Chapter 6

General Principles and Processes of Isolation of Elements

Minerals, Ores & Concentration of Ores

Minerals, Ores and Concentration of Ores:

Minerals: Naturally occurring chemical substance in which metal exist either in its free state or in combined state is called mineral.
Ore: Mineral from which metal can be conventionally and economically extracted is called ore & impurities associated with it is called gangue or matrix.
Types of Ores:

Sulphide Ores:	
Galena: PbS,	Cinnabar: HgS,
Zinc blend: Zns,	Chalcopyrite: $CuFeS_2$
Copper glance: Cu_2S	Fool's Gold: FeS_2

Fig: Galena

Oxide Ores:	
Bauxite: $Al_2O_3.\ 2H_2O$	Haematite: Fe_2O_3
Limonite: $Fe_2O_3.\ 3H_2O$	Tin stone or Cassiterite: SnO_2

Carbonate Ores: Siderite: $FeCO_3$ Calamine $ZnCO_3$
Malacite: $Cu(OH)_2CuCO_3$ Dolomite $CaCO_3.\ MgCO_3.\ 2H_2O$

lime stone: $CaCO_3$

Fig: Lime stone

Sulphate Ores:	
Gypsom: $CaSO_4.2H_2O$	Anylesite $PbSO_4$
Glauber's salt: Na_2SO_4. 10 H_2O	Mohr's salt: $FeSO_4$. $(NH_4)_2SO_4$. $6H_2O$
Halide Ores:	
Rock salt: NaCl	Cryolite: Na_3AlF_6
Fluorspar: CaF_2	Carnallite: KCl. $MgCl_2$. $6H_2O$

Nitrate Ores: Chile Saltpeter: $NaNO_3$
Indian Salt petre: KNO_3

Native Ores: Those metals which are chemically less reactive. They occur in the earth crust in form of free state (lumbs)
e.g: Cu, Ag, Au, Hg, Pd, Pt, Bi.

General principles and processes involved in the extraction of metal from its ore:

The extraction of metal from its ore is completed in five steps:

Step I: Pulverization: The crushing of ore to powdered state is called pulverization.
Step II: concentration or Dressing or Beneficiation of ore
Step III: Conversion of Concentrated ore into oxide form
step IV: Reduction of oxide to the metal
Step V: Purification or refining of crude metal:

Step I: Pulverization: The crushing of ore to powdered state is called pulverization
This process in stamp mill or ball mill

Step II: Concentration or Dressing or beneficiation of Ore

(a) **By Gravity separation:** Ore particles are heavier than the gangue particles. This is used for the separation of most of the gangue particles:

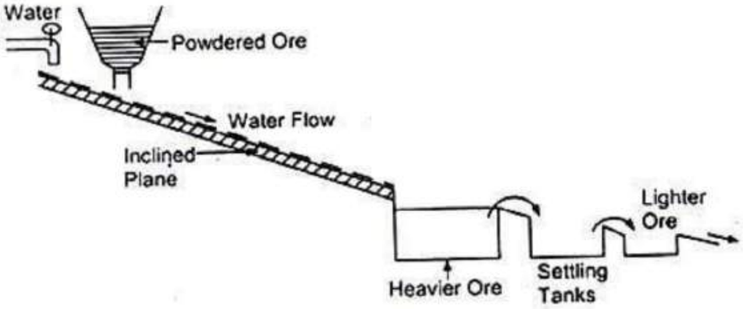


Fig: Gravity separation

(b) ⇒ By Wilfley Table Method

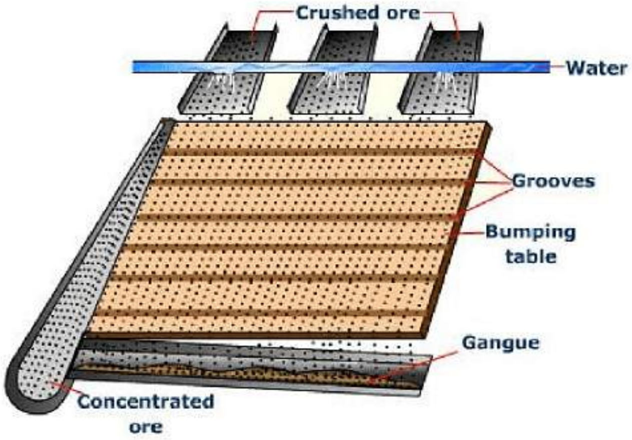


Fig: Wilfey Table method

⇒ By Hydraulic Classifier

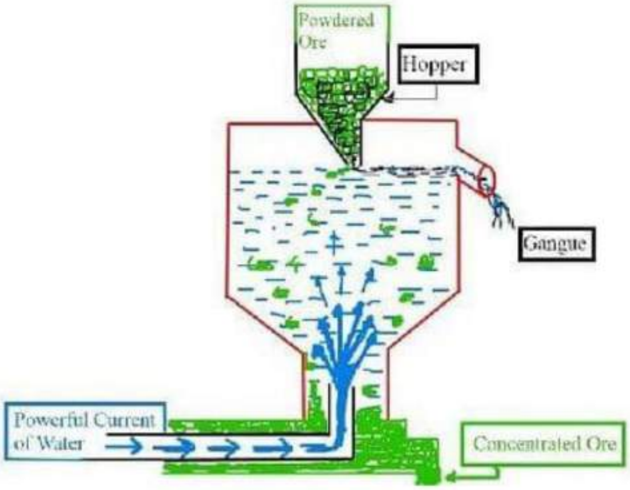
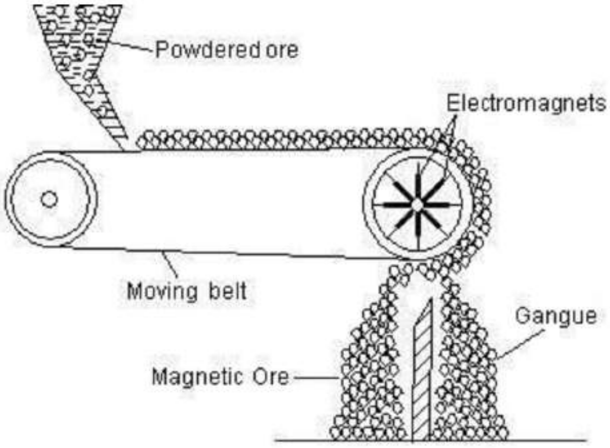


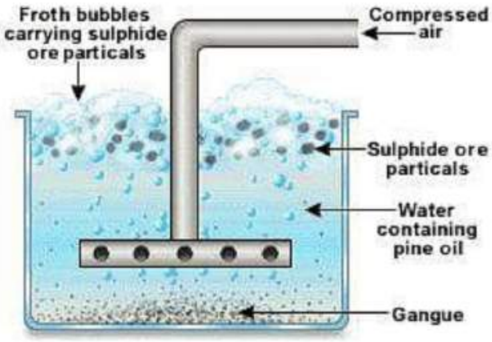
Fig: Hydraulic classifier

(c) By Magnetic separator:



Cassiterite or Tinstone contains impurities of wulframite or wulframates of Fe & Mn.
⇒ Tin stone: $SnO_2 \rightarrow$ Diamagnetic
⇒ Wulframites or wulframates of
Fe & Mn: $FeWO_4$, $MnWO_4 \Rightarrow$ Paramagnetic.
Ulframates of Fe & Mn from Tin stone by magnetic separator.

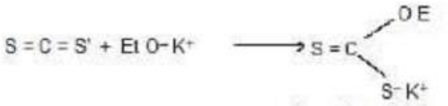
(c) By Froth Floatation Process: This method is used for the concentration of sulphide ores.
It is based on the concept that the sulphide ores are preferentially wetted by pine oil, camphor oil while gangue particles are preferentially by water.
This is based on the physical phenomenon of adsorption.



Frother: Pine oil, Camphor oil
Froth Stabilizers: They reduce surface tension of water e.g. cresols, amines.

Collector: Sodium or Potassium xanthates. It combines with sulphide ore & makes them water replent so that its affinity towards pine oil increases (Adsorption tendency increases)

$KOH + EtOH \rightarrow EtO^{-} + K + H_2O$



Potassium ethyl xanthate

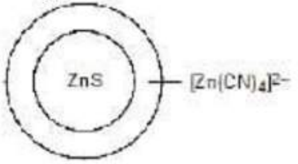
Depressant: KCN or NaCN

ZnS is found to be an impurity with the lead sulphide. There fore to separate out PbS from ZnS depressant KCN or NaCN added.

$PbS\ NaCN \rightarrow$ No complex formation due to very law K_{sp} of PbS.

$ZnS\ 4NaCN \rightarrow 4Na\ [Zn\ (CN)_4]^{2-}\ S^{--}$

(water soluble)



Thus, ZnS becomes water soluble & it remains with gangue while PbS comes out with the froth.

Activator: $CuSO_4$

From galena (PbS.ZnS) ZnS is removed

$ZnS + 4NaCN \rightleftharpoons 4\ Na + [Zn\ (CN)_4]^{2-} \xrightarrow{CuSO_4} [Cu\ (CN)_4]^{3-} + ZnS^{-} + S^{--}$

(water soluble)
(more stable)

& ZnS is taken out by froth floatation second time.

(ii) Chemical Method of Concentration:

Leaching: It involves dissolution of metallic ore in a suitable reagent in which metallic ore is soluble and impurities are insoluble.

Leaching of alumina from bauxite:

$Al_2O_3(s)\ 2NaOH(aq)\ 3H_2O(I) \rightarrow 2Na[Al(OH)_4](aq)$

Having F_2O_3 as important leachant.

The aluminate in solution is acidified by adding acid and hydrated Al_2O_3 is precipitated.

$2Na[Al(OH)_4]_{(aq)} + H^{+}\ (aq) \rightleftharpoons Al(OH)_3{}^{-} + H_2O + Na^{+}{}_{(aq)}$.

(white ppt)

Hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 :

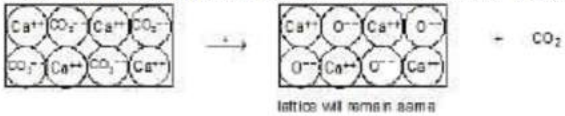
$Al(OH)_3^- \xrightarrow{\Delta} Al_2O_3(s) + 3H_2O(g)$
white (pure)

Other examples:

In the metallurgy of silver and gold, the respective metal/ore is leached with very dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained by displacement reaction.
$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$
(M = Ag Or Au)
$2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s)^-$
Step III : Conversion of Concentrated ore into oxide form :
It is done either by calcination or by roasting.

(i) Calcination:

Calcination is carried out for carbonate, hydrated metal oxide & metal hydroxide ores.
It is carried out in the absence of air i.e., heating in absence of air.



Due to calcination ore becomes porous.
Volatile organic impurities get evaporated

$$CaCO_{3(s)} \xrightarrow{\Delta} CaO + CO_2$$

$$CaCO_3MgCO_3.2H_2O \xrightarrow{\Delta} CaO + MgO + 2CO_2 \uparrow + 2H_2O$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 2H_2O \uparrow$$

$$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O \uparrow$$

$$Pb(OH)_2.\ PbCO_3 \xrightarrow{\Delta} 2PbO + CO_2 \uparrow + H_2O$$

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

$$Fe_2O_3.\ 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 2H_2O \uparrow$$

$$Cu(OH)_2.\ CuCO_3 \xrightarrow{\Delta} 2CuO + CO_2 \uparrow + H_2O$$

Black powder

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2 \uparrow$$

(ii) Roasting: In the presence of air the sulphide are heated in free supply of air below m.p. Impurities of sulphur, phosphorus, arsenic & antimony are converted into their corresponding volatile oxide & thus get removed.
Moisture & Water of crystallization are also removed.

(1) $PbS + \frac{3}{2}O_2 \xrightarrow{\Delta} PbO + SO_2 \uparrow$

$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$

(2) $ZnS + \frac{3}{2}O_2 \xrightarrow{\Delta} ZnO + SO_2 \uparrow$ (Utilised in manufacturing of H_2SO_4)

$ZnS + 2O_2 \longrightarrow ZnSO_4$

Step IV: Reduction of oxide to the metal :

(b) Reduction of Metal oxide / conc. ore into free metal.

This can be carried out
(i) chemical reduction
(ii) By self reduction or auto reduction or Air Reduction
(iii) Metal - displacement method
(iv) By electrolytic Reduction
(v) By amulgamation.
(i) & (ii) method are collectively known as Pyrometallurgy
e.g. Sn, Pb, Fe, Hg, Cu, B, Zn, (Based on Ellinghum diagram)
(iii) step is called hydrometallurgy — Cu, Ag, Au are extracted
(iv) step is called Electrometallurgy, Alkali, Alkaline earth metals & Al & base electrolysis
(v) is used for Ag & Au

(i) Chemical Reduction:

1. Smelting i.e., carbon Reduction - Reduction of metal oxide by coke, coal & RO
Reduction of the metal oxide usually involves heating it with some other Substance acting as a reducing agent, e.g., C or CO or even another metal. The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.
$M_xO_y + yC \rightarrow xM\ y + CO$

Some metal oxides get reduced easily while others are very difficult to be reduced. To understand the variation in the temperature requirement for thermal reductions and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are done, which is explained by ellingham diagram.

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

If ΔH is greater than zero then reduction will be feasible on increasing temprature i.e., $|T\Delta S| > |\Delta H|$

Ellingham diagram:

$M_{(s)} + \frac{x}{2} O_{2(g)} \xrightarrow{\Delta} M_2O_{x(s)}$

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

Therefore, For forward rxn $\Delta S < 0$

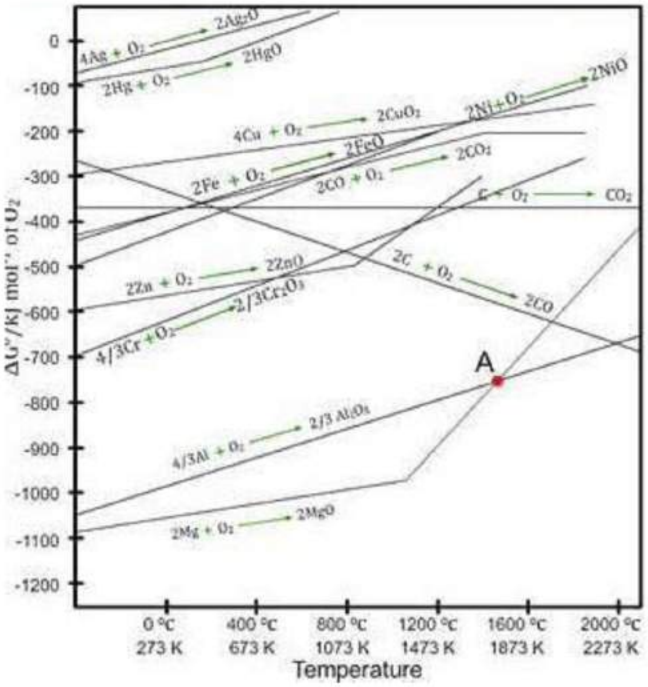


Fig: Ellingham diagram

(Ellingham diagram for formation of M_2O_x)

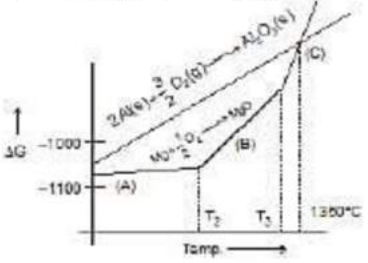
Ellingham diagram is a plot of formation of an element oxide between ΔG & ΔT

Ex. Which of the following statements are true:

$A \rightarrow Mg(s) + \frac{1}{2} O_2(g) \xrightarrow{T_1} MgO(s)$

$B \rightarrow Mg(l) + \frac{1}{2} O_2(g) \xrightarrow{T_2} MgO(s)$

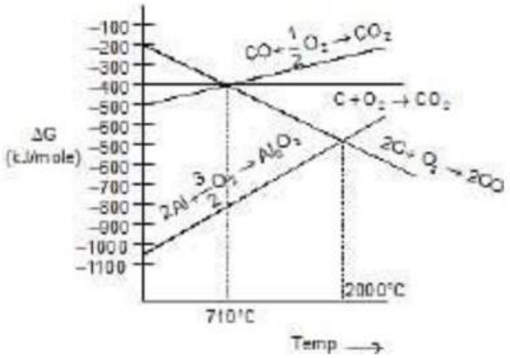
$C \rightarrow Mg(g) + \frac{1}{2} O_2(g) \xrightarrow{T_3} MgO(s)$



I: Below 1350° Mg can reduce Al_2O_3
II: Above 1350° C Mg Will reduce Al_2O_3
III: Below 1350° Al can reduce MgO
IV: Above 1350° Al can reduce MgO
V: At 1350° C there is no change in free energy i.e., $\Delta G = 0$

Sol. $3MgO + 2Al \xrightarrow{\text{then Above 1350°C}} Al_2O_3 + 3Mg$ $\Delta G < 0$
(Its ΔG high) (Its ΔG less)
$Al_2O_3 + 3\,Mg \xrightarrow{\text{Below 1350°C}} 3\,MgO + 2Al$

At 1350° C both reactions have same G There fore ,$\Delta G = 0$
To carry out smelting below 800°C, CO is used as reducing agent while above 800°C, smelting is carried out by coke.
$2C(s) + O_2(g) \rightarrow 2CO\,(g) + \Delta H = -221.0$ kJ/mole
DS = 179.4 J kJ/mol
$C(s) + O_2(g) \rightarrow CO_2(g) + \Delta H = -\,393.5$ kJ/mol
$\Delta S = 2.89\ JK^{-1}\ mole^{-1}$



Aluminium can be extracted from Alumina by carbon reduction but the method is highly uneconomical because -
(i) As the smelting occurs above 200°C hence a part of the aluminium will go into vapour phase (M.P. = 2520°C)

(ii) At this high temperature the liberated Al will combine with the carbon & aluminium carbide will be formed.
(iii) ΔH_{for} of alumina is high - ve value
Therefore,It is thermodynamically more stable & reduction is more difficult
To extract metal from sulphide ore is carried out by firstly roasting it into metal oxide & followed by its smelting. Metal sulphide or sulphide ore is not directly smelted to metal.
$2PbS + C \xrightarrow{\Delta} 2Pb + CS_2$ (Thermodynamically Not feasible)
$Pbs + \frac{3}{2} O_2 \xrightarrow{\Delta} PbO + SO_2$
$PbO + C \xrightarrow{\Delta} Pb\ CO$ Thermodynamically feasible
ΔG_f of PbS = -21.9 kcal/mol
ΔG_f of CS_2 = 17.15 kcal/mol
ΔG_f of PbO = -45.1 kcal/mol
ΔG_f of SO_2 = -71.7 kcal/mol
ΔG_f of CO = - 32.8 kcal/mol

Flux: Additional substances which are used during metal extration to remove acidic or basic impurity are called flux depending upon nature of impurity flux are of two types.

(i) **Basic Flux:** It is used to remove acidic impurity eg : CaO, MgO, $CaCO_3$, $MgCO_3$ $FeCO_3$ etc.

(ii)**Acidic Flux :** It is used to remove basic impurity eg : SiO_2, B_2O_3, P_2O_5, $Na_2B_4O_7$. (Borax)

Smelting: Phenomenon of slag formation by combining flux with impurity is called smelting.
Flux + Impurity → Slag (Smelting)
(Basic or acidic)

Properties of slag:

(i) Slag has low melting point than metal.
(ii) Slag is lighter than metal therefore it floats over the molten metal and prevents further oxidation of molten metal by air.
(iii) Slag immiscible with molten metal therefore it can be easily separated from molten metal.
(b) Gold Schmidt Thermite Reduction:
Thermite: Al powder
$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$

(DG_f = -540 kJ/mole) (DG_3 = -827 kJ/mole)
$B_2O_3 + 2Al \xrightarrow{\Delta} 2B + Al_2O_3$
$2Mn_3O_4 + 8Al \xrightarrow{\Delta} 9Mn + 4\,Al_2O_3$
$Fe_2O_3 + 2Al \xrightarrow{\Delta} 2Fe + Al_2O_3$
This method is used for reduction of those metal oxides which are highly stable if they are reduced by coke it will occur at very high temperature & at this high temperature the liberated metal will combine with the coke & carbide will be formed hence Al powder i.e., thermite is used

(c) Reduction by Hydrogen:

Because of inflammable nature of hydrogen its use as a reducing agent is very restricted.
$Cu_2O + H_2 \xrightarrow{\Delta} 2Cu + H_2O$
$M_OO_3 + 3H_2 \xrightarrow{\Delta} M_0 + 3H_2O$
$BCl_3 + 3/2H \xrightarrow[\text{Filament}]{\text{Ta/W}} B + 3HCl$

Reduction by other metals:

$SiCl_4 + 2Mg \xrightarrow{\Delta} 2MgCl_2\ Si$
Kroll process used for extraction of Ti & Zr
$TiCl_4 + 2Mg\ Ti\ 2MgCl_2$
$ZrCl_4\ 2Mg \xrightarrow{\Delta} Zr\ 2MgCl_2$

I.M.I Process (Imperial Metal Industries)

$TiCl_4\ 4Na \xrightarrow{\Delta} Ti\ 4NaCl$

(ii) By Self reduction or Auto reduction or Air Reduction:

This method is used for extraction of copper, lead, mercury i.e., it is used for the extraction of metal from their sulphide ores.
In this method the sulphide ore is roasted in free supply of air to its metal oxide & then air supply is cut off followed by heating by increasing temperature & metal is extracted by self reduction.

$PbS + \frac{3}{2}O_2 \longrightarrow PbO + SO_2$
$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$
Now air supply is cut off followed by heating
$PbS_{(s)} + 2PbO_{(s)} \xrightarrow{\Delta} 3Pb_{(l)} + SO_2$
Self reduction is responsible for acid rain than roasting because SO_2 dissolves in air, (3927cc CO_2 in 1000cc of H_2O)

(iii) By Metal Displacement Method or By Hydrometallurgy:

$$\underbrace{\text{Li K Ca Na Mg Al Zn Fe Sn Pb}}_{\rightarrow \text{ More Electropositive than Hydrogen}}\ \text{H} \qquad \underbrace{\text{Cu Ag Hg Au}}_{\rightarrow \text{ Less Electropositive}}$$

In this method the concentrated ore is treated/ leached with specific chemical reagent that converts the ore into water soluble salt. Now, on adding more electropositive metal into the aqueous salt solution the metal (less electropositive) is displaced

e.g.

Extraction of Copper from Malacite :

$$Cu(OH)_2\,CuCO_3 + H_2SO_4 \longrightarrow 2CuSO_4 + CO_2\uparrow + 2H_2O$$

or

$$Cu(OH)_2.CuCO_3 \xrightarrow{\Delta} 2CuO + CO_2\uparrow + H_2O$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$H_2SO_4 \Rightarrow$ leaching agent, it leached out Cu as $CuSO_4$

Now, on adding more electropositive metal :

$$CuSO_4 + \underset{\text{(Reducing agent)}}{Fe} \longrightarrow FeSO_4 + Cu\downarrow$$

$$\therefore \quad E^\circ_{Cu^{++}/Cu} = +0.34$$

$$E^\circ_{Fe^{++}/Fe} = -0.40$$

$$\therefore \; E^\circ_{Cell} = 0.74 \qquad \Rightarrow \qquad \Delta G < 0$$

Iron is found to be an impurity in the copper ores hence if Zn is added to extract copper, iron will also be displaced along with copper & that is why iron is used. Both metals which extracted & by which we extracted are water insoluble

(iv) Electro Metallurgy: The metal is extracted by passing electricity into its fused salt or in aqueous solution.

Extraction of sodium:

⇒ By electrolysis of Aq. NaCl solution:
$NaCl(s)\ x\ H_2O \rightleftharpoons Na\ (aq)\ Cl^-(aq)$
$H_2O \rightleftharpoons H\ \ OH^-$
On passing electricity
At cathode: $2H\ \ 2e^- \longrightarrow H_2$

$\Delta G = - n FE^{\circ}$

There fore,Na does not discharge at cathode

At anode : $2Cl^{-} \longrightarrow Cl_2\ 2e^{-}$

$E^{\circ}_{\frac{1}{2}Cl_2/Cl^{-}} = -1.36$ Volt

In sol: $Na\ \ OH^{-} \longrightarrow NaOH$

⇒ By electrolysis of fused NaCl:

On Passing electricity

At cathode: $2Na + 2e^{-} \longrightarrow Na$

At Anode: $2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$

In sol. $Na + OH^{-} \longrightarrow NaOH$

Electrochemical Principles of Metallurgy:

We have seen how principles of thermodynamics are applied to pyrometallurgy. Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element. In the reduction of molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$\Delta G^{\circ} = -nE^{\circ}F$ .... (16)

Here n is the number of electrons and E° is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E° values corresponds to a positive E° and consequently negative DG° in equation (16), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

In simple electrolysis, the M^{n} ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

Methods of Refining of Metals

Step V: Purification or refining of crude metal:

(A) By physical Methods:

(a) liquation
(b) Distillation
(c) Zone refining

(B) By Chemical Methods

(a) Oxidation
(b) Poling

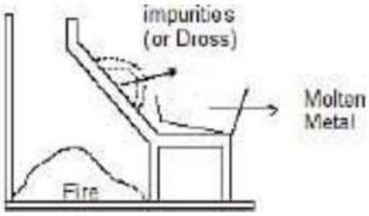
(c) Vapour Phase Refining

(C) By Electrolytic Refining

(A) By Physical Method:

(a) Liquation Method:

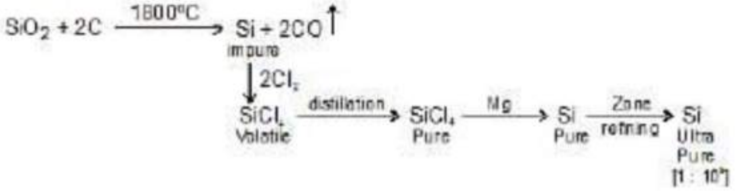
	Metal	M.P.
Impurities	Sn	232°C
	Fe	1535°C
	Mn	1244°C
	W	3380°C

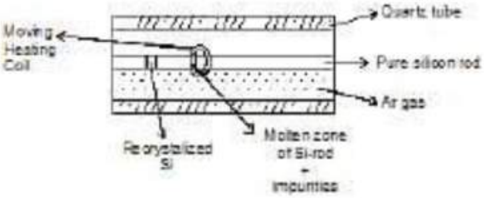


This method is used for refining of those metal which have very low m.p. in comparison to impurity present in them.
e.g. → Sn, Pb, Hg, Bi, Zn

(b) Distillation Method: It is used for refining of those metals which are volatile & hence it is used for refining of Zn, Cd, Hg (i.e., is of filled d orbital metal)

(c) Zone Refining: (Si, Ge, Pb, B, Ga, In)



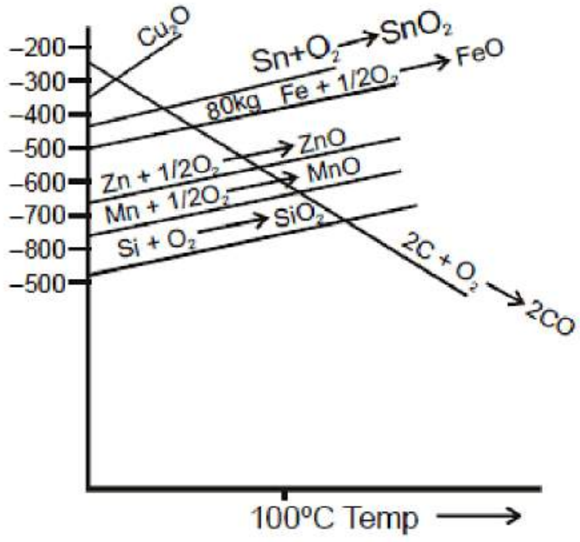


Concept: Impurities are more soluble in the melt than in the solid state. (Fractional crystallization)

(B) By Chemical Methods:
(a) Oxidation: (Fe, Sn, Pb)

eg. Pig iron: M.P. 1080

Impurities: C, P, Mn, Si



$$P_4 + 5O_2 \longrightarrow P_4O_{10} \xrightarrow{CaO} Ca_3(PO_4)_2$$

$$Si + O_2 \longrightarrow SiO_2 \text{(acidic)}$$

$$Mn + \frac{1}{2}O_2 \longrightarrow MnO \text{ (Basic)}$$

$$MnO + SiO_2 \longrightarrow \underset{\text{Slag}}{MnSiO_3} + \text{Heat}$$

$$C + \frac{1}{2}O_2 \longrightarrow CO$$

This method is used for the refining of metals in which impurtities are more oxidisable than metal itself.
When impurities oxidise they are converted into either volatile oxides or non volatile oxides Non-volatile oxides are removed either by slag formation or by removing their scum Oxidation is known by various names bessemerisation (Fe), Cupellation (Ag), Softening (Pb) or Puddling (for iron), tossing (for iron)

(b) Polling: When along with impurities the metal to be refine is also oxidised part then this method is used. In this method the molten impure metal is steared with green wood log, The hydrocarbons released from the log reduce metal oxide into

metal while impurity oxides are not reduced. This method is used for refining of Cu & Tin. In both metals during poling iron get oxidised into FeO which in turn is oxidised into Fe_2O_3 while in case of Sn, SnO_2 is reduced to tin (Sn) & in case of Cu copper (I) oxide i.e., cuprous oxide is reduced to Cu,
$Cu_2O \rightarrow Cu$

(c) Vapour Phase Refining: Impure metal is allowed to react with a suitable reagent such that a volatile unstable compound is formed & then the compound is decomposed to pure free metal when it is subjected to heat.
Mond's Process: used for refining of Ni

(C) By Electrolytic Refining:

Anode: Impure metal
cathode: Pure metal
Electrolyte: Aq. salt sol. of metal/fused metal salt Acid
Anode Mud: Metals which are less electropositive than the metal to be refined.
In electrolyte: More electropositive metals are found.
eg. in Cu: Ag, Au, Fe, Zn
In electrolyte

1. Gold:

Occurrence

Found mostly in free state in quartz veins called auriferous quartz.

Extraction of gold from native ore:

(A) Crushing and concentration:
The gold ore is crushed, powdered finely and concentrated by washing with water.

(B) (Treatment with 0.25-1% sodium cyanide or potassium cyanide solution)
Extraction of Au, from Native ore by **Mac Arthur forest cyanide process.**

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

$$2Na\,[Au\,(CN)_2] + Zn \rightarrow Na_2[Zn\,(CN)_2] + 2Au^-$$

(Impure)

Impure Au is purified by Electrolytic refining method or by amalgamation.

(C) Electrolytic refining method:
Anode: Impure Au

Cathode: Pure Au
Electrolyte: 4% $AuCl_3$ solution acidified with 10% HCl

Purple of Cassius: It is of colloidal gold solution:

$2AuCl_3 + 3SnCl_2 \rightarrow 2Au + 3SnCl_4$
(Very dil.)

The gold thus precipitated is absorbed by Sn $(OH)_4$ formed by hydrolysis of $SnCl_4$

$SnCl_4 + 4H_2O \rightarrow Sn\ (OH)_4 + 4HCl$

This form of gold is purple in colour named after its discoverer, Cassius.

2. Silver:

Ores: (i) Silver glance or argentite Ag_2S (main ore)
(ii) Ruby silver or pyrargyrite $3Ag_2S.\ Sb_2S_3$
(iii) Horn silver or chlorargyrite AgCl.

Extraction of silver from silver glance:

(A) Crushing and concentration: The ore is crushed, powdered and concentrated by froth floatation process.

(B) Extraction of Ag by Mac-Arthur forest cyanide process: (Treatment with 0.4-0.7% sodium cyanide solution)

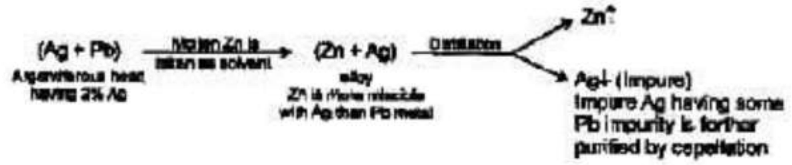
$Ag_2S + 4NaCN \xrightleftharpoons{\text{Atm air}} 2Na\ [Ag\ (CN)_2] + Na_2S$ (soluble)

The role of air is to oxidise Na_2S so that reaction proceed in the forward direction.
Impure Ag is purified by Electolytic refining method or by amalgamation.

(C) Electrolytic refining: Anode Impure Ag
Cathode: Pure Ag
Electrolyte: $AgNO_3(aq)\ HNO_3$.

Silver from (commercial lead) argentiferous lead by Parke's process:
Desilverisation of Lead:

Lead extracted from galena (PbS) contains impurities of Cu, Ag, Bi, As, Fe Zn, Sn, etc. and is called commercial lead or argentiferous lead. This contains Ag upto 2% which is extracted by parkes process. Commercial lead is mixed with a large quantity of Zn and the mixture is melted, where Zn-Ag alloy is formed and Pb remains in the molten state. The alloy is strongly heated where Zn is distilled of leaving Ag. This silver contains some Pb impurity which is removed by cupellation process. Impure Ag is melted in a cupel (a boat shaped dish made of bone ash) by passing Hot blast of air. Pb is oxidised to PbO (litherge) which is either absorbed by cupel or carried away by blast of air leaving pure Ag.



Separation of silver from gold (Parting with conc. H_2SO_4)

Alloy (Au < 20%) is boiled with conc. H_2SO_4 where Ag is dissolved as Ag_2SO_4 and Au remains as spongy mass.

$Ag_2SO_4 + Zn \rightarrow 2Ag + ZnSO_4$ (Metal displacement reaction)

(sparingly soluble solution)

If alloy contains Au > 20%, then some Ag is added to it so as to reduce the % Au below 20.

Silver from silver coin or silver ornaments:

$(AgCu) \xrightarrow[\text{conc. } HNO_3]{\text{dissolve in}} Ag\,(aq) + Cu^{2+}\,(aq) + 3NO_3^-(aq) \xrightarrow{\text{dil HCl}} AgCl^- + Cu^{2+}\,(aq) + 3NO_3^-$

Recovery of Ag from AgCl:

(i) By treating with KCN solution:

$2AgCl + 2NaCN \rightarrow 2Na[Ag(CN)_2] + 2NaCl$

soluble complex

$2Na\,[Ag\,(CN)_2] + Zn(dust) \rightarrow 2Ag + Na_2[Zn\,(CN)_4]$

(ii) Boiling with caustic soda and glucose.

$2AgCl + 2NaOH \rightarrow Ag_2O + 2NaCl + H_2O \xrightarrow{C_6H_{12}O_6} 2Ag + C_6H_{12} + O_7$ (Gluconic Acid)

(iii) $2AgCl + Na_2CO_3 \xrightarrow{\text{Fuse}} 2Ag + CO_2 + O_2 + 2NaCl$

3. Copper:

Ores:

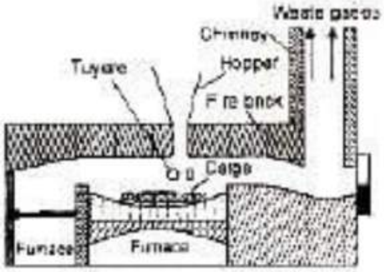
Copper pyrites or Chalcopyrites $CuFeS_2$ (main ore) ; Cuprite or ruby copper Cu_2O ; Malachite $CuCO_3Cu(OH)_2$(green) ; Azurite $2CuCO_3.Cu(OH)_2$(Blue) ; Copper glance Cu_2S, bornite (peacock ore) Cu_5FeS_4.

Extraction of copper from copper pyrites:

(A) Crushing and concentration: Ore is first crushed and then powedered finely and powdered ore is concentrated by froth floatation process.

(B) Roasting: Concentrated ore along with SiO_2 is heated in excess of air in a reverberatory furnace.

$(Cu_2S\ FeS\ FeS_2) + 2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ (Major oxidation)
$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ (Minor oxidation)
$Cu_2O + FeS \rightarrow Cu_2S + FeO$



Reverberatory Furnace

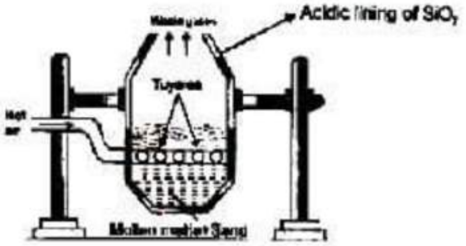
$S + O_2 \rightarrow SO_2$
$4As\ SO_2 \rightarrow 2As_2O_3$
$4Sd\ 3O_2 \rightarrow 2Sb_2O_3$
Volatile impurities are removed in this step.

(C) Slag formation:

Roasted ore mixed with sand and strongly heated in furnace.
$FeO + SiO_2 \rightarrow FeSiO_3$
flux slag
Upper layer containing slag is removed and lower layer contains mostly Cu_2S (98%) with little amount of FeS (2%) is called **matte.**

(D) Bessemerization: (Self - reduction)

$2FeS + 3O_2 \xrightarrow{\Delta} 2FeO + 2SO_2$
$FeO + SiO_2 \xrightarrow{fuse} FeSiO_3$(slag)
$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O\ 2SO_2$ (partial roasting)
(limited air)
$Cu_2S + 2Cu_2O \xrightarrow[\Delta]{high\ temp.} 6Cu + SO_2$ (self reduction)
(R.A.) (impure)
Impure copper obtained has blister appearances and therefore called blister copper.



Poling: Molten Cu is stirred with poles of green wood to reduce any copper oxide impurity into Cu.

Electrolytic refining:
Anode - impure Cu;
Cathode - Pure Cu;
Electrolyte $CuSO_4$, H_2SO_4.
The more electropositive impurities like Zn, Fe, Ni etc. get dissolved in solution and less positive impurities like Ag, Au collect below anode as anode mud.

4. Lead:

Ores: Galena PbS (Main ore); Anglesite $PbSO_4$; Cerussite $PbCO_3$

Extraction of lead from galena:

Crushing and concentration: The ore is crushed, grinded finely and concentrated by froth floatation process.

Roasting: In reverberatory furnace, limited supply of air is passed at moderate temperature.
$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$;
$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

Self reduction: Air supply is cut off and the temperature is increased to melt the change in reverberatory furnace.
$PbS + 2PbO\ 3Pb\ SO_2$
(R.A.) impure
$PbS\ PbSO_4\ 2Pb\ 2SO_2$
(R.A.) impure
$SiO_2 + CaO$ (flux) $\xrightarrow{\text{[illegible]}}$ $CaSiO_3$ (slag)
$PbSiO_3 + CaO$ (lime) $\longrightarrow$ $PbO + CaSiO_3$ (slag)
In this way, lime (CaO) prevents formation of $PbSiO_3$.
Impure Pb is purified by **electrolytic refining method** or by **liquation and poling.**

Electrolytic refining:
Anode - Impure Pb
Cathode - Pure Pb
Electrolyte - $PbSiF_6$ H_2SiF_6 gelatine
5. Tin:

Ores: (i) Cassiterite or Tin stone SnO_2 (Main ore) (It contains impurities of pyrites of Cu and Fe and magnetic impurity of wolframite which is a mixture of $FeWO_4$, $MnWO_4$).

This mineral is also called black tin to distinguish it from the metal Sn which is also called white tin.

Extraction of Sn from cassiterite:

(i) Crushing and concentration:

The ore is crushed and washed with a stream of running water to remove lighter silicious impurities followed by magnetic separation method to remove the magnetic impurity of Wolframite.

(ii) Roasting:

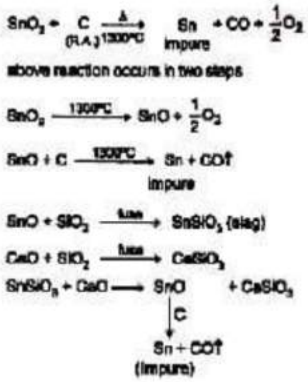
Concentrated ore is heated in pressence of air, and volatile impurities (S as SO_2, As as As_2O_3 and Sb as Sb_2O_3) are removed. The impurities of pyrites of Cu and Fe are converted into their respective oxides and sulphates.

(iii) Washing:

Sulphates of copper and iron are dissolved in water. The ore thus obtained contains 60-70% SnO_2 and is called as black tin.

Carbon reduction:

The black tin is mixed with anthracite coal and heated to about 1300°C. If SiO_2 is present as impurity then CaO is added as flux.



$$SnO_2 + \underset{(R.A.)}{C} \xrightarrow[1300^\circ C]{\Delta} \underset{\text{impure}}{Sn} + CO + \frac{1}{2}O_2$$

above reaction occurs in two steps

$$SnO_2 \xrightarrow{1300^\circ C} SnO + \frac{1}{2}O_2$$

$$SnO + C \xrightarrow{1300^\circ C} \underset{\text{impure}}{Sn} + CO\uparrow$$

$$SnO + SiO_2 \xrightarrow{\text{fuse}} SnSiO_3 \text{ (slag)}$$

$$CaO + SiO_2 \xrightarrow{\text{fuse}} CaSiO_3$$

$$SnSiO_3 + CaO \longrightarrow SnO + CaSiO_3$$

$$SnO \xrightarrow{C} \underset{\text{(impure)}}{Sn} + CO\uparrow$$

Refining:

(i) Liquation and poling:

Impure Sn is melted on the sloping hearth where Sn (m.pt. 232°C) is first melt and flows out leaving behind the less fusible impurities of Cu, Fe, W etc. The liquid Sn is then stirred with poles of green wood to reduce SnO_2 (Impurity) to Sn.

(ii) Electrolytic refining:
Anode: Impure Sn
Cathode: Pure Sn
Electrolyte: $SnSO_4$, H_2SO_4

6. Iron:

Ores: Haematite Fe_2O_3(Main ORE) ; Limonite $Fe_2O_3.3H_2O$; Magnetite Fe_3O_4 ; Siderite $FeCO_3$; Iron pyrites FeS_2

Extraction of Iron from ore haematite:

Crushing and concentration: The oxide ore is first crushed in jaw crushers and then is broken in small pieces. Haematite (non-magnetic) is washed with running water to remove earthy and siliceous impurities by levigation.

Calcination following by roasting:
The concentrated ore is roasted with excess air in a reverberatory furnace. During roasting step, the following changes occur:

(a) If $FeCO_3$ is present as impurity, it gets decomposed into FeO which is oxidised by air to Fe_2O_3.
$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$ (calcination)
siderite
$4FeO + O_2$ (air) $\xrightarrow{\Delta} 2Fe_2O_3$ (Roasting)
In this way, formation of $FeSiO_3$ slag is prevented during melting, and following reaction does not occur.
$SiO_2 + FeO \rightarrow FeSiO_3$ (slag)
(b) The impurities of S, As are also removed as their volatile oxides
$S + O_2 \rightarrow SO_2$
$4As + 3O_2 \rightarrow 2As_2O_3$,
The entire mass becomes porous and hence the reduction of Fe_2O_3 to spongy iron becomes easy at later stage.

Reduction in blast furnace.

(Fe_2O_3 ore lime stone coke) is smelted in blast furnace and following changes take place.

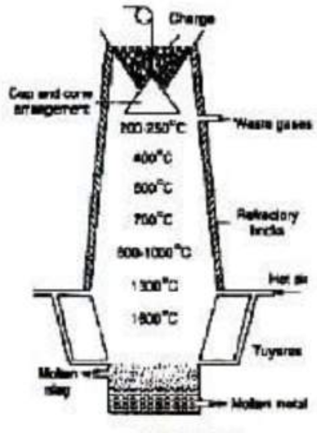
(i) Combustion Zone (155 - 1700°C)

(a) (Combustion zone) a blast of dry preheated air is blown into the furnace from near the bottom of the furnace. Near the bottom, the preheated air comes in contact with the falling coke and combustion of coke into CO_2 takes place.

$C + O \rightarrow CO_2 \Delta H = - 393.5$ kJ

CO_2 produced in the combustion zone rises up and meets with more coke in fusion zone and gets reduced to CO.

$CO_2 + C \rightarrow 2CO$ $\Delta H = 163.0$ kJ



Blast furnace

(ii) Reduction zone (250 - 700°C)

Near the top of the furnace (reduction zone), the temperature varies from 250-700°C. Here the oxide ore (Fe_2O_3) is reduced to spongy iron with the help of uprising vapours of CO produced in the zone of fusion.

$Fe_2O_3 + 3CO \xrightarrow{400-700^\circ C} 2Fe + 3CO_2$

Actually above Reduction, takes in 3 steps:

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

(Spongy iron)

Any Fe_2O_3 which escapes from reduction in reduction zone is reduced in fusion zone.

(iii) Slag formation zone (700-1000°C)

In the middle of the furnace (slag formation zone) where the temperature varies from 700-1000°C, lime stone ($CaCO_3$) present in the change decomposes into CaO and CO_2.

$CaCO_3 \xrightarrow[1000^\circ C]{\Delta} CaO\ CO_2$

CaO combines with the impurity of SiO_2 and forms a fusible slag of $CaSiO_3$. Thus CaO acts as a basic flux.

CaO (basic flux) + SiO_2 (acidic impurity) → $CaSiO_3$(slag)

Slag is lighter than the molten iron. It moves down and floats over molten iron. This region where slag is formed is called slag formation zone.

(iv) Fusion Zone (1000 - 1500°C)

Since the reduction of CO_2 to CO is an endothermic reaction (Heat is required), temperature is decreased to about 1500°C. Fe_2O_3 is reduced to Fe which might not have been reduced in the reduction zone.

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

Impurities are also reduced and get mixed up with spongy Iron.

$MnO_2 + 2C \rightarrow Mn + 2CO$

$2P_2O_5 + 10C \rightarrow P_4 + 10CO$

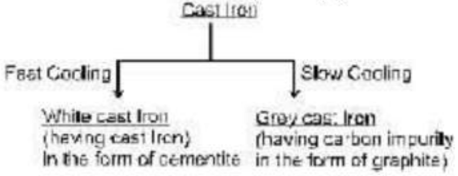
$SO_2 + C \rightarrow S + 2CO$

$SiO_2 + 2C \rightarrow Si + 2CO$

Spongy iron produced in the reduction zone melts here and gets impured in called pig iron, while slag being lighter floats over and thus prevents oxidation of Fe by blast of hot air.

Types of Iron :

1. Cast iron (2% to 5% carbon & other impurity)
2. Steel (0.5% to 2% carbon & other impurity)
3. Wrought iron (< 0.5% carbon & other impurity)



Manufacturing of wrought from cast Iron:

Wrought iron is manufactured from puddling furnace having inner lining of haematite (Fe_2O_3) oxidant for impurities present in cast iron.

$Mn + Fe_2O_3 \rightarrow MnO + 2\ Fe$

(O.A.) (basic)

$Si + Fe_2O_3 \rightarrow SiO_2 + 2\ Fe$

(O.A.) (basic)

$MnO + SiO_2 \rightarrow MnSiO_3$ (slag)

(O.A.) (basic)

$S + Fe_2O_3 \rightarrow SO_2\ 2\ Fe$

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

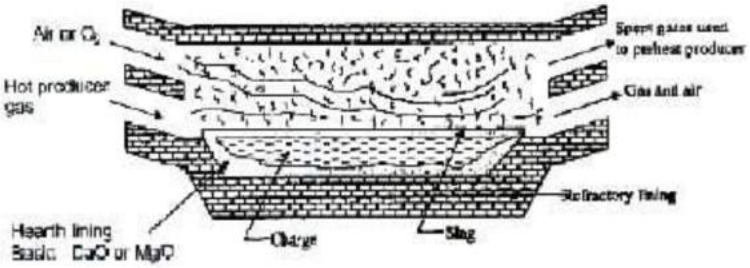
$3P_4 + 10Fe_2O_3 \rightarrow 6P_2O_5 + 20Fe$
$P_2O_5 + Fe_2O_3 \rightarrow 2FePO_4$(slag)

Manufacturing of steel from cast from:

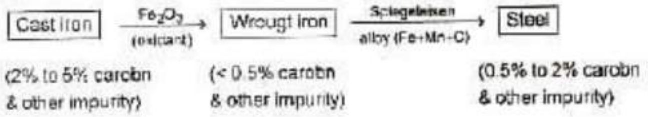
(i) Bassemerisation (already discussed)
(ii) Open-Hearth process (Siemen Martin's process)
(iii) Electrical furnace process

Open hearth process (siemen Martin's process)

$Mn + Fe_2O_3 \rightarrow MnO\ 2\ Fe$
(O.A.) (basic)
$Si + Fe_2O_3 \rightarrow SiO_2 + 2\ Fe$
(O.A.) (Acidic)
$MnO + SiO_2 \rightarrow MnSiO_3$ (slag)
(O.A.) (basic)
$S + Fe_2O_3 \rightarrow SO_2\ Fe$
(O.A.)
$C + Fe_2O_3 \rightarrow 3CO + 2Fe$
$3P_4 + 10Fe_2O_3 \rightarrow 6P_2O_5 + 20Fe$
$P_2O_5 + 3CaO \rightarrow Ca_3(PO_4)_2$ (Thomas slag)



Open hearth furnace for the manufacture steel from cast iron

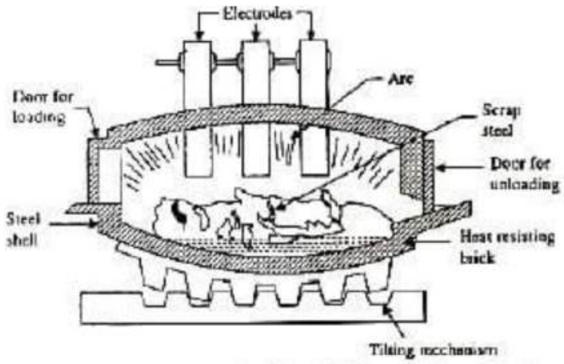


After adding required amount of spiegeleisen steel is formed.

In this method 2 - 5% iron is also oxidised by air because hearth is open therefore this method is discarded is modern age.

In modern age steel is manufactured by electrical furnace process or by L.D. process.

In electrical furnace process heating effect is produced by passing electricity and all chemical reaction are similar to open-hearth process.



Arc furnace (Heroult's furnace) for the manufacture of steel.

Heating Treatment of STEEL

(i) Annealing: Process of heating steel upto redness and then cooling it slowly is called annealing, In this way steel becomes soft, malleable and elastic.

(ii) Quenching: Process of heating steel upto redness and then cooling it suddenly by plunging in into oil or water is called quenching. In this way steel become hard and brittle.

(iii) Tempering: Process of heating quenched steel much below redness and then coiling it slowly is called tempering. In this steel becomes neither so hard nor so brittle.

Surface Treatment of steel:

(i) Case - Hardening: Process of forming hard coating of iron carbide over mild steel by heating it with charcoal is called case - hardening.

(ii) Nitriding : Process of forming hard coating of iron nitride by heating steel with ammonia gas is called nitriding.

7. Zinc :

Ores: Zinc blende ZnS (main ore), Zincite (ZnO), Calamine, $ZnCO_3$.

Extraction of zinc from zinc blende:

(A) Crushing and concentration:
The ore is crushed and concentrated by froth floatation process.
(B) Roasting:
The concentrated ore is roasted in presence of excess of air

$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$
$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$
$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$
$ZnSO_4$ decomposed at higher temperature

(C) Carbon Reduction (Belgian process):
Roasted ore is heated with coke in a vertical fire clay retort.
$ZnO + C \xrightarrow{1100°C - 1400°C} Zn + CO$
(R.A.) vapour
Vapours of zinc are collected by rapid cooling to get zinc spelter (Impure Zn).
Impure Zn is purified either by **electrolytic refining method** or by **distillation.**

Electrolytic Refining

(D) Electrolytic refining:
Anode: Impure Zn
Cathode: Aluminium Electrode
Electrolyte: $ZnSO_4(aq)$ H_2SO_4

Extraction of Cr From $FeCr_2O_4(FeO.Cr_2O_3)$ Chromite ORE:

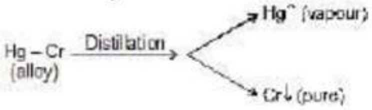
Conc. Step: Chromite ore is concentrated by gravity sep. Method to remove light impurities followed by magnetic sep. method to remove non-magnetic impurities.

Chemical Method to Separate Cr_2O_3:
$4FeO.Cr_2O_3\ \ 7O_2\ (air)\ 8\ Na_2CO_3/16NaOH \xrightarrow[\text{lime}]{\text{fuse}} 2Fe_2O_3\ \ 8Na_2CrO_4\ \ 8CO_2/8H_2O$
Brown
(water insoluble)
↓ Water   yellow solid (water soluble)

$2Na\ (aq)\ Cr_2O_7^{2-}(aq)\ SO_4^{2-}\ (aq) \xleftrightharpoons{H_2SO_4} 2Na\ (aq)\ CrO_4^{2-}\ (aq)$
(Orange Solution) yellow solution
↓ Fractional crystallisation
$Na_2Cr_2O_7.2H_2O \xrightarrow[\text{method}]{\text{Carbon red.}} NaCrO_2 \xrightarrow{H_2O} Cr\ (OH)_3^-$
(orange crystal) (green ppt)
↓ Δ
Cr_2O_3 (green solid)

Al-reduction method: (Goldsmith alumino thermite process)
$\underbrace{\underset{\text{3 part}}{Cr_2O_3} + \underset{\text{1 part}}{Al(R.A.)}}_{\text{Thermite mixture}} \xrightarrow[\text{ignition mixture}]{\Delta,\ \text{Mg Ribbon} - BaO_2} Al_2O_3 + \underset{\text{(Molten impure metal)}}{2Cr\downarrow} + Heat$
Impure Cr is purified by **electrolytic refining method.**
Anode: Impure chromium

Cathode: Hg-electrode
Electrolyte: $CrCl_3$ HCl



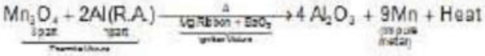
Extraction of Mn from MnO_2 (Pyrolusite):

Pyrolusite is concentrated by gravity separation method followed by magnetic separation method to remove non-magnetic impurity.

Calcination:

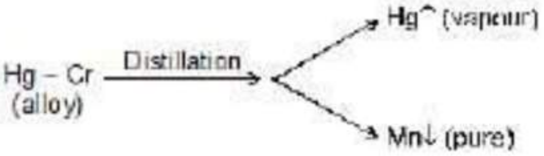
MnO_2 gives explosive rxn. with Al therefore in this step it is converted into mixed oxide Mn_3O_4.
$3MnO_2 \xrightarrow{900°C} Mn_3O_4(MnO\ Mn_2O_3) + O_2$

Al-reduction method: (Goldsmith alumino thermite process)

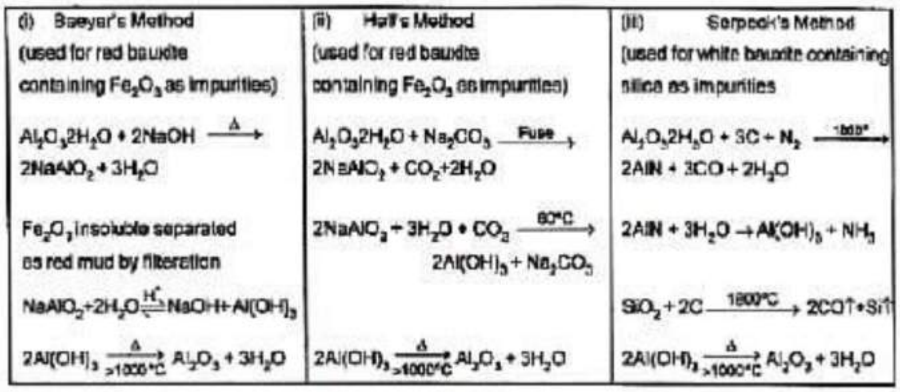


$$\underbrace{\underset{3\,part}{Mn_3O_4} + \underset{8\,part}{2Al(R.A.)}}_{Thermite\ mixture} \xrightarrow[\underbrace{Mg\ Ribbon + BaO_2}_{ignition\ mixture}]{\Delta} 4\,Al_2O_3 + \underset{(impure\ metal)}{9Mn} + Heat$$

Impure Mn is purified by electrolytic refining method.
Anode: Impure Mn
Cathode: Hg-electrode
Electrolyte: $MnSO_4$ H_2SO_4



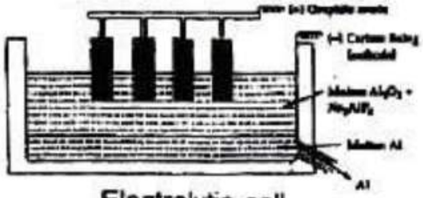
8. Aluminium:
Ores :
(i) Bauxite $Al_2O_3.2H_2O$ (main ORE) ; Diaspore $Al_2O_3.H_2O$; Corundum Al_2O_3
(ii) Mica $K_2O.3Al_2O_3.6SiO_2.2H_2O$; Kaolin $Al_2O_3.2SiO_2.2H_2O$
(iii) Cryolite Na_3AlF_6
Extraction of Al from Bauxite:
Purification of Bauxite:



(i) Baeyer's Method (used for red bauxite containing Fe_2O_3 as impurities)	(ii) Hall's Method (used for red bauxite containing Fe_2O_3 as impurities)	(iii) Serpeck's Method (used for white bauxite containing silica as impurities
$Al_2O_3 2H_2O + 2NaOH \xrightarrow{\Delta} 2NaAlO_2 + 3H_2O$	$Al_2O_3 2H_2O + Na_2CO_3 \xrightarrow{Fuse} 2NaAlO_2 + CO_2 + 2H_2O$	$Al_2O_3 2H_2O + 3C + N_2 \xrightarrow{1800°} 2AlN + 3CO + 2H_2O$
Fe_2O_3 insoluble separated as red mud by filteration	$2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{60°C} 2Al(OH)_3 + Na_2CO_3$	$2AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$
$NaAlO_2 + 2H_2O \overset{H^+}{\rightleftharpoons} NaOH + Al(OH)_3$		$SiO_2 + 2C \xrightarrow{1800°C} 2CO\uparrow + Si\uparrow$
$2Al(OH)_3 \xrightarrow[>1000°C]{\Delta} Al_2O_3 + 3H_2O$	$2Al(OH)_3 \xrightarrow[>1000°C]{\Delta} Al_2O_3 + 3H_2O$	$2Al(OH)_3 \xrightarrow[>1000°C]{\Delta} Al_2O_3 + 3H_2O$

Electrolysis of pure fused Al_2O_3 (Hall - Heroult method)

Cathode - iron tank lined with graphite
Anode - Carbon rods dipped in molten electrolyte
Electrolyte - molten (20% Al_2O_3 60% Cryolite 20% CaF_2) Temp ≈ 1100°C
Cryolite lowers the melting point of mixture and makes the molten mix conducting.
$Na_3AlF_6 \rightleftharpoons 3NaF + AlF_3$
$AlF_3 \rightarrow Al^{3} + 3F^{-}$
At cathode $Al^{3} + 3e^{-} \rightarrow Al$
At anode $3F^{-} \rightarrow 3F + 3e^{-}$
$Al_2O_3 + 6F \rightarrow 2AIF_3 + \frac{3}{2} O_2$
$C + \frac{1}{2} O_2 \rightarrow CO$
$CO + \frac{1}{2} O_2 \rightarrow CO_2$



Electrolytic cell

Anodes are periodically changed as they are consumed by oxygen liberated at anode.

Electrolytic refining (Hoppe's Method)

Iron box lined with carbon, contains the three molten layers.
Bottom layer: Impure Al as anode
Middle layer: (Na_3AlF_6 BaF_2) Molten electrolyte
Tope layer: molten pure Al as cathode.

On passing the current aluminium is deposited at cathode from the middle layer and an equivalent amount is taken from andoe (bottom layer) levaing behind the impurites. In this way aluminium obtained is 99.98% pure.

9. Magnesium: (Dow's process)

Ores:

Carnallite $MgCl_2.KCl\ 6H_2O$ (main ore); Epsom $MgSo_4.7H_2O$ magnesite $MgCO_3$;
Kiesserite $MgSO_4.\ H_2O$; Dolomite $MgCO_3.\ CaCO_3$; Kainite $K_2SO_4.\ MgSO_4.\ MgCl_2.6H_2O$
(Mg is also found in Talc, sabestos and chlorophyll)
Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) Precipitation of magnesium as magnesium hydroxide by slaked lime :

$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$ (ppt. reaction)

(b) Preparation of hexahydrated magnesium chloride :

$Mg\ (OH)_2 + 2HCl(aq) \rightarrow MgCl_2 + 2H_2O$ (Neutralisation reaction)
The solution on concentration and crystallisation gives the crystals of $MgCl_2.6H_2O$

(c) Preparation of anhydrous magnesium chloride:

$MgCl_2.6H_2O \xrightarrow[\text{Dry HCl(g)}]{\Delta} MgCl_2 + 6H_2O$
* It is not made anhydrous by simple heating because it gets hydrolysed.
$MgCl_2.6H_2O \xrightarrow{\Delta} MgO + 5H_2O + 2HCl$

(d) Electrolysis of fused anhydrouns $MgCl_2$:

Magnesium chloride obtained by any of the above methods is fused and mixed with sodium chloride and calcium chloride in the temperature range of 972 - 1023K. The molten mixture is electrolysed. Magnesium is liberated at the carhode (iron pot) and chlorine is evolved at graphite anode.

$MgCl_2 \xrightleftharpoons{700^\circ C} Mg^2\ \ 2Cl^-$
At cathode: $Mg^2 + 2e^- \rightarrow Mg$ (99% pure);
At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$