Metallurgy

→ **Mineral**: Naturally occurring chemical substance from the Earth

Ore: Mineral suitable for extraction of metal

Gangue: Impurities along the ore. Gangue + flux → slag

Abundance : $O_2 > Si > Al > Fe > Ca > Na > K, Mg$

Oxide ores

1. Bauxite – $Al_2O_3 \cdot 2H_2O$
2. Diaspore – $Al_2O_3 \cdot H_2O$
3. Corundum – Al_2O_3
4. Cuprite – Cu_2O
5. Magnetite – Fe_3O_4
6. Magnesite – Fe_2O_3
7. Pyrolusite – MnO_2
8. Cassiterite – SnO_2
9. Zincite – ZnO
10. Pitch Blende – U_3O_8
11. Limonite – $Fe_2O_3 \cdot 3H_2O$
12. Franklinite – $ZnO \cdot Fe_2O_3$

Sulphide ores

1. Copper pyrites – $CuFeS_2$ (Chalcopyrites)
2. Copper glance – Cu_2S
3. Pyrargyrite – Ag_3SbS_3
4. Zinc blende – ZnS
5. Galena – PbS
6. Argentite – Ag_2S
7. Cinnabar – HgS
8. Ruby silver – $3Ag_2S \cdot Sb_2S_3$

Sulphate ores

1. Gypsum – $CaSO_4 \cdot 2H_2O$
2. Epsom salt – $MgSO_4 \cdot 7H_2O$
3. Barytes – $BaSO_4$
4. Kieserite – $MgSO_4 \cdot H_2O$
5. Anglesite – $PbSO_4$
6. Glauber salt – $Na_2SO_4 \cdot 7H_2O$

Halide ores

1. Rock salt – NaCl
2. Horn silver – $AgCl$
3. Sylvine – KCl
4. Carnallite – $KCl \cdot MgCl_2 \cdot 6H_2O$
5. Cryolite – Na_3AlF_6
6. Fluorspar – CaF_2

Phosphate ores

1. Phosphorite – $Ca_3(PO_4)_2$
2. Fluoroapatite – $3Ca_3(PO_4)_2 \cdot CaF_2$
3. Chlorapatite – $3Ca_3(PO_4)_2 \cdot CaCl_2$.

Nitrate ores

1. Chile salt petre – $NaNO_3$
2. Bengal salt petre – KNO_3

Silicate ores

1. Asbestos – $CaSiO_3 \cdot 3MgSiO_3$
2. Feldspar – $K_2O \cdot Al_2O_3 \cdot 6SiO_2$
3. Mica – $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
4. Wollastonite – $ZnSiO_4$
5. Kaolinite – $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
6. Beryl – $3BeO \cdot Al_2O_3 \cdot 6SiO_2$

Carbonate ores

1. Magnesite – $MgCO_3$
2. Dolomite – $CaCO_3 \cdot MgCO_3$
3. Malachite – $CuCO_3 \cdot Cu(OH)_2$
4. Azurite – $2CuCO_3 \cdot Cu(OH)_2$
5. Calamine – $ZnCO_3$
6. Siderite – $FeCO_3$
7. Limestone – $CaCO_3$
8. Strontianite – $SrCO_3$

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

Gemstone → Impure form of Al_2O_3 < Cr^{+3} (Ruby), Co^{+3} (Sapphire)

Extraction of metal from ore

I) Ore concentration II) Extraction of metal from conc ore

III) Refining of metal

I) Ore concentration - Removal of impurities in ore.

1. Handpicking : stones & sand are removed from crushed ore.

Haematite is conc. this method.

2. Hydraulic washing (or) Levigation (or) Gravity separation :

Wilfley's table is used to separate ore & gangue when they differ in their density or specific gravity.

Haematite, tinstone, alluvial sand are concentrated by this method.

3. Electromagnetic method: When ore (or) gangue particles are magnetic.

Ore	Impurity
Cassiterite (SnO_2) non magnetic	wolframite ($FeWO_4$) magnetic
~~Magnetite~~ Chromite ore ($FeCr_2O_4$) Magnetic	Magnetite (Fe_3O_4) non magnetic
Chlorapatite ($3Ca_3(PO_4)_2 \cdot CaCl_2$) - N.M	Pyrolusite (MnO_2) non magnetic
	TiO_2 - Magnetic

4. Froth - flotation process : principle involved in this process is ore particles are wetted by oil & gangue are wetted by water.

low grade Sulphide ore → powder.

Frothers: pine oil, camphor oil, olive oil.

Collectors: potassium or sodium ethyl xanthate

Froth stabilizers: cresol, aniline

Conditioners: Na_2CO_3

Mixture of ZnS & PbS separated by depressant $NaCN$ (or) KCN

$Na_2[Zn(CN)_4]$

$CuSO_4$ & Na_2S acts as activators for ZnS.

- $NaCN$ is used as depressant prevents from ZnS coming to froth but allows PbS with the froth.

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

Bauxite $+ 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4]$

$Na[Al(OH)_4] + CO_2 + H_2O \longrightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$

$Al(OH)_3$

$Al_2O_3 \cdot xH_2O \xrightarrow{\Delta} Al_2O_3 + H_2O$

Leaching agent : NaCN or KCN

M = Au, Ag extracted by this (Mac Arthur's forest cyanidation)

$4M + 8CN^- + 2H_2O + O_2 \longrightarrow 2[M(CN)_2]^- + 4OH^-$

$2[M(CN)_2]^- + Zn \rightarrow 2M\downarrow + [Zn(CN)_4]^{-2}$ M = Ag, Au

II) Extraction of metal from concentrated ore

i) Conversion of other ore into metal

ii) Reduction of metal oxide into metal.

i) 2 < Calcination, Roasting

<u>Calcination</u> : Heating of ore in absence of O_2

Mostly carbonate ores

Carbonate ore $\xrightarrow{\Delta}$ metal oxide $+ CO_2$

<u>Roasting</u> : Process of heating ore in presence of O_2 (sulphide ores)

Sulphide ore $+ O_2 \xrightarrow{\Delta}$ metal oxide $+ SO_2$

Sulphides converted into sulphates after strong heating.

Formed sulphates on heating gives metal oxide, SO_2 & O_2

$2ZnS + 2O_2 \xrightarrow{650°C} 2ZnSO_4$

$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$

Formed SO_2 is used to prepare H_2SO_4

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + [H]$

ii) <u>Reduction of metal oxide into metal</u>

1) Smelting :

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(PbO, ZnO) $SnO_2 + 2C \rightarrow Sn + 2CO$

(WO_3) $MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$

$2NiO + \underbrace{CO + H_2}_{\text{water gas}} \rightarrow 2Ni + CO_2 + H_2O$

(Cr_2O_3) $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$ [Alumino thermite process]

3:1 → $3Fe_2O_3$: Al   Mg powder + BaO_2 - Ignition mixture

Reducing agents: CO, C, H_2, CO + H_2, Al

2. <u>Self reduction (or) Auto reduction :</u>

Cu, Pb, Hg are extracted by this method.

(Cu_2S, HgS) $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$

$2PbO + PbS \rightarrow 3Pb + SO_2$

3. <u>Hydrometallurgy</u> : Reducing less +ve ion with more +ve ion in aq. soln. Ag, Au, Cu are extracted by this method.

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

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

To prevent backward reaction water is added.

$3Na_2S + 2H_2O + 3O_2 \rightarrow Na_2SO_4 + 4NaOH + 2S$

4. <u>Electrolytic reduction</u> : Highly +ve metals like IA & IIA, Al are extracted by electrolytic process $\boxed{\Delta G^\circ = -nFE^\circ}$

(Hall Heroult's process)

Al extracted by electrolysis of $Al_2O_3 + Na_3AlF_6 + CaF_2$

In Down's process electrolyte is NaCl, $CaCl_2$

In Castner process electrolyte is NaOH.

Flux: Gangue + Flux → Slag

Flux
- Acidic flux - SiO_2, $Na_2B_4O_7 \cdot 10H_2O$
  Basic impurities - CaO, MgO, FeO, $CaCO_3$
- Basic flux - CaO, Fe_2O_3, MgO, $MgCO_3$, $CaCO_3$
  Removes acidic impurities like SiO_2, P_4O_{10}

(MgO, FeO) $\underset{\text{flux}}{CaO} + \underset{\text{impurity}}{SiO_2} \rightarrow \underset{\text{slag}}{CaSiO_3} \leftarrow \underset{\text{flux}}{SiO_2} + \underset{\text{impurity}}{CaCO_3} \rightarrow \underset{\text{slag}}{CaSiO_3} + CO_2$

$2NiO + \underbrace{CO + H_2}_{\text{water gas}} \rightarrow 2Ni + CO_2 + H_2O$

(Cr_2O_3) $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$ [Alumino thermite process]

$3:1 \rightarrow 3Fe_2O_3 : Al$ — Mg powder + BaO_2 :- Ignition mix.

Reducing agents: CO, C, H_2, $CO + H_2$, Al

2. Self reduction (or) Auto reduction :

Cu, Pb, Hg are extracted by this method.

(Cu_2S, HgS) $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$

$2PbO + PbS \rightarrow 3Pb + SO_2$

3. Hydrometallurgy : Reducing less +ve ion with more +ion in aq. soln. Ag, Au, Cu are extracted by this method.

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

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

To prevent backward reaction water is added.

$3Na_2S + 2H_2O + 3O_2 \rightarrow Na_2SO_4 + 4NaOH + 2S$

4. Electrolytic reduction : Highly +ve metals like IA & II A, Al are extracted by electrolytic process. $\boxed{\Delta G^\circ = -nFE^\circ}$

(Hall Heroult's process) Al extracted by electrolysis of $Al_2O_3 + Na_3AlF_6 + CaF_2$

In Down's process electrolyte is $NaCl$, $CaCl_2$

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- Acidic flux – SiO_2, $Na_2B_4O_7 \cdot 10H_2O$
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- Basic flux – CaO, Fe_2O_3, MgO, $MgCO_3$, $CaCO_3$
  - Removes acidic impurities like SiO_2, P_4O_{10}

(MgO, FeO) $\underset{\text{flux}}{CaO} + \underset{\text{impurity}}{SiO_2} \rightarrow \underset{\text{slag}}{CaSiO_3}$ ← $\underset{\text{flux}}{SiO_2} + \underset{\text{impurity}}{CaCO_3} \xrightarrow{\Delta} \underset{\text{slag}}{CaSiO_3} + CO_2$

III. Refining of metals

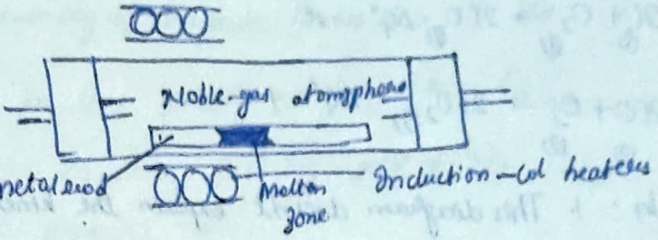
1) Liquation: Metal has low M.P - Sn, Pb, Bi, Hg are extracted.

2) Distillation: Metal has low B.P - Zn, Cd & Hg are refined.

3) Poling: Metal has metal oxide as impurity, green wood poles are used. Cu - CuO, Sn - SnO_2

4) Zone refining: principle involved in this is impurities are more stable in molten state than in solid form.

Highly pure metal obtained - Sb, Ge, Ga, B, In extracted



5) Cupellation: Metal has easily oxidisable "impurity".

Silver (Ag) has lead (Pb) as impurity.

6) Vapour phase refining: i) Impure metal - high volatile.

ii) High volatile - pure metal.

Mond's process - $\underset{(Impure)}{Ni} + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow{450-470K} \underset{pure}{Ni} + 4CO$

Van Arkel method: Ti & Zr

$\underset{Impure}{Zr} + 2I_2 \xrightarrow{1800K} ZrI_4 \xrightarrow{\Delta} \underset{pure}{Zr} + 2I_2$

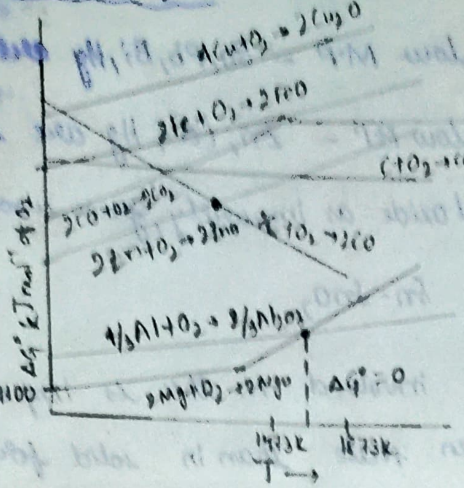
$Ti + 2I_2 \xrightarrow{500K} TiI_4 \xrightarrow{1700K} \underset{(pure)}{Ti} + 2I_2$

7) Electrolytic Refining: Impure metal - Anode

Pure metal - Cathode

Cu, Ag, Al, Au, Zn, Pb, Sn Electrolyte - metal salt

Ellingham Diagram



Metal oxide placed above in the diagram can be reduced by the metal or element present below in diagram

$2Cr_2O_3 + 4Al \rightarrow 4Cr + 2Al_2O_3$

Metal oxides having +ve G° are highly unstable. Ag_2O, HgO

$2Ag_2O \rightarrow 4Ag + O_2$

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta G^\circ = 0$

$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$; $\Delta G^\circ = -ve$

$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ $\Delta G^\circ = +ve$

Draw-backs: 1. This diagram doesn't explain the kinetics of reduction.

2. Reduction of Al by Mg is uneconomical.

3. Reduction of metal oxide is easier if the metal formed is in liquid state at the temperature of reduction.