

INORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Metallurgy

ENGLISH MEDIUM





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METALLURGY

4.1 INTRODUCTION

Metallurgy: The branch of chemistry which deals with 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.

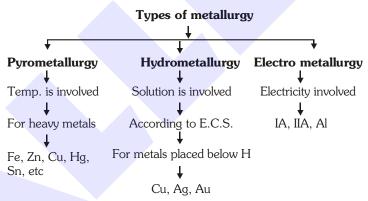
All ores are minerals but all minerals are not ores.

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

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
- **(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.)



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 to the metal (D) Refining of the metal.

(A) Concentration of the ore or benefaction or dressing of ore :

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 CONCENTRATION:

(i) Gravity separation (Levigation) : This method of concentration of the ore is based on the difference in the 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.



Used for concentration of oxygenated ores.

(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 particles are preferentially wetted by water and the ore particles 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 generally of four 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:— They 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 : They stabilise froth.

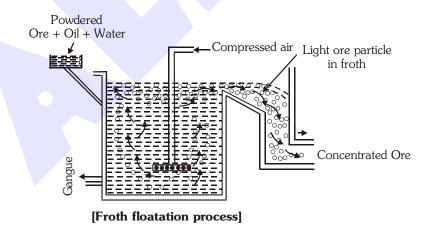
Ex. Cresol, Aniline etc.

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

for eg. 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 come with the froth.

$$NaCN + (ZnS + PbS) \longrightarrow Na_2[Zn(CN)_4] + PbS$$

(remain in (comes to the solution) the froth)

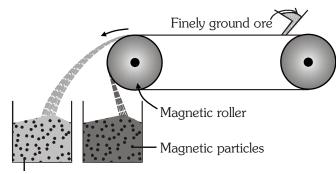


(iii) Magnetic separation:-

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. SnO₂ which is non magnetic having the impurities of FeWO₄ + MnWO₄ (Magnetic)
 - FeO.Cr₂O₃ (Magnetic) having the impurities of SiO₂ (Non magnetic)





Non-magnetic particles

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

Red Bauxite
$$\rightarrow Al_2O_3.2H_2O + Fe_2O_3 / FeO$$

(Major impurities)

White Bauxite
$$\rightarrow Al_2O_3.2H_2O + SiO_2$$

(Major impurities)

for red bauxite:

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

$$\begin{aligned} &\text{Al}_2\text{O}_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 \xrightarrow{\quad \text{H}_2\text{O(excess)} \& \text{CO}_2 \quad} &\text{Al(OH)}_3 \downarrow + \text{NaOH} \\ &\text{Fe}_2\text{O}_3 \ / \ \text{FeO} + \text{NaOH} \longrightarrow &\text{insoluble} \end{aligned}$$

(ii) Hall's process: Na₂CO₃ is used.

$$\mathsf{Al_2O_3} + \mathsf{Na_2CO_3} \longrightarrow \mathsf{2NaAlO_2} \xrightarrow{\mathsf{HOH}} \mathsf{Al(OH)_3} \downarrow + \mathsf{Na_2CO_3}$$

for white bauxite

(i) **Serpeck's process:** a mixture of $(C + N_2)$ is used

$$\begin{split} &\text{Al}_2\text{O}_3 + \text{N}_2 \xrightarrow{1800^{\circ}\text{C}} \text{AlN} \xrightarrow{H_2\text{O}} \text{Al(OH)}_3 \downarrow + \text{NH}_3 \uparrow \\ &\text{C} + \text{SiO}_2 \longrightarrow \text{CO}_2 \uparrow + \text{Si} \uparrow \,. \end{split}$$

- (b) for Ag and Au (CYANIDE PROCESS)
 - (I) for Ag $Ag_2S + 4NaCN \xrightarrow{2O_2} 2Na [Ag (CN)_2] + Na_2SO_4 [in absence of O_2, reaction become reversible]$ $<math>2Na[Ag (CN)_2] + Zn \longrightarrow Na_2 [Zn (CN)_4] + 2Ag \downarrow$
 - (II) for Au Au + KCN + $H_2O \xrightarrow{O_2}$ K [Au (CN)₂] + KOH K[Au (CN)₂] + KOH + Zn \longrightarrow K₂ ZnO₂ + KCN + H_2O + Au \downarrow



(B) Calcination and roasting (Conversion of ore into oxide form)

Concentrated ore must be converted into a form which is suitable for reduction, usually the ore is converted to oxide before reduction because oxides are easier to reduce.

Calcination: Calcination is a process in which ore is heated at temp. below melting point, generally in the absence of air, to expel water from a hydrated or hydroxide ore and carbon dioxide from a carbonate ore.

eg.
$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

 $2Fe_2O_3$. $3H_2O \xrightarrow{\Delta} 2Fe_2O_3 + 3H_2O$
 $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
 $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} CuO + CO_2 + H_2O$

Advantages of Calcination :-

- (i) Moisture is removed.
- (ii) Organic matter is destroyed
- (iii) The ore become porous and easily workable
- **(b)** Roasting: The removal of the excess sulphur contained in sulphide ores in the form of SO₂ 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.

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

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

Some important examples of roasting

Sulphide of Ag and Hg (Ag₂S, HgS) when roasted they give directly metal and oxygen because their oxides are unstable towards heat.

$$\begin{array}{c} \text{Ag}_2\text{S} + \text{O}_2 \xrightarrow{\Delta} \text{Ag}_2\text{O} \xrightarrow{\Delta} \text{2Ag} + \frac{1}{2}\text{O}_2 \\ \text{Unstable} \\ \text{HgS} + \text{O}_2 \xrightarrow{\Delta} \text{HgO} \xrightarrow{\Delta} \text{Hg} + \frac{1}{2}\text{O}_2 \\ \text{Unstable} \end{array}$$

Oxides ores of iron Fe_2O_3 (heamatite), Fe_3O_4 (magnetite) has some amount of FeO and before reduction process these oxide ores of iron should undergo roasting so that FeO can be converted into Fe_2O_3 and it could not form slag with SiO_2 to prevent loss of Fe.

Advantages of Roasting :-

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

$$S + O_2 \rightarrow SO_2 \uparrow$$
 (air)

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

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

 $As_4 + 3O_2 \rightarrow 2As_2O_3 \uparrow$
 $P_4 + 3O_2 \rightarrow 2P_2O_3 \uparrow$

 \bullet For PbS, Cu_2S and HgS partial roasting is carried out because these sulphide ore easily converted into metal by self reduction process.

BEGINNER'S BOX-1

1. Match the following :-

Ore Main element

- (A) Malachite green (P) Fe
- (B) Siderite (Q) Pb (C) Cerrusite (R) Mn
- (D) Pyrolusite (S) Cu
- (1) A-S, B-Q, C-P, D-R (2) A-S, B-P, C-Q, D-R (3) A-Q, B-S, C-P, D-R
- **2.** For which of the following ore, froth floatation method is used?
 - (1) $CaCO_3$ (2) Al_2O_3 .2 H_2O
- (2) $Al_2O_3.2H_2O$ (3) PbS (4) Fe_2O_3
- **3.** Which is correct for chemical concentration (Leaching)?
 - (1) ore form soluble complex with reagent but gangue remain insoluble
 - (2) gangue form soluble complex with reagent but ore remains insoluble
 - (3) both ore and gangue form soluble complex with reagent
 - (4) neither ore nor gangue form soluble complex with reagent
- **4.** Which of the following ore contains both Mg & Ca:
 - (1) Magnesite (2) Calamine
- (3) Carnelite
- (4) Dolomite

- **5.** Argentite is an ore of:-
 - (1) Iron
- (2) Gold
- (3) Platinum
- (4) Silver
- **6.** If Bauxite consists of SiO₂ as impurity, this process employed for concentration is :-
 - (1) Hall's process
- (2) Bayer's process
- (3) Hoope's process
- (4) Serpeck's process

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

- **8.** Chemical leaching is useful in the concentration of:-
 - (1) bauxite
- (2) copper pyrities
- (3) cassiterite
- (4) None
- **9.** Which of the following ore will undergo roasting for conversion into oxide form?
 - (1) CaCO₃
- (2) Al₂O₃.2H₂O
- (3) ZnS
- (4) All
- **10.** Which of the following acts as depressant in froth floatation method?
 - (1) Pine oil
- (2) Cresol
- (3) Xanthates
- (4) NaCN

(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".



Pre-Medical

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced to metal by strongly

heating them with coal or coke, in the blast furnace.

Metal Oxide + Coke + flux \rightarrow Metal + $CO_2 \uparrow$ + Slag.

Ore, limestone and coke

Cone

Exhaust gases (Co, CO₂)
$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
(Iron ore)
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

$$FeO + CO \rightarrow Fe + CO_2$$

$$CaCO_3 \rightarrow CaO + CO_2$$
(Lime Stone)
$$CaO + SiO_2 \rightarrow CaSiO_3$$
(Slag)
$$C + CO_2 \rightarrow 2CO$$
(Coke)
$$C + O_2 \rightarrow CO_2$$

$$FeO + C \rightarrow Fe + CO$$
Blast of air and oxygen

Solid waste

(Blast Furnace)

eg. ZnO + C
$$\longrightarrow$$
 Zn + CO \uparrow

PbO + C \longrightarrow Pb + CO \uparrow

SnO₂ + 2C \longrightarrow Sn + 2CO \uparrow

Fe₂O₃ + 3C \longrightarrow 2Fe + 3CO \uparrow

These reactions are carried out at high temperature because at high temp. C is better reducing agent.

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

Types of flux :-

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

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

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



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

$$\begin{array}{cccc} \text{For example} & & \text{CaO} & + & \text{SiO}_2 & \longrightarrow & \text{CaSiO}_3 \\ \downarrow & & \downarrow & & \downarrow \\ \text{(basic flux)} & \text{(acidic impurities)} & & \text{Slag} \end{array}$$

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 mixture by providing free ions.

For example :
$$(Na_3AIF_6 + CaF_2)$$
, $CaCl_2$ etc.

Smelting in Cu-metallurgy

(ii) Alumino thermite process or thermite welding process: In this process those metal oxide (oxides of Mn, Ti, Cr, Fe) 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 stable oxide (Al₂O₃)
- (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.

In this process metal 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. eg. for sulphides of Cu, Pb, Hg etc.

Self reduction for Pb:

$$\begin{array}{c} \text{2PbS} + 3O_2 \xrightarrow{\text{Partial roasting}} \text{2PbO} + 2SO_2 \uparrow \\ \text{(Galena) (air)} \\ \text{PbS} + 2\text{PbO} \xrightarrow{\text{High temp}} \text{3Pb} + SO_2 \uparrow \\ \end{array}$$

Pre-Medical

TG: @Chalnaayaaar

Chemistry: Metallurgy

Self reduction for Cu (Bessemerisation)

$$Cu_2S + FeS + SiO_2 \longrightarrow Blister copper + slag$$

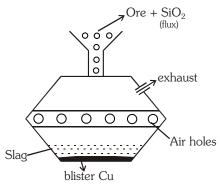
(Copper matte) (flux)

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

FeO +
$$SiO_2 \longrightarrow FeSiO_3$$
 (slag) (gangue) (flux)

$$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$$

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2 \uparrow$$
(Blister copper)



Bessemer convertor

The solidified copper obtained has blistered appearance due to evolution of SO_2 and so it is called blister Copper.

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

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

(IV) Electrolytic reduction

This process is mainly used for the extraction of highly electropositive metals. I A, II A & Al Electrolysis is carried out in a large cell and a small amount of another suitable electrolyte is added which:

- (a) Lowers the melting point of the main electrolyte
- (b) Enhances conductivity of molten mixture
- (c) Reduces corrosion troubles
 e.g. Manufacture of metallic sodium (Down's process)

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

On Fusion : NaCl
$$\rightleftharpoons$$
 Na⁺ + Cl⁻

On Electrolysis : At Cathode :-
$$Na^+ + e^- \rightarrow Na$$

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 Al₂O₃ 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 mixture which decreases the fusion Cryolite Fluospar

temperature of Alumina from 2050°C to 950°C and increases the conductivity of solution.

(i) From cryolite
$$\rightarrow$$
 AlF₃ \longrightarrow Al⁺³ + 3F

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

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

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

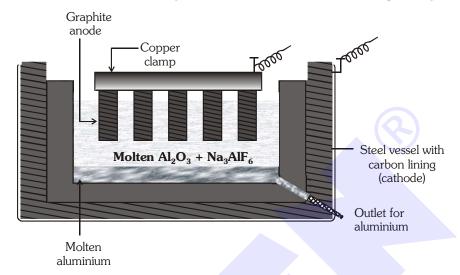


(ii) From Al₂O₃

At Cathode : $Al^{+3} + 3e^{-} \rightarrow Al$

At Anode : $C(s) + 2O^{-2} \rightarrow CO_2(g) + 4e^{-1}$

The oxygen liberated at anode reacts with the carbon of anode producing $CO \& CO_2$ and anode is destroyed, so the main drawback of this process is that anode should be changed frequently.



(D) REFINING OF METALS

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

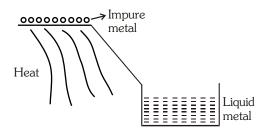
(I) Physical Process:

(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.

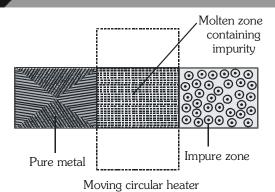
The pure metal flows down leaving behind the non-fusible impurities on the hearth.



- (ii) Distillation: Metals having low boiling point are refined by this method. eg. Zn, Cd, Hg
- **(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 O₂ while metal does not have.

Impure metal +
$$O_2$$

Metal + O_2
 X

Impure metal (Ag)

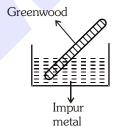
Air holes

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

This process is used for the metal having the impurity of their own oxide. In this process a green wooden pole is heated with molten metal, which provide hydrocarbon (i.e. CH_4) and it reduces impurity of metal oxide to metal.

$$2Cu_2O + CH_4 \longrightarrow 4Cu + CO_2 + 2H_2 \uparrow$$

Impurity



(III) ELECTRO-REFINING OF METALS

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

Anode of electrolytic cell is made from impure metal, 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**. For Example

Electrorefining of 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 : Impure silver Cathode : Pure silver

Electrolyte : aq. solution of $AgNO_3 + 1\%$ dil HNO_3

- Electrorefining of Al (Hoope's process)

Anode : Impure Al, Cathode : Pure Al Electrolyte : A mixture of Na₃AlF₆ + CaF₂

(IV) Vapour Phase Refining / Thermal decomposition

In this method the metal is converted into its volatile compound and collected. It is then decomposed to give pure metal.

Two requirements are -

- (i) The metal should form a volatile compound with available reagent.
- (ii) The volatile compound should be easily decomposable, so that recovery is easy.

(i) Van Arkel method:

for Ti and Zr

useful for removing all the oxygen and nitrogen impurities from metals like Zr and Ti.

$$Ti(s) + 2I_2 \xrightarrow{523 \text{ K}} Ti I_4(g)$$

Impure

$$Til_4(g) \xrightarrow{1800 \text{ K}} Ti(s) \text{ (pure)} + 2l_2(g)$$

(ii) Mond's process

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

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

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. In the extraction of Cu, 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.** Al₂O₃ cannot be reduced to Al by carbon at high temperature because
 - (1) Temperature requirement is high which increases fuel cost
 - (2) Al can form carbide with carbon
 - (3) After reduction collection of metal is to be done very carefully in an inert environment
 - (4) All of the above
- **4.** Identify incorrect match
 - (1) Sn; Liquation
- (2) Zn; Distillation
- (3) Cu; Electrorefining
- (4) Fe; Zone Refining

- Pre-Medical
- **5**. The function of flux during the smellting of ore is:-
 - (1) To make the ore porous

(2) To remove nonfusible impurity

(3) To facilitate reduction

- (4) To facilitate oxidation
- **6.** The following equation represents a method of purification of nickel:-

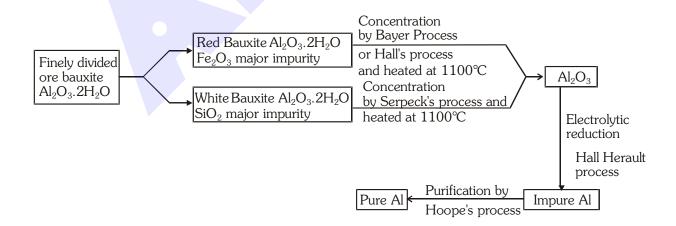
Ni (impure) + 4CO $\xrightarrow{320 \mathrm{K}}$ Ni(CO)₄ $\xrightarrow{420 \mathrm{K}}$ Ni (pure) + 4CO is known as -

- (1) Cupellation
- (2) Mond's process
- (3) Van Arkel method
- (4) Zone refining
- 7. The slag obtained during the extraction of copper from copper pyrities is composed of :-
 - (1) Cu₂S
- (2) CuSiO₃
- (3) FeSiO₃
- (4) SiO₂
- 8. Which acts as a reducing agent in low temperature zone of blast furnace in smelting process of Fe?
 - (1) C

- (2) CO
- (3) CO₂
- (4) All of the above
- **9.** Which of the following cannot reduced by carbon reduction method?
 - (1) Fe_2O_3
- (2) ZnO
- (3) PbO
- (4) Al₂O₃
- **10.** Which of the following metal can be obtained from their ore by self reduction method?
 - (1) Cu
- (2) Hg
- (3) Pb
- (4) All of the above

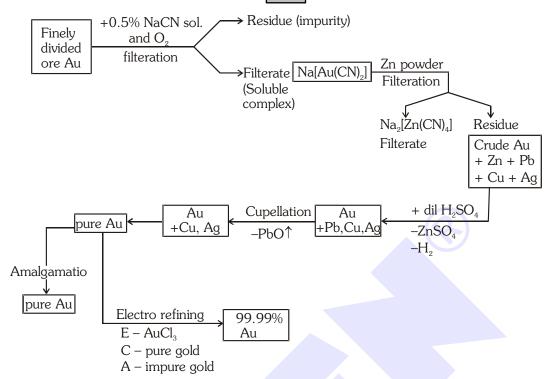
Extraction of metals from their ores









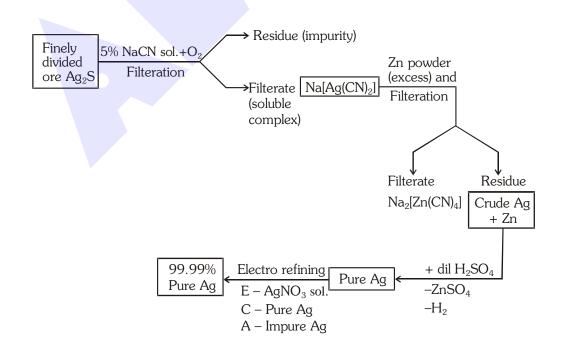


Reaction involved:

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

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

Ag





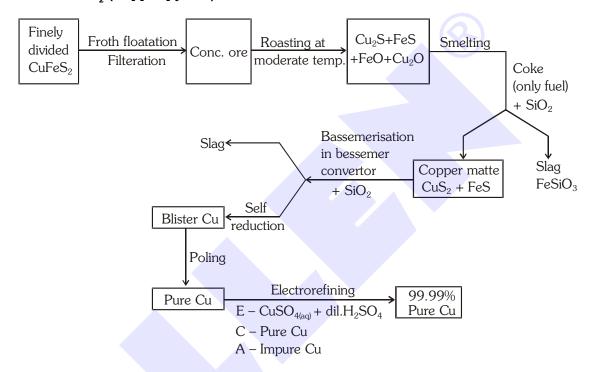
Chemistry: Metallurgy Pre-Medical

Reaction involved:

- $Ag_2S + 4NaCN \Longrightarrow 2Na[Ag(CN)_2] + Na_2S \xrightarrow{O_2+H_2O} Na_2SO_4 + 'S' + 2NaOH$ (a) \Rightarrow O₂ is used to make reaction irreversible which remove Na₂S as Na₂SO₄ + S
- $2Na[Ag(CN)_{2}] + Zn \longrightarrow Na_{2}[Zn(CN)_{4}] + Ag \downarrow$ (b)



Ore - CuFeS₂ (Copper pyrites)



Reaction involved:

(a) Roasting step

$$\begin{aligned} & \text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + \text{FeS} + \text{SO}_2 \uparrow \\ & \text{FeS} + \text{O}_2 \longrightarrow \text{FeO} + \text{SO}_2 \uparrow \\ & \text{Cu}_2\text{S} + \text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2 \uparrow \end{aligned} \quad \begin{aligned} & \text{Very less} \quad & \\ & \text{Cu}_2\text{S} + \text{FeS} + \text{Cu}_2\text{O} + \text{FeO}_2 \\ & \text{less} \quad & \text{less} \end{aligned}$$

(b) Smelting step:-

Cu₂S remain unaffected again because carbon reduction occurs only for oxide and not for sulphide.

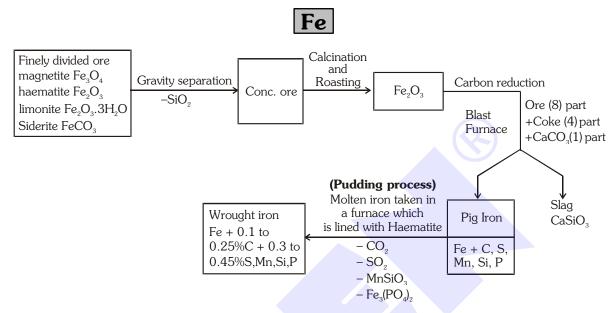
FeS +
$$Cu_2O \rightarrow FeO + Cu_2S$$

FeO + $SiO_2 \longrightarrow FeSiO_3$
(Slag)
 $Cu_2S + FeS$ copper Matte



(c) Bassemer convertor reaction :-

$$\begin{split} \text{FeS} + \text{O}_2 &\longrightarrow \text{FeO} + \text{SO}_2 \uparrow \\ \text{Cu}_2 \text{S} + \text{O}_2 &\longrightarrow \text{Cu}_2 \text{O} + \text{SO}_2 \uparrow \\ \text{Blister Cu} \end{split} \qquad \begin{split} \text{FeO} + \text{SiO}_2 &\longrightarrow \text{FeSiO}_3 \text{ slag} \\ \text{Cu}_2 \text{O} + \text{Cu}_2 \text{S} &\longrightarrow \text{Cu} + \text{SO}_2 \uparrow \\ \text{Blister Cu} \end{split}$$



Reaction involved:

Roasting step:-

$$\begin{aligned} & \text{Fe}_3 \text{O}_4 & \stackrel{\Delta}{\longrightarrow} & \text{FeO} + \text{Fe}_2 \text{O}_3 \\ & \text{FeCO}_3 & \stackrel{\Delta}{\longrightarrow} & \text{FeO} + \text{CO}_2 \\ & \text{FeO} + \text{O}_2 & \stackrel{\Delta}{\longrightarrow} & \text{Fe}_2 \text{O}_3 \\ & \text{Fe}_2 \text{O}_3 \cdot 3 \text{H}_2 \text{O} & \stackrel{\Delta}{\longrightarrow} & \text{Fe}_2 \text{O}_3 + 3 \text{H}_2 \text{O} \\ \end{aligned}$$

GOLDEN KEY POINTS

- Types of Iron :- (i) Pig iron (ii) Cast iron (iii) Steel (iv) Wrought iron
 - (i) Pig iron

It is most impure form of iron and contains the highest proportion of carbon (about 4%) along with traces of S, P, Mn and Si.

(ii) Cast iron

It is different from pig iron and is made by melting pig iron with iron scrap and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

(iii) Steel

It is the most important form of iron and find extensive application. It contains 0.25% – 1% carbon. It is obtained from cast iron.

(iv) Wrought iron / Malleable iron

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%). It is prepared from cast iron.

• Coper from low grade ores and scraps :-

Copper is extracted by hydrometallurgy from its low grade ores.

The solution containing Cu⁺² is treated with scrap iron or H₂.

$$Cu^{+2}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^{+}(aq)$$



Chemistry: Metallurgy Pre-Medical

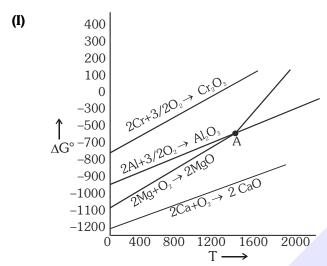
THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM) 4.3

It is explanation of the feasibility of pyrometallurgical process by using gibbs equation $|\Delta G = \Delta H - T\Delta S|$

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

 $\Delta G = +$ ve or Less – ve then process is Unstable or non-Spontaneous

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





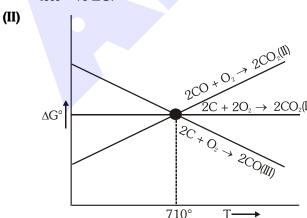
 $\Delta G = +ve$

$$Cr + CaO MgO Al_2O_3$$
 \longrightarrow $Cr_2O_3 + Al Mg Ca$

According to Ellingham diagram, the below metal 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 Cr₂O₃ 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 $-ve \Delta G$ so at Low T, CO is good Reducing agent.

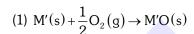
BEGINNER'S BOX-3

- 1. Which of the following statement is true for Ellingham diagram?
 - (1) It consits of plots of ΔG vs T for formation of oxide of metals.
 - (2) It helps in predicting the feasibility of thermal reduction of an ore.
 - (3) Change in slope of a plot indicates the change in physical state of metal oxide
 - (4) All of the above
- 2. 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 CO₂ formed can be easily removed
 - (3) In the lower atmosphere, there is no oxide to be reduced
 - (4) The entropy change during CO/CO₂ is negative
- **3.** 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
- **4.** If in ellingham diagram one plot has more $-ve \Delta G$ then it indicates?
 - (1) Oxidation of metal will be more spontaneous
 - (2) This metal will reduce oxide of metal which has less –ve ΔG in ellingham diagram
 - (3) (1) and (2) both
 - (4) None
- **5.** The true statement is at temperature 'T'



 ΔS is positive

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

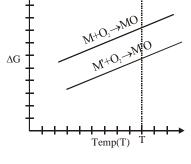
; ΔG is positive

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

 ΔG is negative

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

 ΔS is negative



- **6.** Which is purest form of iron?
 - (1) Pig iron
- (2) Cast iron
- (3) Wrought iron
- (4) Steel

ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	3	1	4	4	4	4	1	3	4
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	3	4	4	2	2	3	2	4	4
				-						-	-
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6				
	Ans.	4	4	1	3	4	3				



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. 3. 4.		MnO_2	Pyrolusite			
		SnO ₂	Cassiterite (Tin stone)			
		Cu ₂ O	Cuprite (Ruby Copper)			
	5.	Fe ₂ O ₃	Haematite			
	6.	$Al_2O_3.2H_2O$	Bauxite			
	7.	FeO. Cr ₂ O ₃	Chromite			
	8.	Fe ₃ O ₄	Magnetite			
	9.	Fe ₂ O ₃ .3H ₂ O	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 (Chalcopyrities)			
	7.	Cu ₂ S.Ag ₂ S	Copper silver glance			
	8.	$Ag_2S.Sb_2S_3$	Pyrargirite (Ruby silver)			
	9.	Cu ₂ S (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 ₂ O	Carnelite			
Carbonate Ore	1.	$MgCO_3$	Magnesite			
2. 3. 4. 5. 6.		CaCO ₃	Lime stone			
		MgCO ₃ .CaCO ₃	Dolomite			
		ZnCO ₃ (Smithosonite)	Calamine			
		PbCO ₃	Cerrusite			
		FeCO ₃	Siderite			
<i>Y</i>	7.	CuCO ₃ . Cu(OH) ₂	Malachite green			
	8.	2CuCO ₃ .Cu(OH) ₂	Azurite			
Sulphate Ore	1.	CaSO ₄ .2H ₂ O	Gypsum			
	2.	MgSO ₄ .7H ₂ O	Epsomite Or Epsom salt			
	3.	K ₂ SO ₄ .Al ₂ (SO ₄) ₃ .24H ₂ O	Alum			
Nitrate Ore	1.	NaNO ₃	Chile- Salt Peter			
	2.	KNO ₃	Salt peter or Indian salt peter			
Phosphate Ore	1.	Ca ₃ (PO ₄) ₂	Rock Phosphate			