

3.1 INTRODUCTION

- Modern Periodic table has 97 metals. Metals with atomic number more than 83 i.e. post Lead (atomic number 82) have unstable nuclei and are radioactive. If one limits attention to Metals which are used frequently for Engineering applications belong to S,P and primarily D block.
- Metals are generally found in associated state in earth crust because of their high chemical reactivity. Most abundant chemical compounds are oxides, carbonate bicarbonate, sulphides, silicates and halides. When metal is required in neat form either to be used as metal or converted to alloy extractive metallurgy is used. Naturally before the development of extractive metallurgy, metals in use would be noble metals which are found in nature in native state. Indeed the first metals reported to be used are Gold, Silver and Copper. As many as 6500 years before in all probability nuggets of gold found in the sands and gravels of riverbeds. Such native metals became known and were appreciated for their ornamental and utilitarian values during the latter part of the Stone Age.
- An essential step toward the Metal Age was the discovery that metals such as copper could be fashioned into shapes by melting and casting in molds; among the earliest known products of this type are copper axes cast in the Balkans in the 4th millennium BC.
- Important step in development of Extractive metallurgy would be the discovery that metals could be recovered from metal-bearing minerals. In that era different minerals probably were collected and distinguished on the basis of color, texture, weight, density and flame color and smell when heated.
- The discovery of Bronze may have been accidental at first, owing to the similarity in colour and flame color between the bright green copper mineral malachite and the weathered products of such copper-arsenic sulfide minerals as enargite, and it may have been followed later by the purposeful selection of arsenic compounds based on their garlic odour when heated. Arsenic contents varied from 1 to 7 percent, with up to 3 percent tin. Essentially arsenic-free copper alloys with

higher tin content in other words, true bronze seem to have appeared between 3000 and 2500 BC. The discovery and use of Bronze is so significant that the era is marked as Bronze Age.

- After Bronze next significant discovery was Iron and steel. This discovery is marked as Iron age which fired major transformations in Science, Engineering and Technology. 1200 BC has been taken as the beginning of the Iron Age. Smelting of iron oxide with charcoal demanded a high temperature and, since the melting temperature of iron at 1,540° C was not attainable then, the product obtained was spongy mass of pasty globules of metal slag.
- This product, on repeated reheating and hot hammering on elimination of the slag, produced wrought iron. Bronze, iron, and brass were, the metallic materials on which successive people built their civilizations and made their equipments for both war and peace.

3.2 OCCURRENCE OF METALS

- Occurrence of native metal is very rare as very few metals can resist natural weathering processes like oxidation, which is why generally only the noble metals, such as gold and platinum, silver and copper are found in neat state. These noble metals were prehistoric man's only access to metal, because melting is thought to have been discovered around 4500 BC. Combining different proportions of metals to form alloys modifies the properties of pure metals to produce desirable characteristics.
- The aim of making alloys is generally to make them less brittle, harder, resistant to corrosion, or have a more desirable color and luster. Metals are often extracted from the Earth by means of mining, resulting in ores that are relatively rich sources of the requisite metal.
- Metals and their compounds are found in earth crust as natural rock, sand, clays known as minerals. Ores are minerals from which metals are extracted profitably and conveniently. Ores contain metal compounds with a lower percentage of impurities. All the ores are minerals, but all minerals are not necessarily ores. The rest of the metals other than noble metals occur in the

combined form as compounds such as oxides, carbonates, sulphides, sulphates, silicates, chlorides, nitrates, phosphates etc.

- Copper and silver are two metals which occur in free as well as in combined state as sulphide, oxide or halide ores. Metals at the top of the activity series (K, Na, Ca, Mg and Al) are so reactive that they are never found in nature as free elements. The metals in the middle of

the activity series (Zn, Fe, Pb, etc.) are moderately reactive. They are found in the earth's crust mainly as oxides, sulphides or carbonates.

- Alkali metals occur as metal halides which are highly water soluble, Alkali earth metals are found as carbonates, transition metals occur as oxides and p-block metals generally occur as Sulphides. The table below shows important ores and their chemical forms.

Table 3.1 : Types of Ores

Oxides	Carbonates	Halides	Sulphides	Sulphates
Zincite (ZnO)	Marble or limestone (CaCO_3)	Fluorspar (CaF_2)	Zinc blende (ZnS) Galena (PbS)	Anglesite (PbSO_4)
Haematite ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)	Calamine (ZnCO_3)	Cryolite (Na_3AlF_6)	Iron pyrites (FeS_2)	Baryl (BaSO_4)
Magnetite (Fe_3O_4)				Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)	Siderite (FeCO_3)	Horn Silver (AgCl)	Cinnabar (HgS)	
Cuprite (Cu_2O)	Magnesite (MgCO_3)	Rock salt (NaCl)		Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)

3.3 TYPES OF ORES

Definition: Ore is rock that contains economic amounts of a particular element, e.g. iron ore, molybdenum ore, or Copper ore. In contrast, rock that is not judged to contain economic quantities of an element is categorized as waste rock.

The metals in ore can occur in many different minerals (compounds) in the rock. As an example, copper occurs in more than 50 minerals with varying percentages of copper in the chemical formulas of those minerals. The richest grade of copper ore is native copper, which is pure copper (100%).

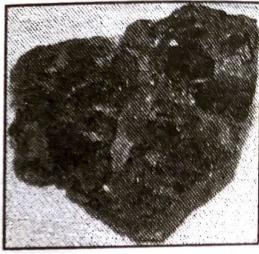
3.3.1 Classification of Ores

[May 19]

- The basis for classification of different ore may be chemical composition or geological location. From extraction process chemical classification will present an advantage like for same chemical compound the steps required for extraction of metal from the ore will be similar. On the basis of chemical composition ores are classified as : Sulfide or Sulfosalts, oxides and hydroxides, oxysalts and halides and silicates.
- Sulfides and Sulfosalts:** Many metallic ores occur as sulfide minerals. Examples of sulfide minerals are **Galena** (lead sulfide, PbS), **Sphalerite** (zinc sulfide ZnS), **Covellite** (copper sulfide CuS), or **Pyrite** (iron sulfide FeS_2).



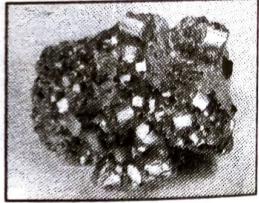
Galena



Sphalerite



Covellite



Pyrite

Fig. 3.1

- These sulfide minerals crystallize from the ore-forming fluids at fairly high temperatures. As erosion brings the sulfide ores to the surface they often become weathered, or oxidized. Thus, new ore minerals are formed in the oxidized zone. **Galena** might be oxidized to anglesite (PbSO_4), **Sphalerite** to hemimorphite [$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$], **Covellite** to malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})$ and **Pyrite** to goethite $\text{FeO}(\text{OH})$.
- Oxides and Hydroxides:** Haematite (Fe_2O_3), Magnetite (Fe_3O_4), Pyrolusite (MnO_2), Rutile(TiO_2), Cuprite(Cu_2O), Ilmenite (FeTiO_3), Uranite (Pitchblende- UO_2), Gibbsite ($\text{Al}(\text{OH})_3$) are very important ores from Oxide and hydroxide family.
- Oxysalts:** Carbonate, bicarbonate, basic carbonate or oxides are collectively called as oxysalts. Calcite

(CaCO_3) , Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$, Apatite $\text{Ca}_8(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ are few important members.

- **Halide:** Very reactive metals are found as halide minerals e.g. Halite (NaCl), Fluorite (CaF_2),
- **Silicate:** Very important type of silicate minerals are beautiful natural zeolites or sodium alumino silicates. Presence of other metal salts gives them gem stone like quality e.g. Beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$), Garnet silicate of $\text{Al},\text{Mg},\text{Fe}$, Zircon ZrSiO_4 are very precious gemstone minerals.
- The classification based on geology will primarily consider the extent of depth upto which excavation or mining is practically possible should be considered while mapping area on the lithosphere where a

particular ore is present. If precious metal is present at depth more than 5 km it is not practically possible to dig that deep and carry out mining activity at that depth hence availability or ore mapping considers a depth upto 5km only.

- Through the 20th century many classifications were based on the types of rocks that host the ore deposits or on the geological context the geometry of the deposit and its relation to its host rocks. A popular classification developed by Lindgren, an American economic geologist who was very influential in the mid 20th century, distinguished deposits that formed at different levels.

Table 3.2 : Lindgren's Classification of Ore Deposits (Modified from Lindgren 1933; Evans 1993)

Name	Depth	Temperature	Occurrence	Metal
Telethermal	Near surface	± 100	In sedimentary rocks or lava flows; open fractures, cavities, joints. No replacement phenomena.	Pb, Zn, Cd, Ge
Epithermal	surface to 1.5 km	50–200	In sedimentary or igneous rocks; often in fault systems; simple veins or pipes and stockworks; little replacement phenomena.	Pb, Zn, Au, Ag, Hg, Sb, Cu, Se, Bi, U
Mesothermal	1.2–4.5 km	200–300	Generally in or near intrusive igneous rocks; associated with regional faults; extensive replacement deposits or fracture fillings; tabular bodies, stockworks, pipes.	Au, Ag, Cu, As, Pb, Zn, Ni, Co, W, Mo, U
Hypothermal	3–15 km	300–600	600 In or near deep-seated felsic plutonic rocks in deeply eroded areas. Fracture-filling and replacement bodies; tabular or irregular shapes.	Au, Sn, Mo, W, Cu, Pb, Zn,

- It is practically impossible to extract beyond Mesothermal layer and hence though precious metals are present in this layer they are in accessible.
- Ore deposits are not distributed uniformly across the globe. Vast areas of land are devoid of viable deposits while others constitute what are known as 'metallogenic provinces' regions containing an unusually high concentration of deposits of one or several types.
- Notable examples include the numerous copper deposits in the southwestern United States, the clusters of lead-zinc deposits in northeastern Australia, and the tin deposits of south east Asia or rich Iron ore in Germany or Coal in Chota Nagpur Plateau. For both geological and economic reasons, it is important to have some knowledge of this distribution prior to metallurgical activity.

3.4 EXTRACTIVE METALLURGY

- **Extractive Metallurgy** is a branch of metallurgy and materials science. It studies the process and methods of extraction of metals from their natural minerals, the types of ore, washing, concentration, separation, chemical processes and extraction of pure metal and their alloying to suit various applications, sometimes for direct use as a finished product.
- It is important to note that looking at the volumes of ores and minerals handled annually worldwide the metallurgy is divided into Ferrous metallurgy and non ferrous metallurgy . Ferrous metallurgy focuses on extraction, separation and alloying Iron ore and coal and manganese and making different types of Steels. All other ores and minerals are grouped under Non ferrous metallurgy. The field of ferrous and non ferrous metallurgy have different unit operations that are generically grouped into the categories of mineral processing, hydrometallurgy, pyrometallurgy, and

electrometallurgy based on the process adopted to extract the metal.

- **Mineral Processing :** The methods used to separate valuable minerals (or metals) from waste minerals based on physical or surface chemistry properties
- **Hydrometallurgy :** The utilization of aqueous environments to "leach" metals from minerals (or other sources), to separate dissolved metals from each other or dissolved impurities, and to recover metals from solution.
- **Pyrometallurgy :** The use of high temperatures to modify the chemistry of minerals (or other sources), to reduce minerals to metals, and to refine metals.
- **Electrometallurgy :** The use of electricity to recover and/or to refine metals in aqueous or molten salt solutions.
- Several processes are used for extraction of same metal depending on occurrence and chemical requirements but most important aspect is economy of each process.

3.5 PHYSICAL METHODS OF ORE PROCESSING

[May, Dec. 18]

In this section we will discuss Physical and Chemical processes undertaken in Extractive metallurgy. Generally after excavation Physical separation begins first which is called as mineral processing.

3.5.1 Mineral Processing

- Mineral processing begins with beneficiation, consisting of initially breaking down the ore to required sizes depending on the concentration process to be followed, by crushing, grinding, sieving etc. Thereafter, the ore is physically separated from any unwanted impurity, depending on the form of occurrence and/or further process involved. Separation processes take advantage of physical properties of the materials.
- These physical properties can include density, particle size and shape, electrical and magnetic properties, and surface properties. Major physical and chemical methods include magnetic separation- useful for ferrous ore, froth floatation is useful for ores where low density impurities are to be separated, leaching uses acid matic to partially dissolve the ore etc.
- All these processes are aimed at separation of the impurities and unwanted materials from the ore and the concentration of metal is increased in the ore.
- This concentrate is then either processed to remove moisture or else used as it is for extraction of the metal

or made into shapes and forms that can undergo further processing, with ease of handling. Ore bodies often contain more than one valuable metal.

3.5.2 Crushing

- Technically called as comminution which means particle size reduction; sizing means separation of particle sizes by screening or classification; concentration by taking advantage of physical and surface chemical properties; and dewatering – solid/liquid separation. Comminution is particle size reduction of ore. It may be carried out on either dry materials or slurries.
- Crushing and grinding are the two primary comminution processes. Crushing is normally carried out on stone, rock as received from mine, while grinding is done on dry or slurry material. In comminution, the size reduction of particles is done by three types of forces: compression, impact and attrition.
- The equipment used for crushing are-jaw crushers, gyratory crushers and cone crushers whereas grinding uses rod mills and ball mills. Crushing is a dry process whereas grinding is generally performed on wet mixture and hence it requires more energy.

3.5.3 Sizing

- The general term for separation of particles according to their size. The simplest sizing process is screening, or passing the particles through a screen or number of screens. Screening equipment different types of sieves and screens like wedge wire screens, radial sieves, banana screens and wire mesh screens. Screens can be static (typically the case for very coarse material) or they can incorporate shaker or vibrater.
- Classification refers to sizing operations that exploit the differences in settling velocities exhibited by particles of different size. Classification equipment may include ore sorters, gas cyclones, hydrocyclones, rotating trommels, rake classifiers or fluidized classifiers.
- Primary function of communication and sizing operations is the determination of the particle size distribution of the materials being processed.

3.5.4 Froth Floatation

[May 19]

- Flotation is the most widely used method for the concentration of fine-grained minerals. When the mineral contains mixture of high and low density metals or their compounds, on addition of water and churning the mixture; low density compound will

separate and under gravitational force the heavier one will settle down.

- The technique involves use of water, hydrophilic liquids, air bubbles while churning the mixture. The air bubbles pass to the upper surface of the pulp and form a froth, which together with the attached hydrophobic minerals, can be removed. The tailings, containing the hydrophilic minerals, can be removed from the bottom of the cell. The Fig. 3.2 below shows typical unit used for froth floatation.

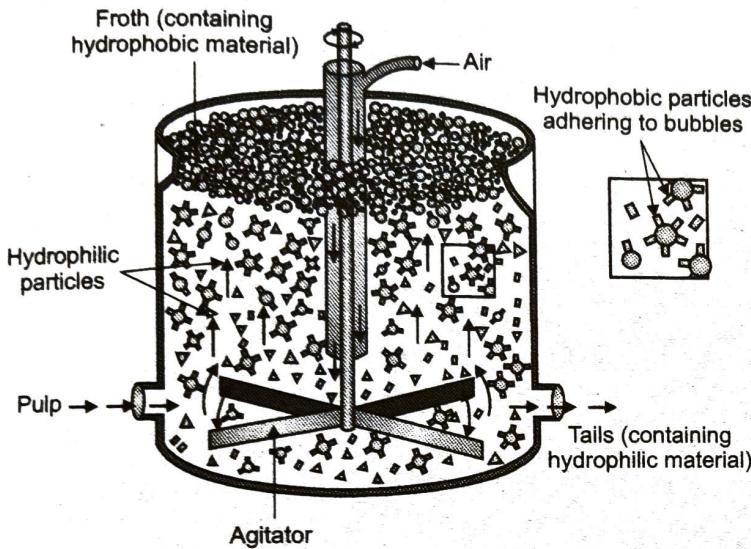


Fig. 3.2 : Curtsy Encyclopedia Britannica, Inc.

- Flotation makes possible the processing of complex inter grown ores containing copper, lead, zinc, and pyrite into separate concentrates and tailings an impossible task with gravity, magnetic, or electric separation methods.
- In the past, these metals were recoverable only with expensive metallurgical processes.

3.5.5 Magnetic Separation

[Dec. 17, May 19]

- Magnetic separation is based on the differing degrees of attraction exerted on various minerals by external magnetic fields. This techniques is primarily useful for separation of ferrous metals from non ferrous metals.
- Success requires that the feed particles fall within a special size spectrum (0.1 to 1 millimetre). With good results, strongly magnetic minerals such as magnetite, franklinite, and pyrrhotite can be removed from gangue minerals by low-intensity magnetic separators.
- High-intensity devices can separate oxide iron ores such as limonite and siderite as well as iron-bearing manganese, titanium, and tungsten ores and iron-bearing silicates.

3.5.6 Electrostatic Separation

- The electrostatic method separates particles of different electrical charges and, when possible, of different sizes. When particles of different polarity are brought into an electrical field, they follow different motion trajectories and can be caught separately.
- Electrostatic separation is used in all plants that process heavy mineral sands bearing zircon(mineral of Zirconium), rutile (Ti metal ore), and monazite(thorium metal ore). In addition, the cleaning of special iron ore and cassiterite concentrates as well as the separation of cassiterite -scheelite (Tin and Tungsten ores respectively) are conducted by electrostatic methods.

3.5.7 Gravity Separation

[Dec. 17]

- Gravity methods use the difference in the density of minerals as the concentrating agent. In heavy-media separation (also called sink-and-float separation), the medium used is a suspension in water of a finely ground heavy mineral such as magnetite or arsenopyrite or ferrosilicon.
- Such a suspension can simulate a fluid with a higher density than water. When ground ores are fed into the suspension, the gangue particles, having a lower density, tend to float and are removed as tailings, whereas the particles of valuable minerals, having higher density, sink and floating impurities are removed.
- The magnetite or ferrosilicon can be removed from the tailings by magnetic separation and recycled. In principle this method has similarity with froth floatation. Gravity concentration on inclined planes is carried out on shaking tables, which can be smoothed or grooved and which are vibrated back and forth at right angles to the flow of water.
- As the pulp flows down the incline, the ground material is stratified into heavy and light layers in the water; in addition, under the influence of the vibration, the particles are separated in the impact direction. Shaking tables are often used for concentrating finely grained ores of tin, tungsten, niobium, and tantalum.

3.6 CHEMICAL METHODS OF SEPARATION

- Physical metallurgy refers to physical treatment or physical changes in the ore but its chemical composition remains same. In chemical methods of separation heat, chemical, catalyst, and/or a combination of all these is acting on the chemical composition of the mineral or chemical compound and

the unwanted matrix is separated from metal leaving pure metal behind.

- This is the set of steps which are designed to carry out chemical modifications primarily reduction of the ore. The different chemical processes include one or more of the following processes Calcination, roasting, Reduction of ore - by pyrolysis, Chemical reduction and Refining of metals.

3.6.1 Calcination

[May 17]

- The IUPAC defines calcination as a process of heating concentrated ore to high temperatures in air or oxygen. However, calcination is also used to mean a thermal treatment process in the absence or limited supply of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition. It is carried out in a steel cylinder that rotates inside a heated furnace and performs indirect high-temperature processing 550 – 1150 °C within a controlled atmosphere.
- Industrial processes of calcination is described below. An oven for calcination of limestone (Ore of Calcium) is shown in Fig. 3.3 below. The process of calcination derives its name from the Latin calcinare which means burning of lime, due to its most common application, the decomposition of calcium carbonate (limestone) to calcium oxide (lime) and carbon dioxide, in order to create cement.
- The product of calcination is usually referred to in general as "calcine", regardless of the actual minerals undergoing thermal treatment. Calcination is carried out in furnaces or reactors sometimes referred to as kilns or calciners of various designs including shaft furnaces, rotary kilns, multiple hearth furnaces, and fluidized bed reactors.

The chemical changes which occur during calcination processes include the following:

- Decomposition of carbonate minerals during calcination of limestone to drive off carbon dioxide.
- Decomposition of hydrated minerals during the calcination of bauxite and gypsum, to remove crystalline water as water vapor.
- Decomposition of volatile matter contained in raw petroleum coke.
- Heat treatment to effect phase transformations, as in conversion of anatase to rutile or devitrification of glass materials.
- Removal of ammonium ions in the synthesis of zeolites.

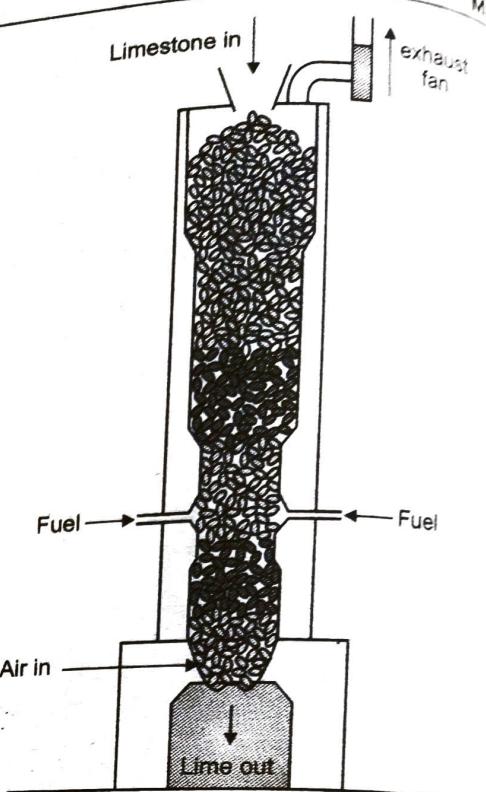


Fig. 3.3 : Reactor used for calcination of limestone

- Calcination Reactions:** Calcination reactions take place at or above, the thermal decomposition temperature (for decomposition and volatilization reactions) or the transition temperature (for phase transitions).
- This temperature is usually defined as the temperature at which the standard Gibbs free energy for a particular calcination reaction is equal to zero. For example, in limestone calcination, a decomposition process the chemical reaction is



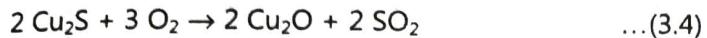
The standard Gibbs free energy of reaction is approximately $\Delta G^\circ = 177, 100 - 158 T$ (J/mol) respectively for above reactions. The standard free energy of reaction is 0 in the case when the temperature T is equal to 848 °C.

3.6.2 Roasting

[May 18]

- Roasting is a process of heating of sulphide ore to high temperature in presence of air this leads to serious concern of air pollution as the products of roasting are directly subjected in to air. Roasting is a metallurgical process involving gas-solid reactions at elevated temperatures with the goal of purifying the metal. Often before roasting, the ore has already been partially purified, e.g. By froth flotation. The concentrate is mixed with other materials called fluxes to facilitate the process.

- Roasting consists of thermal gas-liquid reactions, which can include oxidation, reduction, chlorination, and hydrolysis. In roasting, the ore is treated with very hot air. This process is generally applied to sulfide minerals. During roasting, the sulfide is converted to an oxide, and sulfur is released as sulfur dioxide, a gas. For the ores Cu_2S (chalcocite) and ZnS (sphalerite), balanced equations for the roasting are:



- The gaseous product of sulfide roasting is sulfur dioxide (SO_2) which is often used to produce sulfuric acid. Many sulfide minerals contain other components such as arsenic that are released into the environment. Tarnishing of Taj mahal is an example of air pollution caused by Sulfide base ore used in cement industry nearby. Up until the early 20th century, roasting was started by burning wood on top of ore.
- This would raise the temperature of the ore to the point where its sulfur content start spontaneous combustion, and the roasting process could continue without external fuel sources. Early sulfide roasting was practiced in this manner in "open hearth" roasters, which were manually stirred (a practice called "rabbling") using rake-like tools to expose unroasted ore to oxygen as the reaction proceeded. This process released large amounts of acidic, metallic, and other toxic compounds. Roasting is an exothermic process. Important roasting operations includes oxidizing as used to convert sulfide ore to metal oxide, Volatalizing as used in conversion of Sb_2O_3 , ZnO , Chloridizing which is conversion of metal compounds to Metal chloride, sulfating, magnetic roasting, reduction roasting and sinter roasting.

3.6.3 Reduction of Ore: By Pyrolysis [May 18]

- Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen or any halogen. In earlier stage i.e. calcination and roasting heating of ore was carried out in presence of air or oxygen, here in pyrolysis however no air or oxygen is used during heat treatment. This will enable sulphide/ oxide/ carbonate to undergo reductive reaction for separation of all matter other than metal to be extracted.

It involves the simultaneous change of chemical composition and physical phase and these changes are irreversible. The word is coined from the Greek-derived

- elements pyro "fire" and lysis "separating" means separation of matrix from metal using heat in this case.
- Pyrolysis is a type of thermolysis, and is most commonly observed in organic materials exposed to high temperatures. It is one of the processes involved in charring of wood, starting at 200–300 °C. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content, char. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization. In case of extraction of Iron ore and process steel making carbonization plays a significant role.
- Pyrolysis differs from other processes like combustion and hydrolysis is that, it usually does not involve reactions with oxygen, water, or any other reagents. In practice, it is not possible to achieve a completely oxygen-free atmosphere. Because some oxygen is present in any pyrolysis system, a small amount of oxidation occurs. Pyrolysis can be carried out using carbon in varius chemical forms like coke, carbon fiber or pyrolytic carbon.
- Pyrolysis by Coke:** Coal is used on a massive scale to turn into coke for metallurgy, especially in process steelmaking. Coke can also be produced from the solid residue left from petroleum refining. Those starting materials typically contain hydrogen, nitrogen, or oxygen atoms combined with carbon into molecules of medium to high molecular weight. The coke-making or "coking" process consists of heating the material in closed vessels to very high temperatures (up to 2,000 °C) so that those molecules are broken down into lighter volatile substances, which instantly evaporate and a porous but hard residue that is mostly carbon and inorganic ash. The amount of volatiles varies with the source material, but is typically 25–30% of it by weight.
- Pyrolysis by Carbon Fiber:** Carbon fiber is a filament of carbon that can be used to make very strong yarns and textiles. Carbon fiber items are often produced by spinning and weaving the desired item from fibers of a suitable polymer, and then pyrolyzing the material at a high temperature from 1,500–3,000 °C. The first carbon fibers were made from rayon, but at present polyacrylo-nitrile has become the most common starting material.

3.6.4 Chemical Reductions

[May 17, 19]

- Chemical reduction using any form of carbon is called as carbo-thermic reduction. As compared to reduction by using heat alone carbo-thermic reduction is much more efficient. Smelting is a process of heating the ore with carbaceous flux and fuel above melting point of the metal under purification. In reductive smelting as in case of Iron ore, molten matte i.e. mixture of purified sulphides and molten slag are produced. When this mixture is heated by carbaceous fuel mostly coke it simultaneously reduces the oxide ore to metal



(above 1000°C, CO₂ gets reduced to CO by C)

- An important advantage of smelting is the removal of gangue which was not separated till this stage. Gangue has higher melting point hence flux is added; this mixture becomes easily fusible mass called as slag. Acidic gangue like silica and alumina are removed by adding basic flux like lime or magnesia and basic gangue is added with acidic flux. If the gangue contains both acidic and basic compounds no external flux is required; they are called as self fluxing gangue for e.g. SiO₂ (Acidic Gangue) + CaO (Basic Gangue) → CaSiO₃ (molten slag).
- An important principle which must be noted that all substances in a reduced state precipitate together and all oxidized substances shows tendency to go together. Hence impurities which are reduced go with metal which is being extracted and all impurities which are oxidized go with slags. A metal which occurs as sulphide ore can't be smelted to give metal directly; initially it is converted to oxide and oxide is then reduced to give metal.

3.7 REFINING OF METALS

- In converting the molten metal or matte it is taken in a converter and air is blown through it. No external heat is supplied. When a metal is taken the objective is to convert impurities into oxide and obtain metal of higher purity; this is called as refining of metal. Metals like Copper, Nickel, Zinc are purified by refining process.
- Distillation is used for metals with low melting points. Low boiling metals are obtained by reducing ore above its boiling point of the metal. The ore is added with reducing agent and boiled; the low melting metal is

evaporated and collected. ZnO is added with carbon and heated in retort where Zinc is collected as vapour and condensed.

- Mercury is also separated from mercuric sulphide by process of distillation but this process does not require any reducing agent.
- The impure metal or solution may be refined further to remove impurities and give a product of the required purity. Alternatively the feed stock could be treated to give an essentially pure chemical compound of the metal, and the compound may be reduced to give a pure metal.
- This procedure, is more commonly used for the more reactive metals: titanium, niobium, and the light metals. It's noteworthy that same refining process can be used for purification of low melting metals and refractory metals both.
- Separation of Nickel by process of refining presents an interesting situation. Fine particles of nickel are heated at 60°C in a strong current of carbon monoxide. It produces Ni(CO)₄ leaving behind all heavier, higher-boiling impurities like iron.
- Desilverising of lead is achieved by Parkes's process. In this process zinc is added with molten lead and the mixture is heated over 800°C. While cooling the solubility of zinc reduces and crystallization of zinc takes away gold, silver like noble metal contaminating lead. Later zinc and noble metal mixture on distillation evaporates zinc and gives precious noble metal. Thus lead, noble metal and zinc all are purified.
- Most metals obtained by the reduction process are not very pure. These have to be further refined or purified. Purification of the metal is the last step in metallurgy. Refining is based on the difference between the properties of metals and their impurities. Liquation, distillation, oxidation, electro refining. These processes are discussed in brief below.

3.7.1 Liquation

- In this method the metals are melted and made to go into the liquid state. Metals that have low melting points such as lead, tin etc., can be purified by this method. A sloping hearth of a furnace is used on which the metal is placed and melted. The temperature of the furnace is maintained slightly above the melting point of the metal. Due to the heat the pure metal melts and flows down, leaving behind infusible impurities having higher melting point.

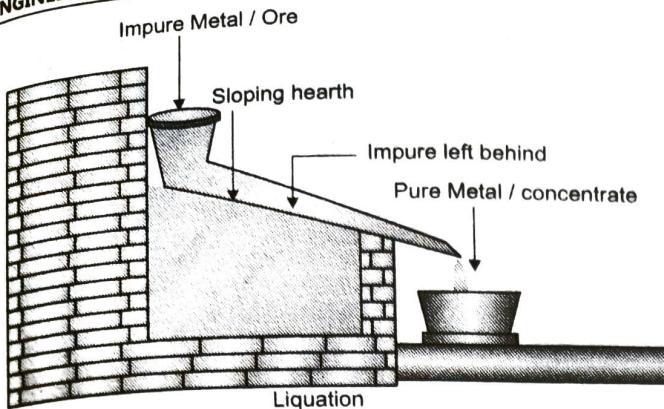


Fig. 3.4 : Schematic diagram of Liquation process

3.7.2 Distillation

Refining of volatile metals like mercury, zinc etc. is done by distillation. The impure form of these metals can be distilled to get their vapours, which are then condensed to get the pure metal. The metal to be refined is heated above its boiling point when the impurities do not vaporize. Pure metal vapourises and is condensed while the impurities are left behind.

3.7.3 Oxidation

Impurities of sulphur, carbon, phosphorous etc. can be removed from the impure metals by passing calculated amount of oxygen or air through the molten metal. These impurities get oxidized to gaseous products like sulphur dioxide, carbon dioxide, phosphorous (V) oxide respectively. These then escape out from the metal.

3.7.4 Electrorefining

[May 17, 19]

Electrolysis can be used for, both extractions of metal (which cannot be separated by chemical reduction process) as well as for further purification of metals obtained by any other method. In the electrorefining process a block of impure metal is made the anode and a thin sheet of pure metal is made the cathode of an electrolytic cell containing an aqueous solution of the metal salt. When electric current of a suitable voltage is passed, impure metal at the anode gets dissolved to deposit the pure metal at the cathode.



Metal ions from the anode enter the electrolyte as follows:



The impurities are left behind as anode mud near the anode. The anode finally disintegrates while the cathode gains in weight due to the collection of pure metal.

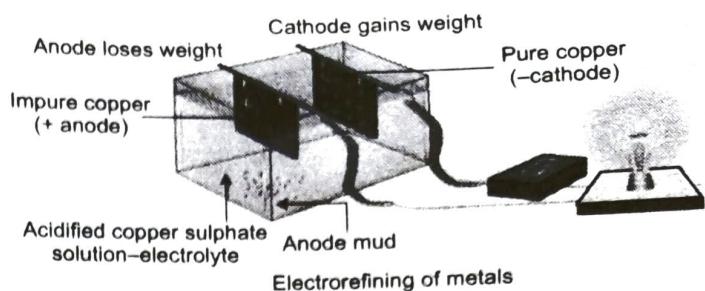


Fig. 3.5 : Schematic of electro-refining of metals

This method is used for refining volatile metals like copper, silver, tin, nickel that have boiling points lower than their impurities. e.g., zinc, mercury.

Electro-refining often provides a particularly high purity of metal. Electrorefining processes using a molten salt or non-aqueous electrolyte are used and, indeed, are the subject of further development. This is due to the possibilities they offer for increasing current densities and refining via lower oxidation states not stable in water (e.g. refining of copper via Cu+ would almost halve the energy requirement). However, aqueous processes presently predominate due to their ease of handling, more developed chemistry and familiarity with aqueous process liquors and electrolytes.

1. Aqueous Electrorefining

The electrolyte and other conditions must be selected so that both the anodic dissolution and the deposition of the metal occur with high efficiency while none of the impurity metals can transfer from the anode to the cathode. Certainly there must be no passivation of the anode and the objective is to obtain a good-quality, often highly crystalline, deposit at the cathode. Where necessary, additives are added to the electrolyte to enforce the correct behavior at both electrodes. Chloride ion is a common addition to enhance the dissolution process and, where essential, organic additives are used to modify the cathode deposit. Since, however, organic compounds can be occluded to some extent and reduce the purity of the metal, their use is avoided when possible.

2. Copper Refining

[Dec. 17, 18]

The process for electrorefining copper is typical of those carried out in aqueous solution. The electrolyte is copper sulfate (0.7 molar) and sulfuric acid (2 molar) and the way in which the purification of the copper occurs can be seen by considering the metals likely to be found as impurities:

Important Considerations During Copper Refining:

- Ag, Au and Pt are more noble than copper and therefore will not dissolve anodically. They will be found as metals in the anode slime;
- Sn, Bi and Sb dissolve anodically but will precipitate in the electrolyte as oxide or hydroxide compounds which will be found in the anode slime;
- Pb is oxidized anodically but will form insoluble lead sulfate in this electrolyte. Again, this will fall to the slime in the base of the cell;
- Fe, Ni, Co and Zn all dissolve anodically and in the sulfate medium form species which are soluble in the electrolyte. The species formed, however, only reduce at potentials more negative than that at which the copper deposits and therefore remain in the electrolyte.

Hence, the impurities accumulate in either the electrolyte or the cell slime and these can be processed further to recover the significant metals.

- The electrolytic cells are generally of a very simple open-tank and parallel-plate electrode design, similar to that described above for copper winning except that the anodes are now of the impure copper (Fig. 3.6). The copper anodes must have the correct size and geometry (i.e. flat plates larger than the starter sheets of aluminum, titanium, steel, or thin Cu foil for the cathodes to avoid heavy edge deposits) and have a homogeneous composition. The flow rate of the electrolyte through the cells is low so that the slime drops to the base of the cell and does not come into contact with the cathode.

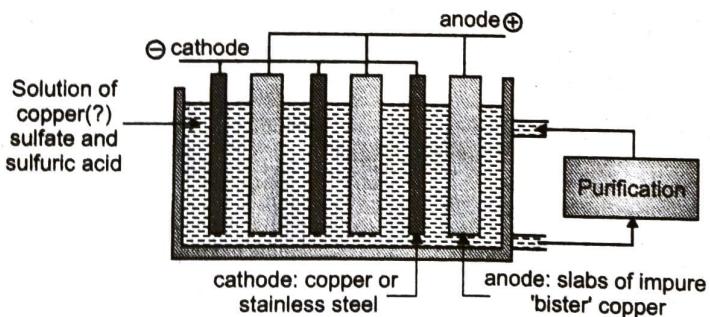


Fig. 3.6 : Electro refining of copper

- Fig. 3.6 Diagram showing the structure of the cells in which the electrolytic refining of copper is carried out. The anodes and cathodes are connected to the + and - current lines respectively. The elements which are more noble than Cu and the compounds are anodically insoluble and precipitate on the bottom of the cells

beneath the anodes as 'anodic slimes' or 'anodic sludge'.

- In the figure, the 'anodic sludges' are shaded, giving some idea of the greater purity of the copper cathode as compared with that of the anode is shown by the smaller density of spots on the cathodes. It should be added that, to reduce the effects of the ohmic drop, the anodes and cathodes are closer together than indicated in the figure.
- The electrolyte additionally contains organic additives which serve to control copper electrocrystallization at the cathode (levellers and brighteners) and help prevent insoluble particulates from co-depositing (surfactants).
- Temperature is usually maintained via steam-heating at 60-65°C (inlet to cell), falling to 55-60°C (cell outlet). Circulation rates are typically 0.01-0.03 m³/min, a cell achieving a nominal change of electrolyte every 4-6 h. This circulation helps to control temperature, gently increase the mass transport, prevent composition gradients, replenish addition agents and serve as a convenient stream for bleeding-off impurities. The electrolyte composition is maintained by purification of the bleed stream in three sequential steps:
 1. Removal and recovery of copper, usually by electro-refining in stage-1 "liberator" cells.
 2. Removal of As, Sb and Bi via electro-refining them onto an impure Cu deposit.
 3. Evaporation of water and precipitation of Ni, Fe and Co as sulfides.

3.7.5 Zone Refining

It's a relatively new technique and used especially where very high purity metal is required for application. Solar cell, photodiode, silicon chip or wafer used to built IC chip, are some examples where high chemical purity is required and hence the metal is purified by zone refining technique.

- Zone melting** (or **zone refining** or **floating zone process** or **travelling melting zone**) is a group of similar methods of purifying crystals, in which a narrow region of a crystal is melted, and this molten zone is moved along the crystal. The molten region melts the impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot. The impurities concentrate in the melt, and are moved to one end of the ingot. Zone refining was

invented by John Desmond Bernal and further developed by William Gardner Pfann in Bell Labs as a method to prepare high purity materials, mainly semiconductors, for manufacturing transistors. Its early use was on germanium for this purpose, but it can be extended to virtually any solute-solvent system having an appreciable concentration difference between solid and liquid phases at equilibrium. This process is also known as the float zone process, particularly in semiconductor materials processing.

- Principle and Process Method of Zone Refining:** The principle is that the segregation coefficient k (the ratio of an impurity in the solid phase to that in the liquid phase) is usually less than one. Therefore, at the solid/liquid boundary, the impurity atoms will diffuse to the liquid region. In short zone refining is an application of Phase rule or Lever rule where impurities are separated from the purified bulk and retained in other solid state by repeated distillation processes over a short length of metal which is being purified. Thus, by passing a crystal boule through a thin section of furnace very slowly, such that only a small region of the boule is molten at any time, the impurities will be segregated at the end of the crystal. Because of the lack of impurities in the leftover regions which solidify, the boule can grow as a perfect single crystal if a seed crystal is placed at the base to initiate a chosen direction of crystal growth. When high purity is required, such as in semiconductor industry, the impure end of the boule is cut off, and the refining is repeated.
- In zone refining, solutes are segregated at one end of the ingot in order to purify the remainder, or to concentrate the impurities. In zone leveling, the objective is to distribute solute evenly throughout the purified material, which may be sought in the form of a single crystal. For example, in the preparation of a transistor or diode semiconductor, an ingot of germanium is first purified by zone refining. Then a small amount of antimony is placed in the molten zone, which is passed through the pure germanium. With the proper choice of rate of heating and other variables, the antimony can be spread evenly through the germanium. This technique is also used for the preparation of silicon for use in computer chips.

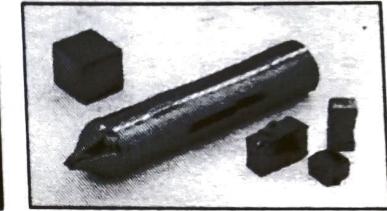
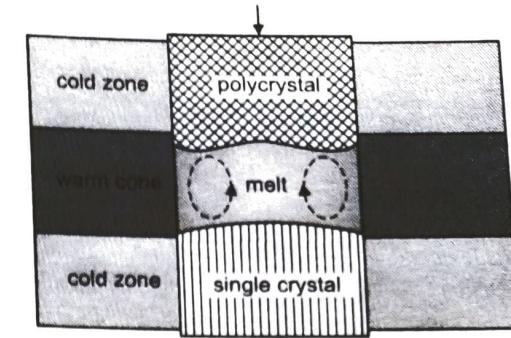


Fig 3.7 : (a) Principle, (b) In process sample during zone refining process and (c) Purified metal rod

Application of Zone Refining

- In solar cells float zone processing is particularly useful because the single crystal silicon grown has desirable properties. The bulk charge carrier lifetime in float-zone silicon is the highest among various manufacturing processes. Float-zone carrier lifetimes are around 1000 microseconds compared to 20-200 microseconds with Czochralski process, and 1-30 microseconds with cast multi-crystalline silicon. A longer bulk lifetime increases the efficiency of solar cells significantly.
- Zone remelting is another related process is zone remelting, in which two solutes are distributed through a pure metal. This is important in the manufacture of semiconductors, where two solutes of opposite conductivity type are used. For example, in germanium, pentavalent elements of group V such as antimony and arsenic produce negative (n-type) conduction and the trivalent elements of group III such as aluminum and boron produce positive (p-type) conduction. By melting a portion of such an ingot and slowly refreezing it, solutes in the molten region become distributed to form the desired n-p and p-n junctions.

3.8 EXTRACTION OF IRON FROM ORE

Extraction of iron from its ore is the most significant process in the Metallurgy. The extraction of metals and its isolation occurs in following steps:

- Concentration of Ore
- Extraction of metal from the concentrated Ore
- Purification of the metal

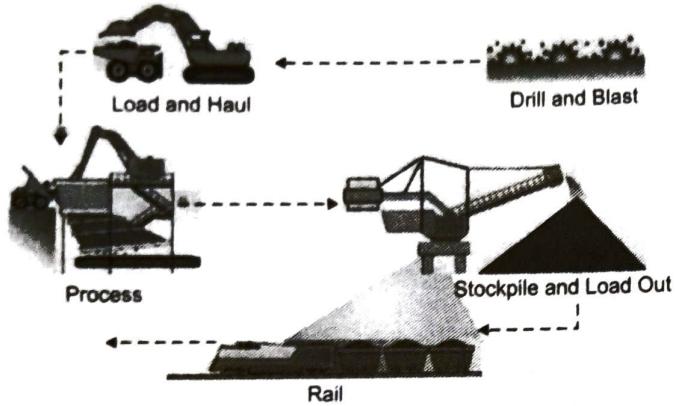


Fig. 3.8 : Schematic of extraction of Iron from ore

- **Iron Extracted from its Ore:** It's a process which begins with Concentration through calcination and roasting. Concentration removes the water and other volatile impurities such as sulphur and carbonates. This concentrated ore is mixed with limestone (CaCO_3) and Coke and fed into the blast furnace from the top. It is in the blast furnace that extraction of iron occurs.
- **Chemical Modifications Happening in Blast Furnace:** The purpose of a Blast Furnace is to reduce the concentrated ore chemically to its liquid metal state. A Blast furnace is a gigantic, steel structure lined with refractory brick where the concentrated iron ore, coke and limestone are charged from the top. A blast of hot air is blown into the bottom. All the three ingredients are crushed into small round pieces and mixed and put on a hopper which controls the charge.
- Hot air is blown from the bottom and coke it burned to generate temperatures up to about 1920°C . Burning of coke provides the heat required for carbothermic reduction process. At such high temperatures, Coke reacts with the oxygen in the hot air to form Carbon Monoxide (CO). The CO and heat move upwards and meet the raw material running down from the top. The temperature in the upper parts of the Blast Furnace is considerably lower than the 1920°C at the bottom. In this part, Haematite (Fe_2O_3) and Magnetite (Fe_3O_4) are reduced to Ferrous Oxide (FeO).

- **Drill and Blast:** Iron ore is excavated from mine by processes like drilling and blasts using dynamite like explosives. The rock lumps are heavy and huge. They are carried to the processing area using heavy JCB machines. At the processing unit the concentration of ore is carried out by number of steps like crushing and grinding, sieving and sifting, then physical methods like froth floatation, gravity separation, magnetic separation is carried out. These processes are followed by chemical processing like carbothermic reduction in Blast furnace.
- The Fig. 3.9 shows details of high temperature reactions taking place in blast furnace. After the process the purified metal goes either to process steel making or stored as blooms, billets, rods, structural sections as per end use requirement.

Reactions Taking Place in the Blast Furnace:

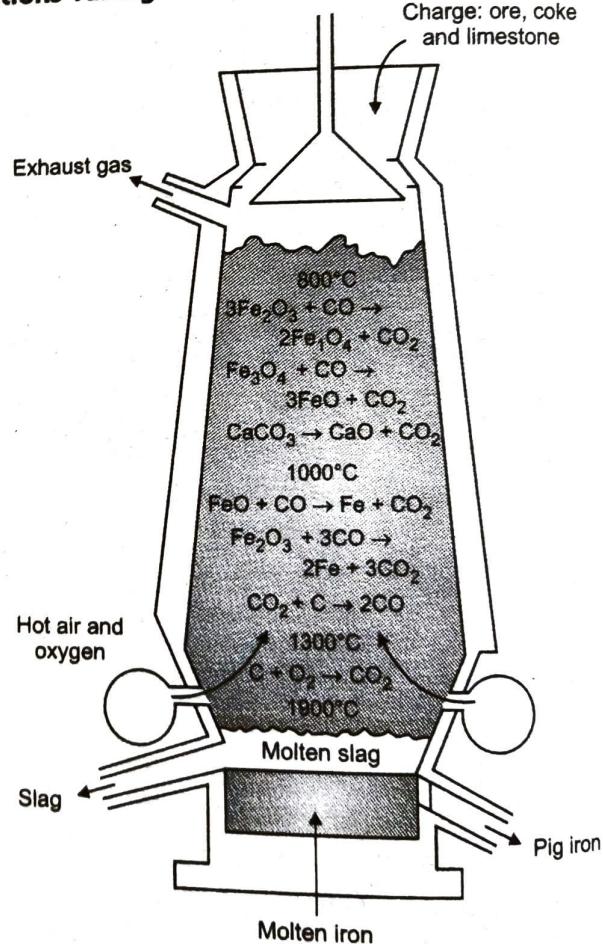
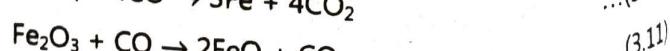
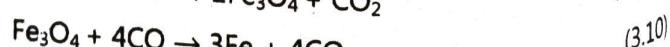
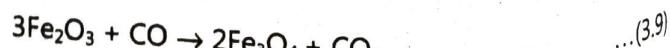
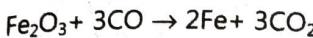
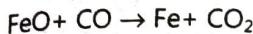


Fig. 3.9
Process of Extraction of Iron: Inside the Blast Furnace at temperature $> 800^\circ\text{C}$



At temperature above 1000C



At temperature above 1300C, In the lower sections of the furnace,



At temperature above 1900



The limestone also decomposes to CaO which removes the silicate impurity of the ore in the form of Slag. It can be easily separated out of molten iron. The iron manufactured in Blast Furnaces contain about 3 – 4 % of Carbon and smaller quantities of many other impurities such as sulphur, Silicon, etc. This is called Pig Iron. It is a hard but brittle metal and the impurities severely hamper its strength. Carbon seems to play a significant role in influencing the brittleness and hardness balance in iron. To further reduce the carbon content of pig iron, it is melted again with scraps of iron and coke and subjected to the blast of hot air. This kind of iron is called Cast Iron and has a slightly lower carbon content 2 – 3 %. This is even harder than pig iron.

• Wrought Iron/ Malleable Iron:

Wrought Iron is the purest form of iron available commercially available and is prepared from cast iron by heating cast iron in a furnace lined with Haematite (Fe_2O_3). The Haematite reacts with Carbon in the cast iron to give pure iron and carbon monoxide gas which escapes.



Limestone is then added as flux, and it creates the slag. Impurities such as S, Si pass into the slag and the slag later can be easily separated to yield pure iron.

SUMMARY

- Metals are very useful, and used for variety of engineering applications
- They are chemically very reactive and hence found in earth crust in associated form.
- Oxides, halides, sulphides and sulphates, carbonate and bicarbonate, sodium alumino silicates (zeolite minerals) are stable chemical form of various metals
- The process of separation of metals from their compounds or minerals is studied in metallurgy and materials science

Important Steps in Ore Extraction are:

- Excavation → ore dressing → comminution (Crushing and grinding) → physical metallurgy i.e. gravity separation → froth floatation → calcinations → roasting → Chemical separation i.e. → smelting → pyrolysis by reduction → refining.
- Extraction of Iron from Haematite is described in detail: The steps involved are Concentration of Ore → Extraction of metal carbothermic reduction → Purification of the metal
- The chemical reduction is carried out in Blast furnace
- Different reactions take place inside blast furnace at various temperatures ranging from 550 to 1800C.
- The product is used as wrought Iron or converted to Steel.

EXERCISE

- What is an ore?
- What are different types of ores?
- What is the difference between Ore and Mineral?
- What are steps involved in Ore dressing?
- What is meant by refining of metal?
- Name 5 ores and metals extracted from them.
- What are different type of reduction reactions?
- Name the device used for reduction of Haematite.
- Why separation of metal from ore should be done?
- Differentiate between calcination and roasting.
- Differentiate between Ore and Mineral
- What are different types of reductive processes.
- What do you understand from Extractive Metallurgy? What are different steps involved in Extractive metallurgy.
- What is the difference between Ore and Mineral? What are different types of Ore?
- Why metals generally occur as metal compounds? Give classification of different ore on the basis of chemical composition.
- Explain Physical methods of separation of Ores namely Froth floatation, magnetic separation and electrostatic separation.
- Explain Gravity separation.

18. Compare between chemical and physical methods of separation of ores.
19. Describe Chemical methods of separation of ores namely calcination, roasting, smelting, reduction
20. Explain different methods of Pyrolysis. Write down Different reactions taking place during pyrolysis.
21. Explain with suitable diagram details of Extraction of Iron from Haematite.
22. Draw a diagram of Blast furnace and enlist different reactions taking place in different zones inside a blast Furnace.
23. What are various chemical modifications taking place during smelting of Iron ore?

UNIVERSITY QUESTIONS**May 2017**

1. Describe smelting process for reduction of Ore. [5]
2. Hoe Ores can be concentrated by calcinations and Roasting process? [5]
3. What is purification of metal? Explain electrolytic refining of metal with suitable example. [5]

December 2017

1. Describe the process of electrolytic refining of crude copper metal. [6]
2. Explain the Gravity separation and Magnetic separation method for physical concentration of metal. [6]

May 2018

1. Explain any two physical methods of concentration of ore. [6]
2. What is Smelting? Explain the process of isolating metals by Pyrolysis. [6]

December 2018

1. Explain any two physical methods of concentration of ore. [6]
2. Describe the process of Electrolytic Refining of crude copper metal. [6]

May 2019

1. Write various types of ore. [6]
2. Explain the Froth Flotation and Magnetic separation method of concentration of ore. [6]
3. Explain the reduction of ore by smelting process. [6]
4. Explain the electrolytic refining of metal. [6]

