Engineering materials constitute the backbone of the modern civilization, in every sphere of human activity; engineering materials are used in one form or the other. In order to make extensive use of engineering materials for human utility, a critical analysis and knowledge of structure of different materials is necessary. Before determining a material for a given application or modifying it according to the requirements, it is very necessary to understand the fundamental nature and structure of the material.

Material science—a branch of applied science helps us for investigating the relationship existing between the structure of materials and their properties as well as for making inter-disciplinary study of the materials for practical considerations. In order to cater to the needs of higher standard of performance and reliability required for modern civilization, material science has developed tremendously to provide right materials in complex industrial situations and serve service requirements.

Material Science

According to John Von Neumann, the father of computers, he signifies material science as the interdisciplinary study of matter for entirely practical purposes (*i.e.* the scientific disciplines of chemistry and physics).

Material science is a combination of two popular engineering words—materials and science. The word 'materials' does not refer to all matters that are found in the universe. Here the word 'materials' refers only to the study of that part of the inanimate matter or materials which are required to fulfill the needs of man-kind and are used by the engineer or technologist in the practice of his profession. They are the solid materials required by the engineer for fulfilling the needs of the modern civilization.

Science refers to the knowledge arranged under general truths and principles. Today it covers a wide range of subjects. It refers particularly to physical sciences—physics and chemistry. In material science, it mainly refers to solid materials only; therefore, the subject is mainly confined to solid state physics and solid state chemistry. The engineering usefulness of the materials is always taken into consideration in material science without any basis whether the laws of science are applicable or not. The material science mainly deals with engineering sciences like metallurgy, ceramics and polymer sciences. These sciences have developed out of the interaction with the scientific disciplines of chemistry and physics which have developed in their own respective spheres and time.

Therefore, the material science is defined as that branch of applied science concerned with investigation of the relationship existing between the structure of materials and their properties. For entirely practical purposes, it also concerns with the inter-disciplinary study of materials. For an engineer, it is the study of the nature and behavior of solid materials which are useful to him during his profession.

1(b) Classification of Engineering Materials

1. According to their mode of occurrence, engineering materials are classified in the following broad groups:

a) Metals and their alloys ***e.g.,*** copper, iron, aluminum, steel, silver, gold, brasses, bronzes, invar.

b) Non-metals ***e.g.,*** carbon, sulphur, phosphorus, acetylene, petrol etc.

c) ceramics and glasses **e.g.,** Mg, CdS, Zn, SiC, $BaTi0_2$ silica, soft-lime, graphite, glass, concrete, cement, ferrite and granite, Urania (UO_2), Beryllia (BeO), Ruby laser.

d) Organic polymers, e.g., plastics, PVC, PTFE, polyethlene, fibres, terylene, nylon, cotton, natural and synthetic rubber, leather etc.

e) Composites (made up of two groups)

1. Metals and alloys, and ceramics **e.g.,** Steel-reinforced concrete, dispersion hardened alloys.
2. Metals and alloys, and organic polymers, **e.g.,** Vinyl- coated steel, Whisker-reinforced plastics.
3. Ceramics and organic polymers, **e.g.,** Fiber-reinforced Plastics, Carbon reinforced rubber.

2. According to the major areas of use. (Requiring materials of all the above types).

a) Structures (objects without moving components) concrete dams, steel melting furnace (refractory oxide and steel), a suspension bridge, an oil-refinery tower, safety helmets (glass reinforced plastics).

b) Machines [lathe, steam turbines (nickel blades with dispersed oxide particles) jet engines, electric motors, generators].

c) Devices (Most recent innovations of engineering like transistors, photo-electric cell, piezo-electric pressure gauges ceramic magnets, lasers etc.).

Inter-relation between materials and their applications:

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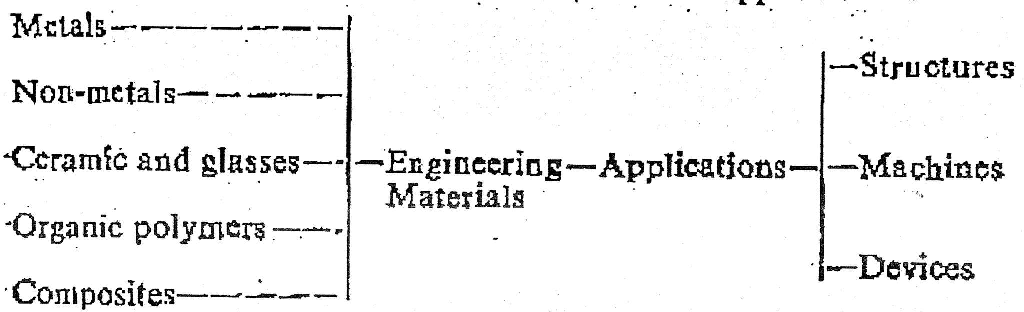
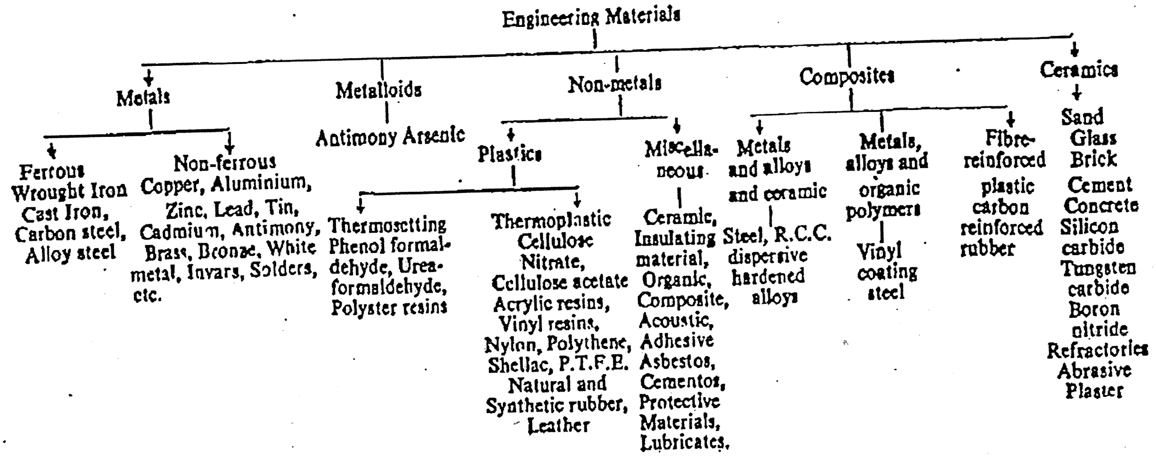
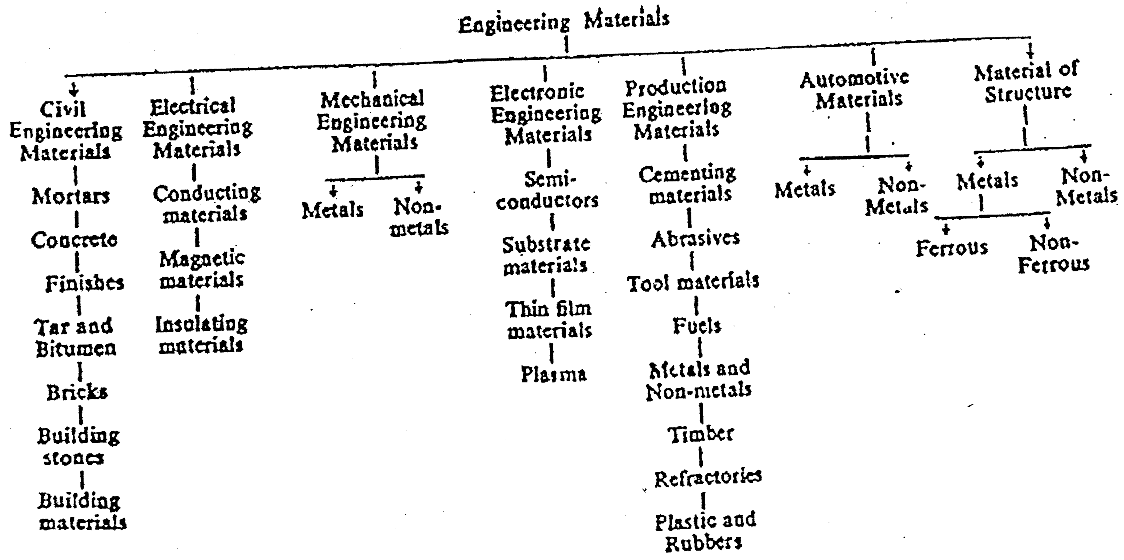


Dr. V. K. SINHA

Further classification of these materials is given in the chart.





Metals.

These electropositive elements are usually given basic oxides although higher valency atom also give acidic oxides. They also form halogen compounds stable in presence of water (KC1, $PbCl_2$). In certain cases, they decompose only to a limited extent because the reaction is reversible ($BiCl_3+H_2O \longrightarrow BiOCl+2HCI$ and $SbCl_3+H_2O \longrightarrow SbOCl+2HCl$). They also form complex salts in which the metals are present either in the form of electropositive radical (cation) as in $[Ag(NH_3)_2]Cl$ or as electronegative radical (anion) as in $K[AgC_2N_2]$. They are normally solid (with the exception of mercury) at ordinary temperatures.

Non-metals.

These are the electronegative elements and show only very feeble electrochemical properties, *(e.g.,* carbon). They give acidic oxides in which the element has its normal valency (in some cases metallic oxides with normal valency can function as feebly acidic oxides in the presence of a strong base ; zinc oxides, ZnO can give a stable chloride, $ZnCl_2$, with hydrochloric acid or an amphoteric oxide. Their halogen compounds are decomposed by water completely, *e.g.* $PC1_8+3H_a0=H_8P0_3+3HCl$. Carbontetrachloride and tetra bromide which are not decomposed by water are the exceptions. Non-metals exist in all the three forms, *(i.e.* solid, liquid and gaseous).

There are certain elements like Antimony and Arsenic which possess characteristics of both the metals and non-metals. They are called ***Metalloids.***

Different types of metals, non-metals and metalloids as classified above will be discussed in detail in further chapters.

1(c) Engineering Requirements of Materials

In material science, the mere knowledge of various types of engineering materials is not sufficient. The practical use and applications of the engineering materials must be known to a technocrat. Further for using the various materials for a purpose or product like a machine, bridge, concrete dams, a road, a computer or a road vehicle to be manufactured, detailed and intimate knowledge of their characteristics and behavior is necessary. For acquainting with various properties and behavioral characteristics, a technocrat must have a firm grasp of the underlying principles governing the engineering requirements of various materials. For this purpose, it is necessary that the evaluation of service conditions followed by the evaluation of material characteristics and properties like Mechanical, Thermal, Electrical, Chemical, Optical etc. should be done. The service conditions will include the effects of mechanical loading or operating, stress level, temperature, electric and magnetic field, chemical environment, exposure to radiation etc. In order to study the various engineering requirements of materials, they are classified as under:

Physical. Shape, size, finish, colour, specific gravity, density, porosity, structure.

Mechanical. Strength, stiffness, elasticity, plasticity, ductility, creep, brittleness, hardness, toughness, resilience, impact, fatigue.

Thermal. Specific heat, heat of transformation, thermal capacity, thermal expansion, heat transfer and thermal conductivity, thermal stresses, thermal fatigue, thermal shocks, latent heat of fusion.

Electrical. Resistivity, conductivity, relative capacity or dielectric constant, dielectric strength, semi-conductivity, superconductivity.

Chemical. Corrossion resistance, atomic weight, valency, molecular weight, acidity, alkalinity, atomic number.

Magnetic. Permeability coercive force, hysteresis, reducti- vity, retentivity, susceptibility, residual inductance, saturation value.

Optical. Colour, lustre, diffraction, fluorescence, reflectivity, luminescence.

Technological. Hardness, weldability, machinability, form- ability, castability.

1(d) Level of Structures

There are different levels of observations for studying the internal 'structure of the material. The measure of the level of observation is the degree of magnification or resolution of the physical aid used to study them by diffemt methods. The details which are revealed or disclosed at a certain level of observation are usually different from the details disclosed at some other level of magnification or resolution. It was Henry Sorby in 1886, when he realize this. He said in 1886: ' 'Though I had studied the microscopical structure of iron and steel for many years, it was not until last autumn that I employed what may be called high powers. This was partly because I did not see how this could be satisfactorily done, and partly because it seemed to be unnecessary. I had found in almost every case a power (magnification) of 50 linear showed on a smaller scale as much as one of 200, and this led me to conclude that I had seen the ultimate structure. Now that the results are known, it is easy to see that my reasoning was false, since a power of 650 linear enables us to see a structure of an almost entirely new order."

The concept of relative sizes must be had in mind while considering structures at a various levels. The "logarithmic scale of the universe" one method of comparison used for the purpose. This is detailed in the table below:

Relative Sizes within the Universe

Object	*Average size*	*Logarithmic scale*
Distance to nearest galaxy	1 million light year	10^{21}
Distance to nearest star	1 light year	10^{16}
Diameter of sun	1 million kilometres	10^{9}
Diameter of earth	10,000 kilometres	10^{7}
Man (average dimensions)	1 metre	10^{0}
Sand grain	1 millimetre	10^{-3}
Dust particle	1 micrometre	20^{-6}
Molecule	10^{-1} nanometre	10^{-9}
Atom	10^{-2} nanometre	10^{-10}

Far studying the internal structure of a material at different level of observation a measure of level of observation is necessary as the magnification or resolution of the physical aid. The structure of materials can be classified as under depending upon the level.

1) Macrostructure
2) Microstructure
3) Substructure
4) Crystal structure
5) Electronic structure
5) Nuclear structure

Macrostructure

The structure of material as examined by the naked eye or a low power magnification is known as macrostructure. It relates to the size, shape and atomic arrangements in a crystalline material. For example, in a crystalline material like quartz, the internal symmetry of the atomic arrangement is reflected in its external form. In a polycrystalline material like a cast brass door knob when polished and etched by constant contact with human hand sweat, its individual crystals are visible. When large, thin zinc crystals are seen on the surface of the heavily galvanized objects, they are known as macroscopic. A macrostructure seems very similar to a sand grain and has more or less similar dimension.

To reveal flaws and segregation in a material, standard procedure available are used for their macro-examination. The study of the macrostructure of a material, is performed either directly on the surface of the work (a casting) or on a fracture or more frequently on specimens or samples cut out of large billets (ingots, forging etc.) or finished articles.

Microstructure

When the structure of a material is observed under a optical microscope with magnifications from x75 to x 1500, it is known as micro-structure. This structure looks very similar to a dust particle. Some type of special specimen preparation and mounting is necessary for each microscopic examination which generally reveals greater details of the structure of a material.

In order to investigate structure of materials in magnification range larger than 0.15 to 0.2 microns or 1,500 to 2,000 **A^0** (where **A^0**, abbreviated Angstrom is 10^{-10} m or 10^{-7} mm).

Both the macrostructure and microstructure are the two terms relating to the same general type of phenomena. The degree of .magnification required to study them is the only basis which differentiate them.

Sub-structure

The structure of a material obtained with the help of a microscope having much higher magnification and resolution than the optical microscope is known as Sub-structure. An electron microscope used for this purpose provides an effective magnification of X 100,000. Details of the material of the order of 50—500 **A^0** are resolved by this microscope. It provides a new wealth of new information on crystal imperfections like dislocation as well as on every small particle of a few hundred angstroms in size. Further the identification of the crystal structure of particle of utility and interest is also provided by the electron diffraction patterns obtained along with the photograph of sub-structure. An electron microscope cannot resolve individual atoms. For this purpose, a powerful and upcoming technique like field iron microscope producing images of individual atom is used.

Crystal Structure

Details of the atomic arrangement within a crystal obtained by means of X-rays and electron diffraction are known as crystal structure. The structure analysis of crystalline *solids* due to their regularity o\f internal structure can be\

obtained by means of various types of radiation. Electron beams are only restricted to surface studies due to the electron being charged particles getting easily deflected by other charged particles within the material.

Electronic Structure

The structure of solid providing information about the electrons in the outermost shells of the individual atoms forming the solids is known as its electronic structure. It is determined by the spectroscopic techniques.

Nuclear Structure

It is the structure of a solid obtained and studied by nuclear spectroscopic techniques like nuclear magnetic resonance (NMR) and Mossbauer studies.

1(e) Structure-Property Relationships in Materials

Due to tremendous increase in the number and variety of engineering materials and their applications, it is not possible to mention the composition, treatment, properties and uses of all the materials. Moreover different materials respond differently to the same stimuli and constraints. The nature of the material determines the quality of the response to imposed stimuli and constraints. This quality of material known as a material property is defined in general as a factor which affects qualitatively or quantitatively the response of a given material to imposed stimuli and constraints. Instead of going for fully descriptive details of a large number of materials, it is appropriate to know the factors which determine the structure-property relationship as well as how much and how a particular material responds to imposed stimuli and constraints.

Further, the composition, treatment, properties and uses of the materials do not provide appropriate knowledge about their improvement. This has created a growing need to study the relationship between the structure and properties of materials. It has also been fully realized now that the properties of all materials develop from their structure, i.e. from the way from which their atoms aggregate to form molecules or crystals or distorted amorphous structures. The nature and distribution of imperfections, either chemical or architectural greatly affect the properties of bulk materials. Different properties of materials observed and exploited in them are not the properties of constituent atoms and molecules, but they are the co-operative properties of the aggregate.

In material science the structure-property relationships greatly help to create a basic background for understanding the nature and behavior of a wide variety of materials. The properties of materials yet to be studied and yet to be developed can also be anticipated with this basic background. This structure-property relationship in metals, ceramics and polymers which are the basic concepts pertaining to the levels of structure (the macro-structure, the sub-structure and the crystal structure) are given in the table below.

S. No.	*Material*	*Crystallinity*	*Bonding*	*Important properties*
1.	Metals	Crystalline	Predominantly metallic	They are excellent conductors with high to moderate strengths, malleable and ductile to certain degree. They are the opaque, lustrous and moderate to high melting points.
2.	Ceramics	(*i*) Crystalline	Ionic and covalent	They are non-conductors with high melting points. They are also brittle, hard and dull to lustrous.
		(*ii*) Non-crystalline (Vitreous)	Ionic and covalent	They are non-conductors and brittle with no definite melting points. They are hard transparent to translucent.
		(*iii*) Crystalline and non-crystalline phase	Ionic and covalent	They are very poor conductors or insulators which are brittle, hard, low strength opaque with high melting ranges.
3.	Polymers (plastics and Rubbers)	Predominantly non-crystalline	Covalent plus secondary	They are also very poor conductors-insulators. They have low strengths, low setting temperatures and deform plastically with little applied load. They are dull and usually translucent to opaque.

1(f) Selection of Materials

For proper and effective utility of engineering materials as well as for development and manufacture of satisfactory products, their selection should be appropriate, sound and economical. It is the direct responsibility of the material engineer to make correct choice of the right materials for given engineering requirements and their proper use including the new ways of using them for greater effectiveness. For this purpose, he must have a thorough knowledge and understanding of the nature and behavior of the materials. Their nature is based upon the chemistry and physics of materials. The behavior of the material involves the application or the principles of the nature of materials under varied conditions found in engineering. The composition, structure, service conditions and the interaction among themselves determine the behavior of the materials.

Selection of material is a problem solving process like most engineering efforts. For a specific application, it is invariably a thorough, lengthy and expensive process. It is just possible that one material may be suited to more than one application. This relative advantages and disadvantages may be a compromise for final selection.

Following three requisites are basis of most of the varied demands of many materials:

a. Service requirements. The material selected must stand up to service requirements due to important role played by them in material selection. Dimensional stability, corrosion resistance, adequate strength, toughness, hardness, heat resistance as well as low electrical resistance, high or low heat conductivity, fatigue resistance etc. are the basic service requirements which should be taken into consideration for material selection.

b. Fabrication requirements. Two basic requisites which should be present in material selection, i.e. possibility to shape the material and to join it to other materials. Qualities like machinability, hardenability, heat treatability, ductility, castability and weldability which are quite difficult to assessment of fabrication requirements of a material.

c. Economic requirements. Final shape in material selection is given by the economic requirements. Material selected should provide goods at lower cost to procure higher profit with all requisite qualities present in it. Minimum overall cost of the component to be made is the basic requirement considered for material selection.

Important Questions

1. Explain 'Material Science' as a subject. What are its uses to an engineer?
2. How engineering materials are classified? Explain.
3. Describe the engineering materials.
4. Discuss the factors that are taken into account in selecting materials for engineering design.
5. Define factor of safety and its significance. As a material engineer, what measures can you suggest to lower the factor of safety to levels lower than the conventional one?

15

Inorganic Cementing Materials

"Portland cement is the most vital inorganic bonding material, used in civil engineering works."

15.1 INTRODUCTION

Inorganic cements *are materials that exhibit characteristic properties of setting and hardening, when mixed to a paste with water.* This makes them capable of joining rigid masses (like bricks, stones, tiles, etc.) into coherent structures. Inorganic cements can be divided into *hydraulic* and *non-hydraulic* types, according to the way in which they set and harden. **Hydraulic cementing materials** (like *Portland cement*) *are capable of setting and hardening under water ; while* **non-hydraulic cements** (like *ordinary lime*) *harden in air and hence, cannot be used under water.*

15.2 LIME

Lime may be defined as *"consisting essentially either of calcium oxide* (CaO) *or of calcium oxide together with a smaller proportion of magnesium oxide* (MgO), *formed by burning a natural rock* (like *limestone,* $CaCO_3$) *at such a temperature that it will slake, when brought in contact with water".*

(1) **High-calcium** or **fat limes** *are produced by burning* **nearly pure** *calcium carbonate.* They contain from 95 to 98% calcium oxide. The balance being mainly silica (SiO_2), a little alumina (Al_2O_3) and manesia (MgO). These limes are *rapid slaking,* with evolution of large amount of heat and afford large volumes (2 to 2.5 times) of powder. These are *non-hydraulic* and the setting of fat lime paste (or mortar) is by *drying only*; and *when continuously moist, they never-set.* Hence, they are unsuitable for use in *damp* situations.

Uses : Fat lime is suitable for making mortars, used in joining thin brick-works and coarse stone masonry works. It is, generally, also used for white-washing, water softening, in metallurgy, and in glass industries.

(2) **Lean** or **poor limes** *contain about 70-80% calcium oxide plus over 5% magnesium oxide* (MgO), *together with little silica* (SiO_2) *and iron oxide impurities.* These limes *slake very slowly.* They show very low shrinkage, better plasticity and workability than fat limes. Therefore, these limes are better suited for *plaster finishing.* These limes must be thoroughly slaked ; otherwise they will slowly expand in the finished work, producing symptoms of *unsoundness.*

Uses : They are employed mainly for mortar purposes and interior works. They are also used in places, where good fat lime is not available.

(3) **Hydraulic limes** *are limes containing 5–30% clayey matter (silica and alumina), but not more than 2% magnesia. The calcium oxide content ranges from about 70 to 80%.* Such limes exhibit *hydraulic properties* (*i.e.,* setting hard, when immersed in water). Hydraulic limes *slake with difficulty,* so these must be finely ground before use. Such limes do not shrink or crack and so they require only a *small* quantity of sand to be added.

Uses : As hydraulic limes set slowly without cracking, they are used as a *substitute for cement.* For example, new foundations, marine works, shafts of tall chimneys and thick walls, where there is *no much access of air.*

Table 1 : *Comparison between fat lime and hydraulic lime.*

	Fat lime	**Hydraulic lime**
1.	It is obtained by the calcination of a pure or nearly *pure variety of limestone.*	It is obtained by the calcination of limestone, containing nearly 30% clay or alternatively from a mixture of 30% *clay + 70% ordinary limestone.*
2.	When mixed with water, it *slakes vigorously* with a hissing sound and evolution of lot of heat.	It *does not slake* or slakes very slowly without any hissing sound and evolution of small or no heat.
3.	In present of moisture, it *absorbs* CO_2 from the atmosphere forming inert material, $CaCO_3$, thereby losing its cementing properties.	It *does not absorb* CO_2 and its slaking takes place, even after months by absorbing atmospheric moisture. Consequently, it causes serious damage, if used before proper slaking.
4.	It *shrinks* and *cracks*, after setting and drying.	It *does not* undergo much shrinkage.
5.	It sets only in presence of CO_2.	It can set, even in the absence of air.
6.	$CaCO_3$ crystals, formed after setting and hardening of fat lime, are *not very strong*. Consequently, fat lime sets to give comparatively *poor strength.*	It sets to form *strong and stone-like* silicates and aluminates.
7.	Suitable for *plastering* walls in exposed positions.	Suitable in all positions, where *strength* in required. Unsuitable for plaster-works.

Classes of hydraulic limes : Depending upon the *percentage of clayey matter,* hydraulic limes are sub-divided into *three* classes.

1. ***Feebly hydraulic limes*** contain from *5 to 15%* clayey matter. They slake very slowly, with some expansion and cracking. During slaking, they evolve heat and form fine powder. They set in *2-3 weeks* and after a period of about one year, they form a *soapy hard mass.* They are used for mortar works.

2. ***Moderately hydraulic limes :*** Their clayey matter content varies from *15 to 20%.* They slake after a period of 1-2 hours, producing small expansions. They set in a *week's time* and become hard and stony in about one year. Such limes form stronger mortars than feebly hydraulic limes. They are used for making mortars suitable for good class brick-works and masonries.

3. ***Eminently hydraulic limes*** contain *20–30%* clayey matter. They resemble *very closely* to ordinary Portland cement. They slake very slowly, without any appreciable expansion. These limes must be very finely ground and screened (to eliminate coarse unslaked particles), before use. They set firm in about *7 days* and form hard stony structures with six months. This class of lime is used as a *substitute for cement.*

4. ***Dolomitic limes*** *are obtained by calcining (heating in presence of a limited supply of air) dolomite (an equimolar mixture of* $CaCO_3$ *and* $MgCO_3$*).* Such limes, usually, contain 30–40% of MgO, but the percentage of clayey impurities (SiO_2 and Al_2O_3) is small. They slake very slowly, with very little expansion and comparatively lesser amount of heat evolution. They yield *very plastic mortars,* which work easily, smoothly and set to hard masses.

Uses : They are used as *fluxes* in metullugical industries and for manufacturing *basic refractories.*

15.3 MANUFACTURE OF LIME

Lime is obtained by ***calcining*** *(i.e., heating in limited supply of air) limestone.*

$$\underset{\text{(Limestone)}}{CaCO_3\ (solid)} \rightleftharpoons \underset{\text{(Lime)}}{CaO\ (solid)} + CO_2\ (gas)$$

Raw materials employed for making fat lime are rocks like *limestone* (CaCO$_3$), containing least amount of impurities such as silica, alumina, iron oxide and magnesium carbonate. For the manufacture of *hydraulic lime*, either limestone containing fairly good quantity of clayey matter ($SiO_2 + Al_2O_3$) or alternatively a mixture of a *pure limestone and clay* in pre-determined proportions are used. In case of dolomitic limes, rocks like dolomite ($CaCO_3 \cdot MgCO_3$) are used.

Theoretically, limestone decomposes when heated at 880°C, but the reaction :

$$CaCO_3 \rightleftharpoons CaO + CO_2 + 43.25\ \text{kcal}$$

is *exothermic and reversible*. Consequently, in order that this reaction takes place in forward direction to yield lime, it is essential that : *(i) CO$_2$ produced during the reaction is* ***removed quickly*** *; and (ii) the temperature of the reaction is* ***not allowed*** *to come down below 900°C.*

Any magnesium carbonate present in the limestone also dissociates into magnesium oxide and carbon dioxide, even earlier than limestone dissociates.

$$MgCO_3 \longrightarrow MgO + CO_2$$

In practice, calcination is carried out at temperatures as high as **1,000 – 1,200° C**, so that *complete dissociation* of carbonate occurs. *If a temperature much above 1,200°C is employed, the lime will be partially vitrified on the outerside of the lumps,* due to the combination of calcium oxide with silica, alumina And iron oxide present. *This causes the lime to be very slow-slaking, which is undesirable.* Such slow-slaking lime escapes hydration and consequently, expands or blows in the walls. This manifests itself in small *blisters* in the finished plaster-workds.

For the manufacture of *hydraulic limes*, still higher temperature as high as 1,500–1,700°C are employed. *In such cases, carbonate dissociation is followed by combination of so-produced lime with silica and alumina (clayey matter), resulting in the formation of calcium silicates, calcium aluminates, etc.*

Calcination (or *burning*) of limestone is almost invariably carried out in *continuous vertical kilns*. The heating or firing of these kilns are carried out either

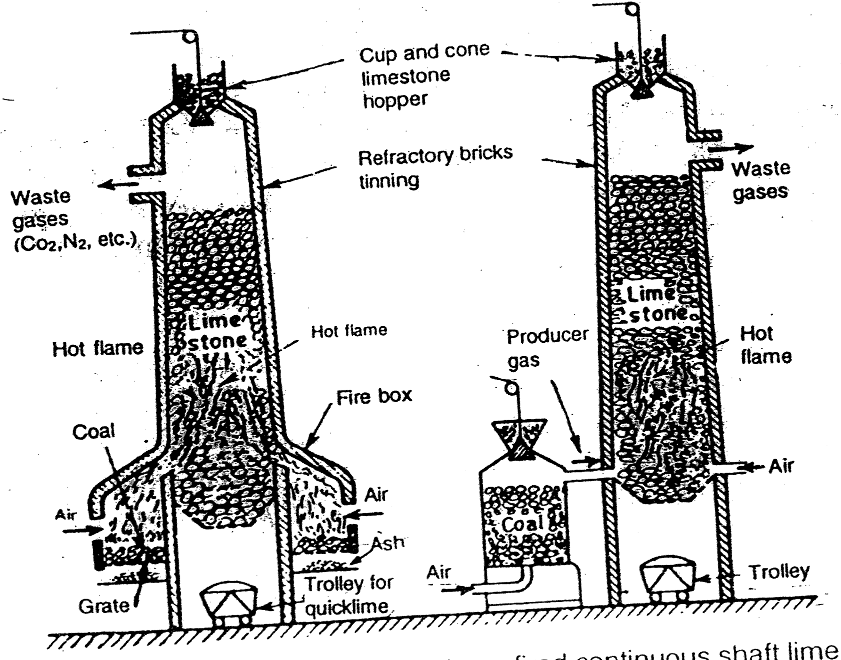


Fig. 1. Vertical section of a coal-fired and gas-fired continuous shaft lime kilns.

by burning *solid fuel* (like coal) inside fire-boxes or in the more modern plants by the use of *gaseous fuel* (such as producer gas). A vertical section of a **modern lime kiln** is shown in Fig. 1. The kiln is a large chimney-like tower (approximately **15** to 40 m in height and 1.5 to 2.5 m in diameter) lined with *refractory bricks*. *Fire*-boxes are built in the sides, around the lower part, so that the fuel or its ash is not mixed with stone. Limestone, fed into the *hopper* at the top, passes slowly down through the heated portion of the kiln. The flame of the burning fuel sweeps in from the sides, causing the decomposition of limestone. *The bottom of the furnace is so-constructed that a current of air is blown in at base.* This serves the purposes of : (*i*) cooling the hot lime at the base of the furnace : (*ii*) furnishing heated oxygen for combustion of fuel, and (*iii*) removing the carbon dioxide from the kiln. The lime is finally dumped into a *trolley*, run under the furnace.

In more advanced countries, *rotary kilns* (similar to those used in cement manufacture) are used for the manufacture of lime.

Manufacture of artificial hydraulic limes : The *fat lime* is slaked and to this *clay* is added in the right proportion and the two are *mixed* thoroughly. The mix is then made into a *stiff paste* with water. This is *kneaded* and made into small balls (2-3 cm) and dried. These balls are burnt in a kiln at 1,500 to 1,700°C. The burnt product is ground to a fine powder and screened, before putting to use.

15.4 PROPERTIES OF LIME

1. Slaking : Lime is a high-melting white solid. When water is added to pure lime (called *quick-lime*) lumps, it is readily absorbed through the pores, forming calcium hydroxide. $Ca(OH)_2$.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15.9 \text{ kcal}$$

This change, called **slaking** (or **hydration**), is of fundamental importance in the use of lime as binding material. The slaking of lime is accompanied : (*i*) *evolution of a considerable amount of heat* (about 2.25 kcal/kg); (*ii*) *expansion in volume to 2–2.5 times* ; (*iii*) *development of "hissing and crackling sound"*, due to : (*a*) conversion of water into steam, and (*b*) breaking of lime to extremely fine white powder, called *slaked lime*. Thus, ***slaked lime** is extremely fine white powder, obtained by the absorption of water by lime*. For making mortar/plaster, lime in "slaked lime" form is used.

Lime is most commonly supplied by manufactures in *hydrated lime* form (*i.e.*, a fine white powder, obtained by adding limited amount of water to lime), because it : (*i*) is easier to handle, (*ii*) can be used immediately, (*iii*) can be stored with less danger, and (*iv*) can be slaked, before it is but to use, with greater safety, because of comparatively much lesser evolution of heat. The ***hydrated lime** is thus, "partially-slaked lime"* and it should, therefore, be slaked completely, before using for making mortars, etc.

2. Plasticity *is the ability of lime to spread during application*. Pure calcium limes are poorly plastic, rather sticky and hard to work. They are also called *'short'* limes. On the other hand, limes containing some magnesium oxide spreads easily and smoothly and hence, are termed *'plastic'*.

3. Sand-carrying capacity : When lime is used either as a mortar or plaster, it is mixed with *sand* with the following *objectives* : (*i*) To decrease the shrinkage of lime on setting ; (*ii*) To get a proper plastic mix ; (*iii*) To make the resultant mix economical. *High-calcium limes show higher sand-carrying capacity than dolomitic limes.*

4. Exposure to air : When lime is kept exposed to air, it slowly absorbs moisture, CO_2, and swells and disintegrates to fine powder, giving *air-slaked lime,* which is of no use for making mortars and plaster. This is because air-slaked lime contains mostly $CaCO_3$ (formed by action of CO_2 with CaO) and very little $Ca(OH)_2$ and hence, a mortar made from it will *not harden.*

5. Setting and hardening : The process of setting (and consequent hardening) of lime or lime-mortar involves, essentially, the following chemical reactions :

(*a*) *Dehydration, i.e.,* loss of water from slaked-lime by evaporation ;

(*b*) *Carbonation, i.e.,* reaction of atmospheric carbon dioxide with lime, forming limestone.

$$CaO + CO_2 \longrightarrow CaCO_3 \text{ (limestone)}$$

or

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

(*c*) It is also believed that *part of calcium hydroxide in the mortar is in the form of a colloidal gel,* which gradually hardens.

Thus, the net effect of setting is *transformation of lime into a hard substance, $CaCO_3$, which serves as a binding/finishing material.* This process of setting involves loss of water, so *shrinkage in the volume* of mortar takes place. In order to overcome this shrinkage, a material like sand (or surkhi) is added to lime, while preparing mortars.

Setting of hydraulic lime is mainly due to *the decomposition of complex silicates of calcium and aluminium,* in presence of water, into simpler compounds like calcium silicate, calcium aluminate, and calcium hydroxide. *These crystallize and form a hard mass in the interior ; while calcium hydroxide, which is soluble in water, comes to the surface and crystallizes to form calcium carbonate, under the action of atmospheric carbon dioxide.* Due to this fact, *hydraulic limes can set and harden under water also.*

6. Hardness *is the capacity of the lime mortars to resist abrasion and impact on setting.* High-calcium lime mortars set *least* hard as compared to the high-magnesium (or dolomitic) limes.

15.5 GYPSUM PLASTER

The mineral **gypsum** [which consists essentially of hydrated calcium sulphate, $CaSO_4 . 2\,H_2O$] *is extensively used as raw material for the manufacture of plasters,* which are almost universally used for coating the inner walls of dwellings. As mined, however, it usually contains a considerable percentage of impurities, the chief of which are clay, calcium and magnesium carbonates, and iron oxide.

Plaster of Paris [$CaSO_4 . \frac{1}{2} H_2O$] *is produced by heating fairly pure gypsum to a temperature of about 120–160°C.* If the gypsum by heated above 200°C, the anhydrous sulphate is produced, which *loses* the power of readily combining with water. The various changes may be depicted as follows :

$$\underset{\text{(Gypsum)}}{CaSO_4 . 2\,H_2O} \rightleftharpoons \underset{\substack{\text{(Orthorhombic}\\ \text{dihydrate)}}}{CaSO_4 . 2\,H_2O} \overset{120°}{\rightleftharpoons} \underset{\text{(Plaster of Paris)}}{CaSO_4 . 1/2\,H_2O} \xrightarrow{200°C} CaSO_4$$

The operation of manufacturing plaster of Paris from gypsum consists in first crushing and grinding of gypsum, and then calcining the ground product in kilns (heated to about 150°C) and finally, pulverizing the calcined product.

Setting and hardening : *When plaster of Paris is mixed with water, the powder forms a plastic mass, which quickly hardens or sets,* ***expanding slightly*** *in the process and regains the closely-packed crystalline structure of gypsum* ($CaSO_4 . 2H_2O$). Setting of plaster of Paris can be *accelerated* by admixing it with alkali sulphates like K_2SO_4, Na_2SO_4 (or alums), which initiate as well as hasten the crystallization process.

Uses : (1) Its *slight expansion on setting*, renders plaster of Paris suitable for making moulds, since details are thereby accurately reproduced. (2) It is used in making castings structural tiles and in *surgical bandages.* (3) Its chief uses are as *plaster for walls* and in *plaster-board*, which is made up of alternate layers of a fibrous material such as felt or paper and gypsum plaster.

15.6 CEMENT

Cement may be broadly be described as *"a material possessing adhesive and cohesive properties, and capable of bonding materials like stones, bricks, building blocks, etc."* The principal constituents of cement used for constructional purposes are *compounds of Ca* (calcarious) *and Al + Si* (argillaceous). *The cements have property of setting and hardening under water, by virtue of certain chemical reactions with it and are, therefore, called* ***'hydraulic cements'.***

CLASSIFICATION : (1) Natural cement *is made by calcining a naturally occurring argillaceous limestone (i.e., 20-40% clay-containing limestone) at a high temperature and subsequently, pulverizing the calcined mass.* During calcination, silica and alumina, present in sufficient quantities, combine with the calcium oxide to form the corresponding calcium silicates and aluminates.

Properties : Natural cement possesses *hydraulic* qualities, but is quick-setting and of relatively low strength. Mortar made from natural cement and sand is satisfactorily used in laying bricks and setting stones. It is also used in large masses of concretes such as dams and foundations. After the discovery of Portland cement, the use and production of natural cement has been nearly dropped.

(2) ***Puzzolana cement*** is among the oldest cementing materials known. It was invented by Romans and used by them in making concrete for the construction of walls and domes. By definition, ***puzzolana cements*** *"are materials which when mixes with lime, without the use of heat, form hydraulic cementing materials".* Such cements consist, essentially, of silicates of aluminum, iron and calcium. Puzzolana cements are made by simply mixing and griding : (*i*) *natural puzzolana* (which are deposits of volcanic ash) consisting of a glassy material, produced by rapid cooling of *lava* (a molten mixture of silicates of calcium, iron and aluminium), and (*ii*) *slaked-lime.*

Properties : Puzzolana cements possess *hydraulic* properties. They are seldom used as such at present time, but are mixed with Portland cement.

(3) **Slag cement** *is made from blast furnace slag and hydrated lime.* The blast furnace slag (consisting largely of a mixture of calcium and aluminium silicates) is granulated by pouring it into a stream of cold water. It is then dried and mixed with hydrated lime, and then the mixture is finely pulverized. Slag cements are *slow to harden*, so an accelerator like clay, salt or caustic soda is sometimes added.

Properties : Slag cements *set more slowly than Portland cement.* They have lower strength and are poor in abrasion-resistance. Slag cements are used, to a limited extent, for making concrete in bulk construction, where strength is relatively unimportant.

(4) **Portland cement** is defined as *"an extremely finely ground product obtained by calcining together, at about 1.500°C, an intimate and properly proportioned mixture of argillaceous (clay-containing) and calcareous (lime-containing) raw materials, without the addition of anything subsequent to calcination, excepting the retarder gypsum".*

Properties : Portland cement is the most important and reliable cementing material, used for constructional works. It was discovered in 1824 by Joseph Aspidin, a brick layer of Leeds. It was so-named, because *a paste of cement with water on setting and hardening resembled in colour and hardness to Portland stone, a limestone quarried in Dorset.*

15.7 MANUFACTURE OF PORTLAND CEMENT

Raw materials for the manufacture of cement are : (1) *Calcaerous materials,* CaO [such as limestone, chalk, marl, etc.] ; (2) *Argillaceous materials,* Al_2O_3 and SiO_2 [such as clay, shale, slate, etc.] ; (3) *Powdered coal or fuel oil,* and (4) *Gypsum* ($CaSO_4 . 2 H_2O$)

Functions of the ingredients of cement : (1) ***Lime*** is the principal constituent of cement. Its proportion must be properly regulated. However, *excess of lime reduces the strength of cement,* because it makes the cement to expand and disintegrate. On the other hand, presence of lesser amount of lime than required also reduces the strength of cement and makes it quick-setting.

(2) ***Silica*** imparts strength to cement.

(3) ***Alumina*** makes the cement quick-setting. Excess of alumina, however, weakens the cement.

(4) ***Calcium sulphate*** (gypsum) helps to retard the setting action of cement. *It actually enhances the initial setting time of cement.*

(5) ***Iron oxide*** provides : (*a*) colour, (*b*) strength, and (*c*) hardness to the cement.

(6) ***Sulphur trioxide***, in small proportion, is desirable. When present in small amount, it imparts *soundness* to cement. However, its excess reduces the soundness of cement.

(7) ***Alkalis***, if present in excess, cause the cement efforescent.

Manufacture of Portland cement involves the following **steps** :

(1) **Mixing of raw materials** can be done either by : (*a*) dry process or (*b*) wet process.

(*a*) **Dry process :** The raw materials [limestone (or chalk) and clay (or shale)] are *crushed* (in gyratory crushers) into roughly 2-5 cm size pieces. Then, these are ground to *fine powder* (in ball mills/tube mills). 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 (called *silos*) 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 :

Component	*Percentage range by mass*
Lime (CaO)	60–69
Silica (SiO_2)	17–25
Alumina (Al_2O_3)	3–8
Iron oxide (Fe_2O_3)	2–4
Magnesium oxide (MgO)	1–5
Sulphur trioxide (SO_3)	1–3
Alkali oxides ($Na_2O + K_2O$)	0.3–1.5

(*b*) **Wet process :** The calcareous raw materials are crushed, powdered and stored in big storage tanks (called *silos*). The argilaceous material (say clay) is thoroughly mixed with water in wash mills, to remove any adhering organic matter, etc. The basin-washed clay is also stored. Powdered limestone (from silos) and washed wet-clay (from basins) are allowed to flow in a channel, in the right proportions. From the channel, the two raw materials are led to *'grinding mills'*, where they are mixed intimately to form a paste, called *slurry* [Grinding operation is carried out in either tube mill or ball mill or both]. The slurry is led to a *'correcting basin'*, where its chemical composition may be adjusted, if necessary. *This slurry contains about 38 to 40 per cent water.* The slurry is finally stored in storage tanks and kept ready for feeding to a rotary kiln.

Table 2 : *Merits and demerits of dry and we processes.*

Dry process	*Wet process*
1. It is adopted when the raw materials are *quite hard*.	It can be used for *any type* of raw materials.
2. Fuel consumption is *low*.	Fuel consumption is *higher*.
3. Process is *slow*.	Process is comparatively *faster*.
4. Cement produced is of *inferior* quality.	Cement produced is of *superior* quality.
5. Cost of production of cement is *less*.	Cost of production of cement is somewhat *higher*.
6. On the whole, the process is *costly*.	On the whole, the process is *cheaper*.

(2) Burning 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*. The kiln is laid in *slightly inclined* position at a gradient of 1 in 25 to 1 in 30. This rests on *roller bearings*, which are supported on column of masonry or concrete. The kiln is *capable of rotating* at 1 r.p.m. (revolution per minute) about its longitudinal axis. *Burning fuel* (usually powdered coal or oil) and *air* are injected at the lower end. A long hot flame is produced, which heats the interior of the kiln upto a maximum temperature of about 1,750°C.

Process : The *'raw-mix'* or *'corrected-slurry'* is injected into the kiln at its upper end; while *hot flames* is forced into the kiln from the lower 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.* As the mixture or slurry gradually descends, the temperature *rises*.

Chemistry : (*i*) In the upper part of kiln, where the temperature is around 400°C, most of the water in the slurry gets evaporated (**drying zone**).

(*ii*) 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* [**calcination zone**].

$$\underset{\text{Limestone}}{CaCO_3} \rightleftharpoons \underset{\text{Quicklime}}{CaO} + CO_2\uparrow$$

(*iii*) In the lower part of the kiln, the temperature is between 1,500 to 1,700°C. Here lime and clay (of nodules) undergo chemical interaction or fusion, yielding *calcium aluminates and silicates* (**clinkering zone**).

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

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

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

$$4\,CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tricalcium aluminoferrite } (C_4AF)}{Ca_4Al_2Fe_2O_{10}}$$

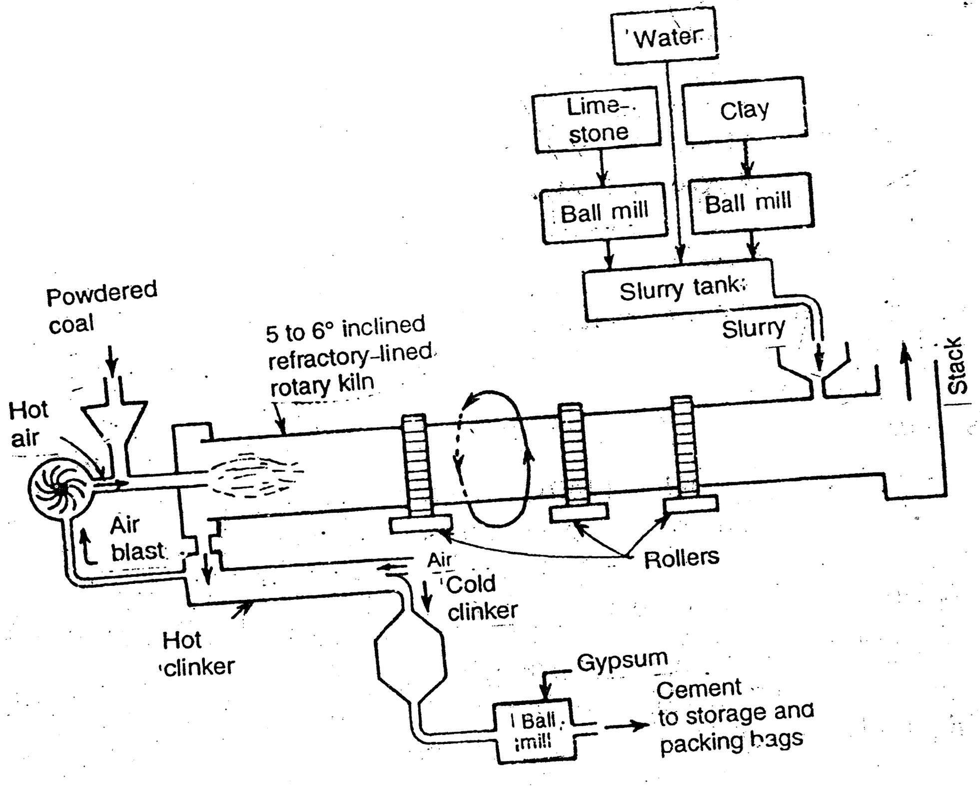


Fig. 2. Rotary cement kiln.

The aluminates and silicates of calcium then fuse together to form small (of about 0.5 to 1 cm diameter) hard, greyish stones, called *clinkers*. These clinkers are very hot (at about 1,000°C). 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 / oil*. The cooled clinkers are collected in small *trolleys*.

(3) Grinding : The cooled clinkers are ground to a fine powder in ball mills or tube mills. During final grindings, a small quantity (2-3%) of powdered gypsum is added, so that the resulting cement *does not set very quickly*, when it comes in contact with water. *Gypsum, thus, acts as a retarding agent for early setting of cement.*

After the initial set, the cement-water paste becomes stiff, but *gypsum* ***retards** the dissolution of C_3A* by forming tricalcium sulphoaluminate ($3\,CaO \cdot Al_2O_3 \cdot x\,CaSO_4 \cdot 7\,H_2O$), which is *insoluble*. Thus :

$$\underset{\text{After initial set}}{3\,CaO \cdot Al_2O_3} + \underset{\text{Gypsum}}{x\,CaSO_4 \cdot 7\,H_2O} \rightarrow \underset{\substack{\text{Tricalcium sulphoaluminate}\\ (\textit{Insoluble})}}{3\,CaO \cdot Al_2O_3 \cdot x\,CaSO_4 \cdot 7\,H_2O}$$

Formation of insoluble tricalcium sulphoaluminate prevents too early further reactions of setting and hardening.

(4) Packing : The ground cement is stored in *silos*, from which it is fed to automatic packing machines. Each bag, usually, contains 50 kg of cement.

FLOW DIAGRAM FOR WET PROCESS

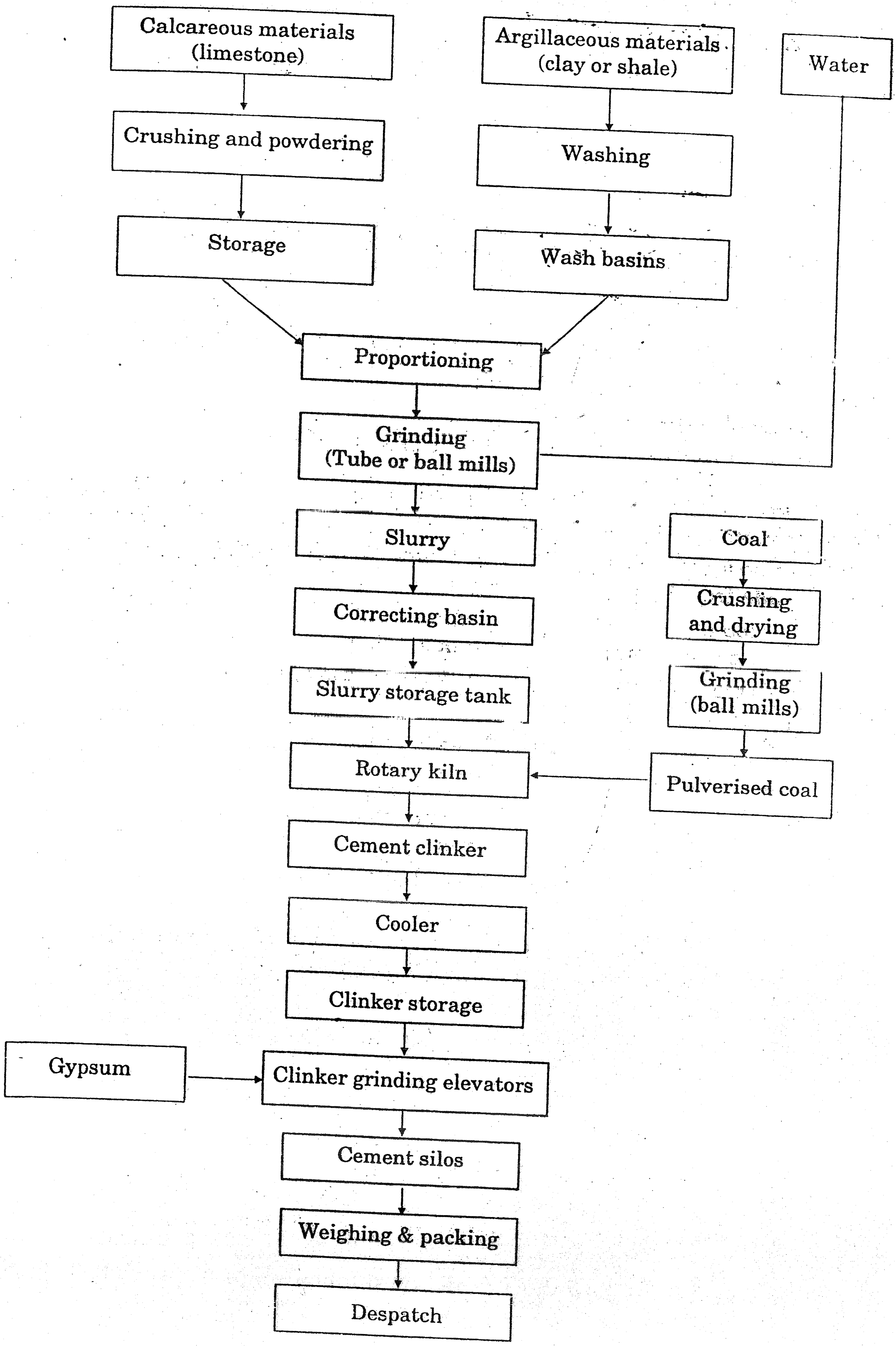


Fig. 3. Flow diagram of cement manufacture.

15.8 CHEMICAL COMPOSITION OF CEMENT

According to **I.S. 269 – 1975**, composition of ordinary Portland cement shall satisfy the following conditions :

(1) Ratio of the percentage of lime (CaO) to that of silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3), when calculated by the formula :

$$\frac{CaO - 0.7\ SO_3}{2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3}$$

shall not be less than 0.66 and more than 1.02.

(2) Ratio of percentage of alumina (Al_2O_3) to that of iron oxide (Fe_2O_3) shall *not be less that 0.66*

(3) Weight of *insoluble residue* shall not exceed 2 percent.

(4) Weight of magnesia shall not be more than 6 percent.

(5) Total sulphur contents, calculated as sulphuric anhydride (SO_3), shall not be more than 2.75 percent.

(6) Total loss on ignition shall not exceed 4 percent.

Notes : In the manufacture of Portland cement, great care is taken to see that the composition satisfies the above.

(i) If too much lime is present, the cement will be 'unsound', that is, after sometime concrete made from it will expand and crack.

(ii) If too little lime is present, the concrete will be low in strength and may 'set quickly', *i.e.*, hardens before the mason has a chance to place it in the forms.

(iii) Cement in which alumina is high is also apt to be quick-setting and hard to burn uniformly.

(iv) High silica cements are, usually, very slow hardening and do not attain their full strength for a considerable period.

Physical requirements of cement : (1) ***Setting time*** : *Initial* : Not less than 30 minutes ; *Final* : Not more than 600 minutes.

(2) ***Compressive strength*** (of 1 : 3 cement mortar cube of cement and Ennore sand) :

3 days : Not less than 1.6 kg/mm^2 (or 16 N/mm^2).

7 days : Not less than 2.2 kg/mm^2 (or 22 N/mm^2).

(3) **Soundness :** By *Le-Chatelier's method :* It expresses the expansivity of the cement set in 24 hours between 25°C and 100°C.

Unaerated cement : Maximum 10 mm.

Aerated cement : Maximum 5 mm.

Note : Soundness : *If a cement on hydration produces only very small volume changes, the cement is said to be* **'sound'**. Soundness is directly related to the presence of excessive amount of crystalline magnesia (MgO), which contributes to unsoundness. In Le-Chatelier's test, a test-piece of specific dimensions is placed in boiling water for 3-5 hours and its expansion then measured.

(4) *Fineness* : Not less than 215 m^2/kg. *Finer* the grinding, the *greater* is the rate of reactions, thereby *hastening* the early development of strength. However, finer cement *generates heat quickly*, thereby the cement mortar/concrete is likely to develop *cracks*.

15.9 CHEMICAL CONSTITUTION OF PORTLAND CEMENT

Average compound composition of Portland cement is :

Name of compound	*Chemical formula*	*Abbreviation used*	*Average %*	*Setting time*
Tricalcium silicate	$3CaO . SiO_2$	C_3S	45	7 days
Dicalcium silicate	$2CaO . SiO_2$	C_2S	25	28 days
Tricalcium aluminate	$3CaO . Al_2O_3$	C_3A	1	~~1 day~~
Tetracalcium aluminoferrite	$4CaO . Al_2O_3 . Fe_2O_3$	C_4AF	9	1 day
Calcium sulphate	$CaSO_4$	–	5	–
Calcium oxide (*free*)	CaO	–	2	–
Magnesium oxide	MgO	–	4	–

Characteristics of constituents : (*i*) ***Tricalcium silicate*** (C_3S) has "*medium*" rate of hydration ; and *develops high ultimate strength quite rapidly.* Moreover, its ultimate-strength is also the *highest* amongst all the constituents. So it is responsible for ultimate-strength. The heat of hydration is about 880 kJ/kg.

(*ii*) ***Dicalcium silicate*** (C_2S) has quite low early-strength, but develops ultimate-strength of *slightly less than* that of C_3S. It hydrates *very slowly*. It is also responsible for ultimate-strength. It possesses the heat of hydration of 420 kJ/kg.

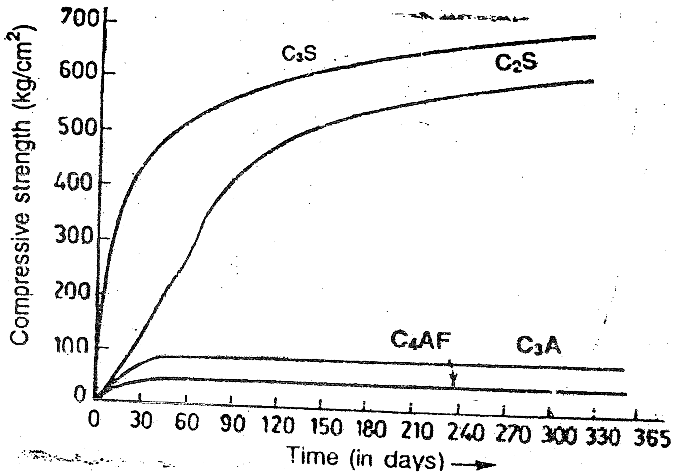


Fig. 4. Development of strength by major constituents in cement.

(*iii*) ***Tricalcium aluminate*** (C_3A) hydrates slowly and *does not* contribute much to the strength of cement, since its early-strength and ultimate-strength are *poorest* amongst all the constituents. Its heat of hydration is about 250 kJ/kg.

15.10 SETTING AND HARDENING OF PORTLAND CEMENT

When cement is mixed with water to a plastic mass, called "cement paste", *hydration reaction begin, resulting in the formation of gel and crystalline products.* The interlocking of the crystals, finally bind the inert particles of the aggregates into a compact rock-like material. The process of solidification-comprises of : (*i*) *setting,* and then (*ii*) *hardening.* '**Setting**' is defined as *stiffening of the original plastic mass, due to initial gel formation.* "**Hardening**" *is development of strength, due to crystallization.*

After setting, hardening starts, due to the gradual progress of crystallization in the interior of the mass. *The strength developed by cement paste at any time, depends upon the amount of gel formed and the extent of crystallization.*

Initial setting *of cement-paste is mainly due to the hydration of tricalcium aluminate* (C_3A) *and gel formation of tetracalcium aluminoferric.*

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

or

$$\underset{\text{Tricalcium aluminate}}{C_3A} + 6\ H_2O \longrightarrow \underset{\text{Hydrated tricalcium aluminate (\textit{Crystalline})}}{C_3A\ .\ 6\ H_2O} \quad + 880\ kJ/kg$$

$$\underset{\text{Tetracalcium aluminoferrite}}{4\ CaO\ .\ Al_2O_3\ .\ Fe_2O_3} + 7\ H_2O \longrightarrow \underset{(\textit{Crystalline})}{3\ CaO\ .\ Al_2O_3\ .\ 6\ H_2O} + \underset{(\textit{Gel})}{CaO\ .\ Fe_2O_3\ .\ H_2O} + 420\ kJ/kg$$

or

$$C_4AF + 7\ H_2O \longrightarrow C_3A\ .\ 6\ H_2O\ (\textit{crystalline}) + CF\ .\ H_2O\ (\textit{gel}) \quad + 420\ kJ/kg$$

Also *dicalcium silicate starts hydrolysing to tobermonite gel* (which possesses a very high surface area* and thus, very high adhesive property), which also contributes to initial setting

$$2\ [2\ CaO.SiO_2] + 4\ H_2O \longrightarrow 3\ CaO.2SiO_2.6\ H_2O + Ca(OH)_2 + 250\ kJ/kg$$

or

$$\underset{\text{Discalcium silcate}}{2\ C_2S} + 4\ H_2O \longrightarrow \underset{\text{Tobermonite gel}}{C_3S_2\ .\ 6\ H_2O} + \underset{\text{Crystailine calcium hydroxide}}{Ca(OH)_2} \quad + 250\ kJ/kg$$

Final setting and hardening *of cement-paste is due to the formation of tobermonite gel (formed above) plus crystallization of calcium hydroxide and hydrated tricalcium aluminate.*

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

or

$$2\ C_3S + 6\ H_2O \longrightarrow C_3S_2\ .\ 3\ H_2O + 3\ Ca(OH)_2 \quad + 500\ kJ/kg$$

The setting and hardening of cement may be depicted in Fig. 5.

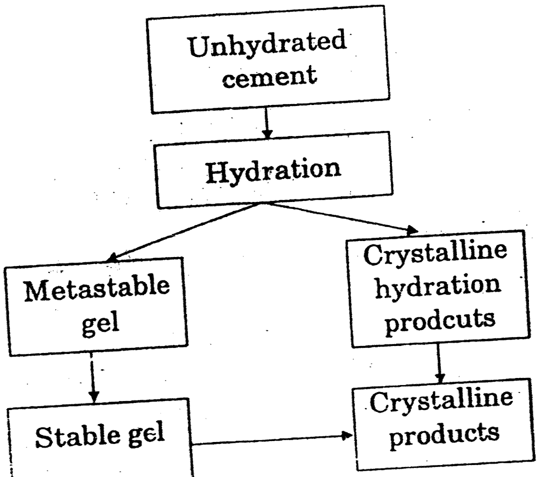


Fig. 5. Setting and hardening of cement.

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* 1 g of *cement* has a surface area of above 10^3 cm^3 ; whereas 1 g of *tobermonite gel* has a surface area of 10^6 cm^3.

Sequence of chemical reactions during setting and hardening of cement : When water is added to cement, its various constituents undergo hydration and crystallization at different rates. (*i*) At first, hydration of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) takes place. (*ii*) Next, the hydration of tricalcium silicate (C_3S) begins within 24 hours and gets completed in 7 days. (*iii*) The gel of aluminate begins to crystallize and at the same time, dicalcium silicate (C_2S) begins to hydrate in 7 to 28 days. Thus, the *initial set* of cement is due to the *hydration of aluminate.* The development of *early-strength,* between 1 to 7 days, is due to the *hydration of tricalcium silicate* and the further hydration of aluminate. The *increase of strength,* between 7 to 28 days, is due to *hydration of dicalcium silicate and continued hydration of tricalcium silicate.*

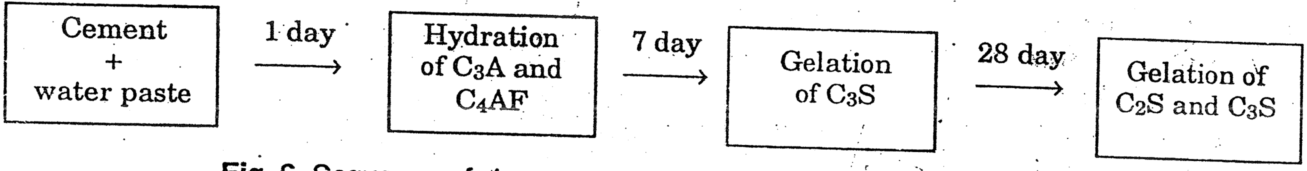

Fig. 6. Sequence of changes during setting and hardening of cement.

Function of gypsum in cement : Tricalcium aluminate (C_3A) combines with water very rapidly with the evolution of a large amount of heat.

$$C_3A + 6\,H_2O \longrightarrow C_3A\,.\,6\,H_2O + \text{Heat}$$

After the initial-set, the paste becomes somewhat stiff. However, the added gypsum retards the dissolution of C_3A by forming *insoluble calcium sulpho-aluminate* :

$$3CaO\,.\,Al_2O_3\,.\,xCaSO_4\,.\,7H_2O.$$

This reaction prevents a high concentrations of alumina in the cement solution, thereby *retarding the early initial-set of the cement.*

15.11 HEAT OF HYDRATION OF CEMENT

When water is mixed with cement, hydration, hydrolysis and gelation reactions start and some heat is liberate simultaneously. On an average, 500 kJ/kg of heat is evolved during complete hydration of cement. The heats of hydrations of various constituents of cement are as follows :

Constituent of cement	C_3A	C_3S	C_4AF	C_2S
Heat of hydration (kJ / kg)	880	500	420	250

Consequently, in order to avoid the shrinkage cracks on setting and hardening, it is quite necessary to pour concrete in position in such amounts that the *heat liberated during hydration is dissipated as quickly as possible.*

15.12 SPECIAL CEMENTS

(1) **Aluminous** or **high-alumina cements** *are made by fusing a mixture of bauxite and limestone at 1,500 to 1,600°C in rotary kiln and then grinding the resulting mass to the same fineness as that of Portland cement.*

Typical composition of such a cement is : 35 to 40% CaO : 35 to 55% Al_2O_3 ; 5 to 15% FeO + Fe_2O_3, and 5 to 10% SiO_2. The most important constituents of such cements are *monocalcium aluminate* (CA) and *tricalcium pentaluminate* (C_3A_5), besides some dicalcium silicate (C_2S) and tetracalcium aluminoferrite (C_4AF). Both CA and C_3A_5 hydrate initially to a gel, $CaAl(OH)_5\,.\,3H_2O$, which gradually changes to a very stable crystalline complex, $Ca_3Al_2(OH)_{12}\,.\,3H_2O$ and a gel of aluminium hydroxide, $Al(OH)_3$. The setting time of high-alumina cement is similar to that of

Portland cement, but its *rate of hardening is very rapid and full-strength is attained in 24 hours*. Since the crystalline complexes formed from high-alumina cements are stable, even on heating, so the *aluminous cement retains its strength at high temperatures*. Another advantage of high-alumina cement, as compared to Portland cement, is its *superior chemical-resistance to sea-water and sulphate-bearing ground water*. Moreover, such a cement *is resistant to very dilute acid solutions* (frequently occurring in industrial wastes), *dilute sulphourous acid solutions* (resulting from the combustion of sulphur-containing fuels) and to hydrogen sulphide solutions.

The advantages of *rapid-hardening* of aluminous cement is, however, offset to some extent by a *rapid evolution of heat of hydration*, which cannot be easily dissipated in a short time. This causes a considerable rise in the temperature of the concrete mass, if in a layer of more than 5 cm thickness, but it is an asset when *concreting is done under freezing conditions*. High-alumina cement should not be mixed with Portland cement, when fresh, because a *flash set occurs*, resulting in a *very weak bond*. However, hardened Portland cement can be bonded to high-alumina cement to get a strong bond.

(2) **High early-strength (H.E.S.) cements** *are made from materials with a high lime to silica ratio*. They contain a *higher proportion of tricalcium silicate* than regular Portland cements and hence, *harden more quickly and with greater evolution of heat*. During the manufacture of such rapid hardening cements, addition of gypsum, during the final grinding, is usually *avoided* and also such cements are *grinded much finer* than ordinary cements. Such cements have only 5 minutes and 30 minutes initial and final setting times respectively.

(3) **White Portland cement** *is white in colour, owing to the absence of iron compounds*. Such cements are made from raw materials which are *free from iron oxide*. It is very expensive and finds useful applications, *e.g.*, repairing and joining marble pillars and blocks, manufacture of tiles and for mosaic works. For the latter purpose, the cements may be coloured by means of colouring matters like yellow ochre, venetain red, etc.

(4) **Sorel cement** *is made by the addition of a strong solution of magnesium chloride to finely ground calcined magnesia*. The material, sometimes known a *magnesium oxychloride cement* [$3MgO \cdot MgCl_2 \cdot 11H_2O$], *sets hard in three to four hours*. This material is principally used in composite flooring. Such floorings have the advantage of being non-slip, fire-proof, not easily scratchable, durable and capable of taking a good wax or oil polish.

The rate of hardening of cement is still increased by addition of *calcium chloride or formate*. The accelerated rate of setting is especially useful during cold weather. It is believed that $CaCl_2$ accelerates the hydration of C_2S and C_3S, the strength-contributing components of the cement. On the other hand, the hydration of C_3A is retarded. The optimum quantity of $CaCl_2$ to be used for such purposes is 1.5% by weight of the total weight of cement. However, if this is exceeded, the corrosion of the steel embedded in the concrete is promoted, especially if the concrete is less compact or porous.

(5) **Barium and strontium cements** *are obtained by replacing calcium by barium or stronium*. So, such as a cement contains tribarium and dibarium silicates, instead of calcium silicates. Such cements show increased resistance to penetrations by radioactive radiations. Hence, they find extensive applications in *concrete shields for atomic piles*.

(6) **Silicate cements** or **acid-resistant cements** *are produced by mixing an inert acid-resisting aggregate (such as finely ground quartzite) with sodium or potassium or silicon ester, in suitable proportions*. Their cementing propety is due to the precipitation of the silica gel, caused by adding suitable setting agents such

as sodium silicon fluoride or ethyl acetate or by evaporation of water. The bond developed by silicate cement is hard, but also brittle. On drying, this cement becomes very porous and permeable to liquids. For this reason, it should always be kept wet or immersed in a liquid to prevent shrinking of the gel.

(7) Water-proof cement : Such a cement is obtained by adding *water-proofining substances* (like calcium stearate, aluminium stearate and gypsum with tannic acid) to ordinary Portland cement, during grinding. The characteristics of such cements depend on the type and quantity of admixture added. A water-proof cement has to do *two* distinct functions, *viz.*, (*i*) *to make concrete impervious to water under pressure, and* (*ii*) *to resist the absorption of water*. Chemically inactive substances added are like calcium soaps, aluminium soaps, resins, vegetable oils, waxes, coal-tar residues and bitumen, which acts as *pore-blocking agents*. These act as *water-repelling agents*. Moreover, they increase appreciably the *resistance to the penetration of moisture*.

15.13 CONCRETE AND RCC

Concrete *is a building and structural material, obtained by mixing a binding material (cement or lime), inert mineral aggregates (sand, crushed stone, gravel, broken brick, slag, etc.) and water in a suitable proportion and which can be readily worked or moulded into almost any desired shape and when sel, it is compact, rigid, strong and durable.*

When *lime* is the binding material, the concrete is known as *lime concrete* and when *cement* forms the binding material, the concrete is called as *cement concrete*. The proportions of cement and aggregates in concrete vary with the use to which it is to be put. For *water-tight works*, concrete is made up of 1 part cement, 1 part sand and 2 parts gravels. If not required to be water-tight, the mixture can be changed to 1 part cement, 3 parts sand, and 5 parts gravels. *The more the cement, within limits, the more water-proof the concrete will be.*

Uses of concrete : Concrete is by far the most important of all non-metallic materials of construction. It ranks *second* only to steel in its wide and varied constructional importance. Its typical uses are in roads, buildings, floors, roofs, columns, arches, tanks, sewers, foundations, abutments, piers, reinforce-works, water-proof structures and other purposes where compressive strength is required.

Curing of concrete : *The hardening of concrete is due to hydration reaction of the constituent cement compounds.* These processes continue indefinitely, but the greatest amount of strength and hardness is developed during the first few days, immediately following placement, *So it is essential to keep the concrete damp for at least a week, to enable the hydration reactions to occur completely.* Moreover, the chemical reactions of the cement and water progresses only under favorable temperature conditions. *Reactions are slowed down in concrete at low temperature and completely stops, when the water in the concrete is frozen.* ***Curing*** *is the process of maintaining a satisfactory moisture content and favorable temperature in concrete during the period immediately following placement, so that hydration of the cement may continue, until the desired properties are developed to a sufficient degree to meet the requirement of service.* During hydration of cement, lot of heat is evolved. So special care has to be taken to dissipate this heat ; otherwise cement work is likely to develop *cracks. Thus, curing also helps in dissipation of heat.*

Reinforced concrete construction (R.C.C.) : *Plain concrete has a great compressive strength, but little ability to withstand tension.* Consequently, structures which are required to bear tensile stresses are *reinforced* (or strengthened) by embedding steel bars or rods and metal meshes in such a way that the tension is taken up by the steel ; while the concrete carries the compression. *This combination of steel and concrete produces structure, called* ***reinforced concrete construction* (*R.C.C.*)**, *which can bear all types of loads.* Reinforced concrete work is mostly used in floor-beams, piers, lintels, girders, arches, slabs, bridges, etc.

Advantage of R.C.C. over plain concrete : (1) R.C.C. is easier to make and cast into any desired shapes, which can bear *all types of loads.* (2) It possesses *greater* rigidity, moisture and fire-resistances. (3) Steel reinforcement also tends to *distribute the shrinkage cracks*, thus preventing the formation of large cracks. (4) Its maintenance cost is *practically negligible*.

15.14 DECAY OF CONCRETE

Although cement concrete is mechanically quite strong, yet it highly susceptible to chemical attack, because concrete contains some free lime (CaO). In acidic water (*viz.*, pH < 7), lime of concrete dissolves, thereby making it *weak*, pH of most natural waters is slightly greater than 7 (*i.e.* they are slightly alkaline), consequently, such waters do not have any marked effect on the strength of concrete. However, as the acidity increases (or pH decreases), the deterioration of concrete enhances. It may be pointed here that *lime is more soluble in soft water than hard water*. Consequently, deterioration of concrete is more quick, when in contact with soft water. Lime of concrete is also removed by sulphates and chlorides, present in water. If concrete is soaked in mineral oil for sometime, its resistance to abrasin decreases. Sugar also causes concrete failure. If even as low as 0.1% sugar is added to cement, the setting time is delayed and its strength is greatly reduced, during the first four weeks. The cause of concrete failure, due to presence of sugar has been traced in the use of old sugar sacks for carrying sand or for covering the freshly concrete used during curing.

The most serious type of damage to concrete takes place in the presence of *sulphates*. The sulphates combine with tricalcium aluminate to form sulphoaluminates, which occupies *more volume*. This causes expansion, thereby the life of concrete is greatly reduced. Such a danger can be avoided by eliminating tricalcium aluminate from the cement composition and manufacturing cement containing tetracalcium aluminoferrite, instead of aluminate.

Protection of concrete : (1) *By giving a coating of bituminous material.* This prevents direct contact between concrete and water. This is a very cheap method.

(2) *By coating the surface with silicon fluoride* in a soluble form together with oxides of Zn, Mg or Al. The precipitate of calcium fluoride so-formed in the capillaries prevents dissolution of lime.

16

Refractories

> ***"The great importance of refractories is evident, when it is pointed that the steel shells of Portland cement kilns, of Bessemer steel converters, of gas producers, and water-gas generators are lined with refractory bricks."***

16.1 INTRODUCTION

Broadly speaking, ***refractory*** *is any material that can withstand high temperatures, without softening or suffering a deformation in shape.* Refractories are the essential materials of construction in metallurgy, engineering and chemical industries and without their use, it is impossible to maintain required high temperatures. The main objective of a refractory is to *confine heat* (*i.e.,* to resist loss of heat) and at the sametime to *resist the abrasive and corrosive action of molten metals, slags and gases* at high operating temperatures, without undergoing softening or distortion in shape.

Refractories are mostly used for the construction of the linings of the furnaces, tanks, converters, kilns, crucibles, ladles, etc., employed for the manufacture of metals (ferrous as well as non-ferrous), cement, glass, ceramics, paper, steel, etc.

Characteristics : A good refractory possesses the following characteristics : It should : (1) be *infusible* at the temperature to which it is liable to be exposed ; (2) be *chemically inerts* towards corrosive action of gases, metallic liquids and slags, produced in its immediate contact in furnaces ; (3) *resist the abrading action* of flue gases, flames, etc. ; (4) be able to *withstand the overlying load* of structure, at operating temperatures ; (5) *not crack and suffer loss in size,* at the operating temperatures ; (6) *expand and contract uniformly*, with temperature rise and fall respectively.

Classification of refractories : Refractories are classified into *three* main types, on basis of the *chemical properties* of their constituent substances ;

1. Acid refractories are those which consist of *acidic materials* like alumina (Al_2O_3) and silica (SiO_2). *They are not attacked by acidic materials, but easily attacked by basic materials.* Important members of this group are *alumina, silica* and *fireclay* refractories.

2. Basic refractories are those which consist of *basic materials* like CaO, MgO, etc. *These are not attacked by basic materials, but easily attacked by acidic materials.* Important members of this group are *magnesite* and *dolomite* refractories.

3. Neutral refractories are made from *weakly acid/basic materials* like carbon, chromite ($FeO \cdot CrO_2$), zirconia (ZrO_2), etc. Important members of this group are *graphite, chromite, zirconia,* and *carborundum* (*SiC*) refractories.

16.2 PROPERTIES OF REFRACTORIES

More important ***characteristics*** of refractories are :

(1) **Refractoriness** *is the ability of a material to withstand the heat, without appreciable deformation or softening under particular service conditions.* Refractoriness is, generally, measured as the *softening or melting temperature* of the material. As most of the common refractory materials are mixtures of several metallic oxides,

so they *do not have a sharp fusion temperatures.* It is common practice to determine *softening temperature*, rather than fusion temperature. The softening temperatures of refractory materials are, generally, determined by using "**pyrometric cones** (also called *Seger cones*) **test**". *It is necessary that a material, to be used as refractory, should have a softening temperature much* ***higher*** *than the operating temperature of the furnace in which it is to be used.* It is, however, notworthy that the inner refractory lining in a furnace is at a much higher temperature than the outer ones. So, unless the refractory melts away completely, it can, usually, be employed to withstand a temperature higher than its softening temperature, since the outer end of refractory is at a lower temperature and still in solid state and it provides requisite strength.

Measurement : Refractoriness is, usually, determined by comparing the behaviour of heat on *cone of material to be tested* with that of a series of *Seger cones* of standard dimensions. The refractoriness is expressed in terms of *Pyrometric cone equivalent* (PCE). These cones are small pyramid-shaped, 38 mm high and have a triangular base, with 19 mm long sides. They melt or fuse at definite temperatures, when heated under standard condition of 10°C per minute. The temperature at which the fusion or softening of the test-cone occurs is indicated by its *apex touching the base* (*see* Fig. 1). The PCE value of the given refractory is taken as the number of the standard cone, *which fuses alongwith* the test-cone. If the test cone softens earlier than one standard cone, but latter than the next cone, the PCE value of the test sample is approximately measured as the average value of the two.

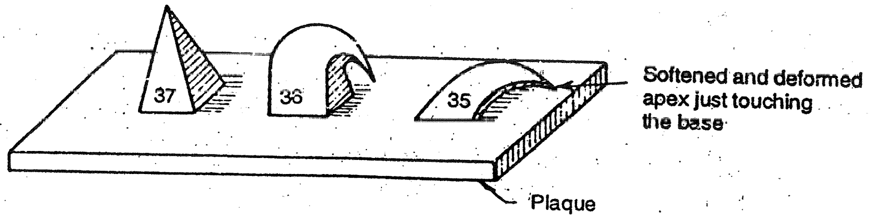

Fig. 1. Seger cone-test.

Table 1 : *Seger-cone number and fusion temperature.*

Seger-cone number	*Temperature °C*	*Seger-cone number*	*Temperature °C*	*Seger-cone number*	*Temperature °C*
1	1,110	12	1,350	27	1,610
2	1,120	13	1,380	28	1,630
3	1,140	14	1,410	29	1,650
4	1,160	15	1,435	30	1,670
5	1,180	16	1,460	31	1,690
6	1,200	17	1,480	32	1,710
7	1,230	18	1,500	33	1,730
8	1,250	19	1,520	34	1,760
9	1,280	20	1,530	35	1,770
10	1,300	23	1,550	36	1,790
11	1,320	26	1,580	37	1,825
				38	1,850

(2) Strength or **refractiorines-under-load :** Refractories in use, in industrial furnaces, have invariably to withstand varying loads of the products, being manufactured at high operating temperatures. *It is, therefore, essential that refractory materials must also possess high mechanical strengths, even at operating temperatures, to bear the maximum possible load, without breaking.* Some refractories, like fireclay and high-alumina bricks, soften gradually over a range of temperature, but under appreciable load, they collapse, far below their true fusion point, as determined by Seger cones. On the other hand, other refractories like silica bricks soften over a relatively narrow range of temperature and exert good load-bearing characteristics close to their fusion points.

R.U.L. test *is performed by applying a constant load (of 3.5 or 1.75 kg/cm^2) to the refractory specimen (of size 5 cm^2 and 75 cm high) and heating in a carbon-resistance furnace at a standard rate (of 10°C/minute).* The record of the height of the specimen *vs.* temperature is made by a plot, until the test-piece deforms or collapses by 10%. The R.U.L. is expressed as the temperature at which 10% deformation takes place. Under a load of 3.5 kg/cm^2 : (*i*) ***a high heat-duty brick should not deform a great deal (i.e., more than 10%) at 1,350°C*** ; (*ii*) ***an intermediate heat-duty brick at 1,300°C*** and (*iii*) ***a moderate heat-duty brick at 1,100°C***. Most of the applications of refractories find use only under *compressive* load ; and in rare cases, they may be subjected to tension or shear alone.

(3) Dimensional stability *is the resistance of a material to any volume changes, which may occur on its exposure to high temperature, over a prolonged time.* These dimensional changes may be *permanent* (*irreversible*) or *reversible*.

Irreversible changes *may result either in the* ***contraction or expansion*** *of a refractory. The* ***permanent contraction*** *is due to the formation of increasing amounts of liquid from the low fusible constituent of the refractory brick, when it is subjected to a long period of soaking at the high temperature. The liquid gradually fills the pores of the refractory body, causing a high degree of vitrification and shrinkage.* A typical example of such a behaviour as *fireclay brick*. The ***shrinkage*** of a refractory can also be caused by *the transformation of one crystalline form of material into another more dense form*. For example, *in a magnesite brick, amorphous MgO, which is relatively light* (*sp. gr* = 3.05), *is gradually converged to a more dense crystalline form, periclase* (*sp. gr.* = 3.54). *With the increase in density, there is a natural shrinkage of the material.* On the other hand, *the transformation of quartz* (*sp. gr.* = 2.65) *in silica bricks to tridymite* (*sp. gr.* = 2.26) *and cristobalite* (*sp. gr.* = 2.32) *at high service temperature is accompanied by a considerable increase in volume.* This thus accounts for *permanent* expansion of silica bricks in service.

(4) Chemical inertness : A refractory should be selected that is *chemically inactive in use and does not easily form fusible products with slags, fuel ashes, furnace gases,* etc. Usually, the environment in most furnaces is either acidic or basic. *It is inadivisable to employ* ***an acid refractory in contact with an alkaline product or vice-versa***.

(5) Thermal expansion : In a furnace design, *allowance has to be made for* ***thermal expansion,*** *since practically all solids expand, when heated and contract, when cooled.* The expansion affects *all dimensions* (*i.e.*, length, area and volume) of a body. So, it is necessary that *a refractory material should have* ***least*** *possible thermal expansion,* because : (*i*) expansion of a refractory *decreases the capacity* of the furnace ; (*ii*) repeated expansion and contraction contribute much towards *rapid breakdown*, and wear and tear of the refractory material structure.

(6) Thermal conductivity : In industrial operations, refractory materials of both high thermal conductivity and low thermal conductivity are required, depending upon the type furnace. In most cases, furnace is lined with refractories of ***low heat conductivities*** *to reduce the heat losses to the outside by radiation ;* otherwise maintenance of high temperatures inside the furnace will become difficult. However, ***a good heat conductivity*** *of refractory is desirable for effective heat transmission in some furnace construction,* as in muffle furnace walls, coke-oven batteries, in which *charge is separated from the flame.*

The ***densest and least porous*** *brick have the* ***highest*** *thermal conductivity, owing to the absence of air-voids.* On the other hand, *in* ***porous bricks,*** *the entrapped air in the pores, acts as a non-heat conducting material.* For making *porous* refractory bricks, the refractory material is mixed with a liberal amount of *carbonaceous* material, then moulded into bricks and burnt. The carbonaceous material burns off ; leaving behind *minute voids, which enhances the insulating quality.*

(7) Porosity : All refractories contain pores, either due to manufacturing methods or deliberately (by incorporating saw-dust or cork during manufacture). The pores may be *open* or *closed,* the latter are encountered in an oven-fired refractory. ***Porosity*** *in the ratio of its pore's volume to the bulk volume.* Thus, porosity,

$$P = \frac{W - D}{W - A} \times 100 \quad \text{where} \quad \left[\begin{array}{l} W = \text{Wt. of saturated specimen.} \\ D = \text{Wt. of dry specimen.} \\ A = \text{Wt. of saturated specimen} \\ \quad\;\; \text{submerged in water.} \end{array}\right.$$

Porosity is an important property of refractory bricks, because it affects many other characteristics, *e.g.,* chemical stability, strength, abrasion-resistance and thermal conductivity. In a *porous* refractory, molten charge, slags, gases, etc., are likely to *enter more easily* to a greater depth and may react and *reduce the life* of refractory material. *Porosity* ***decreases*** *the strength, resistance to abrasion, resistance to corrosion/penetration by slags, gases etc., but* ***increases*** *resistance to thermal spalling (i.e., thermal shock-resistance).* Moreover, *the* ***densest and least porous*** *bricks have the* ***highest thermal conductivity,*** owing to the absence of air-voids. In *porous bricks, the entrapped air in the pores, acts as a non-heat conducting material.* A good refractory, in general, should have *low porosity.*

(8) **Thermal spalling** *is breaking, cracking, peeling off or fracturing of a refractory brick or block, under high temperature.* So a good refractory must show a *good resistance to thermal spalling.* Spalling is, generally, due to *rapid changes in temperature,* which cause uneven expansion and contraction within the mass of refractory, thereby leading to development of internal stresses and strains. Spalling may also be due to *slag penetration* into the refractory brick, thereby causing *variation in the coefficient of expansion.* It has been found that ***spalling can be decreased by*** : (*a*) *using high porosity, low coefficient of expansion and good thermal conductivity refractory bricks,* since all these resist the development of internal stresses ; (*b*) *avoiding sudden temperature changes ;* (*c*) *by overfiring the refractories* (during manufacture) at high temperatures for a sufficiently long time, whereby *mineral inversion,* etc., takes place, making the material less susceptible to uneven expansion or contraction, when heated ; (*d*) *by modifying the furnace design* so that stresses are not set up, when the furnace is heated.

(9) Resistance to abrasion or erosion : *For a refractory to last longer, it is desirable that it is* ***least abraded*** *by descending hard charge, flue gases escaping at high speeds, particles of carbon or grit, etc.,* Resistance to erosion is very important for such constructions as by-product coke-oven walls, and linings of the discharge-ends of rotary cement kilns, etc.

(10) Electrical conductivity : Refractories to be used for lining *electric furnaces* should have *low electrical conductivity*. Except *graphite*, all other refractories are poor conductors of electricity. *However, electrical resistance of refractories decreases rapidly with temperature rise.*

(11) Heat capacity of furnace depends on : (*a*) *thermal conductivity* ; (*b*) *specific heat,* and (*c*) *specific gravity of refractory. In case of intermittently-operated furnaces, light-weight brickwork has an advantage,* since the working temperature can be achieved *in less time with less fuel*. Conversely, *the dense and heavy fire-bricks would be best* for regenerators, checker-works as in coke ovens, glass furnaces, and stoves for blast furnaces.

(12) Texture : *Coarse or light-textured bricks, because of their large porosity, are light in weight and hence, they are more resistant to sudden changes in temperatures.* However, their *crushing strength is low*. Such bricks are *more susceptible to the action of abrasion and corrosion.* On the other hand, *fine or dense-textured bricks* possess low porosity and hence, are heavier in weight. These are not so resistant to sudden changes in temperature. However, such bricks are less susceptible to action of abrasion and corrosion.

(13) Permeability *is a measure of rate of diffusion of gases, liquids and molten solids through a refractory,* Permeability depends upon the *size* and *number of connected pores*. With the rise of temperature, the permeability increases, since the viscosity of molten metals decreases with an increase of temperature. An increase in *bulk-density* (*i.e.*, ratio of weight to its volume) of a refractory increases the resistance to slag-penetration and spalling.

Conditions leading to failure of a refractory material :

(*i*) Using a refractory of refractoriness *less* that of the operating temperature.

(*ii*) Using *lower-duty* refractory bricks in a furnace than the actual load of raw materials and products.

(*iii*) Using bricks of *higher* thermal expansion.

(*iv*) *Rapid changes* in temperature of the furnace.

(*v*) Using *heavy-weight* refractory bricks.

(*vi*) Using refractory bricks which are *not properly fired.*

(*vii*) Using bricks which *undergo considerable volume changes* during their use at high temperatures.

(*viii*) Using *acidic / basic refractory* in a furnace in which *basic / acidic reactants* and/or products are being processed.

16.3 MANUFACTURE OF REFRACTORIES

Manufacture of refractories consists of the following ***steps*** *:*

1. Crushing : The raw materials in the form of big lumps are crushed to about 25 mm size.

2. Grinding : The crushed materials are ground, in suitable grinding machine, down to 200 mesh size.

3. Screening : It is employed to *purify* the refractory raw materials. For producing better refractories, it is essential to remove the *unwanted materials* from the raw materials and this done by : (*i*) settling, (*ii*) magnetic separation, and (*iii*) chemical methods.

5. Storage : After screening and mineral dressing, the pure materials are stored in storage bins with bucket elevators.

6. Mixing : It is done so that proper distribution of the plastic materials throughout the mass takes place. *This makes moulding easier.*

7. Moulding : Moulding may be done either manually or mechanically by the application of high pressure. *Hand-moulding* produces refractories of low density and low strength ; while *mechanical-moulding* produces refractories of high density and strength. In order to increase the density and strength of refractory by mechanical-moulding, the *de-airing* of refractory material is essential. De-airing is done : (*i*) by applying *vacuum* through vents in the moulds ; (*ii*) by allowing *air* inside the void space in the refractory to go out by decreasing the rate of pressure application and release of air ; (*iii*) by *double-pressing* : The material is first pressed and allowed to crack. Then, it is repressed again so as to close the voids.

8. Drying : Drying is carried out to remove the moisture from refractories. Generally, drying is carried out *very slowly* and under well-set conditions of humidity and temperature, depending upon the types of refractory. Drying is, usually, carried out in *tunnel driers*. Rack cars of bricks are placed in a long tunnel and heat is supplied by steam, which passes through the tunnel.

9. Firing : The refractories are fired to stabilize and strengthen their structures. The bricks are, generally, *fired at a temperature as high as or higher than their use temperature*. Firing of bricks is done in *tunnel kilns* or *shaft kilns* or *rotary kilns*. The firing temperature of different bricks are : 1,480°C for high-fired super duty bricks ; 1,700°C for kaolin bricks, and 1,870°C for some basic bricks.

16.4 COMMON REFRACTORY BRICKS

(1) **Silica bricks** *contain 90 to 95%* SiO_2 *and about 2%* ***lime*** *is added during grinding to* ***furnish the bond***. Basic raw materials used for their manufacture are quartz, quartzite, ganister, sand, sandstone, etc. For their manufacture, the siliceous rock is crushed and ground with 2% lime and water. The thick paste is then made into bricks either by *hand moulding* or by *machine-pressing*. The bricks are dried in air or in heated rooms and then, burnt in kilns. During heating, temperature is *slowly* raised, in about 24 hours, to about 1,500°C and this is maintained for nearly 12 hours, so as to allow *quartzite* to be converted into *cristobalite*. Then, cooling is done carefully and it takes about 1 to 2 weeks. *During cooling, cristobalise is slowly changed into tridymite, so that a mixture of tridymite and cristobalite results in the final bricks.*

Properties : Silica bricks are yellowish in colours with brown specks throughout the body and contains about 25% pores. Silica bricks *do not contract* in use, but they have a *permanent expansion* of about 15%, when reheated. This effect is *reversible* and the brick returns to its original size. when cooled. This expansion is caused by *reversible allotropic transformation :*

$$\underset{\substack{\text{(Crystalline)}\\ \text{Sp. gr} = 2.65}}{\text{Quartzite}} \quad \overset{87^\circ\text{C}}{\rightleftharpoons} \quad \underset{\substack{(\alpha\text{–form of silica})\\ \text{Sp. gr} = 2.26}}{\text{Tridymite}} \quad \overset{117^\circ\text{C}}{\rightleftharpoons} \quad \underset{\substack{(\beta\text{–form of silica})\\ \text{Sp. gr} = 2.32}}{\text{Cristobalite}}$$

Thus, if during firing of silica bricks, quartzite is *not* converted into tridymite and crystobalite, the bricks will *expand* to the extent of about 17.2%, during use in the furnace and, consequently, the refractory structure will *fall*. *That is why heating at 1,500°C for about 12 hours in necessary, during the making of silica bricks.*

Silica bricks have homogeneous texture, free from air-pockets and moulding defects. They can withstand a load of about 3.5 kg/cm^2 upto about 1,500–1,600°C. They are thus remarkable for their load-bearing capacity, especially at high temperatures. They possess low permeability to gases and are not susceptible to thermal spalling at temperatures below 800°C. *These properties make silica bricks* *very satisfactory for places subjected to* ***uniform high temperatures****, but fails badly otherwise.* Silica bricks are relatively light (sp. gr. = 2.3 to 2.4) and possess high rigidity and mechanical strength.

Uses **:** The main applications of silica bricks are roofs of open-hearth furnaces, open-hearth steel making furnaces, coke-oven walls, cowper stove domes, roofs of electric furnaces, linings of acid converters, glass furnaces, etc. Because of their high thermal conductivity, they are also used in by-products coke-ovens and gas retort settings.

(2) Fireclay bricks *are made from finely ground soft plastic material fireclay* ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) *with* ***powdered calcined fireclay*** *(called 'grog').* The exact proportions of the constituents depend on the type of bricks to be made. *Greater is the percentage of grog, the lesser will be the spalling tendency.* General composition of fireclay bricks ranges from 55% SiO_2 and 35% Al_2O_3 (*feebly acidic*) to 55% Al_2O_3 and 40% SiO_2 (*nearly neutral bricks*), the balance consists of accessory oxides in the clay like K_2O, FeO, CaO, MgO, etc.

Properties : Fireclay bricks are light-yellow to reddish-brown in colour, depending on the content of iron oxides. They are *slightly acidic* in character, the extent of acidic character depends upon the SiO_2 content. They possess low porosity and lower refractoriness than silica bricks. They, usually, fuse at 1,350°C under a load of 2 kg/cm^2. Their crushing-strength is *quite high* (about 200 kg/cm^2). A very useful property of the fireclay bricks is *better resistance to thermal spalling* than silica bricks and *this makes them very suitable for making a checker-works of regenerative furnaces and charging doors, etc., which are subjected to temperature fluctuations.* Fireclay bricks are much *cheaper* than silica bricks.

Uses : Fireclay bricks are *most widely used* of all the refractory bricks, since they are *very cheap and are well-suited for many applications*. They are used for the construction of blast furnaces, open-hearth furnaces, stoves, ovens, crucible furnaces, flues, kilns, boiler-settings, regenerators, charging doors, etc.

(3) High-alumina bricks *contain 50% or more of* Al_2O_3 and are, generally, made by mixing calcined bauxite (Al_2O_3) with clay bind.

Properties : They possess very low coefficient of expansion, high porosity, great resistance to slags, very little tendency to spall, high temperature load-bearing capacity, excellent wear-resistance and stability, both in oxidizing and reducing conditions, and are particularly inert to the action of gases like CO_2, H_2 and natural gas. They are thus very good refractories, but they are *very costly*, so not used much.

Uses : *'Medium-duty bricks'* (*i.e.*, containing 50 to 60% Al_2O_3) are used for zones of vertical shaft kilns for burning limes, linings of Portland cement rotary kilns, soaking pits, reheating furnaces, hearths and walls, etc., which are subjected to high abrasion. On the other hand, *'high-duty bricks'* (*i.e.*, containing 75% Al_2O_3) find applications specially in the sintering or hottest zones of cement rotary kilns, lower parts of soaking pits, brass melting reverberatories, lead dressing reveberatory furnaces, aluminium melting furnaces, combustion zones of oil-fired furnaces, etc.

(4) Magnesite bricks are important and the *most widely used basic refractories. Calcined magnesite* (MgO) is powdered to a proper size, and then mixed with *caustic magnesia or sulphite lye* (a waste product of paper industries) or *iron oxide* as *binding material*, and then ground with water, and moulded into bricks. The bricks are then slowly heated to 1,500°C, and kept for about 8 hours at this temperature and then, *cooled slowly*.

Properties : Magnesite bricks can be used up to 2,000°C without load, and upto 1,500°C under a load of 3.5 kg/cm^2. They possess good crushing strength, good resistance to basic slags, very little shrinkage, but have *lot of spalling*, due to their sensitiveness to sudden changes of temperature. *Their resistance to abrasion is poor. Moreover, they show a tendency to combine with water and CO_2.*

Uses : They are used where *high temperature* is required to be maintained, together with *great resistance to basic materials* like molten liquids of basic nature. Their chief use is in the steel industry for the lining of basic converters and open-hearth furnaces. Other applications are in hot mixer linings, copper converters, reverberatory furnaces for smelting lead, copper and antimony ores, hot zones of cement rotary kilns, refining furnaces for gold, silver and platinum, etc.

(5) **Dolomite bricks** *are made by mixing calcined dolomite (CaO + MgO mixture in equimolecular proportions) with* **silicate binder**. *They are fired at 1,500°C of about 24 hours.*

Properties : Dolomite bricks possess less strength, more softness and porosity, greater shrinkage and high hygroscopicity than magnesite bricks. However, they can withstand a load of 3.5 kg/cm^2 at 1,650°C. They are also not very resistant to thermal-shocks. *Properties of dolomite bricks can be modified by "stabilization", in which dolomite is mixed with serpentine* ($MgO.SiO_2$) *and the mixture is calcined, resulting in the formation of di-and tri-calcium silicates, which do not absorb water and carbon dioxide.* After calcination, it is mixed with a *silicate binder* and made into bricks, which on firing at 1,500°C for a day or so give *stabilized bricks*. Stabilized dolomite bricks are quite stable towards basic slags.

Uses : *Dolomite is rarly used as a direct refractory*, but is useful as *repair* material. Stabilized dolomite bricks are, however, used for basic electric furnace linings, Bessemer converters, open-hearth furnaces, ladle-linings, etc., and as a cheap substitute for magnesite bricks.

(6) **Carbon bricks** *are made by firing crushed coke with* **pitch** *or* **tar** *(binding material) or graphite mixed with* **clay** *at about 1,300–1,400°C.* During firing, *contact of the bricks with air is minimized* by filling the space in-between the bricks with a mixture of sand and powdered coke.

Properties : Graphite and carbon refractories are excellent refractory materials, but *they can only be used under neutral or reducing conditions*, because they are oxidized readily in air at elevated temperatures. They are practically infusible, insensitive to spalling, highly thermal conductive, close-textured and can withstand temperature fluctuations and chemical attack of acids, alkalis and all solvents, except the oxidizing ones.

Uses : Carbon and graphite bricks are widely used as materials of construction for electrodes, linings of highly chemically-resistant equipments, atomic reactors, electric furnaces, heat-transfer systems, and in copper, aluminium and lead smelting furnaces.

(7) **Chromite bricks** *are made by firing at 1,500–1,700°C crushed chromite are* ($FeO_2 . Cr_2O_3$) *mixed with a little* **clay** *as binding material.*

Properties : Chromite bricks are *neutral* in character. They possess high density, *resistance to acidic as well as basic slags* and moderate resistance to spalling. They can be used upto 1,800°C and their refractoriness under a load of 3.5 kg/cm^2 is 1,430°C. They possess good crushing strength (350 to 550 kg/cm^2). They have moderate thermal conductivities.

Uses : Their most important use is *in separating acidic and basic refractory lining*, so as to prevent their interaction, even at high temperatures, *e.g.*, between acid-roofs of basic open-hearth furnace and the basic bricks of side walls. Other applications are in bottoms of soaking pits, sodium carbonate recovery furnaces, etc.

(8) **Carborundom** (SiC) **bricks :** ***Silicon carbide* (*SiC*)** *is made in an electric furnace at a temperature of 1,500°C from sand (60%) and coke (40%) with the addition of some saw-dust and a little salt.* When burned, saw-dust evolves gases, which by circulation, increases the porosity of the charge. Salt reacts with iron and similar impurities, present in the raw materials, forming volatile chlorides. *This increases the porosity of the final product.* The silicon carbide, removed from the furnace, is a mass of inter-locking iridescent crystals. The product is then mixed with *bonding agent* (like clay, silicon nitride, etc.), and then shaped, dried and fired. Recently, *self-bond type silicon carbide bricks* have been prepared. The silicon carbide particles are mixed with a *temporary binding agent* (such as glue) and then pressed and dried at 2,000°C, when *inter-crystalline bonds* of silicon carbide develop.

Properties : "*Clay-bonded*" silicon carbide bricks can be used upto 1,750°C, as this product softens near this temperature, '*Silicon nitride bonded* "bricks have a high strength and superior thermal-shock resistance than clay-bonded products. "*Self-bonded*" product has high refractoriness, superior strength, high density, high abrasion-resistance and high chemical-resistance. Silicon carbide refractories, in general, are characterized by ***high thermal conductivity and low thermal expansion. However, they tend to oxidise to silica, when heated in air at a temperature range of*** *900 to 1,000°C*. But this drawback in overcome by *coating* them with a thin layer of *zirconium.*

Uses : They are used for *partition walls* of chamber kilns, coke ovens, muffle furnaces, recuperators and floors of heat-treatment furnaces. Moreover, due to their high electrical conductivity, they are used as *heating elements* in furnaces in the form of rods and bars (*globars*).

(9) **Zirconia brick** *is obtained by heating zirconite mineral* (ZrO_2) *and using colloidal zirconia (prepared by drying zirconium nitrate solution and making the residue into solution and again drying) or alumina as binding material at 1,700°C.* Since mineral zirconite undergoes volume changes on heating and cooling, so it is *stabilized* by adding MgO or CaO.

Properties : Zirconia refractories are, usually, classed as neutral refractories, but *they are not quite resistant to acidic slags* and hence, they are actually on the border-line between neutral and basic refractories. They can be used upto 2,000°C, but specially prepared bricks can be used even up to 2,600°C. Their refractoriness under a load to 3.5 kg/cm^2 is about 1,900°C. They are also quite resistant to thermal-shocks.

Uses : Zirconia bricks are *very costly* and hence, used only where *very high temperature* is maintained, *e.g.*, high-frequency electric furnaces.

(10) **Beryllia bricks** *are made by firing moulded articles from powdered pure beryllia mineral at 1,900–2,000°C.*

Properties : *They possess high melting point* (2,550° C), *low electrical conductivity, high thermal conductivity, good resistance to thermal-shocks, and inertness to carbon dioxide and carbon monoxide* upto 2,000°C. They have considerable ***hot-strength***

Uses : In jet propulation fields (due to hot strength), making crucibles (to melt uranium and thorium), in nuclear engineering as *moderator* (in view of its low neutron absorption capacity), and *radiation shields* in carbon resistance furnaces. However, its only drawback is that beryllia is capable of volatilizing, even at 1,000°C, especially in the presence of water vapour ; and beryllia dust, if inhaled even in small quantities, cause series health hazards. Hence, *greater precautions* must be taken to have correct ventilation, etc.

(11) **Chrome-magnesite refractory** *is obtained by blending chrome ore with magnesite, followed by moulding and firing.* During firing, the serpentine ($3\,MgO\,.\,2\,SiO_2\,.\,H_2O$) present in the chrome ore decomposes to yield *forsterite* ($2\,MgO\,.\,SiO_2$) and *magnesium silicate* ($MgSiO_3$). The latter then combines with MgO (of magnesite) to form forsterite.

$$\underset{\text{Serpentine}}{3\,MgO\,.\,2\,SiO_2\,.\,H_2O} \xrightarrow{\Delta} \underset{\text{Forsterite}}{2\,MgO\,.\,SiO_2} + \underset{\text{Mag. silicate}}{MgSiO_3} + H_2O$$

$$MgSiO_3 + MgO \longrightarrow \underset{\text{Forsterite}}{2\,MgO\,.\,SiO_2}$$

Depending upon the *relative proportions* of chromite and magnesite blended before firing, the chrome-magnesite refractories are mainly of *two* types :

(*i*) ***Magnesite-chrome refractories*** *contains about 60% MgO and 8-18% Cr_2O_3.* These refractories are used in place of comparatively costlier 'silica bricks', due to their : (*a*) higher refractoriness (about 2,300°C), (*b*) higher thermal spalling, (*c*) higher thermal conductivity, and (*d*) higher resistance to erosion and consequent corrosion by high-speed flowing gases, slags and molten metals.

(*ii*) ***Chrome-magnesite refractories*** *contains about 40-50% Mg and 15-35% Cr_2O_3.* These possess properties similar to those of (*i*), but they are more prone to undergo *structural spalling.*

16.5 CERMETS

Cermets *are hot-pressed or sintered materials, consisting of combinations of* ***ceramics and metals.*** They possess : (*i*) *high refractoriness of ceramics,* (*ii*) *high thermal conductivity of metals,* (*iii*) *high thermal-shock resistance of metals, and* (*iv*) *high shapeability.* The *metal* serves as a *binder* for high refractory *ceramics particles.*

Refractory ceramics used in cermets manufacture are ***highly refractory carbides*** (such as zirconium carbide, molybdenum carbide, tungsten carbide, titanium carbide, chromium carbide, etc.), *borides* (such as of molybdenum, titanium, tungsten, and zirconium), *oxides* (such as of magnesium and aluminium) as well as certain *silicides* and *sulphides.* The *metals* used are iron, aluminium, chromium, cobalt, nickel and molybdedum. *Most cermets contain about 80% of ceramic materials, and 20% of the metal.* They are, usually, fabricated by *powder metallurgy* techniques.

Uses : Cermets are used as high refractories in various applications in which high temperature and high shock-resistance are required, as in rocket and jet engine parts, spinning tools for hot metals, hot-forging dies, and similar applications.

16.6. INSULATING REFRACTORIES

In order to minimize, either externally or internally, heat losses from a furnace (due to conduction), *refractories of low thermal conductivities* are used as *heat-insulators.* For low operating temperatures (below 900°C), ***diatomaceous-earths*** (*hydrated silicates of iron, containing magnesia*) like *kieselguhr, vermiculite, asebesos* are, usually, employed as heat-insulators. However, these are not suitable for high temperature operations, because kieselguhr undergoes a large contraction ; while vermiculite expands to a large extent on heating. Consequently, *porous refractories* are employed under such circumstances. *The air inside the voids acts as poor conductor of heat. Porous refractories* are made by incorporating *combustibles* like saw-dust, cork, husks, etc., to the usual refractory materials, before firing. Alternatively, a *slip* made up of clay, grog and water is mixed with chemically prepared *foam* [made by of rosin (45%), caustic soda (7%) and rest water and *stabilized* [with glue and alum]. The mixture is poured into moulds and fired.

Table 2 : *Properties of common refractories.*

Refractory	*Major component (% by wt.)*	*Refractoriness (°C)*	*Porosity (%)*	*Thermal resistance*	*Abrasion resistance*	*Acidic slags & fluxes*	*Basic slags & fluxes*
1. Silica	$SiO_2 = 93 - 96$	1,700	16 – 18	Good (1,600°C)	Good	Fair	Poor
2. Fireclay	$SiO_2 = 40 - 55$ $Al_2O_3 = 35 - 55$	1,700 – 1,830	20 – 23	Good	Good	Good	Medium
3. High-alumina	$Al_2O_3 = 50 - 60$ $SiO_2 = 40 - 45$	1,750	20 – 29	Good	Good	Good	Poor
4. Magnesite	$MgO = 80 - 95$ $Fe_2O_3 = 2 - 7$ $Al_2O_3 = < 4$	< 2,000	20 – 23	Poor	Medium	Poor	Good
5. Dolomite	$CaO = 58$ $MgO = 40$	1,650	= 20	Poor	Medium	Poor	Good
6. Carbon	$C = 85 - 90$	< 2,000	22 – 32	Good	Poor	Good	Fair
7. Chromite	$Al_2O_3 = 15 - 23$ $Cr_2O_3 = 30 - 15$ $Fe_2O_3 = 10 - 17$ $MgO = 14 - 20$	1,800 – 1,900	18 – 25	Fair	Medium	Fair	Good
8. Carborundum	$SiC = 89 - 91$	< 2,100	17 – 20	Good	Good	Good	Poor
9. Zirconia	$ZrO_2 = 67$	= 2,500	–	Good	Good	Good	Poor
10. Beryllia	$BeO = 99$	= 2,500	= 30	Good	–	Poor	Good

17

Glasses and Ceramics

"Let there be light", said the Lord and there was light. Man invented glass to let the precious gift enter the shelter of his house to dispel the darkness.

17.1 INTRODUCTION

Glass *is an amorphous, hard, brittle, transparent or tranlucent,* ***super-cooled liquid of infinite viscosity,*** *obtained by fusing a mixture of a number of metallic silicates, most commonly of Na, K, Ca and Pb. It possesses no sharp melting-point, definite formula or crystalline structure.* Within certain limits, it may be represented as x R_2O . y MO . 6 SiO_2, where R is an atom of *monovalent* alkali metal like Na, K, etc., M is an atom of a *bivalent* metal like Ca, Pb, Zn, etc., x and y are *whole numbers*. Thus, approximate composition of ordinary glass (called *soda-lime glass*) is N_2O . CaO . 6 SiO_2. In some glasses, SiO_2 may be replaced by Al_2O_3 . B_2O_3 . P_2O_5, etc.

General properties of glass : Glass : (1) is amorphous, (2) has no definite melting-point. (3) can absorb, reflect or transmit light, (4) can take high polish, (5) is a good electrical insulator, (6) is affected by alkalis, (7) is not affected by air, water or acids or chemical reagents, except HF, which converts its silica into SiF_4, (8) can be formed into articles, even of intricate shapes, (9) is very brittle, (10) softens on heating, (14) is light, because it has homogeneous internal structure similar to liquids, (15) has no crystal structural and hence, no slippage between planes can occur. Hence, glass has a high compressive strength.

Ceramics (from Greek *keramos* meaning burnt stuff) *are inorganic, non-metallic materials that are processed and / or used at high temperatures*. They include silicates, metallic oxides, and their combination. Ceramics can be grouped into *three* broad divisions–clay products, refractories and glasses, according to their common characteristic features. Clay products can be sub-divided into *three* main types, namely :

1. **The structural clay products,** all of which contain *iron oxides*. They are used for *bricks, tiles* and similar products.
2. **The whitewares**, which are *paler substances* such as *Porcelain,* and *China,* and
3. **Chemical stonewares,** which have been *specially-treated* to be hard, resilient and non-porous.

Closely related to ceramics, in chemical composition, are natural rocks and their disintegration products such as clay, sand and gravels.

Clay : The term **clay** *denotes certain earths, which are highly plastic, when wet and which, when heated to redness, loses their plasticity and are converted into a hard mass, which is unaffected by water. Clays are formed by the weathering of igneous,* (*e.g.*, granite), *and felspathic rocks by various agencies through time and are composed essentially of* ***hydrated aluminium silicates*** (such as

$Al_2Si_2O_7 . 2H_2O$), together with other substances such as *mica* and *quartz*, which were present with the feldspar in the original rocks (*e.g.*, granite).

$$\underset{\text{Potash feldspar}}{2\,KAlSiO_8} + 2\,H_2O + CO_2 \longrightarrow K_2CO_3 + \underset{\text{Clay}}{Al_2O_3 . 2\,SiO_2 . 2H_2O} + 4SiO_2$$

The alkali is *leached-out* by water.

If the clay remains at the original location, it is a **primary clay,** *usually white with a low content of iron, so that it 'burns' white : and it is called* **'Kaolin'** *or* **'China clay'**. If in the course of geological changes, the clay has been *transported* (by water, glacier or wind) to *another location,* it is a **secondary clay** ; it now contains limestone powder, hydrated oxides, mud and organic impurities in varying amounts.

17.2 MANUFACTURE OF GLASS

Raw materials : Chief ***source*** of incorporating :

(*a*) *Sodium* is soda, Na_2CO_3. (*Soft glass*)

(*b*) *Potassium* is potash, K_2CO_3. (*Hard glass*)

(*c*) *Calcium* are limestone, chalk and lime.

(*d*) *Lead* are litharge, and red lead. (*Flint glass*)

(*e*) *Silica* are quartz, white sand, and ignited flint.

(*f*) *Zinc* is zinc oxide. (*Heat and shock-proof glass*)

(*g*) *Borate* are borax, and boric acid, (*Heat and shock-proof glass*)

(*h*) *Cullets* or pieces of broken glass to *increase the fusibility*.

(*i*) ***Colours*** : *Yellow*–ferric salt ; *Green*–ferrous and chromium salts ; *Blue*–cobalt salts ; *Purple*–manganese dioxide ; *Red*–nickel salts or Cu_2O; *Lemon-yellow*–CdS. ; *Fluroescent greenish-yellow*–uranium oxide ; *Opaque milky-white*–cryolite (Na_3AlF_6) or calcium phosphate.

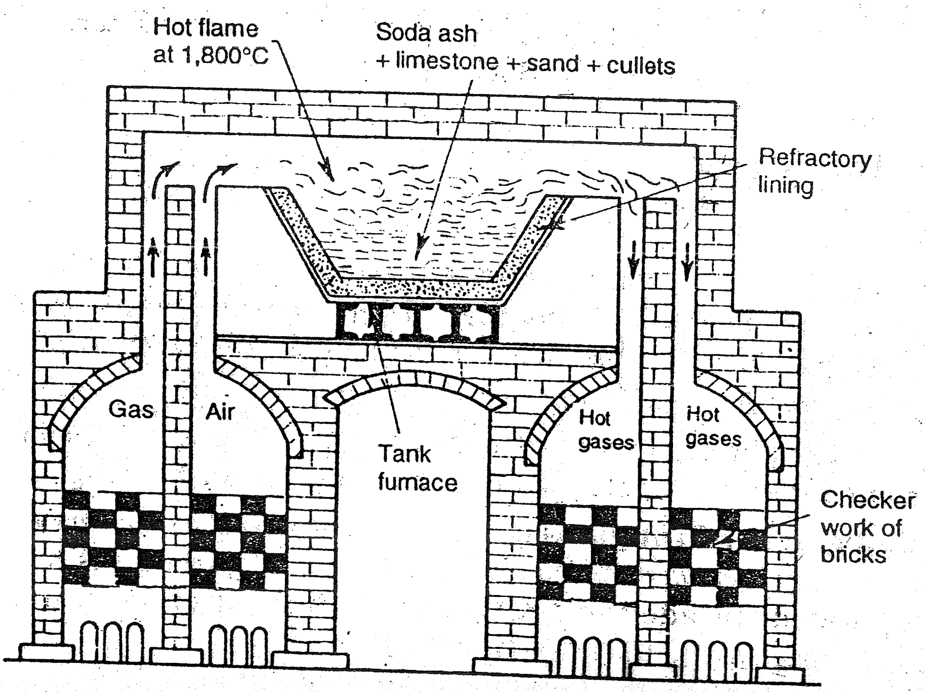

Fig. 1. Manufacture of glass.

Manufacturing steps : (1) ***Melting*** : Raw materials, in proper proportions (*e.g.*, sand, soda ash and limestone for *common glass*) mixed with cullets, are finely powdered and intimate mixture (called '*batch*') is fused in either *fireclay pots* (in case of *high-grade glass*) or *tanks* that form part of an open-hearth furnace, in which heating is done by burning *producer gas* and *air* mixture over the charge. At high prevailing temperature (about 1,800°C), the charge melts and fuses. The melting process in case of ordinary *soda-glass* involves the following series of reactions :

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2 \uparrow$$

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

When all the carbon dioxide has escaped out of the moten mass, *decolorizers* (such as MnO_2 or nitre) are added to do away with ferrous compounds and carbon, if present. *If a coloured glass is desired, the colouring salts are added at this stage.* Heating is continued, till the moten mass is free from bubbles and glass-balls ; and then cooled to about 800°C.

(ii) ***Forming and shaping :*** Molten glass is then worked into articles of *desired shapes* by either blowing or moulding or pressing between rollers.

(iii) ***Annealing :*** Glass articles are then allowed to *cool gradually* to room temperature by passing through different chambers with *descending* temperatures. *If allowed to cool rapidly, glass being bad conductor of heat, the superficial layer cools down first ; leaving the interior portion in a state of strain. Owing to this unequal expansion, the articles are likely to crack to pieces.* The *longer* the annealing period, the *better* the quality of the glass.

(iv) ***Finishing :*** All glass articles, after annealing, are subjected to finishing processes such as cleaning, grinding, polishing, cutting, sand-blasting, etc.

17.3 TYPES OF GLASSES

Commercial glasses can be *classified* as follows :

(1) Soda-lime or **soft glass :** The raw materials are *silica* (sand), *calcium carbonate* and *soda ash*. Their approximate composition is $Na_2O \cdot CaO \cdot 6\,SiO_2$. They are low in cost, resistant to devitrification and relatively resistant to water. They *melt easily* and hence, can be hot-worked easily. Such glasses are, however, *attacked by common reagents like acids*.

Uses : They are widely used as *window glasses, electric bulbs, plate-glasses, bottles, jars, building blocks, and cheaper tablewares,* where high temperature-resistance and chemical-stability are not required.

(2) Potash-lime or **hard glass** *is obtained from silica (sand), calcium carbonate, and potassium carbonate.* Their approximate composition is $K_2O \cdot CaO \cdot 6\,SiO_2$. They possess *high melting-point, fuse with difficulty* and are *less acted upon by acids, alkalis and other solvents than ordinary glasses.*

Uses : These glasses (*costlier* than soda-lime glasses) are used for *chemical apparatus, combustion tubes,* etc., which are to be used for heating operations.

(3) Lead glass or **flint glass** *is made by using lead oxide, instead of calcium oxide, for fusing together with silica.* For *dense optical glasses,* as much as 80% of PbO is incorporated. In addition, K_2O is used, instead of sodium oxide. So, its approximate composition is $K_2O \cdot PbO \cdot 6\,SiO_2$.

Lead glass is a good deal *more expensive* to make than ordinary lime-soda glass, but much *easier to shape and work with*. Lead glass has a lower softening temperature than soda-glass and also a *higher refractive–index*. It has excellent electrical properties. It is bright, lustrous and possesses high specific gravity (3 to 3.3).

Uses : Lead glasses are used widely for *high-quality tablewares, optical purposes* (like lenses, etc.) ; *neon sign tubings, cathode-ray tubes, electrical insulators* and *in art objects,* because of their high lustre. High lead-content glasses are used for *extra-dense optical glasses* for windows and shields to protect personnel from X-rays and gamma-rays in medical and atomic energy fields respectively.

(4) **Borosilicate glass** or **pyrex glass** or **jena glass** *is the most common of the hard glasses of commerce.* Such glasses contain virtually *only silica and boron,* with a small amount of alumina and some alkali oxides. A typical formula for such a glass would be following :

Percentage	80.5	13	3	3	0.5
Component	SiO_2	B_2O_3	Al_2O_3	K_2O	Na_2O

The substitution for alkali (Na_2O) and basic alkaline-earth oxides (CaO) of the soda-lime glasses by boron and aluminium oxides, results in a glass or *low thermal coefficient of expansion, and high chemical-resistance.* Borosilicate glasses have *very high softening points* and excellent resistivity (*i.e., shock-proof*).

Uses : They are used extensively in industry for pipelines for corrosive liquids, gauge glasses, superior laboratory apparatus, kitchenwares, chemical plants, television tubes, electrical insulators, etc.

(5) **Aluminosilicate glass :** A typical analysis of such a glass would be following :

Percentage	55	23	7	9	5	1
Component	SiO_2	Al_2O_3	B_2O_3	MgO	CaO	$Na_2O + K_2O$

This type of glasses possess *exceptionally high softening temperatures.*

Uses : For high-pressure *mercury discharge tubes, chemical combustion tubes, certain domestic equipments, etc.*

(6) **99.5% silica glass** or **vitreosil** *is produced by heating pure sand (SiO_2) to its melting point (or about 1,750°C).* Because of absence of fluxing agents, it is extremely difficult to get rid of all air-bubbles. Moreover, owing to the *high viscosity of this glass at its working temperature, shaping is rather difficult.* The final product is *translucent.* Its softening-temperature is about 1,650°C. Its thermal expansion is *lowest*, namely, only 0.55×10^{-6} cm cm^{-1} °C^{-1}.

If vitreosil glass is heated for long periods, above its melting point, it finally becomes ***transparent*** *and is then known as* **"clear silica glass"**, *i.e.,* glass of considerable *light transmission properties, e.g.,* 1 m thick of this material allows no less than 93% of light to pass.

Uses : It is used mainly for *chemical plants, chemical laboratory wares, electrical insulating materials in electrical heaters, furnaces, etc.*

(7) **Safety glass** *is made by taking two or three flat sheets of glass and in-between them* ***alternate thin layer of vinyl plastic*** *is introduced and the whole is subjected to slight pressure. It is then heated, till the glass layers and plastic layers merge into one another to give a sandwich.* On cooling, the glass becomes quite *tough*. When such a glass breaks, it *does not fly into pieces,* since the inner plastic layer tends to hold back the broken pieces of the glass.

Uses : It is mostly used in *automobile* and *aeroplane* industries as *wind shields,* etc.

(8) **Optical** or **crookes glasses** *contain phosphorus and lead silicate, together with a little* ***cerium oxide***. The latter is capable of *absorbing ultra-violent light* (which is injurious to eyes). Moreover, they are given *thorough homogeneity*. This is secured by a very careful manufacturing process and by careful heating the molten mass for a *prolonged time*. In general, optical glasses have low melting-points and are relatively soft. Their chemical-resistance and durability are appreciably lower than those of ordinary glass.

Uses : They are used for making *lenses*.

(9) **Polycrystalline glass** or **pyroceram** *is produced by adding one or more nucleating agents to a special or conventional glass batch, which is then shaped into a desired forms. The material is then subjected to a controlled heat-treatment*. The *nucleating agents* induce the formation of a large number of sub-microscopic crystallites, which act as centres for further crystal growth. Crystalline glass is *not* ductile, but has much greater impact-strength than ordinary glass. It exhibits high strength and considerable hardness and can be formed and shaped into articles by any methods of moulding.

(10) **Toughened glass** *is made by dipping articles, still hot, in an oil-bath, so that same chilling takes place*. By doing so, *the outer layers of the articles shink and acquire a state of compression ; while the inner layers are in a state of tension*. Such a glass is more elastic and capable of withstanding mechanical and thermal-shocks. When such a glass breaks, it *does not fly, but is reduced to fine powder*.

Uses : It is used for *window shields of fast moving vehicles* (like cars, trucks, aeroplanes), *window shields of furnaces, automatic opening doors and large show-cases*, etc.

(11) **Insulating glass** *is a transparent unit, prepared by using two more plates of glass separated by 6 to 13 mm thick gap, filled up with dehydrated air and then, hermetically sealing around the edges*. This provides a *high insulation against heat*. Thus, if such glass is used for separating apartments, it *does not transmit heat* and consequently, the apartments will remain cool, during summer and warm, during winter.

(12) **Wired glass** *is formed by embedding a wire mesh at the centre of the glass sheet, during casting*. The main advantage of this glass is that when it breaks, it *does not fall apart into splinters*. Moreover, it is more *fire-resistant* than ordinary glass.

Uses : For making *fire-resisting doors, windows, skylights, roofs*, etc.

(13) **Laminated glass** *is made by pressing (or bonding) together two or more sheets/plates of glass with one or more alternating layer of bonding material like plastic resin, asphalt or synthetic rubber*. The laminated glass is : (*i*) *shatter-proof* (*i.e.*, its pieces do not fly off, when suddenly broken) ; (*ii*) *shock-proof* (*i.e.*, it can withstand sudden changes of temperature and even some pressure, without breaking).

A ***bullet-resistant laminated glass*** *is obtained by pressing together several layers of glass with vinyl resins in alternate layers*. Ordinarily, thickness of such glass varies from 12.7 mm to 76.5 mm. Even thicker types are made for *specific uses*.

Uses : As an ideal material for use as *safety glass in aircrafts, automobiles, helicopters, submarines*, etc. *Bullet-resistant laminated glass* finds application in *making automobile wind-screens, looking windows*, etc.

(14) **Glass wool** *is a fibrous wool-like material, composed of intermingled fine threads or filaments of glass*. Glass used for this purpose should be completely *alkali-free*. Glass filaments are obtained by forcing molten mass of glass through

small orifices (or holes), of average diameter of 0.0005 to 0.007 mm. continuously. The filaments of glass so-obtained are thrown over a rapidly revolving drum to get the material in wool-like form.

Properties : (1) It is non-combustible and fire-proof. (2) Its electrical conductivity is low. (3) It is completely heat-proof *i.e.*, heat has no effect on it size and volume. (4) It does not absorb moisture or water. (5) It resists actin of most chemicals. (6) Its density is low (about 65 kg/m^3). (7) Its *thermal conductivity is low* (about 0.033–0.034 kcal/m^2/°C/hr. (8) its tensile strength is about *eight times* that of steel.

Uses : (1) It is employed for *heat-insulation purposes, e.g.*, in domestic and industrial appliances like oven, insulation of metal pipelines, motors, vacuum-cleaners, walls and roofs of houses. (2) Being resistant to chemicals, glass wool is used for *filtration of corrosive liquids* like acid and acidic solutions. (3) It is used for *elctrical insulation*. (4) It is also used for *sound insulation*. (5) It is also employed in air-filters as dust-filtering materials. (6) It is also used for manufacturing *fibre-glass*, by blending with plastic resins.

17.4 PLASTICITY OF CLAYS

The ***plasticity of clay*** can be defined as *its ability to form a plastic mass (dough) with water. The mass can be easily moulded to any shape, but retains sufficient rigidity to prevent deformation on standing.* Dry clay is ***not plastic***, and a certain amount of *water* has necessarily to be added to produce the required plasticity. *The function of water is to form a* ***film*** *around the flaky clay particles, so that their parallel orientation and movement under pressure is facilitated. The amount of water required to make a clay plastic, depends on the size and shape of the clay particles, their surface characteristics, and presence of electrolytes (salts).* For every clay, there is a certain minimum water-content, below which it ceases to behave as plastic material and becomes crumbly. This is called, the ***plastic-limit*** of a clay. *As the proportion of water increases, the clay becomes more and more plastic, until the point is reached at which it starts flowing and becomes wet and sticky.* This point, is called the ***liquid-limit***. The difference in the water-content between the liquid limit and the plastic-limit, is called the ***plasticity index***, which represents the *plasticity-range* of the clay.

Plasticity of clay and its effect on moulding : Depending on the methods employed, *different plasticities* of raw mixes are required to produce a product of desired size and properties. Thus :

(*i*) ***Hand-moulding and machine-extrusion*** require a mass of *plastic* consistency, classified as *'stiff mud'*.

(*ii*) ***Machine-pressing*** is best accomplished on *'stiff plastic'*, and *semi-dry mixes*.

(*iii*) ***Slip-casting*** requires a mix of *semi-liquid consistency*, so that it can be easily poured in a mould.

The *required plasticity* can be secured by :

(*i*) ***Weathering and grinding*** produces a *uniform clay-water paste*, in which clay particles are well dispersed and surrounded by water-films. This treatment *greatly improves the plasticity and homogeneity of the mass*.

(*ii*) ***Blending,*** *i.e., mixing two or more ingredients in such proportions that a mass of required composition and plasticity is obtained.* The usual ingredients are *clay, non-plastic materials* (like finely ground quartz or flint), and *fluxes*. This is particularly used in the manufacture of *high-grade products* such as whitewares, chemicalwares and porcelain. *Blending of clay with* ***non-plastic materials*** *reduces the proportion of water required in the clay to get mass of a* ***desirable plasticity****, thereby preventing an excessive drying shrinkage.* ***Fluxes*** *are substances added to a mix to* ***lower its fusion-point****, thereby making possible more complete vitrification, even at not too high temperature.*

17.5 WHITEWARES OR WHITE-POTTERY

~~The genetic~~ name is given to materials that give products, after firing, which are ***white*** *or* ***pale-cream*** *in colour.* The raw materials used for the manufacture of whitewares contain *little or no compounds of iron*. Whitewares are made by mixing *China clay*, *feldspar* ($KAlSiO_8$) and *flint* (SiO_2). The proportions of these components are adjusted according to the properties desired in the finished article. Whitewares possess *good strength, translucency* and *very low porosity*. This is attained by firing the products at high temperatures (*viz.*, 1,450–1,500°C), when *partial vitrification* of the ceramic constituents takes places.

Whiteware products *consist of refractory body and glossy coating, called the* ***glaze***. They are made by *two* main processes, namely :

(*i*) *Porcelian process,* in which the glaze and the body are developed in *one* firing process .

(*ii*) *China process,* in which the glaze is applied in a *separate* state. In consequence, the glaze of China objects is definitely *better* than that of porcelian objects.

Manufacture of white-pottery involves the following **steps** :

Step I. The body of ware : The ingredients, *kaolin* and *felspar*, are reduced to a state of fine powder, and then suspended in water in the form of a *cream*. Surplus of water is removed by means of a *filter press*. Then, article from the paste is produced by either *moulding* (pressing by hand in a plaster mould) or *throwing* (shaping on a potter's wheel) or *casting* (pouring slip into a porous mould). Next, the article so-produced is dried slowly and fired to the desired density in a *biscuit-oven* to get porous-ware, called "*bisque*".

Step II. The glaze : In order to get *water-tight* article, the porous article is covered with a glaze by melting it over the surface of body. The constituents of the *glaze* (quartz, feldspar and a little boric oxide ; sometime, a little lead oxide) are finely ground and then mixed with water to form a *slip* or *slurry*. The bisque is dipped into the slip and then *fired again* at a high temperature, until the material composing the glaze fuses and produces a smooth and glossy surface. *The glaze must be so-chosen as to resist the reagents to which it is to be exposed, and must have the* ***same coefficient of expansion*** *as the body ; otherwise it will crackle, when the vessel is exposed to changes of temperature.*

Step III. Decoration : If the article is to be decorated, the *design* may either be painted upon the body before glazing, when it is said to be '*under-glazed*', or be painted upon the glazed-article and the article *fired again* so that the pigment melts into the glaze. In the latter case, it is said to be '*over-glazed*'. In the former case, the pigments used as a rule are *metallic oxides* ; while in the latter case are often *coloured glasses*.

Uses of whitewares : Whitewares find applications as spark-plugs, electrical insulators, laboratory equipments, crucibles, dishes, high-class potteries, etc.

17.6 GLAZING

A glaze *is a fine powder, consisting of a mixture of glass-forming materials of proper composition, e.g., lead silicates, borosilicates, etc.* The glazing mixture, free from iron and other colouring *pigments*, form *colourless glaze* ; while for *colour* *glazing*, coloured metal oxides (or *pigments*) are mixed in proper proportions, *e.g.*, *iron oxide* for red and brown colours ; *iron oxide and lime* for cream and yellowish tints ; *copper oxide* for green colours ; *cobalt blue* for blue colours are used.

Purpose of glazing: The glazing is applied for the following purposes : (1) To produce *decorative effect.* (2) To make the surface *impervious to liquids, water,* etc. (3) *To improve appearance* of the article/material. (4) To *increase duability* of ceramic materials. (5) To provide a *smooth* and *glossy surface* to treated material. (6) To *protect the surfaces from the environment / atmospheric actions.*

Methods of glazing : Glazing is accomplished by any of the following *two* methods :

(1) ***Salt glazing*** employs *common salt* (or sodium chloride) for getting "*glossy-films*" over the earthenwares. The process consists in throwing common salt into the furnace, in which the articles are in red-hot condition. Intensive heat causes sodium chloride to volatilize and then react with silica of articles to form glossy and impervious film of '*sodium silicate*'.

(2) ***Liquid glazing*** is much *superior method*, in which fine powder of glaze mixture plus requisite quantity of colouring pigments are mixed with water to form a colloidal solution, called *glaze-slip*. The articles to be glazed are then burnt at a low temperature in kilns. They are then taken out and *dipped momentarily* in the 'glaze-slip', thereby the glaze material enters and *fills up the pores* in the articles. Then, the articles are fired in the kilns at a *higher* temperature so that *glaze material fuses and forms thin glossy-films* over them. *During firing, every care should be taken to see that* ***articles do not come in direct contact with fire*** *; otherwise dust and soot are likely to discolour them.* Delicate articles are, therefore, bunt in *Muffle furnace,* which is heated *externally* ; while the articles are kept *inside.*

17.7 EARTHENWARES AND STONEWARES

These refer to clay products, which are stone-like hard and strong, Comparatively softer variety of clay products, obtained by burning at lower temperatures, are called **earthenwares** *; whereas the harder and more compact variety, obtained at higher temperatures, are known as* **stonewares.** Earthenwares are obtained from mixed earths or clays, or clay mixed with sands, crushed pottery, etc.; whereas stoneware are, generally, made from refractory clays, mixed with crushed stone, crushed pottery, etc. *Both earthenwares, and stonewares are invariable* ***glazed*** *to made them compact, stronger, and impervious to water and most liquids.*

Chemical stonewares *differ from whitewares in colour and they are, generally, coarse and more robust.* The purity requirements for stonewares is *not rigid* as for porcelain and appreciable amount of iron oxide is permissible in stonewares. Chemical stonewares have low absorption power, high density and considerably physical strength and chemical-resistance. During firing, they get *semivitrified,* so that their porosity approaches *zero.* A typical formulation of stonewares would be : (1) ordinary clay = 50% ; (2) kaolin = 5%, (3) feldspar = 20%, (4) grog (or ground scrap stonewares) = 10% ; (5) flints =15%.

Stonewares are shaped either by *moulding* or *throwing* (on a potter's wheel) or *casting*. After shaping, the articles are dried and fired at *high* temperature (above 1,000°C). They are then given a suitable glaze, usually, by a *salt glazing,* in which fired articles are raised to about 1,100°C and common salt is thrown on them. The vapour of the salt produces a more fusible *sodium aluminium silicate*, which fills the surface pores. This glaze is quite resistant to ordinary acids and makes the articles impermeable to liquids.

Uses of stonewares : Stonewares are used for the construction of sanitary fixtures (sinks, closet-towels, bath-tubs), piping vessels, drainage pipes, underground cable sheathings, sewerage pipes, hume-pipes, absorption towers, valves and pumps in chemical industry. They are *cheap* in comparison to many other materials of construction, but suffers from the defects that they are *rather fragile* and once broken, they have *no resale value.*

17.8 OPTICAL FIBRES

Optical fibres represent a relatively new, high technology application of glass making. Optical fibres are made from high purity, low-loss, low-dispersion glass. Basis of operation of optical fibres is the *total internal reflection,* at the interface between the high refractive index core, usually made of vitreous silica doped with *germania* (Ge_2O) and the lower refractive index sheath or cladding of pure glass. Optical fibres are of *two* types, namely,

(*a*) *Monomode fibre,* where the diameter of inner core (of higher refractive index) is comparable with the wavelength of light; this results in there being *only one mode* of light propagation.

(*b*) *Multimode fibre,* where the diameter of the core is sufficiently larger than the wavelength of light, thereby allowing propagation of light in a *large number of modes.*

The key to success of optical fibres is glass purity. To achieve this, impurities must be reduced to the level of 1 ppm. Optical fibres transmits information, using light waves to pass through the fibre. Such fibres are capable of carrying much more information for a given cross-section of fibre than can be transmitted via the conventional coaxial cable. Optical fibres are used as medium for telecommunications by transmission of light of high-frequency pulses.

SHORT ANSWER QUESTIONS

19

Metals and Alloys

"Characteristics of a metal can be modified by alloying it with another metal(s) and/or non-metals(s)."

19.1 INTRODUCTION

Metals and their alloys are the backbone of all engineering projects and products. Various metals are used in one form or the other. In all the jobs, ranging from primitive-type agricultural implements to advanced aircrafts, automobiles, building and bridge construction, railway, light and heavy machinery and equipments, shipping and transportation, and in all such fields, metals occupy a place of prime importance.

19.2 PHYSICAL PROPERTIES OF METALS

Metals used in industry possess some definite physical characteristics, which render them suitable for particular use and their choice for a particular use is governed mostly by these properties. Some important *physical properties* of metals are described as follows :

1. **Specific gravity** *is the relative mass of a certain volume of a material compared to mass of the* ***same*** *volume of water.* Consequently, it is the ratio of the densities (*i.e.*, mass per unit volume) of the material to that of water.

2. **Specific heat** *is the quantity of heat in calories required to raise the temperature of 1 g of a material by one degree Centigrade.* Different substances possess different specific heats. Of all the known substances, *water* has the *highest* specific heat.

3. **Fusibility and fluidity** *signify the ease with which a material is melted by heat and the ease with which it flows in a mould.* Fluidity plays an important role in the production of *castings*.

4. **Weldability** *is the ability of a material to be welded together by the application of heat and/or pressure.*

5. **Elasticity** *is the property due to which a material is capable of regaining the initial shape, when the load producing the deformation is removed.* Material which *recovers completely* its original state (or condition), on removal of the deforming force, is said to *perfectly elastic, e.g.,* steel and glass are highly elastic. There is *no perfectly elastic material* known.

6. **Plasticity** is just apposite of elasticity. *It is the inability of a material to regain the initial shape, when the load producing the deformation is removed.* Thus, plasticity is just *reverse* of elasticity. Plasticity of *wet clay* is used for making earthenwares, bricks, tiles, etc.

7. **Porosity** *is the ratio of volume occupied by pores to the volume of a material.* Low porosity of a material makes it *light* in mass. More, porous material, in general, are *better insulating materials, i.e.,* thermal conductivity of a material can be *decreased* by increasing its porosity.

8. **Stiffness** *is the property due to which a material is capable of resisting deflection by an externally applied force.* It is a great importance in design of girders, bridges, etc.

9. **Ductility** *is the property of a material which allows it to be drawn into wires.* Gold is the *most ductile* of all metals.

10. **Malleability** *is the property of a material which allows it to be beaten into thin sheets.* Gold is the *most malleable* of all metals.

11. **Hardness** *is the property possessed by a material which enables it to resist peneration or abrasion or scratching by other materials.* It is also measured by its own ability to scratch on a comparatively softer material. Diamond is the *hardest* of known materials.

12. **Toughness** *is the property of a material which enables it to withstand bending or torsion without fracture.* It is a highly *desirable* properly for any metal.

13. **Brittleness** is just the opposite of toughness. *It is the property of a material which does not permit permanent deformation without breakage.* Dropping a brittle material from a certain height on a hard floor causes it to break into pieces. Brittleness characterises the *fragility* of the material. Thus, a highly brittle material (like glass) is also highly fragile. Brittleness is an *undesirable* property of an engineering material.

14. **Machinability** *is the property due to which a material can be easily cut by cutting tools to produce a desired shape and surface finish on it.*

15. **Refractoriness** *is the property due to which a material is able to withstand high temperature without fusing, e.g.,* silica (SiO_2), alumina (Al_2O_3), and fireday ($Al_2O_3 . 2SiO_2 . 2H_2O$)

16. **Tensile-strength** *is the property possessed by a material which enables it to withstand a force acting upon it with a tendency to break it by tearing.* It is expressed in kg/cm^2 of cross-section or N/m^2.

17. **Shear-strength** *is the property possessed by a material which enables it to withstand a force acting upon it with a tendency to distort its shape.*

18. **Fatigue-resistance** *is the property of a material which enables it to overcome fatigue, caused by repeated stresses.* Fatigue is failure attributed to repeated loading and unloading. Fatigue-resistance is a *highly desirable* quality of material used for engineering purposes. This property of a metal can be enhanced by *annealing.*

19. **Impact-resistance** *is the property of a material which enables it to withstand heavy shocks* such as in power hammering.

20. **Creep-resistance** : Machine parts which are to work under high temperature, suffer *continual deformation* by the action of the loads they are to carry. This phenomenon is called *"creep"*. Material which possesses a low value of continual deformation under load at high temperature, is said to possess *"high creep-resistance"*. Consequently, such a material can be used at elevated temperatures.

21. **Resilience** *is the ability of a material to return to the original form or position, after the bending/compressing/stretching force been removed.* Resilience is a *desirable* property for springs.

22. **Thermal conductivity** *is the ability of a material to conduct heat from the hot-end to the cold-end.* Silver is the *best* conductor of heat. A material that conducts heat very badly, is called *heat insulator.* The insulating materials are, frequently, employed to *prevent the loss of heat.*

23. **Electrical conductivity** *is the ability of a material to conduct electricity.* A material which allows electric current to pass through it with minimum loss, is called a *"good conductor"* of electricity. Silver is the *best* electrical conductor, and copper is that next one. Material which offers great resistance to the flow of electric current, is called *electrical insulator* or *dielectric.*

24. **Magnetic property** : *Materials which are attracted by a magnet, are called* '**magnetic**'. For example, iron, nickel, steel, cobalt, chromium and manganese. *Materials not attracted by a magnet, are called* '**non-magnetic**'. On the other hand, *materials which are repelled feebly by a magnet, are called* '**diamagnetic**', *e.g.*, copper, zinc, lead, antimony and bismuth.

25. **Foreability** *is the ability of a material to get welded by hammering in hot condition.*

26. **Rollability** *is the property of a material by virtue of which one side of its bar (round or square or rectangular) of short length can be toppered by hammering at or below dull red-heat.* This is used for making chisels, axles, tapper tubes, knife blades, etc.

27. **Coefficient of elasticity** : When an external force acts on a material/body, relative displacement of its constituent particles takes place. In order to restore the original state, the displaced particles of the material/body tend to come back to their original positions. Due to this inherent tendency (of the displaced particles to restore their original positions), *a resorting force* is thus acting within the body. *This restoring force per unit area, is known as* ***stress***. It may be noticed that *the restoring force is equal and opposite to the deforming force (or stressing force) so long as no permanent change is produced in the body.* Hence, stress can indirectly be measured as the *external force applied per unit area'*. Thus, if a deforming force F is acting on a surface area A, then :

$$\text{Stress} = F/A$$ [SI unit of stress is N/m^2.]

When a force acting on a body causes a *relative displacement*, then a change in length, volume or shape takes place. Then, ***strain*** produced by a given force is measured as "*the ratio of change in length, volume or shape to the, original length, volume or shape respectively*. Strain has *no units*. Strains are of *three* types :

(i) ***Longitudinal strain*** *is the ratio of the change in length* (Δl) *to the original length* (l) *of the body.*

(ii) ***Volumetric strain*** *is the ratio of the change in volume* (ΔV) *to the original volume* (V) *of the body.*

(iii) ***Shearing strain*** *in the ratio of the relative displacement of one plane* (Δl) *to its distance from the fixed plane* (l).

The ratio of the stress to strain, is called the ***coefficient of elasticity***.

19.3 METALLURGY

Metallurgy *is the process of* ***extracting*** *a metal in the free form from its ore.* Various *steps* involved in the extraction of metals from their ores are :

1. **Concentration of ore** : The ore is, generally, associated with useless rocky impurities (like clay, sand, etc.), called '*gangue*' or *matrix*. *The* '**concentration**' *of ore means removal of gangue from the powdered ore.* Thus, the percentage of the metal in the concentrated ore is *higher* than that in the original ore. The concentration of ore can be brought about in the *following ways*, depending upon the type of ore :

(i) ***Gravity separation process*** or ***hydraulic washing*** is especially suitable for *heavy 'oxide' ores* like haematite, tinstone, etc. In this, the powdered ore is placed on a sloping floor (or plateform), and washed by directing on it a strong current of water. The lighter sandy, and earthy impurities are washed away ; while the heavier ore particles are left behind.

(ii) ***Froth flotation process*** is especially suitable for '*sulphide ores*' like zinc blende (ZnS), and copper pyrites ($CuFeS_2$). This process is based on the fact that the *sulphide ore particles are only moistened by* **oil** ; *while those of oxide, and gangue particles are moistened only by* **water**. In this process, the powdered ore is mixed

with *water*, and a *little pine oil* (a foaming agent), and the whole mixture is then stirred vigorously by *blowing compressed air*. The oil forms a *foam* (or forth) with air. *The ore particles stick to the froth, which rises to the surface* ; while the rocky, and earthy impurities (gangue) are left in water (*see* Fig. 1). The froth is skimmed off, collected, and allowed to subside to get concentrated ore.

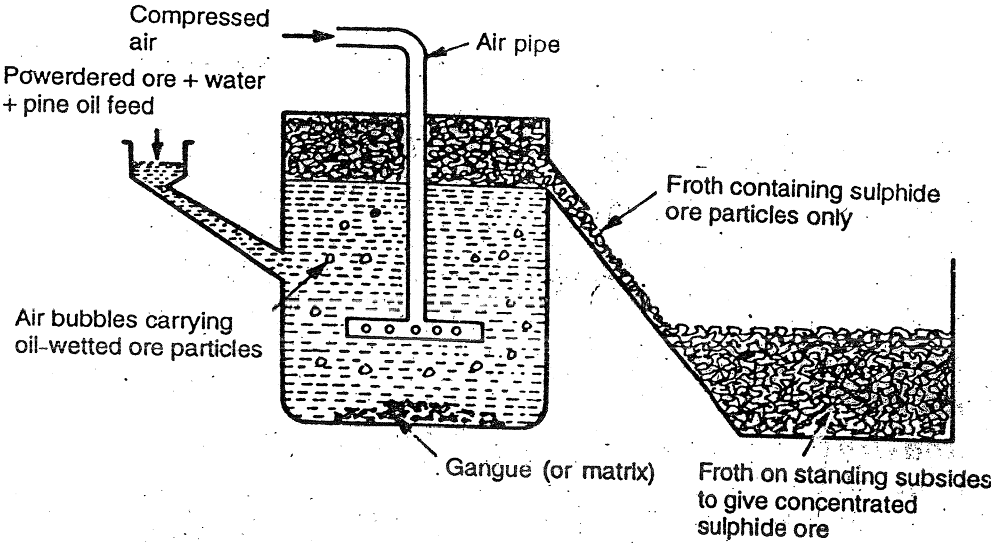

Fig. 1. Froth flotation process.

(*iii*) "***Electromagnetic separation process***" *is used especially for separating* ***magnetic impurities from non-magnetic ore particles***, *e.g.*, *tinstone* (*a tin ore*) *in which tinstone is non-magnetic* ; *while impurities, iron and maganese tungstates are magnetic*. The powdered ore (containing the associated magnetic impurities) is *made to fall (from a hopper) on a belt, moving over electromagnetic roller*. The magnetic impurities fall from the belt in a *heap near the magnet*, due to attraction ; while the non-magnetic concentrated ore falls in a *separate heap, away from* the magnet, due to the influence of centrifugal force (*see* Fig. 2).

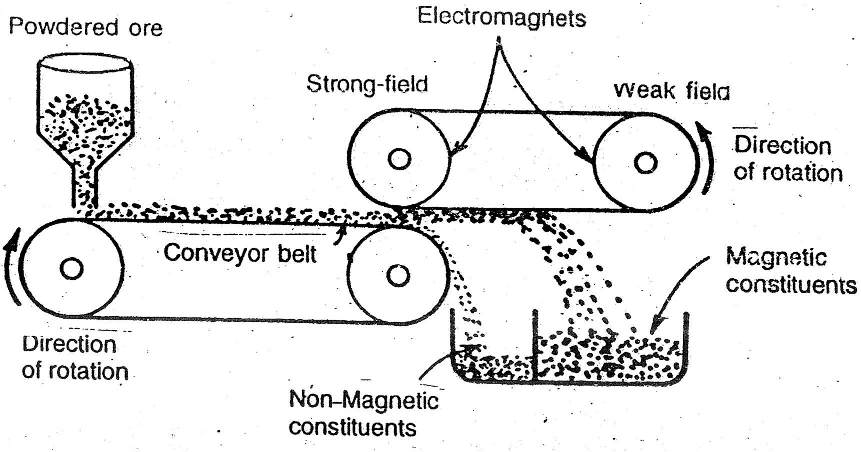

Fig. 2. Electromagnetic separation method.

(*iv*) **Chemical method** *is employed in case where the ore is to be in a very pure form, e.g.*, aluminium extraction. *Bauxite* (Al_2O_3), an ore of aluminium, contains SiO_2 and Fe_2O_3 as impurities. When bauxite ore is treated with NaOH, the Al_2O_3

goes into solution as *sodium meta-aluminate* ; leaving behind the undissolved impurities [Fe_2O_3, SiO_2, $Fe(OH)_3$, etc.], which are then filtered off.

$$\underset{}{Al_2O_3} + 2\,NaOH \longrightarrow \underset{\substack{\text{Sod. meta-aluminate}\\ \textit{(In solution form)}}}{2\,NaAlO_2} + H_2O$$

The filtrate (containing sodium meta-aluminate) on dilution, and stirring gives a precipitate of *aluminium hydroxide*, which is *filtered*, and *ignited* to get pure alumina.

$$NaAlO_2 + 2\,H_2O \longrightarrow \underset{\text{Ppt.}}{Al(OH)_3} + NaOH$$

$$2\,Al(OH)_3 \xrightarrow{\Delta} \underset{\text{Pure}}{Al_2O_3} + 3\,H_2O$$

2. **Conversion of ore into metal oxide** is carried out by either of the following *methods* :

(*i*) '**Roasting**' *is heating strongly the concentrated ore in* **excess of air** *to a temperature at which the ore does not melt*, Roasting is, usually, done to *sulphide ores*. The purpose of roasting is to convert sulphide into oxide, *e.g.*,

$$2\,ZnS + 3\,O_2 \xrightarrow{\text{Roasting}} 2\,ZnO + 2\,SO_2\uparrow$$

(*ii*) '**Calcination**' *is heating strongly the ore in the* **absence of air** *to such a temperature that the ore does not melt*. Calcination is, usually, done to *carbonate, and oxide ores*. The purpose of calcination is to convert carbonate into oxide, and to remove moisture, *e.g.*,

$$ZnCO_3 \xrightarrow{\text{Calcination}} ZnO + CO_2\uparrow$$

3. **Conversion of metal oxide into metal :** This operation can be carried out by using *different methods of reduction* :

(*i*) ***Reduction by heating in air*** : Metals like *mercury*, which occupy *low* position in activity series, are obtained by this method. Thus, concentrated cinnabar (HgS) is roasted in air, when mercuric oxide (HgO) is formed, which on strong heating to about 300°C decomposes to give mercury.

$$2\,HgS + 3\,O_2 \xrightarrow{\text{Roasting}} 2\,HgO + 2\,SO_2$$

$$2\,HgO \xrightarrow{300°C} \underset{\text{Mercury metal}}{2\,Hg} + O_2$$

(*ii*) ***Reduction with carbon*** : Metals like *zinc, copper, nickel, tin, lead,* etc. are obtained by using *coke* (*carbon*) as reducing agent. *Carbon is mixed with metal oxide, and heated in a furnace, when carbon reduces the metal oxide to free metal.* For example :

$$\underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Reducing agent}}{C} \xrightarrow{\Delta} \underset{\text{Zinc metal}}{Zn} + CO\uparrow$$

$$\underset{\text{Lead oxide}}{PbO} + \underset{\text{Reducing agent}}{C} \xrightarrow{\Delta} \underset{\text{Lead metal}}{Pb} + CO\uparrow$$

(*iii*) ***Smelting*** *is the process in which the roasted or calcined ore along-with a reducing agent (generally anthracite coal), and a flux (generally, lime) is heated to a high temperature*. The *reducing agent converts the ore into molten metal*, which is tapped out ; while *the* ***flux*** *removes the last traces of gangue in the form of fusible mass,* ***slag*** (which floats on the molten metal), and is removed separately. For example, in the smelting of iron, following reactions take place :

$$\underset{}{Fe_2O_3} + \underset{\text{(Reducing agent)}}{3\,CO} \xrightarrow{\text{Heat}} \underset{\text{(Metal)}}{2\,Fe} + 3\,CO_2$$

$$\underset{\text{(Flux)}}{CaO\ \text{(lime)}} + \underset{\text{(Gangue)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}\ \text{(calcium silicate)}$$

(*iv*) ***Reduction with aluminium*** (or ***aluminothermic reduction***) : Oxides like Cr_2O_3, Mn_3O_4, etc., *cannot be reduced by carbon*. In such a case, the reduction is brought about by reducing agent, *aluminium* powder. The reduction reaction is *highly exothermic, e.g.*,

$$\underset{\text{(Ore)}}{Cr_2O_3} + \underset{\text{(Reducing agent)}}{2\,Al} \longrightarrow \underset{\text{(Metal)}}{2\,Cr} + Al_2O_3 + 112\ \text{kcal}$$

The chromium so-produced forms the *lower layer* ; while alumina (Al_2O_3) forms the *upper layer*. The two layers are then separated. It is a method used in extraction of metals like chromium, manganese, etc.

(*v*) ***Electrolytic-reduction*** is a process in which *very active metals* (like Na, K, Ca, Al, etc.) are extracted *by the electrolysis of their fused anhydrous salts*. For example, sodium is obtained by the electrolysis of fused sodium chloride.

$$NaCl \rightleftharpoons Na^+ + Cl^- \qquad \textit{(In fused state)}$$

On electrolysis :

$$Na^+ + e^- \longrightarrow \underset{\text{(Metal)}}{Na} \qquad \textit{(At cathode)}$$

$$\left.\begin{aligned} Cl^- &\longrightarrow Cl + e^- \\ Cl + Cl &\longrightarrow Cl_2 \end{aligned}\right\} \qquad \textit{(At anode)}$$

(Secondary reaction)

4. **Purification or refining of metals :** The metal obtained by any of the above reduction methods is invariably impure, and is known as *crude metal. The process of purifying the crude metal to get pure metal, is called* ***refining***. The method of metal refining depends on : (*i*) the nature of the metal to be purified, and (*ii*) the type of impurities present. Common *methods of refining* crude metals are :

(*i*) ***Liquation :*** *Easily fusible metals* (like Pb, Sn, etc.) are heated on the sloping hearth of a reverberatory furnace. The metal in pure form melts, and flows down ; leaving behind the infusible impurities, called *"dross"*.

(*ii*) ***Electrolytic refining :*** *Most of the metals are refined by this method*. In this, large block of *impure metal* is made the *anode* in an electrolytic cell, and a thin sheet of *pure metal* is made the *cathode*. Suitable metal salt solution is made as an *electrolyte*. On passing electric current, pure metal deposits on the cathode sheet ; while some of impurities are left in solution, and other noble metal impurities settle below the anode as *'anode mud'*.

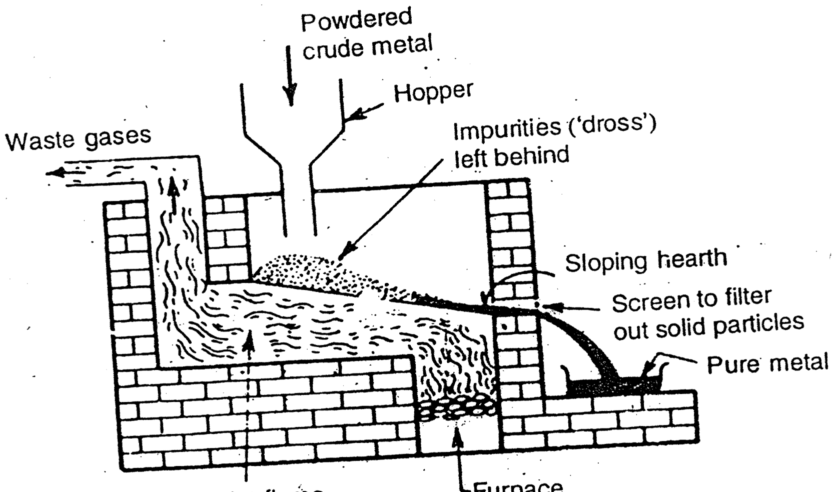

Fig. 3. Refining of metal by liquation.

For example, during the electrolytic refining of a copper, a thick block of impure copper is made anode, and thin plate of pure copper is made cathode. Copper sulphate solution is used as an electrolyte (*see* Fig. 4). On passing electric current, following *reactions* take place :

(1) Cu^{2+} ions (from copper sulphate solution) go to the cathode (negative electrode), where they are reduced to copper, which gets deposited on the cathode.

$$\underset{\text{(From solution)}}{Cu^{2+}} \quad + \quad 2e^- \longrightarrow \underset{\substack{\text{(Deposits on cathode)}\\ \textit{(At cathode)}}}{Cu}$$

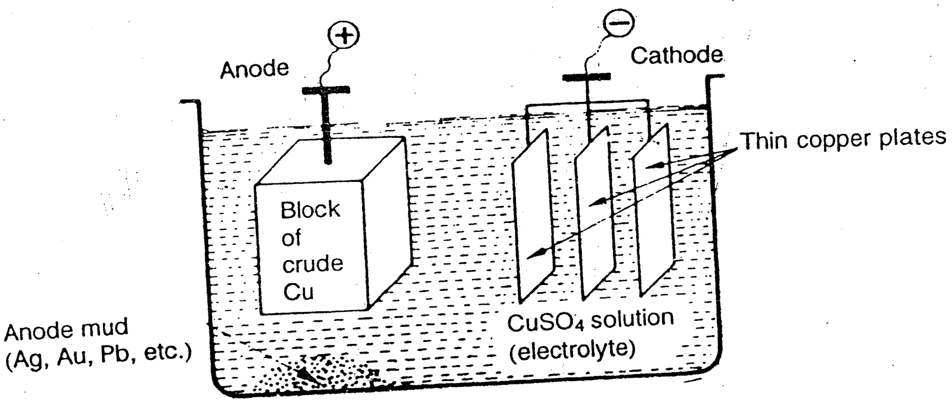

Fig. 4. Electrolytic refining of copper.

(2) Copper (of impure anode) forms copper ions, and these go into solution of electrolyte.

$$\underset{\text{(From anode)}}{Cu} \longrightarrow \underset{\substack{\text{(Goes into solution)}\\ \textit{(At anode)}}}{Cu^{2+}} \quad + \quad 2e^-$$

Thus, the net result is transfer of pure copper from anode to the cathode. Impurities like zinc, iron, etc., go into *solution* ; while noble impurities like silver, gold, etc., are left behind as *anode mud.*

(*iii*) ***Zone-refining*** : This method is employed for preparing *highly pure metals* (such as silicon, tellurium, germanium), which are used as semiconductors (in transistors, solar batteries, etc.). It is based on the principle that *melting point of a substance is lowered by the presence of impurities*. Consequently, when an impure molten metal is cooled, crystals of the pure metal are solidified, and the impurities remain behind in the remaining metal.

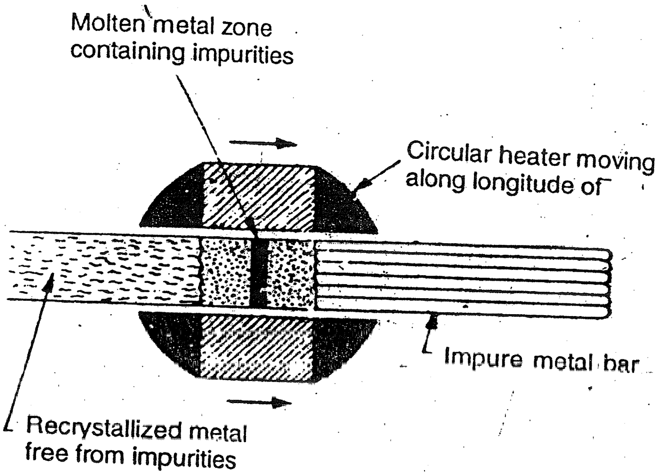

Fig. 5. Zone refining.

The process consists in casting the impure metal in the form of a *bar*. A *circular heater* fitted around this bar is slowly moved longitudinally from one end to the other. At the heated zone, the bar melts, and as the heater move on, pure metal crystallizes ; while the impurities pass into the adjacent molten part. In this way, the impurities are swept from one end of the bar to the other. By repeating the process, *ultra-pure metal* can be obtained.

(*iv*) ***Van Arkel method :*** *Ultra-pure metals* (like titanium, zirconium, etc.) are obtained by this method. In this method, the crude metal is converted into a *volatile compound* (generally metallic iodide); leaving behind impurities. The compound so-obtained is then decomposed to get pure metal. For example :

$$\underset{\text{Crude}}{\text{Ti}} + 2\,\text{I}_2 \longrightarrow \underset{\text{Titanium iodide } (pure)}{\text{TiI}_4\,(g)}$$

$$\text{TiI}_4 \xrightarrow{\text{Heated}} \underset{\text{(Pure)}}{\text{Ti}} + 2\,\text{I}_2$$

19.4 CAST IRON

The term **'cast iron"** *refers to the metal from which iron castings are made.* Pig iron is *not* suitable for being cast direct to give suitable castings for engineering uses. Cast iron is obtained by purifying pig iron, to some extent, by melting it in a ***'cupola furnace*** [in presence of coke and a little limestone].

Varieties of cast iron : (1) **Grey cast** is the most common in which carbon is present mostly in *"well-defined flakes of graphite"*. *It is produced when silicon content is high and molten metal is cooled slowly.* It possesses a ***greyish*** colour fracture, because of evenly distributed graphite. The usual composition of grey cast iron is : iron, 92-93% ; carbon (graphite), 3.5-4% ; carbon (combined), 0.5% ; silicon, 2.3% ; phosphorus, 0.15% to 1.0% ; sulphur, 0.02 to 0.15%, and manganese, 0.4 to 1.0%.

The metal is *soft* and can be machined with ordinary tools. It can be cast into moulds of intricate shapes. It possesses good fusibility, high compressive-strength and brittleness. Since carbon is present in the form of *flakes* or *thin plate-like* *crystals*, and these flakes are quite weak, consequently, they act as gaps within strong metal, iron. Therefore, grey cast iron possesses low tensile-strength, low toughness, and low ductility. It may be pointed here that due to *the presence of graphite flakes, the vibrations of machines are easily transformed* and consequently, grey cast iron is employed for making *bases for heavy machines*.

Uses: The metal finds applications mostly in making of casting, dies, moulds, machine frames, pipes, bodies of electrical machines, bases of heavy machineries, pistons and cylinders for automobiles, beds of engines, etc.

(2) **White cast iron** *is produced when silicon content is low and the molten metal is cooled rapidly*. In this, carbon is mostly present in combined form as *iron carbide* (Fe_3C) and *not* as graphite. Its fracture shows a *fine white* colour. Since cementite is a very hard and brittle compound, so white cast iron is also quite hard and brittle. Consequently, white cast iron *cannot be machined* with ordinary tools. It is rustless, and less soluble in acids. The metal is quite resistant to wear. Its usual compositions is : iron = 94% ; carbon = 2.5% to 3.0% (mostly in the combined state) ; silicon = 0.5 to 1% ; phosphorus = upto 0.2% ; sulphur = upto 0.12%, and manganese = upto 0.5%.

Uses: Due to its hardness, brittleness and poor machinability, white cast iron does not find much use. It is used where good abrasion-resistance is required, such as in railway-carriage brakes. The chief industrial use of white cast iron is in making malleable cast iron.

(3) **Malleable cast iron :** In order to combine the advantages of both white and grey cast irons, new variety of cast iron has been developed by '*heat-treatment*' of white cast iron. The white cast iron is subjected to the process of *annealing, i.e.,* heating in an oven to high temperature of about 875°C and keeping it at that temperature for sufficient time (say 24 – 27 hours) and then, cooling it gradually to room temperature. During heating period, Fe_3C (the iron carbide) dissociates giving graphite in the form of *nodules* (small round particles). Because of the absence of hard Fe_3C, the malleable cast iron is not hard and brittle. *As the graphite is present* ***in nodular form and not as large flakes****, consequently, its weakening effects are reduced.* The materials is called malleable, but it may be pointed here that it *cannot* be drawn into wires or made into sheets by hammering. Malleable cast iron possesses useful characteristics of both cast iron and mild steels. Thus, it possesses good toughness, ductility, shock-resistance and machinability.

Uses : It finds applications in making automobile parts like hubs, pedals, stearing-gear housings, rear-axle housings, agricultural machineries, railway equipments, carpentry tools, and intricate parts like toothed wheels, screw propellers, etc.

19.5 WROUGHT IRON

Wrought iron *is highly refined metallic iron, containing a little slag, which is distributed throughout the iron in fine-fibrous and film forms.* Its carbon content varies from 0.12 to 0.15%.

Properties : (1) Wrought iron is very malleable and ductile and can also be formed, extruded and *hammer-welded*, the latter being a very important characteristic. (2) It cannot be hardened as in the case of the high-carbon steel, but can be case-hardened. (3) A torn fracture of the metal shows a remarkable *fibrous structure*, due to the presence of slag (about 2 per cent maximum). (4) It contains upto 0.2 per cent combined carbon ; and has a tensile-strength greater than that of cast iron. (5) It cannot be cast into shapes. (6) Its m.p. is about 2,750°F (1,510° C).

Uses : Wrought iron is mostly used for making small-size water-pipes and fittings, corrugated sheets, ornamental sheets, metal works, wires, blacksmith's work like making of chains, bolts, nails, anchors, etc. Also used for making cores of electro-magnets and for conversion into hard steel.

19.6 STEEL

Steel *is essentially iron, containing 0.15 to 1.5% carbon.* In addition to carbon, all so-called **plain-carbon steels** (*i.e., which own their distinctive properties to their carbon contents*) contain Mn (upto 1%), S (upto 0.3%), Si (upto 0.03%), and P (upto 0.5%). Depending upon carbon content, steels are classified into *three* classes as follows :

1. Mild steels : Steel wherein the carbon content ranges from 0.15 to 0.3 per cent, is called the *mild steel* or *low-carbon steel* or *soft steel.* If the carbon content is 0.15 per cent, then the steel, is called *'dead-mild' steel.*

Properties : (*i*) They are quite tough. (*ii*) They are ductile. (*iii*) They are weldable by forging. (*iv*) They can be permanently magnetised. (*v*) They can withstand shock and impact well. (*vi*) They are difficult to harden and temper. (*vii*) Their density is about 7.8 g cm^{-3}. (*viii*) They undergo corrosion quickly. (*ix*) Their strength is about 40 kg/mm^2. (*x*) They are not much affected by saline water. (*xi*) Their structure is fibrous, with dark-bluish colour.

Uses : In the manufacture of rail tracks, cranes, transmission towers, industrial building structures in the form of I-sections, T-sections, angle irons, plates, channel sections, round and square rods. M.S. (mild steel) round bars are extensively used for reinforcement in *reinforced cement concrete* (RCC). M.S. sheets are used as roof covering. M.S. is also used for the manufacture of bolts, nuts, rivets, screws, plates for boilers and ships.

2. Medium-carbon steels have carbon content between 0.30 to 0.8%.

Properties : (*i*) They are tougher and harder than mild steels. (*ii*) They are shock-resistant. (*iii*) They are not easily weldable like mild steels. (*iv*) They exhibit greater strength (about 50 kg/mm^2) than mild steel. (*v*) They can be hardened to some extent.

Uses : Medium-carbon steels are used in the manufacture of wheels, gears, wires, hammers, hydraulic fittings (like cylinders, rams, turbine rotors, shafts, spindles), rifle barrels, gun parts, heavily stressed parts in general engineering, castings for automobile engine components, agricultural tools and implements, aero-engine cylinders, wire ropes, steels spokes, clutch plates, large forging dies, helical springs, boiler marine shafts and axles, connecting rods, turbine discs, etc.

3. High-carbon steels *contain carbon from 0.8 to 1.5%.* High-carbon steel with carbon content over 1%, is also known as *cast-steel* or *carbon-tool steel.*

Properties : (*i*) Their structure is granular. (*ii*) They can be permanently magnetised. (*iii*) They are quite hard. (*iv*) They possess high strength (about 65 kg/mm^2). (*v*) Their hardness and strength increase with increase in C content. (*vi*) With increasing carbon content, their ductility and wearability decrease. (*vii*) They can be hardened and tempered easily. (*viii*) They can be hardened further by heating to a high temperature, followed by quenching in water/oil. (*ix*) They are difficult to forge (*i.e.*, welding by hammering in hot condition). (*x*) They can withstand shocks and vibrations better. (*xi*) They are resistant to wear.

Uses : High-carbon steel are used in the manufacture of springs, blades, chisels, hammers, dies, wood-working tools, cutters, saws, drills, files, razors, metal-cutting tools (for lathes, planers and slotters), mandrels, gauges, engraving tools, wear-resistant forgings, smith's cutlery, knives, boring tools, screw drivers, safes, etc.

Function of carbon in steels : It is now well-established that carbon is responsible for : (*i*) the *strength of steel, which increases* with the *increase* in the proportion of carbon, till it reaches 0.83%, after which the effect is in the reverse direction ; (*ii*) *the ductility* which *decreases with increase in the carbon content. This correspondingly affects the workability of the steel* ; (*iii*) the *hardness,* which *increases* with the *increased* amounts of carbon ; (*iv*) the *susceptibility to heat-treament,* which *increases* with the *increased* carbon content.

Whatever its effects, the extent of carbon required to be present in steel is never more than 1.5%, even in the highest carbon steels.

19.7 EFFECT OF IMPURITIES IN STEEL

Carbon steels, usually, contain following *four* chemical elements, is addition to iron and carbon ;

(1) **Manganese** is the most important element in steel. *It deoxidises* ferrous oxide, which is harmful, and combines with sulphur to form manganese sulphide, the latter as impurity is relatively *harmless* in small amount.

(2) **Silicon** in ordinary amount is used in steel manufacture as a *scavenger.* It eliminates gases, thus making the metal *sound and free from blow-holes.* It improves tensile-strength and deep-hardening properties. Only small amount of silicon is added, a fraction of that added is found in the finished steel, seldom exceeding 0.25%.

Note : Both silicon and manganese are introduced into iron in the smelting of the iron ores. Nearly all these elements are lost, when the iron is converted into steel. It is, therefore, necessary to add them to the molten metal run into moulds. *Ferro-manganese* and *ferro-silicon* are employed for this purpose.

(3) **Sulphur** is *valueless* to the metal, and so is kept as low as possible in all steels. Sulphur above 0.06 percent should *not* be present in steels ; otherwise the steel becomes *very brittle and red short* (*i.e.*, the condition of iron and steel in which it cannot be worked by hammering or rolling at or above a dull-red heat). *When sulphur is present alongwith manganese, it improves the machinability of steel.*

(4) **Phosphorus** should *not* be present above 0.06 per cent ; otherwise the steel becomes *cold short* (*i.e.*, the condition of iron and steel in which it cannot be worked by hammering or rolling at or below a dull-red heat). This property is developed in steels containing more than 0.1 per cent phosphorus and is marked, when the amount of carbon and phosphorus together is more than 0.3 per cent. *In low-carbon steels, phosphorus improves yield-stength, and tensile-strength.*

19.8 HEART-TREATMENT OF STEEL

Heat-treatment may be defined as "*the process of heating and cooling of solid steel article under carefully controlled conditions, thereby developing in it certain physical properties, without altering its chemical composition*". Heat-treatment cause : (*i*) *refinement of grain structure* ; (*ii*) *removal of the imprisoned gases,* and (*iii*) *removal of internal stresses.* The main characteristics and the relevant heat-treatment *processes* adopted are given below :

1. **Annealing** means *softening.* This is done *by heating the metal to a certain high temperature, followed by very slow cooling in a planned manner in a furnace.* Annealing *increases machinability,* and *also removes the imprisoned gases and internal stresses* (caused in it, during casting or cold working). The process is classified into *two* categories as follows :

(*a*) ***Process annealing*** (or *low-temperature annealing*) involves in heating steel to a temperature *below the lower critical point*, followed by slow cooling. The main purpose of process annealing is to *improve machinability* by *relieving the internal stresses* (caused due to uneven contraction during casting) or *relieving internal strains* (caused during cold rolling or wire drawing). The process *increases ductility and shock-resistance, but reduces hardness.*

(*b*) ***High-temperature annealing*** (or *full-annealing*) involves in heating steel to a temperature about *30 to 50°C above the higher critical temperature*, holding it at that temperature for sufficient time to allow the internal charges to take place and then, cooling gradually to room temperature. The approximate annealing temperatures of various grades of carbon steels are : (*i*) mild steel (840 – 870°C) ; (*ii*) medium-carbon steel (780 – 840°C) ; (*iii*) high-carbon steel (760 – 780°C).

The net effect of full-annealing is that during the period of high temperature heating, *an intimate solution of the carbon and other elements present occurs, leading to an increase in the ductility and hence, machinability*. This process makes the *steel softer*, together with an appreciable *increase in its toughness.*

2. **Hardening** (or **quenching**) *is a process of heating steel beyond critical temperature and then suddenly cooling it either in oil or brine-water or some other fluid.* The net result yields steel of *great hardness*. The *faster* the rate of cooling, *harder* will be the steel produced. Medium and high-car-bon steels can be hardened, but low-carbon steels *cannot* be hardened. By hardening the steel, we *increase its resistance to wear, ability to cut other metals and strength,* but the steel becomes *extra-brittle as well.*

The object of hardening is to *increase abrastion-resistance*, and also to enable the hardened steel to cut other metals, so that it can used for making *cutting tools*.

3. **Tempering** consists in *heating the* ***already hardened steel*** *to a temperature lower than its own hardening temperature and then, allowing it to cool slowly.* In tempering, the temperature to which hardened steel is re-heated is of great significance and controls the development of the final properties. Thus : (*i*) *for retaining strength and hardness, temperature should* ***not exceed 400°C*** ; (*ii*) *for developing better ductility and toughness, reheating temperatures should be* ***within*** *400 – 600°C.*

Tempering removes any stress and strains that might have developed during quenching. By this operation, the brittleness and also some hardness are reduced ; but toughness and ductility are simultaneously increased. Cutting-tools (like blades, chisels, cutters, tool-bits) always require tempering.

4. **Normalising** *involves in heating steel to a definite temperature* (*above its higher critical temperature*) *and allowing it to cool gradually in air*. By normalising : (*i*) the homogeneity of the steel structure is recovered ; (*ii*) grains are refined ; (*iii*) internal stresses are removed, and (*iv*) toughness is increased. Normalised steel is suitable for use in engineering works. A normalised job will *not* be as soft as an annealed job of the same material. Also normalising takes *much lesser* time than annealing process. Sometimes, normalizing is done as a preparatory step for other heat-treatment processes, *e.g.*, tempering.

5. **Case-hardening** *is a process through which a* ***hard-wearing surface*** *is produced on steel having a* ***soft core inside***. It is chiefly employed for *low-carbon steels,* which cannot be hardened by quenching process. *The process involves in heating the steel to red-heat and then, forcing the carbon content into its surface structure so that at a certain depth, all along its surface becomes* ***rich in carbon****. It is then hardened as usual*. The process of case-hardening is carried out in *two* stages ;

(*i*) **Carburizing** : The mild steel article is enclosed in a cast iron box, containing a material *rich in carbon* (such as small pieces of charcoal). Heat it to 900 to 950°C and allow to remain at that temperature for sufficient time, so that the carbon is *absorbed to the required depth*. The article is then allowed to cool slowly, within the box. *The outer skin of the article is converted into high-carbon steel, containing about 0.8 to 1.2% carbon*. The depth to which this hardening takes place, depends upon the time allowed to the metal article to remain in contact with charcoal at the elevated temperature. The usual depth of 0.08 mm to 1.6 mm is attained in 3 to 4 hours.

(*ii*) **Hardening** : The carburised article is re-heated to about 900°C and then, *quenched in oil* so that brittleness is removed and the core becomes tough and soft. The article is then re-heated to about 700°C and *quenched in water* so that the outer-casing, which had been rendered soft during the preceding operation, is hardened again.

6. **Flame hardening** *is essentially a* **localised hardening**. *It consists in heating an area to be surface-hardened by means of oxy-acetylene (or oxy-hydrogen) flame, followed by abrupt cooling by spraying water on it.* The hardened depth can be controlled easily by adjusting the heating time, the temperature of the flame and the water spray. This method possesses an added advantage of consuming comparatively *less time* for heating in a furnace.

7. **Gas carburizing** *is another method of getting* **hard-wearing surface, containing a tough and relatively soft core inside**. In this operation, *the metal is subjected to gas rich in hydrocarbons (such as coal gas) at high temperature. This causes the infusing of carbon into the outer layer*. However, this method requires a lot of skill on the part of the operator to yield good results.

8. **Nitriding** *is a process of getting* **super-hard surface**. However. it can only be employed effectively for *alloy steels*. In this operation, *the metal alloy is heated in presence of ammonia at a temperature of about 550°C*. The nitrogen (obtained by the dissociation of ammonia) combines with the surface constituents of the alloy to form *extremely hard nitrides*. This process is quite time-consuming.

9. **Cyaniding** *is also a type of case-hardening process*. It consist in producing a layer of hard surface on low or medium-carbon steels by *immersing the metal in a molten salt, containing* **cyanide** *(like KCN or NaCN) at a temperature of about 870°C and then, quenching in oil or water*. The hard surface is produced, due to the *absorption of carbon and nitrogen* by the metal surface.

19.9 NICKEL

Occurrence : The most important ore of nickel is *pentlandite* (Fe.Ni.Cu)S. Other important ores are : (1) *garnierite* (Ni, Mg) $SiO_2.xH_2O$; *smaltite* (Fe, Co, Ni) As ; (3) *kupfer-nickel* (Ni, As) ; (4) *nickel-glance* (Ni, As, S).

Extraction from *pentlandite* (sulphides of Ni, Fe and Cu) involves :

(1) **Concentration :** The finely divided ore is first concentrated by "*froth flotation process*", *i.e.*, pulverized ore is fed into a flotation tank in which water and pine oil (frothing agent) are maintained in condition of violent agitation by forcing compressed-air. *The mineral particles are preferentially "wetted" by the froth so-produced, which is carried over a weir*. On the other hand, the gangue particles (impurities), which are not wetted, remain behind in flotation tank. The froth is collected and washed with water to get concentrated ore.

(2) **Roasting :** The concentrated ore is then heated on the hearth of reverberatory furnace is free supply of air, whereby :

(*a*) most of the sulphur is oxidised to SO_2,

$$S + O_2 \longrightarrow SO_2 \uparrow$$

(*b*) ferrous sulphide is partially oxidised to ferrous oxide.

$$2\,FeS + 3\,O_2 \longrightarrow 2\,FeO + 2\,SO_2 \uparrow \qquad \textit{(Main)}$$

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2 \uparrow \qquad \textit{(In small proportion)}$$

$$2\,NiS + 3\,O_2 \longrightarrow 2\,NiO + 2\,SO_2 \uparrow$$

(3) **Smelting :** The roasted one is mixed with coke, silica, and limestone, and smelted in a small blast furnace with a *regulated blast of air*. Residual iron sulphide is oxidised to ferrous oxide, which combines with silica (flux) to form fusible ferrous silicate (*slag*).

$$\underset{}{FeO} + \underset{\text{(Flux)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

The product forms *two* layers, *i.e.*, lower layer of *molten matte* and upper layer of fusible *slag*. The two layers are separated.

(4) **Bessemerization :** The molten matte (containing sulphides of Cu and Ni, alongwith a small quantity of FeS) is mixed with requisite quantity of *silica* and then introduced in a Bessemer converter, provided with a *basic lining*. Blast of air is blown in, when most of sulphur is converted into SO_2 and iron is changed into ferrous silicate (slag). The resulting *bessemerized matte* contains about 56% Ni, 25-30% Cu, 1.4 1.7% S and 0.25% Fe.

(5) **Removal of copper (*Mond's process*) :** It is based on the following facts : (*a*) only nickel (and *not* Cu, Fe, etc.) forms a volatile carbonyl, $Ni(CO)_4$, when CO is passed over it at 50°C ; (*b*) the nickel carbonyl decomposes at 180°C to yield pure nickel.

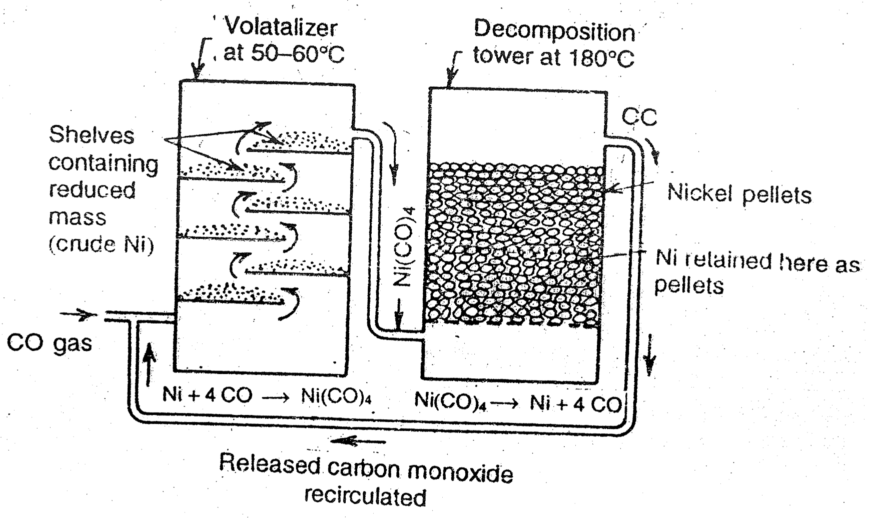

Fig. 6. Mond's process of refining of nickel.

Process : The baseemerized matte is first heated in air in a special type of furnace, when sulphides of Ni and Cu are converted into oxides. These oxides are then extracted with hot 15% dilute H_2SO_4, which dissolves oxides of Cu and Fe to form soluble sulphates ; while NiO is left be behind undissolved and is separated.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

The residue, consisting mostly of NiO, is heated carefully in a tower at 350°C, in which a current of water gas (CO + H_2) is passed. At this temperature, only NiO is reduced to metallic state.

$$\underset{\text{(Water gas)}}{2\,\mathrm{NiO} + \mathrm{CO} + \mathrm{H_2}} \xrightarrow{350°\mathrm{C}} 2\,\mathrm{Ni} + \mathrm{CO_2}\uparrow + \mathrm{H_2O}$$

The reduced mass is then placed on the shelves in a tower (called '*volatilizer*'), which is kept at 50–60°C, and a current of CO is passed through it. Nickel *alone* forms a *volatile carbonyl*, $Ni(CO)_4$; while Cu and Fe are left behind unaffected.

$$\mathrm{Ni} + 4\,\mathrm{CO} \xrightarrow{50\text{–}60°\mathrm{C}} \mathrm{Ni(CO)_4}\uparrow$$

The *vapour of nickel carbonyl* is led through a tower (called '*decomposition tower*"), which is filled with pellets of nickel and maintained at 180°C. Here *nickel carbonyl undergoes decomposition*, and the nickel (99.8% pure) so-formed gets deposited on the pellets.

$$\mathrm{Ni(CO)_4} \xrightarrow{180°\mathrm{C}} \mathrm{Ni} + 4\,\mathrm{CO}\uparrow$$

Carbon monoxide thus set free is pumped to volatilizer for re-use.

(6) **Refining :** Nickel obtained as above is 99.8% pure. Further purification, if needed, is carried out by electrolysing a solution of nickel ammonium sulphate at 20–25°C in cell consisting of crude nickel as *anode* and a thin strip of pure nickel as *cathode*. Pure nickel is deposited on the cathode. Impurities like Hg, Au, Pb, etc. form *anode-mud*.

Properties : Nickel is a silvery-white metal, capable of taking high polish. It is malleable, ductile and hard. It density and m.p. are 8.69 g/cm^3 and 1,455°C respectively. *Nickel is extremely resistant to corrosion and has excellent strength at low temperatures*. For this reason, nickel and its alloys are widely used in chemical industry, where corrosion-resistance is of importance. Nickel is not tarnished by air, as it has the ability to form a minutely thin *protective oxide film* on its surface. Nickel is not attacked by dilute non-oxidizing acids, organic compounds and dilute alkalis, and at the same time is *non-toxic*, so it is widely used for making equipments used in pharmaceutical and food industries.

Uses of nickel : (1) *In nickel-plating* : Due to its silvery-white luster and great resistance to atmospheric corrosion, it is used for electroplating iron and other baser metals. (2) *As a catalyst* in the manufacture of vegetable ghee and converting unsaturated into saturated organic compounds. (3) *In preparing important alloys* like : (*a*) *Monel metal* (67% Ni, 30% Cu, 3% Fe). It is bright, strong, tough and resists corrosion effects of atmosphere, sea-water, alkalis, and most of acids (other than HNO_3 and H_2SO_4). It is easily cleaned and has attractive appearance. Used for acid-proof impellers, food processing equipments and trubine blades ; (*b*) *Nichrome* (60% Ni, 25% Cr, 15% Fe) possesses a very high melting-point and marked resistance to heat, electricity and chemical reagent. Used for making resistance coils, heating elements in stoves, electric irons, toasters and other electrical appliances ; (*c*) *German silver* (Cu = 55%, Ni = 20%, Zn = 25%) is used in ornaments, and cutlery (like spoon, forks, etc) ; (*d*) *Platinoid* (Cu = 60%, Zn = 24%, Ni =14%, and a little W) is used in electric bulbs and radio-valves, since its *co-efficient of expansion is equal to that of glass*.

19.10 CHROMIUM

Occurrence : Its principles ores are : (1) *chromite or chrome iron* (FeO . Cr_2O_3) : (2) *chrome ochre* (Cr_2O_3), and (3) *chrometite* ($Fe_2O_3 \cdot Cr_2O_3$). However, the chief ore is chrome iron or chromite.

Extraction from chromite involves the following *steps* :

(1) **Concentration :** The finely powdered chromite ore is washed in a strong and rapidly flowing current of water, when lighter siliceous impurities (called, gengue) are washed away ; while the heavier ore particles are left behind (*Gravity process*).

(2) **Roasting :** The concentrated ore is mixed with excess of sodium carbonate and a little lime and the mixture heated on the hearth of a reverberatory furnace in a free supply of air, when chromite is converted into soluble sodium chromate. The lime serves to keep the mass porous.

$$2\,[FeO \cdot Cr_2O_3] + 4\,Na_4CO_3 + \frac{1}{2}\,O_2 \longrightarrow \underset{\text{(Soluble)}}{4\,Na_2CrO_4} + \underset{\text{(Insoluble)}}{Fe_2O_3} + 4\,CO_2$$

The roasted mass is extracted with hot water (to dissolve sodium chromate) and filtered. The filtrate is acidified with a calculated quantity of sulphuric acid to change it into sodium dichromate.

$$2\,Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

On fractional crystallization, less soluble sodium sulphate separates out ; leaving behind sodium dichromate.

(3) **Reduction of dichromate to Cr_2O_3 :** The dicnromate is heated with carbon, when it is converted into green powder of chromic oxide.

$$Na_2Cr_2O_7 + 2\,C \longrightarrow Cr_2O_3 \downarrow + Na_2CO_3 + CO \uparrow$$

Alternatively, the reduction may be brought about by boiling the dichromate with ammonium choride.

$$Na_2Cr_2O_7 + 2\,NH_4Cl \longrightarrow (NH_4)_2Cr_2O_7 + 2\,NaCl$$

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 \uparrow + 4\,H_2O$$

(4) **Reduction of Cr_2O_3 to Cr.** This is done by *Goldschmidt's aluminothermic process*. The Cr_2O_3 (mixed with requisit quantity of Al power) is taken in a fireclay crucible, which is surrounded by sand (to prevent the loss of heat by radiation). The charge is covered with an ignition mixture of Mg powder plus BaO_2. The mixture is fired by means of piece of magnesium ribbon. Large quantity of heat thus-produced

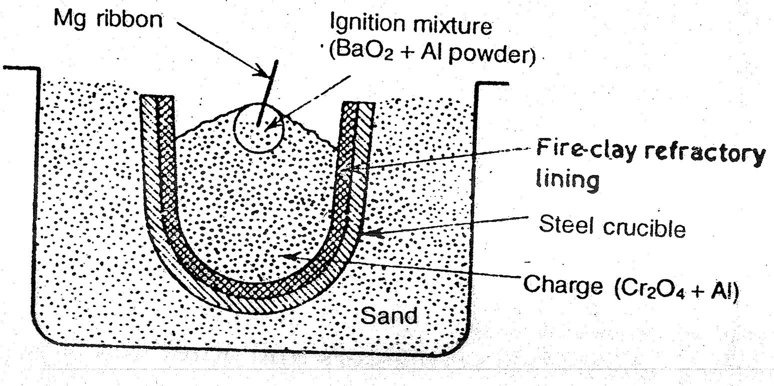

Fig. 7. Goldschmidt's process for reduction of Cr_2O_3.

fuses the alumina and Cr metal is produced. The latter forms the lower layer, which is separated.

$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr + 112\ kcal$$

Uses : (*i*) *Ferro-chrome* (an alloy of 35% Fe ; 65% Cr) is used for making special teels. It is prepated by heating chromite ore with C in an electric furnace.

$$FeO\ .\ Cr_2O_3 + 4\ C \xrightarrow{\text{Heat}} \underbrace{Fe + 2\ Cr}_{\text{Ferro-chrome}} + 4\ CO \uparrow$$

(*ii*) *In chrome plating* : Cr is highly resistant to corrosion by air, water and CO_2 and hence,. is used in electroplating of iron articles. The surface layer of Cr not only protects them from rusting, but also improves their appearance.

(*iii*) *In the manufacctures of alloy steels and alloys*, since Cr imparts great strength, hardness, brightness and resistance to corrosion. Important chromium alloy steels are : (*a*) *Stainless steel* (13% Cr ; 0.1 to 0.2% C ; rest Fe) is used for making cutlery, surgical instruments, etc. (*b*) *Nichrome* (Ni = 58.62% ; Cr = 8.13% ; Fe = 22 – 28% ; C= 0.2 - 1%) is used for making resistance wires for furnaces. (*c*) *Satelite* (Cr, Co and W) is used for making surgical instruments, high-speed tools and automobile parts. (*d*) *Chrome steel* (25% Cr ; 1.5% C ; rest Fe) is used for making safes and armour plates, due to its extreme hardness.

19.11 TITANIUM

Occurrence : Titanium is found in nature as : *ilemenite, rutile, onatase* and *brooklite,* all of which are different varieties of TiO_2.

Extraction : This presents great difficulty, owing to the *great affinity of the molten metal for electronegative elements* such as carbon, nitrogen and oxygen. Following *steps* are involved in its extraction :

Step I **:** The ilemenite ore is digested with hot concentrated H_2SO_4. The soluble material, which contains titanium sulphate and ferrous sulphate, is then diluted with water. Under the action of water, *hydrolysis of only titanium sulphate takes place* ; while ferrous sulphate remains in solution.

$$Ti(SO_4)_2 + 3\ H_2O \xrightarrow{\text{(Hydrolysis)}} \underset{\text{(Titanium hydroxide)}}{TiO(OH)_2} \downarrow\ +\ 2\ H_2SO_4$$

The precipitated titanium hydroxide is filtered and then roasted to form titanium dioxide.

$$TiO(OH)_2 \xrightarrow{\Delta} TiO_2 + H_2O \uparrow$$

Step II **:** Titanium dioxide is reacted with carbon in presence of chlorine to form volatile titanium tetrachloride, which is then condensed.

$$TiO_2 + 2\ C + 2\ Cl_2 \longrightarrow TiCl_4 \uparrow\ + 2\ CO \uparrow$$

Step III **:** Titanium tetrachloride is then heated with magnesium or sodium a 850°C in an *inert atmosphere of argon*.

$$TiCl_4 + 2\ Mg \longrightarrow Ti + 2\ MgCl_2$$

$$TiCl_4 + 4\ Na \longrightarrow Ti + 4\ NaCl$$

When heated strongly in an electric furnace, the by-products vaporize ; leaving molten titanium, which solidifies on a rod of titanium, used as one pole of the arc.

Step IV : For getting *very pure* titanium, the impure metal is *heated with iodine* in an evacuated vessels (*see* Fig. 8). The *titanium tetraiodide* vapour is formed, which decomposes thermally, when it comes near the tungsten filament, which is kept at about 1,700°C by an electric current. Pure titanium is deposited on the filament, which slowly grows in thickness ; and the iodine vapour combines with more of the impure metal. This method depends upon the volatility of titanium tetraiodide and its low decomposition temperature compared with the boiling point of titanium.

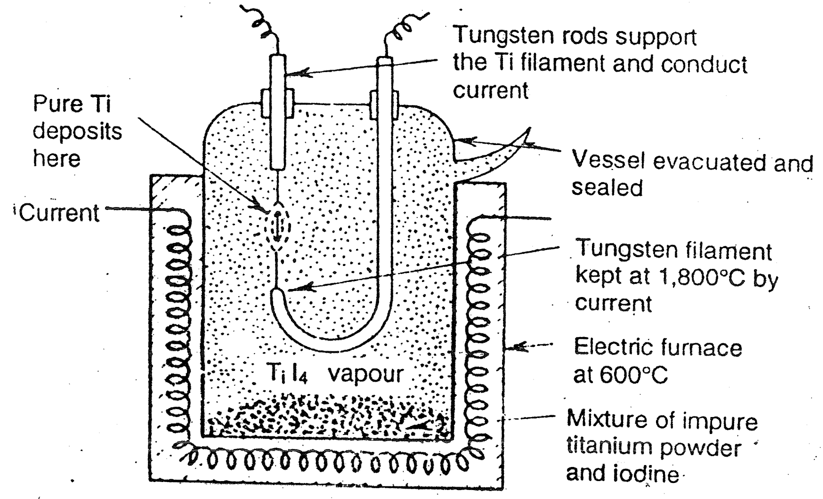

Fig. 8. Filament growth method for making pure titanium.

$$TiI_4 \rightleftharpoons Ti + 2\,I_2$$

Properties : Titanium has a very high boiling-point (1,800°C) and low density (4.5 g/cm^3), but its strength is of the same order as that of heat-treated steel ; while the corrosion-resistance and thermal conductivity compare favourably with those of steel. When pure, it is ductile even at room temperature. Acids and alkalis have little action on titanium at room temperature, but it reacts readily with halogen forming tetrahalide, when heated. Molten titanium has high affinity for oxygen, carbon, nitrogen and hydrogen. *The presence of such impurities diminishes very greatly the strength of the metal.* Solid metal resists the action of oxygen and air well up to about 360°C. *A tightly adhering thin oxide film also protects it against acids, alkalis, and salts.*

Uses : (1) Titanium has great stability at elevated temperatures and for this reason, it is widely used for casting and forgings in the aircraft industry. (2) Its alloy with iron, called *ferro-titanium,* is added to molten steel to remove dissolved gases. (3) Titanium and its alloys are of growing importance in the construction of *aircrafts and missiles,* where its high melting point, great resistance to corrosion and low density are valuable properties. Its remarkable resistance to attack by sea-water has led to many *marine uses*. Its common alloy, which is widely used, has Cr = 1.8 to 3% ; Fe = 0.9 to 1.5%, C = 0.15 to 0.5%. (4) It is also used in *surgery* for pining together broken bones or repairing damaged skulls, because the light, but strong pieces of titanium remain *uncorroded* in the body throughout the life-time of the patient.

19.17 ALLOYS

Metals, in general, are insoluble is ordinary solvents (like water, alcohol, ether, benzene, etc.). However, a metal can dissolve in another metal in molten state forming a homogeneous liquid mixture, which on cooling solidifies to a solid mixture, called an ***alloy***. Most of the metals can mix up in all proportions, *e.g.*, tin and lead mix up in all proportions, forming alloys. Alloys are formed *not only by metals among themselves, but also by metal and non-metal*. From the above, it is clear that an alloy contains *at least one metal*. Thus, an ***alloy*** *is a metallic, intimately mixed solid mixture of two or more different elements, one of which at least is essentially a metal.* Alloys containing mercury (a liquid at ordinary temperature) as the constituent element, are called *amalgams, e.g.*, sodium-amalgam is an alloy of sodium and mercury.

Note : It may be made clear that the alloys are homogeneous in molten state, but they may or may not be homogeneous upon solidification. Hence, *an alloy in solid state may be either homogeneous or heterogeneous.*

19.18 PURPOSE OF MAKING ALLOYS

Pure metals, in general, possess a few useful physical properties (like high malleability, ductility, lustre, good electrical conductivity, etc.). However, they are very soft and highly chemically reactive. The properties of a given metal can be improved by alloying it with some other metal/non-metal. Main *purposes* of making alloys are :

(1) **To enhance the hardness of the metal :** Pure metal are, generally, soft. The hardness of a metal is enhanced on alloying it with another metal/non-metal. *In other words, an alloy is harder than its component elements.* For example, addition of 0.5% arsenic makes lead so hard that it is used for making bullets (lead shots). Also pure iron is very soft. However, when iron is alloyed with a small quantity (0.15% to 1.5%) of carbon to get steel, hardness is imparted to it. Thus, presence of carbon imparts hardness to iron-carbon alloy, steel.

(2) **To lower the melting point :** In general, *the melting point of an alloy is lower than those of its constituent elements*. In other words, alloying makes the metal *easily fusible*. This fact is utilized in making useful alloys, called *solders*. For example, wood's metal, an alloy of bismuth, lead, cadmium and tin, possesses melting-point of only 71°C, which is much lower than those of its components, Bi, Pb, Cd and Sn.

(3) **To enhance tensile-strength :** *Alloy formation, in general, enhances the tensile strength of the parent/base metal.* For example, addition of 1% carbon increases the tensile-strength of pure iron by about *ten* times.

(4) **To enhance corrosion-resistance** : Metals in pure form are quite reactive and easily corroded by surrounding atmospheric gases, moisture, etc., thereby their life is reduced. But if a metal is alloyed, it resists corrosion. In other words, *alloys are more resistant to corrosion than pure metals*. For example, *bronze*, an alloy of copper with tin, is more corrosion-resistant than copper. Pure iron is corroded even in moist air, but *stainless steel*, an alloy of Fe with Cr and Ni, is even acid-proof.

(5) **To modify colour :** *The colour of metal can be modified to a desired one by alloying it with another suitable element.* Thus, an alloy can be prepared having a colour quite different from the colour of the base metals. For example, *brass*, an alloy of copper (red) and zinc (silver-white) is *yellow* in colour.

(6) **To provide better castability :** One of the most essential requirements to get good castings is *expansion of metal on solidification*. But pure molten metals, in general, undergo *contraction* on solidification. Hence, in order to get good castings, metals have to be alloyed, because alloys expand on soldification. Moreover, alloys are *easily fusible*, so they also give good castings easily. For example, pure lead on alloying with tin (5%) and antimony (2%) yields '*type metal*', which is used for casting printing type, due to its exceptionally good casting properties.

19.19 PREPARATION OF ALLOYS

The following are the commonly employed *methods* for the manufacture of *binary* (two-component) alloys :

(1) **Fusion method :** In this, components of the alloy in proper proportions are fused together in a refractory bricks-lined crucible or melting pot. The component metal, with higher melting point, is first melted and the other components, having lower melting points, are then added to the melt. The molten mass is well-stirrred with graphite rods to bring about a thorough and uniform mixing. It may be pointed here that the densities of the alloy constituents have also to be taken into account during mixing. *The heavier component metals are, generally, mixed later in order to avoid its setting ; otherwise alloy of uneven composition results.* Since the molten metals are at high temperatures, so they are likely to undergo oxidation by atmospheric oxygen to form oxides. Consequently, the surface of the molten mass is covered with *a layer of powdered carbon* to avoid the oxidation of the molten alloy components. The molten mass, after through mixing, is finally allowed to cool slowly, when solid alloy is obtained. For example, *brass*, an alloy of copper (m.p. 1,089°C), is obtained by melting first copper, followed by addition of requisite amount of solid zinc. To avoid the oxidation of molten copper and zinc, the surface is covered with *charcoal powder*. The molten mass is stirred thoroughly with graphite rods and then, allowed to cool slowly to get brass.

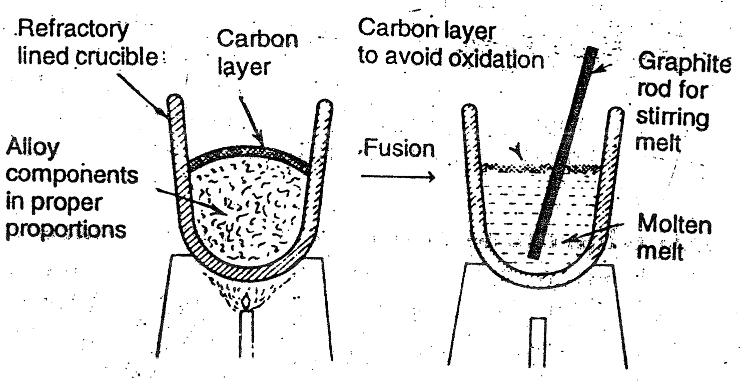

Fig. 9. Fusion method of alloy making.

(2) **Electrodeposition method** *involves in simultaneous deposition of the different component metals from the electrolytic solution, containing their salts solution mixture, by passing D.C. electricity.* For example, *brass* is obtained by the electrolysis of mixed solution of *copper* and *zinc cyanides* dissolved in *potassium cyanide*.

(3) **Reduction method** *involves in reduction of a suitable compounds of one component of alloy in the presence of other component metal.* Generally, oxide of one component metal is reduced in presence of other component metal. For example, *aluminium bronze* is prepared by reducing alumina (Al_2O_3) in the presence of copper in an electric furnace.

19.20 POWDER METALLURGY

Powder metallurgy *is the art or science of manufacturing useful metallic and alloy articles by compacting the metal (or alloy constituent) powders and other powders in a die, with little or no melting, followed by sintering. When compaction and sintering is done simultaneously, then the process, is called* ***pressure sintering*** *or* ***hot pressing.***

The power metallurgy involves the following *steps* :

(1) **Preparation of metal/alloy powder** is carried out by following *methods* :

(*a*) ***Mechanical pulverization*** *involves the use of mechanical pulverizers, consisting of either counter-rotating plates or rapidly moving hammers*. Due to the mechanical forces, it '*disingtegrates*' the metal particles to fine powder. Usually, pulverization is followed by ball milling. This method is used for Mg, Al, Pb, and Zn.

(*b*) ***Atomization*** *involves in forcing molten metal through a 'nozzle' into a stream of compressed air or water, when molten metal breaks to a fine powder*. The process requires careful control of temperature, pressure, and oxidation can be prevented by providing an *inert gas atmosphere*. This method is commonly used for Zn, Pb, Sn, Al, Cd, Mg, etc.

(*c*) ***Chemical reduction*** *involves heating metal oxide* (*e.g.*, WO_2) *in a current of hydrogen, which reduces oxide to get pure spongy metal* (*e.g.*, tungsten) *powder, which is suitable for cold pressing, due to its softness and plasticity*. *Nickel powder* is obtained by forming $Ni(CO)_4$, which on decomposition (by heat only) precipitates *nickel powder*. Fe, Cu, and Zn powders are obtained by this method.

(*d*) ***Electrolytic process*** is useful for getting powders of Fe, Cu, Zn, Ag, W, Ta, etc. ***When conventional electrolysis is carried out, a powdery deposit is obtained on the cathode. The deposited powder is scrapped, washed, dried and then pulverized further to get powder of desired size.*** This method possesses an advantage that the power so-obtained is ***resistant to oxidation***.

(*e*) ***Decomposition*** is used specially to iron and nickel carbonyls. The gaseous carbonyles [$Fe(CO)_5$ or $Ni(CO)_4$] on decomposition yield very pure metal (Fe or Ni] powders, which are usually *spherical*.

(2) **Mixing and blending :** Metal powders in desired proportions are uniformly mixed into order to get uniform and best results, especially when an alloy is to be made. For special purposes, lubricants, volatilizing agents are also included for homogeneous distribution of powder.

Note : Similar shape and density particles provide excellent mixing ; whereas particles of different size, shape and density give uneven mixing.

(3) **Compacting** (or **briquetting**) *is the process of converting loose powder into an accurately defined dimension (i.e, shape and size). It involves taking a premeasured quantity of blended powder in a cavity* (*female die*) *of desired shape and size. Then, the powder is compressed with the use of top 'die'* (*male die*). The pressure used ranges from 100 – 1,000 MN/m^2 ; and the dies are usually made of high grade hardened steel with fine finish. The solid mass, is called '*green compact*'.

Note : By compacting : (*i*) voids between powder particles are reduced, thereby the density of the compact is raised ; (*ii*) adhesion and cold weld of the powder is produced ; (*iii*) deformation of powder plasticity occurs, so as to allow recrystallization during subsequent sintering. This in-turn increases the contact area between the powder particles.

(4) **Presintering** *refers to the process of heating the 'green compact' to a temperature below the sintering temperature*. Its objects are to remove the lubricants and binders (added during blending). This also enhances the strength of the "green compact." *Presintering is essential for metals like tungsten (for getting carbide), which cannot be machined after sintering.*

(5) **Sintering :** Compaction (and presintering) does not provide enough cohesiveness and strength. In sintering, *the compacted (and presisntered) pieces are heated in a furnace to a temperature below, but close to the melting point of the basic*

metal, usually in an atmosphere of hydrogen gas. During this process, the metal particles *sinters, i.e.*, a proportion of them partly meet and bond the remaining particles into coherent bodies. *The sintering temperature and time of sintering vary*, depending upon : *the compressive load used during compacting, the nature of the metal, and the final strength of the finished work pieces required.*

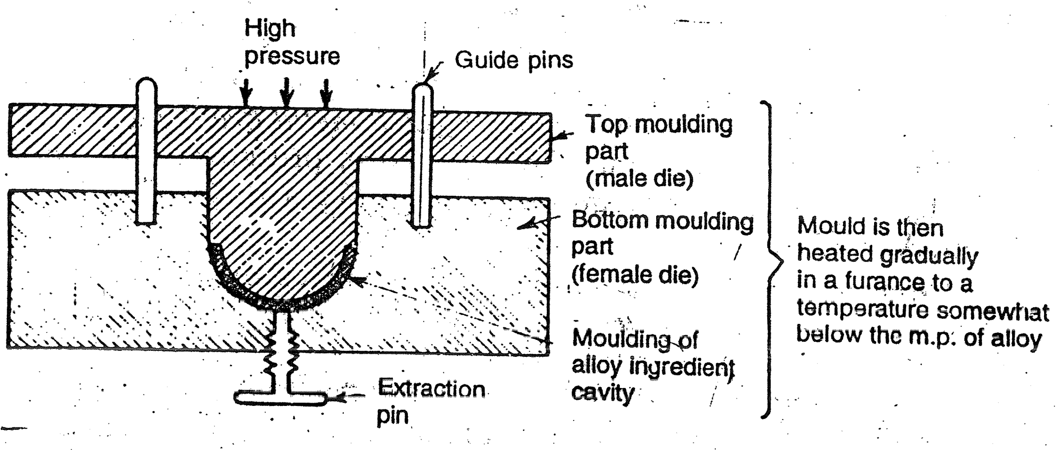

Fig. 10. Compounding during powder metallurgy.

The sintering operation consists in : (*i*) *heating*, (*ii*) *soaking*, and (*iii*) *cooling cycle*. It may be pointed that : (*i*) sintering conditions, and (*ii*) sintering atmosphere governs the properties of the final products, such as toughness, hardness, density, etc.

Notes : (*i*) Furnaces used in sintering include belt-type, pusher-type, roller-type, vacuum-type furances.

(*ii*) Controlled atomsphere used are endothermic gas, cracked ammonia, nitrogen-hydrogen mixture.

(6) **Secondary operations :** Generally, the work pieces cannot be used as such, *since during sintering they may expand or contract*, depending upon the nature of basic metal. Consequently, the work pieces are, generally, subjected to finishing operations like machining (sizing), plating, etc., to get the perfect dimensions of the work pieces.

Uses of power metallurgy : Important products manufactured by powder metallurgy are : porous bearing, *filaments of electric bulbs* of tungsten, electric clocks, sewing machines, gears, cams, parts of gas turbines, cutting tools (hard carbide of tungsten, titanium, tantalum, etc.), *refractory metal composites* (Mo, W, Pt, etc., with ceramic oxides, carbides, nitrides, etc.), *diamond-impregnated cutting tools* ; *magnetic metarials* (alnico, permalloy, Ni–Zn ferrites, Mn–Mg ferrites, etc), oil pump gears (Fe–C composites), surgical implants (Ti – Ta composites), bearings (for automobiles), clutches, brakes, generator bushes, filters, etc.

Advantages of power metallurgy : (1) Rate of production is high. (2) Dimensional accuracy and good surface finish is obtained. So, products hardly require machining, etc. (3) Cleaner and quieter operation. (4) Life of the components parts is longer. (5) Products with relatively much uniforms structures (*i.e.*, free from defects like voids, blow-holes, etc.,) are produced. (6) Quite complex shapes can be produced. (7) No material is wasted (*i.e.*, the process makes use of 100% raw materials). (8) Parts with wide variations in compositions and materials can be produced. (9) Highly skilled labour is *not* required. (10) Complex shapes obtained, possess excellent reproducibility. (11) Porous parts can also be produced. (12) Impossible parts like super-hard cutting-tools can also be produced.

Limitations of powder metallurgy : (1) *The derived size and shape of a part is limited* by the avaialble press capacity, since relatively high pressure is needed to compact the powder. (2) Since the compacted mass has to be ejected from the die without fracture, so *shapes that can be made are limited*, *i.e.*, more intricate shapes cannot be produced. (3) The precision dies used for pressing are *very expensive.*

19.21 ALLOY STEELS

Plain-carbon steel finds only limited use, Addition of small amounts of one or more metals (such as nickel, chromium, cobalt, etc.) imparts *special properties* to the steel. *Such steels, are called* ***alloy steels*** *or* ***special steels***.

Need for alloying steels : Main purposes of alloying steel are to : (*i*) improve tensile-strength ; (*ii*) improve ductility ; (*iii*) improve toughness ; (*iv*) improve elasticity ; (*v*) improve heat-resistance ; (*vi*) improve corrosion-resistance ; (*vii*) improve hardenability ; (*viii*) improve resistance to abrasion ; (*ix*) improve acid and chemical-resisting property ; (*x*) improve hardness ; (*xi*) improve ability to retain shape in hot condition ; (*xii*) minimise the coefficient of expansion ; (*xiii*) improve the ability to undergo milling operations (*e.g.*, drawing, rolling, pressing, hammering, etc.) smoothly ; (*xiv*) improve weldability ; (*xv*) improve oxidation-resistance ; (*xvi*) improve magnetic permeability ; (*xvii*) improve forgeability ; (*xviii*) improve shock-resistance ; (*xix*) improve *red-hardness, i.e.,* hardness in outer surface layer only ; (*xxi*) improve ability to retain physical properties at high temperatures ; (*xxii*) improve cutting ability.

Specific effects of alloying elements : The properties of steels are greatly affected by the presence of alloying elements. A brief description of their effects is given below :

(1) **Nickel :** It improves tensile-strength, ductility, toughness, elasticity, heat and corrosion-resistances.

(2) **Chromium :** It is added in proportions upto 18%. Below 1.5%, addition of chromium enhances tensile-stength ; while 12% addition imparts high corrosion-resistance. In general, chromium *improves hardness and toughness simultaneously.*

(3) **Manganese :** Addition of 1.0 to 1.5% increases strength and toughness plus brittleness. Addition of still higher proportions, say between 11 to 14%, provides a high degree of hardness.

(4) **Molybdenum :** Strength at elevated temperature, corrosion-resistance, and abrasion-resistance are increased ; while temper-brittleness is eliminated.

(5) **Tungsten :** Red hardness, toughness, abrasion-resistance, and shock-resistance are increased.

(6) **Vanadium :** Tensile-strength, ductility, and shock-resistance are increased.

19.22 APPLICATIONS OF ALLOY STEELS

Important applications of alloy or special steels, on the basis of particular *type of their use*, are described below :

1. ***Heat-resisting steels*** *are alloy steels suitable for making equipments exposed to high temperatures.* For getting such steels : (1) *molybdenum is an alloying element, which gives strength and creep-resistance to steel at high temperatures.* Steels containing 3.5% Mo are used as heat-resisting steels ; (2) *chromium* is a universal constituent of all heat-resisting steels, because it increases corrosion-resistance at high temperatures. *Heat-resisting steels, generally, contain more than 12% chromium.* Important heat-resisting alloy steels are :

(*i*) **Nichrome,** a steel alloyed with 60% nickel and 12% chromium can be used at 1,000 to 1,100°C.

(*ii*) Steels containing 16 to 20 percent chromium with low (0.06 to 0.15%) C possess oxidation-resistance up to 900°C.

(*iii*) Steels containing 18% nickel, with small amounts of columbium can withstand temperature as high as 900°C

Uses : In making parts of boilers, steam-lines, stills, gas-turbrines, aero-engine valves, retorts, annealing boxes, and other machineries/equipments exposed to high temperatures.

2. ***Spring-steels*** or ***shock-resistant steels :*** *Spring (coil or leaf) are used in situations, where sudden shock-absorption in required.* They possess high elastic limits. *Chrome-vanadium steels* containing 0.8 to 1.1% chromium, 0.25% vanadium, and 0.35 to 0.9% carbon possess great impact-resistance, and are used in making laminated springs, leaf springs, coil springs, etc.

3. ***Magnetic steels*** *possess good ferromagnetic properties.* They are used for making pole-pieces of electromagnets, transformer cores, dynamos, motors, loud-speakers, etc. *Alnico* (or aluminium-nickel-cobalt steel) containing 12% Al, 20% Ni and 6% Co is highly magnetic and used for making powerful magnets.

4. ***Stainless steels*** or ***corrosion-resistant steels*** *are alloy steels which resist corrosion by atmosphere and also by chemicals.* They contain, essentially, chromium, together with other elements such as nickel, molybdenum, etc. *Chromium is especially effective, if its content is 16 per cent or more.* The protection against corrosion is due to the formation of *dense, tough film of chromium oxide at the surface of metal.* If this film is broken in service, it gets *healed-up automatically* by oxygen of air. There are *two* main types of stainless steels :

(*a*) **Heat-treatable stainless steels** *contain upto 1.2 per cent carbon and less than 18 percent chromium (generally 12 to 16 percent).* Their typical characters are that they are *magnetic, tough* and *can be worked in cold state.* They can be used at temperatures upto 800°C. They are satisfactory for resisting weather, and water. Such steels find use in making surgical instruments., scissors, blades, cutlery, etc.

(*b*) **Non-heat-treatable stainless steels** *show less strength at high temperatures, but are more resistant to corrosion.* According to their composition, they may be *magnetic* or *non-magnetic.*

(*i*) ***Magnetic-type*** *contains 12–22 percent chromium, with carbon content below 0.35%.* They can be forged, rolled or cold drawn, and machined by the use of specially designed tools. They resist corrosion *better* than heat-treatable ones. They are used in making chemical equipments and automobile parts.

(*ii*) ***Non-magnetic-type*** *contains 18 to 26% chromium, 8 to 21 percent nickel, and upto 0.15% carbon.* Total percentages of Cr and Ni in such steels is more than 23 percent. These exhibit *maximum* resistance to corrosion. *Most widely used common stainless steel contains 18% Cr and 8% Ni is, usually, referred to as "18/8 stainless steel".* To increase corrosion-resistance further, a little quantity of molybdenum is added to such stainless steels. Such steels find use in making household utensils, decorative pieces, sinks, dental instruments, surgical instruments, etc.,

5. ***Tools steels*** *are steels used for making tools such as hammers, shears, drills, dies for drawing wires, etc.* They, in general, possess great strength, toughness, hardness and resistance to wear and softening.

(*i*) ***Tool-steels*** *used, particularly, in making cutting-tools* (which require resistance to wear and softening at high temperature) contain tungsten (4-21%), chromium (4-4.5%), vanadium (1-2%), besides 0.5 to 0.75% C. Such steels, are called ***high-speed steels*** or ***cutting tools.***

(*ii*) ***Cobalt high-speed steel*** contains 5 to 8% cobalt and shows better properties than 18-4-1 HSS.

(*iii*) ***Molybdenum high-speed steel*** *contains 6 to 8% Mo*. It retains hardness at red-heat. It is used in high-speed cutting tools.

Besides the above high-speed steels, there are some *non-ferrous alloys* used like high-speed steels. *Two* such alloys are :

(*a*) **Satellite** : *An alloy containing 50-65% Co. 30% Cr, 4-15% W, with very little iron and varying amounts of carbon* possesses very high water-resistance and very high cutting-hardness.

(*b*) **Carboloy** (*tungsten carbide =80-97%, cobalt=rest*) is cheaper and less brittle, but almost as hard as diamond and probably the best material available for the tips of high-speed cutting-tools and wear-resistant dies.

6. ***Nickel steels*** : *Nickel improves tensile-strength, ductility, toughness, elasticity, heat, and corrosion-resistance of steel.*

(*i*) ***Invars*** or *steels with 0.3% to 0.5% C, and 30-36 Ni* have practically *zero coefficient of expansion.* They are used for making metre scales, measuring tapes, chronometers, clock pendulums, survey instruments, scientific measuring devices, wheels of watches, balances, etc.

(*ii*) ***Platinite*** or *steels with 0.15% C and 46% Ni* possess *co-efficient of expansion equal to glass.* They are used in armoured glass (*i.e.*, glass plates containing steel nets inside), metal seals to glasses, wire in electric light bulbs, etc.

7. ***Nickel-chromium steels*** *are the best alround alloy steels in commercial use.* The presence of Ni confers increased ductility and toughness ; while Cr provides hardness and corrosion-resistance.

"Allgheny metal" or ***18/8 steels*** or *stainless steels containing 18% Cr, 8% Ni and less then 0.15% C* are extremely tough, ductile, strong and highly corrosion-resistant.

Uses : In cutlery, boiler and pump parts, acid and alkalis (*e.g.*, ammonia synthesis) plants, turbines in petroleum-refining units, ornamental trims of buildings, and other decorative purposes.

8. ***Chrome-vanadium steels*** *have the composition 0.8% to 1.1% Cr. 0.25% V, and 0.35 to 0.93% C.* They possess great tensile-strength, toughness and impact-resistance. They are used where great strength, toughness, and resistance to fatigue are a necessity as in piston-rods, gears, axles, crank-pins, car frames, leaf-springs, high-grade coils, laminated springs, heavy locomotive forgings, etc.

9. ***Molybdenum steels*** *possess the composition 0.2 to 0.7% Mo, 0.15 to 0.3% C, 0.3 to 1% Mn, and 0.1 to 0.35% Si.* They possess great toughness and deep-hardening properties. They are used as rolled sections, forgings, and for casting gears, bearings for gears, axle-bearings, shafts, etc.

10. ***Chromium-molybdenum steels*** *possess the composition 0.4% to 10% Cr and 0.2% to 1.5% Mo.* Steels containing low percentages of Cr and Mo have mechanical properties similar to low alloy structure steels, and are used for general purposes ; while steels containing high percentage of Cr have high elognation (18–20%), high ultimate strength (12–25 tonnes/cm^2) and are corrosion-resistant. They are mainly used as rolled sections, forgings and castings, where acid and corrosion-resistances are required.

11. ***Alnico*** or ***aluminium-nickel-cobalt steel*** *has the composition 12% Al, 20% Ni, and 6% Co.* It is highly magnetic and used for making powerful permanent magnets.

12. ***Silicon steel* :** *Duriron* or *12-14% Si steel* is very hard, easily castable, extremely resistant to corrosion by acids and alkalis. Used for making retorts, pipes, valves and fittings, used in acid and alkali industries.

19.23 NON-FERROUS ALLOYS

These *do not* contain iron as one of their *main components. Usual main components of non-ferrous metals are aluminium, copper, lead, zinc, tin, nickel, etc.* Usually, their melting points are *lower* than those of ferrous alloys. They find wide applications, because of their : (*i*) good formability, (*ii*) softness ; (*iii*) attractive/good colours ; (*iv*) cold-working characteristics ; (*v*) special electrical properties ; (*vi*) magnetic properties ; (*vii*) easy castability ; (*viii*) low coefficient of friction ; (*ix*) atmospheric corrosion-resistance ; (*x*) low density, etc. The composition, properties and uses of some important non-ferrous alloys are given below :

1. **Copper alloys :** Copper and its alloys rank next to steel as engineering materials. The most important copper alloys of commercial importance are listed in Table 1.

Table 1 : *Copper alloys.*

Alloys	*Composition*	*Characteristics*	*Uses*
1. **Brasses.**	Cu = 60 – 90% Zn = 40 – 10%	They possess greater strength, durability and machinability than pure copper. They have lower m.p. than Cu and Zn. They are good corrosion-resistant against water.	
The main forms of the **brasses** are :			
(*i*) *Commercial brass* or Guilding metal or French gold.	Cu = 90% Zn = 10%	Stronger and harder than pure copper. Golden in colour.	Forgings, rivets, hardwares, screws, costums, jewellery, etc.
(*ii*) *Dutch-metal* or low brass.	Cu = 80% Zn = 20%	It has golden colour. It is suitable for all drawing and forming operations.	Cheap jewellery, musical instruments, battery caps, flexible hoses, tubes, name plates, etc.
(*iii*) *Cartridge brass* or spinning brass.	Cu = 70% Zn = 30%	Soft, ductile in the annealed state, harder and stronger than copper, can be severely cold deformed by drawing, pressing, and extrusion, and work hardens quickly.	General purpose brass, cartridge cases, condenser tubes, sheet fabrication, household articles, etc.
2. **Special brasses.**	Contain metal(s) other than Cu and Zn.		

Alloys	*Composition*	*Characteristics*	*Uses*
(*i*) *German silver*	Cu = 25–50% Zn = 10–35% Sn = 5–35%	It possesses good strength and corrosion-resistance to salt water. It is extremely ductile, malleable, and looks like silver.	Utensils, tablewares, bolts, screws, ornaments, cutlery, corrosion-resistant implements, coinage, decorative articles, etc.
(*ii*) *Admiraly brass or Tobin bronze.*	Cu = 59–62% Zn = rest Sn = 0.5–1.5%	It possesses high corrosion and abrasion-resistances.	Propellers and marine works.
3. **Bronzes.**	Cu = 80 – 95% Sn = 20 – 5% Besides these other metals are also added.	They are tough, strong, corrosion resistant, can readily be casted and machined.	
The main ***bronzes*** are :			
(*i*) *Coinage-bronze* or common bronze.	Cu = 89 – 92% Sn = 11 – 8%	It is soft, ductile and durable.	Pumps, valves, wires, flanges, utensils, coins, statues, etc.
(*ii*) *Gun-metal.*	Cu = 85% Zn = 4% Sn = 8% Pb = 3%	It is hard, tough, strong to resist the force of explosion.	Foundry works, hydraulic fittings, heavy-load bearings, parts of high-pressure steam plants, water fittings, marline pumps, etc.
(*iii*) *High-phosphorus bronze.*	Cu = rest Sn = 10 – 13% P = 0.4 to 1%	They are hard, brittle and abrasion-resistant. They possess low co-efficient of friction.	For making bearings and gears, taps, bushes, springs, turbine blades, fibres for moving coil galvanometers, fuses, etc.
(*iv*) *Aluminium bronze.*	Cu = 90 – 93% Al = 10 – 7%	It is quite strong, readily fusible, gives good castings, resistant to corrosion, even at high temperatures. It possesses good abrasion-resistance. It has magnificent golden yellow colour.	For all casting operations, bushes and bearings, which retain strength upto 400°C, jewellery, utensils, coins, photo-frames, etc.
(*v*) *Nickel bronzes.*	Cu = 90% Ni = 9% Fe = 1%	They are hard, higher in tensile strength and better corrosion-resistant than copper.	For rolling purposes, unhardened shafts, valves, and general purpose semi-hard bearings.

2. **Nickel alloys :** Important nickel alloys are : (*i*) **Constantan** (Cu = 60%, Ni = 40%). It possesses high electrical-resistance and very low temperature coefficient. It is used as winding resistance and thermo-couple alloy.

(*ii*) **Nichrome** (Ni = 60%, Cr = 12%, Mn = 2%, Fe = 26%). It is chemical and heat-resistant. It possesses high m.p. and oxidisability. It has a high electrical-resistance. It is used for making resistance coils, heating elements in stoves, electric irons, toasters, and other electrical appliances.

(*iii*) **Iocanel** contains approximately 77% Ni, 15% Cr, and 8% Fe. It is very ductile and can be wrapped around its own diameter. It is very good corrosion-resistant. It retains hardness, even at 400°C. It is used for springs, used under conditions of elevated temperatures of 400°C and exposed to corrosive action. It is also used in exhaust manifolds, aircraft engines, and aero-engines.

(*iv*) **Monel metal** contains of 66 – 67% Ni ; 28 – 30% Cu ; 1 – 2% Fe ; 0.9 to 1% Mn, with very small amounts of sulphur and carbon.

Properties : (1) It is bright, strong and tough ; (2) It is very much corrosion-resistant. It resists corrosion effects of atmosphere, sea-water, alkalis and acids, other than nitric and sulphurous ; (3) It can easily be cleaned and is attractive in appearance ; (4) It can be hot rolled, cold drawn and annealed ; (5) It maintains its physical properties like strength at elevated temperatures ; (6) Its tensile-strength is around 5,500 kg/cm^2, after proper heat-treatment ; (7) It has low magnetic permeability.

Uses : It is used for making : (1) chemical, textile, dye, petroleum, and food-processing plants ; (2) turbine blades, corrosion-resistant bolts, screws, nails, etc. ; (3) sinks, water heaters, laundry equipments, etc. ; (4) fittings for ships ; (5) fire-box trays, gaskets and other parts of steam plants ; (6) resistance wires, welding electrodes and transistor capsules ; (7) automobile engine parts, exposed to high temperatures ; (8) filter-pumps, impellers, etc.,

3. **Aluminium alloys** (or *light-weight alloys*) : With the modern advancement of aircrafts and automobiles, *the utility of light-weight alloys have increased considerably*. Aluminium and magnesium are the two important components of such alloys. The *main alloys* of this type are :

(*i*) **Duralumin** *contains Al = 95% ; Cu = 4% ; Mn =0.5%, and Mg = 0.5%.*

Properties : (*i*) It is light, tough, highly ductile, easily castable, good conductor of heat and electricity, and corrosion-resistant ; (*ii*) It approaches steel in strength and yet its density is one-third that of steel ; (*iii*) It can easily be worked and possesses high machinability ; (*iv*) Its tensile-strength can be raised, by heat-treatment, up to about 2,000 kg/cm^2, without affecting its ductility.

Uses : (*i*) Due to good strength and low density, it finds extensive use in *aircraft industry* in the form of aclad (*i.e.*, duralium clad on either side with pure Al). It also finds use in making automobile and locomotive parts ; (2) Due to high ductility and good electrical conductivity, it finds use in making surgical instruments, cables, fluorescent-tube caps, etc.

(*ii*) **Magnalumin** *contains Al = 70 – 90%, and Mg = 30.10%.* It is quite strong, tough and lighter than Al and possesses mechanical properties similar to brass. It is used for making cheap balances, airplane parts, and scientific instruments.

(*iii*) **Electron** *contains Al = 9 – 11%, Zn = upto 3.5%, Mn = 0.5%, and Mg=rest.* It is used for crank-cases of engines, covers, brackets and similar lightly-stressed components and also in construction of pans, petrol and oil tanks, break components, gear-boxes, etc.

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4. **Solders** *are low-melting alloys of tin and lead.* Important solders are :

(i) ***Soft solders*** ***(Pb = 37.67%, Sn = 31 – 60%, and Sb = 0.12 – 2%).*** They melt at low temperatures. They are used for soldering electrical connections, sealing tin cans, and joining lead pipes.

(ii) ***Brazing alloys*** (Sn = *92%*, ***Sb*** *= 5.5%,* ***and*** ***Cu*** = *2.5%*). Used for soldering steel joints by the process of fusing.

(iii) ***Tinman's solders (Sn = 66, and Pb = 34)*** : Used for soldering and tinning.

5. **Type metal** (Pb = *75%, Sb = 20%, and Sn = 5%*). It *expands slightly* upon solidification and gives good castings. Used for the production of printer's type.

6. **Low melting alloys** are : (i) ***Wood's metal*** *contain Bi = 50% , Pb = 25%, Sn = 12.5%, and Cd = 12.5%.* It is readily fusible (m.p. 70°C). Used : (1) For making fire-alarms and automatic sprinklers ; (2) For making safety plugs for cookers, milk pot, etc. ; (3) As a soft solder for joining two metallic parts/pieces ; (4) As castings for dental works ; (5) For boiler and electric fuses, etc.,

(ii) ***Rose metal*** *(Bi = 50%, Pb = 28% and Sn = 22%)* is readily fusible (m.p. = 89°C). Used for making fire-alarms, fuse-wires, castings for dental works, and in automatic sprinkler systems.

7. **Bearing alloys** *are essentially, modified bronzes designed to provide in bearing : (i) a* ***hard constituent****, which resists wear and furnish a surface with a low coefficient of friction, and (ii) a* ***soft constituent****, which distributes the load uniformly to avoid binding and over-heating.* Bearing alloys take most of the wear and must, therefore, be replaced ; whereas the axle that runs in them, as a result suffers very little wear.

A bearing or anti-friction alloy should have the following properties : (1) Low co-efficient of friction ; (2) Good wearing quality ; (3) Non-corrosive properties ; (4) Ability to withstand continuous bearing pressure and impact ; (5) Good casting qualities ; (6) High melting point ; (7) High thermal conductivity ; (8) Low shrinkage after casting ; (9) Desired plasticity, under the load it is called upon to bear ; (10) Economy of cost ; (11) Ability to work satisfactory with suitable lubrication at the rubbing-speeds at which it required to run. *Important bearing alloys* are :

(i) ***Bronze metal alloys*** contain Cu = 80-87% , Sn = 1011%, and Sb = 1.5 to 10%.

(ii) ***Babbit metal*** is an alloy extremely variable composition, but contains Sn = 50-90%, Cu = 2-6%, Sn = 7-10% and Pb = 5-30%. It is a silvery-while metal. It does not tarnish easily and can be polished easily. It is used for making engine bearings, since it distributes the load uniformly.