Chapter-2

Metallurgy

Introduction

The processes involved in the extraction of metals from their respective ores economically and easily is known as "Metallurgy". Earth crust is the biggest source of the elements. Oxygen is the most (49%) abundant non-metal while Al (8%) is the most abundant metal in the earth's crust.

Three-fourth of the known elements are metals. About 85 metals, 17 non-metals and 7 metalloids. Metals are electropositive, can undergo oxidation and can act like a reducing agent. They are good conductors of heat and electricity (free electron) are malleable and ductile, show metallic lustre.

Being more reactive, most of the metals exist in their combined form known as minerals but a few of them are found in uncombined native forms *i.e.*, is free state. (Cu, Au, Ag etc.).

Minerals

Minerals are the naturally accruing chemical substances in which metal are present in either native state or combined forms.

Ore

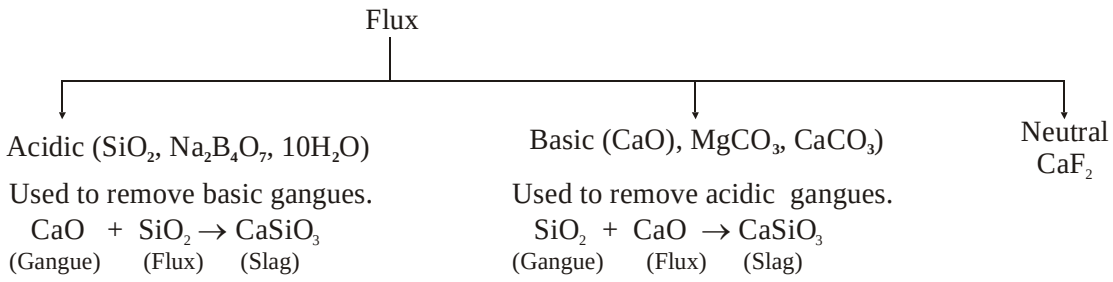
Ore is these mineral from which metals can be extracted economically and conveniently.

Gangue or Matrix

Gangue or matrix is the non-metallic impurities present in the ore. In fact impurities associated with an ore is known as gangue.

Flux

Fluxes are chemical substances which are generally added to an ore in order to remove the impurities or gangue. e.g., CaO, SiO_2 etc.

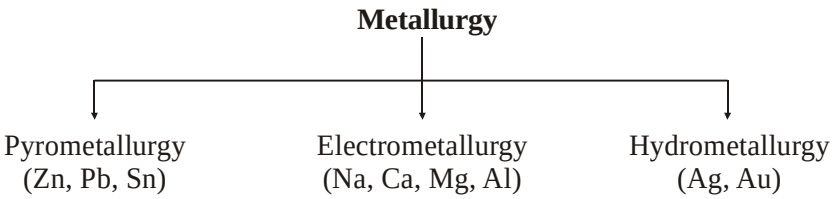


Slag

$$\text{Gangue} + \text{Flux} \rightarrow \text{Slag}$$

"Slag" is the fusible, light and floatable substances, formed due to combination between the gangue and the flux.

Types of Metallurgy



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

$ZnO + C \xrightarrow{\Delta} Zn + CO \uparrow$

$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$

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

Processes involved in extraction of metals

All the methods depend upon the nature of ore and gangue.

(1) Concentration of ores

(2) Conversion of ore into oxides (Calcination and roasting)

(3) Reduction of oxides

(4) Purification of metals

Concentration of ores : Concentration is the removal of impurities from an ore. Actually, it is the enrichment of metal in an ore.

(i) Gravity separation method (Hydraulic Washing Method): Heavier ore particles are eliminated from lighter impurities. e.g.,

Haematite + SiO_2, Tin stone + SiO_2

(ii) Magnetic separation : Ore and gangue are separated if one of them will be magnetic.

$FeWO_4$ + SiO_2

(magnetic) (diamagnetic)

$TiO_2 + Ca_3(PO_4)_2CaCl_2$

(magnetic) chlorapatite

(iii) Froth floatation method : Most suited for sulphide ores. It is fundamentally based on the different wetting property of the ore and gangue with oil and water.

Ore → More wetted by oil

Gangue → More wetted by H_2O

Powdered ore + water + pine oil → froth

* froth is a colloidal solution of gas and liquid. It has good adsorption capacity.

Activators : Which can activate the frothing nature of a frothing agent. e.g., $CuSO_4$.

Collectors : These compounds form water repellant or hydrophobic molecules with ore particles and go to the surface making froth. e.g., Pot. Xanthate → K_2COS_2

Pot. ethyl xanthate — $K(C_2H_5)COS_2$

Collectors get attached to the ore particles and make them hydrophobic so that ore particles can be

carried out to the surface by air bubbles. Collectors are long chain organic molecules with a polar end.

Depressants : Depressants can suppress the frothing tendency of the frothing agent. e.g., KCN, NaCN, e.g., extraction of Pb from PbS (galena).

Leaching : It is the selective dissolution of an ore in a suitable reagent whereas gangue will remain undissolved and gets separated.

Chemical method of concentration. e.g., Concentration of Al.

$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

$2NaAlO_2 + 4H_2O \rightarrow 2Al(OH)_3 + 2NaOH$

$2Al(OH)_3 \xrightarrow[1200]{\Delta} Al_2O_3 + 3H_2O$

e.g., Al, Ag, Au concentration.

Conversion of ore into Metal Oxide:

(i) Calcination : ore is heated in absence of air below its melting point in order to

(a) expel H_2O, CO_2, SO_2

(b) remove organic matters

(c) make the ore more porous and reducible

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

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$

$2Fe_2O_3 . 3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$

(ii) Roasting : Process of heating an ore below its melting point in presence of air in order to

(a) Dry the ore

(b) Remove volatile impurities

(c) Convert ore into oxide

(d) Convert water insoluble sulphides into water soluble sulphates

$CuS + 2O_2 \xrightarrow{\Delta} CuSO_4$

(Insoluble) (Soluble)

$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$

(Insoluble) (Soluble)

$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$

$AgCl + 2Hg \rightarrow Ag\text{-}Hg + HgCl$

$Ag_2S + 2NaCl \rightarrow 2AgCl + Na_2S$

Reduction of metallic oxides

(i) Carbon-reduction method :

$MO + C \xrightarrow{\Delta} M + CO$

Less electropositive (R.A.)

Not applicable for those metallic oxides which can form carbide with carbon e.g., Al_4C_3, CaC_2 etc.

$ZnO + C \xrightarrow{\Delta} Zn + CO$

$Fe_2O_3 + C \xrightarrow{\Delta} 2FeO + CO$

$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO \uparrow$

* $Al_4C_3 + water \rightarrow 3CH_4 + 4Al(OH)_3$

  $CaC_2 + water \rightarrow C_2H_2 + Ca(OH)_2$

(ii) Self reduction :

$2HgS + 3O_2 \xrightarrow{\Delta} 2HgO + 2SO_2$

$2HgO^{+2} + Hg^{o}S \rightarrow 3Hg + SO_2 \uparrow$

$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + SO_2$

$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 \uparrow$

(iii) Reduction with Al :

Metallic oxides of those metals whose melting point are very high and are reduced by heating with Al. It is an exothermic process.

$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2CrO + Heat$

$3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3 + Heat$

(iv) Electrolytic reduction :

Oxides of highly electropositive metals are reduced by this method

$NaCl \xrightarrow{\Delta} Na^+ + Cl^-$

$Na^+ + e \rightarrow Na$, Cathode

$2Cl^- \rightarrow Cl_2 + 2e^-$

$Al_2O_3 + AlF_3 \rightarrow$ Fused $Al_2O_3 . AlF_3$

$AlF_3 \rightarrow Al^{+3} + 3F^-$

AlF_3 catalytic $F^- \rightarrow {}^1/_2F_2 + e$

F^- is R.A. $Al_2O_3 + 3F_2 \rightarrow 2AlF_3 + 3/2\ O_2$

$Al^{+3} + 3e \rightarrow Al$

(v) Reduction by precipitation (Hydrometallurgy) :

$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$

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

Metal is obtained by adding more reactive metal.

Purification of Metals

(i) Distillation :

Based on difference in B.P. of metals and impurities, metals of low boiling point are purified.

$Zn \xrightarrow{\Delta} Zn(Vap) \xrightarrow{-\Delta} Zn\ (Pure)$

$Hg \xrightarrow{+\Delta} Hg\ (Vap) \xrightarrow{-\Delta} Hg(Pure)$

(ii) Liquation :

Based on the difference in the fusibility of the metal and the impurities. Easily fusible metals are purified. e.g., Sn, Pb.

(iii) Zone-refining :

Method is based on the principle that an impure metal on solidification will deposit crystals of pure metal and the impurities will remain behind in the molten part in the metal. Ge, Si, Ga (semiconductors) are purified.

(iv) Van-Arkel method :

Metal is converted into a volatile unstable compound (e.g., Iodene) and impurities are not affected during compound formation.

e.g., Zr, Ti

$Ti + 2I_2 \rightarrow TiI_4(g)$

$TiI_4(g) \xrightarrow{1700\,K} Ti(s) + 2I_2(g)$

(v) Chromatography and Ion exchange :

By this method Lanthanides and Actinides are purified.

(vi) Cupellation : Pb, Ag

Impure metals are heated in a cupel or oval shaped crucible where impurities get oxidised and then removed.

(vii) Poling : Molten metal is stirred with green wooden poles which releases hydrocarbons (gas) which reduces the oxide e.g., Cu

$Cu_2O + CO \rightarrow 2Cu + CO_2$

$Cu_2O + H_2 \rightarrow 2Cu + H_2O$

(viii) Electrorefining :

Purification by electrolysis Cathode – pure metal and Anode - impure metal

(ix) Mond's method :

Nickel is purified by CO gas

$Ni + 4CO \rightarrow [Ni(CO)_4]$ impurities are left unaffected.

$[Ni(CO)_4] \xrightarrow{\Delta} Ni\downarrow + CO\uparrow$

Metallurgy of some important metals :

Aluminium

Sources :

Bauxite	$Al_2O_3 . 2H_2O$ (chief ore)
Cryolite	Na_3AlF_6
Feldspar	$KAlSi_3O_6$
Mica	$KAlSi_3O_{10}(OH)_2$
Beryl	$Be_3Al_2Si_6O_{18}$
Cribbsite	Al_2O_3

Diaspore	Al_2O_3
Kaolinite	$Al_2O_3 . H_2O$
Corundum	Al_2O_3
Alunite (Alum stone)	$K_2SO_4 . Al_2(SO_4) . 4Al(OH)_3$

Extraction of Aluminium

Aluminium is obtained by the electrolysis of the oxide (alumina) dissolved in fused cryolite. This involves the following steps :

1. Purification of the ore

Naturally occurring bauxite usually contains silica as impurity. These impurities must be removed before electrolysis, since Aluminium, once prepared, cannot be freed of other metals (which will be simultaneously deposited during electrolysis) by refining it. The bauxite is purified by any one of the following three methods :

(i) Baeyer's process

$$\text{Finely powdered bauxite} \xrightarrow[FeO \rightarrow Fe_2O_3]{\text{Roasted}} \text{Roasted ore} \xrightarrow[\text{High pressure (150°C, 80 atm)}\\ \text{filtered, } Fe_2O_3 \text{ as residue}]{+\text{Caustic soda solution}}$$

$$\text{Filtrate (sod. aluminate + sod. silicate)} \xrightarrow[\text{Filtered}]{CO_2} Al(OH)_3 \xrightarrow{\text{Heat}} \text{Pure } Al_2O_3$$

(ii) Hall's process

$$\text{Finely divided bauxite} \xrightarrow[\text{Fused, extracted with water}\\ \text{Residue } SiO_2, Fe_2O_3]{+Na_2CO_3} \text{Solution} \xrightarrow[\text{50–60°C and filtered}\\ \text{filtrate } (Na_2CO_3)]{CO_2} \text{Precipitate } Al(OH)_3$$

$$\xrightarrow{\text{Heat}} \text{Pure } Al_2O_3$$

(iii) Serpeck's process

$$\text{Finely powdered bauxite ore} \xrightarrow[\text{Heated to 1800°C}]{\text{Coke} + N_2} \text{Silica reduced to Si which volatilises +}$$

$$\text{Alumina form Aluminium nitride AlN} \xrightarrow{\text{Hydrolysis}} Al(OH)_3 \xrightarrow{\text{heated}} \text{Pure } Al_2O_3$$

2. Electrolysis

Pure alumina, is a bad conductor of electricity. Hence it is dissolved in molten cryolite, $NaAlF_6$ to decrease its fusion temperature. Alumina is then, electrolysed at 800–900ºC, using a number of carbon (graphite) blocks as anodes and a carbon (graphite) lined iron bath as cathode.

A low voltage is used to avoid decomposition of cryolite and a very high current density is employed. Molten aluminium collects at the floor of the graphite lined bath and is run off from time to time. Oxygen is evolved at the anode.

A solid crust of the electrolyte is deposited on the surface of the molten electrolyte which prevents heat loss, loss of aluminium fluoride and burning of carbon anodes.

3. Refining of aluminium (Hoope's electrolytic process)

In this process the electrolysis is carried out in a graphite lined bath which acts as the anode. Carbon cathodes are used. The refining cell consists of three fused layers differing in specific gravity.

(a) The bottom layer is of molten impure Aluminium

(b) The middle layer is of fused cryolite and barium fluoride and

(c) The upper layer is of pure Aluminium

Iron

Source of Fe or Ores

(1) Haematite.Fe_2O_3 (Chief ore)

(2) Magnetite.Fe_3O_4

(3) Siderite.$FeCO_3$ or spalthic ore

(4) Iron pyrites.FeS_2

(5) Pyrehotite.FeS

(6) Chalcopyrites.$CuFeS_2$

(7) Lemonite $Fe_2O_3 . 3H_2O$

Extraction - From Haematite

Concentration - By gravity separation and electromagnetic separation

Roasting

(1) To remove moisture, Carbon, Sulphur and Arsenic

$S + O_2 \rightarrow SO_2$

$4As + 3O_2 \rightarrow 2As_2O_3$

(2) Carbonate and sulphide ores are changed into oxides and mass becomes porous.

$FeCO_3 \rightarrow FeO + CO_2$

$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8\ SO_2$

(3) FeO is oxidised to Fe_2O_3

$4FeO + O_2 \rightarrow 2Fe_2O_3$

Smelting - In blast furnace

(1) **Charge** - (ore + coke + lime)

(2) Reaction in the **zone of combustion**

$C + O_2 \rightarrow CO_2$

$CO_2 + C \rightarrow 2CO$

(3) Reaction in the **zone of reduction** - (300 - 800ºC)

$$2Fe_2O_3 + C \underset{400^oC}{\overset{300^oC}{\rightleftharpoons}} 2Fe_3O_4 + CO$$

$$Fe_3O_4 + CO \underset{700^oC}{\overset{600^oC}{\rightleftharpoons}} 3FeO + CO_2$$

$$FeO + CO \underset{800^oC}{\overset{700^oC}{\rightleftharpoons}} Fe + CO_2$$

(4) Reactions in the **zone of fusion** - (800ºC - 1200ºC)

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$ Slag

$$\left.\begin{array}{l} MnO_2 + 2C \rightarrow Mn + 2CO \\ SO_2 + 2C \rightarrow S + 2CO \\ P_2O_5 + 5C \rightarrow 2P + 5CO \end{array}\right\} \text{Along with Fe called pig iron or cast iron.}$$

Pig iron	:	It contains about 4% of Carbon and many other impurities (such as *S*, *P*, Si & Mn).
Cast iron	:	It is specially made by igniting pig iron with scrap Iron & coke in hot air, cast Iron contain 3% Carbon.
Wrought iron	:	It contains approximately 0.5% impurities of which about half is Carbon.
Steel :		Broadly classified as mild steel (0.1 – 005% C) and hard steel (0.6 – 1.5% C).
Alloy Steel	:	A lot of variety of steel prepared by the addition of the appropriates alloying metal or metals.
Stainless Steel	:	It contains 18% of Chromium.
Tungsten Steel	:	It contains about 5% of Tungsten (very hard).
Manganese Steel	:	It contains about 13% of Manganese (very tough).

Manufacture of wrought Iron

Charge - Cast iron + haematite

Furnace - Pudding furnace lined with Fe_2O_3

Reaction

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

$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2$

$Fe_2O_3 + 3Mn \rightarrow 2Fe + 3MnO$

$$\left.\begin{array}{l} SiO_2 + MnO \rightarrow MnSiO_3 \\ Fe_2O_3 + P_2O_5 \rightarrow 2FePO_4 \end{array}\right\} \text{Slag}$$

Copper (Cu)

Source

Copper pyrite (cheif ore)	-	$CuFeS_2$ (Chief ore)
Copper glance	-	Cu_2S
Azurite	-	$2CuCO_3.\ Cu(OH)_2$
Malachite	-	$Cu(OH)_2.CuCO_3$
Ruby Copper or cuperite	-	Cu_2O

Extraction

(1) Hydrometallurgical process - About 105 tonnes of ore is exposed to water and air. In about one year following reaction takes place.

$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4$

$2Cu_2S + 5O_2 \rightarrow 2CuSO_4 + CuO$

$CuS + 2O_2 \rightarrow CuSO_4$

In the case of non sulphide ores, the ore is treated with dil. H_2SO_4

$CuCO_3.\ Cu(OH)_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 + 3H_2O$

Copper is then separated by the reaction

$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$

(2) Pyrometallurgical process

(1) Concentration - Froth floatation process

(2) Roasting - In reverberatory furnace in the current of air

$S + O_2 \rightarrow SO_2$

$4As + 3O_2 \rightarrow 2As_2O_3$

$2CuFeS_2 + O_2$ (air) $\rightarrow Cu_2S + 2FeS + SO_2$

$2FeS + 3O_2$ (air) $\rightarrow 2FeO + 2SO_2$

(3) Smelting - (Charge - Roasted ore + Coke + Sand + air)

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

$FeO + SiO_2 \rightarrow FeSiO_3$

(4) Bessemerisation

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

$FeO + SiO_2 \rightarrow FeSiO_3$ (Slag)

$2CuS + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

The molten copper is run off into moulds and on cooling, Sulphurdioxide, Nitrogen and Oxygen escape from the metal giving the surface blistered appearances and known as blister Copper.

(5) Purification

(a) Poling - Green wood is used.

$Cu_2O + CO \rightarrow 2Cu + CO_2$

$Cu_2O + H_2 \rightarrow 2Cu + H_2O$

(b) Electrolytic refining

Anode - Impure Copper

Cathode - Pure Copper

Electrolyte - 15% $CuSO_4$ + 5% H_2SO_4

Reaction

Anode - $Cu \rightarrow Cu^{+2} + 2e^-$

At Cathode - $Cu^{+2} + 2e^- \rightarrow Cu$

Alloy of Cu : Brass (Cu + Zn)

Bronze (Cu + Sn)

Coinage alloy (Cu + Ni)

Silver (Ag)

Source

Argentite or Silver glance	-	Ag_2S (Chief ore)
Pyrargyrite or ruby silver	-	Ag_3SbS_3
Proustite	-	Ag_3AsS_3
Chloragyrite or Horn silver	-	AgCl
Argentigorons lead	-	PbS
		(0.01 to 0.1% Ag)

Extraction

(1) Mac Arthur - Forest cyanide process

(a) Concentration - Froth floatation process

(b) Treatment with Sodium cyanide -

$Ag_2S + 2NaCN \rightarrow 2AgCN + Na_2S$

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

$4Na_2S + 2H_2O + 5O_2\ (air) \rightarrow 2Na_2SO_4 + 4NaOH + 2S.$

(c) Recovery of Silver -

$2Na\ [Ag(CN)_2] + Zn \rightarrow Na_2\ [Zn\ (CN)_4] + 2Ag$ (This is known as spongy Silver)

Sod. tetra cyanozincate (II)

(d) Refining - Electrolytic refining

Anode - Impure Ag

Cathode - Pure Ag

Electrolyte - $AgNO_3$ with about 1% HNO_3

(2) Amalgamation Process

$Ag_2S + 2CuCl_2 \rightarrow 2AgCl + Cu_2Cl_2 + S$

$2AgCl + 2Hg \rightarrow Hg_2Cl_2 + 2Ag$

The amalgam so obtained is distilled to recover mercury.

Metallurgy of Au is same as that of Silver. Gold mostly occurs in native state. It may be extracted by Mac-Arthur Forest cyanide process.

Zinc

Occurence

Zinc has been known from very early times especially in the form of its alloys (brass and bronze). It does not occur in native form. In combined state it occurs as :

(i) Zinc blende, ZnS (Chief ore)

(ii) Calamine, $ZnCO_3$

(iii) Zincite, ZnO

(iv) Franklinite, $ZnO.Fe_2O_3$

The first two ores are more abundant and are generally employed for the extraction of the metal. In India, Zinc blende is mined in Zewar mines located near Udaipur in Rajasthan.

Extraction

The various steps involved in the extraction of Zinc from Zinc blende are :

1. The ore is concentrated by froth floatation process.

2. The concentrated ore is roasted in air to convert it into oxide.

$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

Sulphur dioxide so formed is used in the manufacture of Sulphuric acid.

3. The oxide obtained is mixed with crushed coke and heated to 1673 K in a fire clay retort where it is reduced to Zinc metal.

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

The CO evolved burns at the mouth of retort. When the flame changes colour from blue to greenish white, condenser is fitted to the retort. Being volatile at this temperature, the metal distills over and is condensed.

4. The metal is further purified by fractional distillation or by electrolysis.

In case of calamine, instead of roasting the ore is calcined and subsequently reduced with coke.

In order to prepare Zinc dust the molten metal is atomised with a blast of air. Granulated Zinc is prepared by pouring molten Zinc into cold water.

Mercury

The only important ore of Mercury is Cinnabar, HgS which is found mainly in Spain and Italy. Mercury is extracted by roasting concentrated Cinnabar in sufficient air at 773 — 873 K.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

Mercury volatilises and is condensed. Mercury, thus, obtained is about 99.7% pure. It contains traces of Lead, Zinc and Tin as impurities. It can be purified by distillation under reduced pressure.

OBJECTIVE QUESTIONS

Choose the correct answers :

1. In presence of oxygen, removal of sulphur from an ore is included in

(a) Calcination (b) Roasting (c) Smelting (d) Fluxing

2. In the extraction of copper from its sulphide ore, the metal is formed by reduction of Cu_2O with

(a) FeS (b) CO (c) Cu_2S (d) SO_2

3. Pyrolusite is a/an

(a) oxide ore (b) sulphide ore (c) carbide ore (d) not an ore

4. The metal always found in the free state is

(a) Au (b) Ag (c) Cu (d) Na

5. In the extraction of iron, slag is produced. Slag is

(a) CO (b) $FeSiO_3$ (c) $MgSiO_3$ (d) $CaSiO_3$

6. Cryolite is

(a) Na_3AlF_6 and is used in the electrolysis of alumina for decreasing electrical conductivity

(b) Na_3AlF_6 and is used in the electrolysis of alumina for lowering the melting point of alumina

(c) Na_3AlF_6 and is used in the electrolytic purification of alumina

(d) Na_3AlF_6 and is used in the electrolysis of alumina

7. Cassiterite is an ore of

(a) Mn (b) Ni (c) Sb (d) Sn

8. When an aqueous solution of sodium chloride is electrolysed using platinum electrodes, the ions discharged at the electrodes are

(a) Sodium and hydrogen (b) Sodium and chloride

(c) Hydrogen and chloride (d) Hydroxyl and chloride

9. The lustre of a metal is due to

(a) its high density (b) its high polishing

(c) its chemical inertness (d) presence of free electrons

10. Which metal can't be obtained from electrolysis ?

(a) Ca (b) Mg (c) Cr (d) Al

11. During smelting, an additional substance is added which combines with impurities to form a fusible product. It is known as

(a) Slag (b) Mud (c) Gangue (d) Flux

12. Purification of silicon element used in semiconductors is done by

(a) Zone refining (b) Heating (c) Froth floatation (d) Heating in vacuum

13. Aluminothermic process is used for metallurgy of

(a) Pb (b) Ag (c) Al (d) None of these

14. In electrorefining of copper some gold is deposited as

(a) Anode mud (b) Cathode mud (c) Cathode (d) Electrolyte

15. Mac Arthur process is use for

(a) Ag (b) Fe (c) Cl (d) O_2

16. Use of electrolysis is

(a) Electroplating (b) Electrorefining (c) Both (a) and (b) (d) None of these

17. Calcination is used in metallurgy for removal of

(a) Water and sulphide (b) Water and CO_2

(c) CO_2 and H_2S (d) H_2O and H_2S

18. In blast furnace, maximum temperature is in

(a) Zone of fusion (b) Zone of combustion

(c) Zone of slag combustion (d) Zone of reduction

19. Which one of the following beneficiation processes is used for the mineral, $Al_2O_3 . 2H_2O$?

(a) Froth floatation (b) Leaching (c) Liquation (d) Magnetic separation

20. The extraction of which of the following metals involves bessemerisation ?

(a) Fe (b) Ag (c) Al (d) Cu

21. One of the characteristic properties of non-metals is that they

(a) are reducing agents (b) form basic oxides

(c) form cations by electron gain (d) are electronegative

22. Of the following which cannot be obtained by electrolysis of the aqueous solution of their salts ?

(a) Ag (b) Mg and Al (c) Cu (d) Cr

23. Van Arkel method of purification of metals involves converting the metal into a

(a) Volatile stable compound (b) Volatile unstable compound

(c) Non volatile stable compound (d) None of the above

24. In the froth floatation process for the purification of ores, the ore particles float because

(a) they are light

(b) their surface is hydrophobic i.e., not easily wetted by water

(c) they bear electrostatic charge

(d) they are insoluble

25. Which is not a basic flux ?

(a) $CaCO_3$ (b) Lime (c) SiO_2 (d) CaO

26. The substance which is added to remove impurities is known as

(a) Slag (b) Flux (c) Gangue (d) Catalyst

27. Electrolytic reductio method is used in the extraction of

(a) highly electronegative elements (b) highly electropositive elements

(c) transition metals (d) noble metals

28. The role of calcination in metallurgical operations is

(a) to remove moisture (b) to decompose carbonate

(c) to drive off organic matter (d) to achieve all the above

29. Which method of purification is represented by the following equations ?

$Ti + 2I_2 \xrightarrow{773\,K} TiI_4 \xrightarrow{1675\,K} Ti + 2I_2$

(a) Cupellation (b) Poling (c) Van Arkel (d) Zone refining

30. Calcination is the process of heating the ore

(a) in a blast furnace (b) in absence of air (c) in presence of air (d) none of these

31. Which one of the following metals cannot be extracted by carbon reduction process ?

(a) Pb (b) Al (c) Hg (d) Zn

32. Cyanide process is used for obtaining

(a) Cr (b) Ag (c) Cu (d) Zn

MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

33. Which of the following is (are) correctly matched?

(a) Copper-Bessemer converter (b) Iron-Blast furnance

(c) Chromium-Aluminothermic process (d) Tin-Electrolytic reduction

34. In which of the following pair(s), the minerals are converted in to metals by self-reduction process?

(a) Cu_2S, PbS (b) PbS, HgS (c) PbS, ZnS (d) Ag_2S, Cu_2S

35. The reaction (s) which does not occur in the reduction zone in the extraction of iron from haematite ore is (are);

(a) $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$ (b) $FeO + CO \longrightarrow Fe + CO_2$

(c) $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$ (d) $CaO + SiO_2 \longrightarrow CaSiO_3$

36. Which of the following statement (s) is (are) true?

(a) In process of the precipitation of silver from sodium dicyano argentate (I), the zinc acts as reducing agent as well as complexing agent.

(b) In the process of roasting, the copper pyrnes is converted into a mixture of Cu_2S & FeS which, in turn, are partially oxidised

(c) Limonite, haematite and magnesite are ores of iron

(d) Tin and lead both are extracted from their ores by self-reduction

37. Why lime stone is added in the extraction of lead form galena?

(a) It prevents the formation of $PbSO_4$

(b) It remove the impurity of silica as fusible slag

(c) It converts lead silicate to lead oxide

(d) It remove the impurity of iron oxide as fusible slag

38. The role of fluorispar (CaF_2) which is added in the electrolytic reduction of alumina dissolved in fused cryolite is (are):

(a) to acts as a catalyst

(b) to make the fused mixture very conduction

(c) to increase the temperature of the melt

(d) to decrease the rate of oxidation of carbon at the anode

39. Which of the following statement (s) is (are) correct about slag?

(a) The chemical composition of slag obtained in the extraction of copper from copper pyrites is $PbSiO_3$

(b) The calcium silicate, $CaSiO_3$ is obtained in slag formation zone in the extraction of iron from hematite one

(c) In blast furnace/Bessemer converter, the upper layer of molten liquid (i.e molten metal) is of slag.

(d) The slag is fusible matter

40. Which of the following common element (s) is (are) present in the anode mud in electrolytic refining of copper

(a) Selenium (b) Tellurium (c) Silver (d) Gold

MISCELLANEOUS ASSIGNMENT

Comprehension-I

A black coloured compound (A) on reaction with dil H_2SO_4 form a gas 'B' and a solution of compound (C). When gas B is passed through solution of compound (C), a black coloured compound 'A' is obtained which is soluble in 50% HNO_3 and forms blue coloured complex 'D' with excess of NH_4OH and chocolate brown ppt. 'E' with $K_4[Fe(CN)_6]$

1. 'A' is

(a) CuS (b) FeS (c) PbS (d) HgS

2. 'B' is

(a) H_2S (b) SO_2 (c) NH_3 (d) SO_3

3. 'C' is

(a) CuS (b) $CuSO_4$ (c) $Cu(NO_3)_2$ (d) $HgSO_4$

4. 'D' is

(a) $Cu(OH)_2$ (b) $[Cu(NH_3)_2]SO_4$ (c) $[Cu(NH_3)_4]\ (NO_3)_2$ (d) $[Cu(NH_3)_6]SO_4$

5. 'E' is

(a) $Cu_2[Fe(CN)_6]$ (b) $Cu_4[Fe(CN)_6]$ (c) $Cu_3[Fe(CN)_6]_2$ (d) none of these

Comprehension-II

Amongst the various ores of a metal (M) (sulphide, carbonates, oxides, hydrated or hydroxides) two ores [X] and [Y] show that following reactivity

(i) [X] on calcination gives a black solid (S), carbon dioxide and water

(ii) [X] dissolved in dil. HCl on reaction with KI gives a white precipitate (P) and iodine

(iii) [Y] on roasting gives metal (M) and a gas (G) which turns acidified $K_2Cr_2O_7$ solution green.

(iv) [Y] on reaction with dil. HCl gives a white precipitate (Q) and another gas (G_2) which turns lead acetate solution black and also reacts with gas (G_1) to precipitate (Q) and another gas (G_2) which turns lead acetate solution black and also reacts with gas (G_1) to precipitate colloidal sulphur in presence of moisture.

The M, S, [X] and [Y] gives greenish blue flame.

6. The metal ores [X] and [Y] are respectively:

(a) carbonate and sulphite ores (b) sulphite and carbonate ores

(c) carbonate and hydroxide ores (d) carbonate and oxide ores

7. Which of the following statements is correct about [Y]?

(a) [Y] is converted to metal (M) by self reduction

(b) Carbonate extract of [Y] gives yellow precipitate with suspension of $CdCO_3$

(c) [Y] is chalococites of chalcopyrites

(d) All of these

8. The gas (G_1) acts as

(a) Oxidising agent (b) reducing agent

(c) oxidisng and reducing agent (d) fluxing agent

9. The white precipitate (P) is of

(a) Cu_2I_2 (b) CuI_2 (c) $K_2[CuI_4]$ (d) none of these

MATRIX MATCH TYPE QUESTIONS

10. Match the reactions given in column (I) with the appropriate method(s) listed in column (II)

Column-I	**Column-II**
A. $4Au + B\ NaCN + 2H_2O + O_2$ (air) $\longrightarrow 4\ Na[Au(CN)_2] + 4NaOH$	(p) Sulphate ore
B. $CuFeS_2 + 2H_2SO_4 \longrightarrow CuSO_4 + FeSO_4 + 2H_2S$	(q) Carbonate ore
C. $Fe_3O_4 + 4CO \xrightarrow{823K} 3Fe + 4CO_2$	(r) Roasting
D. $MgCl_2.6H_2O \xrightarrow[\text{Dry HCl(g)}]{\Delta} MgCl_2 + 6H_2O$	(s) Calcination

11. Match the following metals given in column-I with the appropriate metal extraction process (es) listed below in column-II

Column-I	**Column-II**
A. Silver	(p) Fused salt electrolysis
B. Lead	(q) Cyanide process
C. Iron	(r) Carbon monoxide reduction
D. Magnesium	(s) Self reduction

INTEGER TYPE QUESTIONS

12. Amongst the following, total number of elements which occur in combined state in the earth's crust is: F, Au, Na, Pt, Cl, Ag, K, Hg, Pb.

13. Amongst the following, the total number of carbonate ores are: Argentite, magnesite, cerussite, sylvine, siderite, azurite, anglesite, barytes, calcite, willemite, calamine, malachite.

14. The total number of ores which are concentrated by electromagnetic separation out of the following is: Cassiterite, epsomite, chromite, magnetite, cryolite, pyrolusite, fluorite, dolomite, rutile.

15. Amongst the following, the total number of ores which are calcined to convert them into their corresponding metal oxides is: Bauxite, Zinc blende, Diaspore, Limestone, Magnesite, Copper glance, Calamine, Siderite, Cerussite, Rock salt.

16. How many of the following are basic fluxes? SiO_2, $CaCO_3$, $MgCO_3$, $Na_2B_4O_7$. $10H_2O$, Fe_2O_3.

17. Considering Ellingham diagram, the number of oxides which are reduced by Zn is: MgO, FeO, Al_2O_3, Cu_2O.

18. How many of the following metals are obtained by auto reduction of their sulphide ores on heating? Al, Mg, Hg, Cu, Ca, Pb, Sb, Ba, K.

19. How many of the following metals are purified by liquation method? Cu, Fe, Hg, Pb, Al, Sn, Bi, Ni.

20. Iron sulphide on heating in air gives an oxide of sulphur A which dissolves in water to give an acid. The basicity of the acid is.

21. Total number of ores each containing two different metal ions out of the following are : Dolomite, Malachite, Azurite, Copper pyrites, Pentlandite, Carnallite, Cryolite, Felspar.

PREVIOUS YEAR QUESTIONS

IIT-JEE/JEE-ADVANCE QUESTIONS

1. An aqueous solution of sodium sulphate is electrolysed using inert electrodes. The products at the cathode and anode are respectively

(a) H_2, O_2 (b) O_2, H_2 (c) O_2, Na (d) O_2, SO_2

2. The compound which gives off oxygen on moderate heating is

(a) Cupric oxide (b) Mercuric oxide (c) Zinc oxide (d) Aluminium oxide

3. Amongst the trihalides of nitrogen, which one is least basic?

(a) NF_3 (b) NCl_3 (c) NBr_3 (d) NI_3

4. Which one of the following are prepared by electrolytic method?

(i) Mg (ii) Sn (iii) S (iv) F_2

(a) (i) & (ii) (b) (ii) & (iv) (c) (iii) and (iv) (d) (i) and (iv)

5. A metal nitrate gives black ppt. with KI and on adding excess of KI it gives orange colour. It is

(a) Hg^{+2} (b) Bi^{+3} (c) Sn^{+2} (d) Pb^{+2}

6. The compound which gives off oxygen on moderate heating is

(a) Cupric oxide (b) Mercuric oxide (c) Zinc oxide (d) Aluminium oxide

7. Which of the following will not be oxidised by O_3?

(a) KI (b) $FeSO_4$ (c) $KMnO_4$ (d) K_2MnO_4

8. Which gelatinous ppt. is soluble in $NH_4OH + NH_4Cl$

(a) $Zn(OH)_2$ (b) $Al(OH)_3$ (c) $Ca(OH)_2$ (d) $Mg(OH)_2$

9. When $MgSO_4$ in presence of NH_4Cl is treated with Na_2HPO_4. The white ppt. formed is of

(a) $MgSO_4$ (b) $Mg(NH_4)PO_4$ (c) $Mg_3(PO_4)_2$ (d) $MgCl_2$

10.

(*i*)	Ag	A.	C reduction
(*ii*)	B	B.	Self reduction
(*iii*)	Pb	C.	Complex formation followed by ppt. of metal
(*iv*)	Cu	D.	tetra iodide

11. Extraction of zinc from zinc blende is achieved by

(a) electrolytic reduction

(b) roasting followed by reduction with carbon

(c) rosting followed by reduction with another metal

(d) roasting followed by self-reduction

12. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of

(a) nitrogen (b) oxygen (c) carbon dioxide (d) argon

13. A solution of colourless salt **H** on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) **H** is (are)

(a) NH_4NO_3 (b) NH_4NO_2 (c) NH_4Cl (d) $(NH_4)_2SO_4$

Paragraph for Question 14 to 16

Copper is the most noble of the first now transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4 \cdot 5H_2O$, atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

14. Partial roasting of chalcopyrite produces

(a) Cu_2S and FeO (b) Cu_2O and FeO (c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3

15. Iron is removed from chalcopyrite as

(a) FeO (b) FeS (c) Fe_2O_3 (d) $FeSiO_3$

16. In self-reduction, the reducing species is

(a) S (b) O^{2-} (c) S^{2-} (d) SO_2

17. Match the entries in Column I with the correctly related quantum number(s) in column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

Column I	**Column II**
(A) $PbS \rightarrow PbO$	(p) roasting
(B) $CaCO_3 \rightarrow CaO$	(q) calcination
(C) $ZnS \rightarrow Zn$	(r) carbon reduction
(D) $Cu_2S \rightarrow Cu$	(s) self reduction

18. Match each of the reactions given in **Column I** with the corresponding product(s) given in **Column II**

Column I	**Column II**
(A) Cu + dil. HNO_3	(p) NO
(B) Cu + conc. HNO_3	(q) NO_2
(C) Zn + dil. HNO_3	(r) N_2O
(D) Zn + conc. HNO_3	(s) $Cu(NO_3)_2$
	(t) $Zn(NO_3)_2$

19. Extraction of metal from the ore **cassiterite** involves

(a) carbon reduction of an oxide ore (b) self-reduction of a sulphide ore

(c) removal of copper impurity (d) removal of iron impurity

20. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are

(a) O_2 and CO respectively (b) O_2 and Zn dust respectively

(c) HNO_3 and Zn dust respectively (d) HNO_3 and CO respectively

21. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is

(a) Fe(III) (b) Al(III) (c) Mg(II) (d) Zn(II)

22. Sulphide ores are common for the metals

(a) Ag, Cu and Pb (b) Ag, Cu and Sn (c) Ag, Mg and Pb (d) Al, Cu and Pb

23. The carbon-based reduction method is **NOT** used for the extraction of

(a) tin from SnO_2 (b) iron from Fe_2O_3

(c) aluminium from Al_2O_3 (d) magnesium from $MgCO_3 \cdot CaCO_3$

24. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are)

(a) Impure Cu strip is used as cathode

(b) Acidified aqueous $CuSO_4$ is used as electrolyte

(c) Pure Cu deposits at cathode

(d) Impurities settle as anode-mud

25. Match the anionic species given in Column I that are present in the ore(s) given in Column II.

Column I	**Column II**
(A) Carbonate	(P) Siderite
(B) Sulphide	(Q) Malachite
(C) Hydroxide	(R) Bauxite
(D) Oxide	(S) Calamine
	(T) Argentite

DCE QUESTIONS

1. If a non-metal is added to the interstitial sites of a metal then the metal becomes

(a) softer (b) less tensile (c) less malleable (d) more ductile

2. Railway wagon axles are made by heating rods of iron embedded in charcoal powder, the process is known as

(a) Cast hardening (b) Tempering (c) Annealing (d) Shevadizing

3. Most Acidic oxide amount following is

(a) Cl_2O_5 (b) Cl_2O (c) Cl_2O_3 (d) Cl_2O_7

AIEEE/JEE-MAINS QUESTIONS

1. Which one of the following nitrates will leave behind a metal on strong heating?

(a) Copper nitrate (b) Manganese nitrate (c) Silver nitrate (d) Ferric nitrate

2. In context with the industrial preparation of hydrogen from water gas ($CO + H_2$), which of the following is the correct statement?

(a) CO is removed by absorption in aqueous Cu_2Cl_2 solution

(b) H_2 is removed through occlusion with Pd

(c) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali

(d) CO and H_2 are fractionally separated using differences in their densities

3. Which of the following factors is of *no significance* for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?

(a) CO_2 is thermodynamically more stable than CS_2

(b) Metal sulphides are less stable than the corresponding oxides

(c) CO_2 is more volatile than CS_2

(d) Metal sulphides are thermodynamically more stable than CS_2

4. Boron cannot form which one of the following anions?

(a) BF_6^{3-} (b) BH_4^- (c) $B(OH)_4^-$ (d) BO_2^-

5. Which method of purification is represented by the following equation:

$$Ti(s) + 2I_2(g) \xrightarrow{523K} TiI_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$

(a) Zone refining (b) Cupellation (c) Poling (d) Van Arkel

6. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is

(a) Cu (b) Cr (c) Ag (d) Ca

ANSWERS

Objective Questions

1.	(b)	2.	(c)	3.	(a)	4.	(a)	5.	(d)
6.	(b)	7.	(d)	8.	(c)	9.	(d)	10.	(c)
11.	(d)	12.	(a)	13.	(d)	14.	(a)	15.	(a)
16.	(c)	17.	(b)	18.	(b)	19.	(b)	20.	(a)
21.	(a)	22.	(b)	23.	(a)	24.	(b)	25.	(c)
26.	(b)	27.	(b)	28.	(d)	29.	(c)	30.	(b)
31.	(b)	32.	(b)	33.	(a,b,c)	34.	(a,b)	35.	(c,d)
36.	(a,b)	37.	(a,b,c)	38.	(b)	39.	(b,c,d)	40.	(a,b,c,d)

Miscellaneous Assignment

1.	(a)	2.	(a)	3.	(b)	4.	(c)	5.	(a)
6.	(a)	7.	(d)	8.	(c)	9.	(a)		
10.	A-(p); B-(p); C-(q); D-(s)			11.	A-(q); B-(s); C-(r); D-(p)				
12.	(6)	13.	(7)	14.	(5)	15.	(7)	16.	(3)
17.	(2)	18.	(4)	19.	(4)	20.	(2)	21.	(6)

Previous Year Questions

IIT-JEE/JEE-ADVANCE QUESTIONS

1.	(a)	2.	(b)	3.	(a)	4.	(d)	5.	(b)
6.	(b)	7.	(c)	8.	(a)	9.	(b)		
10.	(i)-C, (ii)-A, (iii)-B, (iv)-B			11.	(c)	12.	(b)	13.	(a,b)
14.	(a)	15.	(d)	16.	(c)	17.	A-(p);B-(q);C-(p),(r);D-(p), (s)		
18.	A-(p),(s); B-(q),(s); C-(r),(t); D-(q),(t)					19.	(a,d)	20.	(b)
21.	(d)	23.	(a)	23.	(c,d)	24.	(a,c,d)		
25.	A–(P), (Q), (S); B–(T); C–(Q), (R); D–(R)								

DCE QUESTIONS

1. (b) 2. (a) 3. (d)

-MAINS QUESTIONS

1. (c) 2. (c) 3. (d) 4. (a) 5. (d)
6. (d)