6. General Principles and Processes of Isolation of Elements

Occurrence of metals:

Metal	Ores	Composition
Aluminium		$AlO_x(OH)_{3-2x}$
	Bauxite	
		[where $0 < x < 1$]
	Kaolinite (a form of clay)	[Al ₂ (OH) ₄ Si ₂ O ₅]
Iron	Haematite	Fe ₂ O ₃
	Magnetite	Fe ₃ O ₄
	Siderite	FeCO ₃
	Iron pyrites	FeS ₂
Copper	Copper pyrites	CuFeS ₂
	Malachite	CuCO ₃ .Cu(OH) ₂
	Cuprite	Cu ₂ O
	Copper glance	Cu ₂ S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	ZnCO ₃
	Zincite	ZnO

- Metallurgy: Process of extracting pure metal from their ore
- Minerals: Mixture of metal compounds, soil, sand, limestone and rock
- Gangue: Impurities present in ore like mud, silica etc.
- Ores: Minerals from which metals can be extracted economically at low cost and with minimum cost
- Flux: Substance added in furnace to remove gangue
- Slag: The fusible mass formed when flux combined with gangue
- Smelting: Process of extracting metal from their oxide ores by reducing the roasted oxides

The major steps involved in the extraction and isolation of metals from ores are:

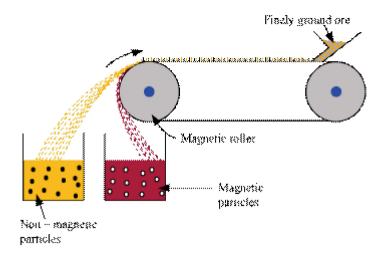
- 1. Crushing and grinding ore
- 2. Concentration of the ore
- 3. Roasting and Calcination of the ore
- 4. Reduction of the metal oxide
- 5. Refining of the pure metal

Concentration of ores:

- Hydraulic washing: It is the washing away of lighter gangue particles from the heavier ore. It is based on the gravity difference between the ore and the gangue particles.
- Magnetic separation: This separation is carried out if either the ore or the gangue is attracted by a magnetic field.







- Froth floatation method: This method is used for removing gangue from sulphide ores. 'Depressants' are used for separating two sulphide ores. E.g., for separating ZnS and PbS, NaCN is used as the depressant.
- Leaching: If the ore is soluble in some suitable solvent, then this process is used. For example, ores of aluminium (bauxite), silver and gold
 - 1. Leaching of alumina

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \otimes 2Na[Al(OH)_4]_{(aq)}$$

$$2\mathsf{Na}[\mathsf{Al}(\mathsf{OH})_4]_{(aq)} + \mathsf{CO}_{2(\mathsf{g})} \circledast \mathsf{Al}_2\mathsf{O}_3.\mathsf{xH}_2\mathsf{O}_{(s)} + 2\mathsf{Na}\mathsf{HCO}_{3(aq)}$$

$$Al_2O_3.xH_2O_{(s)} \xrightarrow{\text{HDE}} Al_2O_{3(s)} + xH_2O_{(s)}$$

Isolation of crude metal from concentrated ore: It involves two steps –

- (i) Conversion into oxide and (ii) Reduction of the oxide to metal
 - Conversion into oxide:
 - 1. Calcination → Involves heating

 Generally, carbonate ores are converted into oxides by this process.

$$ZnCO_{3(s)} \longrightarrow ZnO_{(s)} + CO_{2(g)}$$

1. Roasting → Involves heating in a regular supply of air, at a temperature below the melting point of the metal.

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

Generally, sulphide ores are converted into oxides by this process.







• Reduction of the oxide to metal: Involves heating with some reducing agents such as C, CO or another metal.

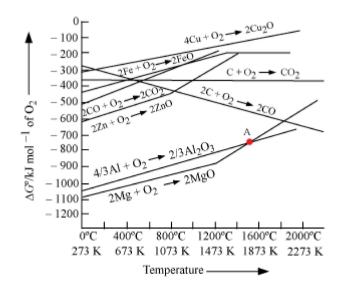
Thermodynamic principles of metallurgy: For any process, the change in Gibbs energy at a temperature is given by

$$\Delta G = \Delta H - T\Delta S$$

and $\Delta G^{\Theta} = -RT \ln K$

A reaction will proceed when the value of ΔG is negative.

• Applications:



If $\Delta G(X, XO)$ is lower than $\Delta G(Y, YO)$, then X can reduce YO.

Extraction of iron from its oxides:

- 1. Reaction taking place in a blast furnace
- 2. At 500 800 K

$$3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$$

 $\text{Fe}_3\text{O}_4 + 4\text{CO} \rightarrow 3\text{Fe} + 4\text{CO}_2$
 $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2$

1. At 900 – 1500 K
$$C + CO_2 \rightarrow 2CO$$

$$FeO + CO \rightarrow Fe + CO_2$$

1. Limestone is decomposed to CaO, which removes silicate impurity as slag.

$$CaCO_3 \rightarrow CaO + CO_2$$







$$CaO + SiO_2 \rightarrow CaSiO_3$$
 (slag)

- 1. Pig iron is the iron obtained from a blast furnace, which contains about 4% carbon and impurities like S, P, Si, Mn in smaller amounts.
- 2. Cast iron (contains about 3% carbon) is obtained by melting pig iron with scrap iron and coke, using hotair blast.
- 1. Extraction of copper from cuprous oxide:

$$Cu_2O + C \rightarrow 2Cu + CO$$

1. Copper matte contains Cu₂S and FeS. It is put in the silica-lined converter to convert the remaining Cu₂S/Cu₂O into metallic copper.

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

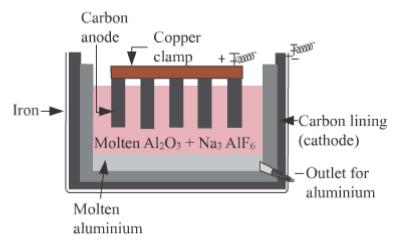
 $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

1. Extraction of zinc from zinc oxide:

$$Z_{nO} + C \xrightarrow{\text{color, 673 II.}} Z_{n} + CO$$

Electrochemical principles of metallurgy: A more reactive metal displaces a less reactive one from its salt solution.

• Extraction of aluminium:



- 1. Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 to lower the melting point and bring conductivity.
- 2. The overall reaction —

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

- 1. This electrolytic process is known as Hall-Heroult process.
- 2. The electrolytic reactions are -

Cathode:
$$Al^{3+}_{(melt)} + 3e^{-} \rightarrow Al_{(l)}$$

Anode: $C_{(s)} + O^{2-}_{(melt)} \rightarrow CO_{(g)} + 2e^{-}$







$$C_{(s)} + 2O^{2-}_{(melt)} \rightarrow CO_{2(g)} + 4e^{-}$$

Copper from low-grade ores and scraps:

Copper is extracted by hydrometallurgy from low-grade ores. The solution containing Cu^{2+} is treated with scrap iron or H_2 .

$$Cu^{2+}_{(aq)} + H_{2(g)} \rightarrow Cu_{(s)} + 2H^{+}_{(aq)}$$

Extraction of Chlorine from Brine

• oxidation reaction

$$2\text{NaCl}_{(aq)} + 2\text{H}_2\text{O}_{(l)} \longrightarrow 2\text{NaOH}_{(aq)} + \text{H}_{2(g)} + \text{Cl}_{2(g)}$$

- $E^0 = 2.2 \text{ V}$
- Requires an external emf greater than 2.2 V. But the
- Electrolysis requires an excess potential to overcome some other hindering reactions.
- Electrolysis of molten NaCl produces Na metal in the place of NaOH.

Extraction of Gold and Silver

- Metal is leached with NaCN or KCN.
- Ag is oxidised to Ag+ and Au is oxidised to Au⁺

$$\begin{split} &4M_{(s)} + 8CN_{(aq)}^{-} + 2H_{2}O_{(aq)} + O_{2(g)} \longrightarrow 4\left[M(CN)_{2}\right]_{(aq)}^{-} + 4OH_{(aq)}^{-} \\ &(M = Ag \text{ or } Au) \\ &2\left[M(CN)_{2}\right]_{(aq)}^{-} + Zn_{(s)} \longrightarrow \left[Zn(CN)_{4}\right]_{(aq)}^{2-} + 2M_{(s)} \end{split}$$

Refining (Purification):

Distillation –

The impure forms of low-boiling metals like zinc and mercury are evaporated to obtain pure metals as distillate.

• Liquation -

Low-melting metals (like tin) are separated from higher-melting liquids by allowing them to flow on a sloping surface.

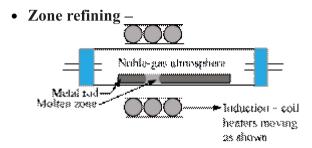
• Electrolytic refining –

Anode: $M \rightarrow M^{n+} + ne^{-}$ Cathode: $M^{n+} + ne^{-} \rightarrow M$





- a. Impure metal is taken as anode and a strip of pure metal is taken as cathode.
- b. Copper and zinc are refined by this process.
- c. Anode mud obtained during electrolytic refining of copper contains antimony, selenium, tellurium, silver, gold and platinum.



- a. Principle The impurities are more soluble in the molten state than in the solid state of a metal.
- b. Germanium, silicon, boron, gallium, indium are refined by this process.
- Vapour-phase refining –
- a. Requirements -
- b. The metal should form a volatile compound with an available reagent.
- c. The volatile compound should be easily decomposed so that it can be recovered easily.
- a. Mond process for refining nickel:

Ni + 4CO
$$\xrightarrow{330-350 \text{ K}}$$
 Ni(CO)₄
Ni(CO)₄ $\xrightarrow{450-470 \text{ K}}$ Ni + 4CO

a. van Arkel method for refining ziroconium (Zr) or titanium (Ti):

Used for removing oxygen and nitrogen present as impurities

$$Zr + 2I_2 \rightarrow ZrI_4$$

 $ZrI_4 \rightarrow Zr + 2I_2$

- Chromatographic methods:
- a. Principle Different components of a mixture are differently adsorbed on an adsorbent.
- b. Chromatography involves a mobile phase and a stationary phase.
- c. There are several chromatographic techniques –
- d. Paper chromatography
- e. Column chromatography
- f. Gas chromatography



