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1. METALLURGY

1. What are the differences between minerals and ores?

Minerals	Ores
Naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds are called a Minerals.	Minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called ores.
Ex: Clay	Ex: Bauxite

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

(i) Concentration of the ore

(ii) Extraction of crude metal

(iii) Refining of crude metal

3. What are the steps in the extraction of the crude metal?

(i) Conversion of the ore into oxides of the metal

(ii) Reduction of the metal oxides to elemental metals.

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

- Limestone acts as a Flux in this process
- It combine with silica and get converted into Calcium silicate called as Slag

$$\underset{\text{Flux}}{CaO\ (s)} + \underset{\text{Gangue}}{SiO_2\ (s)} \longrightarrow \underset{\text{Slag}}{CaSiO_3\ (s)}$$

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

- Sulphide ores can be extracted by froth floatation method

Examples:

- ✓ Galena (PbS)
- ✓ Zinc blende (ZnS)

6. Out of coke and CO, which is better reducing agent for the reduction of ZnO? Why?

- Out of Coke and CO, coke is better reducing agent than CO for the reduction of ZnO
- Reduction by carbon can be applied to zinc which does not form carbides with carbon at the reduction temperature.

$$ZnO\ (s) + C\ (s) \longrightarrow Zn\ (s) + CO\ (g)\uparrow$$

- ZnO lies above CO in Ellingham diagram
- Hence, carbon can be used as a reducing agent for the reduction of ZnO

7. Describe a method for refining nickel.

- Nickel is refined by Mond's process in two steps

<u>Step – I : Formation of a volatile compound with the metal:</u>

$$\underset{\text{Impure metal}}{Ni} + 4\,CO \xrightarrow{350K} \underset{\text{Nickel Tetra carbonyl}}{Ni(CO)_4}$$

<u>Step – II : Volatile compound decomposed to give pure metal:</u>

$$Ni(CO)_4 \xrightarrow{460K} \underset{\text{pure metal}}{Ni} + 4\,CO$$

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8. Explain zone refining process with an example.

- This method is based on the principles of fractional crystallisation.
- When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten region.
- 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 which results in melting of the metal on that portion of the rod.
- When the heater is slowly moved to the other end the pure metal crystallises while the 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.
- The 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 .

Example:

- Elements such as germanium (Ge), silicon (Si) and galium (Ga) that are used as semiconductor are refined using this process.

9. Using Ellingham diagram,
(A) Predict the conditions under which
(i) Aluminium might be expected to reduce magnesia.
(ii) Magnesium could reduce alumina.
(B) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K

(A) (i) Aluminium might be expected to reduce magnesia:

- Ellingham diagram for the formation of Al_2O_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) Magnesium could reduce alumina:

- In Ellingham diagram below 1600K magnesium line lies below aluminium line
- Hence, below 1600K magnesium can reduce alumina.

(B) Reduce Fe_2O_3 by coke at a temperature around 1200K:

- 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

10. Give the uses of zinc.

- zinc is used in **galvanising** metals to protect them from rusting and corrosion.
- Zinc is also used in electrical and hardware industries.
- Zinc oxide is used to prepare paints, rubbers and ink.

11. Explain the electrometallurgy of aluminium.

- Aluminium is extracted by Hall-Herold process.
- Cathode : Iron tank coated with Carbon
- Anode : Carbon rod
- Electrolytes : A 20% solution of alumina mixed with molten cyrolite
- Temperature :1270K($CaCl_2$ helps to lower the melting point of mixture)

Ionisaiton of alumina	$Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$
Reaction at cathode	$2Al^{3+}$ (melt) $+ 6e^- \longrightarrow 2Al$ (l)
Reaction at anode	$6O^{2-}$ (melt) $\longrightarrow 3O_2 + 12e^-$

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

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$$C(s) + O^{2-}(melt) \longrightarrow CO + 2e^-$$
$$C(s) + 2O^{2-}(melt) \longrightarrow CO_2 + 4e^-$$

- Due to the above two reactions, anodes are slowly consumed during the electrolysis.
- The pure aluminium is formed at the cathode and settles at the bottom.
- The net electrolysis reaction can be written as follows.

$$4Al^{3+}(melt) + 6O^{2-}(melt) + 3C(s) \longrightarrow 4Al(l) + 3CO_2(g)$$

12. Explain the following terms with suitable examples.
(i) Gangue **(ii) slag**

(i) Gangue:
- Non metallic impurity, Silicon impurity and rock present in the ore is called as Gangue.

$$FeO(s) + \underset{\text{Gangue}}{SiO_2(s)} \longrightarrow FeSiO_3(s)$$

(ii) slag:
- Slag is a fusible chemical substance formed by the reaction of gangue with flux

$$\underset{\text{Flux}}{FeO(s)} + \underset{\text{Gangue}}{SiO_2(s)} \longrightarrow \underset{\text{Slag}}{FeSiO_3(s)}$$

13. Define Concentration.
- The process of removal of the gangue from the impure ore is called as concentration.

14. Give the basic requirement for vapour phase refining.
(i) Reagent which can form a volatile compound with the metal.
(ii) The volatile compound is decomposed to give the pure metal.

15. 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) Silica in the extraction of copper:
- In the extraction of copper silica acts as an acidic flux to remove FeO as slag $FeSiO_3$

$$\underset{\text{Flux}}{FeO(s)} + \underset{\text{Gangue}}{SiO_2(s)} \longrightarrow \underset{\text{Slag}}{FeSiO_3(s)}$$

(ii) Cryolite in the extraction of aluminium:
- As Al_2O_3 is a poor conductor cryolite improves electrical conductivity.
- In addition, cryolite lowers the melting point of the electrolyte.

(iii) Iodine in the refining of Zirconium:
- 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 zirconium tetraiodide (ZrI_4)
- The impurities left behind as they do not react with iodine.

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(iv) Sodium cyanide in froth floatation:

- Sodium Cyanide acts as a depressing agent which prevents other metal sulphides from coming to the froth.

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

- Let us understand this process by considering electrolytic refining of silver as an example.
  - ✓ Cathode : Pure silver
  - ✓ Anode : Impure silver rods
  - ✓ Electrolyte : Acidified aqueous solution of silver nitrate.
- When a current is passed through the electrodes the following reactions will take place

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

- 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.

17. 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 reaction, the change in free energy (ΔG) should be negative.
- Therefore, thermodynamically, the reduction of metal oxide with a given reducing agent can occur if the free energy change 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.
- Hence the reducing agent is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal.

Example:

- From the Ellingham diagram at 1500K

$$2Fe_{(s)} + O_{2(g)} \rightarrow 2FeO_{(g)} \quad \Delta G_1 = -350\ KJmol^{-1} \ ....1$$
$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \quad \Delta G_2 = -480\ KJmol^{-1} \ ....2$$

- Reverse the reaction (1)

$$2FeO_{(s)} \rightarrow 2Fe_{(s)} + O_{2(g)} \quad -\Delta G_1 = 350\ KJmol^{-1} \ ....3$$

- Couple the reactions (2) and (3)

$$2FeO_{(s)} + 2C_{(s)} \rightarrow 2Fe_{(s)} + 2CO_{(g)} \quad \Delta G_3 = -130\ KJmol^{-1} \ ....4$$

- The standard free energy change for the reduction of one mole FeO is

$$\frac{\Delta G_3}{2} = -65\ KJmol^{-1}$$

18. What are the observations of Ellingham diagram?

- The formation metal oxides gives a positive slope. The value of ΔS value is negative and the randomness decreases.
- The formation of Carbon monoxide gives a negative slope. The ΔS value of value is positive. So Carbon monoxide is more stable at high temperature
- For MgO, due to phase transition, there is a sudden change in the slope at a particular temperature.

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19. What are the applications of Ellingham diagram?

- The Ellingham diagram for the formation of Ag_2O and HgO is at the upper part of the diagram. So, these oxides are unstable and decompose on heating.
- Ellingham diagram is used to predict the thermodynamic feasibility of reduction of metal oxides by another metal.

Example:

- ✓ Aluminium can be reduce Chromic oxide.
- Carbon line cuts the line of many metal oxides. Hence it can reduce all metal oxides a high temperature.

20. Give the limitations of Ellingham diagram.

- It does not explains the rate of the reaction
- It does not explain the possibility of other reactions taking place.
- When the reactants and the products are in equilibrium, the value of ΔG is not true value.

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

- The 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 technique, the metal salts are taken in a fused form or in solution form.
- The metal ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.
- Gibbs free energy change for the electrolysis process is given by the following expression

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

- Where,
  - ✓ n = number of electrons involved in the reduction process,
  - ✓ F is the Faraday
  - ✓ E^0 is the electrode potential of the redox couple.
- If E^0 is positive then the ΔG is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.
- When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution.

Example:

$$Cu(s) + 2Ag^+(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

22. Explain the refining method of Titanium.

- Titanium can be purified by Van-Arkel Method

Step – I:

- 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.(TiI4).
- The impurities are left behind, as they do not react with iodine

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

Step – II :

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

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

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23. Explain the Gravity separation or Hydraulic wash process

- The ore is finely powdered and washed with a current of water.
- The lighter gangue particles are washed away by water.

Example:

- ✓ This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe_2O_3), tin stone (SnO_2)

24. Define Roasting.

- The Ore is oxidised by heated in the presence of Oxygen in a furnace below the melting point of the metal.
- This method is usually applied for the conversion of sulphide ores into their oxides.

Example:

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

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2\uparrow$$

25. Define Calcination

- The ore is heated in the absence of oxygen in a furnace.
- The water molecules are removed as moisture.
- This method can also be carried out with a limited supply of air.

Example:

- During calcination of carbonate ore, carbon dioxide is expelled

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

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

26. Define Smelting

- The ore is heating above the melting point in the presence of Flux and reducing agents like Carbon in a smelting furnace.
- The water molecules are removed as moisture.

Example:

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

$$FeO\,(s) + \underset{\text{Gangue}}{SiO_2\,(s)} \longrightarrow FeSiO_3\,(s)$$

27. Explain the Froth Floatation process

- Frothing agent : Pine oil
- Collector : Sodium Ethyl Xanthate
- Depressing agent : Sodium cyanide

Example :

- ✓ Sulphide ore (Galena)

- The ore is finely powdered and mixed with water and pine oil.
- When air is passed, it produces froth.
- The ore particles rise to the surface and collected separately.
- The Impurities settles at the bottom of the container.

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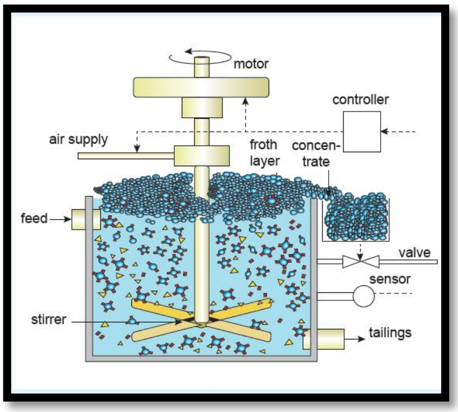
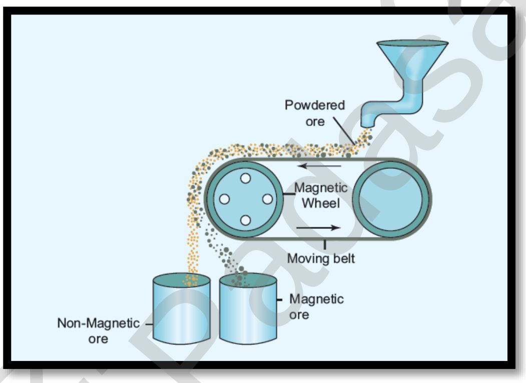


28. Explain the magnetic separation method.

- 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.
- 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.



29. What is Leaching?

- 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.
- The gangue remains insoluble.

30. Explain cyanide leaching (or) Explain the extraction of gold by 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.

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

31. What is 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**.

$$Zn\ (s) + 2[Au(CN)_2]^-\ (aq) \longrightarrow [Zn(CN)_4]_2^-\ (aq) + 2Au\ (s)$$

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32. What is called Blister Copper?

- 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.

33. Write a note on alumino thermic process.

- Metallic oxides such as Cr_2O_3 can be reduced by an alumino thermic process.
- In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible.

Aluminothermic process

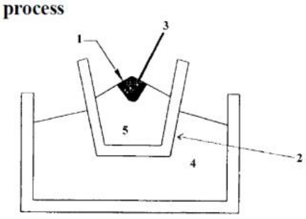

Fig. 4.1 Aluminothermic process

1. BaO_2 + Mg Powder 2. Fireclay crucible 3. Magnesium ribbon, 4. Sand 5. Cr_2O_3 + Al

- To initiate the reduction process, an ignition mixture (usually magnesium and barium peroxide) is used.

$$BaO_2 + Mg \longrightarrow BaO + MgO$$

- During the above reaction a large amount of heat is evolved (temperature up to 2400°C, is generated and the reaction enthalpy is : 852 kJ mol^{-1}) which facilitates the reduction of Cr_2O_3 by aluminium power.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$$

34. Write a note on auto reduction.

- Simple roasting of some of the ores give the crude metal.
- In such cases, the use of reducing agents is not necessary.

Example:

- ✓ Mercury is obtained by roasting of its ore cinnabar (HgS)

$$HgS\,(s) + O_2\,(g) \longrightarrow Hg\,(l) + SO_2\uparrow$$

35. What is ment by reduction by carbon? Give example.

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

Example:

$$ZnO\,(s) + C\,(s) \longrightarrow Zn\,(s) + CO\,(g)\uparrow$$

36. Explain the extraction of copper.

- Important Ore : copper pyrite ($CuFeS_2$)
- Concentration : froth-floatation process
- Roasting :
  - ✓ The concentrated ore is heated strongly in the reverberatory furnace, in excess of air. During roasting,

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

- Smelting:
  - ✓ The roasted ore is mixed with powdered coke and sand and is heated in a blast furnace.
  - ✓ It is made of steel plates lined inside with fire clay bricks. Hot air at 800°C is introduced from the tuyers near the base of the furnace. As a result, the following changes occur.

    $$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
    $$FeO + SiO_2 \rightarrow FeSiO_3 \text{ (fusible slag)}$$
  - ✓ Some of the cuprous sulphide undergoes oxidation to form cuprous oxide which then reacts with more cuprous sulphide to give copper metal.

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

37. List out the uses of Aluminium.
- Aluminium foil is used for packing food items
- Aluminium is used to make cooking vessels
- Aluminium alloy is used to make Aero planes
- Aluminium is used to make gas pipes
- Aluminium is used to make electric cables

38. Write the uses of Iron.
- It is used to make Bridges and cycle chain
- It is used to make pipes and valves
- The alloys of iron is used to make Magnets

39. Give the uses of Copper.
- It is used to make coins
- It used to make wires and water pipes
- Copper and gold are used to make ornaments

40. List the uses of Gold.
- It is used to make coins
- Copper and gold are used to make ornaments
- It is used as catalyst
- It is used in electro plating of watches.

Prepared by,

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Class : 12th

Subject : Chemistry

Unit : 1. Metallurgy

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