UNIT – 1 METALLURGY

Answer the following questions

1. What is the difference between minerals and ores?

Minerals	Ores
Naturally occuring substances obtained by mining which contain the metals in free state or in the form of compounds like oxides, sulphides etc. are called minerals.	Minerals that contain high percentage of metal from which it can be extracted conveniently and economically are called ores.
All minerals are not ores	All ores are minerals
Ex : Clay – Mineral of aluminium	**Ex :** Bauxite –Ore of aluminium

2. What are the various steps involved in extraction of pure metals from their ores?

i)Concentration of the ore.

ii) Extraction of the crude metal.

iii) Refining of the crude metal.

3. **What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3?**

The silica gangue present in the ore is acidic in nature, the limestone a basic flux combines with it to form calcium silicate (slag).

$CaO (s) + SiO_2 (s) \longrightarrow CaSiO_3 (s)$

Flux **Gangue** **slag**

4.Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.

Sulphide ores can be concentrated by froth floatation method.

E.x : Galena (PbS), Zinc blende (ZnS)

5. **Out of coke and CO, which is better reducing agent for the reduction of ZnO? why?**

- Above 1073 K , Gibb's free energy for formation of C_2 from C is less than that of Gibb's free energy for formation of ZnO .Therefore C can easily reduce ZnO to Zn
- On the other hand Gibb's free energy for formation of CO_2 from C is higher than that of Gibb's free energy of formation of ZnO . Therefore CO cannot reduce ZnO

6. Describe a method for refining nickel.

Impure nickel is heated in a stream of carbon monoxide at around **350K**. Nickel reacts with CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$Ni(s) + 4CO(g) \longrightarrow NiCO_4(g)$

On heating nickel tetra carbonyl around 460K, the complex decomposes to give pure nickel.

$Ni(CO)_4(g) \longrightarrow Ni(S) + 4CO(g)$

7. Explain zone refining process with an example

- The principle used in this process is fractional crystallisation.
- When an impure metal is melted and allowed to solidify, the impurities will prefer to remain in the molten region. i.e impurities are more soluble in the melt than in the solid state metal.
- In this process the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater, melting the metal on that portion of the rod.
- When the heater is slowly moved to the other end pure metal crystallises while impurities will move on to the adjacent molten zone formed due to the movement of the heater.
- As the heater moves further away, the molten zone containing impurities also moves along with it.
- This process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level.
- This process is carried out in an inert gas atmosphere to prevent the oxidation of metals.
- Germanium, Silicon and gallium which are used as semiconductor are refined by this process.

8. **A) Predict the conditions under which**

i) Aluminium might be expected to reduce magnesia.

ii) Magnesium could reduce alumina.

B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above

this temperature, the reverse is true - Explain.

c) It is possible to reduce Fe2O3 by coke at a temperature around 1200K

A) i) Ellingham diagram for the formation of $A_{l2}O_3$ and MgO intersects around 1600K. Above this temperature aluminium line lies below the magnesium line. Hence we can use aluminium to reduce magnesia above 1600K.

ii) In Ellingham diagram below 1600K magnesium line lies below aluminium line. Hence below 1600K magnesium can reduce alumina.

B) The two lines for C →CO2 and C →CO cross at about 983K. Below this temperature the reaction to form CO_2 is energetically more favourable hence CO is more effective reducing agent than carbon below 983K. But above 983K the formation of CO is preferred, hence carbon is more effective reducing agent than CO above this temperature.

C) In Ellingham diagram above 1000K carbon line lies below the iron line. Hence it is possible
to reduce Fe_2O_3 by coke at a temperature around 1200K.

9. Give the uses of zinc.

- Metallic zinc is used in **galvanisation** to protect iron and steel structures from rusting and corrosion.
- **Zinc is used to produce die - castings** in the automobile, electrical and hardware industries.
- **Zinc oxide** is used in the manufacture of paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment.
- **Zinc sulphide** is used in making luminous paints, fluorescent lights and x - ray screens.
- **Brass an alloy of zinc** which is highly resistant to corrosion is used in water valves and communication equipment.

10. Explain the electrometallurgy of aluminium.

Hall - Herold Process

Cathode : Iron tanked lined with carbon

Anode : Carbon blocks

Electrolyte : 20% solution of alumina obtained from bauxite + Molten Cryolite + 10% calcium chloride (lowers the melting point of the mixture)

Temperature: Above 1270K

Ionisation of Alumina : $Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$

Reaction at cathode : Al^{3+} (melt) + $3e^- \longrightarrow Al_{(l)}$

Reaction at anode : $2O^{2-}$ (melt) $\longrightarrow O_2 + 4e^-$

Since carbon acts as anode the following reaction also takes place on it.

$C(s) + O_2^-$ (melt) $\longrightarrow CO + 2e^-$

$C(s) + 2O_2^-$(melt) $\longrightarrow CO_2 + 4e^-$

During electrolysis anodes are slowly consumed due to the above two reactions. Pure aluminium is formed at the cathode and settles at the bottom.

Net electrolysis reaction is

$4Al^{3+}$ (melt) + $6O_2^-$ (melt) + $3C_{(s)} \longrightarrow 4Al_{(l)} + 3CO_{2(g)}$

11.Explain the following terms with suitable examples. i) Gangue ii) Slag

i) Gangue :

The non metallic impurities, rocky materials and siliceous matter present in the ores are called gangue.

E.x : SiO_2 is the gangue present in the iron ore Fe2O3.

ii) Slag :

Slag is a fusible chemical substance formed by the reaction of gangue with a flux.

$CaO (s) + SiO_2 (s) \longrightarrow CaSiO_3 (s)$

Flux **Gangue** **slag**

12.Give the basic requirement for vapour phase refining.

- The metal should f**orm a volatile compound** , when treated with a suitable reagent
- Then the volatile compound should **decomposed** to give the pure metal.

13. **Describe the role of the following in the process mentioned.**

i) Silica in the extraction of copper.

ii) Cryolite in the extraction of aluminium.

iii) Iodine in the refining of Zirconium.

iv) Sodium cyanide in froth floatation.

i) In the extraction of copper silica acts as an acidic flux to remove FeO as slag $FeSiO_3$.

$FeO(s) + SiO_2(s) \longrightarrow FeSiO_{3(s)}$

Flux **Slag**

ii) Cryolite serves as an added impurity and lowers the melting point of the electrolyte.

iii) First Iodine forms a Volatile tetraiodide with impure metal, which decomposes to give pure metal. Impure zirconium metal is heated in an evacuated vessel with iodine to form the volatile zirconium tetraiodide (ZrI_4). The impurities are left behind, as they do not react with iodine.

iv) Sodium cyanide acts as a depressing agent in froth floatation process. When a sulphide ore of a metal of interest contains other metal sulphides the depressing agent **sodium cyanide selectively prevent other metal sulphides from coming to the froth.**

14. Explain the principle of electrolytic refining with an example.

Crude metal is refined by electrolysis carried out in an electrolytic cell.

Cathode : Thin strips of pure metal.

Anode : Impure metal to be refined.

Electrolyte : Aqueous solution of the salt of the metal with dilute acid.

As current is passed, the metal of interest dissolves from the anode and pass into the electrolytic solution.

At the same time same amount of metal ions from the electrolytic solution will be deposited at the cathode.

Less electro positive impurities in the anode settle down as anode mud.

Electro refining of silver :

Cathode : Pure silver

Anode : Impure silver rods.

Electrolyte : Acidified aqueous solution of silver nitrate.

On passing current the following reactions will take place.

Reaction at anode : $2Ag (s) \rightarrow Ag^{+} (aq) + 1e^{-}$

Reaction at cathode $Ag^{+} (aq) + 1e^{-} \rightarrow 2Ag (s)$

During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode.

15. The selection of reducing agent depends on the thermodynamic factor: Explain with an example.

- A suitable reducing agent is selected based on the thermodynamic considerations.
- For a spontaneous reactionΔG should be negative.
- Thermodynamically, the reduction of metal oxide with a given reducing agent can occur if ΔG for the coupled reaction is negative.
- Hence the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.
- Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal.

For example

- Above 1623 K , Al has more negative ΔG^{o} value than Mg
- Hence Al is used to reduce magnesia
- Below 1623 K , Mg more negative ΔG^{o} value than Al
- Hence Mg is used to reduce Al

16. Give the limitations of Ellingham diagram.

- Ellingham diagram is constructed based only on thermodynamic considerations.
- It gives information about the thermodynamic feasibility of a reaction.
- It does not tell anything about the rate of the reaction.
- More over it does not give any idea about the possibility of other reactions that might be taking place.
- The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the product which is not always true.

17. Write a short note on electrochemical principles of metallurgy.

- Reduction of oxides of active metals such as sodium, potassium etc. by carbon is thermodynamically not feasible.
- Such metals are extracted from their ores by using electrochemical methods.
- In this method the metal salts are taken in fused form or in solution form.
- The metal ion present can be reduced by treating the solution with suitable reducing agent or by electrolysis.
- Gibbs free energy change for the electrolysis is

  $\mathbf{\Delta G^{0} = - nFE^{0}}$

  n = number of electrons involved in the reduction

F = Faraday = 96500 coulombs

E^0 = electrode potential of the redox couple.

- If E_0 is positive, ΔG^0 is negative and the reduction is spontaneous.
- Hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.
- A more reactive metal displaces a less reactive metal from its salt solution.

eg : $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

- Zinc is more reactive than copper and displaces copper from its salt solution.

Book inside

Two Mark Questions

1. What is concentration of ores?

The removal of non metallic impurities, rocky materials and siliceous matter (called as gangue) from the ores is known as concentration of ores.

2. What is leaching?

The process of dissolving metal present in an ore in a suitable solvent to form a soluble metal salt or complex leaving the gangue undissolved is called leaching.

3. What is ammonia leaching?

Crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure.

Ammonia selectively leaches these metals by forming their soluble complexes namely $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$ from the ore.

4. In the extraction of metal ore is first converted into metal oxide before reduction into metal. why?

- In the concentrated ore the metal exists in positive oxidation state and hence it is to be reduced to elemental state.
- From the principles of thermodynamics the reduction of oxide is easier compared to the reduction of other compounds of metal.
- Hence before reduction the ore is first converted into metal oxide.

5. How will you extract the metal by the process of reduction by carbon.

- In this method oxide ore of the metal is mixed with coal (coke) and heated strongly in a blast furnace.
- This method can be applied to metals which do not form carbides with carbon at the reduction temperature.

$ZnO_{(S)} + C \rightarrow Zn_{(S)} + CO_{(g)}\uparrow$

6. What is auto reduction of metallic ores?

Simple roasting of some of the metallic ores give the crude metal.

Use of reducing agent is not necessary.

E.x Cinnabar is roasted to give mercury.

$HgS_{(S)} + O_{2(g)} \rightarrow Hg_{(l)} + SO_2(g)\uparrow$

7. Write the applications or uses of copper.

Used for making coins and ornaments along with gold and other metals.
Copper and its alloys are used for making wires, water pipes and other electrical parts.

8. Write the applications or uses of gold.

- Used for coinage and has been used as standard for monetary systems in some countries.
- Extensively used in jewellery in its alloy form with copper.
- Used in electroplating to cover other metals with a thin layer of gold in watches, artificial limb joints, cheap jewellery, dental fillings and electrical connectors.
- Gold nanoparticles are used for increasing the efficiency of solar cells.
- Used as catalyst.

9.What do you meant by Refining process

- The metal extracted from its ore contains some impurities such as unreacted oxide ore, other metals, nonmetals etc...
- Removal of such impurities associated with the isolated crude metal is called refining process.

10.How will you refine the metal by distillation

- This method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K).
- In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

11. How will you refine the metal by liquation

- This method, is employed to remove the impurities with high melting points from metals having relatively low melting points such as tin (Sb; mp= 904 K), lead (Pb; mp=600 K), mercury (Hg; mp=234 K), and bismuth (Bi; mp=545 K).
- In this process, the crude metal is heated to form fusible liquid and allowed to flow on a sloping surface.
- The impure metal is placed on sloping hearth of a reverberatory furnace and it is heated just above the melting point of the metal in the absence of air, the molten pure metal flows down and the impurities are left behind.
- The molten metal is collected and solidified.

12.What do you meant by cementation?

Gold can be recovered by reacting the deoxygenated leached solution with zinc. In this process the gold is reduced to its elemental state (zero oxidation sate) and the process is called **cementation**.

Long answers

1. Explain froth floatation method.

- This is used to **concentrate sulphide ores** such as galena (PbS) Zinc blende (ZnS) etc.
- Metallic ore particles **preferentially wetted by oil** can be separated from gangue.
- **Crushed ore is mixed with water** and a frothing agent like pine oil or eucalyptus oil.
- A small amount of **sodium ethyl xanthate** is added as a **collector**.
- A froth is formed by blowing air through the mixture.
- The collector molecules attach to the ore particles and make them water repellent.

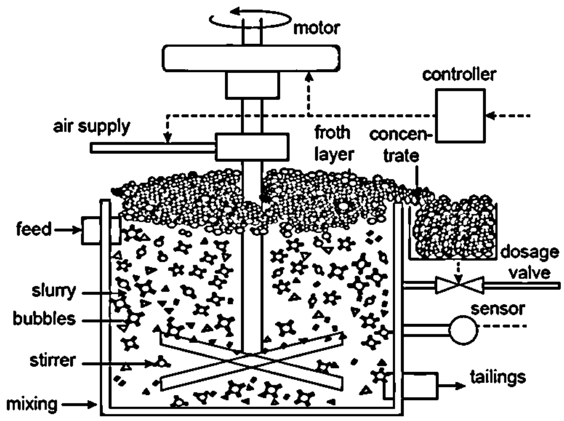

Figure 1.1 Froth Flotation

- As a **result ore particles wetted by the oil rise to the surface along with the froth.**
- The froth is skimmed off and dried to recover the concentrated ore.
- Gangue particles preferentially wetted by water settle at the bottom.
- If the sulphide ore contains other metal sulphides as impurities, they are selectively prevented from coming to the froth by using depressing agents like sodium cyanide, sodium carbonate etc.
- Sodium cyanide depresses the floatation property of the impurity ZnS present in galena
- (PbS) by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of ZnS.

2. Explain about concentration of ore by Gravity separation or Hydraulic wash

- In this method, **the ore having high specific gravity is** separated from the gangue that has low specific gravity by simply washing with running water.
- Ore is crushed to a **finely powdered form** and treated with rapidly flowing current of water. During this process the lighter gangue particles are washed away by the running water.
- This method is generally applied to concentrate the native ore such as gold and oxide ores such as **hematite (Fe_2O_3), tin stone (SnO_2**) etc.

3. Explain about Magnetic separation

- This method is applicable to **ferromagnetic ores** and it is based on the difference in the magnetic properties of the ore and the impurities.

- For example tin stone can be separated from the wolframite impurities which is magnetic. Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities.
- **The crushed ore is poured on to an electromagnetic separator** consisting of a belt moving over two rollers of which one is magnetic.

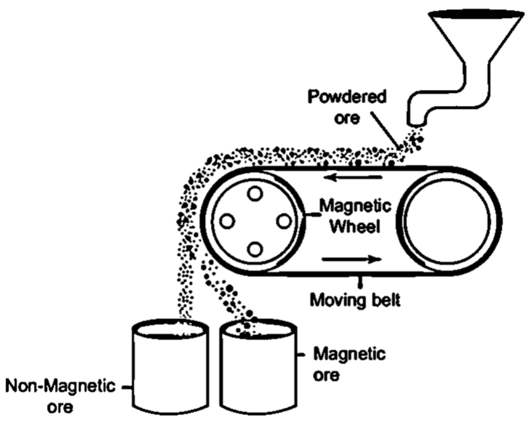

Figure 1.2 Magnetic separation

- The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it

4. Explain about Van-Arkel method for refining zirconium/titanium:

- This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals.
- Titanium and zirconium can be purified using this method. For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide.(TiI_4).
- The impurities are left behind, as they do not react with iodine

$$\mathbf{Ti\ (s) + 2I_2\ (s) \longrightarrow TiI_4\ (vapour)}$$

- The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K.
- The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.

$$\mathbf{Ti\ (s) + 2I_2\ (s) \longrightarrow TiI_4\ (vapour)}$$

5.What are Application of Al

- Aluminium is the most abundant metal and is a good conductor of electricity and heat. It also resists corrosion. The following are some of its applications.
- Many heat exchangers/sinks and our day to day cooking vessels are made of aluminium.
- It is used as wraps (aluminium foils) and is used in packing materials for food items,
- Aluminium is not very strong, However , its alloys with copper, manganese, magnesium and silicon are light weight and strong and they are used in design of aeroplanes and other forms of transport.
- As Aluminium shows high resistance to corrosion, it is used in the design of chemical reactors, medical equipments ,refrigeration units and gas pipelines.

- Aluminium is a good electrical conductor and cheap, hence used in electrical overhead electric cables with steel core for strength.

6.Explain about leaching

This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution. In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble.

Cyanide leaching

The crushed ore of gold is leached with aerated dilute solution of sodium cyanide. Gold is converted into a soluble cyanide complex. The gangue, aluminosilicate remains insoluble.

$$4Au (s) + 8CN^- (aq) + O_2 (g) + 2H_2O (l) \longrightarrow 4[Au(CN)_2]^- (aq) + 4OH^-(aq)$$

Ammonia leaching

When a crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure, ammonia selectively leaches these metals by forming their soluble complexes viz. $[Ni(NH_3)_6]^{2+}$, $[Cu(NH3)4]^{2+,}$ respectively from the ore leaving behind the gangue, iron(III) oxides/hydroxides and aluminosilicate.

Alkali leaching

In this method, the ore is treated with aqueous alkali to form a soluble complex. For example, bauxite, an important ore of aluminium is heated with a solution of sodium hydroxide or sodium carbonate in the temperature range 470 - 520 K at 35 atm to form soluble sodium meta-aluminate leaving behind the impurities, iron oxide and titanium oxide.

$$Al_2O_3 (s) + 2NaOH (aq) + 3H_2O (l) \longrightarrow 2Na[Al(OH)_4] (aq)$$

The hot solution is decanted, cooled, and diluted. This solution is neutralised by passing CO2 gas, to the form hydrated Al2O3 precipitate.

$$2Na[Al(OH)_4] (aq) + CO2 (g) \longrightarrow Al_2O_3.xH_2O (s) + 2NaHCO_3 (aq)$$

The precipitate is filtered off and heated around 1670 K to get pure alumina Al_2O_3.

Acid leaching

Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.

$$2ZnS (s) + 2H_2SO_4 (aq) + O2(g) \longrightarrow 2ZnSO_4 (aq) + 2S (s) + H_2O$$

In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur

7.How will you convert metal into metal oxide by roasting and calcination

Roasting

Roasting is the method, usually applied for the conversion of sulphide ores into their oxides.

In this method, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2 \uparrow$$

Roasting also removes impurities such as arsenic, sulphur, phosphorous by converting them into their volatile oxides.

Calcination

- Calcination is the process in which the concentrated ore is strongly heated in the absence of air.
- During this process, the water of crystallisation present in the hydrated oxide escapes as moisture.
- Any organic matter (if present) also get expelled leaving behind a porous ore.
- This method can also be carried out with a limited supply of air.
- During calcination of carbonate ore, carbon dioxide is expelled

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$$

8.Explain about Smelting

In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace. For example the oxide of iron can be reduced by carbon monoxide as follows.

$$Fe_2O_3\,(s) + 3CO\,(g) \longrightarrow 2Fe\,(s) + 3CO_2\,(g)$$

9.Explain about extraction of copper from copper pyrite

- Ore is concentrated by froth flotation process
- The concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed due to melting is basic in nature and it combines with silica to form ferrous silicate (slag).
- The remaining metal sulphides Cu2S and FeS are mutually soluble and form a copper matte.

$$2CuFeS_2\,(s) + O_2\,(g) \longrightarrow 2FeS\,(l) + 2Cu_2S\,(l) + 2SO_2\,(g)$$

$$FeS\,(l) + O\,(g) \longrightarrow FeO\,(l) + SO_2\,(g)$$

$$FeO\,(s) + SiO_2\,(s) \longrightarrow FeSiO_3\,(s)$$

Flux Gangue Slag

- The matte is separated from the slag and fed to the converting furnace. During conversion, the FeS present in the matte is first oxidised to FeO. This is removed by slag formation with silica. The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper as shown below.

Cu_2S (l,s) + $3O_2$ (g) $\longrightarrow$ $2Cu_2S$ (l,s) + $2SO_2$ (g)

$2Cu_2O$ (l) + Cu_2S (l) $\longrightarrow$ 6Cu (l) + SO_2 (g)

- The metallic copper is solidified and it has blistered appearance due to evolution of SO_2 gas formed in this process. This copper is called blistered copper.