Elements are classified into three categories namely metals, non-metals and metalloids.

#### **METALS:**

Generally lustrous solids, malleable, ductile and good conductors of heat and electricity. For example, Fe, Cu, Al, Pb, Au, Ag, Hg etc.

#### **NON-METALS:**

Generally non-lustrous, brittle and poor conductors of electricity (except Graphite). For example, O,H,C,S,P etc.

#### **METALLOIDS:**

The elements which show common characteristics of metals and non-metals. For example, Sb, As etc. These elements are classified into three categories namely metals, non-metals and metalloids.

#### MODES OF OCCURANCE OF METALS:

Elements occur in nature in two states:

#### 1. Native State:

If metals are found in elemental form, they are said to be in native state. Generally less reactive metals are found in native state. For example, Au, Ag, Cu, Pt etc.

#### 2. Combined State:

The metals are said to occur in combined state if they are found in nature in the form of their compounds. Generally the reactive metals occur in the form of their compounds.

In the combined state the metals are found in the earth's crust as oxides, carbonates, sulphates, silicates, phosphates etc.

#### MINERALS:

A mineral is a naturally occurring substance, representable by a chemical formula, that is usually solid and inorganic, and has a crystal structure. It is different from a rock, which can be an aggregate of minerals or non-minerals and does not have a specific chemical composition. The study of minerals is called mineralogy

#### ORE:

An **ore** is an occurrence of rock or sediment that contains sufficient minerals with economically important elements, typically metals, that can be economically extracted from the deposit. The ores are extracted from the earth through mining, they are then refined to extract the valuable element, or elements.

#### TYPES OF ORES:

Ores may be divided into four groups-

#### . Native Ores:

These ores contain the metal in free state eg. Silver gold etc. These are usually formed in the company of rock or alluvial impurities like clay, sand etc.

#### Oxidised Ores:

These ores consist of oxides or oxysalts (eg. carbonates, phosphate) and silicate of metal. Important oxide ore includes, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O etc. and important cabonate ores are limestone (CaCO<sub>3</sub>), Calamine (ZnCO<sub>3</sub>) etc.

#### Sulphurised Ores:

These ores consist of sulfides of metals like iron, lead, mercury etc. Examples are iron pyrites (FeS2). galena (PbS), Cinnabar (HgS)

#### · Halide ores:

Metallic halides are very few in nature. Chlorides are most common examples include horn silver (AgCl) carnallite KCl. MgCl<sub>2</sub>.6H<sub>2</sub>O and fluorspar (CaF<sub>2</sub>) etc.

#### **GANGUE:**

The economically worthless materials associated with the ores are collectively called as gangue or matrix, consisting of sand, clay and other impurities.

# PRINCIPLES AND METHODS OF EXTRACTION OF METALS (METALLURGY):

Metallurgy is the branch of science and technology concerned with the properties of metals and their production and purification. It is a domain of materials science and engineering that studies the physical and chemical behavior of metallic elements, their inter-metallic compounds, and their mixtures, which are called alloys. Metallurgy is used to separate metals from their ore.

Metallurgy is subdivided into ferrous metallurgy (also known as *black metallurgy*) and non-ferrous metallurgy (also known as *colored metallurgy*). Ferrous metallurgy involves processes and alloys based on iron while non-ferrous metallurgy involves processes and alloys based on other metals. The production of ferrous metals accounts for 95 percent of world metal production.

#### OCCURRENCE OF METALS

METAL	ORES	COMPOSITION
ALUMINIUM	BAUXITE	AlOx(OH)3-2x
		{Where 0 <x<1}< td=""></x<1}<>
	KAOLINITE{a form of clay}	{Al2(OH)4Si2O5}

IRON	HAEMATITE	Fe2O3
	MAGNETITE	Fe3O4
	SIDERITE	FeCO3
	IRON PYRITES	FeS2
COPPER	COPPER PYRITES	CuFeS2
	MALACHITE	CuCO3.Cu(OH)2
	CUPRITE	Cu2O
	COPPER GLANCE	Cu2S
ZINC	ZINC BLENDE OR SPHALERITE	ZnS
	CALAMINE	ZnCO3
	ZINCITE	ZnO

### The steps involved in the metallurgical operations are:

- 1. Crushing and grinding of the ore
- 2. Concentration or benefication of the ore
- 3. Preliminary treatment of the concentrated ore
- 4. Reduction
- 5. Purification or refining of crude metal

#### 1. CRUSHING OR GRINDING OF THE ORE:

The ore in the form of big rocks is broken into small pieces with the help of crushers. These small pieces are then powdered with the help of a ball mill or stamp mill.

### 2. CONCENTRATION OR BENEFICATION OF THE ORE:

The removal of gangue from the pulverized ore is called concentration, dressing or benification of the ore. It involves several steps and selection of these steps depends upon the differences in physical properties of the compound of the metal present and that of the gangue. The type of the metal, the

available facilities and the environmental factors are also taken into consideration.

It is carried out by any of the following processes:

#### PHYSICAL METHODS:

#### I.HYDRAULIC WASHING:

This is based on the differences in the mass of the ore and the gangue particles. Hydraulic washing process is done by washing the ores with streams of water. If an ore is heavier or denser than the gangue, then the gangue particles are washed way with the stream. The heavier or denser ore particles remain behind and can be collected. Hydraulic washing is done for ores that have tin or lead, as they are found to be heavier than the gangue.

#### II. FROTH FLOTATION PROCESS:

This method is based on the principle of difference in the wetting properties of the ore and the gangue particles with water and oil.

This method is used for the concentration of sulphide ores of copper, zinc, lead, etc.

The powdered ore is mixed with water, containing small quantity of oil (pine oil or turpentine oil) in a large tank. The sulphide particles in the ore get wet with oil while dust and sand particles do not get wet with oil. The water containing ore is agitated violently by blowing air to form froth. Sulphide particles being lighter float along with the froth at the surface which is removed from the top of the tank and collected. Impurities being heavier collect at the bottom. The froth is then washed, filtered and dried.

#### **III.MAGNETIC SEPARATION:**

This method uses the principle of difference in the magnetic properties of the ore and the gangue (impurities).

A magnetic separator consists of a leather conveyer belt moving over two rollers. One of the rollers has a strong magnet in it. Powdered ore is dropped on the moving belt at one end through a hopper. When it reaches the other end, nonmagnetic impurities fall down first whereas the magnetic particles fall later forming a separate heap. This method is generally used for the concentration of the iron ore.

For example, in the metallurgy of aluminium, aluminium oxide is subject to leaching by alkali solutions:

Al2 O3 + 3H2 O + 
$$2$$
NaOH  $\rightarrow$   $2$ NaAl(OH)4

Leaching of sulfides is a more complex process due to the refractory nature of sulfide ores.

#### CHEMICAL METHODS:

Ores of highly reactive metals are concentrated by chemical method.

#### **LEACHING:**

In this process the powdered ore is dissolved in certain acids, bases or other suitable reagents. The impurities remain undissolved as sludge. The solution of ore is filtered and the ore is removed by precipitation or crystallization.

### 3. PRELIMINARY TREATMENT OF THE CONCENTRATED ORE:

The objective of preliminary treatment of the concentrated ore is:

- i. To get rid of the impurities which would cause difficulties in the later stages.
- ii. To convert the ore into oxide of the metal because it is easier to reduce an oxide than the carbonate or sulphide.

There are two processes employed for preliminary treatment:

#### **I.CALCINATION:**

Calcination is the process of heating the ore strongly in absence of air to remove (i) volatile impurities (ii) water [from hydrated ore] or (iii) to convert carbonate ore into metal oxide.

$$ZnCO3 \rightarrow ZnO + CO2$$

#### II.ROASTING:

Roasting is used to convert sulphide ores into oxides by heating for a longer period in presence of air.

$$2 \text{ ZnS} + 3 \text{ O2} \rightarrow 2 \text{ ZnO} + 2 \text{ SO2}$$

#### 4. REDUCTION:

The conversion of metal oxide into metal is called 'Reduction'.

The following steps can be used for reduction-

#### I. SMELTING:

The roasted or calcined ore is mixed with coke or charcoal (reducing agent) and heated above its melting point. The metal oxide during the reduction process gets reduced to metal.

$$ZnO+$$
  $C$   $\rightarrow$   $Zn$  +  $CO$   
 $Fe_2O_3$  +  $3C$   $\rightarrow$   $2Fe$  +  $3CO$ 

During reduction, an additional reagent is also added to the ore to remove the impurities still present in the ore. This reagent is called Flux.

Flux combines with the impurities to form a fusible product called Slag.

Flux + Impurities 
$$\rightarrow$$
 Slag

If impurities are acidic in mature, the flux is basic and vice versa.

P4010 + 6CaO 
$$\rightarrow$$
 2 Ca3(PO4)2
Acidic impurity Basic flux Slag

CaO Basic + SiO<sub>2</sub>  $\rightarrow$  CaSiO<sub>3</sub>
impurity Acidic Slag

flux

#### II. REDUCTION WITH ALUMINIUM:

Aluminium is used as reducing agent for the reduction of certain oxides of metals like chromium (Cr2O3), manganese (Mn3O4) and iron (Fe2O3) which can not be reduced with C. A large amount of heat is produced during the process and the metal is obtained in liquid (molten) state. The process is known as Thermite Process or Aluminothermy.

Cr2O3 + 2Al 
$$\rightarrow$$
 Al2O3 + 2 Cr  
Fe2O3 + 2 Al  $\rightarrow$  Al2O3 + 2 Fe  
3 Mn3O4 + 8Al  $\rightarrow$  4 Al2O3 + 9 Mn

#### **III. AUTO-REDUCTION:**

Certain metals like copper, silver and mercury commonly occur in sulphide ores that can be easily reduced by roasting. For example, mercury can be obtained by roasting its ores Cinnabar (HgS).

$$2 \text{ HgS} + 3O2 \rightarrow 2 \text{ HgO} + 2 \text{ SO2}$$
  
 $2 \text{ HgO} + \text{ HgS} \rightarrow 3 \text{ Hg} + \text{ SO2}$ 

#### IV. HYDROMETALLUGY:

Some metals like gold and silver are extracted from their concentrated ores by leaching. They are dissolved in suitable reagent leaving behind insoluble impurities. The metal is recovered from the solution by re-precipitation or crystallization. For example,

Silver ore is leached with dilute solution of sodium cyanide. Silver dissolves in it forming a complex sodium argentocyanide. The solution is treated with scrap zinc which displaces silver from the complex.

Ag2S + 4 NaCN 
$$\rightarrow$$
 2 Na[Ag(CN)2] + Na2S  
2 Na[Ag(CN)2] + Zn  $\rightarrow$  Na2[Zn(CN)4] + 2 Ag

### V. ELECTROLYTIC REDUCTION OR HALL-HEROULT PROCESS:

Oxides of highly reactive metals like sodium, potassium and aluminium cannot be reduced by using chemical reduction (by carbon or aluminium). If carbon is used large amount of heat is required and metal carbide is formed. These metals are obtained by electrolysis of their fused (molten) salts. The cathode acts as the reducing agent as it supplies electrons to metal ions.

The addition of cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and fluorspar (CaF<sub>2</sub>) makes alumina a good conductor of electricity and lowers its Fusion temperature from 2323 TO 1140K

The reaction taking place during electrolysis-

```
Na_3AIF_6 \Longrightarrow 3NaF + AIF_3

AIF_3 \Longrightarrow AI^{3+} + 3F^-

At cathode

AI^{3+} + 3e^- \longrightarrow AI

At anode

F^- \longrightarrow F + e^-

2AI_2O_3 + 12F \longrightarrow 4AIF_3 + 3O_2

2C + O_2 \longrightarrow 2CO

2CO + O_2 \longrightarrow 2CO_2
```

### 5. PURIFICATION OR REFINING OF CRUDE METAL:

#### I. LIQUATION:

This method is used when the melting temperature of the metal is lower than that of the impurity and the impurities are not miscible with the metal. Metals like Bi, Sn, Pb, Hg etc., are purified by this method. The sloping floor of a furnace is used to melt crude metal, when the pure metal flows down, the impurities are left behind.

#### II. ELECTROLYTIC REFINING:

It is used to refine metals like zinc, lead, aluminium, copper, silver, gold, etc. The impure metal works as anode, a strip of pure metal is taken as cathode and a suitable salt of the metal to be purified in aqueous solution is taken as an electrolyte. The impure metal enters the solution from anode and then gets deposited on cathode. The impurities remain in the solution as anode mud.

#### Process of refining-

The apparatus consist of Electrolytic tank containing acidified copper sulphate solution as electrolyte. A thick block of impure

copper metal is made anode .A thin strip of pure copper metal is made as cathode.

On passing electricity, Impure copper from the anode dissolves and goes into CUSO4 solution and pure copper from the copper sulphate solution deposits on the cathode .

Thus pure copper metal is produced at cathode. The soluble impurities goes into the solution whereas insoluble impurities settles down at anode as anode mud.

#### Chemical reaction:

At cathode:  $Cu^{2+} + 2e^{--->}Cu$ 

At anode: Cu - 2e---->Cu2+

#### III. ZONE REFINING:

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. This method is used for obtaining ultra pure metals like germanium, silicon and gallium.

A circular mobile heater is fixed at one end of a rod of the impure metal . The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off.

#### IV. VAPOUR PHASE REFINING:

In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. So, the two requirements are:

- (i) the metal should form a volatile compound with an available reagent,
- (ii) the volatile compound should be easily decomposable, so that the recovery is easy.

There are two processes:

#### A. MOND'S PROCESS:

In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

$$Ni + 4 CO \rightarrow [Ni(CN)_4](330 - 350 K)$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal

#### **B**. VAN-ARKEL METHOD:

In the Van Arkel-de Boer method impure metal is first converted into one of its unstable compounds. Heating the unstable compound of the metal at higher temperatures, decomposes it to give pure metal. Zr or Ti is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI4 --- > Zr + 2I2$$

#### **METALLURGY OF IRON:**

#### ORES OF IRON

Common Name	Chemical Name	Formula
Haematite	Ferric oxide	Fe <sub>2</sub> O <sub>3</sub>
Magnetite	Tri iron tetroxide	Fe <sub>3</sub> O <sub>4</sub>
Iron Pyrites	Iron sulphide	$FeS_2$
Spathic iron ore	Ferrous carbonate	FeCO <sub>3</sub>

#### 1. <u>Dressing and Concentration of Ore:</u>

The iron ore is split into small pieces and washed in water to remove sand, clay etc.

#### 2. Calcination:

The washed ore is strongly heated in the absence of air to expel water sticking to it. The calcination converts the carbonate ore into oxide.

#### 3. Reduction:

The washed and dried hematite is mixed with measured quantities of coke and lime stone and fed into the blast furnace.

## REACTIONS IN BLAST FURNACE IN DIFFERENT REGIONS

#### **COMBUSTION ZONE:**

Reaction: Combustion of coke Temperature of the

region: 2000<sup>0</sup>C

$$C + O_2 \rightarrow CO_2 + Heat$$

#### **FUSION ZONE:**

Reaction: Reduction of carbon dioxide to carbon monoxide Temperature of the region: 1300° C

$$CO_2$$
+  $C \rightarrow 2 CO - Heat$ 

#### **DECOMPOSITION OF LIMESTONE:**

The lime stone (CaCO<sub>3</sub>) decomposes to give carbon dioxide and quicklime (CaO)

$$CaCO_3 \rightarrow CaO + CO_2 - Heat$$

The above reaction is endothermic and the temperature in the region falls to about 800-1000°C.

#### FORMATION OF SLAG:

The CaO reacts with acidic impurities such as silica (SiO2) and forms a slag which melts and collects above the iron at the bottom of the furnace. Slag is an easily fusible mass having a low melting point

$$CaO + SiO_2 \rightarrow CaSiO_3$$

#### **REDUCTION ZONE:**

Reduction of haemetite to molten iron takes place here. Temperature of the region: 500-700° C

In the upper region of the furnace, the CO reduces the haemetite to molten iron and oxidizes it self to CO<sub>2</sub>.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

The molten iron produced is collected, poured into moulds and solidified to give pig iron. Pig iron contains carbon, sulphur, phosphorus, silicon and manganese as impurities.

#### **METALLURGY OF COPPER:**

#### ORES OF COPPER

Common Name	Chemical Name	Formula
Copper pyrites	Chalcopyrite	CuFeS <sub>2</sub>
Copper glance	Chalcocite	Cu <sub>2</sub> S

#### **CONCENTRATION**

The finely crushed ore is concentrated by Froth-Floatation process. The finely crushed ore is suspended in water containing a little amount of pine oil. A blast of air is passed through the suspension. The particles get wetted by the oil and float as a froth which is skimmed. The gangue sinks to the bottom.

#### **ROASTING:**

The concentrated ore is then roasted in a furnace in the presence of a current of air. Sulphur is oxidized to SO<sub>2</sub> and impurities of arsenic and antimony are removed as volatile oxides.

The following reaction takes place.

$$2CuFeS2 + O2 \longrightarrow Cu2S + 
2FeS + SO2S + O2 \longrightarrow SO2$$

$$4As + 3O2 \longrightarrow As2O3$$

$$4Sb + 3O2 \longrightarrow 2Sb2O3$$

Cuprous sulphide and ferrous sulphide are further oxidized into their oxides.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
  
 $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ 

#### SMELTING:

The roasted ore is mixed with coke and silica (sand) SiO<sub>2</sub> and is introduced in to a blast furnace. The hot air is blasted and FeO is converted in to ferrous silicate (FeSiO<sub>3</sub>).

FeSiO3 (slag) floats over the molten matte of copper.

#### **BESSEMERIZATION:**

Copper metal is extracted from molten matte through bessemerization. The matte is introduced in to Bessemer converter which uphold by tuyers. The air is blown through the molten matte. Blast of air converts Cu2S partly into Cu2O which reacts with remaining Cu2S to give molten copper.

$$2Cu2S + 3O2 \rightarrow 2Cu2O + 2SO2$$
  
 $2Cu2O + Cu2S \rightarrow 6Cu + SO2$ 

#### REFINING OF COPPER:

Blister copper is refined by electrolysis. Blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes. The cathode plates are coated with graphite in order to remove depositing copper. The electrolyte is copper sulphate (CuSO4) mixed with a little amount of H2SO4 to increase the electrical conductivity. Optimum potential difference is 1.3 volt for this electrolytic process. During electrolysis, pure copper is deposited on the cathode plates and impurities which are soluble and fall to the bottom of the cell as anode mud or sludge

$$Cu \rightarrow Cu^{+2} + 2e^{-}$$
 (at the anode)  
 $Cu^{+2} + 2e^{-} \rightarrow Cu$  (at the cathode)

This electrically refined copper is 100% pure.

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