B.Sc. I (Hons), Paper-IB (Inorgchem) Unit-2

Principles of Metallurgy

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CLASSMATE Page:

* **Occurrance of metals:** Metals occur in nature (Earth's crust) in following two states:

(1) **Free or Native state:** Those metals which are least reactive w.r.to O_2, H_2O etc. or noble occur in free state in the nature. e.g. Silver (Ag), Gold (Au), Platinum (Pt) etc.

(2) **Combined state:** Metals are generally found in combined state or in combination with other elements, since reactive in nature. Metals found in combined states or ores in different forms e.g. Oxides, Sulphides, Carbonates, Sulphates, phosphates, halides etc (Table-1).

Table-1

Metal	Form	Name	Formula or Composition
1. Magnesium (Mg)	Chloride	Carnalite	$KCl.MgCl_2.6H_2O$
	Carbonate	Magnesite	$MgCO_3$
		Dolomite	$MgCO_3.CaCO_3$
2. Aluminium (Al)	Oxide	Bauxite	$Al_2O_3.2H_2O$
		Alumina or Corundum	Al_2O_3
	Fluoride	Cryolite	Na_3AlF_3 or $3NaF.AlF_3$
3. Tin (Sn)	Oxide	Tinstone or Cassiterite	SnO_2
	Sulphide	Tin pyrites	SnS_2
4. Lead (Pb)	Sulphide	Galena	PbS
	Oxide	Red Lead	Pb_3O_4
5. Copper (Cu)	Sulphide	Chalcocite or Copper glance	Cu_2S
		Copper pyrites	$CuFeS_2$
	Carbonate	Malachite	$Cu(OH)_2.CuCO_3$
6. Zinc (Zn)	Carbonate	Calamine	$ZnCO_3$
	Sulphide	Zinc blende	ZnS

* **Metallurgical terms:** 1. **Minerals:** Those natural substances (impure) in which metals or their compounds occur in the earth are known as minerals. The mineral has a definite composition. It may be a single compound or a complex mixture & contains large amt. of impurities. e.g. clay ($Al_2O_3.2SiO_2.2H_2O$).

2. **Ores:** Those minerals from which the metals can be extracted/obtained conveniently and economically are known as ores. e.g. Bauxite ($Al_2O_3.2H_2O$).

All ores are minerals but all minerals need not be ores. For example, Both clay ($Al_2O_3.2SiO_2.2H_2O$) & Bauxite ($Al_2O_3.2H_2O$) are mineral of Al. But Bauxite is an ore of Al, but clay is not, since Al can be extracted conveniently & economically from Bauxite, but not from clay.

3. **Gangue or Matrix:** The undesired substances (impurities) such as soil, silicates etc. present in the ores are known as gangue or matrix. Gangue may be physical (e.g. soil, sand, stone etc.) or chemical (acidic, e.g. SiO_2 / basic, e.g. Fe_2O_3). e.g. Bauxite ore contains SiO_2, Fe_2O_3 as impurities. Here SiO_2, Fe_2O_3 are gangue.

4. **Flux:** A chemical substance which is added from outside in the ore during process of

smelting to remove gangue is known as flux. Flux may be two types: (i) Acidic flux: Acidic substance which removes basic impurities (gangue) from the ore. e.g., SiO_2 (silica)
(ii) Basic flux: Basic substance which removes acidic impurities (gangue) from the ore, e.g. CaO, MgO etc.

5. Slag: Light, fusible and waste material(s) obtained during process of smelting (metallurgy) is/are called slag. Thus, slag is combined form of gangue & flux, i.e. Slag = Gangue + Flux. For example, Haematite (Fe_2O_3) ore contains SiO_2 as impurities (gangue) which forms light & fusible mass $CaSiO_3$ with CaO (lime) or $CaCO_3$ (limestone) as flux. Here $CaSiO_3$ is a slag. It is neutral substance (salt).

$$SiO_2 + CaO \xrightarrow{\Delta} CaSiO_3$$

6. Calcination: Calcination is the process of heating an ore with/without air below its melting point to remove volatile impurities (e.g. S, As etc) / moisture from the ore giving metal oxide. This process is done for oxy ores, viz. hydrated oxide, carbonate etc, and in reverbetory furnace.
e.g., Calamine ($ZnCO_3$) ore is converted into zinc oxide (ZnO) by calcination.

$$\underset{\text{(Calamine ore)}}{ZnCO_3} \xrightarrow{\Delta} \underset{\text{(Zinc oxide)}}{ZnO} + CO_2\uparrow$$

7. Roasting: Roasting is the process of heating an ore below its melting point in presence of excess air (O_2) in order to remove volatile gangue and oxidize metal into metal oxide. This is done for non-oxy ores, viz. sulphide, and in reverbetory furnace.
e.g. Zinc blende ore (ZnS) is converted into zinc oxide (ZnO) by roasting.

$$\underset{\text{(Zinc blende)}}{2ZnS} + 3O_2 \xrightarrow{\Delta} 2SO_2\uparrow + \underset{\text{(Zinc oxide)}}{2ZnO}$$

8. Smelting: Smelting is the process of heating an ore above its melting point with coke and/or flux to remove non-volatile gangue (impurities) and ore is reduced into metal. This process is used for such ores in which gangue could not be removed by roasting, and done in blast furnace.
e.g. Iron metal is obtained/extracted from Haematite ore by smelting.

$$Fe_2O_3 + C + \underset{\text{or } CaCO_3}{CaO} \xrightarrow{\Delta} \underset{\text{(Iron)}}{2Fe} + 3CO\uparrow + \underset{\substack{\text{Calcium Silicate}\\ \text{(Light, fusible mass; slag)}}}{CaSiO_3}$$
(SiO_2)

9. Metallurgy? Metallurgy is the science of extracting metals in pure form from their ores/naturally occurring substances. It also include preparation of alloys.
For example, extraction of pure Al metal from bauxite ores is called metallurgy.
The extraction of metals, i.e. metallurgy cannot be carried out by any universal method because extraction of each metal requires different procedure/science of extraction, which depends upon nature/reactivity of metals. Thus, metallurgy is of three types: (i) Thermo or pyrometallurgy (ii) Electro-metallurgy (iii) Hydrometallurgy.

(i) Thermo or pyro metallurgy: Heavy metals (e.g. Cu, Hg, Fe, Pb, Sn etc.) are extracted by thermal reduction (Carbon, Al or Self) method from their ores.

(ii) Electrometallurgy: Highly reactive metals (e.g. Na, K, Mg, Ca, Al etc. are extracted by electro-reduction method, i.e. by reduction of ore/metal compd: electric energy/electricity in fused or solution.

(iii) Hydro metallurgy: Noble or less reactive metals (e.g. Ag, Au etc) are extracted by precipitation/cyanide method from their ores in aqueous solution.

* Steps or stages of Metallurgy/Extraction of metals: Extraction of pure metals (i.e. metallurgy) from its ores occurs in following steps:

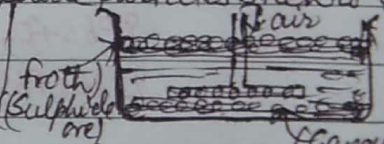
Step-1. Crushing 2. Concentration 3. Reduction 4. Refining.

1. Crushing (& Pulverisation): The ore obtained from earth crust/nature is in the form of big lumps/piece rock, which is unsuitable for further treatment. So, it is crushed into suitable size (3-3.5 cm) in big jaw crushers and then mills/stamps to get fine powder.

Step-2. Concentration/Dressing of the ore: Removal of impurities or gangues from the ore is called concentration or dressing of the ore. It is done by different methods depending upon nature of gangue/ore.

(A) Physical methods: (i) Gravity separation method/levigation: This is used for those ores in which gangues are lighter (e.g. $ZnCO_3$ carbonate, oxide ores). This is based on the difference of specific densities of substances present in the ore. In this method, powdered ore is agitated with water or washed with a running stream of water. The heavy ore particles settle down while lighter particles are washed away. Wilfley table or Hydraulic classifier is used in this method.

(ii) Froth floatation method: This is used for non-ferrous sulphide ores, e.g. PbS, ZnS, HgS, $CuFeS_2$ etc. It is based on fact that metal sulphide is attracted/wetted by oil (froth) while gangues by water. In this method, powdered ore is added to water containing pine oil (as froth), fatty acid (as frother), sodium ethyl xanthate (as collector) and aniline, cresols (as stabilisers). Air is blown in the mixture and agitated with rotating paddle when sulphide particles stick to the oil drops and rise to the froth while gangues remain in water.



(iii) Magnetic separation method: This is used for ferromagnetic ores (e.g. FeS_2, SnO_2, $FeWO_4$). In this method, powdered ore is added on leather/brass belt moving on magnetic wheel/roller, when magnetic substance (ore/gangue) collected below magnetic wheel/roller while non-magnetic substance at far position.

(B) Chemical methods: (i) Calcination (ii) Leaching: Removal of non-volatile gangue/impurities by treating with an acid/a base/a reagent/water solution by chemical reaction is called leaching. e.g. Removal of SiO_2 & Fe_2O_3 from bauxite ore by NaOH solution (Bayer's process).

Step-3 Reduction of concentrated ore: This is done by different ways/methods depending upon nature of metals.

(A) Thermometallurgy: Heavy metals (e.g. Zn, Cu, Hg, Fe etc.) are generally extracted from concentrated ore by heat treatment in two steps: (i) Conversion of concentrated ore into metal oxide either by calcination (e.g. $ZnCO_3$) (Oxy ores) or roasting (e.g. ZnS) (non-oxy ores).

(ii) Reduction of metal oxide into metal: Metal oxides are reduced either by coke (C), aluminium (Al), or by heat or own compd. So, this step involves following methods:

(a) Carbon reduction method (b) Alumino-thermic process (c) Self or Auto reduction method.

(a) Carbon reduction method:— Oxides of Zn, Fe, Sn, Pb, Hg (Mercury) etc can be reduced by coke (C), so these metals are extracted by this method. The concentrate ore/calcined/roasted ore is mixed with C and mixture is heated in suitable furnace when metal oxide is reduced into metal & CO escaped. Sometimes a flux is also added/mixed to remove non-volatile gangue if any.

e.g. $SnO_2 + 2C \xrightarrow{\Delta} Sn + 2CO\uparrow$
(Tinstone ore) (Blast furnace) (Tin)

(b) Alumino-thermic process/Goldsmidt thermite process: This process is used for high melting metals (e.g. Cr, Mn etc) whose oxides cannot be reduced by C. In this method, a mixture of metal oxide & aluminium powder (thermite) covered with Mg powder & BaO_2 is taken in a steel crucible placed on bed of sand. The mixture is ignited when reaction started with evolution of high heat and so metal fused (as lower layer) and alumina (as upper layer) obtained. e.g. $Cr_2O_3 + Al \xrightarrow{\Delta} 2Cr + Al_2O_3$
(Chromium oxide) (Chromium) (Alumina)

(c) Self or Auto reduction method: This method is used for less electro positive metals e.g. Pb, Cu, etc. whose sulphides are reducing in nature. In this method, metal sulphide ore is heated in air as to convert part of the ore into oxide or sulphate which then reacts with (reduced) remaining sulphide to give metal. Here no external reducing agent is used.

e.g. Pb is obtained from Galena (PbS) ore (rich) by self reduction method,

$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2\uparrow$; $PbS + 2O_2 \longrightarrow PbSO_4$ (Partial oxidation)

$2PbO + PbS \longrightarrow 3Pb + SO_2\uparrow$ (Self reduction)
(Lead)

(B) Electrometallurgy / Electro-reduction method: High electro positive or reactive metals e.g. Na, K, Mg, Ca, Al etc) which are strong reducing agents, not reduced by C or Al are extracted by electro-reduction method. In this method, a suitable electric current is passed through molten ore/electrolytic solution of the metal in electrolytic cell. As a result of electrolysis, metal deposited at cathode. Sometimes, a small amount of strong electrolyte is added to lower the melting point or to increase conductivity or both.

e.g. Na metal is extracted from Rocksalt($NaCl$) by electroreduction method.

$NaCl(s) \xrightarrow[575-585^{\circ}C]{KF \text{ or } KCl} NaCl(fused) \xrightarrow{Electricity} Na^+ + Cl^-$

(Rocksalt)

At anode: $2Cl^- \xrightarrow{(-2e)} 2Cl \longrightarrow Cl_2\uparrow$; At cathode: $2Na^+ + 2e \longrightarrow 2Na$ (Reduction)

(+) (Sodium)

(C) Hydrometallurgy: This is used for very less reactive or noble metals, e.g. Ag, Au etc. The method/process involving it is known as wet/precipitation/Cyanide process. In this method, ore or impure metal is first converted into a soluble complex compound/salt by treating with a suitable reagent (leaching) and then high electropositive metal is added to the salt solution, when metal precipitated. e.g. Silver metal is extracted from Argentite ore(Ag_2S) or Argentiferrous rock by Cyanide process (Hydrometallurgy).

$4Ag \text{ or } Ag_2S + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$

sodium dicyano argentate(I) solution.

$2Na[Ag(CN)_2] + Zn \longrightarrow 2Ag\downarrow + Na_2[Zn(CN)_4]$

(Silver)

Step-4 Purification or Refining of metals: Impure metals are purified by different methods which depend upon nature of metals/impurities present in them.

(A) Physical methods:

(i) Liquation method: This method is used for low melting (lower melting point) metals e.g. Sn, Pb, Bi etc. In this method, impure metal is heated on the curved surface of Shallow hearth furnace when pure metal melted and collected at bottom of the furnace leaving behind impurities.

(ii) Distillation: This method is used for volatile (lower boiling point) metals, e.g., Hg, Zn, Cd etc. In this method, impure metal first melted if solid and then distilled in a retort. Vapours of pure metal evolved which on cooling condensed in receiver leaving behind impurities in the retort.

(iii) Zone refining: Si, Ge, Ga etc, which used as semiconductors, are purified by this method. This method is based on the difference in solubility of impurities in molten & solid state of the metal. In this method, impure metal rod is heated at one end by a movable burner and slowly moved across it to another end. The metal melts at the point of heating and crystallised at once burner is removed while impurities pass on the adjacent portion and finally dropped.

(B) Chemical methods: (i) Mond's process: Nickel is purified by this method. In this method, impure nickel is heated with carbon monoxide gas at 60-80°C when volatile nickel carbonyl is formed. On heating at 180°C it decomposes to give pure nickel.

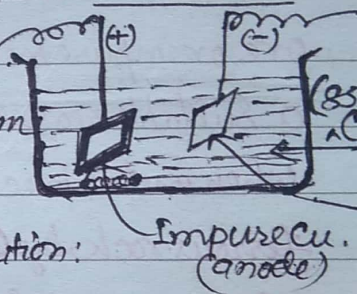
$Ni + 4CO \xrightarrow{60-80^{\circ}C} [Ni(CO)_4]$; $[Ni(CO)_4] \xrightarrow{180^{\circ}C} Ni + 4CO$

(Impure) (Pure)

(ii) Bessemerisation: This method is used in purification of iron (Pig Cast). In this method, impure metal is heated by hot air in a bessemer converter, when impurities such as S, Mn, As etc removed either as volatile oxides or slag (light fusible mass). $S + O_2 \longrightarrow SO_2\uparrow$, $Si + O_2 \longrightarrow SiO_2$

$4P + 5O_2 \longrightarrow P_4O_{10}$, $4As + 3O_2 \longrightarrow As_4O_6\uparrow$, $2Mn + O_2 \longrightarrow 2MnO$, $MnO + SiO_2 \longrightarrow MnSiO_3$.

(iii) Electrolytic method/Electro refining: Metals are generally purified by electrolysis. In this method, impure metal (thick plate) is made as anode, a thin sheet of pure metal as cathode and aqueous solution of the metal salt as an electrolyte. When electricity is passed through electrolytic solution, pure metal dissolved from anode as metal ion and deposited (reduced) on cathode. Impurities collected below the anode as 'anode mud'. This method gives high purity (≈ 99.9%) of metal, e.g. Purification of impure copper.



Impure copper - Anode, Pure copper - cathode, An aqueous solution of $CuSO_4$ (85%) containing 15% H_2SO_4 - Electrolyte. The following reactions when an electric current passed through the solution:

$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$; At cathode: $Cu^{2+} + 2e \longrightarrow Cu$ (pure)

At anode: $Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e$.