Chapter 5

Extraction of metals

Day - 1

EXTRACTION OF METALS

Metallurgy: - The entire scientific and technological process used for isolation of the metal from its ore

Minerals are naturally occurring chemical substances in the earth's crust obtainable by mining.

Ores: minerals from which a metal can be extracted profitably are known as **ores**.

All ores are minerals but all minerals are not ores.

Gangue An ore does not contain only the desired substance. It is usually contaminated with earthly or undesired materials known as **gangue**.

Flux: The substance which reacts with gangue to form slag is called flux

Slag: Compound or mixture of flux and gangue is called slag. Slag separates more easily from the ore than the gangue. This way, removal of gangue becomes easier

Native ores: The ores which contain metals in free stste ex. Silver, Gold, Platinim etc. are called native ores.

Chief Ores and Methods of Extraction of Some Common Metals:

Metals	Occurrence	Extraction Method	Remark
Sodium	Rock salt: NaCl Feldspar:$Na_3AlSi_3O_8$	Electrolysis of fused NaCl or NaCl/ $CaCl_2$	Sodium is highly reactive, it reacts with water
Copper	Copper pyrites:$CuFeS_2$ Malachite:$CuCO_3.Cu(OH)_2$ Cuprite: Cu_2O Copper glance: Cu_2S	Roasting of sulphide partially and reduction $2Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2$	It is self reduction in a specially designed converter. Sulphuric acid leaching is also employed
Aluminium	Bauxite: $AlOx(OH)_{3-2x}$ where $0<x<1$ Cryolite: Na_3AlF_6 Kaolinite: $[Al_2(OH)_4Si_2O_5]$	Electrolysis of Al_2O_3 dissolved in molten cryolite or in Na_3AlCl_6	A good source of electricity is needed in the extraction of Al
Zinc	Zinc blende ZnS Zincite: ZnO Calamine: $ZnCO_3$	Roasting and then reduction with C	The metal may be purified by fractional distillation

Lead	Galena: PbS	Roasting of the sulphide ore and then reduction of the oxide	Sulphide ore is concentrated by froth floatation process
Silver	Argentite: Ag_2S	Sodium cyanide leaching of the sulphide ore and finally replacement of Ag by Zn	It involves complex formation and displacement

EXTRACTION OF METALS CAN BE BROADLY DIVIDED IN FOUR STEPS

I. Concentration of ore
II. Conversion of concentrated ore to oxide
III. Reduction of oxide to metal
IV. Refining of metal.

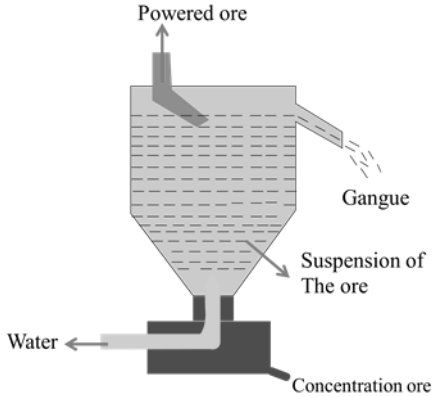
I. Concentration of Ores

Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as concentration, dressing or benefaction. 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. Some of the important procedures are described below.

DIFFERENT PROCEDURES FOR CONCENTRATION OF ORES

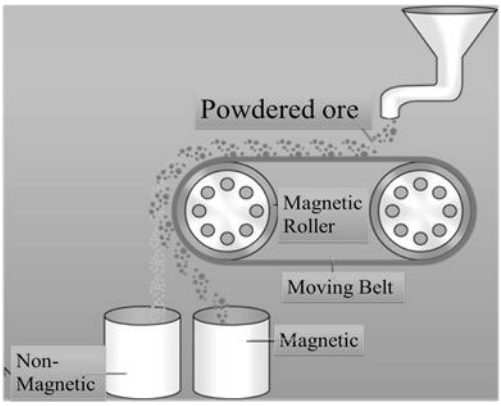
(a) Hydraulic Washing

This is based on the differences in gravities of the ore and the gangue particles. It is therefore a type of gravity separation. In one such process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.



(b) Magnetic Separation

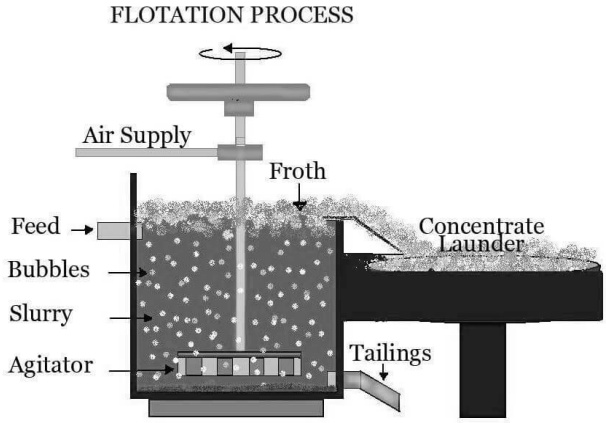
This is based on differences in magnetic properties of the ore components. If either the ore or the gangue is capable of being attracted by a magnetic field, then such separations are carried out as per the attached figure. This method is used to remove tungsten ore particles from cassiterite (SnO_2). It is also used to concentrate magnetite (Fe_3O_4), chromite ($FeCr_2O_4$) and pyrolusite (MnO_2) from unwanted gangue



(c) Froth Floatation Method

The principle of froth floatation process is that sulphide ores are preferentially wetted by the pine oil, whereas the gangue particles are wetted by the water. Collectors are added to enhance the non-wettability of the mineral particles. Examples are pine oil, fatty acids and xanthates. Froth stabilizers are added to stabilize the froth. Examples are cresols, aniline. . A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.

If two sulphide ores are present, it is possible to separate the two sulphide ores by adjusting proportion of oil to water or by adding depressants. For example- In the case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to froth but allows PbS to come with the froth



(d) Leaching

It is a process in which ore is treated with suitable solvent which dissolves the ore but not the impurities.

Example Purification of Bauxite by Leaching: Baeyer's process:

Step 1: Al_2O_3 (s) + 2NaOH (aq) + $3H_2O$ (l) → $2Na[Al(OH)_4](aq)$

Step 2: $2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$

Step 3: $Al_2O_3.xH_2O(s)$ –1470K → $Al_2O_3(s) + xH_2O(g)$

Concentration of Gold and Silver Ores by Leaching:

$4M(s) + 8CN^-(aq)\ 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$

$2[M(CN)_2]^-$ (aq) + Zn(s) → $[Zn(CN)_2]^-$ (aq) + 2M(s) Where : [M Ag or Au]

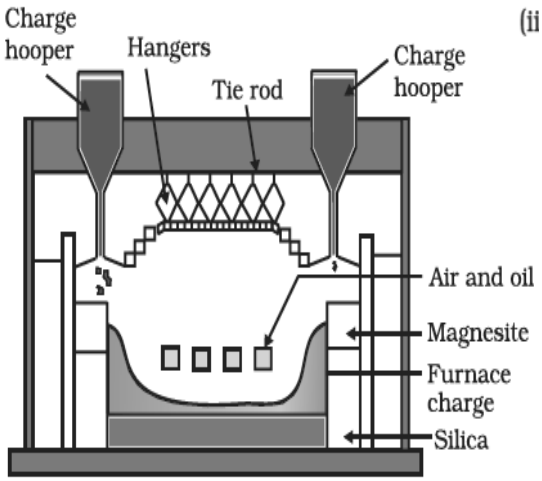
II. Conversion of concentrated ore to oxide

Conversion to oxide. There are two methods. (i) Calcination: and (ii) Roasting

Roasting	Calcination
It is a process in which ore is heated in a regular supply of air at a temperature below melting point of the metal so as to convert the given ore into oxide	It is a process of heating ore in limited supply of air or no air so as to convert carbonate ores into oxides.
It is also used to remove impurities as volatile oxides	It is also used to remove moisture and volatile impurities
Sulphide ores are converted into oxide by roasting	Carbonate ores are converted into oxide by roasting
$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$ $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$	$Fe_2O_3.xH_2O(s)$ _ Fe_2O_3 (s) + $xH_2O(g)$ $ZnCO_3$ (s) → ZnO(s) + $CO_2(g)$ $CaCO_3.MgCO_3(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g)$

The sulphide ores of copper are heated in **reverberatory furnace**. If the ore contains iron, it is mixed with silica before heating. Iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte which contains Cu_2S and FeS.

- $FeO + SiO_2 \rightarrow FeSiO_3$ (slag)
- The SO_2 produced is utilised for manufacturing
- H_2SO_4



III. Reduction of oxide to the metal

The process of converting metal oxide into metal is called reduction. It needs a suitable reducing agent depending upon the reactivity or reducing power of metal. The common reducing agents used are carbon or carbon monoxide or any other metals like Al, Mg etc.

Thermodynamic principles of metallurgy: Some basic concepts of thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in metallurgical processes:

- Gibbs free energy change at any temperature is given by $\Delta G = \Delta H - T\Delta S$ where ΔG is free energy change, ΔH is enthalpy change and ΔS is entropy change.
- A negative ΔG means +ve value of K i.e., products are formed more than the reactants. The reaction will proceed in forward direction.

Ellingham diagrams: The plots between $\Delta_f G^\Theta$ of formation of oxides of elements vs. temperature are called Ellingham diagrams. It provides a sound idea about selecting a reducing agent in reduction of oxides. Such diagrams help in predicting the feasibility of a thermal reduction of an ore. ΔG must be negative at a given temperature for a reaction to be feasible

Limitations of Ellingham Diagrams: It does not take kinetics of reduction into consideration, i.e., how fast reduction will take place cannot be determined

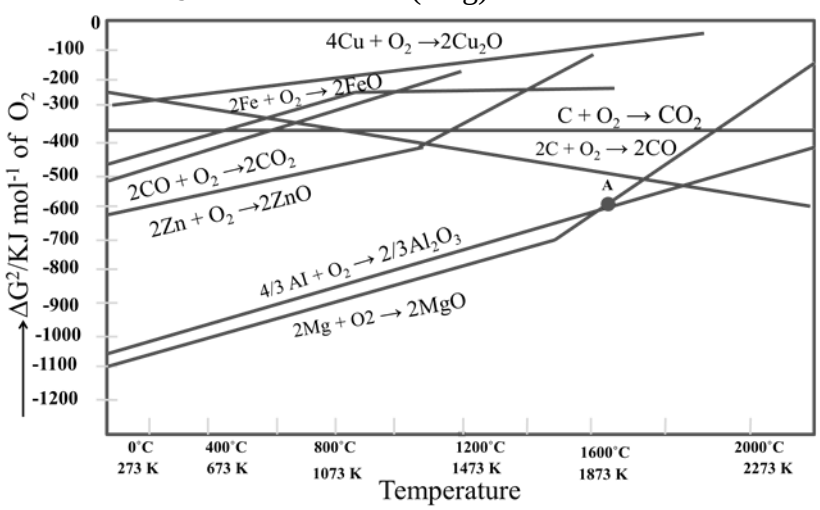
Reduction of iron oxide in blast furnace: Reduction of oxides takes place in different zones.

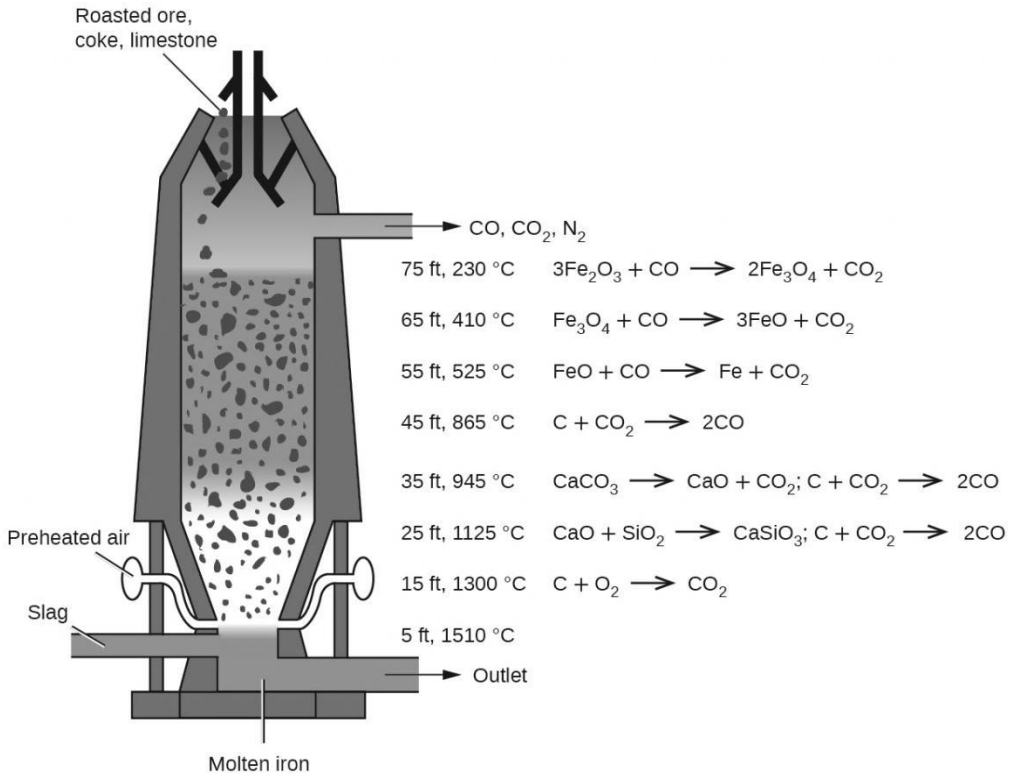
At 500 – 800 K (lower temperature range in blast furnace)

- $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
- $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$
- $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

At 900 – 1500 K (higher temperature range in blast furnace)

- $C + CO_2 \rightarrow 2CO$
- $FeO + CO \rightarrow Fe + CO_2$
- Limestone decomposes to CaO and CO_2
- $CaCO_3 \xrightarrow{-heat} CaO + CO_2$
- Silica (impurity) reacts with CaO to form calcium silicate which forms slag. It floats over molten iron and prevents oxidation of iron.
- $CaO + SiO_2 \rightarrow CaSiO_3$ Calcium silicate (Slag)





TYPES OF IRON

- **Pig iron:** The iron obtained from blast furnace is called pig iron. It is impure from of iron contains 4% carbon and small amount of S,.P, Si and Mn. It can be casted into variety of shapes.
- **Cast iron:** It is made by melting pig iron with scrap iron and coke using hot air blast. It contains about 3% of carbon content. It is extremely hard and brittle.
- **Wrought iron**: It is the purest form of commercial iron. It is also called malleable iron. It is prepared by oxidative refining of pig iron in reverberatory furnace lined with haematite which oxidises carbon to carbon monoxide

WROUGHT IRON

- $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
- $S + O_2 \rightarrow SO_2$
- $4P + 5O_2 \rightarrow 2P_2O_5$
- $Si + O_2 \rightarrow SiO_2$
- $CaO(flux) + SiO_2 \rightarrow CaSiO_3$ (slag)
- $3CaO(flux) + P_2O_5 \rightarrow Ca3(PO_4)_2$ (slag) The metal is removed and freed from slag by passing through rollers

DIFFERENT TYPES OF STEEL

Alloy	Composition	Uses
Mild steel	Chromium 0.1 - 0.5%,	Making chain bolts and framework.

Hard steel	Chromium 0.6 - 1.5%,	Making chain bolts and framework.
Stainless steel	Cr 11-26%, Ni-1-8%, Co, Mo etc. in different proportion. C<0.5%	utensils, various specialty uses