

METALLURGY

Metallurgy

The branch of chemistry deals with the method of extraction of metals from their ores.

Most abundant metal in earth crust is Al.

(1)	(2)	(3)	(4)
Minerals	Ores	Flux	Gangue or Matrix
Elements or other substances obtained from earth crust	Minerals from which metal can be extracted easily + profitably	Compounds which are used to remove non volatile impurities <ul style="list-style-type: none">• acidic flux (used to remove basic impurities)• basic flux (used to remove acidic impurities)	Impurity present in ores

All ores are mineral but all minerals are not an ores

Types of Metallurgy

- (1) Pyro metallurgy
- (2) Hydro metallurgy
- (3) Electro metallurgy

Different steps are used in pyro metallurgy

- (a) Crushing & grinding of ore
- (b) Concentration of ore

It is done by different methods

- (1) Froth floatation method used for sulphideore
 - (2) Froth floatation method (water soluble impurities remove)
 - (3) Gravity separation method (Heavy/light impurities remove)
 - (4) Magnetic separation method (Magnetic/non-magnetic impurities remove)
 - (5) Leaching method (In this method chemicals are used which react with pure metal)
- (c) Calcination (done in absence or controlled air)
 - (d) Roasting (Done in excess of air) (sulphide ore convert to oxide ore and SO_2 , P_2O_5 , As_2O_5 evolve out)
 - (e) Main advantage of roasting is to convert sulphide or into oxide ore because oxide ore easily reduced than sulphide.
 - (f) Smelting (non volatile impurities remove)
 - (g) Bessemerisation
 - (h) Purification of metal (by Electrolysis)

Hydro metallurgy

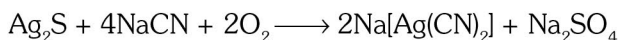
Cyanidation method

- (a) Crushing ore
- (b) Concentration of ore
- (c) Complex formation
- (d) Metal displacement

[Extraction of Ag from Ag_2S]

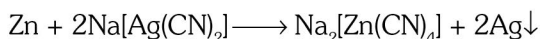
- (a) Crushing of ore

- (b) Ore reacts with excess of NaCN in presence of excess of air.



Use of oxygen is to convert reversible reaction into irreversible

- (c) Displacement of Ag by Zn



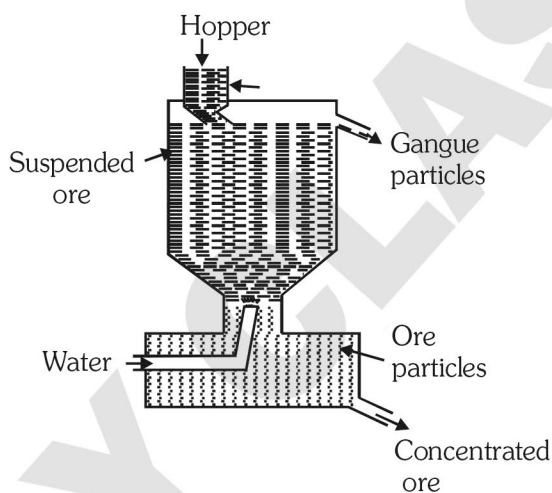
Here Zn acts as reducing agent.

(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 and 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 stabilisers :** To stabilise froth.

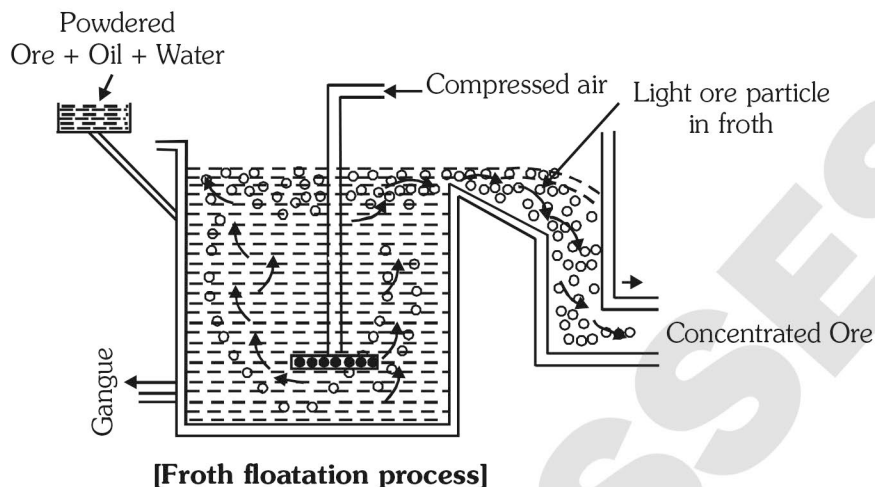
Ex. Cresol, Aniline etc.

- (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

$\text{NaCN} + [\text{PbS} + \text{ZnS}] \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + \text{PbS} \rightarrow \text{form froth}$

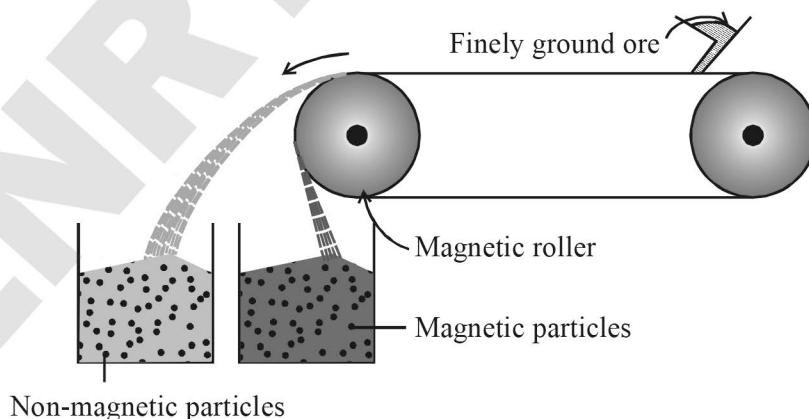


- Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'.
- For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to go along with the froth.

(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 $\text{FeWO}_4 + \text{MnWO}_4$ (Wolframite)
 - $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ having the impurities of SiO_2 .

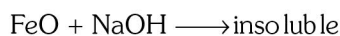


2. **CHEMICAL SEPARATION (LEACHING)** : In this process we use suitable agent which react with ore to form water soluble complex while impurities remain insoluble. Applicable for Al, Ag, Au.

- (a) **Aluminium** :
- Red Bauxite $\rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Fe}_2\text{O}_3$ (Major impurity)
 - White Bauxite $\rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{SiO}_2$ (Major impurity)

(I) **RED BAUXITE** : Two processes

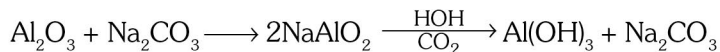
(i) **Baeyer's process** : NaOH is used.



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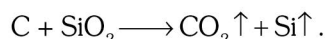
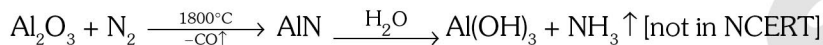
Basic

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

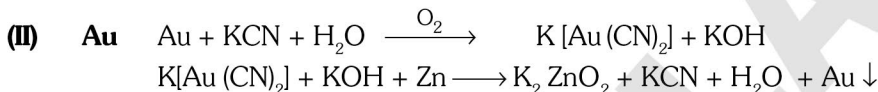
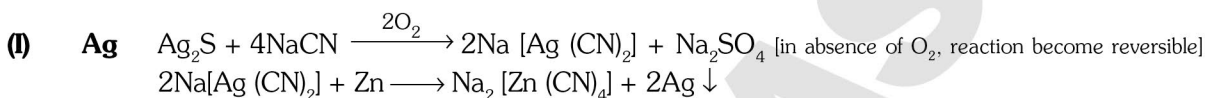


(II) **WHITE BAUXITE** : One process.

Serpeck's process : $(\text{C} + \text{N}_2)$ is used



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

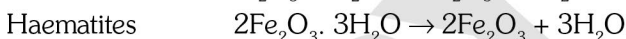


(B) **Conversion of concentrated ore into oxide form**

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

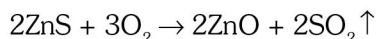


Advantages of Calcination :-

- (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

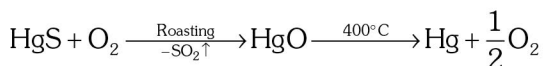
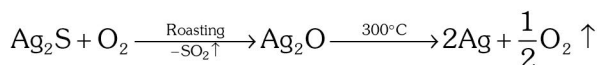
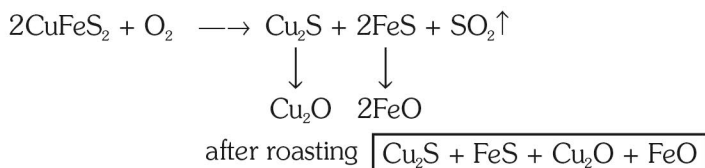
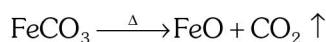
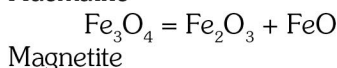
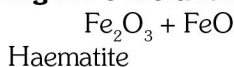
(b) **Roasting** : The removal of the excess sulphur contained in sulphide ores in the form of SO_2 by heating in an excess of air is called roasting.

The concentrated sulphide ore is heated in reverberatory furnace, below its melting point in the presence of an excess of air with or without the addition of an external substance.



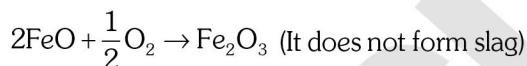
Thermal reduction

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

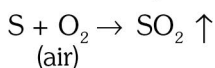
**Partial roasting****Roasting in Fe metallurgy**

Siderite

Roasting \rightarrow to prevent wastage of Fe as slag in reduction step

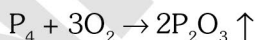
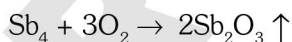
**In reduction step****Advantages of Roasting :-**

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



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

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

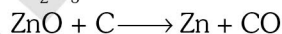


• For PbS, CuS and HgS partial roasting is carried out because these sulphide ore easily convert into metal by auto reduction process.

Reduction of metal oxide to metal

Different methods are used to convert metal oxide to metal

(a) Reduction by Carbon - Oxide of less reactive metal can be convert to metal on strongly heating with coke.



Note :- Some metal oxides like Al_2O_3 , Cr_2O_3 , Mn_3O_4 , MnO_2 are not reduced by coke.

Note :- CO is better reducer but not for Zn.

(b) **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.

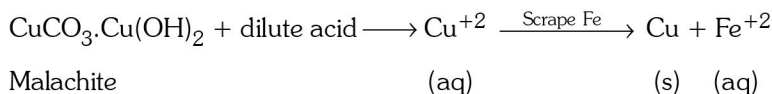
Self reduction for Cu (Extraction of Cu from copper glance.)



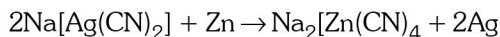
(c) **Metal displacement method**

In this method, a water soluble compound is obtained from the ore. The aqueous solution of the compound is reacted with a more electropositive metal which displaces, the metal from the solution.

Ex. (i) Extraction of Cu from low grade (lean) ore



Ex. (ii) Separation of Ag by Complex formation (Cyanide process).



(d) **Electrolytic reduction**

This process is mainly used for the extraction of **highly electropositive metals**.

Electrolysis is carried out in large cells and a small amount of another suitable electrolyte is added which:

- (i) Lowers the melting point of the main electrolyte
- (ii) Enhances its conductivity
- (iii) Reduces corrosion troubles

Ex. Na, K, Mg, Ca, Al, etc.

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

Molten NaCl containing a little CaCl₂ is electrolysed between graphite anode and iron cathode. The various reactions that take place are

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

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

At Anode : $2\text{Cl}^- \rightarrow \text{Cl}_2 (\text{g}) + 2e^-$

Note : Hall heroult process : This process is used for extraction of Al from alumina. The extraction of Al from Al₂O₃ is quite difficult because –

- (i) Fusion temperature of Alumina is quite high (2050°C). Even more than boiling point of Al (1150°C).
- (ii) It is a bad conductor of electricity.

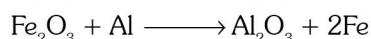
To overcome these difficulties we mix some amount of neutral flux [Na₃AlF₆ + CaF₂]. Neutral flux provide free ions to the solution which decreases the fusion temperature of Alumina from 2050°C to 950°C.

(e) **Alumino thermite process :** In this process those metal oxide will be reduced which required high temperature and at high temperature carbon react with metal to form 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 stable oxide (Al₂O₃).
- (ii) This reaction is highly exothermic in nature and once it starts it will continue till all the metal oxide reduces to metal.

For Cr, Mn, Fe :



Commercial use of this method is in aluminothermite weldings.

Note :- (Fe₂O₃ : Al) mixture in 3 : 1 is used.

REFINING OF METALS

Depending upon the nature of the metal and impurities, the following methods are used for purification of the metals.

(1) Distillation

Metals having low boiling point are refined by this method, for example, zinc, cadmium and mercury.

(2) Liquefaction

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

Ex. Pb, Sn, Sb, Bi and Hg.

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

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

(3) Electro-refining of Metals

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

Anode mud - Deposition of noble metals like Au Y Pt below anode.

Anode - made of impure metal

Cathode - made of pure metal

Electro refining of Copper

Anode : Blister copper (98%)

Cathode : Pure copper

Electrolyte : An aqueous solution of CuSO_4 (15%) + 5% dil H_2SO_4

Electro refining of Pb (Bett's process)

Anode : Impure lead.

Cathode : Pure lead.

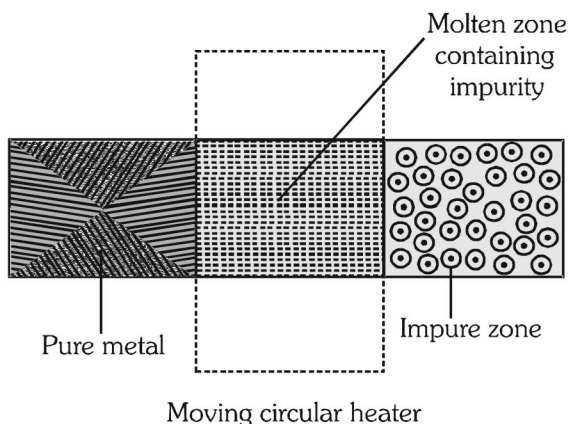
Electrolyte : A mixture of PbSiF_6 and H_2SiF_6

(4) Zone refining or fractional crystallisation

Metals of very high purity are obtained by zone refining.

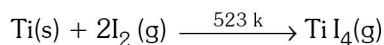
This refining method is based on the fact that impurities tend to remain dissolved in molten metal than solid.

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

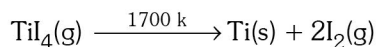


(5) Vapour phase refining**(i) Van - Arkel process**

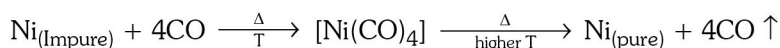
- Employed for purification of metals like **titanium(Ti)** and **zirconium(Zr)**.



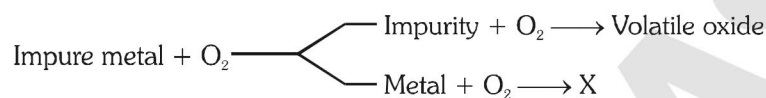
Impure

**(ii) Mond's process**

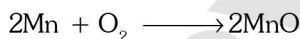
Nickel is purified by using CO gas. This involves the formation of nickel tetracarbonyl.

**(6) Some chemical processes****(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) Polling :** Used to purify Cu, Pb.

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

**(iii) Bessemerisation :** Impure metal is heated in a furnace and a blast of compressed air is blown which oxidises the impurity into their oxides and that can be removed in the form of slag .**GOLDEN KEY POINTS****Types of Iron**

Pig iron \rightarrow Cast iron \rightarrow Steel iron \rightarrow Wrought iron

(i) Cast iron and 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 mid-way 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.

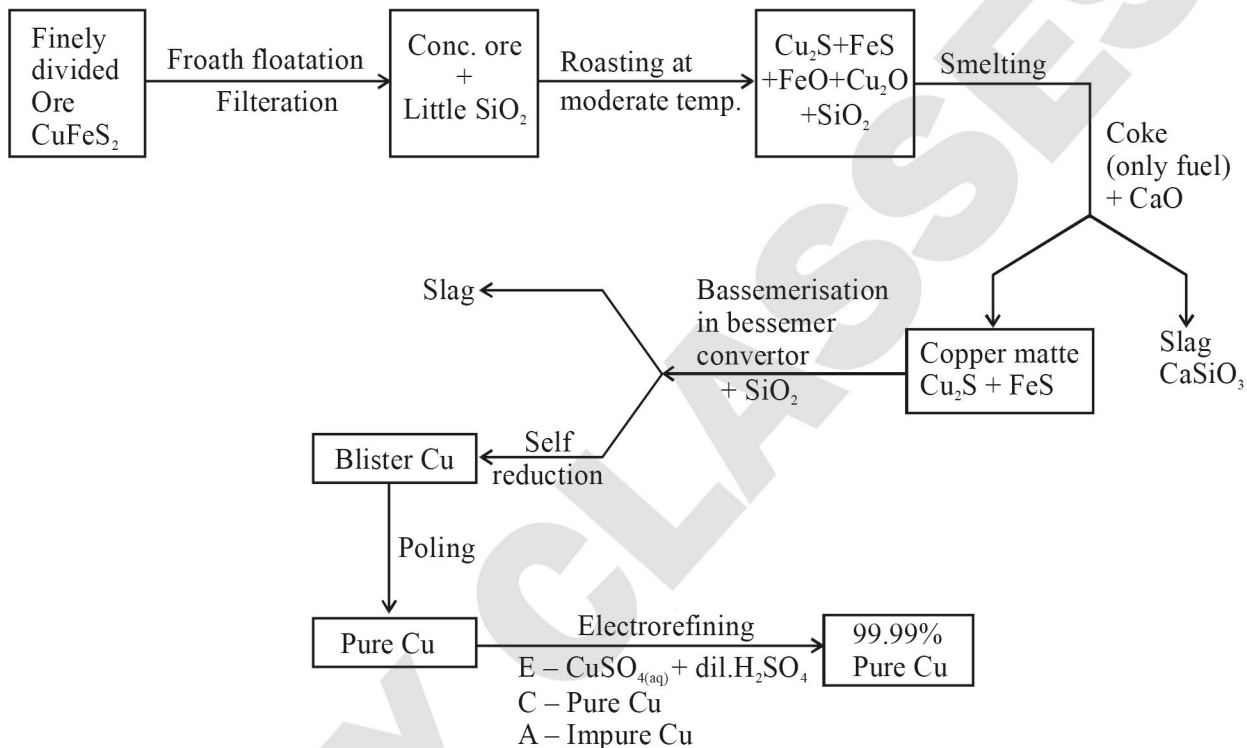
Order of M.P. :- Wrought iron > Steel > Cast iron or Pig iron

Heat Treatment of Steel

- (a) **Quenching or hardening** : Steel is heated to red hot temp. and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.
- (b) **Annealing** : The steel is heated to red hot temp. and then cooled slowly. It makes steel soft.
- (c) **Tempering** : If quenched steel is heated to temp. between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.

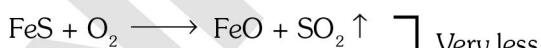
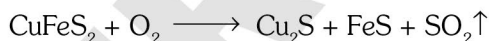
Extraction of Cu

Ore - CuFeS_2 copper pyrites



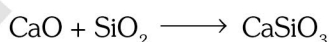
Reaction involved :

(a) Roasting step

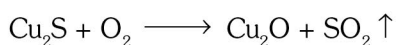
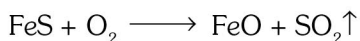


(b) Smelting step :-

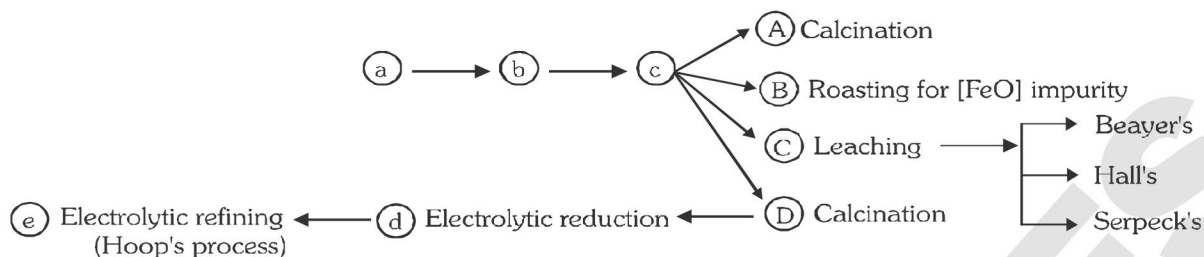
Cu_2S remain unaffected again becoz carbon reduction occurs only for oxide and not for sulphide.



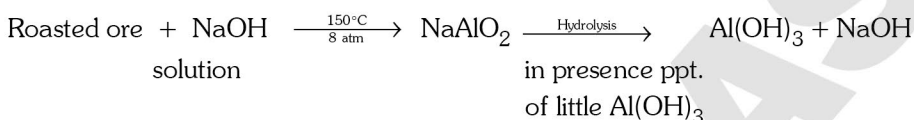
(c) Bassemer convertor reaction :-



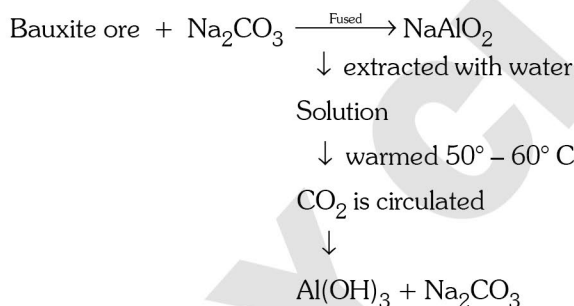
Extraction of Aluminium

Short chart of Al from $Al_2O_3 \cdot 2H_2O$ (Bauxite)**BAUXITE****Concentration of Bauxite ore**

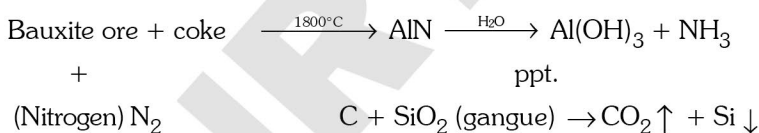
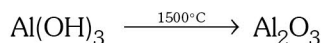
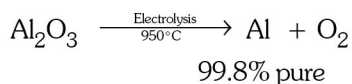
- (a)
- Baeyer's process**
- : (Used for red bauxite in which main impurity is iron oxide)

Bauxite ore $\xrightarrow{\text{Roasted}}$ as to convert FeO into Fe_2O_3 

- (b)
- Hall's Process**
- : (Red bauxite)



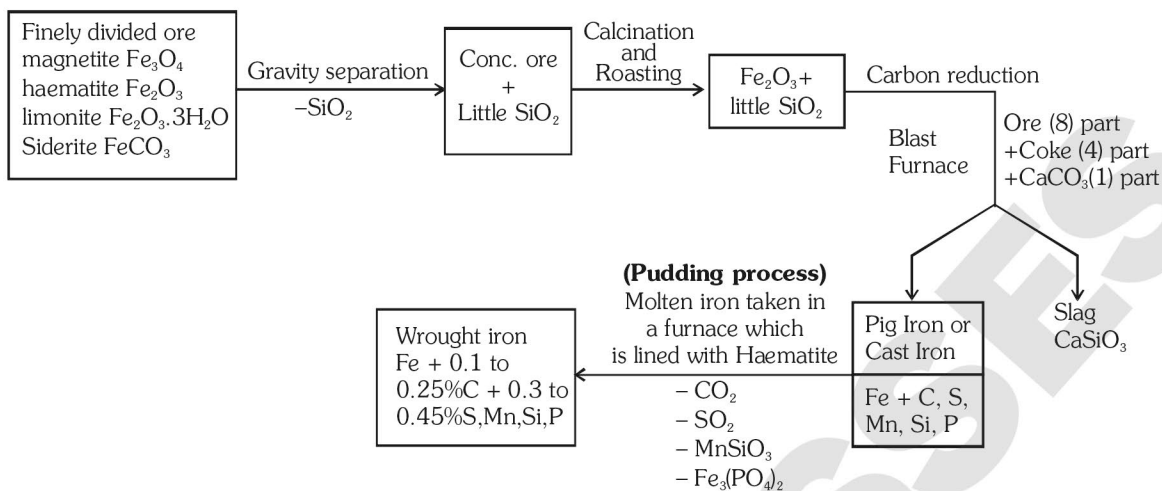
- (c)
- Serpeck's process**
- : (Used for white bauxite in which main impurity is silica)

**CALCINATION****Electrolytic Reduction**Electrolyte Al_2O_3 dissolved in Na_3AlF_6 and CaF_2 **Cathode** – Carbon lining**Anode** – Graphite rods**Electrolytic Refining**

(Hoop's process)

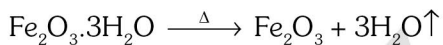
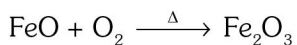
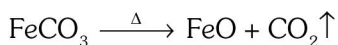
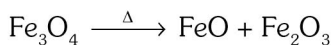
Pure Al (99.98 % pure)

Extraction of Fe



Reaction involved :

(1) Roasting step :-



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.