INTRODUCTION

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

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 profitably and easily extracted is called an ore.

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

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 concentration ore into oxide form.
- (C) Reduction to the metal

(D) Refining of the metal.

(A) Concentration of the 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:

(i) Magnetic separation:-

If the ore and not the gangue or the gangue and not the ore is attracted by a magnet, the two can be separated by this method.

 SnO_2 having the impurities of FeWO₄. FeO.Cr₂O₃ having the impurities of SiO₂.



(ii) Froth Floatation method

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



Froth floatation process 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 preferrentially 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, Eucliptus oil, etc.

(b) Collectors or floating agents :-

These attach themselves by polar group to the grains of the ores which then become water repellant and pass on into the froth. Example: sodium ethyl xanthate.

(c) Activators or Depressants :-

These reagents activate or depress the flotation properly and help in the separation of different sulphide ores present in a mixture.

An example of depressant is NaCN. An activator is CuSO₄.

(iii) Gravity separation (Lavigation)

This method of concentration of the ore is based on the difference in the specific lavigation gravities of the ore and the gangue particles.



Gravity Separation or Hydraulic Washing

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

CHEMICAL SEPARATION (LEACHING): (2)

In this process we use suitable agent which react with ore to form water soluble complex while impurities will remain insoluble. Applicable for Al, Ag,Au.

(A) Aluminium:

 $\neg \operatorname{Re} d \operatorname{Bauxite} \rightarrow \operatorname{Al}_2O_3.2H_2O + FeO$ (Impurities)

White Bauxite \rightarrow Al₂O₃.2H₂O + SiO₂ (Impurities)

- (I) **RED BAUXITE**: Two process
 - (i) **Baeyer's process :** NaOH is used.

 $Al_2O_3 + NaOH \longrightarrow NaAlO_2 =$ нон $Al(OH)_3 + NaOH$ $FeO + NaOH \longrightarrow X$ Basic

(ii) Hall's process : Na₂ CO₃ is used.

$$Al_{2}O_{3} + Na_{2}CO_{3} \longrightarrow 2NaAlO_{2}$$
$$\xrightarrow{HOH} CO_{2} \rightarrow Al(OH)_{3} + Na_{2}CO_{3}$$

(II) WHITE BAUXITE : One process.

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

$$\begin{array}{rcl} Al_2O_3 &+ & N_2 & \underline{1800^{\circ}C} & AlN & \underline{H_2O} \\ Al(OH)_3 + NH_3 & & \\ C + SiO_2 \longrightarrow CO_2 \uparrow + Si\uparrow. \end{array}$$

(B) Ag and Au (CYANIDE PROCESS)

(I) Ag

 $Ag_2S + NaCN \xrightarrow{O_2} Na [Ag (CN)_2] + Na_2 SO_4$

$$Na[Ag(CN)_{2}] + Zn \longrightarrow Na_{2}[Zn(CN)_{4}] + Ag \downarrow$$

(II) Au

 $\begin{array}{l} \operatorname{Au}+\operatorname{KCN}+\operatorname{H}_2\operatorname{O} & \stackrel{\operatorname{O}_2}{\longrightarrow} \operatorname{K} \left[\operatorname{Au} \left(\operatorname{CN}\right)_2\right] + \operatorname{KOH} \\ \operatorname{K} \left[\operatorname{Au} \left(\operatorname{CN}\right)_2\right] + \operatorname{KOH} + \operatorname{Zn} \longrightarrow \operatorname{K}_2 \operatorname{ZnO}_2 + \operatorname{KCN} \\ + \operatorname{H}_2\operatorname{O} & + \operatorname{Au} \downarrow \end{array}$

- (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

$$\begin{array}{l} \mathrm{Al_2O_3.}\ 2\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + 2\mathrm{H_2O}, \quad 2\mathrm{Al(OH)_3} \rightarrow \\ \mathrm{Al_2O_3} + 3\mathrm{H_2O} \\ 2\mathrm{Fe_2O_3.}\ 3\mathrm{H_2O} \rightarrow 2\mathrm{Fe_2O_3} + 3\mathrm{H_2O} \\ \mathrm{CaCO_3} \rightarrow \mathrm{CaO} + \mathrm{CO_2} \end{array}$$

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 mass become porous and easily workable

(b) Roasting

The removal of the excess sulphur contained in sulphide ores in the form of SO_2 then in the 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. $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ $ZnS + 2O_2 \rightarrow ZnSO_4$ $CuS + 2O_2 \rightarrow CuSO_4$

Advantages of Roasting :-

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

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

- (ii) The metal sulphide is converted into metal oxide.
- (iii) Impurities of arsenic antimony & phosphorous are removed as their volatile oxides.

$$Sb_4 + 3O_2 \rightarrow 2Sb_2O_3 \uparrow$$
$$As_4 + 3O_2 \rightarrow 2As_2O_3 \uparrow$$
$$P + 3O_2 \rightarrow 2PO$$

$$\mathbf{P}_4 + \mathbf{SO}_2 \rightarrow \mathbf{2P}_2\mathbf{O}_3$$

(C) Reduction to the metal

The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

(a) Chemical reduction :

(i) Reduction by carbon (Smelting)

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

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

Metal Oxide + Coke + flux \rightarrow Metal + CO₂ \uparrow +Slag.

FLUX:

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

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

For example

CaO +	$SiO_2 \longrightarrow$	CaSiO ₃
(basic imp.)	✓ (acidic flux)	(Slag)
Acidic flux are	non metal oxide	$(SiO_2, P_2O_5 \text{ etc.})$

(II) Basic flux : Substance used to remove acidic (III)Metal displacement method impurities (non metal oxide)In this method, compound is r

For example

 $\begin{array}{cccc} CaO & + & SiO_2 & \longrightarrow & CaSiO_3 \\ \downarrow & & \downarrow & & \downarrow \\ (basic flux) & (acidic impurities) & Slag \\ Basic flux are metal oxide. (CaO, MgO, etc.) \end{array}$

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

For example : $(Na_3AlF_6 + CaF_2)$, $CaCl_2$ etc.

(B) 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 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 (Al_2O_3)

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

For Cr, Mn, Fe:

$$Cr_2O_3 + Al \longrightarrow Al_2O_3 + 2Cr$$

 $Fe_2O_3 + Al \longrightarrow Al_2O_3 + 2Fe$

(II) Self reduction

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

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

Self reduction for Pb :-

 $\begin{array}{c} 2PbS + 3O_2 \xrightarrow{Roasting} 2PbO + 2SO_2 \uparrow \\ (Galena) \text{ (air)} \end{array}$

PbS + 2PbO $\xrightarrow{\text{High temp}}$ 3Pb + SO₂ \uparrow

(Self reduction)

Self reduction for Cu :-

 $2 \operatorname{Cu}_2 O + \operatorname{Cu}_2 S \xrightarrow{\Delta} 6 \operatorname{Cu} + SO_2$

In this method, compound is reacted with a more electropositive & more reactive metal which displaces, the metal from the solution.

For Example

(i) Zairvogel process for silver.

$$Ag_{2}S + 2O_{2} \xrightarrow{85^{0}C} Ag_{2}SO_{4}$$
Argentite
$$Ag_{2}SO_{4}(aq) + Cu \rightarrow CuSO_{4}(aq) + 2Ag(S)$$
(Scrap Copper)

(IV) Complex formation

Silver and gold are extracted by a method involving complex formation.

Powdered argentite is reacted with a dilute solution of sodium cyanide in the presence of air. The silver from the ore is dissolved in the cyanide solution forming sodium argentocyanide.

$$Ag_2S + 4NaCN \xrightarrow{air} 2Na [Ag(CN)_2] + Na_2SO_4$$

(Powdered argentite)

Now metallic zinc is added to the complex salt solution which being more electropositive element than silver, displaces it from the solution.

 $2Na [Ag(CN)_{2}] + Zn \rightarrow Na_{2} [Zn(CN)_{4}]$ $(aq) + 2Ag \downarrow$

Black ppt.

(V) Electrolytic reduction

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

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

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

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

On Fusion : NaCl \implies Na⁺ + Cl⁻

(Ions become mobile)

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

(Metallic sodium)

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

HALL HEROULT PROCESS: This process is used for extraction of Al from alumina. The extraction of Al from Al_2O_3 is quite difficult because –

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

Mechanism : No specifie mechanism

(I) From Cryolite

 $AlF_3 \longrightarrow Al^{+3} + 3F^{-1}$

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

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

 F_2 reacts with Al_2O_3 .

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

So liberated gas at anode is O_2 . Which on reaction with graphite anode convert into $/CO_2$ and enode the anode

 $C + O_2 \longrightarrow CO_2 \uparrow$

(II) From Al₂O₃

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

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

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

(D) Refining of Metals

Metals obtained by the reduction of its compound still contains some objectionable substance 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.

Examples, 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 nonfusible material on the hearth.

(ii) Distillation

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

(iii) Zone refining

Metals of very high purity are obtained by zone refining.



This refining method is based on the fact that impurities tend to remain dissolved in molten metal. Ge, Si and Ga used as semiconductors are refined in this manner.

(iv) Distribution method

The parke's process is used for the desilverization of argentiferous lead is based on distribution principle. The principle follows as

- (a) Molten zinc and molten lead form a two phase system.
- (b) Silver is more soluble in molten zinc than the molten lead.

- (c) The Zn Ag alloy is lighter than Pb and freezes fast. For Example
- (d) The floating solidified Zn Ag alloy can be easily removed from molten Pb.
- (e) From Zn Ag alloy, zinc is separated by distillation.

(II) CHEMICAL PROCESS :-

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

This porcess is used when impurity have greater affinity towards O_2 while netal 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 poles is heated with molten metal, which provide C and H to metal oxide which reduced impurity of metal oxide to metal.

 $\begin{array}{c} \mathrm{CuO} + \mathrm{H_2} \longrightarrow \mathrm{Cu} + \mathrm{H_2O} \uparrow \\ \mathrm{CuO} + \mathrm{C} \longrightarrow \mathrm{Cu} + \mathrm{CO} \uparrow \end{array}$

(iii) Bessemerisation : Impure metal is heated in a furnace and a blast of compressed air is blown which oxidised the impurity into their oxides and that can be removed in the form of slag.

 $2Mn + O_2 \longrightarrow 2MnO$ Si + O₂ \longrightarrow SiO₂

(III) ELECTRO-REFINING OF METALS

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

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

Electrolyte is the solution of a double salt of the metal.

On passing the electric current pure metal from the

anode dissolves and gets deposited at the cathode.

The soluble impurities go into the solution while insoluble or less electropositive impurities settle down below the anode as **anode mud** or sludge. *Electrorefining of Copper* Anode : Blister copper (98%)

Cathode : Pure copper

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Electrolyte : An aqueous solution of CuSO₄

 $(15\%) + 5\% \text{ dil } \text{H}_2\text{SO}_4$

- Electrorefining of Silver

Anode : Impure silver

Cathode : Pure silver

Electrolyte : $Aq Ag NO_3 + 1\%$ dil HNO_3 on passing electricity anode

dissolves and pure Ag is deposited at the cathode.

Electrorefining of Pb (Bett's process)
 Anode : Impure lead., Cathode : Pure lead.
 Electrolyte : A mixture of PbSiF₆ and H₂SiF₆

(IV) THERMAL DECOMPOSITION

- (i) Van Arkel process
- (i) Employed to get metal in very pure form of small quantities.
- (ii) In this method, the metal is converted into a volatile unstable compound
 (e.g.iodide), and impurities are not affected during compound formation.
- (iii) The compound thus obtained is decomposed to get the pure metal.
- (iv) Employed for purification of metals like titanium and zirconium.

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

Impure

 $\operatorname{TiI}_{4}(g) \xrightarrow{1700 \text{ k}} \operatorname{Ti}(s) + 2I_{2}(g)$

- (ii) Mond's process
- (i) Nickel is purified by using CO gas. This involves the formation of nickel tetracarbonyl.

$$Ni_{(Impure)} + 4CO \longrightarrow [Ni(CO)_4]$$

 $\longrightarrow Ni_{(pure)} + 4CO \uparrow$

COPPER (Cu)

Occurrence

Copper occurs in free as well as in combined state. The main ores are as follows.

(i) Copper pyrites $CuFeS_2 \text{ or } Cu_2S. Fe_2S_3$

- (ii) Cuprite (Ruby copper)Cu₂O
- (iii) Copper glance Cu_2S
- (iv) Malachite $Cu (OH)_2$. $CuCO_3$
- (v) Azurite $Cu(OH)_2$. $2CuCO_3$

Extraction

Copper is extracted from the ores (sulphide) by two process.

1. Pyrometallurgical Process

This is a dry process and applied to high grade ores (containing 4% or more copper).

2. Hydrometallurgical Process

This is a wet process and applied to low grade ores.

1. Extraction from pyrites by pyrometallurgical process (Smelting Process)

(i) Concentration

The finely powdered ore is concentrated by froth floatation process.

(ii) Roasting

The concentrated ore is heated strongly in presence of air.

Sulphur, arsenic, and antimony are removed in form of their volatile oxides while the proper ore is converted into a mixture of cuprous and ferrous sulphides.

These sulphides are partially oxidised to oxides.

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

(b)
$$2As_2S_3 + 9O_2 \rightarrow 2As_2O_3\uparrow + 6SO_2\uparrow$$

(c)
$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 \uparrow + 6SO_2 \uparrow$$

(d)
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

 $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

(iii) Smelting

The roasted ore is mixed with sand (flux) and coke (fuel) and then heated in water jacketed blast furnace called smelter.

The oxidation of ferrous sulphide which started during roasting now goes a step further. Ferrous oxide formed, reacts with sand to form ferrous silicate (slag).

Here some FeS reacts with Cu_2O to form Cu_2S again.

- (a) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$ (Slag)
- (b) $Cu_2O + FeS \rightarrow Cu_2S + FeO$

Slag (forming upper layer) and molten mass consisting of Cu_2S and a little Fe (forming lower layer and commonly called matte) are removed from separate holes.

(iv) Bessemerisation

Molten matte is heated in a Bessemer converter and a blast of air mixed with sand is blown through the molten mass.

Here iron (FeS) is completely removed as slag, a part of Cu_2S is oxidised to Cu_2O and a part of Cu_2S reduces Cu_2O to metallic copper.

- (a) $2\text{FeS} + 3\text{O}_2 \rightarrow 2\text{FeO} + 2\text{SO}_2 \uparrow$ FeO + SiO₂ \rightarrow FeSiO₃
- (b) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow 2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2\uparrow$

The molten copper is poured off into sand moulds. As it cools it gives up the dissolved sulphur dioxide which forms blister on the surface of the metal. Hence the metal thus obtained is called blister copper and contains 98 percent copper.

(v) Refining of copper

(a) **Poling**

The molten blister copper is heated in pressure of air and stirred with green wood **poles**.

S and As are oxidised to their volatile oxides.

Iron is oxidised and forms a scum or slag which is **skimmed** off.

The cuprous oxide is reduced to Cu by CO and $\rm H_2$ from green wood.

$$Cu_{2}O + CO \rightarrow 2Cu + CO_{2} \uparrow$$

$$Cu_{2}O + H_{2} \rightarrow 2Cu + H_{2}O$$

(b) Electrolytic refining

The electrolytic bath contains an acidified solution of copper sulphate.

Impure copper acts as anode while cathode is of the pure copper strip.

When electric current is passed, there is transfer of pure copper from anode to cathode which gradually grows in size.

The impurities like Fe, Zn, Ni, Co etc. dissolve in the solution as sulphates and others like Au and Ag settle down below the anode as **anode mud.**

The cathode is removed and copper of about 99.99% purity is obtained.



Electrolytic refining of copper

2. Hydrometallurgical Process

Crushed and powdered low grade ore is exposed to air and water then copper sulphide is oxidised to copper sulphate. Some iron sulphate and sulphuric acid is also produced. The process is completed in about a year.

- (a) $CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4$ (Copper pyrite)
- (b) $2Cu_2S + 5O_2 \rightarrow 2CuSO_4 + 2CuO$ (Copper glance) $CuS + 2O_2 \rightarrow CuSO_4$
- (c) $CuCO_3$. $Cu(OH)_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 \uparrow + 3H_2O$

(malachite)

The pale green liquor draining from the bottom of the heaps is $CuSO_4$ which is collected in pans and treated with iron scraps which precipitate out copper.

 $CuSO_4 + Fe \rightarrow FeSO_4 + Cu \downarrow$



Process inbrief



Properties

(A) Physical

- (i) Copper is a reddish coloured Rusturons, heavy metal (sp. gravity = 8.94), It melts at 1080° C and boils at 2325° C.
- (ii) Next to silver it is the best conductor of the heat and electricity.

Ag > Cu > Au > Al

- (B) Chemical :-
- (i) Action of air :- Copper is not affected by dry air at room temperatures, but when exposed to moist air having CO_2 it is superficially coated with a green layer of basic carbonate.

 $2Cu + H_2O + CO_2 + O_2 \rightarrow CuCO_3$. $Cu(OH)_2$

When heated with air it forms cupric and cuprous oxides.

 $2Cu + O_2 \xrightarrow{below 1100^{\circ}C} 2CuO (Cupric oxide)$ $4Cu + O_2 \xrightarrow{above 1100^{\circ}C} 2Cu_2O (cuprous oxide)$

(ii) Action of acids

Non-oxidizing acids (HCl and dil H_2SO_4) do not have any effect on copper. However they dissolve the metal in presence of air.

 $\begin{aligned} & 2\text{Cu} + 4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cu}\text{Cl}_2 + 2\text{H}_2\text{O} \\ & 2\text{Cu} + 2\text{H}_2\text{SO}_4\,(\text{dil}) + \text{O}_2 \rightarrow 2\text{Cu}\text{SO}_4 + 2\text{H}_2\text{O} \end{aligned}$

Acids possessing oxidising properties (Conc. H_2SO_4 and HNO_3) readily attack the copper.

 $Cu + 2H_2SO_4$ (Conc.) → $CuSO_4 + 2H_2O + SO_2$ 3 $Cu + 8HNO_3$ (Dil.) → 3Cu (NO_3)₂ + 4 H_2O + 2NO

 $Cu + 4HNO_3 (Conc.) \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

(iii) Action of aqueous ammonia

Copper dissolves in ammonia solution in presence of air forming deep blue solution of the complex salt tetraamine- copper (II) hydroxide.

 $2Cu + 2H_2O + 8NH_3 + O_2 \rightarrow 2[Cu(NH_3)_4] (OH)_2$ It also dissolves in aqueous solution of potassium cyanide yielding the complex $[Cu(CN)]_4$]⁻

(iv) Metal displacement

Copper displaces less electropositive metals like Ag, Hg, Au and Pt from their salt solutions. More electropositive metals like Fe and Zn displace copper from copper salt solution.

$$2Ag^{+} + Cu \rightarrow Cu^{2+} + 2Ag$$
$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$$

Uses

Copper is the second most useful metal (the first being Iron) because of its stability in air and water and excellent conductivity.

It is used :-

- 1. In the manufacture of electrical wires, cables etc.
- 2. For electroplating.
- 3. As a coinage metal and in ornaments and jewellery.
- 4. For the manufacture of alloys like brass (Cu + Zn), bronze (Cu + Sn) German silver (Cu + Zn + Ni) bell metal (Cu + Sn) gun metal (Cu + Sn + Zn), coppper coins (Cu + Zn + Sn) etc.

Copper sulphate Blue vitrol. Nila–thotha

$(CuSO_4.5H_2O)$



Preparation :- It is prepared by action of dil.

 $\rm H_2SO_4$ on copper scraps in presence of air.

 $2\mathrm{Cu} + 2\mathrm{H}_2\mathrm{SO}_4 + \mathrm{O}_2 \rightarrow \mathrm{Cu}\mathrm{SO}_4 + 2\mathrm{H}_2\mathrm{O}$

Impurities of FeSO_4 can be oxidized by dil. nitric acid which remain in solution after crystallization.

Properties :-

- (i) Readily soluble in water.
- (ii) When heated slowly pentahydrate decomposes in the following stage.

 $CuSO_{4}.5H_{2}O \xrightarrow{35^{\circ}C} CuSO_{4}.3H_{2}O \xrightarrow{100^{\circ}C} CuSO_{4}.H_{2}O \xrightarrow{100^{\circ}C} CuSO_{4} \xrightarrow{400^{\circ}C} CuO+SO_{3}$

- (iii) The crystalline copper (II) sulphate $CuSO_4.5H_2O$ has the structure in which four water molecules are coordinated in central copper cation at the centre of a square and fifth water molecule is held by a hydrogen bond between a sulphate ion a coordinated water molecule.
- (iv) Fifth water molecule is deeply embedde in the crystal lattice and hence hot easily removed
- (v) Aqueous solution of CuSO₄ is slowly hydrolysed forming basic copper sulphate.
- (vi) If aqueous solution of $CuSO_4$ is saturated with ammonia a deep blue solution is formed $CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

(Blue colour)

(vii) It dissolve in excess of KCN to give $K_3[Cu(CN)_4]$

(viii)
$$2\text{CuSO}_4 + 4\text{KI} \rightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$$

 $\text{CuSO}_4 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{CuS}_2\text{O}_3 + \text{Na}_2\text{SO}_4$

Solved Examples

Ex.1 Matte is obtained after this step -

- (C) Smelting (D) Refining
- $\textbf{Sol.} (\textbf{C}) \, \text{Refer process of copper}$
- Ex.2 Copper glance istype of ore -
 - (A) Carbonate (B) Sulphide
 - (C) Oxide (D) Sulphate
- **Sol.** (**B**) Copper glance, chemical formula is Cu_2S .
- Ex.3 High purity copper is obtained by -
 - (A) Zone refining (B) Poling
 - (C) Electrolytic refining (D) Cupelling
- **Sol.** (C) After electrolytic refining. Purity of copper is 99.99% which is enough for **electrical applications.**

IRON (Fe)

Occurrence

It is the second most (first being aluminium) abundant metal occuring in the earth crust (4.5%). It is present in red blood, cells of blood.

Ores of Iron

(i) Haematite (red)	Fe ₂ O ₃
(ii) Limonite (brown haematite)	$2Fe_2O_3 \cdot 3H_2O$
(iii) Magnetite	Fe ₃ O ₄
(iv) Siderite	FeCO ₃
(v) Iron pyrites	FeS ₂
(vi) Copper pyrites	CuFeS ₂

Types of Iron

(a) Cast iron or pig iron

It is most impure form of Iron and contains the higest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si.

(b) 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.

(c) 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 0.5-1.5% carbon. Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

Extraction of Iron

1. Crushing and concentration

The crushed ore is washed with water and then concentrated by electromagnetic process.

2. Roasting and calcination

The concentrated ore is heated in shallow kilns in the presence of excess air. Here

- (a) Most of the moisture is removed.
- (b) Impurities (like C, S, P, As and Sb) are removed in the form of their volatile oxides.

 $S + O_2 \rightarrow SO_2^{\uparrow}$

(c) Carbonates and sulphides are converted into oxides.

 $FeCO_3 \rightarrow FeO + CO_2 \uparrow 4FeS_2 + 11O_2$ $\rightarrow 2Fe_2O_3 + 8SO_2 \uparrow$

(d) Ferrous oxide is oxidised to ferric and thus avoids formation of slag with sand (SiO₂)

 $4\text{FeO} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ FeO + SiO₂ \rightarrow FeSiO₃ (Slag)

3. Smelting or reduction

The calcined ore (8 parts) mixed with coke, a reducing agent (4 parts) and lime stone a flux (1 part) is reduced in a blast furnace.

Since the blast furnace has different temperatures at different zones, different reactions take place at different zones.

(a) **Zone of combustion (1500 - 1600^oC)**

This zone is near at the bottom of the furnace and little above the tuyers. It increases temp. of the furnace because of exothermic reactions.

 $2C + O_2 \rightarrow 2CO + 58$ k cal.

 $C + O_2 \rightarrow CO_2 + 97$ k cal.

(b) **Zone of fusion** (1200-1500°C)

It is just above the zone of combustion. Here the iron melts and trickles down in the hearth while the slag being lighter floats over the molten metal and thus prevents oxidation of Fe by blast of air.

(c) Zone of heat absorption or slag formation (800-1200°C)

This is the middle part of the furnace. Here rising CO_2 is reduced to carbon monoxide.

 $CO_2 + C \rightarrow 2CO - 39$ kCal.

The reaction being endothermic, lowers the temperature of the zone.

 Limestone decomposes forming CaO which reacts with SiO₂ forming slag.

 $CaCO_3 \rightarrow CaO + CO_2$

 $CaO + SiO_2 \rightarrow CaSiO_3$ (Slag)

(d) **Zone of reduction (300-700^oC)**

It is near the top of the furnace. Here the calcined ore is reduced to Fe by rising CO.

$$Fe_2O_3 + CO \Longrightarrow 2FeO + CO_2$$

 $Fe_{3}O_{4} + CO \implies 3FeO + CO_{2}$

 $FeO + CO \rightarrow Fe + CO_2$

To retard the backward reaction, supply of excess of CO is maintained by the following reaction.

 $CO_2 + C \rightarrow 2CO$

Since the temperature of this zone is too low to melt iron, the metal produced is known as spongy iron.

Properties of Cast Iron/Pig iron

- (i) Carbon is present partially as free carbon in the form of graphite and partially in the form of Iron carbide $(Fe_3C \text{ cementite})$.
- (ii) Due to the presence of impurities, its melting point is low (1100 - 1250°C).
- (iii) The molten iron expands on solidification and hence it produces good casting.
- (iv) It does not rust easily.
- (v) It can neither be tempered nor magnetised easily.
- (vi) Due to high carbon contents, it is hard and brittle and therefore can not be easily welded.
- (vii) It possesses very little ductility.

Uses of Cast Iron

It is used for small casting, for railings, hot water pipes, electric poles, bunsen burner bases and many other purposes where strain is minimum. Wrought iron and steel are manufactured from cast Iron.

(4) Refining

Manufacture of Wrought Iron :-

It is manufactured in a special type of reverberatory furnace called pudding furnace the hearth of which lined with haematite Fe_2O_3 .

The impurities of pig iron ore rapidly oxidised by oxygen of haematite. Oxides of C and S, being volatile, escape while those of Mn, Si and P form slags.

 $\begin{array}{l} 3\mathrm{C}+\mathrm{Fe_2O_3}\rightarrow 2\mathrm{Fe}+\mathrm{CO}\ \uparrow\ ;\ 3\mathrm{S}+2\mathrm{Fe_2O_3}\rightarrow \\ 4\mathrm{Fe}+3\mathrm{SO_2}\ \uparrow \\ 3\mathrm{Mn}+\mathrm{Fe_2O_3}\rightarrow 2\mathrm{Fe}+3\mathrm{MnO}\ ;\\ \mathrm{MnO}+\mathrm{SiO_2}\rightarrow \mathrm{MnSiO_3}\ (\mathrm{Slag}) \\ 3\mathrm{Si}+2\mathrm{Fe_2O_3}\rightarrow 4\mathrm{Fe_2O_3}\rightarrow 4\mathrm{Fe}+3\mathrm{SiO_2} \end{array}$

At this stage it is taken out in the forms of balls. These balls are beaten under steam hammers to **squeeze out** as much of slag is possible. The obtained product is wrought Iron.

Properties of Wrought Iron

- (i) It is extremely tough and melts at 1500° C.
- (ii) It is highly malleable and ductile.
- (iii) Presence of slag $MnSiO_3$ and $FePO_4$ makes it tough and resistant towards rusting.
- (iv) It becomes passive when treated with conc. HNO₃, chromic or chloric acids.

Use of wrought Iron

Wrought Iron is used

- (i) For the manufacture of article, chains, nails hooks, bolts etc.
- (ii) For the manufacture of electromagnets and agricultural implements.



Process inbrief

Manufacture of Steel

Bessemer process

This process involves the use of a large pear- shaped furnace (vessels) called Bessemer converter.

This is made of steel plates lined with silica (SiO_2) or magnesia (MgO) depending upon the nature of impurities.

If the impurities are acidic e.g. P_4O_{10} or SiO₂, basic lining of lime (CaO) or magnesia is used (Basic process).

If the impurities are basic e.g. MnO_4 , lining of silica bricks is used (acid process).

Silicon and manganese (in acidic process) or phosphorus (in basic process) are oxidised to their oxides and thus removed as slag.

Acid process :- $Si + O_2 \rightarrow SiO_2$; $2Mn + O_2 \rightarrow 2MnO$; $MnO + SiO_2 \rightarrow MnSiO_3$ (Slag)

Basic process :- $P_4 + 5O_2 \rightarrow P_4O_{10} P_4O_{10} + 6CaO \rightarrow Ca_3(PO_4)_2$ (Thomas slag)

Properties of Steel :-

Steel combines the useful properties of cast iron and wrought iron. It is hard and elastic. The properties of steel depend upon its carbon contents. With the increase in carbon content, the hardness of steel increases while its ductility decreases.

- (i) Low carbon or soft steel contain C upto 0.25%.
- (ii) Medium carbon steel or mild steel contain 0.25–0.5% C.
- (iii) High carbon or hard steels contain 0.5-1.5% C.

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.

- (d) Surface treatment of steel
- (i) Nitriding Process of heating steel at 1000 K in an atmosphere of NH_3 .

This gives hard coating of iron nitride on the surface.

- (ii) **Case hardening** Process of giving a thin coating of hardend steel, by heating steel in contact with charcoal followed quenching in oil.
- It is used for axles of railway wagons.
 Uses of Steel:- For making machinery parts, girders, tools, knives, razors, household utensils etc.

Properties of Fe and its compounds

(i) FeO is basic in nature, which is prepared by reducing Fe_2O_3 -

 $\operatorname{Fe}_2\operatorname{O}_3 + \operatorname{H}_2 \xrightarrow{573 \operatorname{K}} 2\operatorname{FeO} + \operatorname{H}_2\operatorname{O}$

(ii) Fe_3O_4 (magnetite FeO + Fe₂O₃) is more stable than the other two oxides.

– On passivity of Fe with conc. HNO_3 , a stable layer of Fe₃O₄ is formed on the surface.

(iii) Anhydrous Fe_2Cl_6 is very hygroscopic. Its aqueous solution on crystallisation gives $\text{FeCl}_36\text{H}_2\text{O}$. The aqueous solution is strongly acidic, due to hydrolysis-

 $\operatorname{FeCl}_3 + 3\mathrm{H}^+\mathrm{OH}^- \Longrightarrow \operatorname{Fe(OH)}_3 + 3\mathrm{HCl}$

Structure :



 FeCl_3 is used for etching metals like Cu and Ag, this is oxidizing action of Fe^{+3}

$$2Fe^{+3}_{(aq.)} + Cu(s) \rightarrow 2Fe^{2+} + Cu^{2+}$$
$$Fe^{+3}_{(aq.)} + Ag_{(s)} \rightarrow Fe^{2+} + Ag^{+}$$

(iv) $FeSO_4.7H_2O$ (green vitriol) on exposure to air changes to brown due to formation of basic ferric sulphate.

 $2\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)SO}_4$

- It is efflorescent i.e. loses water of crystallisation, white layer forms on the surface of crystal.

 $FeSO_4.7H_2O \xrightarrow{exposure} FeSO_4.H_2O + 6H_2O$ On heating -

$$FeSO_{4}.7H_{2}O \xrightarrow[-7H_{2}O]{Heat} FeSO_{4} \xrightarrow[-7H_{2}O]{Heat} Fe_{2}O_{3} + SO_{2} + SO_{3}$$

(colourless)

With nitric oxide (NO) it changes to brown due to formation of nitrosoferrous sulphate
 FeSO₄.NO

 $FeSO_4 + NO + 5H_2O \rightarrow [Fe(H_2O)_5NO]SO_4$ (Ring test) (brown ring complex)

- (v) Mohr's salt $[FeSO_4(NH_4)_2SO_4.6H_2O]$ does not effloresce like ferrous sulphate.
- (vi) Iron(iii) ammonium sulphate $Fe_2(SO_4)_3$. (NH₄)₂SO₄.24H₂O is known as ferric alum.

Solved Examples

- **Ex.4** Magnetic separation is used for increasing concentration of the following -
 - (A) Horn silver (B) Calcite
 - (C) Hamatite (D) Magnesite
- **Sol.** (C) Haematite ore having magnetic property, can be separated by magnetic separation

Ex.5 In blast furnace, iron oxide is reduced by -

(A) Silica	(B) CO
(C) C	(D) lime stone

Sol. (**B**)

Ex.6 Steel consists of percentage of carbon -

(A) 3.1 – 4.5%	(B) 2.2 – 3.1%
(C) 0.15 – 0.28%	(D) $0.15 - 1.5\%$

Sol. (D)

Zinc (Zn)

Occurrence :-

Its important minerals are :-

(i)	Zinc blende or black jack	ZnS
(ii)	Zincite	ZnO
(iii)	Calamite	ZnCO ₃

Extraction :-

Electrolytic Process

(i) Concentration

The powdered ore ZnS is concentrated by froth flotation method.

(ii) Roasting

Concentrated ZnS is roasted at 700°C. A mixture of ZnO and $ZnSO_4$ is obtained

 $ZnS + 2O_2 \rightarrow ZnSO_4$ $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

(iii) Leaching with dilute sulphuric acid

The roasted ore is treated with dilute H_2SO_4 when ZnO is dissloved by forming

 $ZnSO_4 ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$

(iv) Removal of impurities

The solution of $ZnSO_4$ so obtained contains Cu, Cd, Sb, Mn Al, Fe and As as impurities. They are removed by treatment with Ca(OH)₂, Fe, Al, As and Sb are removed as hydroxides. Mn is removed as MnO(OH) by blowing air through the solution. Impurities of Cu and Cd are removed by their replacement from the solution by treatment with zinc dust.

 $CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$

(dust)

(v) Electrolysis :-

Anode	\rightarrow	Impure Zn
Cathode	\rightarrow	Pure Zn

Electrolyte \rightarrow Pure solution of ZnSO₄ + H_2SO_4 (dil.) on the electrolysis zinc is deposited at cathode.

The metal is scrapped off and melted to give 99.95% pure metal.

Chemical Properties :-

(i) Action of Air :- Zinc is not affected by dry air at room temperature. On long contact with moist air, a protective layer of basic zinc carbonate is deposited. When heated in air, it burns with a bluish - white flame and forms zinc oxide known as philosopher's wool.

 $2 \operatorname{Zn} + \operatorname{O}_2 \xrightarrow{\operatorname{Burning}} 2 \operatorname{ZnO}$

(ii) Action of Water :- Pure zinc has no action on water. Zinc decomposes boiling water slowly and steam readily.

 $Zn + H_2O \rightarrow ZnO + H_2\uparrow$ (Hot) (Steam) (iii) Action of acids :- Zinc is fairly electropositive. So it displaces hydrogen gas from dilute hydracids.

$$\begin{aligned} &Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow \\ & \text{(dil)} \\ &Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow \\ &\text{with hot and Conc. } H_2SO_4 \text{ it gives } SO_2. \\ &Zn + 2H_2SO_4 \xrightarrow{\Delta} ZnSO_4 + 2H_2O + SO_2 \uparrow \\ & \text{(Conc.)} \end{aligned}$$

(iv) Action of alkalis :- Zinc is acted upon caustic alkalis; H₂ is released.

 $Zn\left(S\right)+2\ NaOH\ (aq)\rightarrow Na_{2}ZnO_{2}\ (aq)+H_{2}\uparrow$

$(v) \quad Reaction \ with \ solutions \ of \ salts$

less electropositive metals than zinc are replaced by it from their salt solution.

$$Zn(S) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(S)$$

 $Zn(S) + Pb(NO_2)_2(aq) \rightarrow Zn(NO_2)_2 + Pb(S)$

Uses :

- (i) In making alloys e.g. brass bronze, german silver, electron etc.
- (ii) In the extraction of silver and gold by cyanide process.
- (iii) In dry cells for making cathode container.
- (iv) Zn–Cu couple, Zn-Hg, zinc dust etc. are used as reducing agent in organic reactions.
- (v) large amounts of zinc are used for galvanizing iron.Zinc is deposited on the surface of iron articles. This process is called galvanization.

Zinc sulphate white vitrol : ZnSO₄.7H₂O

Effect of Heat :

$$ZnSO_{4}.7H_{2}O \xrightarrow{375 \text{ K}} ZnSO_{4}.H_{2}O \xrightarrow{725 \text{ K}}$$
$$ZnSO_{4} \xrightarrow{1075 \text{ K}} ZnO + SO_{2} + O_{2}$$
$$Use \qquad as a eye lotion :$$

Zinctie Philospher's wool (ZnO)

Properties :	Amphoteric in nature
Use	as white pigment

Lithopone $(ZnS + BaSO_4)$

Use as a white paint.

SILVER, Ag (Argentum)

Occurrence :

Ag found in free and combined state in nature.

Its main ore is Argentite Ag,S.

Other ores are

Copper silver glance	—	$Cu_2S \cdot Ag_2S$	

- Horn silver AgCl
- Argentiferous lead PbS(0.01 0.1% Ag)

Steps of Metallurgy :-

- (A) From Argentite (Ag₂S)
- (1) Concentration :- As it is a sulphide ore, so froth floatation process is used.
- (2) Leaching and reduction (Mac Arther cyanide process)
- (a) Formation of cyanide complex :-

 $Ag_2S + NaCN \implies Na[Ag(CN)_2] + Na_2S$ In absence of air reaction is reversible.

In presence of air reaction is irreversible.

 $Na_2S + O_2 \rightarrow Na_2SO_4$

 Na_2SO_4 does not reacts with sod. Argento cyanide.

(b) Displacement of Ag metal :-

$$\begin{split} Na[Ag(CN)_2] + Zn \ \rightarrow \ Na_2[Zn(CN)_4] + Ag \\ Sod. \ tetra \ cyanozincate \ (black \ ppt) \,. \end{split}$$

Ag $\xrightarrow{\Delta}$ Ag (Solid) Shining silver (impure)

(3) Purification by electrolytic method :-

Pure Ag	_	Cathode
Impure Ag		Anode
Electrolyte		AgNO ₃
+ 1% HNO ₃	_	To increase ionisation
and to avoid hydrolysis of $AgNO_3$ by common ion		
effect		

- (B) Ag from Argentiferous lead (PbS Galena) :– Galena has a little amount of silver
- (1) Concentration :- (PbS) by froth floatation process
- (2) Reduction of metal :-

- (a) **Park's process :** Based on distribution law.
- (I) Molten Ag is more soluble in molten zinc.

PbS (molten) \rightarrow Zn(molten)



- (II) Melting point of Zn/Ag alloy is greater than lead, so Zn/Ag freezes first.
- (III) Density of Zn/Ag is less than Pb so Zn/Ag forms the upper layer and Pb form lower layer.
- (IV) Upper layer taken out.
- (V) Ag is separated by using distillation method. (Vapourisation of Zn)
- (b) Pattinson method :-
- (I) It is based upon fractional crystallisation.
- (II) Ag/Pb is melted then cooled, the process is repeated again & again, concentration of Ag increases. Pb separate out in crystalline form.
- (3) **Purification :**
- (a) Cupellation :



- * Pb impurities separates (oxidised) out in the form of litharge.
- (b) Electrolytic process :- As discussed earlier.

Properties of Silver :

- (i) It is hard, malleable and ductile.
- (ii) Silver is the best conductor of heat & electricity.
- (iii) **Spitting of silver :** When Ag is melted in air, it absorbs oxygen about 20 times of its volume. This absorbed O_2 is given out on cooling the metal with a spurting sound. This phenomenon is known as spitting of silver.

(iv) Action of acids

When heated with conc. H_2SO_4 silver evolves SO_2 $2Ag + 2H_2SO_4(conc.) \rightarrow Ag_2SO_4 + 2H_2O + SO_2 \uparrow$ Dil. and conc. nitric acid dissolves silver forming silver nitrate.

$$3Ag + 4HNO_{3} \rightarrow 3AgNO_{3}(aq.) + NO + 2H_{2}O$$
(Dilute)
(Nitric oxide)
$$Ag + 2HNO_{3} \rightarrow AgNO_{3} + NO_{2} + H_{2}O$$
(Conc.)

(v) Standard oxidation potential of silver is – 0.80 V.
 Silver is easily displaced from a solution of its salt by metals above it in the electrochemical series but not by metals below it. e.g. Au, Pt etc.

$$Cu(s) + Ag_2SO_4(aq) \rightarrow CuSO_4(aq) + 2Ag \downarrow$$

(more electro positive than silver)

AgBr + Au \rightarrow no reaction.

Silver Nitrate (Lunar Caustic) AgNO₃

It is prepared by discolving metalic silver in dilute nitric acid.

Properties –

- (1) It is not very hygroscopic and very soluble in water.
- (2) $AgNO_3$ is also decomposes by organic matter such as glucose, paper, skin and cork.
- (3) It has also a caustic and destructive effect on organic tissue.
- (4) Aqueous solution are susseptible to decomposition by light.
- (5) AgNO₃ is oxidising in nature (decomposes on heating)

 $2AgNO_{3} \xrightarrow{above MP} 2AgNO_{2} + O_{2}$ $2AgNO_{3} \xrightarrow{Red heat} 2Ag + 2NO_{2} + O_{2}$

(6)
$$2AgNO_3 + 2NaOH \rightarrow Ag_2O + 2NaNO_3 + H_2O$$

(Brown)

(7)
$$\operatorname{AgNO}_3 + \operatorname{NH}_4\operatorname{OH} \rightarrow \operatorname{AgOH} \rightarrow \operatorname{Ag}_2\operatorname{O} + \operatorname{H}_2\operatorname{O}$$

wt. ppt. (Brown)

It dissolves in excess of NH_4OH

$$Ag_2O + 4NH_4OH \rightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

(Complex)

Ammonical AgNO₃ is known is TOLLEN's reagent

(8) Black ppt. with H_2S

$$2AgNO_3 + H_2S \rightarrow Ag_2S + 2HNO_3$$

(9) White ppt. with Hypo :-

 $2 \text{AgNO}_3 + \text{Na}_2 \text{S}_2 \text{O}_3 - -$

In excess of Hypo $\left| \begin{array}{c} H_2O \\ (Hydrolysis) \end{array} \right|$

white ppt. Na, $[Ag(S,O_1)]$ [Ag,S

 $Ag_2S_2O_3 + 2Na_2OH$

Soluble complex

(10) Red ppt. with K₂CrO₄

$$2AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4 + 2KNO_3$$

Red ppt.

Uses

- (i) It is used in silver plating.
- (ii) Silver foils are used in medicine.
- (iii) Silver amalgam is used for dental filling.
- (iv) Compounds of silver are used in silvering of mirrors (AgNO₃ + HCHO + Red Pb), in photography, as laboratory reagents etc.
- (v) Silver is easily alloyed with copper, so it is used in making coins, ornaments, silver ware etc.
- (vi) It gives black spot on skin due to decomposition so it is also used as hairdy and ink.

Halide : Silver Bromide AgBr :-

Preparation : It is prepared by the reaction of silver nitrate with a soluble bromide.

$$AgNO_3 + NaBr \rightarrow AgBr + NaNO_3$$

Properties :

- On heating, it melts to a red liquid. (i)
- (ii) It is partially soluble in strong solution of NH_4OH due to complex formation.

 $AgBr + 2NH_{4}OH \rightarrow Ag(NH_{2})_{2}Br + 2H_{2}O$

(iii) It is most sensitive to light, it undergoes photo reduction.

AgBr $\xrightarrow{\text{light}}$ 2Ag + Br,

(iv) It dissolves in Hypo.

 $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

(v) AgBr is reduced to silver, when treated with zinc and dil. H₂SO₄ $Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$ $2AgBr + 2H \rightarrow 2Ag + 2HBr$

Solubilities of AgX in Water :-

AgF >> AgCl > AgI

soluble Insoluble

glucose

Other Properties

$$AgCl + Na_{2}CO_{3} \xrightarrow{\text{fuse}} 2Ag + 2NaCl + CO_{2} + \frac{1}{2}O_{2}$$
$$Ag_{2}O + C_{6}H_{12}O_{6} \rightarrow 2Ag + C_{6}H_{12}O_{7}$$

gluconic acid

PHOTOGRAPHY

The process involves the following steps -

(I) Ripening and preparation of sensitive plate $AgNO_3 + AgBr + gelatin on a film of celluloid$ (Ammonical)

-AgBr is photosensitive.

(II) Exposure

AgBr decomposed due to light falling on the plate. The extent of decomposition is proportional to the light

 $2AgBr \rightarrow 2Ag + Br_{2}$

(III) **Developing**

The developer is an alkaline solutiion of quinol or pyrogallol or ferrous oxalate which reduces some of the AgBr to black Ag in area exposed to light $2AgBr + C_6H_4(OH)_2 \rightarrow 2Ag + 2HBr + C_6H_5O_2$ quinone

(IV) Fixing

Sodium thio sulphate (Hypo)is used as fixer, which removes unchanged AgBr as a complex ion -

(V) Toning

The print is than dipped in $H[AuCl_{\lambda}]$, where Ag goes partially in solution and beautiful purple tint is imparted to the photograph due to Au particles.

 $H[AuCl_4] + 3Ag \rightarrow 3AgCl + Au \not b + HCl$

Solved Examples

Ex.7 925 fine silver means an alloy of -

- (A) 7.5% Ag and 92.5% Cu
- (B) 92.5% Ag and 7.5% Cu
- (C) 9.25% Cu and 90.75% Ag
- (D) 9.25% Ag and 90.75% Cu

Sol. (B)

Siver being soft is alloyed with copper. The composition of a silver alloy is expressed as its fineness', i.e., the amount of Ag in 1,000 parts of the alloy. 925 fine silver means an alloy of 92.5% Ag and 7.5% Cu.

Ex.8 Heating of Ag with conc. HNO₃ give -

(A) NO	(B) NO ₂
$(C) N_2O$	(D) N_2O_3

Sol. (**B**)

 $2HNO_3 \rightarrow 2NO_2 + H_2O + O$ $2Ag + 2HNO_3 + O \rightarrow 2AgNO_3 + H_2O$

(Adding) $2Ag + 4HNO_3 \rightarrow 2NO_2 + 2AgNO_3 + 2H_2O$

(conc)

if dil. HNO₃ is used, NO is produced.

GOLDAu (Aurum)

Atomic number	- 79
Electronic configuration	- 2, 8, 18, 32, 18, 1
Valency	-+1,+3
Occurance	- Alluvial deposits &
	Quartz veins

(A) Mac Arther Forest's Cyanide Process

(1) Concentration

Sand associated with Au is removed by washing method.

(2) Extraction of metal

 Gold particles – ground and agitated with KCN in alkaline medium and air is simultaneously blown through.

Au + KCN + $H_2O + O_2 \rightarrow K[Au(CN)_2] + KOH$ (Pot. dicyano aurate)

- (II) Impurities filtered out.
- (III) Filtrate is treated with zinc dust Au precipitated.

 $\begin{array}{l} K[Au~(CN)_2] + KOH + Zn \rightarrow K_2ZnO_2 + KCN + \\ H_2O + Au \downarrow \end{array}$

(IV) Au obtained as black mud is treated with dil. H_2SO_4 to remove excess of Zn.

(3) **Purification :**

Crude Au \rightarrow Anode

Pure Au \rightarrow Cathode

Electrolyte \rightarrow HAuCl₄(aq)

Properties

Fineness of Au is expressed in carats.

Pure Au is of 24 carats

22 carats Au – contains 22 parts by weight of Au +2 parts by weight of Cu.

It is very inert. It dissolves in aqua-regia (HCl (3 parts) + HNO₃ (1 part))

 $2Au + 6Cl \rightarrow AuCl_3$; $AuCl_3 + HCl \rightarrow HAuCl_4$

Uses

(i) It is used in Jwellery.

(ii) In the electroplating Gold is used.

(iii)In the Aurvedic medicine.

Solved Examples

Ex.9 Purple of cassius is -

(A) Pure gold

(B) Solid solution of gold

- (C) Gold (I) hydroxide
- (D) Gold (III) chloride

Sol. (B)

It is obtained by treating gold (III) chloride solution with $SnCl_2$

 $2AuCl_3 + SnCl_2 \rightarrow 2Au + 3SnCl_4$

SnCl₄ sor formed hydrolyses as follows

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

stannic acid

The colloidal precipitate of stannic acid absorbs colloidal particles of gold. This has beautiful purple colour and is known as purple of cassius. It is used for colouring glass (ruby red) and pottery.

Ex.10 Percentage of gold in 20 Carat gold -

(A) 80%	(B) 83.33%
(C) 86.66%	(D) 96%

Sol. (B)

20 karat gold means it consists of 20 parts gold out of 24 parts and four parts of copper.

% of gold =
$$\frac{20}{24} \times 100 = 83.33\%$$

ALUMINIUM

Occurence :

It is most reactive so do not found in free state in nature. It is first most abundant metal and third most abundant element. (First two are oxygen, silicon).

Its important minerals are :-

$Al_2O_3.2H_2O$	 Bauxite
Al ₂ O ₃ .H ₂ O	 Diaspore
Al_2O_3	 Corundum
Na_3AlF_6	 Cryolite

Extraction :

It extracted from bauxite in following steps :

- (i) Concentration of bauxite :- removal of ferric oxide and silica
- (ii) Electrolytic reduction of Al_2O_3
- (iii) Electrolytic purification of Aluminium Flow Sheet for the extraction of Al

BAUXITE



(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 Fe₂O₃



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

Bauxite ore + $Na_2CO_3 \xrightarrow{Fused} NaAlO_2$ $\downarrow e$ Solution $\downarrow w$ CO_3

 \downarrow extracted with water



Important points

- (I) Useful gas NH_3 is evolved in the leaching of bauxite by serpeck's process.
- (II) In the electrolytic reduction of Al_2O_3 cryotite (Na₃AlF₆) is added along with CaF₂ (fluorspar) to– – decrease m.p. of Al_2O_3
 - decrease viscocity of electrolyte (Ca F_2 is used) -increase conductivity
- (III) In the electrolytic reduction graphite anode get corrode or finishe due to reaction with O_2 liberates at anode, hence it had to be changed periodically.
- (IV) In the electrolytic refining (4th step) no electrodes are used. In the Hoop's process molten pure Al is used as cathode and molten impure Al is used as anode.
- (V) In the Hoop's process carbon dust is sprayed over molten Al to

-avoid heat lose

– minimise metallic lusture (glaze) which is harmful for the eyes.

Properties :-

- (i) It is very light metal (density 2.7 gm/cc.) It is 4th Good conductor of electricity (Frist three Ag, Cu and gold)
- (ii) With moist air, it forms a oxide layer at surface which protects against corrosion.
- (iii) Al dissolves in alkalis : $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2 \uparrow$ (sod. meta Aluminate)
- (iv) Al when heated in contact of halogens, halides forms. $2Al + 3Cl_2 \xrightarrow{heated} 2AlCl_3$
- (v) Metallic Al is a strong reducing agent. It is due to its great affinity for oxygen. It reduces several metallic oxides to metals.

 $3MnO_2 + 4A1 \longrightarrow 2Al_2O_3 + 3Mn + heat$

Uses :

It is used :

- (i) In the manufacture of alloys, magnalium (Mg + Al), aluminium bronze (Cu + Al) etc.
- (ii) In thermite welding of metals
- (iii) For making containers for nitric acid
- (iv) Aluminium is used in house-hold articles.
- (v) Aluminium foil is used as a wrapping material
- (vi) Al—Hg couple is used as reducing agent.

Aluminium Chloride (AlCl₃):

Solved Examples

- Ex.11 Aluminium is obtained from Al₂O₃ by this method-
 - (A) Thermal reduction
 - (B) Hydro metallurgical method
 - (C) Electrolytic reduction
 - (D) Reduction by iron
- Sol. (C)

For all metals with high electropositive nature, electrolytic reduction is best method.

- **Ex.12** If Bauxite consists of SiO_2 as impurity, this process is employed -
 - (A) Hall's process (B) Baeyer's process
 - (C) Hoope's process (D) Serpeck's process

Sol. (D)

TYPES OF ORES	S. N.	FORMULA OF THE ORE		NAN	ЛЕ
Owida Ora	1	7:0	Zinaita		rf+ sl/h\/ı
Oxide Ore	1. 2	ZIIO	Druchusita	=	
	2. 2		Pyroiusite	=	[INJNYUNV]
	5.	SnO_2	Cassiterite	=	[UBI VJKUV] [Durith)/ uk u chelki iz
	4.		Cuprite	=	
	5.	Fe_2O_3	Hematite	=	[gækvkov]
	6.	$Al_2O_32H_2O$	Bauxite	=	[CKDI KDV]
	7.	FeO. Cr_2O_3	Chromite	=	[ØkækbV]
	8.	Fe ₃ O ₄	Magnetite	=	[e &ut/k bV]
	9.	$Fe_2O_3.3H_2O$	Limonite	=	[ykbekukbV]
	10.	3BeO. Al ₂ O ₃ . 6 SiO ₂	Beryl	=	[C ʃj y]
Sulphide Ore	1.	ZnS	Zinc Blande	=	[ftad (ysMh]
	2.	HgS	Cinabar	=	[fl uckj]
	3.	PbS	Galena	=	[X\$y\$uk]
	4.	Ag ₂ S	Argentine	=	[∨t ß Vkbu]
		2	or Silver glanc	æ	[fl Yoj Xykl]
	5.	FeS_2	Iron pyrites	=	[∨k;ju ik;jkbVht]
	6.	CuFeS ₂ , CuS.FeS	Copper pyrite	s =	[dk₩j ik;jkbVht]
	7.	Cu ₂ S.Ag ₂ S	Copper silver	=	[dkWj fl Yoj Xyka]
			glance		
	8.	$Ag_2S.Sb_2S_3$	Pyrargirite	=	[ikbjkft]kbV]or(;k)
			Rubisilver		[: ch fl Yoj]
	9.	$Ag_5.SbS_4$	Stifenite	=	[LVhQ§ikbV]
Halide Ore	1.	NaCl	Rock Salt	=	[[kfut ued]
	2.	AgCl	Horn Silver	=	[gkWZfl Yoj]
	3.	CaF ₂	Flour Spar	=	[Qykji Likj]
	4.	AlF ₃ .3NaF	Cyrolite	=	[Øk; kykbV]
	5.	KCl.MgCl,.6H,O	Carnelite	=	[dku iy kbV]
		2 2			

APPENDIX

NO. 1 LIST OF ORES AND THEIR NAMES

Carbonate Ore	1.	MgCO ₃	Magnesite	=	[e \$ ku ! kbV]
	2.	CaCO ₃	Lime stone	=	[pwkiłrj = ekcły]
	3.	MgCO ₃ .CaCO ₃	Dolomite	=	[MksykækbV]
	4.	ZnCO ₃	Calamine	=	[dŷkfeu]
	5.	PbCO ₃	Cerusite	=	[h: kbV]
	6.	FeCO ₃	Siderite	=	[fl MjkbV]
	7.	$CuCO_3$. $Cu(OH)_2$	Malachite	=	[e \$ydk bV]
	8.	$2CuCO_3$.Cu(OH) ₂	Azurite	=	[, stýkbV]
	9.	SrCO ₃	Strontianite	=	[LVkufl;ukbV]
Sulphate Ore	1.	$BaSO_4$	Barytes	=	[c j kbVht]
	2.	PbSO ₄	Anglisite	=	[, x yhl kbV]
	3.	CaSO ₄ .2H ₂ O	Gypsum	=	[ftll e]
	4.	$MgSO_4.7H_2O$	Eypsomite	=	[, II kekbV] (Or Epsim salt)
	5.	SrSO ₄	Celestine	=	[\$y\$.Vkbu]
	6.	$K_2SO_4.Al_2(SO_4)_3.$	Alum	=	[fQVdjh]
		24H ₂ O			
Silicate Ore	1.	$LiAl(SiO_3)_2$	Spodumene	=	[LikMehu]
	2.	KAl Si ₃ O ₈	Felsper	=	[Q¥I ikj]
	3.	$Al_2O_3.2SiO_2$	Caolin	=	[d\$vk\$yu]
		.2H ₂ O	(or China- clay)	=	[phuh feêh]
	4.	3BeO.Al ₂ O ₃ .6SiO ₂	Beryl	=	[C ĺj y]
	5.	CaO.3MgO.4SiO ₂	Asbestus	=	[, LCLVI]
	6.	$K_2O.3Al_2O_3.6SiO_2.$	Mica	=	[vHkd]
		2H ₂ O			
		$\mathrm{KH}_{2}\mathrm{Al}_{3}\mathrm{(SiO}_{3})_{4}$			
Nitrate Ore	1.	NaNO ₃	Chili - Salt Peter	=	[fpyhl kYV i hVj]
	2.	KNO ₃	Salt peter	=	[kYVihVj ;k 'kkgik];k
			or Indian salt pete	er=	[bf.M;ulkYVikVj]
Phosphate Ore	1.	$Ca_3(PO_4)_2$	Rock Phosphate	=	[jkkt] QkLQ\$V]
	2.	$\operatorname{Fe}_{3}(\operatorname{PO}_{4})_{2}.8\operatorname{H}_{2}\operatorname{O}$	Vivianite	=	[fofo, ukbV]
	3.	AlPO ₄ .Al(OH) ₃ .H ₂ O	Terguoise	=	[VjDoks]]

SOME IMPORTANT ALLOY

1.	Bronze	-	Cu (75-90 %) + Sn (10-25 %)
2.	Brass	-	Cu (60-80 %) +Zn (20-40%)
3.	Aluminium Bronze	-	Cu (90%) + Al (10%)
4.	Gun metal	-	(Cu + Zn + Sn) (87:3:10)
5.	German Silver	-	Cu + Zn + Ni (2:1:1)
6.	Bell metal	-	Cu (80 %) + Sn (20 %)
7.	Monel metal	-	Cu: Ni: (Fe + Mn) (30: 67: 3)
8.	Nichrome	_	(Ni + Cr + Fe)
9.	Alnico	_	(Al, Ni, Co)
10.	Britania metal	_	(Sn + Pb)
11.	Babbit metal	_	Sn + Pb + Cu
12.	Munz metal	_	Cu + Zn (60-62%) - (68 - 40%)
13.	Type metal	_	Pb + Sn + Sb
14.	Alloys of steel		
	(a) Vanadium steel		V (0.2 - 1%)
	(b) Chromium steel		Cr (2-4%)
	(c) Nickel Steel		Ni (3-5%)
	(d) Manganese steel		Mn (10-18%)
	(e) Stainless steel		Cr (12-14%) & Ni (2-4%)
	(f) Tunguston steel		W (10-20%)
	(g) Invar (buokj)		Ni (36%)
15.	14 Carat Gold	_	54% Au + Ag (14 to 30%) + Cu (12 - 28%)
16.	24 Carat Gold	_	100% Au
17.	Genny Gold	_	Au + Cu
	or Coil of Gold		11:1
18.	Solder		Pb + Sn
19.	Delta metal		Cu + Zn + Fe
20.	Coin of Silver		Ag (92.5%) + Cu (7.5%)
21.	Coin of aluminium		Mg + Al
22.	Coin of steel		3.5% Ni in steel
23.	Magnellium		Mg(10%) + Al(90%)
24.	Duralumin		(Al + Mn + Cu)
25.	Y-alloy		Al(93%) + Cu(4%) + Ni(2%) + Mg(1%)
26.	Dutch metal		Cu (80 %) + Zn (20%)
27.	Artificial Gold		Cu (90%) + Al (10%)
28.	Constantan		Cu (60%) + Ni (40 %)

B % of Carbon in different type of Iron

	NAME	% of C
1. Wrought iron	(fi Voka ykgk)	.1 to .25
2. Steel	(LVhy)	.25 to 2.0
3. Cast Iron	(<nd>(<nd>kgk)</nd></nd>	2.6 to 4.3
4. Pig Iron	(dPpk ykgk)	2.3 to 4.6

INDUSTRIALLY IMPORTANT PROCESS

Ammonia Soda process (Solvay process)	:	Manufacture of NaHCO ₃
Bosch process	:	Manufacture of H ₂
Baeyer's process	:	Manufacture of Al
Birkeland - Eyde process	:	Manufacture of HNO ₃
Castner process	:	Manufacture of Na
Caster - Kellner Cell process	:	Manufacture of NaOH
Cyanide process or (Mac Arthur Forrest process)	:	Manufacture of Ag
Cupellation process	:	Purification of Ag
Carter process	:	Manufacture of basic lead carbonate (white lead)
Contact process	:	Manufacture of H ₂ SO ₄
Down process	:	Manufacture of Na
Dow's process	:	Manufacture of phenol
Deacon's process	:	Manufacture of Cl ₂
Frecht (Magnesia) process	:	Manufacture of K ₂ CO ₃
Gold Smidt process	:	Thermite welding, extraction of metals
Hoop's process	:	Purification of Al
Haber process	:	Manufacture of NH ₃
Hasenclever process	:	Manufacture of Bleaching powder
L.D. process	:	Manufacture of steel
Lead chamber process	:	Manufacture of H ₂ SO ₄
Leblanc process	:	Manufacture of K ₂ CO ₃
Merck process	:	H ₂ O ₂
Nelson cell process	:	Manufacture of NaOH
Ostwald process	:	Manufacture of HNO ₃
Parke process	:	Manufacture of Ag
Pattinson process	:	Manufacture of Ag
Serpeck's process	:	Manufacture of Al