METALLURGY

4.1 INTRODUCTION

Metallurgy : The branch of chemistry which dealswith the method of extraction of metals from their ores by profitable means. ·

Metal : The element which tends to form positive ion is called a metal.

Minerals : The various compounds of metals which occur in the earth's crust and are obtained by mining are called minerals. In earth crust order of abundance of elements is. O > Si > Al > Fe.

A mineral may be single compound or a mixture.

Ore : The mineral from which a metal can be extracted profitably and easily is called an ore.

All ores are minerals but all minerals are not ores. (T/F).

Type of Ores :

(I) **Combined Ore :** Metals placed above H in electrochemical series are generally reactive i.e. why they generally found in combined state.

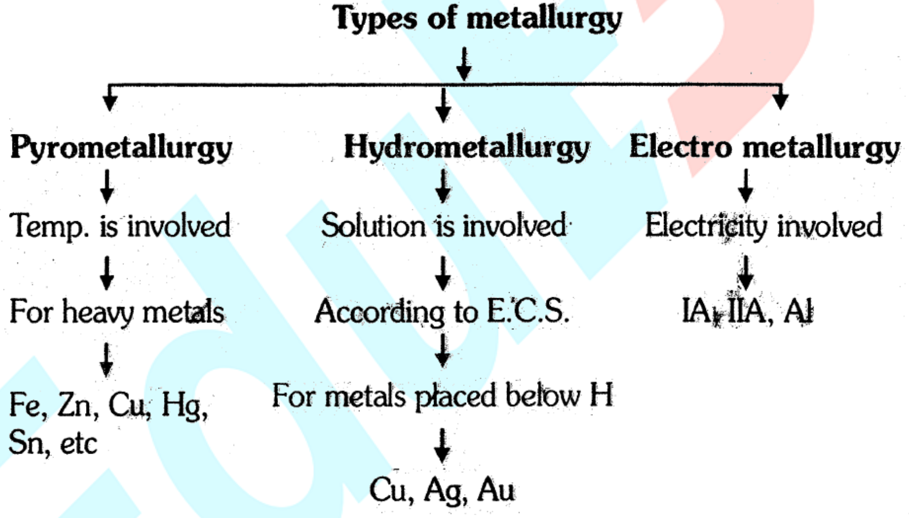
(a) Halide ore / Sulphate ore / Oxy ore : Metals are highly reactive (Li → Mg)

(b) Oxide ore : Reactive metal (Al to Sn)

(c) Sulphide ore : Metal placed near H or below H. (Pb, Hg, Cu, Ag)

(II) **Native Ore :** Metal placed below H in electrochemical series are generally found in native state. (Ag, Au, Cu, Pt etc.)

Gangue or matrix : The undesirable impurities present in an ore are called **gangue**.



4.2 STEPS INVOLVED IN THE EXTRACTION OF METALS

The extraction of a metal from its ore is completed in the following four steps.

(A) Concentration of the ore (B) Conversion of concentrated ore into oxide form.

(C) Reduction of the metal (D) Refining of the metal.

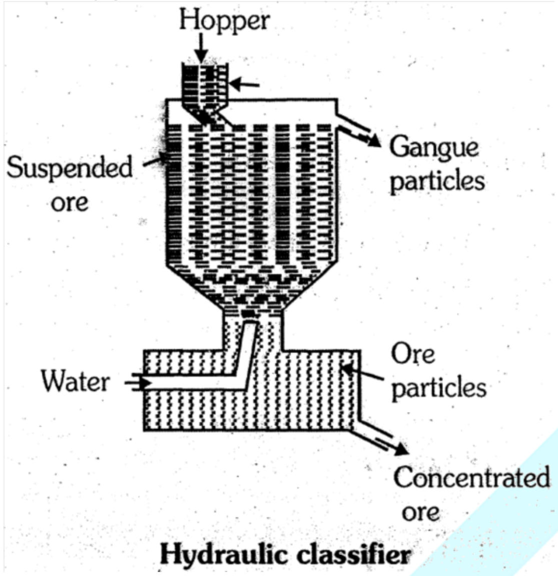
(A) Concentration of the ore or dressing or benefaction

The removal of impurities from the ore is called its concentration or to increase the concentration of ore in ore sample.Two process- (1)Physical (2) Chemical

(1) PHYSICAL

(i) Gravity separation (Levigation) : This method of concentration of the ore is based on the difference in the specific gravities of the ore and the gangue particles. Powdered ore is agitated with a running stream of water. The lighter gangue· particles are taken away by water while heavier ore particles settle down.

Ex. Oxygenated ore



Hydraulic classifier

(ii) Froth Floatation method

This method is mainly employed for the concentration of sulphide ores.

The method is based on the different wetting characteristics of the gangue arid the sulphide ore with water and oil. The gangue preferentially wetted by water and the ore by oil.

The crushed ore along with water is taken in a floatation cell. Various substances are added depending on the nature of the ore and a current of air is blown in. The substances added are usually of three types.

(a) Frothers : They generate a stable froth which rises to the top of the tank

Example of frother is pine oil, Eucalyptus oil, fatty acids etc.

(b) Collectors or floating agents : These attach themselves by polar group to the granules of the ores which then become water repellent and pass on into the froth.

Example : sodium ethyl xanthate, pine oil and fatty acid.

(c) Froth stabilizers : To stabilise froth.

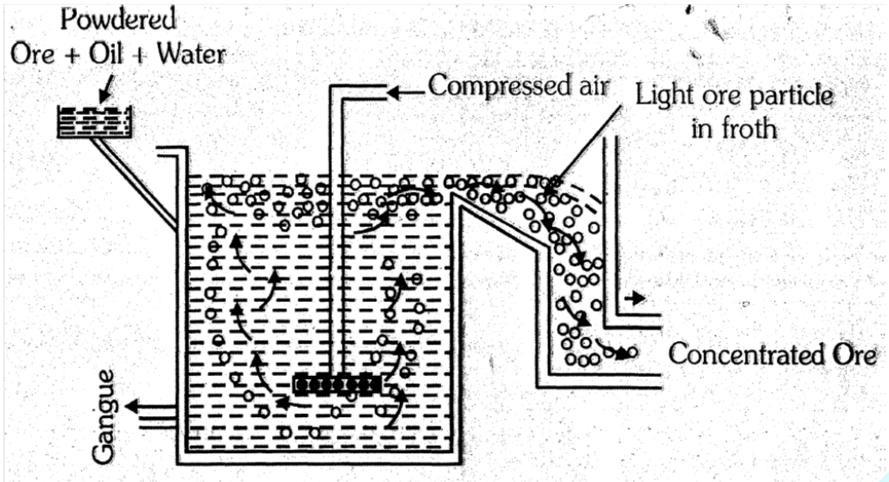
Ex. Cresol, Aniline etc.

(d) Depressants : These reagents activate or depress the floatation property and help in the separation of different sulphide ores present in a mixture.

e.g. NaCN.

Impurity of ZnS in PbS ore removed by NaCN

$NaCN + [PbS + ZnS] \rightarrow Na_2[Zn(CN)_4] + PbS \rightarrow$ form froth



[Froth floatation process]

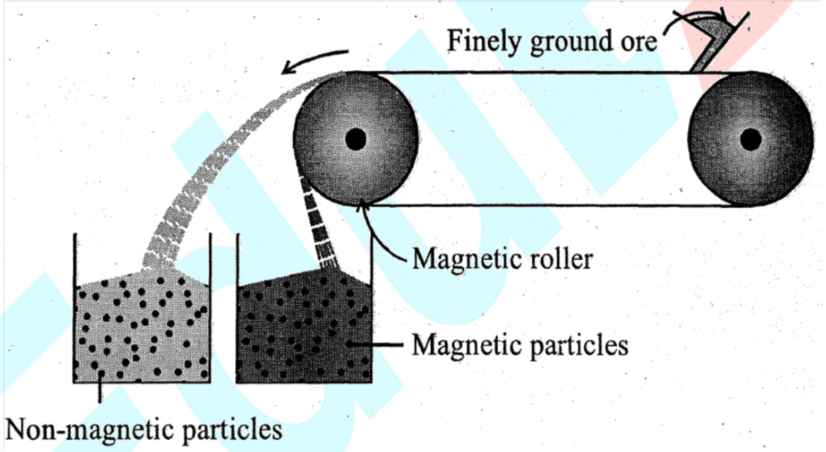
- Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'.
- For example, in· case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to go along with the froth.

(iii) Magnetic separation :

If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g. in case of iron ores)

e.g. • SnO_2 having the impurities of FeW04 + MnW04(Wolframite)

• $FeO.Cr_2O_3$ having the impurities of SiO_2.



2. CHEMICAL SEPARATION (LEACHING) : In this process we use suitable agent which react with ore to form water soluble complex while impurities remain insoluble. Applicable for Al, Ag, Au.

(a) Alluminium :
$$\begin{cases} \text{Red Bauxite} \rightarrow Al_2O_3.2H_2O + Fe_2O_3 (\text{Major impurity}) \\ \text{White Bauxite} \rightarrow Al_2O_3.2H_2O + SiO_2 (\text{Major impurity}) \end{cases}$$

(I) RED BAUXITE : Two processes

(i) Baeyer's process : NaOH is used.

$$Al_2O_3 + NaOH \longrightarrow NaAlO_2 \xrightarrow{\text{excess } H_2O} Al(OH)_3 + NaOH$$

$FeO + NaOH \rightarrow$ insoluble

$\downarrow$

Basic

(ii) Hall's process : Na_2CO_3 is used.

$Al_2O_3 + Na_2CO_3 \longrightarrow 2NaAlO_2$

(II) **WHITE BAUXITE :** One process

Serpeck's process: $(C+N_2)$ is used.

$Al_2O_3 + N_2 \xrightarrow[-CO\uparrow]{1800°C} AlN \xrightarrow{H_2O} Al(OH)_3 + NH_3\uparrow$ (not in NCERT)

$C + SiO_2 \longrightarrow CO_2\uparrow + Si\uparrow$

(b) **Ag and Au (CYANIDE PROCESS)**

(I) Ag $Ag_2S + 4NaCN \xrightarrow{2O_2} 2Na[Ag(CN)_2] + Na_2SO_4$ (in absence of O_2, reaction become reversible)

$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$

(II) Au $Au + KCN + H_2O_2 \xrightarrow{O_2} K[Au(CN)_2] + KOH$

$K[Au(CN)_2] + KOH + Zn \longrightarrow K_2ZnO_2 + KCN + H_2O + Au\downarrow$

(B) **Conversion of concentrated ore into oxide form**

Calcination and roasting

(a) Calcination : Calcination is a process in which ore is heated, generally in the absence of air, to expel water from a hydrated. or hydroxide ore and oxide or carbon dioxide from a carbonate ore at temperature below their melting points.

For Example: All carbonates, hydrated ore and hydroxide ore

Bauxite	$Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O$, $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$
Haematites	$2Fe_2O_3.3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$
Limestone	$CaCO_3 \rightarrow CaO + CO_2$
Siderite	$FeCO_3 \rightarrow FeO + CO_2$
Calamine	$ZnCO_3 \rightarrow ZnO + CO_2$
Cerussite	$PbCO_3 \rightarrow PbO + CO_2$
Malachite green	$CuCO_3.Cu(OH)_2 \rightarrow CuO + CO_2 + H_2O$

Advantages of Calcination :-

(i) Moisture is removed.

(ii) Organic matter is destroyed

(iii) The hydroxide and carbonates ores are converted into their oxides.

(iv) The ore become porous and easily workable

(b) **Roasting :** The removal of the excess sulphur contained in sulphide ores in the form of SO_2 by heating in an excess of air is called roasting.

The concentrated sulphide ore is heated in reverberatory furnace, below its melting point in the presence of an excess of air with or with out the addition of an external substance.

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$

$ZnS + 2O_2 \rightarrow ZnSO_4 \rightarrow ZnO + SO_3\uparrow$

$PbS + O_2 \xrightarrow{Roasting} PbO + SO_2\uparrow$

Thermal reduction

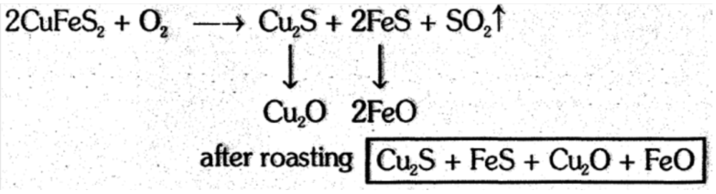
Some less stable metal' oxide further decompose into metal and oxygen.

$$Ag_2S + O_2 \xrightarrow[-SO_2\uparrow]{Roasting} Ag_2O \xrightarrow{300°C} 2Ag + \frac{1}{2}O_2\uparrow$$

$$HgS + O_2 \xrightarrow[-SO_2\uparrow]{Roasting} HgO \xrightarrow{400°C} Hg + \frac{1}{2}O_2$$

Partial roasting

$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$



Roasting in Fe metallurgy

$Fe_2O_3 + FeO$

Haematite

$Fe_3O_4 = Fe_2O_3 + FeO$

Magnetite

$FeCO_3 \xrightarrow{\Delta} FeO + CO_2\uparrow$

Siderite

Roasting → to prevent wastage of Fe as slag in reduction step

$2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$ (It does not form slag)

In reduction step	FeO	+	SiO_2	=	$FeSiO_3$
	(Flux)		(Impurity)		(Slag)

Advantages of Roasting :-

(i) Excess of sulphur is removed as volatile oxide.

$S + O_2 \rightarrow SO_2\uparrow$

(air)

(ii) The metal sulphide is converted into metal oxide.

(iii) Impurities of arsenic, antimony & phosphorous are removed as their volatile oxides.

$Sb_4 + 3O_2 \rightarrow 2Sb_2O_3\uparrow$

$As_4 + 3O_2 \rightarrow 2As_2O_3\uparrow$

$P_4 + 3O_2 \rightarrow 2P_2O_3\uparrow$

- For PbS, CuS and HgS partial roasting is carried out because these sulphide ore easily convert into metal by auto reduction process.

BEGINNER'S BOX-1

1. Match the following :

	Ore		**Main element**
(A)	Malachite	(P)	Fe
(B)	Siderite	(Q)	Pb
(C)	Cerrusite	(R)	Zn

(D)	Pyrolussite	(S)	Cu
(E)	Wurtzite	(T)	Mn

(1) A-S, B-Q, C-P, D-T, E-R
(2) A-S, B-P, C-Q, D-T, E-R
(3) A-Q, B-S, C-P, D-T, E-R
(4) A-R, B-Q, C-P, D-T, E-S

2. Assertion : Froth floatation is concentration method mainly used for sulphide ores.
Reason : Metal sulphides are highly soluble in water.
(1) A (2) B (3) C (4) D

3. Assertion : In cyanide process, the reaching is accomplished using NaCN.
Reason : CN^- ion reduces Ag, Au & Zn ions in the process.
(1) A (2) B (3) C (4) D

4. Match the ores listed in Colurnn-I with their correct, chemical formula listed in Column-H.

	Column I		**Column II**
(A)	Cassiterite	(p)	$FeCO_3$
(B)	Siderite	(q)	SnO_2
(C)	Cerussite	(r)	$PbSO_4$
(D)	Anglesite	(s)	$PbCO_3$

(1) A-q, B-p, C-s, D-r
(2) A-r, B-p, C-s, D-q
(3) A-p, B-q, C-s, D-r
(4) A-q, B-p, C-r, D-s

5. Which of the following contains both Mg & Ca :
(1) Magnesite (2) Calamine (3) Carnelite (4) Dolomite

6. Argentite is an ore of:-
(1) Iron (2) Gold (3) Platinum (4) Silver

7. If Bauxite consists of SiO_2 as impurity, this process is employed :-
(1) Hall's process (2) Bayer's process (3) Hoope's process (4) Serpeck's process

8. The impurities present in the ore is called:-
(1) Slag (2) Flux (3) Alloy (4) Gangue

9. $Ag_2S + NaCN \longrightarrow A, A + Zn \longrightarrow B$
B is a metal Hence A and B :-
(1) $Na_2[Zn(CN)_4]$, Zn
(2) $Na[Ag(CN)_2]$, Ag
(3) $Na[Ag(CN)_4]$, Ag
(4) $Na_3[Ag(CN)_4]$, Ag

10. Chemical leaching is useful in the concentration of:-
(1) bauxite (2) copper pyrities (3) cassiterite (4) None

(C) Reduction to the metal :

The calcined or roasted ore is then reduced to the metallic state by either of the following method :

(I) Chemical reduction :

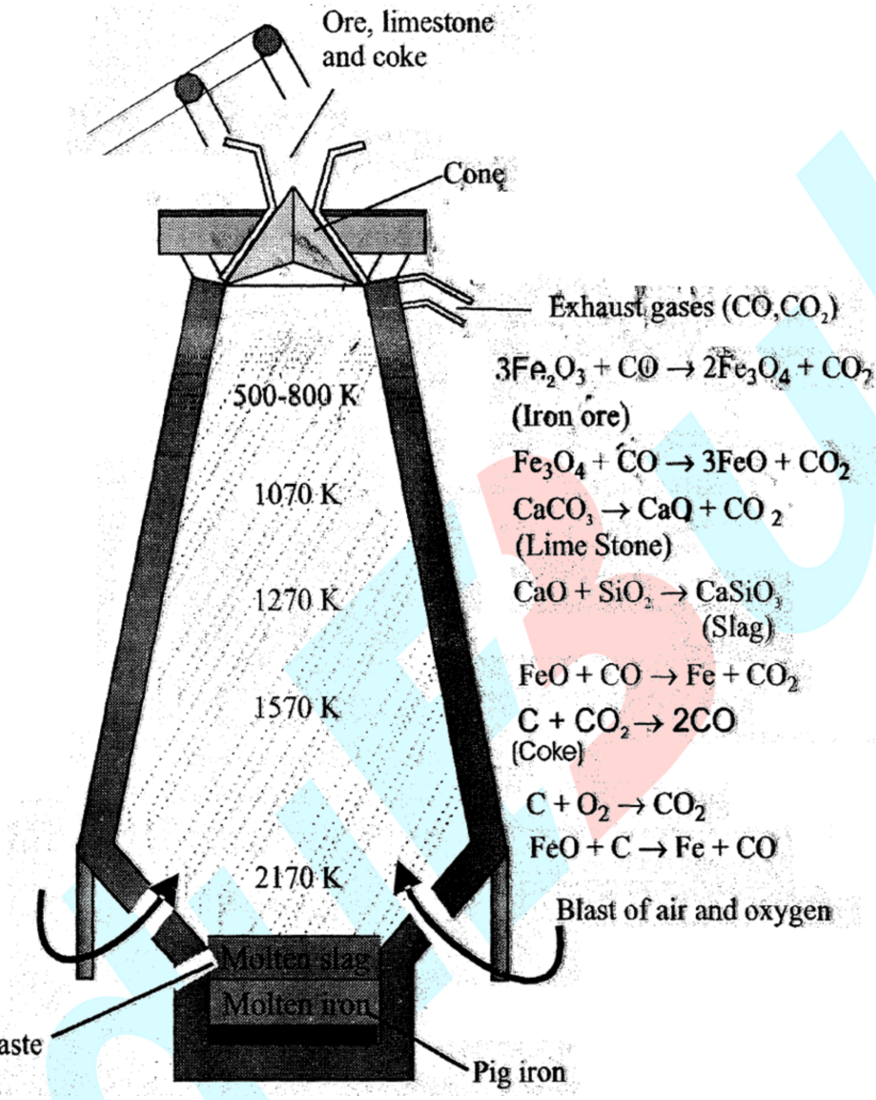
(i) Reduction by carbon (Smelting)

"Reduction of the oxide with carbon at high temperature is known as smelting".

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating them with coal or coke, in the blast furnace.

Metal Oxide + Coke + flux → Metal + $CO_2\uparrow$ + Slag

Example - Reaction in blast furnance :-



Metal oxide		**Coke**		**Molten metal**	
ZnO	+	C	$\longrightarrow$	$Zn + CO\uparrow$	At high temp.
PbO	+	C	$\longrightarrow$	$Pb + CO\uparrow$	
SnO_2	+	$2C$	$\longrightarrow$	$Sn + 2CO\uparrow$	
Fe_2O_3	+	$3C$	$\longrightarrow$	$2Fe + 3CO\uparrow$	

$$\left.\begin{aligned} Fe_2O_3 + 3CO &\longrightarrow 2Fe + 3CO_2\uparrow \\ PbO + CO &\longrightarrow Pb + CO_2\uparrow \\ SnO_2 + 2CO &\longrightarrow Sn + 2CO_2\uparrow \end{aligned}\right\} \text{low temp.}$$

FLUX : Substance used to convert non fusible impurities into fusible one. Three types of flux are used.

(a) Acidic Flux : Substance used to remove basic impurities (metal oxide)

For example $\underset{\text{(basic impurity)}}{CaO} + \underset{\text{(acidic flux)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$

Acidic flux are non metal oxide (SiO_2, P_2O_5 etc)

(b) Basic flux : Substance used to remove acidic impurities (non metal oxide)

For example : $\underset{\substack{\downarrow \\ \text{(basic flux)}}}{CaO} + \underset{\substack{\downarrow \\ \text{(acidic impurities)}}}{SiO_2} \longrightarrow \underset{\substack{\downarrow \\ \text{Slag}}}{CaSiO_3}$

Basic flux are metal oxide. (CaO, MgO, etc.)

(c) Neutral flux : Substance used in electrolytic reduction to decrease the fusion temperature and to increase the conductivity of the solution by providing free ions.

For example: $(\underset{\text{Cryolite}}{Na_3AlF_6} + \underset{\text{Flourspar}}{CaF_2})$, $CaCl_2$ etc.

Smelting in Cu-metallurgy

$$\begin{bmatrix} CuS + FeS \\ Cu_2O + FeO \end{bmatrix} + \underset{\substack{\downarrow \\ \text{only act as fuel (not RA)}}}{Coke} + \underset{\text{(flux)}}{SiO_2} \xrightarrow[\text{furnace}]{\text{In blast}} \underset{\text{(Copper matte)}}{Cu_2S} + FeS + slag$$

$MS + C \longrightarrow M + CS_2$ $\Delta G = +ve$ (non spotaneous)

$Cu_2O + FeS \longrightarrow Cu_2S + FeO$

$\underset{\text{imp}}{FeO} + \underset{\text{flux}}{SiO_2} \longrightarrow FeSiO_3$ (slag)

(ii) Alumino thermite process or thermite welding process : fn this process those metal oxide will be reduced which required high temperature and at high temperature carbon react with metal to from metal carbide.

In this process we use aluminium as a reducing agent due to :-

(i) Al has greater affinity towards oxygen as it forms most stabte oxide (Al_2O_3)

(ii) This reaction is highly exothermic in nature and once it start it will continue till all the metal oxide is reduced into metal.

For Cr, Mn, Fe : (a) $Cr_2O_3 + Al \longrightarrow Al_2O_3 + 2Cr$

(b) $Fe_2O_3 + Al \longrightarrow Al_2O_3 + 2Fe$

Note : Reaction (b) is used in welding of railway tracks.

(II) Self reduction

Compounds of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc.

Their sulphide ores are partially roasted to give some oxide. This oxide is now reduced to the metal by the remaining sulphide ore at elevated temperatures in the absence of air. The process is known as self reduction.

Self reduction for Pb :-

$\underset{\text{(Galena)}}{2PbS} + \underset{\text{(air)}}{3O_2} \xrightarrow{\text{Roasting}} 2PbO + 2SO_2\uparrow$

$PbS + 2PbO \xrightarrow[\text{Absence of air}]{\text{High temp.}} \underset{\text{(Self reduction)}}{3Pb + SO_2\uparrow}$

Self reduction in Cu Metallurgy or bessemerisation

$Cu_2S + FeS + \underset{\text{(flux)}}{SiO_2} \longrightarrow$ Blister copper + slag

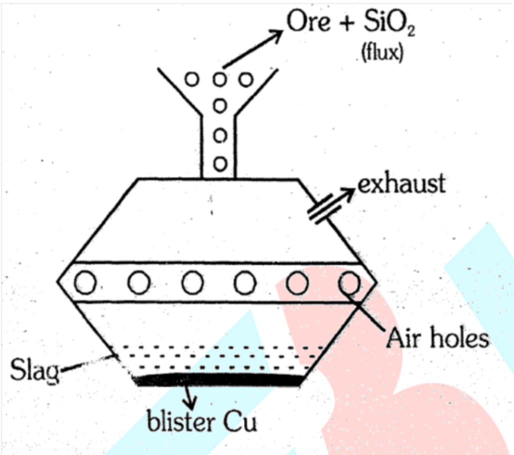
$FeS + O_2 \longrightarrow FeO + SO_2\uparrow$

$\underset{\text{gangue}}{FeO} + \underset{\text{flux}}{SiO_2} \longrightarrow FeSiO_3$ (slag)

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SOI_2\uparrow$

Self reduction for Cu :- $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$



Bessemer convertor

(III) **Metal displacement method :** In this method, compound is reacted with a more electropositive & more reactive metal which displaces, the metal from the solution.

For Example $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$

Kroll's Process

$TiCl_4 + Mg \longrightarrow 2MgCl_2 + Ti$ (Mg acts reducing agent)

(IV) **Electrolytic reduction**

This process is mainly used for the extraction of highly elctropostive metals. IA, IIA & Al Electrolysis is carried out in Cl large cell and a small amount of another suitable electrolyte is added which

(a) Lowers the rnelting point of the main electrolyte
(b) Enhances its conductivity
(c) Reduces corrosion troubles

e.g. Manufacture of metallic sodium (Down's process)

Molten NaCl containing a little $CaCl_2$ is electrolysed between graphite aonode and iron cathode. The various reactions that take place are :

On Fusion : $NaCl \rightleftharpoons Na^+ + Cl^-$ (Ions become mobile)

On Electrolysis : **At Cathode :-** $Na^+ + e^- \rightarrow Na$ (reduction) (Metallic sodium)

At Anode :- $2Cl^- \rightarrow Cl_2\,(g) + 2e^-$

Hall Heroult Process :

This process is used for extraction of Al from alumina. The extraction of Al from Al_2O_3 is quite difficult because

(i) Fusion temperature of Alumina is quite high (2050°C). Even more than boilling point of Al (1150°C).
(ii) It is a bad conductor of electricity. To overcome these difficulties we mix some amount of neutral flux. [$Na_3AlF_6 + CaF_2$]. Neutral flux provides free ions to the solution which decreases the fusion temperature of Alumina from 2050°C to 950°C.

(i) From cryolite → $AlF_3 \longrightarrow Al^{+3} + 3F^-$

At cathode: $Al^{+3} + 3e^- \rightarrow Al$ (reduction)

At anode: $2F^- - 3e^- \rightarrow \frac{3}{2}F_2$

F_2 reacts with Al_2O_3 $3F_2 + Al_2O_3 \longrightarrow 2AlF_3 + \frac{3}{2}O_2$

So at anode O_2 gas is liberated which on reaction with graphite anode convert into CO_2 & destroy the anode.

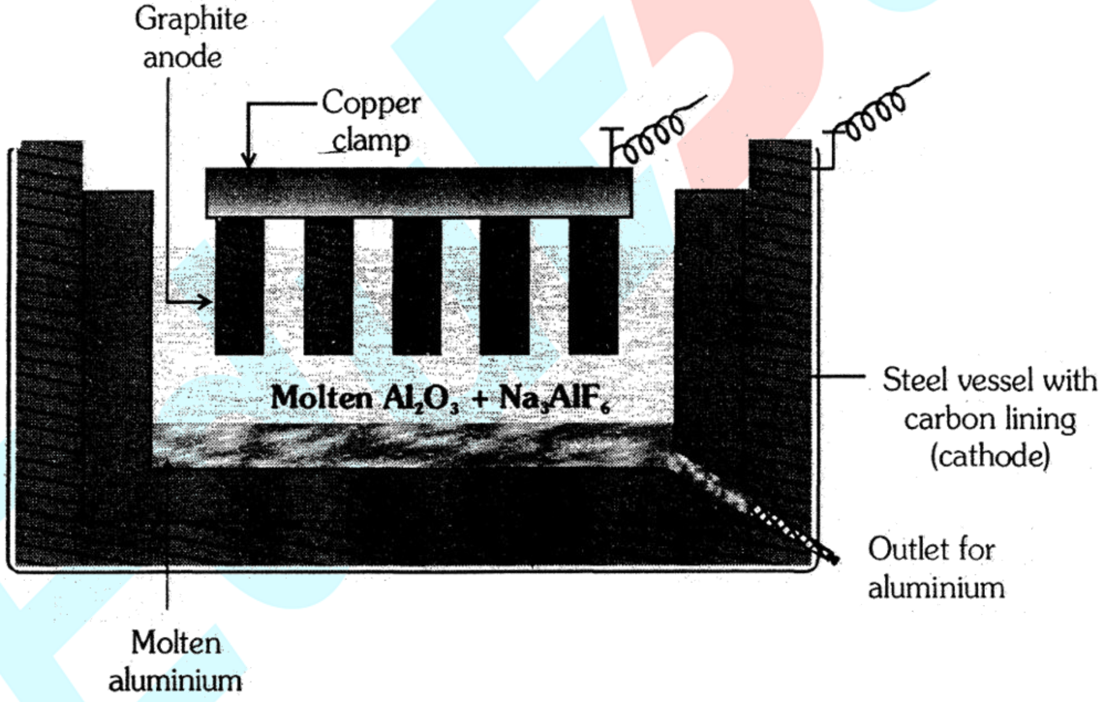
$C + O_2 \longrightarrow CO_2\uparrow$

(ii) From Al_2O_3

At Cathode : $Al^{+3} + 3e^- \longrightarrow Al$ (reduction)

At Anode : $C(s) + 2O^{-2} \longrightarrow CO_2(g) + 4e^-$

The main drawback of this process it that anode should be changed frequently.



REFINING OF METALS

Metals obtained by the reduction of its compound still contains some objectionable and have to be refined. Depending upon the nature of the metal and impurities, the following methods are used for purification of the metal.

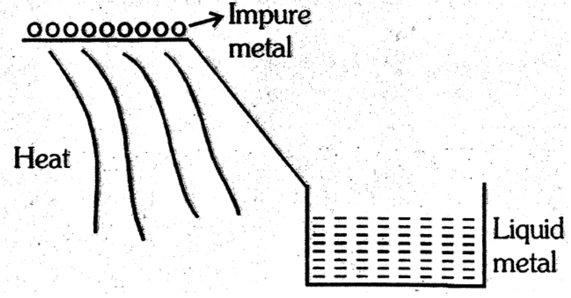
(I) Physical Process :

(i) Liquation : This method is used for the refining of metals having low melting point and are associated with high melting impurities.

Ex. Pb, Sn, Sb and Bi.

The impure metal is heated on the sloping hearth of a furnace.

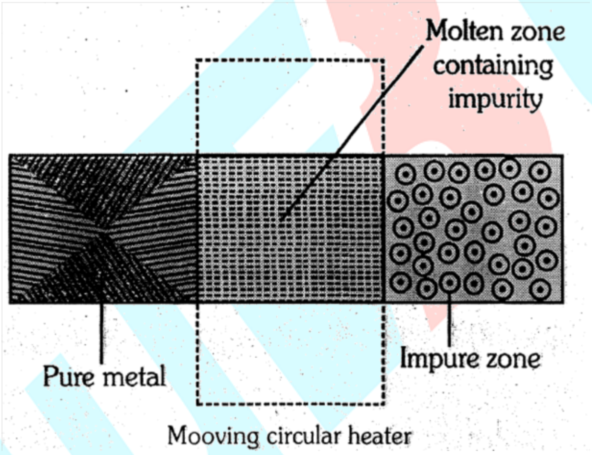
The pure metal flows down leaving behind the non- fusible impurities on the hearth.



(ii) Distillation : Metals having low boiling point are refined by this method, for example, zinc, cadmium and mercury.

(iii) Zone refining : Metals of very high purity are obtained by zone refining. This refining method is based on the fact that impurities tend to remain dissolved in molten metal.

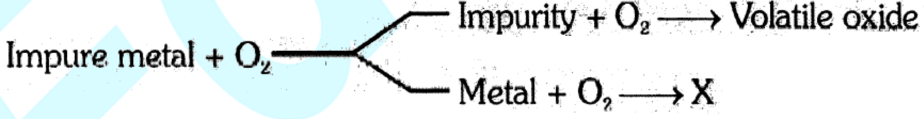
Ge, Si and Ga used as semiconductors are refined in this manner.

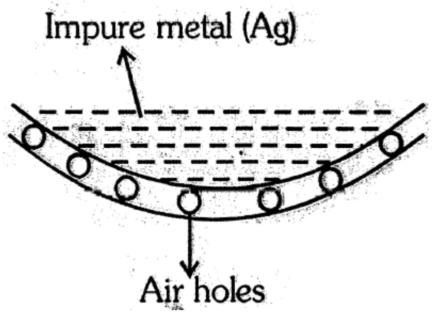


(II) CHEMICAL PROCESS :-

(i) Cupellation : This process is used to purify silver containing the impurities of Pb.

This process is used when impurity have greater affinity towards O_2 while metal does not have.



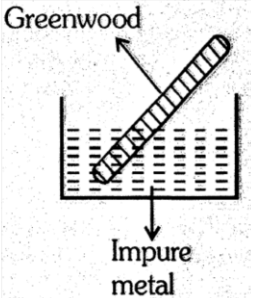


(ii) Poling : Used to purify Cu, Pb.

This process is used for the metal having the impurity o their own oxide. In this process a green wooden pole is heated with molten metal which provide C and H to metal oxide which reduce impurity of metal oxide to metal.

$2Cu + O_2 \longrightarrow Cu_2O\uparrow$

$2Cu_2O + CH_4 \longrightarrow 6Cu + CO + 2H_2\uparrow$



(iii) Bessemerisation : Actually it is the key principle involve to removal of impurities by oxidation with air being blown oxidise to molten metal.

Impure metal is heated in a furnace· and a blast of compressed air is blown which oxidise the impurity into their oxides and that can be removed in the form of slag .

$2Mn + O_2 \longrightarrow 2Mn0$

$Si + O_2 \longrightarrow SiO_2$

(III) ELECTRO-REFINING METALS

Metals such as Cu, Ag, Zn, Sn, Pb, Al, Ni, Cr are refined by this method.

The impure metal is made the anode of an electrolytic cell, while cathode is thin plate of pure metal. Electrolyte is the solution of a salt of the metal.

On passing the electric current pure metal from the anode dissolves and gets deposited at the cathode. The soluble impurities go into the solution while insoluble or less electropositive impurities settle down below the anode as **anode mud** or sludge, For Example

- Electrorefining or Copper
  - Anode : Blister copper (98%)
  - Cathode : Pure copper
  - Electrolyte : An aqueous solution of $CuSO_4$ (15%) + 5% dil H_2SO_4
- Electrorefining of Silver
  - Anode : Aq $AgNO_3$ + 1% dil HNO_3 on passing electricity impure anode dissolves and pure Ag is deposited at the cathode.
- Electrefining of Pb (Bett's process)
  - Anode : Impure lead,
  - Cathode : Pure lead
  - Electrolyte : A mixture of $PbSiF_6$ and H_2SiF_6
- elctrorefining of Al (Hoope's process)
  - Anode : Impure Al,
  - Cathode : Pure Al
  - Electrolyte : A mixture of Na_3AlF_6 + CaF_2

(IV) Vapour Phase Refining (Thermal decomposition)

(i) Van – Arkel process :

This method is very useful for removing all the oxygen & nitrogen present in the form of impurity.

(i) Employed to get metal in very pure form of small quantities.

(ii) In this method , the metal is converted into a volatile unstable compound (e.g. iodide), and impurities are not affected during compound formation.

(iii) The compound thus obtained is decomposed to get the pure metal.

(iv) Employed for purification of metals like titanium and zirconium.

$$\underset{\text{Impure}}{Ti(s)} + 2I_2(g) \xrightarrow{523k} TiI_4(g)$$

$$TiI_4(g) \xrightarrow{1800k} Ti(s)\ (pure) + 2I_2(g)$$

(ii) Mond's process

(i) Nickel is purified by using CO gas. This innvoles the formation of nickel tetracarbonyl.

$$Ni_{(impure)} + 4CO \xrightarrow[350K]{330K} [Ni(CO)_4] \xrightarrow[470K]{450K} Ni_{(pure)} + 4CO\uparrow$$

BEGINNER'S BOX-2

1. Copper matte, consists of:-
(1) Copper oxide and ferrous sulphide
(2) Copper sulphide and ferrous oxide
(3) Copper sulphide and ferrous sulphide
(4) Copper oxide and ferrous oxide

2. Product obtained after Bessemerisation is called as ... because ......
(1) Concentrated copper ; copper percentage is high
(2) Copper matte ; of its appearance
(3) Blister copper ; of its appearance
(4) Ultra pure copper ; 100 percent copper

3. Matte is obtained after this step -
(1) Froth floatation (2) Roasting
(3) Smelting (4) Refining

4. Copper glance is .... type of ore-
(1) Carbonate (2) Sulphide (3) Oxide (4) Sulphate

5. High purity copper is obtained by -
(1) Zone refining (2) Poling
(3) Electrolytic refining (4) Cupellation

6. The function of flux during the smellting of oreis:
(1) To make the ore porous (2) To remove gangue
(3) To facilitate reduction (4) To facilitate oxidation

7. The following equation represents a method of Purification of nickel by:-
$Ni(impure) + 4CO \xrightarrow{320\,K} Ni(CO)_4 \xrightarrow{420\,K} Ni(pure) + 4CO$
(1) Cupellation (2) Mond's process
(3) Van Arkel method (4) Zone refining

8. The slag obtained during the extraction of copper from copper pyrites is composed of :-

(1) Cu_2S (2) $CuSiO_3$ (3) $FeSiO_3$ (4) SiO_2

9. Which of the following reaction is a part of Hall's process :-

(1) $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

(2) $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$

(3) $AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$

(4) $Al_2O_3.2H_2O + 2Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O$

10. Which method of purification is represented by the following equations

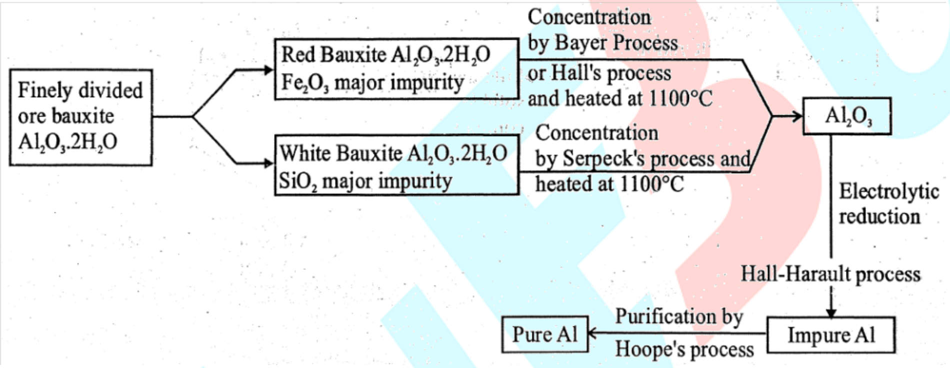
$Ti + 2I_2 \xrightarrow{523\,K} TiI_4 \xrightarrow{1700\,K} Ti + 2I_2$

(1) Cupellation (2) Poling

(3) Van Arkel (4) Zone refining

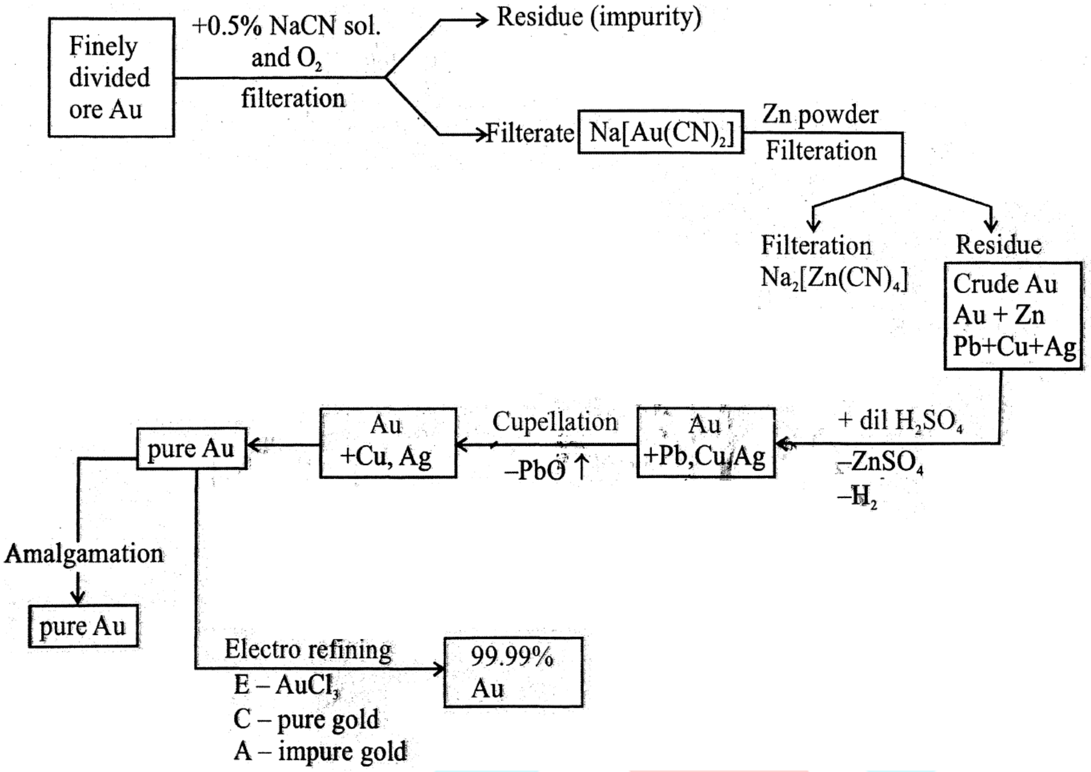
Al

Ore-Bauxite $Al_2O_3.2H_2O$



Au

Ore-Auriferrous Rock



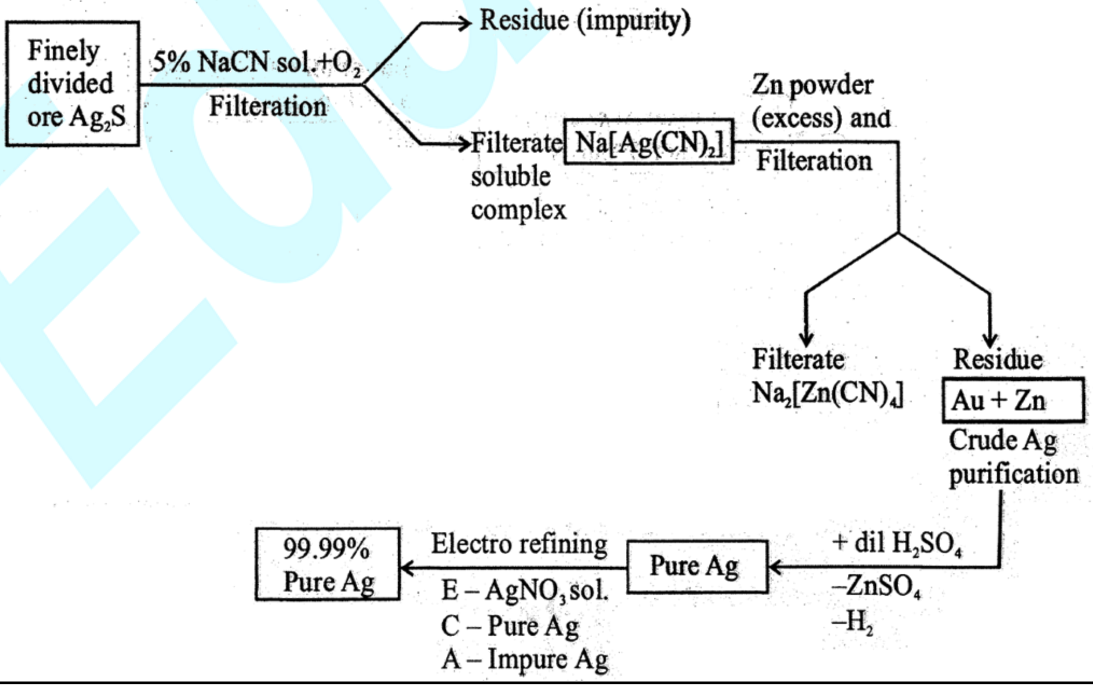
Reaction involved :

(a) $4Au + 8NaCN + O_2 + 2H_2O \longrightarrow \underset{\text{(soluble)}}{4Na[Au[CN)_2]} + 4NaOH$

(b) $\underset{\text{(soluble)}}{2Na[Au(CN)_2]} + Zn \longrightarrow \underset{\text{(soluble)}}{Na_2[Zn(CN)_4]} + 2Au\downarrow$

Ag

Ore – Argentite Ag_2S



Reaction involved :

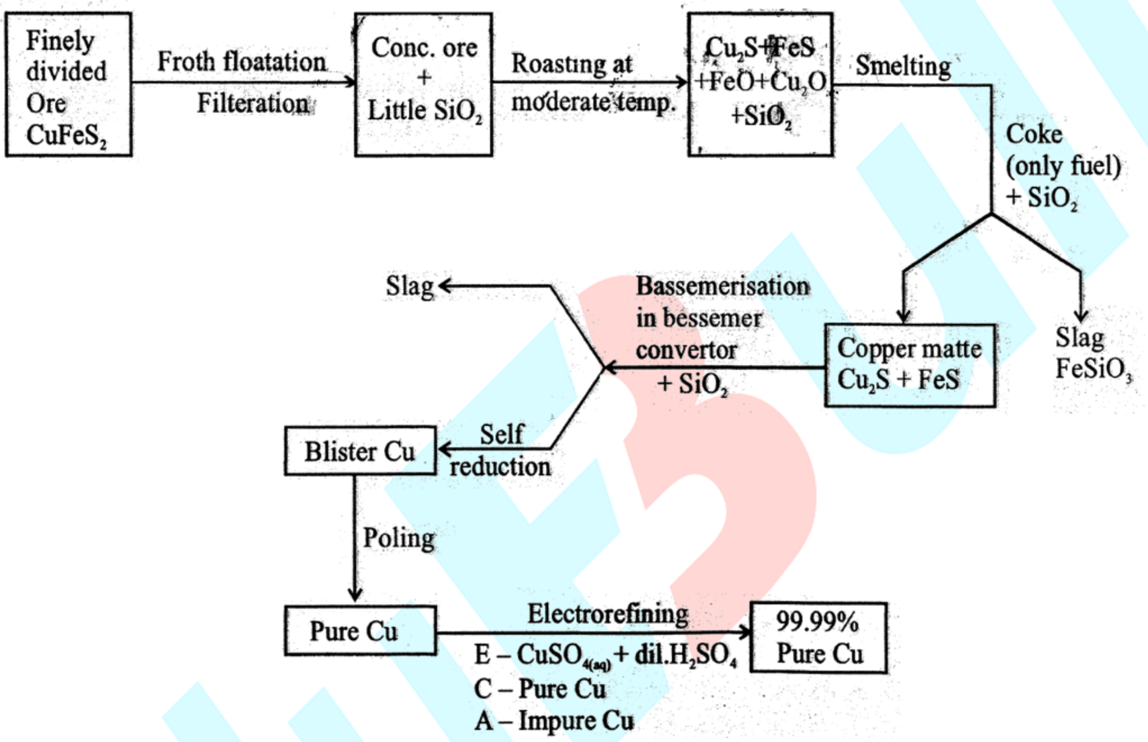
(a) $As_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S \xrightarrow{+O_2+H_2O} Na_2SO_4 + 'S' + 2NaOH$

⇒ O_2 is used to make reaction irreversible which remove Na_2S as $Na_2SO_4 + S$

(b) $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + Ag\downarrow$

Cu

Ore – $CuFeS_2$ copper pyrites



Reaction involved

(a) Roasting step

$$CuFeS_2 + O_2 \longrightarrow Cu_2S + FeS + SO_2\uparrow$$

$$\left.\begin{array}{l} FeS + O_2 \longrightarrow FeO + SO_2\uparrow \\ Cu_2S + O_2 \longrightarrow Cu_2O + SO_2\uparrow \end{array}\right] \text{Very less}$$

$$\boxed{\begin{array}{c} Cu_2S + FeS + \underset{\text{less}}{Cu_2O} + \underset{\text{less}}{FeO} \end{array}}$$

(b) Smelting step :-

Cu_2S remain unaffected again because carbon reduction occurs only for oxide and not for sulphide.

$FeS + Cu_2O \longrightarrow FeO + Cu_2S$

$$\left.\begin{array}{l} FeO + SiO_2 \longrightarrow FeSiO_3 \\ CaO + SiO_2 \longrightarrow CaSiO_3 \end{array}\right] \text{Slag}$$

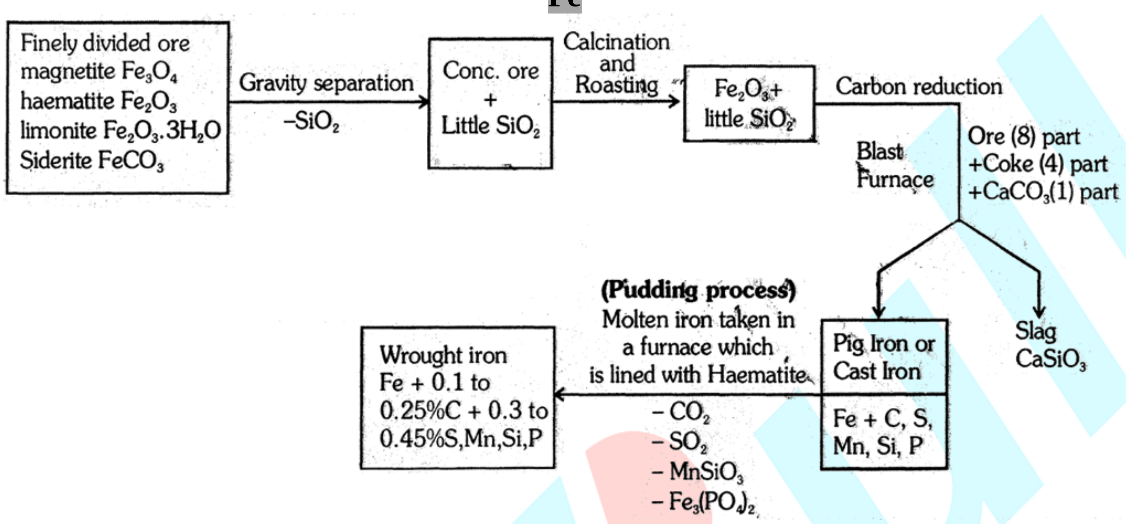
$Cu_2S + FeS$ Copper Matte

(c) Bassemer convertor reaction :-

$FeS + O_2 \longrightarrow FeO + SO_2$-　　　　$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

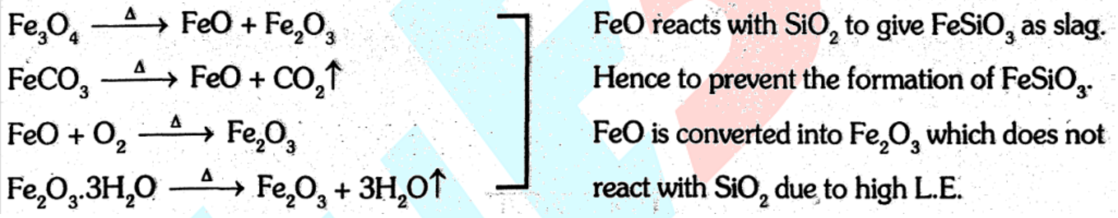
$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$-　　　　$Cu_2O + Cu_2S \longrightarrow \underset{\text{Blister Cu}}{Cu} + SO_2$-

Fe



Reaction involved :

(1)　Roasting step :



$Fe_3O_4 \xrightarrow{\Delta} FeO + Fe_2O_3$

$FeCO_3 \xrightarrow{\Delta} FeO + CO_2\uparrow$

$FeO + O_2 \xrightarrow{\Delta} Fe_2O_3$

$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O\uparrow$

FeO reacts with SiO_2 to give $FeSiO_3$ as slag. Hence to prevent the formation of $FeSiO_3$. FeO is converted into Fe_2O_3 which does not react with SiO_2 due to high L.E.

GOLDEN KEY POINTS

- **Types of Iron :-**

  Pig iron ⟶ Cast iron → Steel iron → Wrought iron

  (i) Cast iron or pig iron

  It is most impure form of Iron and contains the highest proportion of carbon (2.5–4%) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig contain 2.5 to 5%.

  (ii) Wrought iron (Fibrous iron) or malleable iron

  It is the purest form of iron and contains minimum amount of carbon (0.12–0.25%) and less than 5% of other impurities.

  (iii) Steel

  It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is midway between cast iron and wrought iron, it contains 0.25–2% carbon. Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

  Order of M.P. WI > Steel > CI or PI
- Useful gas NH_3 is evolved in the leaching of bauxite by serpeck's process.
- In the electrolytic reduction of Al_2O_3, cryolite (Na_3AlF_6) is added along with CaF_2 (fluorspar) to-

  -decrease m.p. of Al_2O_3

- decrease viscocity of electrolyte (CaF_2 is used)
- increase conductivity

- In the electrolytic reduction, graphite anode gets corroded or finished due to reaction with O_2 liberated at anode, hence it had to be changed periodically.
- In the electrolytic refining (4th step) no electrodes are used. In the Hoope's process molten pure Al is used as cathode and molten impure Al is used an anode.

4.3 THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM)

It is explanation of the feasibility of pyrometallurgical process by using gibbs, equation

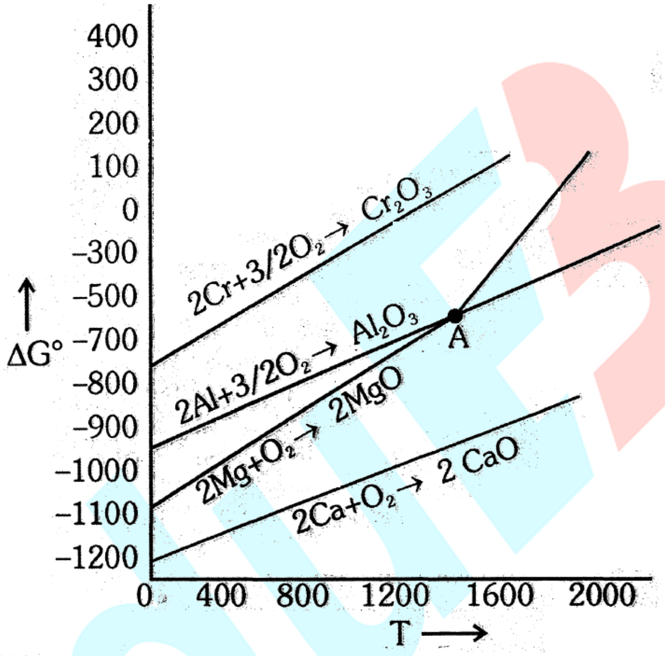
$$\Delta G = \Delta H - T\Delta S$$

If $\Delta G = -ve$ Process is stable or spontaneous

$\Delta G = +ve$ or Less $-ve$ the process is Unstable or non-spontaneous.

When pyrometallurgical process contains more than one type of reaction then s tability of reaction can be explain by Ellingham diagram Ellingham diagram contains plot ΔG vs T

(I)



$\Delta G = -Ve$

$$Ca + \boxed{MgO \mid Al_2O_3 \mid Cr_2O_3} \longrightarrow CaO + \boxed{Mg \mid Al \mid Cr}$$

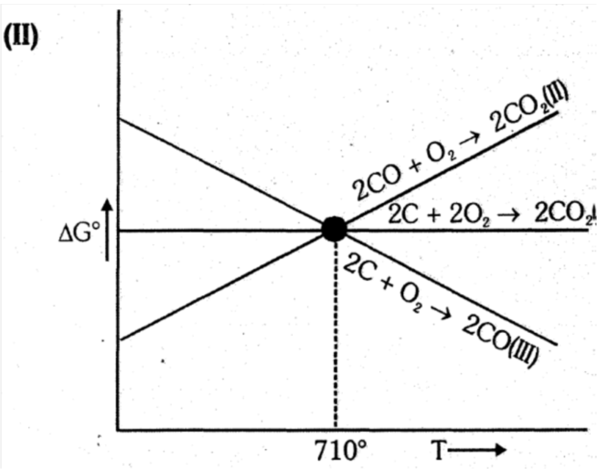
$\Delta G = +Ve$

$$Cr + \boxed{CaO \mid MgO \mid Al_2O_3} \longrightarrow Cr_2O_3 + \boxed{Al \mid Mg \mid Ca}$$

According to Ellingham diagram, the metal below can reduce the oxide of metal above it in the curve, as affinity of metal below for oxygen is more.

Example Al Metal can reduce Cr_2O_3 but can not reduce MgO & CaO .

At very high T after 'A' Point Al metal can reduce MgO because Formation of MgO contains less $-ve$ ΔG.



According to diagram at high T (710°C OR above 710°C) Oxidation of C contains more –ve ΔG so at high T 'C' is good Reducing agent.

At Low T (below 710°C) Oxidation of CO contains more –ve ΔG so at Low T, CO is good Reducing agent.

BEGINNER'S BOX-3

1. The appropriate flux for removing FeO will be ''

(1) SiO_2 (2) CaO (3) MgO (4) Al

2. Match the following :

Metallurgical process	Methods
(A) Copper glance → Cu	(P) Leaching by NaOH followed by electrolytic reduction
(B) Bauxite → Al	(Q) Froth flotation, partial roasting & self reduction.
(C) Cerussite → Pb	(R) Heating in presence of dry HCl followed by electrolysis
(D) $MgCl_2.6H_2O$ → Mg	(S) Calcination followed by carbon reduction

(1) A-R, B-P, C-S, D-Q (2) A-Q, B-P, C-S, D-R
(3) A-P, B-Q, C-S, D-R (4) A-S, 8-P, C-Q, D-R

3. In the metallurgy of iron, during smelting process, CO is main reducing agent at the upper part of blast furnace, because

(1) It is less concentrated in upper atmosphere
(2) The CO_2 formed can be easily removed.
(3) In the lower atmosphere, there is no oxide to be reduced
(4) The entropy change during CO/CO_2 is negative

4. Favourable reducing agent for ZnO/Zn is:-

(1) C at high temperature (2) CO at high temperature
(3) Cu at high temperature (4) Cu at low temperature

5. Which of the following is true regarding recovery of copper from its low grade (lean) ores.

(1) Zn is advantageous economically
(2) Fe is advantageous economically
(3) Both Fe and Zn can he used and are equally advantageous
(4) None of them can be used because Cu is less reactive

6. The slope of a line on Ellingham diagram for a process M/MO is:-

(1) $-\dfrac{\Delta G}{R}$ (2) $-\Delta S$ (3) ΔS (4) $-\dfrac{\Delta S}{T}$

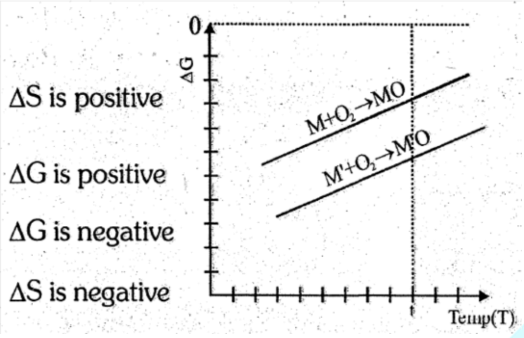
7. The true statement is at temperature T

(1) $M'(s) + \frac{1}{2}O_2(g) \rightarrow M'O(s)$

(2) $M'(s) + MO(s) \rightarrow M'O(s) + M(s)$

(3) $M'O(s) + MO(s) \rightarrow M'O(s) + M(s)$

(4) $M'(s) + O_2(g) \rightarrow M'O(s)$



8. Auto reduction process is used in extraction of :

(1) Cu (2) Hg (3) Ph (4) All of these

9. Which is not the correct process-mineral matching in metallurgical extraction.

(A) Leaching : silver (B) Zone refining : lead

(C) Liquation : tin (D) Van Arkel : Zr

10. Consider the following metallurgical processes:-

(i) Heating impure metal with CO and distilling the resulting volatile carbonyl (boiling point 43°C) and finally decomposing at 150°C to 200°C to get the pure metal.

(ii) Heating the sulphide Ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react with unchanged sulphide.

(iii) Electrolysing the molten electrolyte containing approximately equal amounts of the metal chloride and $CaCl_2$ to obtain the metal.

The process used for obtaining sodium, nickel and copper are respectively.

(1) (i), (ii) and (iii) (2) (ii), (iii) and (i)

(2) (iii), (i) and (ii) (4) (ii), (i) and (iii)

ANSWER KEY

BEGINNER'S BOX-1

1.	(2)	**2.**	(3)	**3.**	(3)	**4.**	(1)	**5.**	(4)	**6.**	(4)	**7.**	(4)
8.	(4)	**9.**	(2)	**10.**	(1)								

BEGINNER'S BOX-2

1.	(3)	**2.**	(3)	**3.**	(3)	**4.**	(2)	**5.**	(3)	**6.**	(2)	**7.**	(2)
8.	(3)	**9.**	(4)	**10.**	(3)								

BEGINNER'S BOX-3

1.	(1)	**2.**	(2)	**3.**	(4)	**4.**	(1)	**5.**	(2)	**6.**	(2)	**7.**	(4)
8.	(4)	**9.**	(2)	**10.**	(3)								

SOME IMPORTANT ALLOY

1. Bronze - Cu (75:90 %) + Sn (10-25 %)
2. Brass - Cu (60-80 %) + Zn(20-40%)
3. Gun metal - (Cu+ Zn+ Sn) (87 : 3 : 10)
4. German Silver - Cu + Zn + Ni (2 : 1 : 1)
5. Nichrome - (Ni + Cr + Fe)
6. Alloys of steel -
   (a) Chromium steel - Cr(2-4%)
   (b) Nickel Steel - Ni(3-5%)
   (c) Stainless steel - Cr (12-14%) & Ni (2-4%) Cr forms oxide layer & Protects Iron From Rusting
   (d) Invar (इनवार) - Ni (36%)

APPENDIX

LIST OF ORES AND THEIR NAMES

TYPES OF ORES	S.N.	FORMULA OF THE ORE	NAME
Oxide Ore	1.	ZnO (Philosopher's Wool)	Zincite
	2.	MnO_2	Pyrolusite
	3.	SnO_2	Cassiterite (Tin stone)
	4.	Cu_2O	Cuprite (Ruby Copper)
	5.	Fe_2O_3	Haematite
	6.	$Al_2O_3.2H_2O$	Bauxite
	7.	$FeO.Cr_2O_3$	Chromite
	8.	Fe_3O_4	Magnetite
	9.	$Fe_2O_3.3H_2O$	Limonite
	10.	TiO_2	Rutile
Sulphide Ore	1.	ZnS	Zinc Blende (Sphalerite)
	2.	HgS	Cinnabar
	3.	PbS	Galena
	4.	Ag_2S	Argentite or Silver Glance
	5.	FeS_2	Iron pyrites (Fool's gold)
	6.	$CuFeS_2$, CuS.FeS	Copper pyrites (Chalcopyrites)
	7.	$Cu_2S.Ag_2S$	Copper silver glance
	8.	$Ag_2S.Sb_2S_3$	Pyargirite (Ruby silver)
	9.	Cu_2S(Copper glance)	Chalcocite
Halide Ore	1.	NaCl	Rock Salt
	2.	AgCl	Horn Silver
	3.	CaF_2	Flourspar
	4.	$AlF_3.3NaF$	Cryolite
	5.	$KCl.MgCl_2.6H_2O$	Carnelite
Carbonate Ore	1.	$MgCO_3$	Magnesite
	2.	$CaCO_3$	Lime stone
	3.	$MgCO_3.CaCO_3$	Dolomite
	4.	$ZnCO_3$ (Smithosonite)	Calamine
	5.	$PbCO_3$	Cerrusite

	6. 7. 8.	$FeCO_3$ $CuCO_3.Cu(OH)_2$ $2CuCO_3.Cu(OH)_2$	Siderite Malachite Azurite
Sulphate Ore	1. 2. 3.	$CaSO_4.2H_2O$ $MgSO_4.7H_2O$ $K_2SO_4.Al_2(SO_4)_3.24H_2O$	Gypsum Epsomite or Epsom salt Alum
Nitrate Ore	1. 2.	$NaNO_3$ KNO_3	Chile-Salt Peter Salt peter or Indian salt peter
Phosphate Ore	1.	$Ca_3(PO_4)_2$	Rock Phosphate