General Principles and Processes of Isolation of Elements

Chapter 6

1 OCCURRENCE OF METALS

- The most abundant metal in the earth's crust is aluminium.
- Gem 'ruby' (impure Al_2O_3) has Cr impurity
- Gem 'sapphire' (impure Al_2O_3) has Co impurity
- The second most abundant metal on earth crust is iron.
- **Minerals:** These are naturally occuring chemical substances containing metal in the earth's crust and are obtain through mining.
- **Ores:** Minerals which are viable to be used as source of the metal are called ores.
- **Gangue:** The undesired impurities such as sand, clay associated with the ore are called gangue or matrix.
- Principal ores of some important metals:

Metal	Ore	Composition
Aluminium	Bauxite	$AlOx(OH)_{3-2x}$ where, $0 < x < 1$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
Copper	Copper pyrite	$CuFeS_2$
	Malachite	$CuCO_3 . Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

2 METALLURGY

The entire scientific and technological process used for isolation of the metal from its ore is known as metallurgy. It involves following main operations

(i) Concentration or dressing of ore
(ii) Isolation of crude metal
(iii) Purification or refining of metal

3 CONCENTRATION OF ORES

The removal of impurities from the ores is known as concentration or dressing or benefaction of ore. The concentration is done in number of ways depending upon the nature of impurities.

(i) **Hydraulic Washing:** The process of removing of lighter particles of sand, clay etc. by washing with water using hydraulic classifer. Separation is based on difference between specific gravity of the ore and gangue particles. It is type of a gravity separation.

(ii) **Magnetic Separation:** This is used when either the ore or the gangue is attracted towards magnetic field. Wolframite ($FeWO_4$), a magnetic ore is separated from non-magnetic ore, cassiterite (SnO_2) by this method.

(iii) **Froth Floatation Method:** This method is used for the concentration of sulphides ore. This process is based on the preferential wetting of ore particles by pine oil and gangue particles by water.

- Pine oil, fatty acids and xanthates are used as collectors.
- Cresols, aniline are used as froth stabilizer.
- In case of ore containing ZnS and PbS, the depressant NaCN is used which prevents ZnS from coming to the froth.

(iv) **Leaching:** It involves the treatment of the ore with a suitable reagent to make it soluble while impurities remain insoluble. The ore or the metal is recovered from the solution by a suitable chemical method. examples

- **Leaching of Alumina from bauxite:** Bauxite is digested with aqueous solution of NaOH, where Al_2O_3 dissolves forming sodium aluminate while impurities such as Fe_2O_3 and TiO_2 remain insoluble

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

The pure alumina is recovered from filtrate.

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

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

- Ores of Ag and Au are treated with aqueous dilution solution of NaCN in presence of oxygen. The Ag and Au particles get dissolved forming complex cyanides. Ag or Au recovered from solution by adding Zn.

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

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

4 EXTRACTION OF CRUDE METAL FROM CONCENTRATED ORE

Extraction involves following two steps

(i) Conversion of ore into metallic oxide
(ii) Reduction of metallic oxide

(i) Two methods ore used for conversion into oxide

(a) Calcination: It involves heating of ore below its fusion temperature in the absence of air

$$Fe_2O_3 \cdot xH_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + xH_2O(g)$$

$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

(b) Roasting: It involves heating of ore below its fusion temperature in regular supply of air.

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

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

- The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, silica is added before heating. Iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte which contains Cu_2S and FeS

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

(ii) Reduction of the oxide ore into free metal is done by a suitable reducing agent.

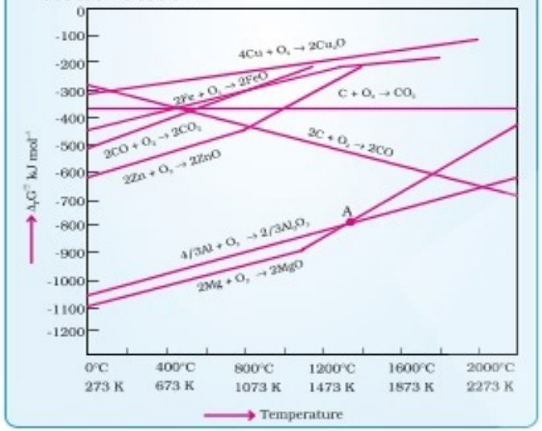
- **Smelting:** When C or CO or other metal are used as reducing agent at high temperature. The process in general known as pyrometallurgy

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

(5) THERMODYNAMIC PRINCIPLES OF METALLURY

- For considering the choice of reducing agent in reduction of oxide, Elligham Diagram is used.
- Ellingham diagram consists of plots of $\Delta_f G^\circ$ vs T for the formation of oxides of metals and reducing agents.

  eg: $2x\,M(s) + O_2(g) \rightarrow 2M_xO(s)$
- The difference in the two $\Delta_f G^\circ$ values determines whether reduction of the oxide of the element of the upper line is feasible by the element of which oxide formation is represented by the lower line. If the difference is large, the reduction is easier.



(6) EXTRACTION OF IRON FROM ITS OXIDE

Reduction of oxides of iron (Fe_2O_3, Fe_3O_4) is done in blast furnace.

- Iron obtained from blast furnace contains 4% carbon, known as pig iron.
- Cast iron is obtained by melting pig iron with scrap iron and coke using hot air blast. It contains about 3% carbon.
- Wrought iron is the purest form of commercial iron and prepared in a reverberatory furnace lined with haematite.

(7) EXTRACTION OF COPPER FROM CUPROUS OXIDE

- The sulphide ores containing iron are roasted/smelted to give oxide

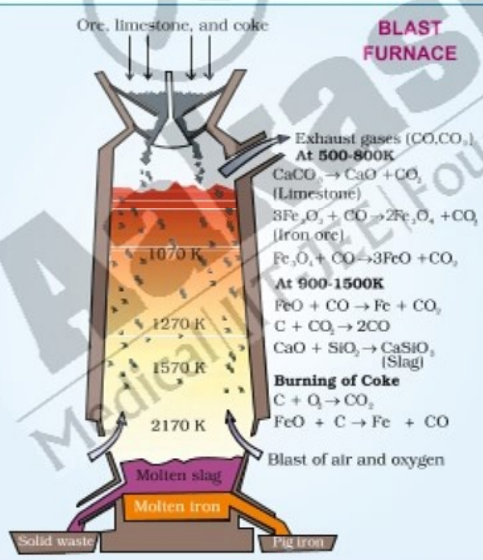
  $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
- The oxide is reduced to copper using coke

  $Cu_2O + C \rightarrow 2Cu + CO$
- The ore is heated in a reverberatory furnace after mixing with silica, where iron oxide "slags of" as iron silicate

  $FeO + SiO_2 \rightarrow FeSiO_3$(slag)
- Copper is produced as copper matte containing Cu_2S and FeS, which is then charged into silica lined convertor in presence of hot air blast.

$$FeS \xrightarrow[-SO_2]{O_2} FeO \xrightarrow{SiO_2} FeSiO_3$$

$$Cu_2S \xrightarrow[-SO_2]{O_2} Cu_2O \xrightarrow[-SO_2]{Cu_2O} Cu\text{(blister copper)}$$



(8) HALL-HEROULT PROCESS

Purified Al_2O_3 is mixed with Na_3AlF_6 (Cryolite) and CaF_2 (fluorspar) to lower the melting point of the mixture and to increase conductivity

$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

- Steel vessel with lining of carbon acts as cathode and graphite is acts as anode.

(9) REFINING

The process of purifying impure metals is called refining.

(i) **Distillation:** It is used for those metals which are volatile. The impure metal is heated and the vapours are separately condensed in receiver. It is used for purification of Zn, Hg etc.

(ii) **Liquation:** When impurities are less fusible than the metal itself then this process is used. The impure metal such as Sn is purified by liquation.

(iii) **Electrolytic refining:** Metal like Cu are purified by this method. The impure metal is made the anode and a strip of a pure metal is made as cathode while the electrolytic solution consists of solution of a suitable salt of metal.

(iv) **Zone refining:** It is based on the concept that impurities are more soluble in melt than in the solid state of the metal. This method is useful for Ge, Si, B for obtaining highly pure metals.

(vi) **Vapour phase refining:**

(a) Mond process: $Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4(\uparrow)$

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

(b) Van Arkel method: (for Zr/Ti)

$$Zr + 2I_2 \rightarrow \underset{\text{(volatile)}}{ZrI_4} \xrightarrow{1800\ K} Zr + 2I_2$$

(vii) **Chromatographic Methods:** Column chromatography is used for purification of elements which are available in minute quantities and impurities are not very different in the chemical properties from the element to be purified.

(10) USES OF METALS

- Zn is used for galvanising iron.
- Zn in Alloys (Brass : Cu + Zn, german silver: Cu + Zn + Ni).
- Al is used in extraction of Cr and Mn from their oxides.
- Cu is used for making wires used in electrical industry
- Wrought iron is used making anchors, wires, bolts.
- Chrome steel is used for cutting tools.

Sharpen Your Understanding

1. Leaching is a process of [NCERT Pg. 154]
(1) Oxidation (2) Reduction
(3) Refining (4) Concentration

2. Which of the following reaction represents calcination process? [NCERT Pg. 155]
(1) $CaCO_3 \rightarrow CaO + CO_2$
(2) $Cu_2S + 2CuO \rightarrow 4Cu + SO_2$
(3) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
(4) $FeO + SiO_2 \rightarrow FeSiO_3$

3. For which reaction ΔG° Vs temperature plot in the Ellingham diagram has negative slope [NCERT Pg. 157]
(1) $CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)$
(2) $C(s)+\frac{1}{2}O_2(g) \rightarrow CO(g)$
(3) $Mg(s)+\frac{1}{2}O_2(g) \rightarrow MgO(s)$
(4) $2Ag(s)+\frac{1}{2}O_2(g) \rightarrow Ag_2O(s)$

4. Among the following which ore is concentrated by froth floatation process? [NCERT Pg. 154]
(1) Cassiterite (2) Bauxite
(3) Zincite (4) Cinnabar

NCERT Based MCQs

5. Cyanide process of leaching is used for which of the following metals? [NCERT Pg. 155]
(1) Al (2) Cu
(3) Ag (4) Na

6. Malachite is an ore of [NCERT Pg. 152]
(1) Fe (2) Zn
(3) Cu (4) Al

7. Extraction of aluminium is usually carried out from its bauxite ore by leaching it with [NCERT Pg. 154]
(1) NaCl (2) NaCN
(3) Na_2SO_4 (4) NaOH

8. The percentage of Zn in german silver is about [NCERT Pg. 166]
(1) 25 - 30% (2) 40 – 50%
(3) 15 – 25% (4) 60 – 80%

9. Which of the following is not used as collectors in froth floatation method? [NCERT Pg. 154]
(1) Pine oils
(2) Aniline
(3) Fatty acids
(4) Xanthates

10. The impurities present in the mineral is called [NCERT Pg. 153]
(1) Alloy (2) Flux
(3) Slag (4) Gangue

11. Gem 'ruby' contains the impurity of [NCERT Pg. 152]
(1) Co (2) Ni
(3) Cr (4) Fe

12. In case of an ore containing ZnS and PbS, the depressant used is [NCERT Pg. 154]
(1) KOH (2) $MgCl_2$
(3) NaCN (4) CsCN

13. Mond process is used for the refining of [NCERT Pg. 165]
(1) Zirconium
(2) Titanium
(3) Cobalt
(4) Nickel

14. The function of flux during the smelting of the ore is [NCERT Pg. 156]
(1) To remove impurities
(2) To make ore porous
(3) To reduce the melting point of ore
(4) To make the reduction of ore easy

15. In the equation, $4M + 8CN^- + 2H_2O + O_2 \rightarrow 4[M(CN)_2]^- + 4OH^-$, the metal M is [NCERT Pg. 155]

(1) Cu (2) Zn

(3) Fe (4) Au

16. Select the correct statement(s) among a, b, c and d for roasting process [NCERT Pg. 155,156]

a. Sulphide ores converted into oxide ores

b. Ore is heated in a regular supply of air

c. Removes sulphur impurity as volatile oxides

d. Solid ore converts into molten ore

(1) a, b and d only (2) a, b and c only

(3) b, c and d only (4) a, b, c and d

17. At which temperature carbon monoxide is used as reducing agent to reduce iron oxide in blast furnace? [NCERT Pg. 157]

(1) 1500 K (2) 300 K

(3) 1073 K (4) 2170 K

18. The correct statement(s) regarding Hall-Heroult process is/are [NCERT Pg. 163]

(1) Fluorspar is added to decrease the melting points of Alumina

(2) Cryolite is added to increase the conductivity of non-conducting molten mass

(3) The surface of molten electrolyte is covered with coke to prevent the oxidation of Al so formed

(4) All of these

19. The impure copper obtained in the Bessemer process is called [NCERT Pg. 162]

(1) Blister copper

(2) Copper pyrites

(3) Copper spelter

(4) Glitter copper

20. The process used for refining of low boiling metals is [NCERT Pg. 164]

(1) Zone refining

(2) Distillation process

(3) Electrolytic refining

(4) Liquation process

Thinking in Context

1. _____ is the third most abundant element in earth's crust. (By weight) [NCERT Pg. 152]

2. Removal of unwanted materials from the ore is known as concentration, dressing or _____ of ore. [NCERT Pg. 153]

3. Hydraulic washing method is based on the difference between _____ of the ore and the gangue particles [NCERT Pg. 153]

4. Froth floatation method is used for removing gangue from _____ ores. [NCERT Pg. 154]

5. Bauxite is a principle ore of _____. [NCERT Pg. 154]

6. In the metallurgy of gold, the gold is leached with a dilute solution of NaCN in the presence of _____. [NCERT Pg. 155]

7. Usually sulphides ores, converted into _____ ores before reduction. [NCERT Pg. 155]

8. Copper matte contains Cu_2S and _____. [NCERT Pg. 156]

9. _____ diagram helps us in predicting the feasibility of thermal reduction of ore. [NCERT Pg. 157]

10. At 500 – 800 K in blast furnace, Fe_2O_3 is first reduced to _____ and then _____. [NCERT Pg. 160]

11. The iron obtained from blast furnace contains about _____ % carbon. [NCERT Pg. 161]

12. The reduction of Zinc oxide is done by using _____. [NCERT Pg. 162]
13. Copper is extracted by _____ from low grade ores. [NCERT Pg. 163]
14. Zone refining method is based on the principle that the impurities are _____ soluble in the melt that in solid state of metal. [NCERT Pg. 165]
15. In Mond process for refining Nickel, the metal is heated in a stream of _____. [NCERT Pg. 165]
16. _____ is used for making wires used in electrical industry and for water and steam pipes. [NCERT Pg. 166]
17. In _____ method, a low melting metal like tin can be made to flow on a sloping surface. [NCERT Pg. 164]
18. In electrolytic refining method, the impure metal is made to act as _____. [NCERT Pg. 164]
19. _____ is the purest form of commercial iron. [NCERT Pg. 161]
20. Cresols act as _____ in froth floatation method. [NCERT Pg. 154]

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