal spalling. A good refractory material should have good resistance to thermal spalling.
5. **Dimensional Stability:** The Resistance of refractory material to any change in volume (expansion or contraction) due to exposure to high temperature is known as dimensional stability. A good refractory material should have high Dimensional stability.
6. **Thermal Conductivity:** The passage of heat through refractory material is called thermal conductivity. A good refractory material must be thermal insulator in order to minimize the heat loss from the furnace.
7. **Corrosion Resistance:** At high temperature during furnace operation, viscosity of slag decreases and hence catalyses the chemical reaction between refractory lining and the slag, this results into corrosion of refractory lining. A good refractory material should have high resistance to corrosion.
8. **Electrical Conductivity:** An electric furnace should be lined with refractory materials having low electrical conductivity. A good refractory material should have low electrical conductivity.
9. **Chemical Inertness:** The refractory material should be chemically inert to the composition taken in furnace. A good refractory material must have high chemical resistance

10. **Thermal Expansion:** The refractory materials expand on rise in temperature and contract on fall in the temperature. A good refractory material should have less thermal expansion.

APPLCATIONS OF REFRACTORY MATERIALS

Refractory materials are useful for the following functions

1. Serving as a thermal barrier between a hot medium and the wall of a containing vessel
2. Withstanding physical stresses and preventing erosion of vessel walls due to the hot medium
3. Protecting against corrosion
4. Providing thermal insulation
5. In the metallurgy industry, refractories are used for lining furnaces, kilns, reactors, and other vessels which hold and transport hot media such as metal and slag.

LUBRICANTS

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other, due to mutual rubbing of one part against another, a resistance is offered to their movement. This resistance is known as friction. Friction causes a lot of wear and tear of surfaces of moving parts and a large amount of energy are dissipated in the form of heat, thereby causing loss in the efficiency of machine. Moreover, the moving parts get heated up, damaged.

"A substance introduced between two moving/sliding surfaces with a view to reduce the frictional resistance between then is known as a lubricant**".** The process of reducing frictional resistance between moving/sliding surfaces, by the introduction of lubricants in-between them is called lubrication.

Function of Lubricants:

1. It reduces wear and tear of the surfaces by avoiding direct metal to metal contact between the rubbing surfaces, i.e. by introducing lubricants between the two surfaces
2. It reduces expansion of metal due to frictional heat and destruction of material
3. It acts as coolant of metal due to heat transfer media
4. It avoids unsmooth relative motion
5. It reduces maintenance cost
6. It also reduces power loss in internal combustion engines

Mechanism of Lubrication: The phenomenon of lubrication can be explained with the help of the following mechanism; (a) Thick-Film lubrication (Fluid-Film or hydrodynamic lubrication) (b) Thin Film lubrication (Boundary lubrication) and (c) Extreme Pressure lubrication

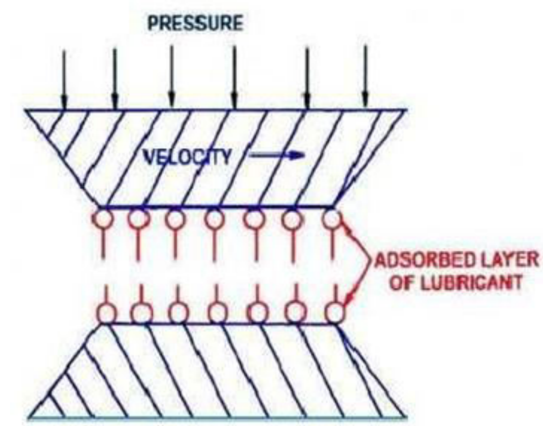
Thick-Film Lubrication:

In this, moving/sliding surfaces are separated from each other by a thick film of fluid (at least 1000 A° thick), so that direct surface to surface contact and welding of welding of junctions rarely occurs. The lubricant film covers/fills the irregularities of moving/sliding surfaces and forms a thick layer between them, so that there is no direct contact between the material surfaces. This consequently reduces friction.

The lubricant chosen should have the minimum viscosity (to reduce the internal resistance between the particles of the lubricant) under working conditions and at the same time, it should remain in place and separate the surfaces. Hydrocarbon oils (mineral oils) are considered to be satisfactory lubricants for thick-film lubrication.

Thin Film Lubrication:

This type of lubrication is preferred where a continuous film of lubricant cannot persist. In such cases, the clearance space between the moving/sliding surfaces is lubricated by such a material which can get adsorbed on both the metallic surfaces by either physical or chemical forces. This adsorbed film helps to keep the metal surfaces away from each other at least up to the height of the peaks present on the surface.



Vegetable and animal oils and their soaps can be used in this type of lubrication because they can get either physically adsorbed or chemically react in to the metal surface to form a thin film of metallic soap which can act as lubricant. Graphite and molybdenum disulphide are also suitable for thin-film lubrication.

Extreme Pressure Lubrication:

When the moving/sliding surfaces are under very high pressure and speed, a high local temperature is attained under such conditions, liquid lubricants fail to stick and may decompose and even vaporize. To meet these extreme pressure conditions, special additives are added to minerals oils. These are called extreme pressure additives. These additives form more durable films on metal surfaces. Important additives are organic compounds having active radicals or groups such as chlorine, sulphur and phosphorus. These compounds react with metallic surfaces at existing high temperatures to form metallic chlorides, sulphides and phosphides. Iron' chloride and iron sulphide melts respectively at 650°C and 1,100°C

Classification of Lubricants: Lubricants can be broadly classified, on the basis of their physical state, as follows:

(a) Liquid lubricants or lubricating oils (b) Semi-solid lubricants or greases (c) Solid lubricants.

a) **Liquid lubricants or lubricating oils:**

Lubricating oils reduce friction and wear between two moving/sliding metallic surfaces providing a continuous fluid film in-between them. Lubricating oils are further classified as

- **Animal and Vegetable Oils**:

Before the beginning of the petroleum industry, oils of vegetable and animal origins were the most commonly used lubricants. They possess good "oiliness". They: (i) are costly, (ii) undergo oxidation easily (iii) haves tendency to hydrolyse when contact with moist-air. Actually they are used as "blending agent" with mineral oils.

- **Mineral or Petroleum Oils**

These are obtained by fractional distillation of petroleum. The length of hydrocarbon chain in petroleum oils varies between about 17 to 30 carbon atoms.

These are the most widely used lubricants, because they are; (i) cheap, (ii) available in abundance (iii) quite stable under service conditions. However, they possess poor oiliness as compared to that of animal and vegetable oils.

- **Blended Oils:**

No single oil serves as the most satisfactory lubricant for many of the modern machineries. Typical properties of petroleum oils are improved by incorporating specific additives. Oiliness increased by the addition of vegetable oils or animal oils. To avoid extreme pressure condition, organic chlorine, organic sulphur and organic phosphorus is added to lubricant.

b) Semi-solid Lubricants or Grease: A semi-solid lubricant obtained by combining lubricating oil with thickening agents is termed as grease. Lubricating oil is the principal component and the thickeners consist primarily of special soaps of Li, Na, Ca, Ba, Al, etc. Grease can support much heavier load at lower speed. Internal resistance of grease is much higher than that of lubricating oils; therefore it is better to use oil instead of grease. Compared to lubricating oils, grease cannot effectively dissipate heat from the bearings, so work at relatively lower temperature.

c) Solid Lubricants: Solid lubricants are used where: (i) lubricating film cannot be secured by use of lubricating oils or greases (ii) contamination lubricating oil by the entry of dust or grit particles (iii) the operating temperatures or load is too high (IV) combustible lubricants must be avoided. The two most usual solid lubricants employed are Graphite and Molybdenum Disulphide. Graphite is stable up to 650 ^{0}C and Molybdenum Disulphide is stable up to 375 ^{0}C.

PROPERTIES OF LUBRICATING OILS

1. **Viscosity Index:** It is the property of a liquid or fluid by virtue of which it offers resistance to its own flow. Viscosity is the most important single property of any lubricating oil.

   Significance: If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving or sliding surfaces. On the other hand (2) if the viscosity is too high, excessive friction will result.

2. **Flash and Fire-points:** Flash-point is "the lowest temperature at which the oil lubricant gives off enough vapors that ignite for a moment, when a tiny flame is brought near it. Fire-point is "the lowest temperature at which the vapors of the oil burn continuously for at least five seconds, when a tiny flame is brought near it". In most cases, the fire-points are **5 to 40** higher than the flash-points.

   Significance: A good lubricant should have flash-point at Least above the temperature at which it is to be used. This safeguards against risks if fire, during the use of lubricant.

3. **Acid Number or neutralization number (saponification number):** Acid number defined as "the number of milligrams of KOH required neutralizing the free acids in 1g of the oil".

   Significance: Good Lubricating oil should possess acid value less than 0.1. Greater than 0.1 indicates that oil has been oxidized**.** This will consequently lead to corrosion, also gum and sludge formation.

4. **Cloud and Pour Points**: The temperature at which the lubricating oil becomes cloudy or hazy on cooling is known as the cloud point. The temperature at which the lubricating oil ceases to flow on cooling is known as the pour point.

   Significance: Cloud and pour points indicate the suitability of lubricant oil in cold conditions. Lubricant oil used in a machine working at low temperatures should possess low pour point; otherwise solidification of lubricant oil will cause jamming of machine.

BUILDING MATERIALS

Cement may be broadly described as material possessing adhesive and cohesive properties and capable of binding materials like stones, bricks, building blocks, etc. The principal constituent of cement used for constructional purposes are compounds of Ca (Calcarious) and Al+Si (argillaceous). The cement has property of setting and hardening under water by virtue of certain chemical reactions with it and therefore it is called hydraulic cement.

MANUFACTURE OF PORTLAND CEMENT

Raw materials for the manufacture of cement are

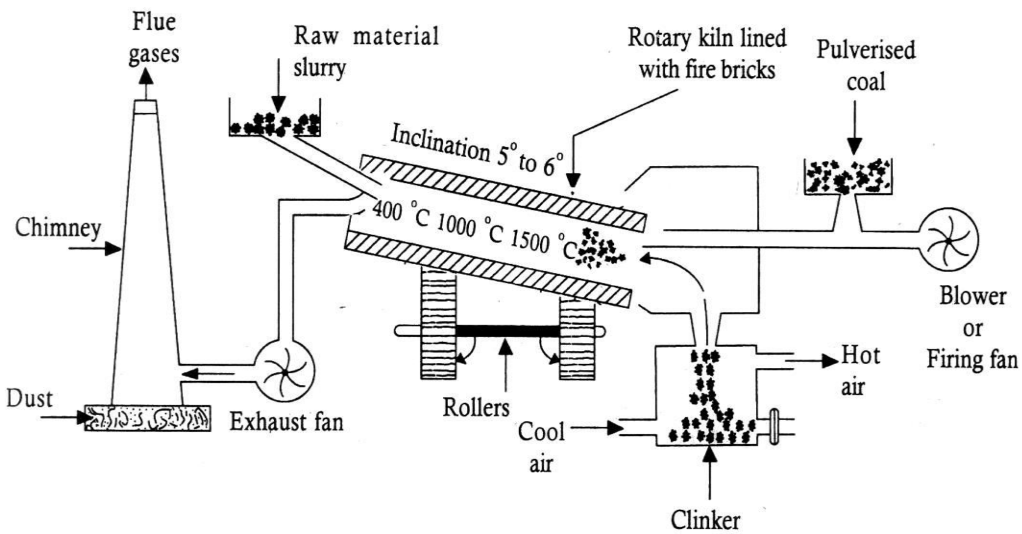
1. Calcareous materials CaO [as limestone].
2. Argillaceous materials, Al_2O_3 and SiO_2 [a clay].
3. Powdered coal or fuel oil.
4. Gypsum ($CaSO_4$ 2 H_20).
5. Iron oxide (Fe_2O_3), Magnesium oxide (MgO).
6. Sulphur trioxide (SO_3).
7. Alkali oxides (K_2O + Na_2O).

S. No	Name of The Component	Percentage Of Mass
01	CaO	60-69%
02	SiO_2	17-25%
03	Al_2O_3	3-8%
04	Iron oxide (Fe_2O_3)	2-4%
05	Sulphur trioxide (SO_3)	1-5%
06	Magnesium oxide (MgO)	1-3%
07	Alkali oxides (K_2O + Na_2O)	0.3-1.5%
07	Gypsum ($CaSO_4$ 2 H_20	Retarding Agent
08	Powdered coal or fuel oil	Fuel for Burning Coal powder

Functions of the ingredients of cement

1. Lime is the principal constituent of cement. However, excess of lime reduces the strength of cement. On the other hand, presence of lesser amount also reduces the strength of cement and makes it quick-setting.
2. Silica imparts strength to cement.

3. Alumina makes the cement quick-setting.
4. Calcium sulphate (gypsum) helps to retard the setting action of cement.
5. Iron oxide provides colour, strength, and hardness to the cement.
6. The presence of the alkali oxides Na_2O and K_2O, sulphur dioxide SO_3 and of MgO were recognized as having an influence on the clinker formation process.
7. Sulphur trioxide in small proportion is desirable it imparts Soundness to cement.
8. Alkalis if present in excess cause the cement efflorescent (Loss of water).



Steps involved in manufacture of Portland cement

Step-I: Mixing of raw materials

It can be done by either dry process or wet process.

Dry process: The raw materials are crushed to roughly 2-5 cm size pieces. Then, these are ground to fine powder. Each separate powdered ingredient is stored in a separate hopper. Then, the powdered materials are mixed in the requited proportions to get dry 'raw mix', which is stored in storage bins and kept ready to be fed in a rotary kiln. Raw materials are mixed in calculated proportions so that the average composition of the final product is as follows:

Wet process: The calcareous raw materials are crushed, powdered and stored in big Storage tanks. The argillaceous material is thoroughly mixed with water in washed mills. The basin-washed clay is also stored. The two raw materials are led to 'grinding mills', where they are mixed intimately to form a paste, called slurry. This slurry contains about 38 to 40 percent water. It is kept ready for feeding to a rotary kiln.

Step-II: Burning:

It is usually done in rotary kiln, which is a steel tube, about 2.5 to 3.0 m in diameter and 90 to 120 m in length, lined inside with Refractory bricks. This rests on roller bearings. The kiln is capable of rotating at 1 r.p.m. (revolution per minute) about its longitudinal axis. Burning fuel (usually powder coal or oil) and air are injected at the lower end. A long hot flame is produced, which heats the interior of the kiln up to a maximum temperature of about 1,750°C.

Chemistry (Chemical Reactions That Take Place in Different Parts of Kiln):

1. In the Upper part of kiln (drying zone): Where the temperature is around 400°C, most of the water in the slurry gets evaporated.
2. In The Central Part of Kiln: where the temperature is around 1,000°c, limestone of dry mix or slurry undergoes decomposition to form quick-lime and carbon dioxide; and the latter escapes out. The material forms small lumps, called nodules. $CaCO_3 \rightleftharpoons CaO + CO_2$
3. In The Lower Part of the Kiln (Clinkering Zone): The temperature is between 1,500 to 1,700°C. Here lime and clay (of nodules) undergo chemical interaction or fusion, yielding calcium alulninates and silicates.

$$2\,CaO + SiO_2 \longrightarrow Ca_2SiO_4\ (C_2S) \text{ - Dicalcium silicate}$$

$$3\,CaO + SiO_2 \longrightarrow Ca_3SiO_5\ (C_3S) \text{ - Tricalcium silicate}$$

$$3\,CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6\ (C_3A) \text{ - Tricalcium aluminate}$$

$$4\,CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}\ (C_4AF) \text{ - Tetracalcium alumino ferrate}$$

Step-III: Grinding

The cooled clinkers are ground to fine powder in ball mills and after grinding process add small quantity of gypsum; so that resulting cement doesn't set very quickly when it comes in contact with water. Here gypsum acts as a retarding agent for early setting of cement.

$$\underset{\text{Cement}}{3CaO.Al_2O_3} + \underset{\text{Gypsum}}{xCaSO_4.2H_2O} \longrightarrow \underset{\text{Tricalcium sulpho aluminate}}{3CaOAl_2O_3\ xCaSO_4\ .2H_2O}$$

SETTING AND HARDENING OF PORTLAND CEMENT

When cement is mixed with water to a plastic mass, called "cement paste", hydration reaction begins, resulting in the formation of gel and crystalline products. This process is known as setting and hardening of cement.

Setting: – Stiffening of original plastic mass (Gelation)

Hardening: – Development of strength due to crystallization.

Initial setting: Initial setting of cement-paste is mainly due to:

1. The hydration of tricalcium aluminate (C_3A)
2. Gel formation of hydrated tetra calcium alumino ferrite (C_4AF)

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3Cao.\ Al_2O_3.\ 6H_2O + 880\ kJ/kg$$

$$4CaO.Al_2O_3.Fe_2O_3{+}7H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O{+}420\ kJ/kg$$

Final setting and hardening: Dicalcium silicate starts hydrolyzing to tobermonite gel (which possesses a very high surface area and thus very high adhesive property).Final setting and hardening of cement-paste is due to the formation of tobermonite gel plus crystallization of calcium hydroxide from tricalcim silicate.

$$\underset{\text{Dicalcium silicate}}{2\,[2CaO.SiO_2] + 4H_2O} \longrightarrow \underset{\text{Tobermonite gel}}{3CaO.2SiO_2.3H_2O} + \underset{\text{crystalline}}{Ca(OH)_2} + 250\ kJ/kg$$

$$\underset{\text{Tricalcium silicate}}{2\,[3CaO.SiO_2] + 6H_2O} \rightarrow \underset{\text{Tobermonite gel}}{3CaO.2SiO_2.3H_2O} + \underset{\text{(Crystalline)}}{3Ca(OH)_2} + 500\ kJ/kg$$

When water is added to cement, its various constituents undergo hydration and crystallization at different rates

- At first hydration of C_3A and C_4AF takes place.
- Next the hydration of C_3S begins within 24 hours and gets completed in 7 days.
- The gel of alumina begins to crystallize and at the same time C_2S begins to hydrate in 7 to 28 days.
- The increase of strength between 7 to 28 days is due to hydration of C_2S and continued hydration of C_3S.