Refining or Preparation of Ultrapure Metals:

The metals obtained by reduction methods from the concentrated ores are usually impure. These impure metals may be associated with small amounts of:

- Unchanged ore,
- Other metals produced by the simultaneous reduction of their compounds originally present in the ore,
- Non-metals like silicon, carbon, phosphorus, etc.,
- Residual slag, flux, etc.

The impure metal is thus subjected to some purifying processes known as refining in order to remove the undesired impurities. The following refining processes may be applied depending upon the nature of the metal under treatment and the nature of the impurities.

Liquation process: This process is based on the difference in fusibility of the metal and impurities. When the impurities are less fusible than the metal itself, this process is employed. The impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and flows down leaving behind the impurities on the hearth. This method is used to purify the metals like Bi, Sn, Pb, Hg, etc.

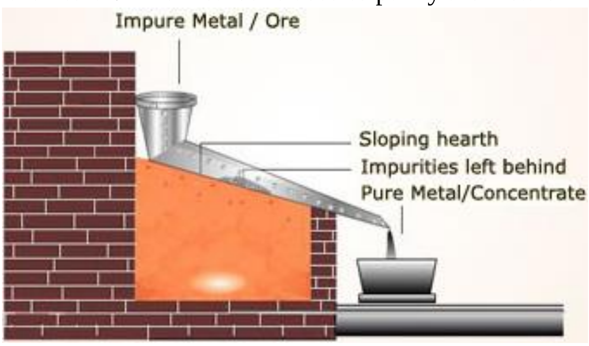

Figure 3: Diagrammatic representation of Liquation.

Distillation: This process is used for those metals which are easily volatile. The impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left-behind in the retort. This is used for the purification of Zn,Cd, Hg, etc.

Pyrometallurgical oxidation process: This process is used when the impurities have a greater affinity for oxygen than the metal itself. This method is usually employed for refining the metals like Fe, Cu, Ag, etc. The oxidation is done by various ways:

(i) **Cupellation**: The impure metal is heated in a cupel or oval shaped crucible made of bone ash or cement and a blast of air is passed over the molten mass. The impurities get oxidised and removed with the blast of air. For example the impurity of lead present in silver is removed by cupellation process.

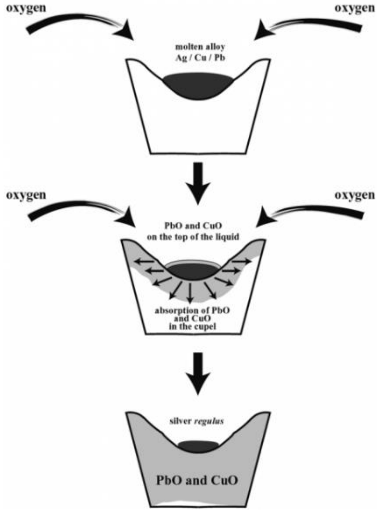

Figure 4: Diagrammatic representation of Cupellation.

(ii) **Bessemerisation**: The impure metal is heated in a furnace and a blast of compressed air is blown through the molten mass. The impurities get oxidised. For example, the molten pig iron is taken in a bessemer converter and compressed air is passed which oxidises the impurities.

$$2Mn + O_2 \longrightarrow 2MnO$$
$$Si + O_2 \longrightarrow SiO_2$$
$$2C + O2 \longrightarrow 2CO$$
$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

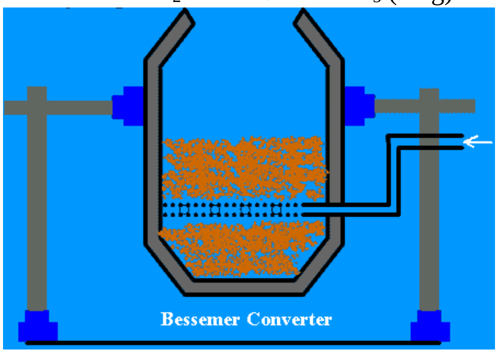

Figure 5: Diagrammatic representation of Bessemerisation.

(iii) **Poling**: The impure metal containing oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. The green poles of wood release the hydrocarbon gases which reduce the oxide impurities. This method is especially used in the purification of copper (old method).

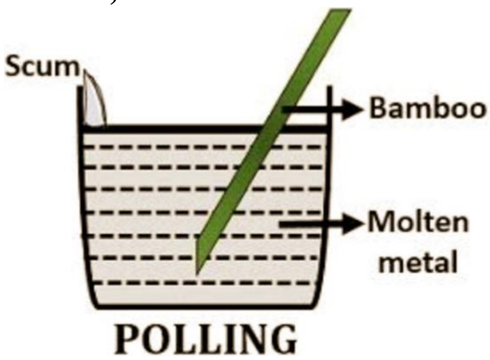

Figure 6: Diagrammatic representation of Bessemerisation.

Electrolytic Refining of Metals: Many of the metals such as copper, silver, gold, aluminium, lead, etc. are purified by this method. This is perhaps the most important method. The impure metal is made anode while a thin sheet of pure metal acts as a cathode. The electrolytic solution consists of generally an aqueous solution of a salt or a complex of the metal. On passing the current, the pure metal is deposited on the cathode and equivalent amount of the metal gets dissolved from the anode. Thus, the metal is transferred from anode' to cathode through solution. The soluble impurities pass into the solution while the insoluble one, especially less electropositive impurities collect below the anode as anodic mud or anode sludge.

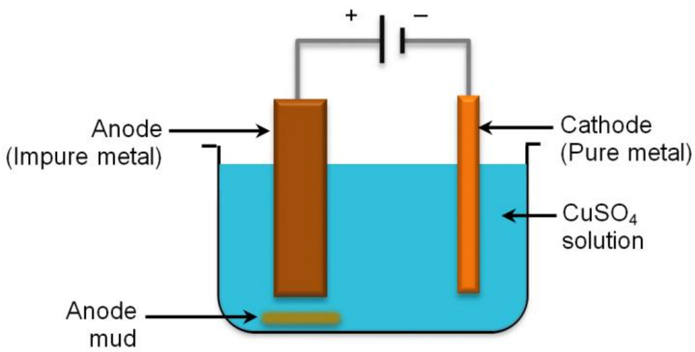

Figure 7: Diagrammatic representation of electrorefining.

Some examples are given below:

(i) **Purification of Copper**:

Impure metal: Anode

Thin sheets of copper: Cathode
Electrolyte-An aqueous solution of copper sulphate containing H_2SO_4
A current of 1.3 volt is used. Anodic mud contains Ag, Au, Pt, Pd, etc. and impurities like Fe, Zn, Ni, etc. pass into the solution. 99.9% pure copper is obtained.

(ii) **Purification of Silver**:
Impure metal-Anode
A thin sheet of pure silver-Cathode
Electrolyte-An aqueous solution of $AgNO_3$ containing HNO_3.

(iii) **Purification of Lead**:
Impure metal-Anode
A sheet of pure lead-Cathode
Electrolyte-A solution of lead silico fluoride $PbSiF_6$ containing 8-10% of H_2SiF_6.

Special methods: Sometime some special methods are used for refining or purification of metals, some of which are given below:

1. **Vapour Phase Refining**: The two essential criteria for vapour phase refining are:
   - ❖ The intermediate compound formed has to be volatile.
   - ❖ The intermediate compound formed has to be unstable, *i.e.* it should decompose on heating at practically achievable temperature.

   This refining technique is used in the following purification processes:

(i) **Mond's Process**: Nickel is purified by this method. Impure nickel is treated with carbon monoxide at 60-80°C when volatile compound, nickel carbonyl, is formed. Nickel carbonyl decomposes at 180°C to form pure nickel and carbon monoxide which can again be used.

$$\underset{\text{Impure}}{Ni(s)} + 4CO(g) \xrightarrow{60\text{-}80\ ^\circ C} Ni(CO)_4\ (g) \xrightarrow{180\ ^\circ C} \underset{\text{Pure}}{Ni(s)} + 4CO\ \text{(recycled)}$$

(ii) **Van-Arkel-de Boer Process**: This method is generally applied for obtaining ultrapure metals. The impure metal is converted into a volatile compound while the impurities are not affected. The volatile compound is then decomposed electrically to get the pure metal. Ti, Zr, Hf, Si, etc., have been refined by this method.

$$\text{Impure metal} + I_2 \longrightarrow \underset{\text{(vapours)}}{\text{Metal iodide}} \xrightarrow[\text{W filament}]{\text{Heating}} \underset{\text{Pure}}{\text{Metal}} + I_2\ \text{(recycled)}$$

$$\underset{\text{Impure}}{Ti(s)} + 2I_2(g) \xrightarrow{523K} TiI_4(g)$$

$$TiI_4(g) \xrightarrow{1700K} \underset{\text{Pure}}{Ti(s)} + 2I_2(g)$$

2. **Zone refining or Fractional crystallisation**: Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method. This process is known as ultrapurification because it results in impurity level decreasing to ppm level.
   Zone refining is based upon fractional crystallization as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod and producing a thin zone throughout the cross-sectional area.
   It is desirable that the diameter of the rod, d is small enough to give a uniform melt.
   When the melted zone in the metal rod is ready, the furnace is allowed to move downwards very slowly together with the melted zone. The furnace is then switched off, cooled down and taken to the top again for repetition of the process. Almost all impurity sweeps out to the bottom after several repetitions of the process.

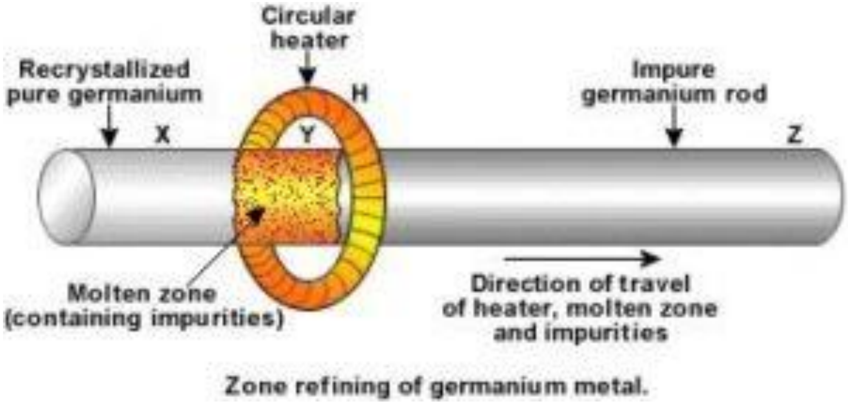

Figure 8: Diagrammatic representation of zone refining.