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Metallurgy

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Metals occur in two forms in nature

(i) In native state

(ii) In combined state

Ore An ore is a complex mixture of a metal-containing mineral and economically worth less material called gangue, consisting of sand, clay and other impurities.

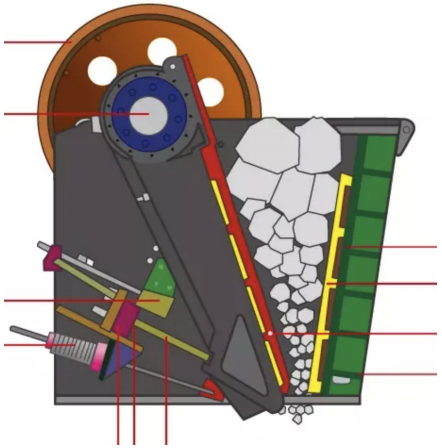
Metals	Ore	Formula
Li	Spodumene	$LiAlSi_2O_6$
	Lepidolite	$(Li, Na, K)_2Al_2(SiO_2)_3F(OH)$
Na	Common salt	NaCl (rock salt)
	Chile salt petre	$NaNO_3$
	Glauberite	$Na_2SO_4 \cdot 10H_2O$ (Glauber's salt)
	Borax	$Na_2B_4O_7 \cdot 10H_2O$
	Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
	Soda ash	Na_2CO_3
	Feldspar	$NaAlSi_3O_8$
K	Sylvine	KCl
	Nitre	KNO_3 (saltpeter)
	Schonite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$

Mg	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3 \cdot CaCO_3$
	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
	Epsom salt	$MgSO_4 \cdot 7H_2O$
Ca	Gypsum	$CaSO_4 \cdot 2H_2O$
	Limestone	$CaCO_3$
	Phosphorite	$Ca_3(PO_4)_2$
	Fluorspar	CaF_2
Al	Bauxite	$Al_2O_3 \cdot 2H_2O$
	Diaspore	$Al_2O_3 \cdot H_2O$
	Corundum	Al_2O_3
	Cryolite	Na_3AlF_6
Sn	Cassiterite	SnO_2 (tin stone)
Pb	Galena	PbS
	Cerussite	$PbCO_3$
	Anglesite	$PbSO_4$

Cu	Chalcopyrite	$CuFeS_2$ (copper pyrite)
	Chalcocite	Cu_2S (copper glance)
	Cuperite	Cu_2O
	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
Ag	Argentite	Ag_2S (silver glance)
	Cerargyrite	AgCl (horn silver)
	Pyrargyrite	$Ag_2S \cdot Sb_2S_3$ (Ruby silver)
Fe	Haematite	Fe_2O_3
	Limonite	$Fe_2O_3 \cdot 3H_2O$
	Magnetite (lodestone)	Fe_3O_4 (magnetic oxide of iron)
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
Hg	Cinnabar	HgS
Zn	Zinc blende	ZnS (black zinc or sphalerite)
	Calamine	$ZnCO_3$
	Zincite	ZnO (red zinc)

Crushing of Ore

Crushing and grinding of ores are done in order to ease the process of concentration of ores. They are crushed into small pieces in gyratory crushers followed by grinding.



Concentration of Ores

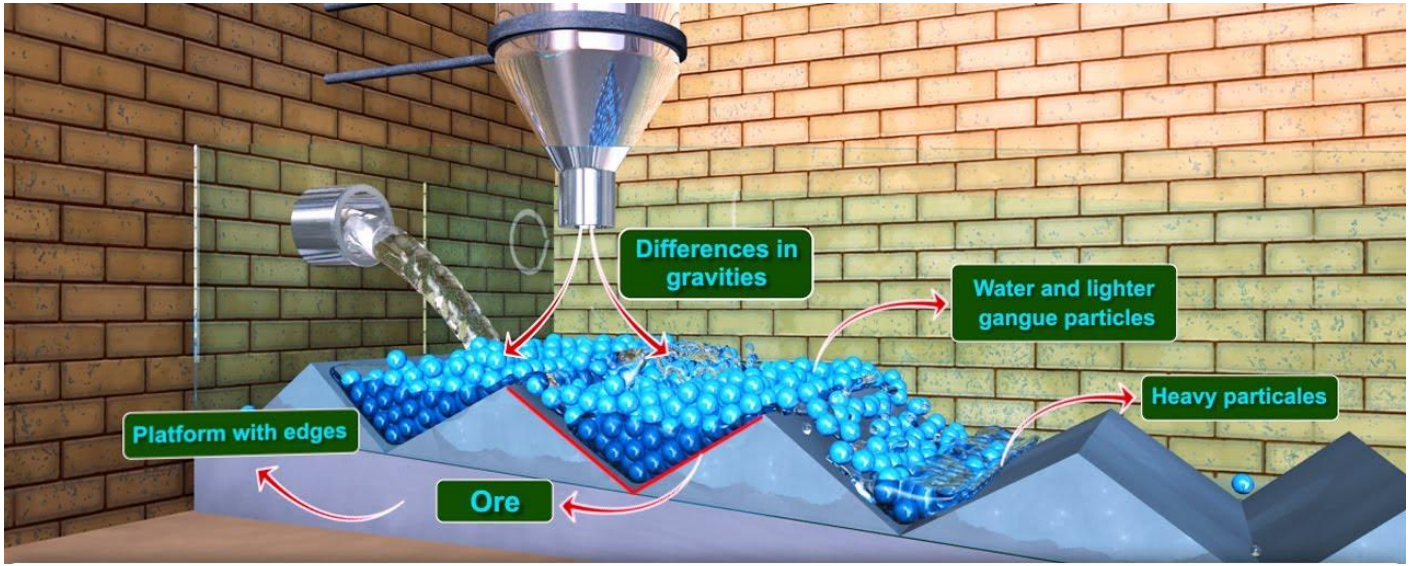
It involves the removal of unwanted materials like sand, clays, etc., from the ore. The procedure followed depends on physical properties of compounds of minerals and impurities present in it.

Some of the important methods involved are:

1. Gravity separation / Hydraulic washing
2. Froth Floatation method
3. Magnetic Separation
4. Leaching

Gravity Separation

It is based on difference in the density of the ores and the gangue particles. The powdered ore is washed in a running stream of water. The lighter gangue particles are washed away leaving the heavier ores. Fe_2O_3, Fe_3O_4, etc., are concentrated by this method.

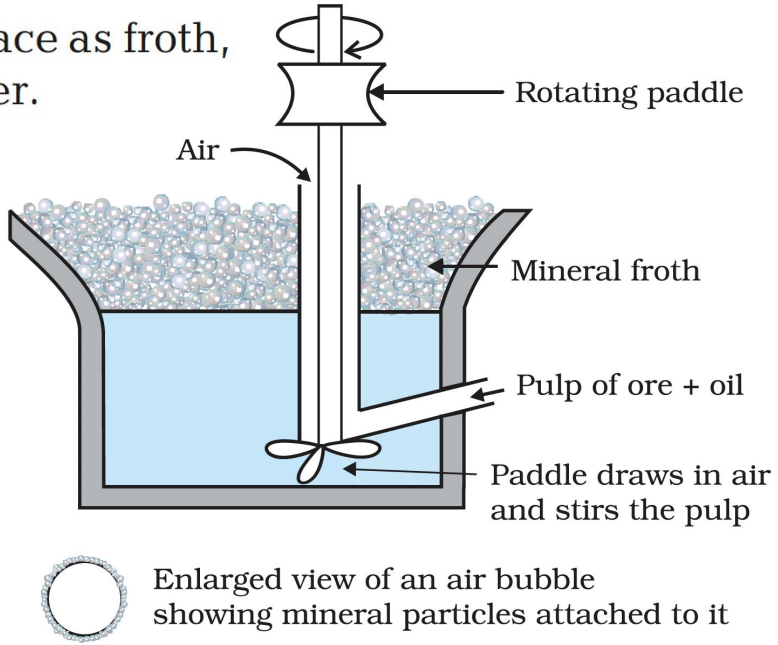


Froth Floatation Method

Sulphide ores of Cu, Ag, Zn, Pb, etc., are concentrated by this process.

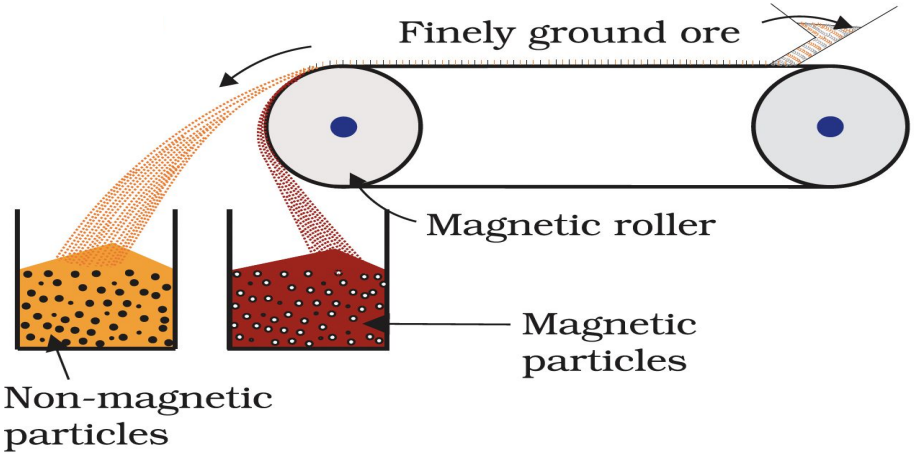
- A suspension of powdered ore in water is made followed by the addition of collectors (pine oil, fatty acids, xanthates, etc.) and froth stabilisers (cresol, aniline, etc.).
- Ore particles are made wet by oil and come to surface as froth, whereas gangue particles remain inside with water.

Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using '*depressants*'. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.



Magnetic Separation

It is based on difference in magnetic properties of gangue and ores. The ore is concentrated by a magnetic separator, that separates magnetic substances from non-magnetic substances. Magnetite (Fe_3O_4), chromite ($FeO \cdot Cr_2O_3$), pyrolusite (MnO_2), tungsten ore, etc., are separated by this method.



Leaching

Leaching is often used if the ore is soluble in some suitable solvent.

(a) Leaching of alumina from bauxite

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

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

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

In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement:

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)\ (M = Ag \text{ or } Au) \quad (6.4)$$

$$2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s) \quad (6.5)$$

Highly Active Metals (e.g. Na, K, Mg etc.)

Electrolytic Reduction The oxides of highly electropositive metals do not reduce easily with coke. Hence, they are extracted by electrolysis of their salts in fused sate. Pure metal is obtained at cathode.

Less Active Metals

Roasting Sulphide ores are converted to oxide ores by roasting. The ore is treated in a furnace in regular supply of air at a temperature below the melting point of the metal. The sulphide ores are converted to metal oxides and the impurities are removed as volatile oxides.

Calcination Hydroxide and carbonate ores do not undergo roasting, hence they are heated below melting point in absence of air forming metal oxides.

Metal Oxide

Reduction of Oxide to Metal Metal oxides are reduced to the corresponding metals by various processes based on standard reduction potential called pyrometallurgical process and hydrometallurgical process.

Impure Metal

Refining of Impure Metal The impure metal obtained from the reduction of metal oxide contains impurities that are refined to get pure metal.

Pure Metal

Smelting The concentrated ore is treated with coke and flux and heated at high temperature and the process is called smelting. The coke reduces metal oxide to metal and flux removes acidic or basic impurities as slag :

With Hydrogen $MO_3 + 3H_2 \longrightarrow M + H_2O$ (M = Mo or W)

Goldschmidt Aluminothermic Process Cr and Mn oxides are reduced by this process.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

With Other Metals Highly active metals reduce less active metal oxides.

$$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$$

Self Reduction or Auto-reduction A part of sulphide ore of less electropositive metals like Hg, Pb, Cu, etc., are converted to oxide ore. The sulphide and oxide ores undergo self-reduction to form the metal.

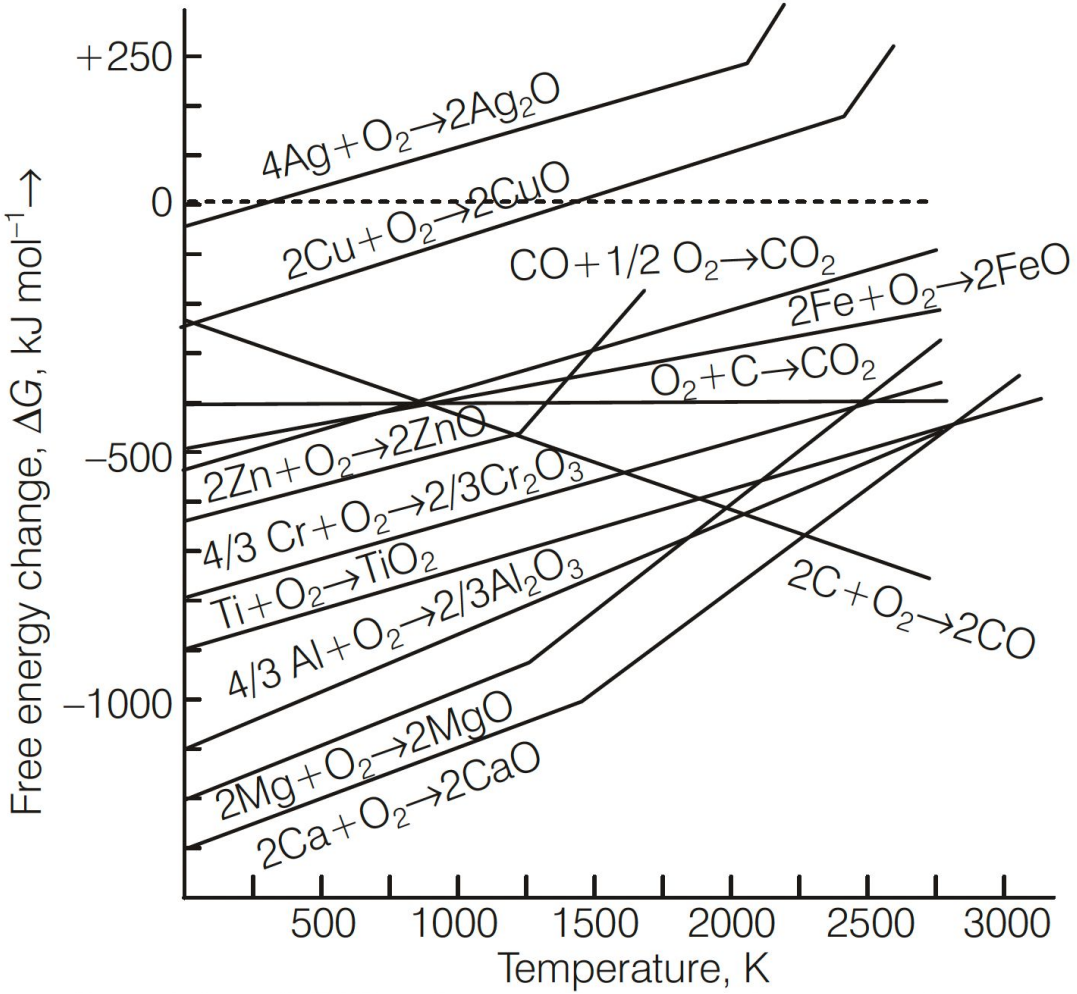
e.g. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2(g)$

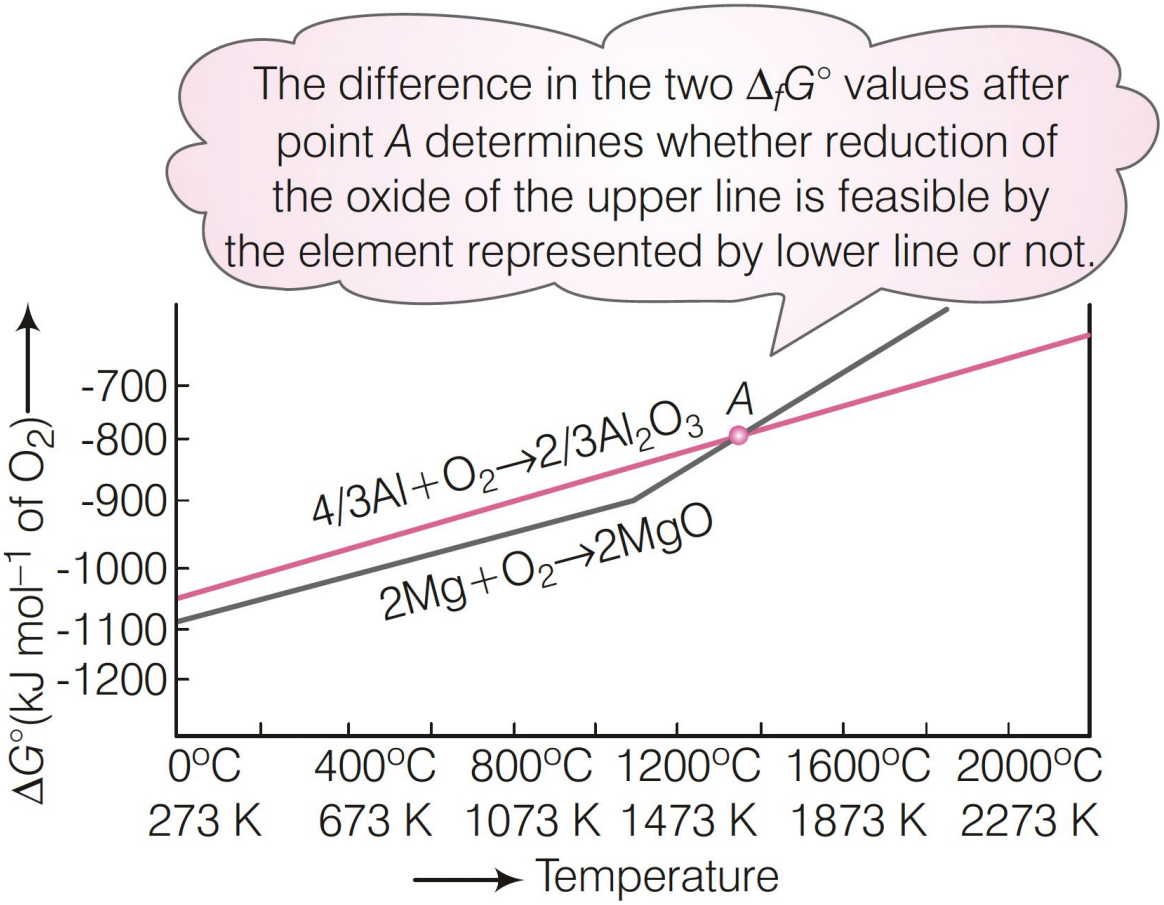
$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2(g)\uparrow$

Ellingham Diagram

It represents $\Delta_f G^\circ$ *versus* temperature for the formation of oxides of elements.

- Each plot is a straight line except when a phase change occurs.
- There is a point in the curve below which $\Delta_f G^\circ$ is negative (the oxide is stable) and above this point the metal oxide is decomposed to form metal.
- This diagram is useful in choosing a reducing agent for the reduction of metal oxides.

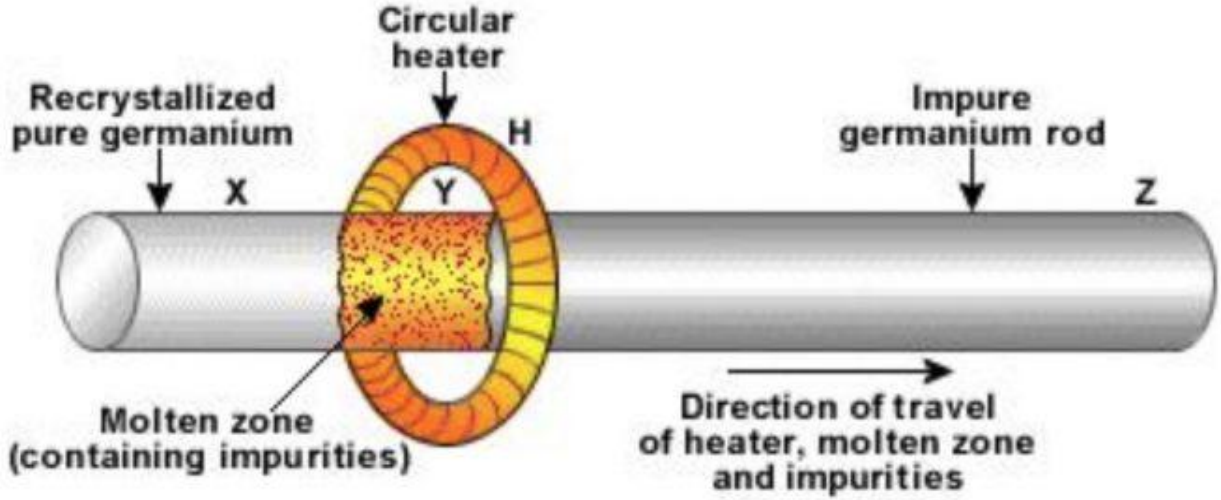

+250
0
−500
−1000
Free energy change, ΔG, kJ mol⁻¹→
4Ag+O2→2Ag2O
2Cu+O2→2CuO
CO+1/2 O2→CO2
2Fe+O2→2FeO
O2+C→CO2
2Zn+O2→2ZnO
4/3 Cr+O2→2/3Cr2O3
Ti+O2→TiO2
4/3 Al+O2→2/3Al2O3
2C+O2→2CO
2Mg+O2→2MgO
2Ca+O2→2CaO
500
1000
1500
2000
2500
3000
Temperature, K


The difference in the two $\Delta_f G^\circ$ values after point A determines whether reduction of the oxide of the upper line is feasible by the element represented by lower line or not.
ΔG° (kJ mol^{-1} of O_2)
-700
-800
-900
-1000
-1100
-1200
$4/3Al + O_2 \rightarrow 2/3Al_2O_3$
A
$2Mg + O_2 \rightarrow 2MgO$
0°C 273 K
400°C 673 K
800°C 1073 K
1200°C 1473 K
1600°C 1873 K
2000°C 2273 K
Temperature

Refining of Metals

1. **Distillation Method** Metals with low boiling point like Zn, Cd, Hg, etc., are evaporated to collect the pure metal.
2. **Liquation Method** Metals with low melting point like, Sn, Pb, Hg, Bi, etc., are separated from high melting impurities by this method.
3. **Electrolysis** The impure metal act as anode and deposited at cathode as pure metal. The electrolysis is carried out in a cell containing aqueous solution of the salt of the metal. The more basic impurities remain in solution and less basic impurities are deposited as anode mud, e.g. Cu, Zn, Ag, Au, Al, etc.

4. **Zone-refining Method** This is based on the principle that impurities are more soluble in molten state than in the solid state of metal. The metal obtained is highly pure. The impure metal on gradual cooling deposit as pure crystal of metal leaving impurities in the remaining part of molten metal. Ge, Si, B, Ga, in are purified by this method.



5. **Vapour Phase Refining Method** The impure metal is converted into its volatile compound, which on heating is decomposed to pure metal.

Mond process

$$Ni + CO \xrightarrow{330 - 350\ K} \underset{\text{Volatile compound}}{Ni(CO)_4}$$

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

van-Arkel Method This method is used to remove oxygen and nitrogen impurities in metals like Zr, Ti, V, Th, etc., e.g.

$$Ti + 2I_2 \xrightarrow{150 - 250\,^\circ C} \underset{\text{Volatile compound}}{TiI_4\,(g)}$$

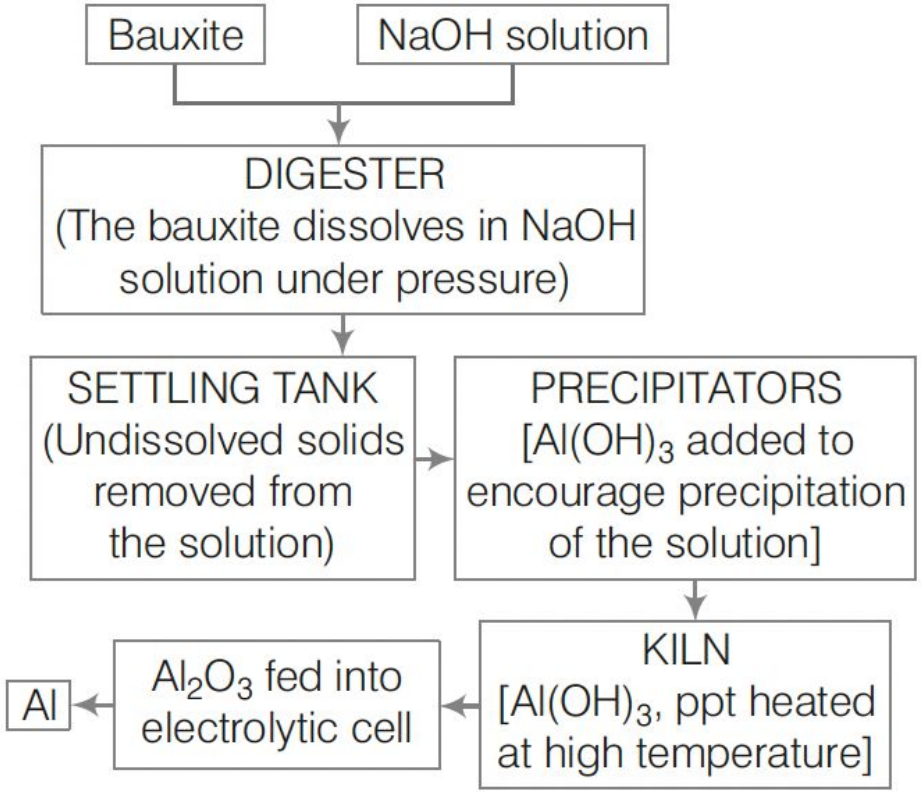
$$TiI_4\,(g) \xrightarrow[\text{Tungsten filament}]{1400\,^\circ C} \underset{\text{(Pure)}}{Ti(s)} + 2I_2\,(g)$$

6. **Hydrometallurgical Process** The ore is treated with reagents like NaCN or Cl_2 in presence of water. The metal forms salt solution that is recovered in pure form either by electrolysis or by replacement reaction in the solution.
7. **Amalgamation Process** Noble metals like Ag, Au when come in contact with Hg form amalgam, from which pure metal is obtained by distillation.
8. **Chromatographic Method** This is based on the principle that different compounds of a mixture are differently adsorbed on an adsorbent. This method is used when the impurities are very close in their chemical properties and the metal is present in very minute quantity.

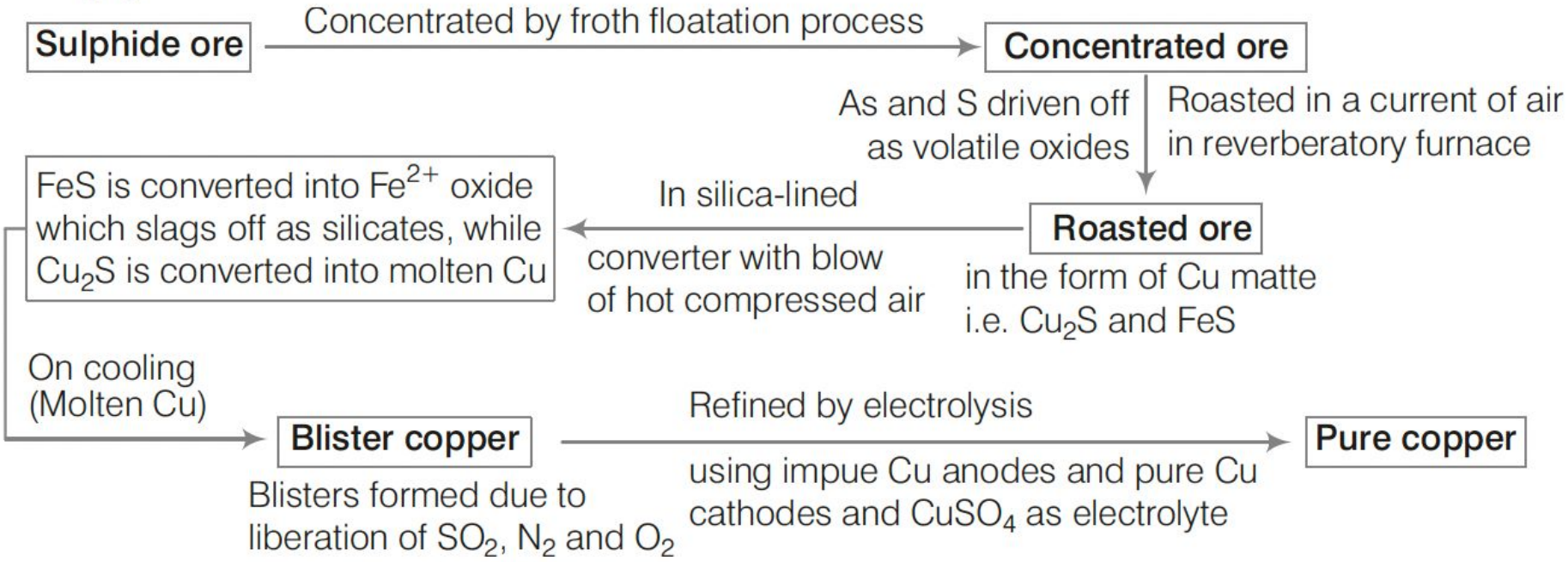
9. **Poling Method** The impure metal containing oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. This pole release hydrocarbon gases which reduce the oxide impurities. This method is used specially in case of copper.
10. **Cupellation** In this process ores or alloyed metals are treated under very high temperatures and have controlled operations to separate noble metals like Ag and Au, from base metals like Zn, Bi, As etc. This method is known as cupellation because impure metal is fused in small boat shaped dishes of bone ash or cement called carpels.

11. **Bessemerisation** In this process, the impure metal is heated in Bessemer converter and a blast of compressed air is blown through the molten mass. The impurities get removed in the form of volatile oxides. This process is used in making steel from cast iron, in purification of Ni etc.

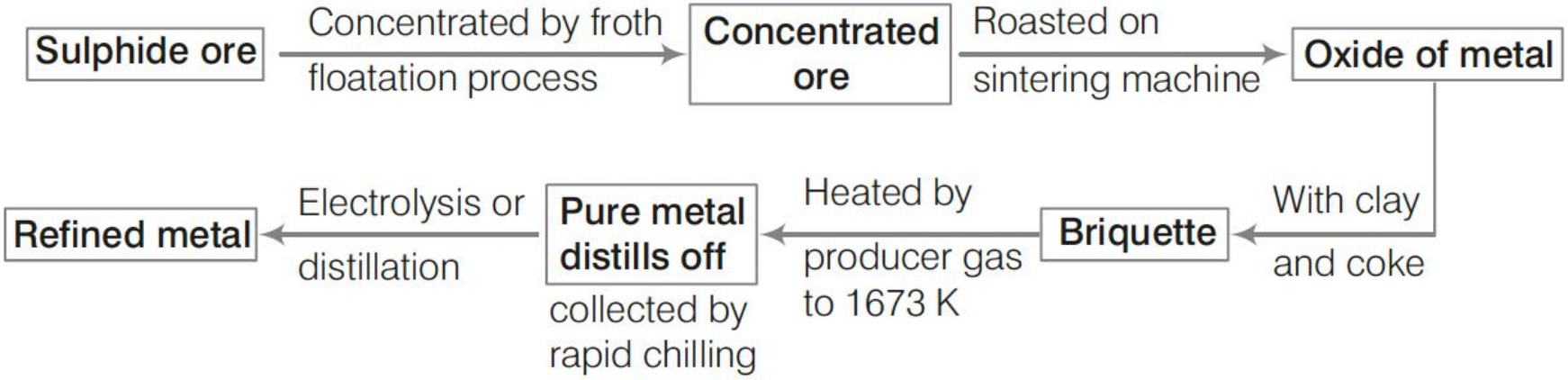
Aluminium



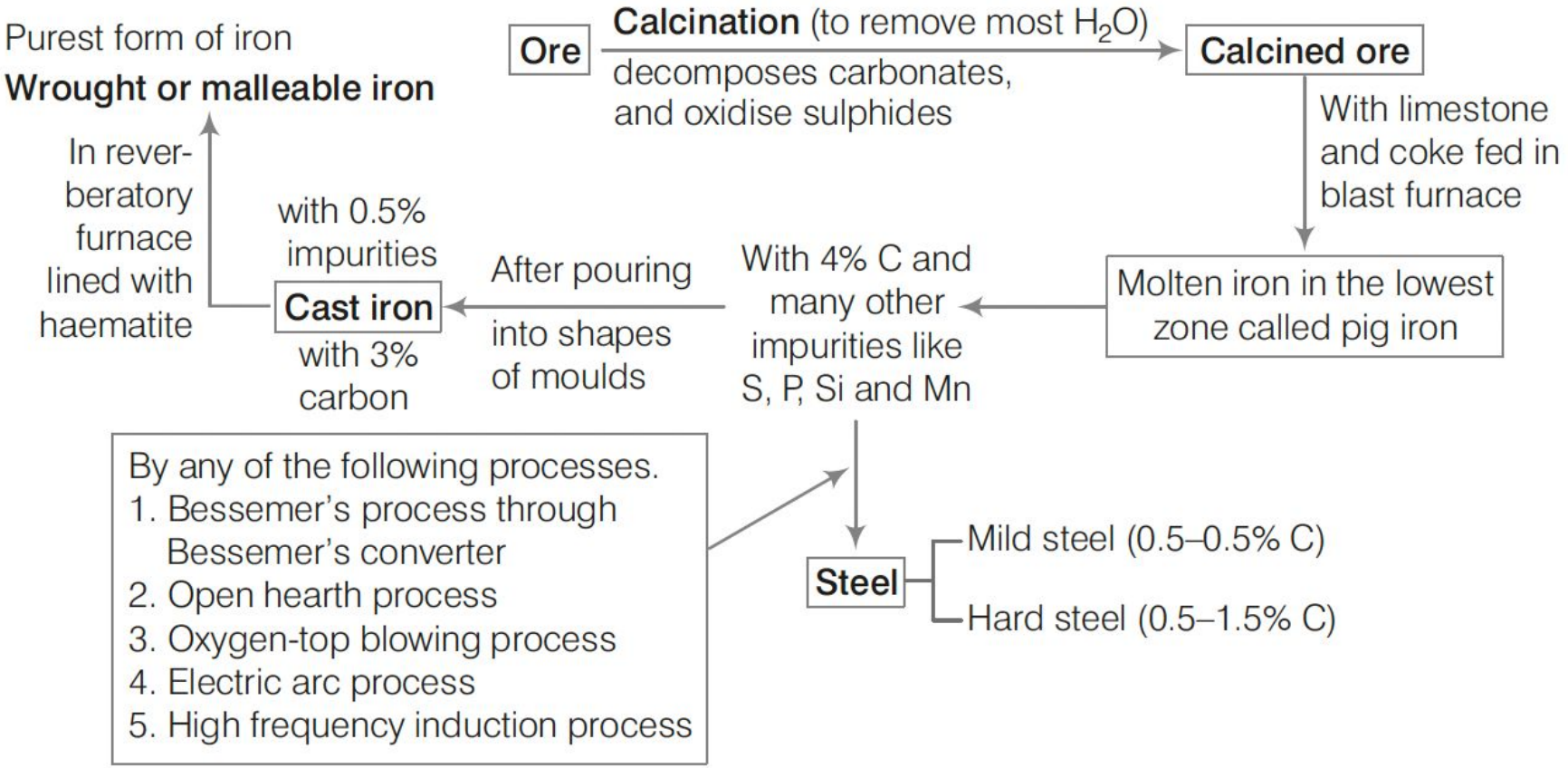
Copper



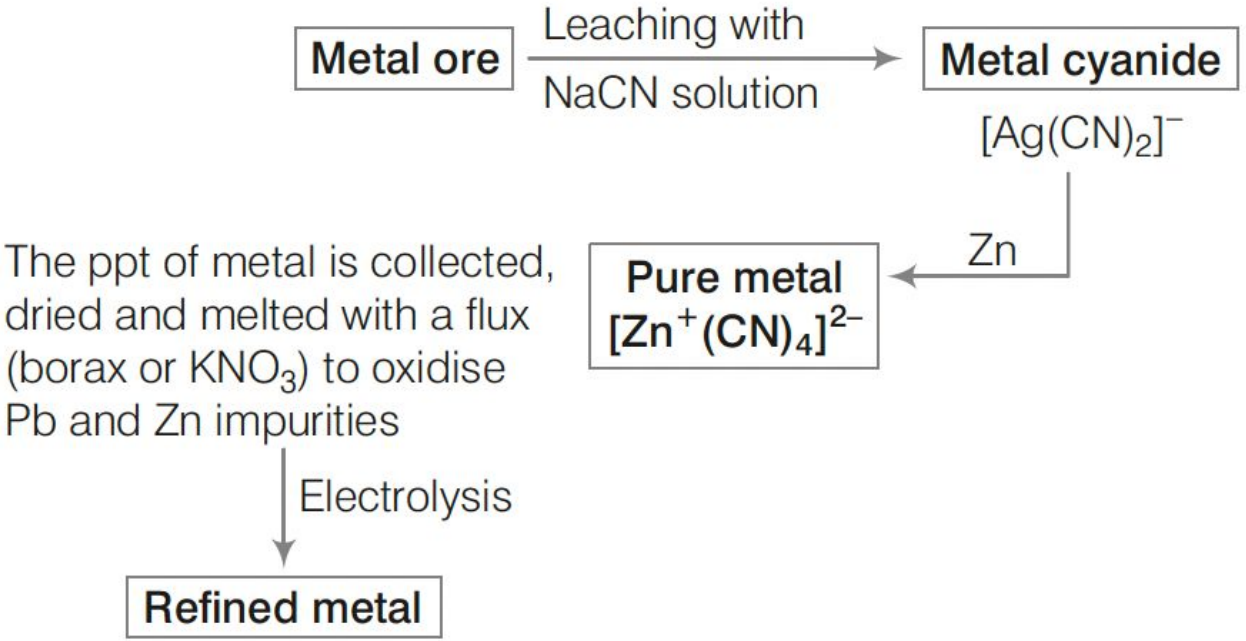
Zinc


Sulphide ore
Concentrated by froth floatation process
Concentrated ore
Roasted on sintering machine
Oxide of metal
With clay and coke
Briquette
Heated by producer gas to 1673 K
Pure metal distills off
collected by rapid chilling
Electrolysis or distillation
Refined metal

Iron


Purest form of iron
Wrought or malleable iron
In reverberatory furnace lined with haematite
with 0.5% impurities
Cast iron
with 3% carbon
After pouring into shapes of moulds
With 4% C and many other impurities like S, P, Si and Mn
Molten iron in the lowest zone called pig iron
With limestone and coke fed in blast furnace
Calcined ore
Calcination (to remove most H_2O) decomposes carbonates, and oxidise sulphides
Ore
By any of the following processes.
1. Bessemer's process through Bessemer's converter
2. Open hearth process
3. Oxygen-top blowing process
4. Electric arc process
5. High frequency induction process
Steel
Mild steel (0.5–0.5% C)
Hard steel (0.5–1.5% C)

Silver


Metal ore
Leaching with
NaCN solution
Metal cyanide
$[Ag(CN)_2]^-$
Zn
Pure metal
$[Zn^+(CN)_4]^{2-}$
The ppt of metal is collected, dried and melted with a flux (borax or KNO_3) to oxidise Pb and Zn impurities
Electrolysis
Refined metal

Mercury

It is found as 1×10^{-5} % of earth crust and its most important ore is cinnabar (HgS).