JEE Advanced Revision Notes
Chemistry
Metallurgy

Introduction:

The process of extraction of pure metal from its ore is called metallurgy.

Steps involved in the operation of metallurgy are:

- Crushing and grinding of the ore.
- Concentration of the ore.
- Extraction of crude metal from concentrated ore.
- Purification or refining of the metal.

Crushing and Grinding of Ore:

Big lumps are crushed into smaller pieces and reduced to fine powder with the help of a ball mill process called pulverization.

Concentration / Dressing of Ore:

- The process of removal of unwanted impurities (gangue or matrix) from the crushed ore is known as the concentration or dressing of the ore.
- It is carried out by the following methods.

Hand-picking:

- The rocks may be removed from ore by hand picking. The stony impurities from the iron ore (haematite) are removed by this method.

Levigating or Hydraulic Washing (Gravity separation):

- This method is based on the difference in specific gravities of the ore and gangue particles.
- It is frequently used when the ore particles are heavier than gangue particles.
- When crushed ore is washed in a stream of water, the lighter impurities are swept away heavier ore particles settle down.
- The process is carried out in specially designed tables called Wilfley tables.
- It is generally used for oxide ores and carbonate ores.

Magnetic separation:

- It is used when either ore or gangue is magnetic.

Froth floatation:

- This process is commonly used for the concentration of sulphide ores.
- It is based upon the principle of difference in the wetting property of the ore and gangue particles with water and oil.

Leaching (Chemical method):

- The powdered ore is treated with a suitable reagent in which the ore is soluble but the impurities are not soluble.
- The impurities left undissolved are removed by filtration.

Extraction of crude metal

- Metals are usually extracted by the reduction of their oxides since they are easier to reduce.
- The extraction of metals from concentrated ore involves the following two major steps.

Conversion of the ore into metallic oxide:

- Hydrated oxide, a carbonate, or a sulphide ore can be converted into oxide form by Calcination and by Roasting.

Reduction of the metallic oxide into free metal:

- Smelting: The charge (ore + suitable reducing agent + flux) is heated above the melting point of the metal in the blast furnace.

Hydrometallurgy:

- The process of reducing less electro-positive metal ions with more electro-positive metal in an aqueous solution is called hydrometallurgy.

Electrolytic reduction:

- Highly electropositive metals like alkali and alkaline earth metals, aluminum, etc., are commonly extracted by the electrolysis of their fused salts.
- Sometimes a small amount of some other salt is added to lower the fusion temperature or increase the conductivity or both.

Refining or Purification of metals:

The metals obtained after reduction may still contain some objectionable impurities which are removed by refining using the following methods:

- **Liquation:**
  It is used for refining the metal such as Sn, Pb, Bi, Hg, etc) having low melting points as compared to impurities.
- **Distillation:**
  It is used for the refining of metals that have low boiling points such as Zn, Cd, Hg, etc.,
- **Zone refining (fractional crystallization):**
  This method is based on the principle that the impurities are more soluble in the melt than in the solid-state of the metal.
- **Poling:**
  This method is used when the impure metal contains impurities of its own oxide.
- **Electrolytic refining:**
  Metals like Cu, Ag, Au, Zn, Al, Pb, etc., are purified by this method. The insoluble impurities settle down below the anode as anode mud or anode sludge.
- **Chromatographic methods:**
  This method is based on the principle that different components of the mixture are differently adsorbed on an absorbent. This mixture is out in a liquid or gas media and moved through the absorbent. The absorbed components are removed(eluted) by using a suitable solvent(eluant).

Vapour phase refining:

Van Arkel method:

- This method is generally applied for obtaining ultra-pure metals.
- This impure metal is converted into a volatile stable compound and is then decomposed to get the pure metal at a higher temperature.
- Ti and Zr are purified by this method.

  $Ti + 2I_2 \xrightarrow{500K} TiI_4$

  $TiI_4 \xrightarrow{1700K} Ti + 2I_2$

Mond's process:

- Nickel is purified by this method.

- Impure Ni is heated with carbon monoxide, forming a volatile nickel tetra carbonyl which decomposes at higher temperature to get the pure metal.

$$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4$$

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

Furnaces:

- Furnace is a device in which high temperature is produced either by burning fuel (or) by using electricity.
- Furnaces are lined with refractory bricks or fine bricks.
- The important parts in a furnace are:
  i. Hearth.
  ii. Fireplace (fire box).
  iii. Chimney.
- In a furnace the fuel burns in the first place. In a furnace, the blue gases escape through the chimney. The fireplace and the hearth are separated by a partition known as a fire bridge.

The different types of furnaces used are

i. Reverberatory furnace.
ii. Retort furnace.
iii. Blast furnace.
iv. Shaft furnace.
v. Open hearth furnace.
vi. Muffle furnace.
vii. Electrical furnace.
viii. Arc furnace.
ix. Bessemer converter.

- The ore along with the substance added to it (if any) is known as a charge.
- The charge is placed on the hearth of the furnace.

Thermodynamic Principle of metallurgy:

- Gibbs energy of thermodynamics helps us in understanding the theory of metallurgical transformations.
- The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation.
  $\Delta G = \Delta H - T\Delta S$.

ΔH=enthalpy change.

ΔS=entropy change for the process.

- If ΔG is negative then the reaction proceeds towards products.
- If two reactions are occurring together in a system and if the sum of ΔG of the two reactions is negative the overall reaction will occur spontaneously.
- The net reaction is called a coupled reaction.
- Such coupling is easily understood through Gibbs energy $(\Delta G)^{\circ}$ *Vs* T plots for the formation of the oxides.

Reducing Nature of Carbon:

Carbon in the form of coke, charcoal, or carbon monoxide is used as a reducing agent in pyrometallurgical operations. Such a reduction process used in the extraction of metal is termed **Smelting.**

Electrochemical principles of metallurgy:

- In the reduction of molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation.

  $\Delta G^{\circ} = -nFE^{\circ}$, n= number of electrons.

  E° =electrode potential of the redox couple formed in the system.
- More reactive metal has a large -ve value of E°, then ΔG° becomes +ve, so their reduction is difficult.
- If the difference of two E° values corresponds to a positive E° and consequently ΔG° becomes negative, then less reactive metal will come out of the solution and the more reactive metal will go to the solution.

  Example: $Cu^{+2}{}_{(aq)} + Fe_{(s)} \rightarrow Cu_{(s)} + Fe^{+2}_{(aq)}$

Metallurgy of Iron:

Haematite Ore (Fe_2O_3)

$\downarrow$

Concentration of ore by gravity process followed by electromagnetic separation

$\downarrow$

$Ore + air \xrightarrow{heat} Moisture, CO_2, SO_2, As_2O_3$ is removed and FeO is oxidized into ferric oxide

$S + O_2 \rightarrow SO_2$

$4As + 3O_2 \rightarrow 2As_2O_3$

Calcination

$Fe_2O_3.3H_2O \rightarrow Fe_2O_3 + 3H_2O$

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

↓

Smelting

Smelting is done in a blast furnace

(ore + coke + Limestone)

Types of iron:

Property	Cast iron	Wrought iron	Steel
Chemical composition	Iron 93% -95% Carbon 2.5% - 5% Impurities about 2%	Iron 99.5% -99.8% Carbon 0.1% -0.21% Impurities about 0.3%	Iron 98% -99.5% Carbon 0.25% - 2.0%
Hardness	Very hard	Soft	Medium hardness
Magnetization	Cannot be permanently magnetized	Magnetization is not permanent but easy	Can be permanently magnetized
Malleability	Brittle	Malleable	Malleable and brittle
Melting Point	Lowest about 1200°C	Highest about 1500°C	Between -1300-1400°C
Structure	Crystalline	Fibrous	Granular

Metallurgy of copper:

Flow chart for the extraction of copper

Copper pyrites $(CuFeS_2)$

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Concentrated by forth floatation

Powdered ore + water + pine oil + air → Sulphide ore in the forth

↓

Roasting in reverberatory furnace in presence of air

$2CuFeS_2+2SiO_2+4O_2 \rightarrow Cu_2S+2FeSiO_3+3SO_2$

↓

$Cu_2S+O_2 \rightarrow 2Cu+SO_2$

↓

Blister copper (98% Cu + 2% impurities)

Electrolytic refining

Anode−Impure copper plates

$Cu(s) \rightarrow Cu^{2+}(aq)+2e^-$

Cathode−pure copper plates

$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$

Pure copper deposited at cathode

↓

PURE COPPER (99.6-99.9%)

Metallurgy of Zinc:

Zinc Blende (ZnS)

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Concentration by froth floatation process

Powdered ore + water + pine oil + air → froth carrying sulphide ore particle

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Roasting in reverberatory furnace

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

↓

Reduction: $ZnO + C \rightarrow Zn + CO$ (**Belgian process**)

Heating is done by producer gas

↓

Zn (impurities)

↓

Electrorefining

Anode: Impure metal

Cathode: Pure metal sheet

Electrolyte: solution of zinc sulfate.

Pure Zn deposits on cathode.

Extraction of Aluminium:

Aluminium is the third most abundant element from 8.3% of the earth's crust. It is a constituent of clay, slat, and many types of silicate rocks.

The important mineral ore:

i. Bauxite $AlO_x(OH)_{3-2x}$ (where $0 < x < 1$)

ii. Kaolinite (a form of clay) $(Al_2(OH)_4Si_2O_5)$

Extraction:

Aluminium is mainly isolated from bauxite ore which is generally contaminated with ferric oxide and silica.

The extraction of aluminum from bauxite ore involves the following steps:

1) Purification of bauxite ore i.e., removal of ferric oxide and silica.

- **Baeyer's process:**

This process is mainly applied to bauxite ore containing ferric oxide as the chief impurity. The color of such ore is usually red and hence called red bauxite.

- $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$
- $2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$
- $Al_2O_3.xH_2O(s) + \text{heat} \rightarrow Al_2O_3(s) + xH_2O(g)$

- **Hall's process**

Bauxite is fused with sodium carbonate.

AlO_3 combines with sodium carbonate forming sodium meta aluminate. The fused mass is extracted with water where Fe_2O_3 and SiO_2 remains as a precipitate.

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$$

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow 2Al(OH)_3 + Na_2CO_3$$

- **Serpeck's process**

This process is used when silica is present in considerable amounts in bauxite ore. The ore is mixed with coke and heated at 1800 °C in presence of nitrogen, where AIN(aluminum nitride) is formed.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AIN + 3CO$$

$$\mathbf{2AlN + 6H_2O \rightarrow 2NH_3 + Al(OH)_3}$$

Calcination of aluminum hydroxide: The aluminum hydroxide precipitate obtained from the above process is calcined at 1500 °C in a rotary kiln to obtain pure alumina (Al_2O_3)

$$2Al(OH)_3 \xrightarrow{1500^\circ C} Al_2O_3 + 3H_2O$$

Electrolytic reduction of pure alumina

The Electrolysis of pure alumina faces two difficulties:

i. Pure alumina is a bad conductor of electricity

ii. The fusion temperature of pure alumina is about 2000 ºC and at this temperature when the electrolysis is carried of fused mass, the formed metal vapourize as the boiling point of aluminum is 1800 ºC.

This can be overcome by using a mixture containing alumina, cryolite (Na_3AlF_6 and fluorspar (CaF_2)) in the ratio of 20: 24 : 20 The fusion temperature of this mixture is 900 ºC and it is a good conductor of electricity.

i. Heating of the electrolyte

   The temperature of the cell is automatically maintained at 900-950 ºC.

ii. Electrolysis:

   On passing current, aluminum is discharged at the cathode, and Oxygen is liberated at the anode. It attacks carbon rods forming CO and CO_2.

First step:

AlF_3 from cryolite ionizes as $AlF \rightleftharpoons Al^{3+} + 3F^-$

Al^{3+} ions discharged at cathode and F^- ions at the anode.

$Al^{3+} + 3e \rightarrow Al$ (at cathode)

$2F^- \rightarrow F_2 + 2e$ (at anode)

The liberated fluorine reacts with alumina to form AlF_3 and O_2

The oxygen attacks the carbon anode to form CO and CO_2.

$$Al_2O_3 + 3F_2 \rightarrow 2AlF_3 + \frac{1}{3}O_2$$

$$2C + O_2 \rightarrow 2CO$$

$$C + O_2 \rightarrow CO_2$$

Metallurgy of silver

Argentite (Ag_2S)

$\downarrow$

Concentrated by the froth floatation process powdered ore + Water +pine oil + air → Froth carrying sulphide ore particles.

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Cyanidation

Concentrated ore + aq.NaCN solution (0.4% -0.6%) + air.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na\left[Ag\left(CN\right)_2\right] + Na_2S$$

$$4Na_2S + 5O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4NaOH + 2S$$

↓

(filter)

Precipitation of silver with zinc

$$2Na\left[Ag\left(CN\right)_2\right] + Zn \rightarrow 2Ag + Na_2\left[Zn\left(CN\right)_4\right]$$

Black precipitation of $Ag + KNO_3 \xrightarrow{Fuse}$ compact mass (silver metal)

↓

Electrorefining

Anode: Impure silver

Cathode: Pure silver plate

Electrolyte: $AgNO_3$ solution + HNO_3

Pure silver deposits on the cathode.