GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

BASIC CONCEPTS

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Minerals -Naturally occurring compounds of an element obtainable from the earth by mining.

Ores -Minerals from which the element can be isolated economically.

‘All ores are minerals, but all minerals are not ores’

Metallurgy - The process used for the isolation of metal from its ore.

Metallurgy involve the following major steps-

I. Concentration or Enrichment of ore

II. Isolation of Metal from the concentrated ore

III. Purification of the metal.

I. Concentration of the Ore

- Removal of Earthy impurities (sand, clay, soil…)
- Earthy impurities are known as Gangue
- Also known as Dressing Or Benefaction
- The ores are graded and powdered to reasonable size prior to concentration by the following methods -

1. Hydraulic Washing

- Used when there is difference in gravities between ore and gangue.
  - Powdered ore is washed in an upward stream of running water.
  - The lighter gangue particles are washed away and heavier ores are left behind.

2. Magnetic Separation

- Used when either the ore or the gangue are capable of being attracted by the magnetic field

3. Froth Floatation Process

- Used for removing Gangue from Sulphide ores.

- Principle behind this process is the preferential wetting of ore particle with oil and gangue by water.
- A suspension of powdered ore is made with water.
- To this Collectors(oil, fatty acids etc) and froth stabilisers(cresols, aniline etc) are added
- Minerals will be wet by oil while gangue by water
- When the mixture is agitated froth will be formed which will carry the ore particle
- It is possible to separate two Sulphide ore by using Depressants

  Eg :-In ore containing ZnS and PbS , NaCN act as a Depressant & selectively

  prevents the ZnS from coming to the froth but allows PbS.

4. Leaching-A chemical method

- Used when the ore is soluble in some suitable solvent

  (i) eg.- Leaching of Alumina From Bauxite
- Bauxite usually contain SiO_2, Iron oxides, TiO_2 etc as impurities
- Powdered ore is digested with conc. NaOH at 473-523K and 35-36 bar pressure
- Al_2O_3 and SiO_2 are leached out as Sodium aluminate and Sodium silicate

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

- The impurities are left behind
- The aluminate is neutralised by passing CO_2 so that hydrated aluminium oxide is precipitated (seeded with fresh Hydrated Al_20_3)

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3\ (aq)$$

- The sodium silicates remains in the solution
- Hydrated alumina is filtered, dried and heated to give pure Al_2O_3

$$Al_2O_3.xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g)$$

(ii) eg. - Leaching of Silver and Gold

- Leached with a dilute solution of NaCN or KCN in presence of air
- The metal is obtained later by Displacement

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq) \quad (M = Ag \text{ or } Au)$$

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

II. Extraction of The Crude Metal

- The metals are extracted from its ore by Reduction
- Oxide ores are easier to be reduced therefore sulphide ores and carbonate ores are first converted into oxides
- Therefore the extraction process consist of two processes
  - Conversion to oxide
  - reduction

Conversion to Oxides

1. **Calcination** - Heating in a limited supply of air or oxygen.
   - Usually carbonate ores are subjected to this process
   - A volatile matter escapes leaving behind the Oxide

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + xH_2O(g)$$
$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$
$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s) + 2CO_2(g)$$

2. **Roasting** - Heating in plenty of Air or oxygen at a temperature below the melting point.

   Usually sulphide ores are subjected to this process.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

Gangue-The impurities present in the ore.

Flux -The substance added to remove the Gangue

Slag-The easily fusible substance formed by the combination of Gangue & Flux.

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

III. Purification of the Metal

1. Distillation- This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

2. **Liquation** - A low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

3. Electrolytic Refining -

- The impure metal is made as anode.
- A strip of the same metal in pure form is used as cathode.
- A soluble salt of the same metal is used as electrolyte.
- The more basic metal remains in the solution and the less basic ones go to the anode mud.
- The reactions are:

Anode: $\mathbf{M \rightarrow Mn^{+} + ne^{-}}$

Cathode: $\mathbf{Mn^{+} + ne^{-} \rightarrow M}$

4. Zone Refining -

- Is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.
- A circular mobile heater is fixed at one end of a rod of the impure metal
- The molten zone moves along with the heater which is moved forward.

- As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone.
- The process is repeated several times and the heater is moved in the same direction.
- At one end, impurities get concentrated. This end is cut off.
- This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

5. Vapour Phase Refining - The metal is converted into its volatile compound and collected. It is then decomposed to give pure metal.

The two requirements are:

1. The metal should form a volatile compound with an available reagent,
2. The volatile compound should be easily decomposable, so that the recovery is easy.

Example. – (a). ***Monds Process for Refining Nickel***

- Nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.
- $Ni + 4CO \xrightarrow{330 - 350 K} Ni(CO)_4$
- It is decomposed at high temperature giving the pure metal.
- $Ni(CO)_4 \xrightarrow{450 - 470 K} Ni + 4CO$

(b). ***Van Arkel Method for Refining Zirconium or Titanium***

- Useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.
- The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4$$

- The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2$$

6. Chromatographic Method – Based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

QUESTIONS FOR LOW ACHIEVERS

Q1. Why the reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction?

Ans. The entropy of metal is higher in its liquid state than its solid state. The value of entropy change in reduction process is more on positive side when the metal formed is in liquid state . Thus the value of change in Gibbs energy becomes more on negative side and the reduction becomes easier.

Q2. Copper can be extracted by hydrometallurgy, but not zinc. Explain.

Ans. Copper is less reactive than Hydrogen and occupies a lower position in the electrochemical series, while Zn is more reactive and has a large negative reduction potential. Hence Zn cannot be extracted by hydrometallurgy, but Cu can be.

Q3. What is the role of depressant in froth floation process?

Ans. Depressants prevent certain ores from forming froth, in a mixture of ores .E.g., NaCN acts as a depressant for ZnS but not for PbS. Hence when an ore containing PbS and ZnS is subjected to froth floation process, only PbS forms the froth. This way PbS can be separated from ZnS.

Q4. Why is the extraction of Copper from pyrite difficult than that from its oxide ore through reduction?

Ans. Copper pyrites contain FeS which must be oxidized to FeO and then removed as $FeSiO_3$ (slag)

Q5. (i)Out of C and CO, which is a better reducing agent at 673 K?

Ans. At 673 K, CO is a better reducing agent.

(ii) How is copper extracted from a low grade ore of it?

Ans. It is extracted by hydrometallurgy. It is carried out in two steps-

- Leaching- low grade copper ores and scrapes are leached by using acid or bacteria.
- Reduction- The solution containing copper ions is treated with H_2

$$Cu^{2+} (aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

Q6. Name the common elements present in the anode mud during the electro refining of copper. Why are they so present?

Ans. The elements Au, Ag, Pt, Sb, Te, Se, are present in the anode mud, as these are less electropositive and do not undergo oxidation at anode. Hence they settle down as anode mud.

Q7. What criterion is followed for the selection of the stationary phase in chromatography?

Ans. In chromatography method , adsorbent acts as the stationary phase. It should have high adsorption power and greater surface area for adsorption. It should not react chemically with the sample component.

Q8. Describe a method for refining Nickel.

Ans. Mond's process - Ni is heated with CO to form a volatile complex

$$Ni + 4CO \rightarrow Ni(CO)_4$$

Now nickel tetra carbonyl is heated at high temperature so that it decomposes into pure metal

$$Ni(CO)_4 \rightarrow Ni + 4\,CO.$$

Q9. Is cast iron different from pig iron?

Ans. Cast iron contains 3% carbon, while pig iron contains about 4% carbon. Pig iron is converted into cast iron by heating molten pig iron with scrap iron and coke in specially designed furnace.

Q10. What is the role of cryolite in the metallurgy of Aluminium?

Ans. Cryolite reduces the melting point of the mixture, acts as a solvent and increases the conductivity of the ions in the electrolytic cell.

Q11. What is the role of collectors in Froth Floatation process?

Ans. Collectors like pine oil, fatty acids, xanthates enhance on wettability of mineral particles.

Q12. Copper matte is charged into a silica lined converter in extraction of copper. What is the role of silica lining here?

Ans. Silica acts as a flux.

Q13. What is meant by the term 'pyrometllurgy'?

Ans. The process of reducing a metal oxide with coke or with any other reducing agent at high temperature is called pyrometallurgy.

Q14. Write the reactions involved in the following process:

Refining of Zirconium by Van Arkel method.

Ans. (i) Van- Arkel Method: It is used to get ultra pure metals. Zr is purified by this process.

Zr is heated in iodine vapours at about 870k to form volatileZrI_4 which is heated over tungsten filament at 2075K to give pure Zr.

$$Zr(s) + 2I_2 \xrightarrow[870k]{heat} ZrI_4(s)$$

$$\text{Impure } ZrI_4\ (s) \xrightarrow{2075K} Zr(pure) + 2I_2$$

Q15. Describe the role of

(i) NaCN in the extraction of gold from gold ore

(ii) SiO2 in the extraction of copper from copper matte.

(iii) Iodine in the refining of zirconium

Write chemical equations for the involved reactions.

A. (i) Extraction of gold:

NaCN forms a complex with gold ore which can be easily reduced

$$4Au(s) + 8NaCN\ (aq) + 2H_2O\ (l) + O_2(g) \longrightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$

Or

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

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

In this reaction, zinc acts as reducing agent.

(ii) SiO_2 acts as flux, reacts with gangue FeO to remove it in form of slag (iron silicate)

$$FeO + SiO_2 \longrightarrow FeSiO_3(slag)$$

(iii) Iodine reacts with impure Zr to form a volatile compound ZrI_4 which on heating decomposes to give pure zirconium

$$Zr + 2I_2 \xrightarrow[870K-2070K]{heat} ZrI_4 \xrightarrow{heat} Zr(pure) + 2I_2$$

16 . Describe the role of the following:

(i) NaCN in the extraction of silver from a silver ore.

(ii) Iodine in the refining of titanium.

Ans (i) dil. NaCN forms a complex with Ag_2S which on reduction with zinc gives silver metal. Impurities remain unaffected and can be filtered off.

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

$$2Na[Ag(CN)2] + Zn \longrightarrow Na_2[ZnCN)_4] + 2Ag$$

(ii) Iodine reacts with Titanium to form titanium iodide which on heating strongly gives pure titanium and iodine back.

$$Ti\ (pure) + 2I_2 \longrightarrow TiI_4$$

$$TiI_4 \xrightarrow{heat} Ti\ (pure) + 2I_2$$

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