

Principles & Processes of Isolation of Elements

Elements in Nature

Earth crust is the source of many elements. Out of these elements, 70% are metals. Aluminium is the most abundant metal of earth crust and iron comes second. The percentage of different elements in earth crust are O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-1%

Metals occur in two forms in nature (i) in native state (ii) in combined state, depending upon their chemical reactivities.

Native State

Elements which have low chemical reactivity or noble metals having least electropositive character are not attacked by oxygen, moisture and CO_2 of the air. These elements, therefore, occur in the free state or in the native state, e.g. Au, Ag, Pt, S, O, N, noble gases, etc.

Combined State

Highly reactive elements which are readily attacked by moisture, oxygen and carbon dioxide of the air, such as F, Cl, Na, K, etc., occur in nature in combined form as their compounds such as oxides, carbonates, sulphides, halides, etc.

Hydrogen is the only non-metal which exists in oxidised form only.

Minerals and Ores

The naturally occurring substances in the form of which the metals occur in the earth crust along with impurities are called **minerals**.

Every mineral is not suitable for the extraction of the metal. The mineral from which the metal is economically and conveniently extracted is called an **ore**.

Thus, all ores are minerals but all minerals are not ores.

Important Ores/Minerals

Combined state	Element	Ore/mineral
Oxides	Fe	Haematite (Fe_2O_3), Magnetite (Fe_3O_4), Limonite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$)
	Al	Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), Diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), Corundum (Al_2O_3)
	Mn	Pyrolusite (MnO_2)
	Zn	Zincite (ZnO)
	Ti	Rutile (TiO_2)
	Cu	Cuprite (Cu_2O)
	Sn	Cassiterite or tin stone (SnO_2)
Carbonates	Ca	Calcite (CaCO_3)
	Mg	Magnesite (MgCO_3)
	Ca, Mg	Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)
	Cu	Malachite [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$]
	Zn	Calamine (ZnCO_3)
	Fe	Siderite or spathic ore (FeCO_3)
	Pb	Cerussite (PbCO_3)
Au	Azurite [$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$]	
Sulphides	Fe	Iron pyrite (FeS_2)
	Cu	Copper glance (Cu_2S)
	Cu, Fe	Copper pyrite or chalcopyrite (CuFeS_2)
	Hg	Cinnabar (HgS)
	Zn	Zinc blende (ZnS)
	Pb	Galena (PbS)
	Ag	Argentite or silver glance (Ag_2S)
Halides	Na	Common salt or Rock salt (NaCl)
	Al	Cryolite (Na_3AlF_6)
	K, Mg	Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)
	Ag	Horn silver (AgCl)

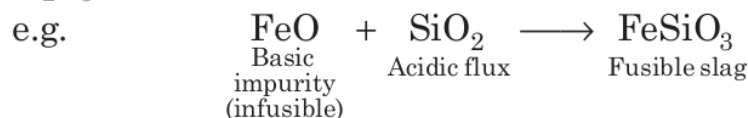
Terms Related to Extraction of Elements

- (i) **Flux** The substance added to convert infusible mass (impurities) into some fusible mass is called flux.

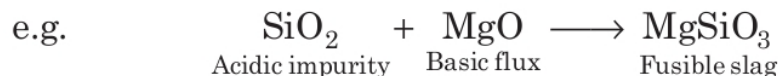


Depending upon the nature of impurity, it may be acidic or basic.

- **Acidic flux** It is used to remove basic impurities. e.g., Silica (SiO_2), boron trioxide (B_2O_3), phosphorus pentoxide (P_2O_5) etc., are acidic flux.



- **Basic flux** It is used to remove acidic impurities e.g., lime (CaO), lime stone (CaCO_3), magnesia (MgO) etc., are basic flux.



- (ii) **Slag** The fusible mass obtained by the reaction of flux and infusible mass is called slag and this process is called **slagging operation**.
- (iii) **Gangue or Matrix** Impurities associated with ores are called gangue or matrix.

Metallurgy

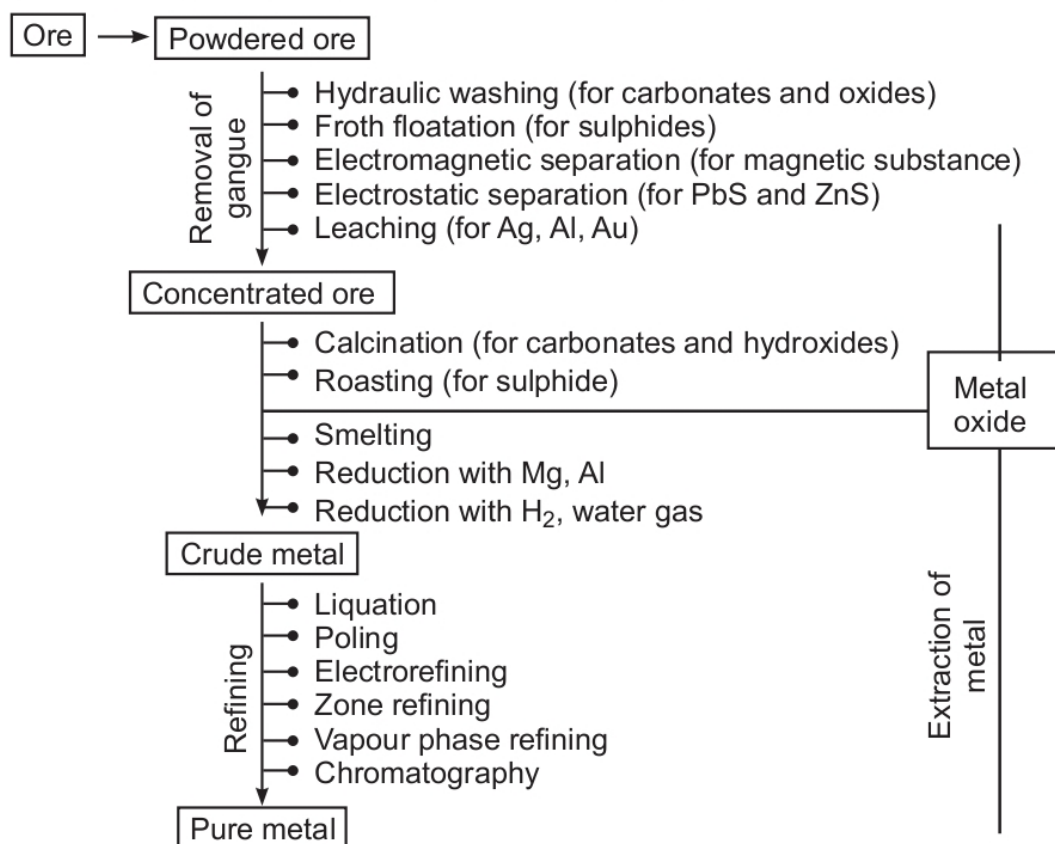
The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Types of Metallurgical Processes

- (i) **Pyrometallurgy** In this type of metallurgy is used to extract the element. Cu, Fe, Zn, Sn, etc., are extracted by this method.
- (ii) **Hydrometallurgical process** In this method, metals are extracted by the use of their aqueous solution. Ag and Au are extracted by this method.
- (iii) **Electrometallurgical process** In this method process of electrolysis is used in the extraction of metals. Na, K, Li, Ca, etc., are extracted from their molten salt solution through electrolytic method.

Steps Involved in Metallurgy

Following steps are involved in the metallurgy :



Crushing of the Ore

The big lumps of ore are crushed into smaller pieces with the help of jaw-crushers. The process of grinding the crushed ore into fine powder with the help of the stamp mills is called **pulverisation**.

Concentration of Ores

Removal of unwanted materials (e.g. sand, clays, etc.) from the ore is known as **ore concentration**, ore dressing or ore benefaction. It can be carried out by various ways depending upon the nature of the ore.

Hydraulic Washing/Gravity Separation/Levigation

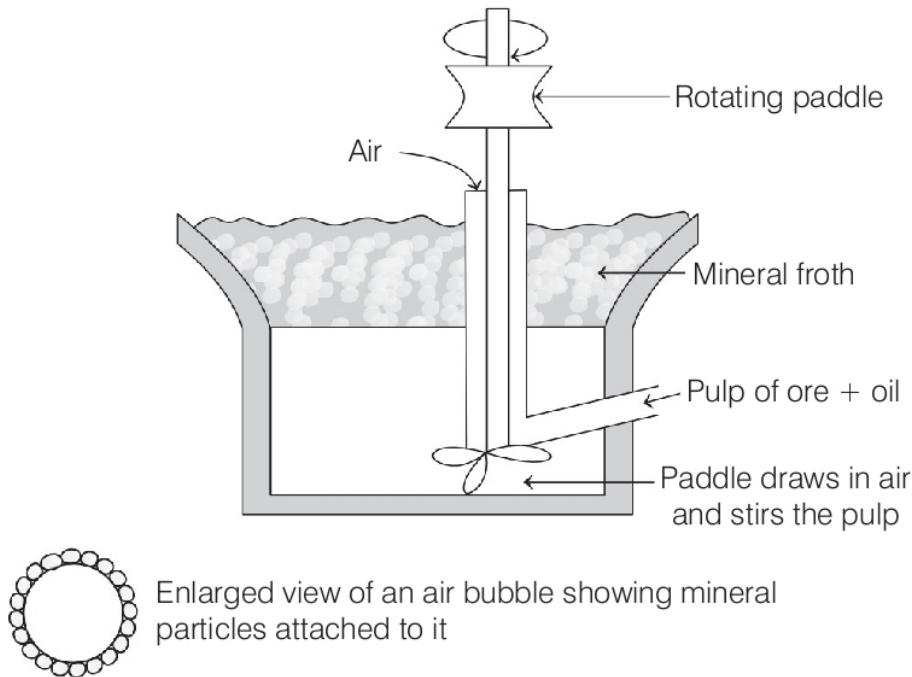
The process by which lighter earthy impurities are removed from the heavier ore particles by washing with water is called **levigation**. The lighter impurities are washed away. Thus, this method is based on the difference in the densities (specific gravities) of ore and gangue.

This method is commonly used for oxide ores such as haematite, tin stone and native ores of Au, Ag, etc.

Froth Flotation

This method is used for the concentration of sulphide ores. The method is based on the preferential wetting of ore particles by oil and that of gangue by water. As a result, the ore particles become light and rise to the top in the form of froth while the gangue particles become heavy and settle down. Thus, adsorption is involved in this method.

The froth can be stabilised by the addition of stabilisers (aniline or cresols).



Froth flotation process (schematic)

Activator They activate the floating property of one of the component of the ore and help in the separation of different minerals present in the same ore. CuSO_4 is used as activator.

Depressants These are used to prevent certain types of particles from forming the froth with air bubbled, e.g. NaCN can be used as a depressant in the separation of ZnS and PbS ores. KCN is an another depressant.

Collectors It increases the non-wettability of ore particles by water, e.g. pine oils, xanthates and fatty acids.

Electromagnetic Separation

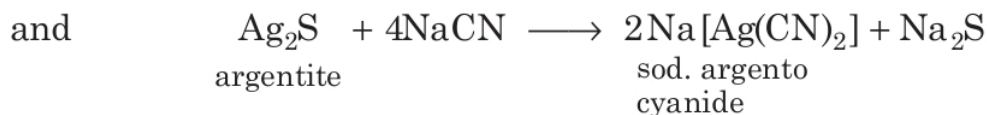
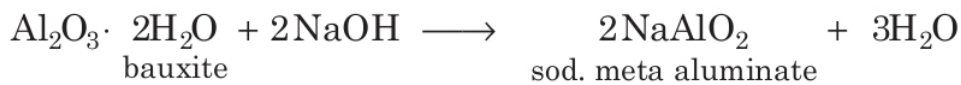
This method of concentration is employed when either the ore or the impurities associated with it are magnetic in nature, e.g. chromite, FeCr_2O_4 , containing magnetic silicious gangue and wolframite, FeWO_4 , containing cassiterite, SnO_2 (non-magnetic impurities) can be separated by this method.

Electrostatic Separation

This method is used for the separation of lead sulphide (good conductor of electricity) which is charged immediately in an electrostatic field and is thrown away from the roller from zinc sulphide (poor conductor of electricity) which is not charged and hence, drops vertically from the roller.

Chemical Method-Leaching

Leaching is the process in which the ore is concentrated by chemical reaction with a suitable reagent which dissolves the ore but not the impurities, e.g. bauxite is leached with a hot concentrated solution of NaOH which dissolves aluminium while other oxides (Fe_2O_3 , TiO_2 , SiO_2), remain undissolved and noble metals (Ag and Au) are leached with a dilute aqueous solution of NaCN or KCN in the presence of air.



Leaching of Ag or Au with NaCN is called cyanide process.

Extraction of Crude Metals from Concentrated Ore

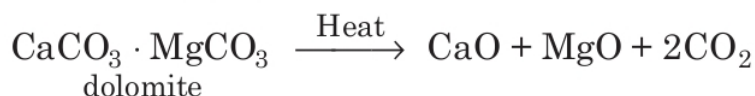
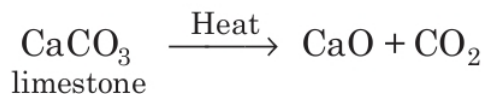
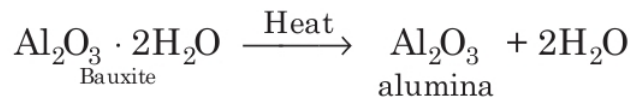
The concentrated ore is usually converted to oxide before reduction, as oxides are easier to reduce. Thus, isolation of crude metal from concentrated ore involves two major steps:

- (i) Conversion to oxide. (ii) Reduction of the oxides to metal.

Conversion to Oxides

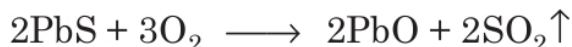
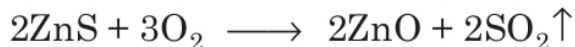
- (i) **Calcination** It is the process of converting an ore into its oxides by heating it strongly, below its melting point in a limited supply of air or in absence of air.

During calcination, volatile impurities as well as organic matter and moisture are removed.



Calcination is used for metal carbonates and hydroxides and is carried out in reverberatory furnace.

- (ii) **Roasting** It is the process of converting an ore into its metallic oxide by heating it strongly, below its melting point in excess of air. This process is commonly used for sulphide ores and is carried out in blast furnace or reverberatory furnace. Roasting helps to remove the non-metallic impurities and moisture.



The furnaces used in calcination and roasting employ refractory materials which resist high temperature and do not become soft. The SO_2 produced is utilised for manufacturing of H_2SO_4 .

Acidic refractories : SiO_2 and $\text{SiO}_2 + \text{Al}_2\text{O}_3$

Basic refractories : CaO and MgO

Neutral refractories : Graphite, chromites, etc.

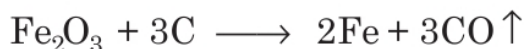
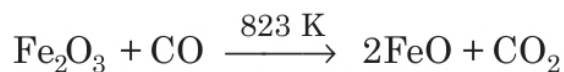
Heavy metals like Cu, Zn, Fe, Sn, etc., are obtained by roasting and smelting.

Reduction of the Oxides to Metal

The roasted or the calcined ore is then converted to the free metal by reduction. Reduction method depends upon the activity of metal.

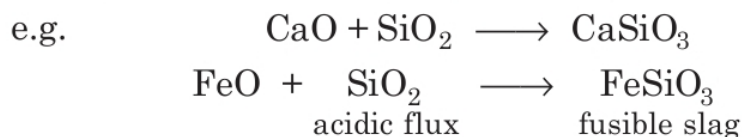
Metals which are low in the activity series (like Cu, Hg, Au) are obtained by heating their compounds in air; metals which are in the middle of the activity series (like Fe, Zn, Ni, Sn) are obtained by heating their oxides with carbon while metals which are very high in the activity series, (e.g. Na, K, Ca, Mg, Al) are obtained by electrolytic reduction method.

- (i) **Smelting** (reduction with carbon) The process of extracting the metal by fusion of its oxide ore with carbon (C) or CO is called **smelting**. It is carried out in a reverberatory furnace.

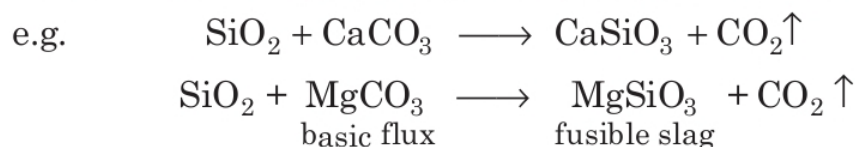


During smelting a substance, called **flux** is added which removes the non-fusible impurities as fusible slag. This slag is insoluble in the molten metal and is lighter than the molten metal. So, it floats over the molten metal and is skimmed off.

Acidic flux For basic impurities, acidic flux is added.



Basic flux For acidic impurities, basic flux is added.



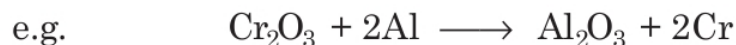
In the extraction of Cu and Fe, the slag obtained are respectively FeSiO_3 and CaSiO_3 .

The obtained slag is used in road making as well as in the manufacturing of cement and fertilizers.

(ii) **Reduction by hydrogen** It is done for W or Mo oxide.

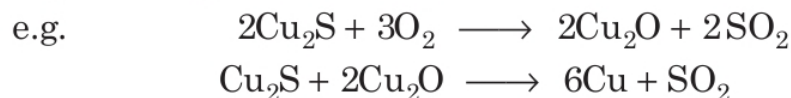


(iii) **Reduction by aluminium** It is known as aluminothermic reduction or Gold Schmidt thermite process. Aluminium powder is used for this purpose.



Mixture of the oxide and Al in the ratio of 3 : 1 is known as **thermite** and mixture of $\text{BaO}_2 + \text{Mg}$ powder acts as ignition powder.

(iv) **Auto reduction** This is used for reduction of sulphide ores of Pb, Hg, Cu, etc. The sulphide ore is heated in a supply of air at 770-970 K when the metal sulphide is partially oxidised to form its oxide or sulphate which then reacts with the remaining sulphide to give the metal.



(v) **Reduction by Mg**



(vi) **Electrolytic reduction or electrometallurgy** It is the process of extracting highly electropositive (active) metals such as Na, K, Ca, Mg, Al, etc by electrolysis of their oxides, hydroxides or chlorides in fused state, e.g. Mg is prepared by the electrolysis of fused salt of MgCl_2 (Dow's process).

Thermodynamic Principle in Extraction of Metals

The free energy change (ΔG) occurring during the reduction processes help in deciding the suitable method for reduction.

For the spontaneous reduction of an oxide, halide or sulphide by an element, the essential condition is that there is a decrease in the free energy of the system (i.e., -ve value of ΔG).

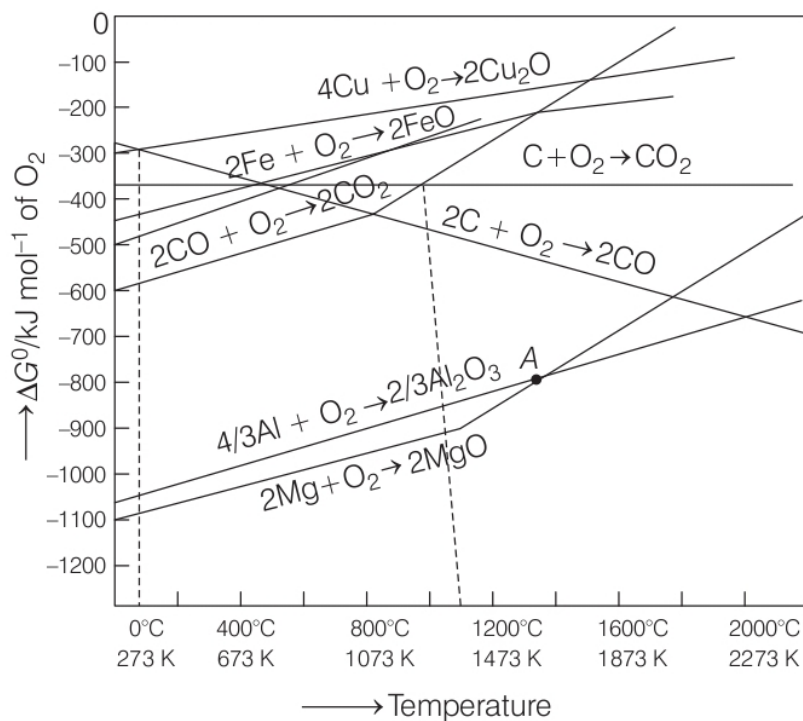
More the negative value of ΔG , the higher is the reducing power of an element. ΔG can be given as

$$\Delta G = \Delta H - T\Delta S$$

where, ΔH = enthalpy change; ΔG = Gibbs free energy

T = temperature; ΔS = entropy change

For the reduction of a metal oxide with a reducing agent, the plot of ΔG° against temperature is studied, which is called **Ellingham diagram**.



Plot of Gibbs energy (ΔG°) vs T (Ellingham diagram)

Characteristics of Ellingham Diagram

1. All the plots slope upwards since ΔG° becomes more positive when temperature increases, i.e. stability of oxides decreases.
2. A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e. the metals for which the free energy of formation (ΔG_f°) of their oxides is more negative can reduce those metal oxides which has less negative ΔG_f° .

3. The decreasing order of the negative values of ΔG_f° of metal oxides is Ca > Mg (below 1773 K) > Al > Ti > Cr > C > Fe
> Ni > Hg > Ag

Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.

Mg can reduce Al_2O_3 below 162 K but above 1023 K, Al can reduce MgO.

4. CO is more effective reducing agent below 1073 K and above 1073 K, coke is more effective reducing agent, e.g. CO reduces Fe_2O_3 below 1073 K but above it, coke reduces Fe_2O_3 . Coke reduces ZnO above 1270 K.

Electrochemical Principle of Metallurgy

In the reduction of molten metal salt, electrolysis is done. It is based on the electrochemical principle.

$$\Delta G^\circ = - nFE^\circ$$

where, n = no. of electrons

E° = electrode potential of redox couple formed in the system. Since, more reactive metals have large negative values of the electrode potential, hence their reduction is difficult. If the difference in two values of E° of redox couple is positive, then ΔG° will be negative and less reactive metal can be obtained from its salt by more reactive metal.

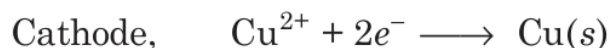
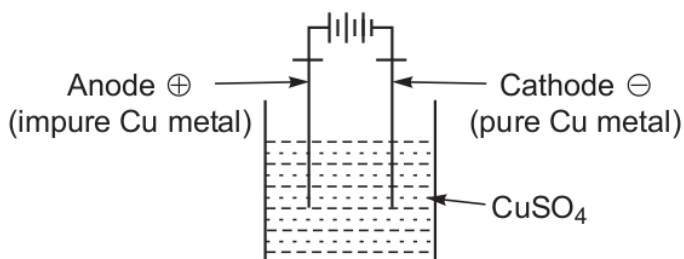
Refining or Purification of Crude Metals

Physical Methods

- (i) **Liquation** This method is used for refining the metals having low melting points (such as Sn, Pb, Hg, Bi) than the impurities. The impure metal is placed on the sloping hearth and is gently heated. The metal melts and flows down leaving behind the non-fusible impurities.
- (ii) **Distillation** This is useful for low boiling metals such as Zn, Hg. The impure liquid metal is evaporated to obtain the pure metal as distillate.
- (iii) **Cupellation** This method is used when impure metal contains impurities of other metals which form volatile oxides, e.g. traces of lead ore removed from silver (as volatile PbO) by this process.

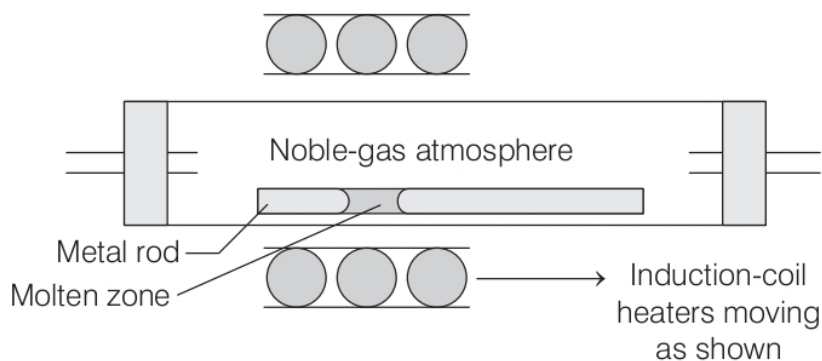
Chemical Methods

- (i) **Poling** This method is used when the impure metal contains impurities of its own oxide, e.g. Cu_2O in blister copper and SnO_2 in impure Sn. The molten impure metal is stirred with green wood poles. At the high temperature, wood liberates gases such as CH_4 which reduces any oxides present in the metal.
- (ii) **Electro-refining** In this method, impure metal forms the anode while the cathode is a rod or sheet of pure metal. The electrolytic solution consists of a soluble salt of the metal.



On passing electricity, the pure metal gets deposited on the cathode while the insoluble impurities settle down below the anode as anode mud or anode sludge. Metals like Cu, Ag, Au, Cr, Zn, Ni, etc are purified by this method.

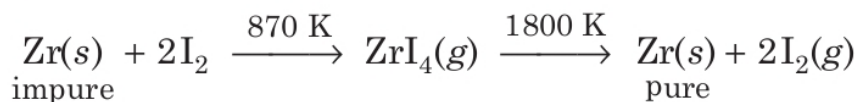
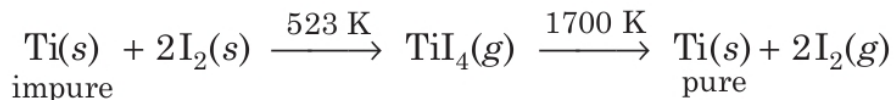
- (iii) **Zone-refining** This method is based upon the principle of fractional crystallisation, i.e. difference in solubilities of impurities in molten and solid state of metal. Semiconductors like silicon, germanium, gallium arsenide and indium antimonide are purified by this method. Elements of very high purity are obtained by this method.



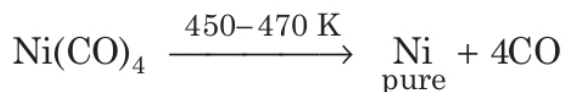
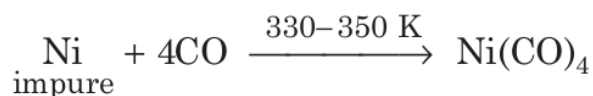
Zone refining process

(iv) **Vapour phase refining** In this method, crude metal is made free from impurities by first converting it into its volatile compound by heating with a chemical reagent at low temperature. After this, the volatile compound is decomposed by heating to some higher temperature to give pure metal.

(a) **van Arkel method** This method is used for preparing ultra-pure metal used in space technology (e.g. Ti, Zr, etc.)



(b) **Mond's process** It is used for refining of nickel.



(v) **Chromatographic method** This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. Adsorption chromatography is generally used. The impure metal is dissolved in a suitable solvent and the solution is allowed to run slowly into an adsorbent column packed with alumina (Al_2O_3). The metal and the impurities present are adsorbed at different rates. These are then eluted with suitable eluent (solvent). In this method, weakly adsorbed component is eluted first and the strongly adsorbed component is eluted afterwards.

Occurrence, Extraction and Uses of Some Metals

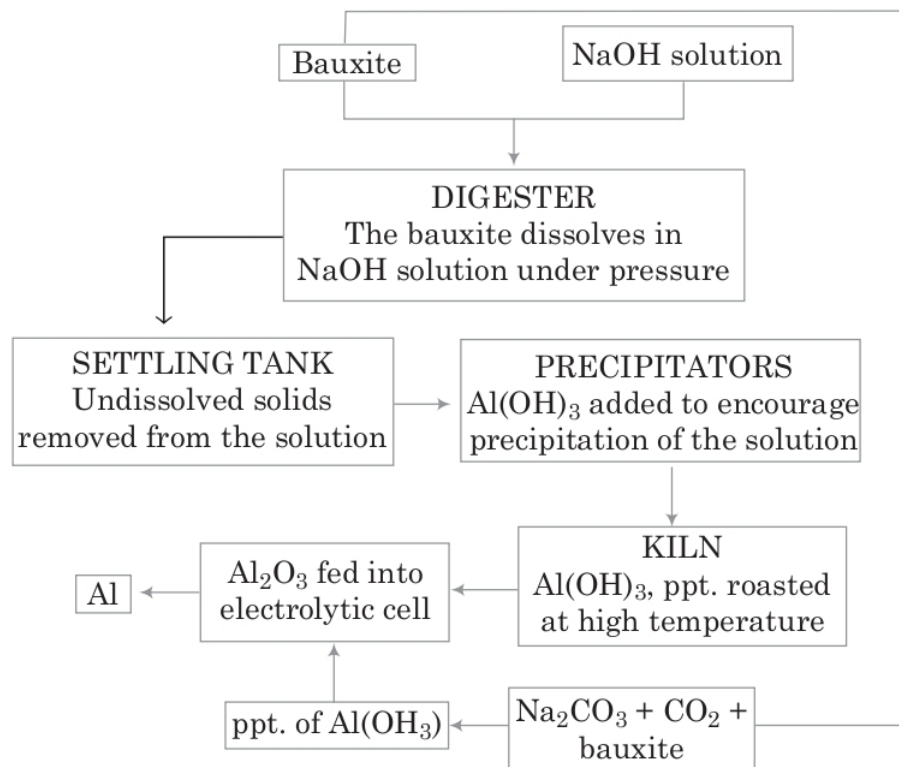
1. Aluminium (Al)

Occurrence

(i) Bauxite — $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (ii) Cryolite — Na_3AlF_6

Common method of extraction Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6 (neutral flux).

Neutral flux is the neutral compound added to the ore to decrease its melting point and to make it conducting, e.g. CaF_2 , cryolite (Na_3AlF_6) etc.



Uses Making electric wires, silver paint, kitchen utensils, food packing, extraction of Mo, Cr, etc.

2. Iron (Fe)

Occurrence

- (i) Haematite — Fe_2O_3 (ii) Magnetite — Fe_3O_4

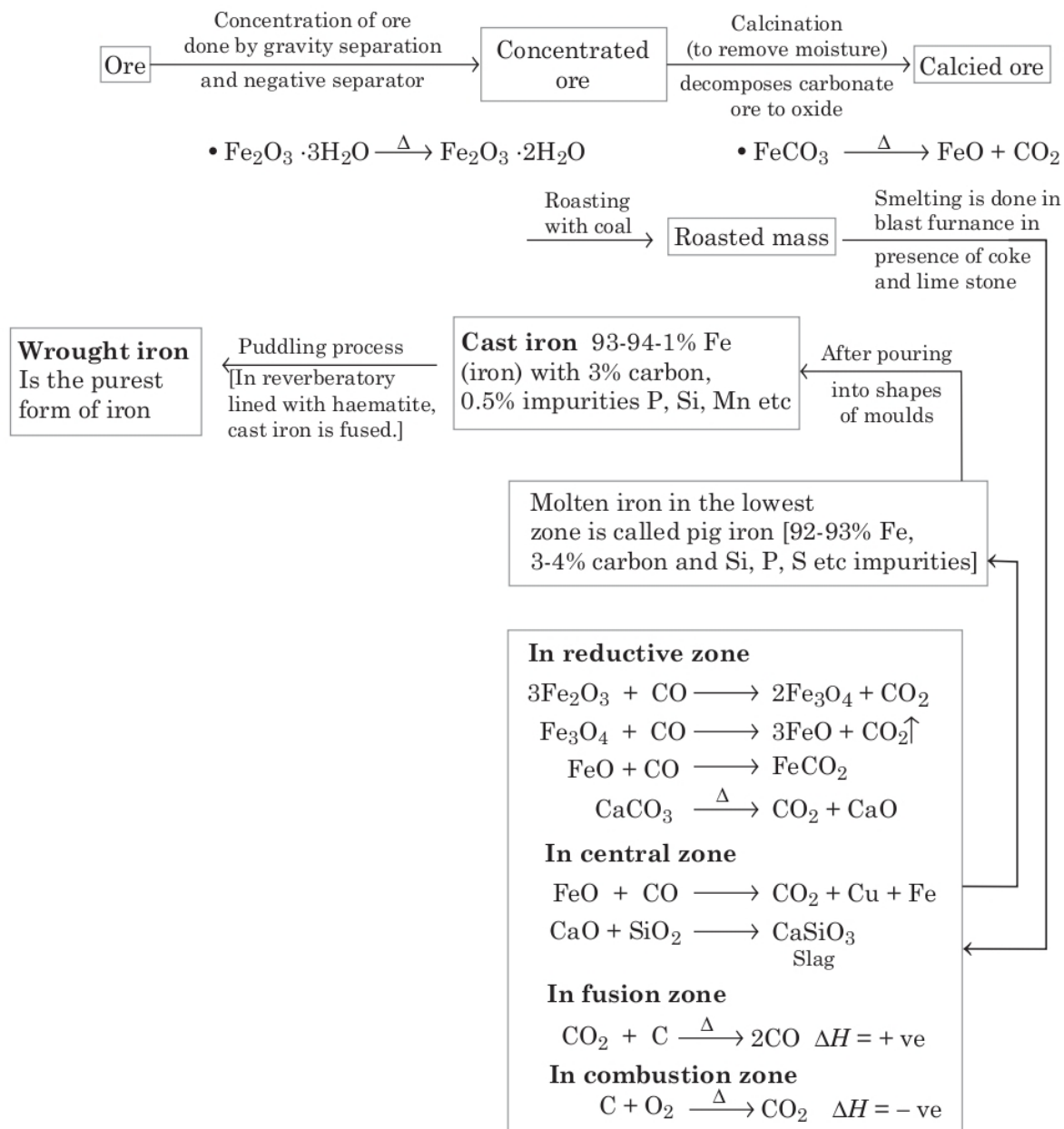
Common method of extraction Reduction of the oxide with CO and coke in blast furnace. The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g. S, P, Si, Mn) and is known as **pig iron**.

Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast.

It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Wrought iron or **malleable iron** is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide.





Uses : Making wrought iron and different varieties of steel.

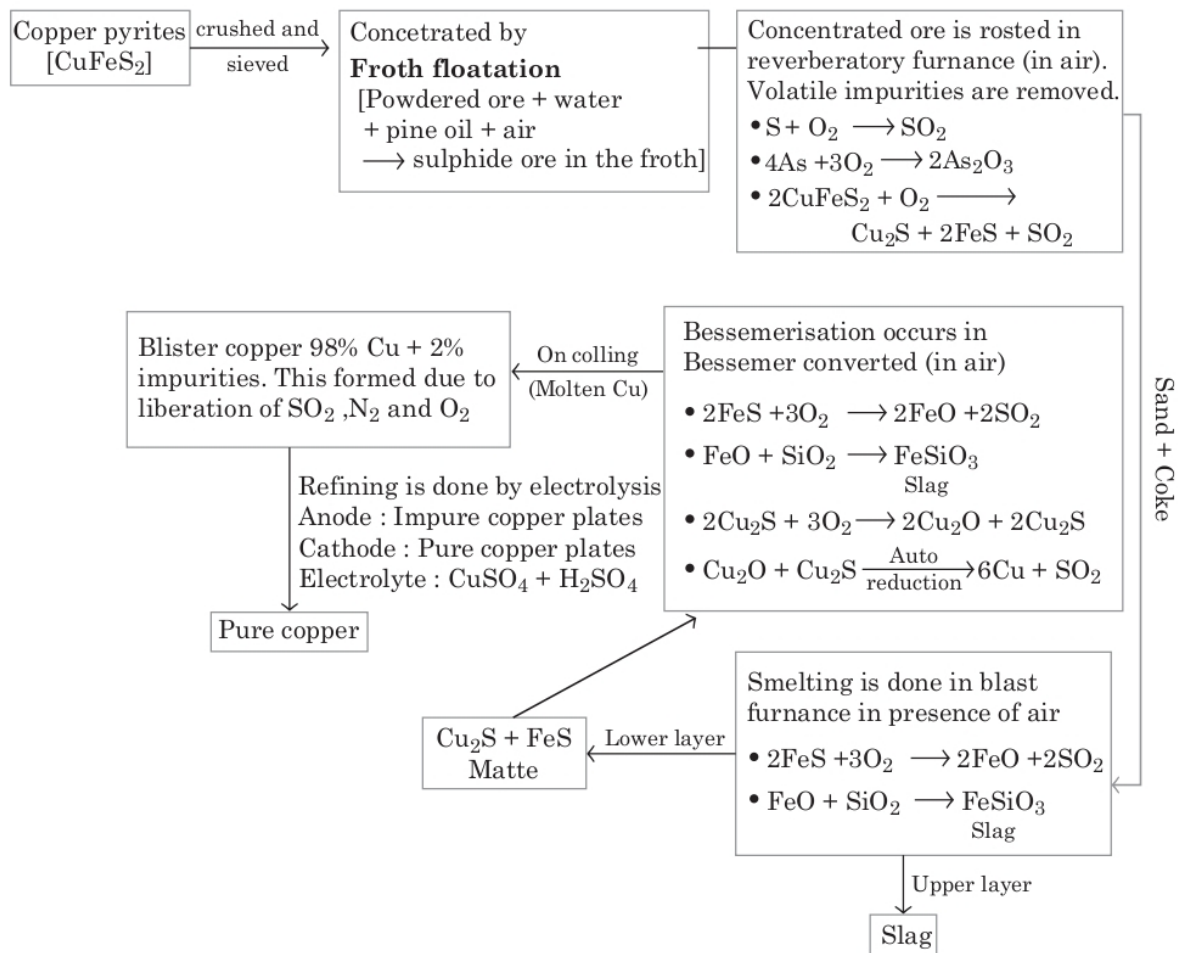
3. Copper (Cu)

Occurrence

- (i) Copper pyrites — CuFeS_2
- (ii) Copper glance — Cu_2S

Common method of extraction Roasting of sulphide partially and reduction.

$\text{Cu}_2\text{S} + \text{FeS}$ is called matte. Blister copper contains 96-98% copper with small amounts of Ag and Au as impurity.



Uses : For the preparation of steam pipes, in making electrical wires, calorimeters, alloys like brass, bronze, etc.

4. Zinc (Zn)

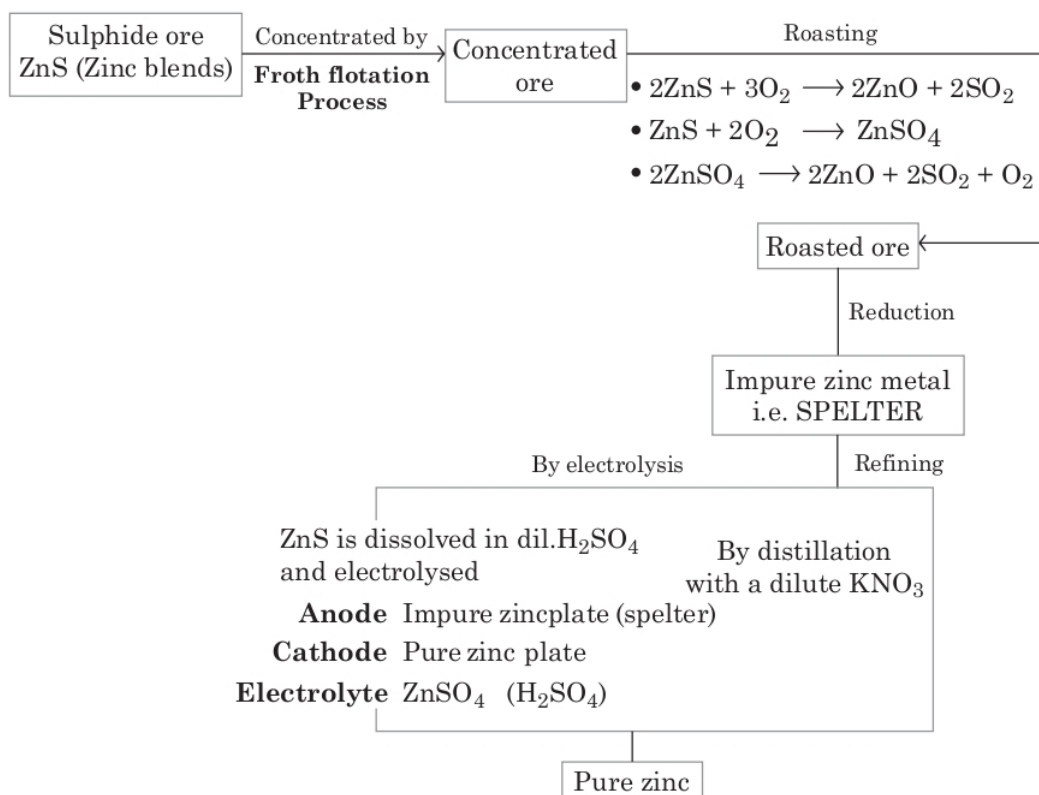
Occurrence

- Zinc blende or sphalerite- ZnS
- Calamine — $ZnCO_3$
- Zincite — ZnO

Common method of extraction Roasting followed by reduction with coke.

The metal may be purified by fractional distillation.

97–98% pure zinc is called **spelter**.



Uses : Making alloys like brass, german silver, for making dry cell, for galvanisation of iron, etc.