Chapter-06

General Principles Of Isolation Of Elements

LECTURE: 1

Minerals and Ores:-

Minerals are naturally occurring chemical substances in the earth crust obtainable by mining ores are the minerals from which metal can be extraction economically and comfortably. “All ores are minerals but all minerals are not ores”.

Gangue:-

The earthly or undesired materials found in the ore are called gangue.

Flux and Slag:-

These are the additional substances added to ore to remove the impurities in the form of slag. Slag is the combustion of flux and impurities.

$$impurities + flux \rightarrow slag \qquad SiO_2 + CaO \rightarrow CaSiO_3$$

Metallurgy:-

The scientific and technological process used for the isolation of metal from its ores is called metallurgy. It involves the following steps

(a) Concentration of ore

(b) Conversion of concentrated ore into metal oxide

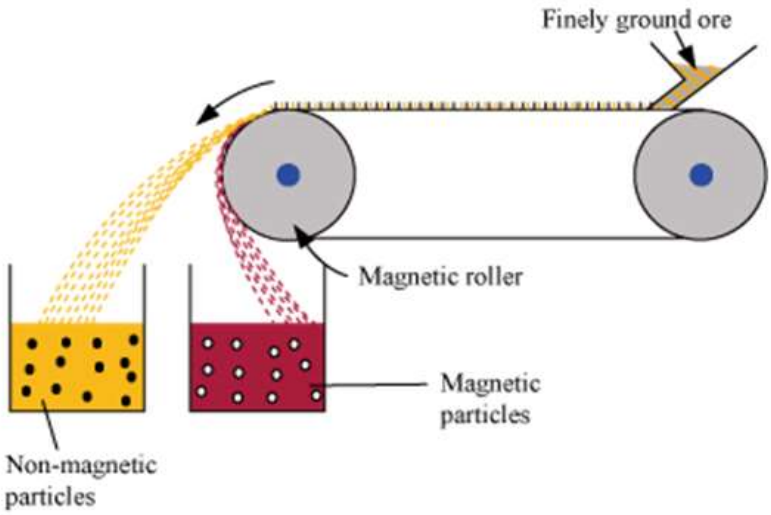
(c) Reduction of metal oxide to metal

(d) Purification of metal

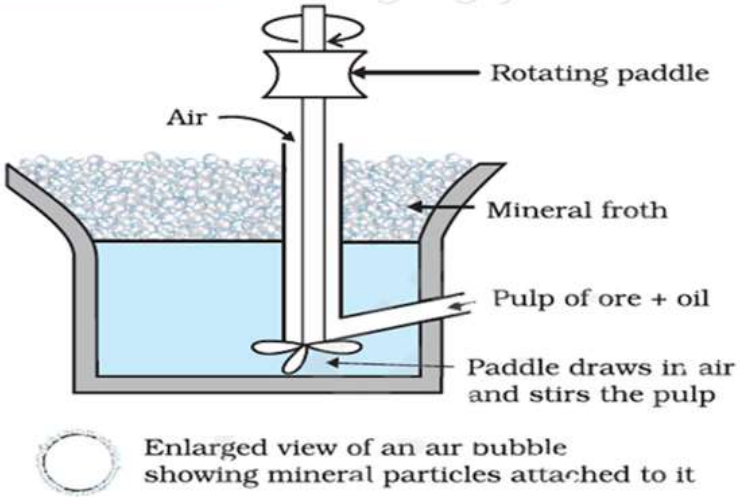
(I) The concentration of ores:- The process of removal of the unwanted materials (e.g sand, clays, etc) of ore is known as concentration dressing or benefaction. It involves the following steps

(a) Hydraulic Washing:- It is based on the principles that the impurities are lighter then the ore particles so when an upward stream of running water is used to wash the ore, the lighter gauge particles will be washed away and the heavier ores are left behind.

(b) Magnetic Separation:- It is based on the difference in magnetic properties of the ore components. If either the ore or the gangue is capable of being attracted by a magnetic field then its method is useful.



(c) Froth floatation process:- It is based on the principle that the mineral particles become wet by oil whole the gangue particles by water. Sulfide ores are concentrated by this process. If this method is the suspension of the powdered ore is made with water and collectors and forth stabilizers are added. Collectors like pine oil enhance the new wettability of the mineral particles and forth stabilizers like aniline and cresol stabilize the forth. Two separate the two supplied ores deprecations are used. Depressants prevent one of the sulfite ore from coming to the froth and allow the other to come with the froth. For example in the separation of ZnS and PbS depressant like NaCl is used, which prevents ZnS from coming to the froth but allows PbS to come with the forth.



Froth floatation process

(d) leaching (chemical method of concentration)

(1) Leaching of alumina from bauxite:- The powder ore of bauxite is treated with concentrated solve of NaOH at 473 – 523 K and 35 – 36 bar pressure so Al_2O_3 is leached out as sodium aluminates leaving behind the impurities.

$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na\left[Al(OH)_4\right]_{(aq)}$. The aluminates in solution are neutralized by passing CO_2 gas and hydrated Al_2O_3 is precipitate $2Na\left[Al(OH)_4\right]_{(aq)} + CO_{2(g)} \rightarrow Al_2O_3.KH_2O + 2NaCl_{(aq)}$. The sodium silicate remains in the solving and hydrated alumina is biltered dried and heated to give balk pure alumina (Al_2O_3).

$Al_2O_3.xH_2O_{(s)} \xrightarrow{1470k} Al_2O_{3(s)} + xH_2O_{(g)}$.

(2) Leaching of gold and silver:- In the metallic of gold and silver the respective metal is loathed with a dilute solution of NaCN or KCN in the presence of our (CrO_2) from which the metal is obtained leather by replacement.

$4M_{(S)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)} \rightarrow 4\left[M(CN)_2\right]^-_{(aq)} + 4OH_{(aq)}$, (M = Au or Ag)

$2\left[M(CN)_2\right]^-_{(aq)} + Zn_{(s)} \rightarrow \left[Zn(CN)_4\right]^-_{(aq)} + 2M_{(s)}$

(II) Conversion concentrated ore into metal oxide:- It can be done by

(a) Calcination:- It is the process of heating of concentrated ore in the absence of air. It is used to convert the carbonate ore into oxide ore to remove the volatile impurities from the ore.

$$Fe_2O_{3(s)}.xH_2O_{(s)} \xrightarrow{\Delta} Fe_2O_{3(s)} + xH_2O_{(g)}$$

$$ZnCO_{3(s)} \xrightarrow{\Delta} ZnO_{(s)} + CO_{2(g)}$$

$$CaCO_3.MgCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + MgO_{(s)} + 2CO_{2(g)}$$

(b) Roasting:- It is the process of heating of concentrated ore in the regular supply of air. It is used to convert supplied ore into oxide ore to remove the volatile impurities from the ore.

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

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cl_2O + 2SO_2$$

(II) Reduction of metal oxide to metal:- It usually involves heating the metal oxide with some other substances acting as a reduction agent (C or CO or even another method)

$$M_xO_y + yC \rightarrow xM + yCO.$$

The process of reduction of metal oxide to metal by heating is called pyrometallurgy metal like aluminum, magnesium et is used for the reduction of metal oxide to metal.

LECTURE-2

Thermodynamic principles of metallurgy:-

Some basic concepts of thermodynamics which help us in understanding the theory of metallurgical transformation ore.

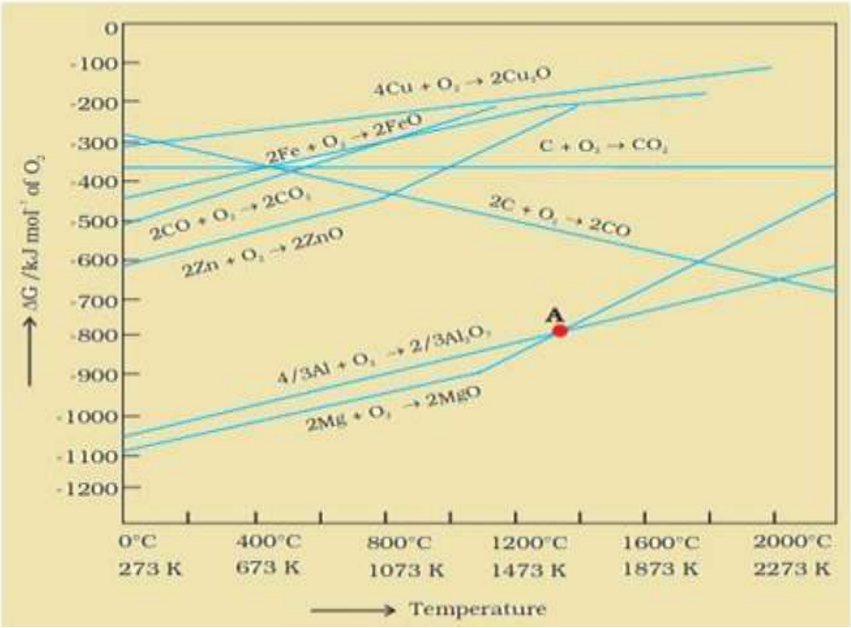
(I) Gibb's energy charge (ΔG) should be negative which can be described by the equation.

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

Where ΔH is the enthalpy charge and ΔS is the entropy charge. This charge could also be explained through the equation. $\Delta G^{\ominus} = -RT \ln K$ 'K' is called equilibrium constant.

(II) If the reduction is not feasible, then the reactant and product of the two reaction are put together in a system and the net ΔG of the two possible reaction is –ve, the overall reaction will occur.

Ellingham Diagram:- The graphical representation of Gibb's energy charge $(\Delta_f G^{\theta})$ for the formation of oxides of metal vs temperature is called the Ellingham diagram. It is useful for the selection of reduction agent reduction of metal oxide to metal.



Extraction of Iron:- The important ore of ion is hematite (Fe_2O3). The extraction process involves the following steps

(I) The concentration of ore:- It can be done by hydrolytic washing in which the ore is washed with a running stream of water to remove the sand, clays, etc from the ore.

(II) Calcination:- the concentrated ore is heated in the absence of air to remove the volatile impunities and to convert the carbonate (if any) into oxide.

$$Fe_2O_3.xH_2O_{(s)} \xrightarrow{\Delta} Fe_2O_{3(s)} + xH_2O_{(g)}$$

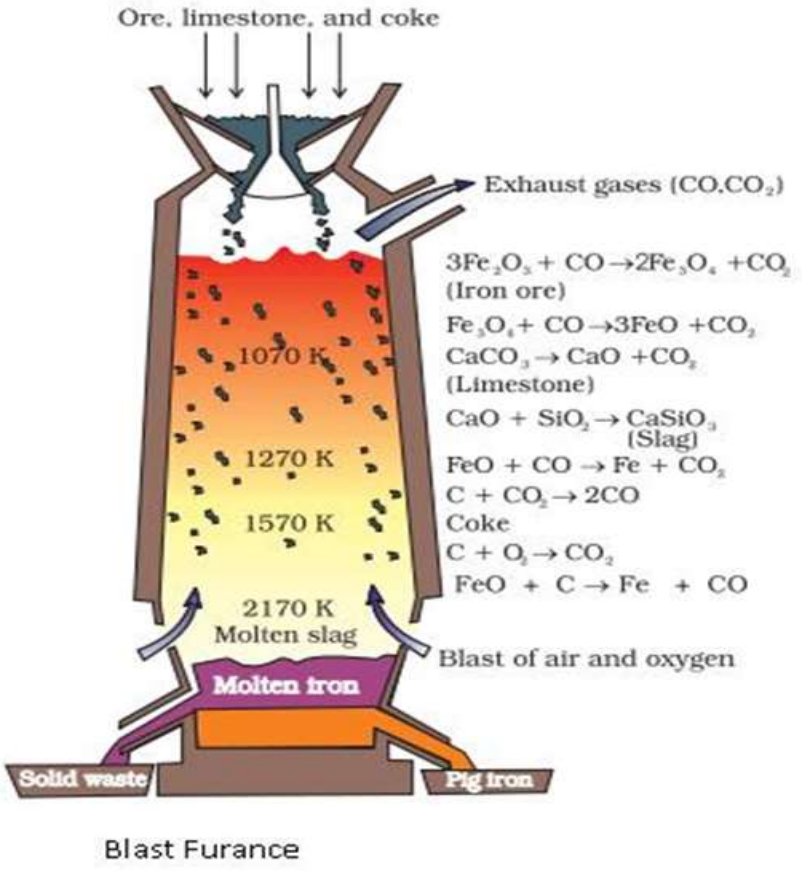
(III) Reduction of iron oxide to iron:- Mixture of ore, coke and limestone in the blast furnace and hot air is blown from the furnace so that coke is bunt and the following relation takes place and molten pig iron is obtained.

(a) $C + O_2 \rightarrow CO_2$ (b) $C + CO_2 \rightarrow 2CO$

(c) $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ (d) $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

(e) $FeO + CO \rightarrow Fe + CO_2$ (f) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

(g) $CaO + SiO_2 \rightarrow CaSiO_3\,(slag)$



Extraction of copper from copper pyrites:- Important ore of copper is copper pyrites ($CuFeS_2$). The metallurgy involves the following steps.

(I) The concentration of Ore:- It can be done by the froth flotation process.

(II) Roasting:- The concentrated ore is heated with a regular supply of our to convert the sulfide ore into oxide ore and to remove the volatile impurities.

$CuFeS_2 + O_2 \rightarrow Cu_2S + FeO + SO_2$ $\qquad 2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

The or is heated in a reverberatory furnace after mixing with silica. Iron oxide is removed as slag in the form of iron silicate and copper is produced in the form of copper matter, which contains Cu_2S and FeS. Copper matte is then charged into a silica lined converter. Some silica is also added and hot air blast is blown to convert the remaining FeS_2,. FeO and Cu_2S / Cu_2O to the metallic copper following reactions take place.

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ $\qquad$ $FeO + SiO_2 \rightarrow FeSiO_3(slag)$

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $\qquad$ $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

The copper obtained is called blister copper due to the evolution of SO_2.

Extraction of Zinc:- The important ore of zinc is zinc blende (ZnS). The metallurgy involves the following steps

(I) The concentration of ore:- By froth floatation process

(II) Roasting:- $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

(III) Reduction of zinc oxide:- $ZnO + C \xrightarrow{COKe,673K} Zn + CO$

LECTURE-3

Electrochemical principles of metallurgy:- The reduction of metal oxide to metal is also based on the electrolysis of a solution of the metal ion or molten state. The electrochemical principles are based on the equation.

$$\Delta G^\theta = -nFE^\theta$$

N = no. of electrons

E^θ = The electrode potential of the redox couple formed by the system more reactive metal have large negative values of the electrode potential. So there reduction is difficult. If the difference of two E^θ values corresponds to a positive E^θ and consequenting negative ΔG^θ then the less reactive method will come out of the solution and the more reactive metal will go to the solution e.g $Cu^{2+}_{(aq)} + Fe_{(s)} \rightarrow Cu_{(s)} + Fe^{2+}_{(aq)}$. Flux are also added for making the molten mass more conducting.

Extraction of Aluminium:- the important ore of aluminum is bauxite ($Al_2O_3.xH_2O$).metallurgy based on the following steps.

(I) Leaching of bauxite:- It can be done by the chemical method of purification which involves.

(a) The powdered ore is treated with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. So that Al_2O_3 is leached out as sodium aluminates leaving the impetrates behind.

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na\left[Al(OH)_4\right]_{(aq)}$$

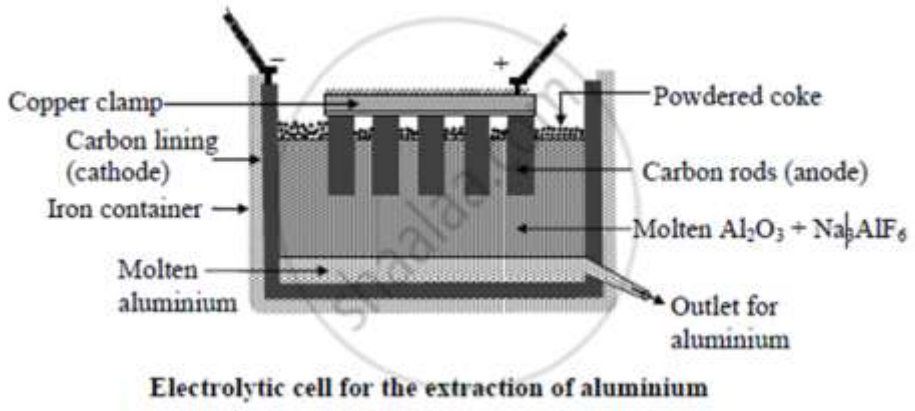
(b) The aluminate solution is neutralized by passing CO_2 gas and hydrated Al_2O_3 is precipitated.

$$2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} \rightarrow Al_2O_3.xH_2O_{(s)} + 2NaHCO_{3(aq)}$$

(c) The sodium silicate remains in the solution and hydrated alumina is filtered, dried, and heated to give back pure This process of leaching is called Baeyer's process.

$$Al_2O_3.xH_2O_{(s)} \xrightarrow{1470k} Al_2O_{3(s)} + 2H_2O_{(g)}.$$

(II) Electrolytic Reduction of Alumina (Al_2O_3):- In the metallurgy of aluminum, purified Al_2O_3 is mixed with Na_3AlF_6 or COF_2 which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolyzed in an electrolytic take made of still in which carbon lining act as a cathode and graphite rod as an anode. This process of electrolysis is called the hall – Heroult process. During electrolysis, the following reactions face place and molten aluminum is collected at the cathode.



Electrolytic cell for the extraction of aluminium

$$Al_2O_{3(molten)} \xrightarrow{electrolyte} 2Al^{3+}_{(melt)} + 3O^{2-}_{(melt)}$$

Cathode:- $Al^{3+}_{melt} + 3e^- \rightarrow Al_{(l)}$

Anode:- $C_{(s)} + O^{2-}_{(melt)} \rightarrow CO_{(g)} + 2e^-$ $\qquad$ $C_{(s)} + 2O^{2-}_{(melt)} \rightarrow CO_{2(g)} + 4e^-$

Extraction of copper from low-grade ores and scraps:-

Copper is extracted by hydrometallurgy from low-grade ores. It is leached out using acid or bacteria.

The solution containing Cu^{2+} is treated with scrap iron or A_2C_2 to obtain metallic copper.

$$Cu^{2+}_{(aq)} + H_{2(g)} \rightarrow Cu_{(s)} + 2H^+_{(aq)} \qquad Cu^{2+}_{(aq)} + Fe_{(s)} \rightarrow Cu_{(s)} + Fe^{2+}_{(aq)}$$

Extraction using oxidation and Reduction:- the extraction of some of the non-metal is based on oxidation. For example.

(I) Extraction of chlorine from brine solution:- Electrolysis of concentrated aqueous solution of NaCl (brine solution) with produce Cl_2 at the anode.

$$2NaCl_{(aq)} + 2H_2O_{(l)} \xrightarrow{Electrolysis} Cl_{2(aq)} + H_{2(g)} + 2NaOH_{(aq)}$$

$$NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$$H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$$

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

At Cathode:- $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

Extraction of Gold and Silver:- It involves the leaching of gold and silver with a dilute solution of NaCN or KCN to form a soluble complex of gold and silver which involves an oxidation reaction. The metal is later recovered by displacement method using zinc as a reducing agent, which involves a reduction reaction.

$$4Au_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)} \rightarrow 4\left[AuC(CN)_2\right]^-_{(aq)} + 4OH^-_{(aq)}$$

$$2\left[Au(CN)_2\right]^-_{(aq)} + Zn_{(s)} \rightarrow 2Au_{(s)} + \left[Zn(CN)_4\right]^{2-}_{(aq)}$$

LECTURE-4

Refining:- A metal extracted by any method is usually contaminated with some importance so for obtaining metal of high party several techniques are used depending upon the difference in properties of the metal and the impurity. Some of these are:-

(a) Distillation:- It is based on the principle that the boiling point of the metal is lower than the impurities. Metals like zinc mercury can be purified by this method.

(b) Liquation:- It is based on the principle that the melting point of the metal is lower than the impurities. Example metal like tin can be purified by this method.

(c) Electrolytic Returning:- It is based on the principle that impure metal acts as an anode, strip of the same metal in pure form act as a cathode the salt solution of the same metal act as an electrolyte. On electrolysis, the more basic metal reaction in the solution and the less basic over go to the anode. Anode mud contains antimony, selenium tellurium, silver gold, and platinum. Metals like copper and zinc are refined by this method.

Anode: - $M \rightarrow M^{n+} + ne$ Cathode:- $M^{n+} + ne \rightarrow M$

(d) Zone Refining:- It is based on the principle that the impurities are more soluble in the metal than the solid-state of the metal. This method is very useful for producing semiconductors and other metals of very high purity e.g germanium, silicon, boron gallium, and indium can be purified by this method.

(e) Vapor phase Refining:- It is based on the principle that the impure metal is treated with suitable resent to form a volatile compound and collected elsewhere. Which then decomposed to form pure metal. Examples:-

Refining of nickel by mond process:- Impure nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetra carbonyl, which is then subjected to a higher temperature so that it decomposed to pure metal.

$$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4 \qquad Ni(CO)_4 \xrightarrow{450-470K} Ni + 4CO$$

Van Arkel method for refining zirconium and titanium:- The impure metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilizes

$$Zr/Ti + 2I_2 \rightarrow ZrI_{(g)}/TiI_4 \qquad ZrI_4/TiI_4 \xrightarrow{Tungsten\ filament\ (1800K)} Zr/Ti + 2I_2$$

LECTURE-5

(f) Chromatographic method:- It is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. This method is very useful for the purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified. Column chromatography is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

Uses of Aluminium, Aluminium, Copper, Zinc, and Iron:

Aluminum foils are used as wrappers for food materials. The fine dust of the metal is used in paints and lacquers. Aluminum, being highly reactive, is also used in the extraction of chromium and manganese from their oxides. Wires of aluminum are used as electrical conductors. Alloys containing aluminum, being light, are very useful. Copper is used for making wires used in the electrical industry and for water and steam pipes. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin), and coinage alloy (with nickel). Zinc is used for galvanizing iron. It is also used in large quantities in batteries. It is a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and German silver (Cu 25-30%, Zn 25-30%, Ni 40–50%). Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc. Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc. It is used in the manufacture of wrought iron and steel. Wrought iron is used in making anchors, wires, bolts, chains, and agricultural implements. Steel finds several uses. Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and airplane parts, pendulum, measuring tapes. Chrome steel is used for cutting tools and crushing machines, and stainless steel is used for cycles, automobiles, utensils, pens, etc.

Questions:-

01. Differentiate between ore and minerals.
02. What are flux and slag? Give an example
03. What is the basic principle of the froth flotation process?
04. What is the role of the collector in the broth flotation process?
05. What is the role of the froth stabilizer in the froth flotation process?
06. State the role of depressant in the froth flotation process.
07. Name the depressant used in the separation of ZnS and PbS.
08. State the role of pine oil in the froth flotation process.
09. State the role of cresol in the froth flotation process.
10. What is the basic principle of the magnetic separation method?

Questions:-

01. Describe the leaching of bauxite ore ($Al_2O_3.xH_2O$).
02. What is the significance of leaching in the extraction of aluminum?
03. State the role of NaCN in the metallurgy of silver
04. Al through thermodynamically feasible, in practice magnesium metal is not used for the reduction of alumina in the metallurgy of aluminum why?
05. Why is the reduction of metal oxide easier if the metal formed is in the liquid state at the temperature of reduction?
06. Differentiate between roasting and collimation.
07. What is hydrometallurgy?

Question:-

01. State the role of limestone in the extraction of ore
02. What is the difference between cast iron and piston?
03. Write the reactions that take place in the blast furnace during the extraction of iron from hematite.
04. Which iron is the present from or iron?
05. What is the composition of copper matte?
06. Why is copper matte put into silica lined conversion?
07. State the role of silica in the metallurgy of copper.
08. Why is the copper obtained from copper pyrites is called blister copper?

Questions:-

01. State the role of cryolite $\left(Na_3AlF_6\right)$ in the metallurgy of aluminum
02. How is launching carried out in the case of low-grade copper ores?
03. Why is zinc not extracted from zinc oxide through reduction using CO?
04. Out of "C" and CO which is a better reducing agent for ZnO.
05. What is the role of the graphite rod in the electrometallurgy of aluminum?
06. How can you separate aluminum from silica in a bauxite ore associated with silica? Give equation if any.

Questions:-

01. State the role of carbon monoxide in the purification of nickel.

02. Describe the mond process for the refining of nickel.

03. Write the principles of the method used for the refining of germanium.

04. Out line the basic principle of

(a) Zone refining (b) vapor phase refining (c) electrolytic refining (d) Chromatographic method.

05. Name the method used for the refining of

(a) Tin (b) Mercury (c) Titanium (d) Copper

06. Name the method of refining which is based on the principle of adsorption.

07. What is meant by the term chromatography?

08. What criterion is followed for the selection of the statement phase in chromatography?

09. Indicate the principle behind the method used for the refining of zinc.

10. A mixture of X and Y was loaded in the column of silica. It was eluted by an alcohol-water mixture. Compound Y eluted in preference to compound X compare the extent of adsorption of X and Y on the column.