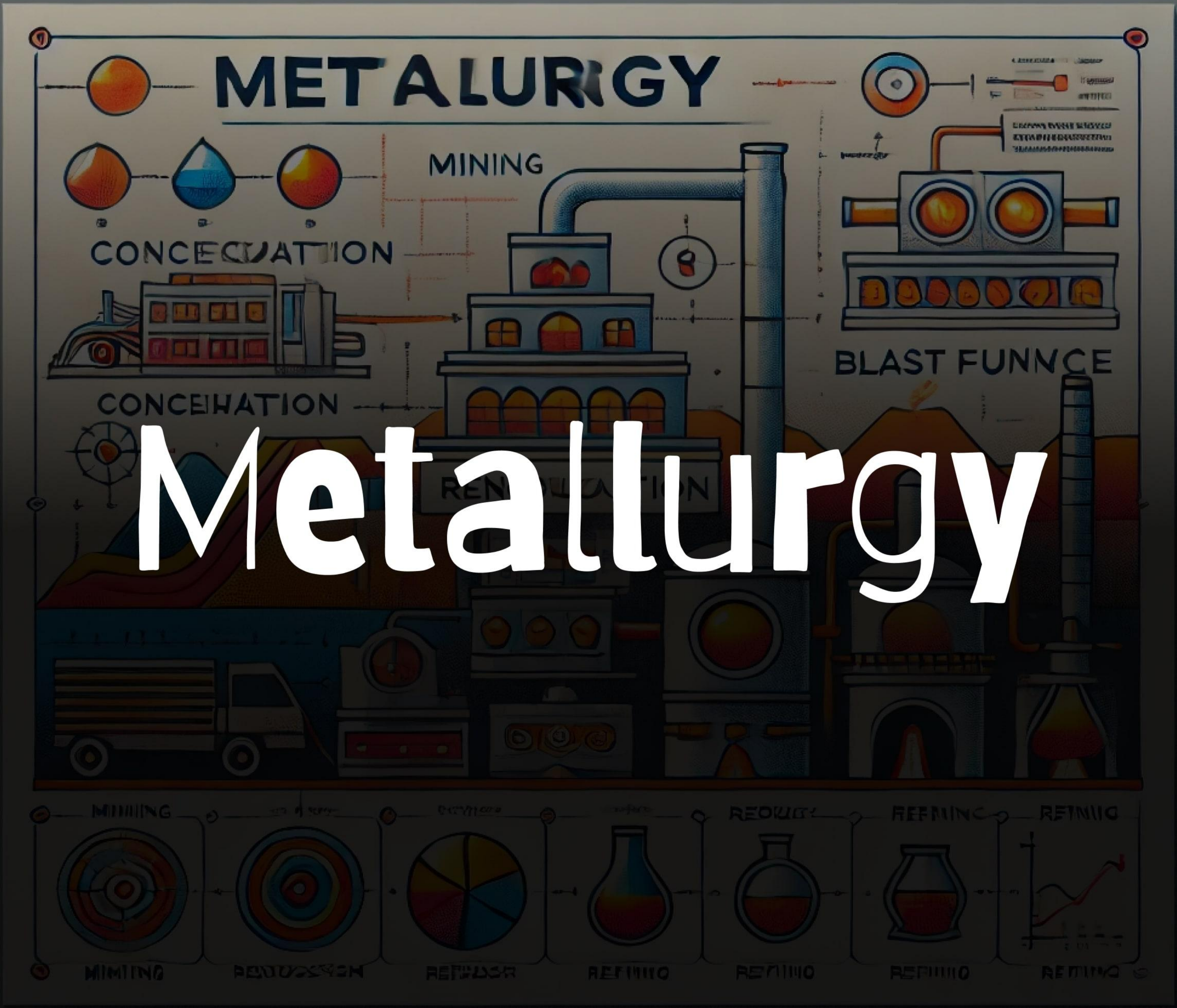
Metallurgy


METALURGY
MINING
CONCECVATION
CONCEHATION
BLAST FUNNCE
RENOUCATION

* Metallurgy *

Mineral - naturally occuring chemical substance which conta some % of metal in it.

Ore - minerals from which metals can be extracted profitably / economically.

Gangue - non - metallic impurities (sand, clay, quartz) (matrix)

Flux - Additional substance added to ore to remove infusible impurity.

Slag - it is lighter than metal & hence floats over metal ; it prevents further oxdn of liq. metal

* Ore

1) Sulphide ore

Ironpyrite - FeS_2
Copper pyrite - $CuFeS_2$
Silver glance - Ag_2S
Copperglance - Cu_2S
zincblende - ZnS
Galena - PbS
Cinnaba - HgS

2) Oxide ore

हे Haematite - Fe_2O_3
मा Magnetite - Fe_3O_4
पारो Pyrolusite - MnO_2
Box ~~Casseterite~~ Bauxite - $Al_2O_3 \cdot xH_2O$
Cassete casseterite - SnO_2
Lithogk Litharge - PbO
Cuprite - Cu_2O
Zincite - ZnO
Limonite - $Fe_2O_3 \cdot 3H_2O$

3) Carbonate Ore

Malachite - $CuCO_3 \cdot Cu(OH)_2$
↳ Green

Azurite - $2CuCO_3 \cdot Cu(OH)_2$
↳ blue

Siderite - $FeCO_3$
Magnesite - $MgCO_3$
Limestone - $CaCO_3$
dolomite - $MgCO_3 \cdot CaCO_3$
Cerrusite - $PbCO_3$

4) Halide ore

CaF_2 - Fluorspar
Na_3AlF_6 → cryolite

* Copper ore -

Cuprite - Cu_2O

Copper pyrite - $CuFeS_2$ → main ore

Copper glance - Cu_2S

malachite - $CuCO_3 \cdot Cu(OH)_2$ - green

azurite - $2CuCO_3 \cdot Cu(OH)_2$ - blue

* Iron ore.

Haematite - Fe_2O_3 } main ore

Magnetite - Fe_3O_4

Limonite - $Fe_2O_3 \cdot 3H_2O$

Iron pyrite - FeS_2

Siderite - $FeCO_3$

* Zinc ore

Zincite - ZnO

Zinc blende - ZnS

Calamine - $ZnCO_3$

* Mercury ore

Cinnabar - HgS

Florospar - CaF_2

* Aluminium ore

Bauxite - $Al_2O_3 \cdot xH_2O$

Cryolite - Na_3AlF_6

* Metallurgy - ① Concentration of ore.
② Roasting / calcination
③ Reduction
④ Refining

Metallurgical process

* Hydrometallurgy	* Pyrometallurgy	* Electrometallurgy
→ aq. soln is used in extraction	→ Heat is used in extraction	→ Electrolysis is used in extraction

* Steps in metallurgy

{Ore}

① {Powdered ore} → concentration / Benefaction / dressing of
Of ore / of ore / ore

→ Hydrolautic washing
→ Froth floatation
→ Magnetic separation } Physical method
→ Leaching.] → chemical method

② {Concentrated ore} ③ {Reduction} {Crademeta}
Refining

→ Roasting →Smelting
→calcination → Reduction with Al

1) Gravity separation or Hydrolic washing or Levigation
→ Difference in gravity of ore particle & gangue particle
→ powdered ore is passed with steam of water.
(Heavy particle of ore - settles down)
(light gangue particle - wash away)
→ eg. Oxide ore, carbonate ore

Cassiterite, Haematite
SnO_2 Fe_2O_3

2) Magnetic separation. diff in magnetic property of ore particle & impurity
→ Powder ore is dropped on belt moving on rollers (magnetic)

→ magnetic particle in ore are attracted by magnet & fall inside

→ Chromite ore - $FeCr_2O_4$ ($FeO \cdot Cr_2O_3$)
Haematite - Fe_2O_3
Magnetite - Fe_3O_4
Wolframite - $FeWO_4$

3) Froth Floatation (O loves O) → Sulphide ores
→ based on preferital wetting of ore particle by oil. & gangue particle with water
→ Frothing agent - Pine oil
→ Collector - Potassium ethyl xanthate.
→ Froth stabilizer - phenol, cresol, Anilline
→ Depressent - Separates two sulphide ore.

$\boxed{Zn + PbS} \rightarrow$ depressant → NaCN
depress → ZnS.

activator - $CuSO_4$ (promote froth floatation
→ Powdered ore is added to water containing pine oil.
→ air is passed to create froth.
→ Sulphide ore sticks to oil droplet & rise to surface & floats with air bubble
→ impurite settle down

4) Leaching - It is used if ore is soluble in suitable solvent
→ Leaching of Alumina from Bauxite ore.
↳ $Al_2O_3 \cdot xH_2O$
↳ Impurity - SiO_2, TiO_2, Iron oxide

Bayers Process

$$\underset{}{Al_2O_3(s)} + \underset{\text{Suitable solvent}}{\text{conc. } NaOH} \longrightarrow \underset{\text{(soluble)}}{Na[Al(OH)_4]}$$

$Na[Al(OH)_4] + CO_2 \longrightarrow Na_2CO_3 + Al_2O_3 \cdot xH_2O$

$Al_2O_3 \cdot xH_2O \xrightarrow{\Delta} \underset{(Pure)}{Al_2O_3} + xH_2O$

impurity- Iron oxide → conc. NaOH → Bayer's Process

impurity- Silicon oxide → Serpeck process.

Ore is heated to 1800°c with carbon & nitrogen

It forms $AlN \xrightarrow{Hydrolysis} Al(OH)_3 + NH_3$

Solvent → conc. NaOH → Bayer's process

→ Na_2CO_3 → Hall's process

Mac Arthur Cyanide process (leaching)

Ag, Au

$Ag + NaCN + O_2 + H_2O \longrightarrow Na[\overset{+}{Ag}(CN)_2] + NaOH$

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

$Au + NaCN + O_2 + H_2O \longrightarrow Na[Au(CN)_2] + NaOH$

$Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + Au\downarrow$

Step 2 Concentrated ore → Oxide

Calcination → Heating (absence of air) below MP

Hydroxide, Hydrated Oxide, Carbonate

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

$Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$

$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$

$CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + CO_2$

Roasting - Heating (presence of air) below MP

→ Sulphide ore

$ZnS + O_2 \longrightarrow ZnO + SO_2$

$PbS + O_2 \longrightarrow PbO + SO_2$

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

if ore contains Fe

$CuFeS_2 \longrightarrow \underbrace{Cu_2S + FeS}_{\text{Copper matte}} + \underbrace{FeO}_{\text{Basic}} + \boxed{SO_2}$ → H_2SO_4 preparation

$FeO + \underbrace{SiO_2}_{\text{Acidic Flux}} \longrightarrow \underbrace{FeSiO_3}_{\text{Slag}}$

Partial Roasting

Cu_2S, कया

HgS, होगा

PbS, प्रभु

Step 3 Reduction of Oxide to metal.

① Smelting - Extracting a metal from metal oxide by Reduction with carbon (coke, coal, CO)

$M_xO_y + yC \longrightarrow xM + yCO$

Reactivity series

Please - Potassium K

Stop - Sodium Na

Calling - Calcium Ca

Me - magnetium Mg

A - Aluminium Al

cute - carbon C

zebra - zinc Zn

I - Iron Fe

never nickel - Ni

today Tin Sn

like lead Pb

her - Hydrogen H

call - Copper Cu

smart - Silver Ag

goat - Gold Au

Poor - platinum Pt

Eg - $ZnO + C \rightarrow Zn + CO$

$Fe_2O_3 + C \longrightarrow Fe + CO_2$

$Fe_3O_4 + C \longrightarrow Fe + CO_2$

$CuO + C \longrightarrow Cu + CO$

$NiO + C \longrightarrow Ni + CO$

$SnO + C \rightarrow Sn + CO_2$

$PbO + C \longrightarrow Pb + CO$

② Pyrometallurgy - Extraction of metal using Heat.

$$HgO \xrightarrow{\Delta} Hg + O_2$$

$$Ag_2O \xrightarrow{\Delta} Ag + O_2$$

$$(Au_2O_3)\ Au_2O \xrightarrow{\Delta} Au + O_2$$

③ Reduction by Al - (Gold Schmidt aluminothermic process) (Thermite process)

→ Oxide of chromium, iron, manganese, are reduction using Aluminium

Cr, Mn, Fe → Al

कौन रोया मन मे फिर से आलिया

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

$$M_3O_4 + Al \rightarrow Mn + Al_2O_3$$

$$Fe_3O_4 + Al \rightarrow Al_2O_3 + Fe$$

④ Auto reduction / Self Reduction

क्या होगा प्रभु

Cu, Hg, Pb → partial Roasting

→ A part of ore converts to oxide then react with remainging sulphide ore to give metal & SO_2.

$$Cu_2S + Cu_2O \longrightarrow \boxed{Cu} + SO_2\uparrow$$

Blister copper
(98% pure)

⑤ Electrolytic Reduction. Highly Reactive metals (alkali + alkaline + Al)

→ Pure metal → cathode

$$(Molten)\ NaCl \longrightarrow \underset{metal}{Na} + Cl_2$$

$$(Molten)\ MgCl_2 \longrightarrow \underset{Metal}{Mg} + Cl_2$$

Cathode

⑥ Hydrometallurgy - Ag, Au (dissolve in suitable reagent then react with more electropositive metal

$$Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + Ag$$

$$Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + Au$$

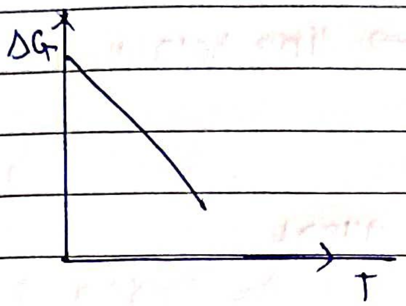
* Thermodynamic principle of metallurgy

Ellingham diagram

→ plot betn ΔG & Temp $\quad y = c - xm$

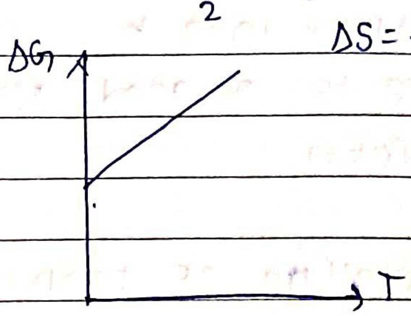
$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ $\quad \Delta G = \Delta H - T\Delta S$

$\Delta S = +ve$



$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$

$\Delta S = -ve$



$Cu(g) + O_2(g) \rightarrow Cu_2O(s)$ $\Delta S = -ve$

$Fe(s) + O_2(g) \rightarrow FeO(s)$ $\Delta S = -ve$

$Cu(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta S = 0$

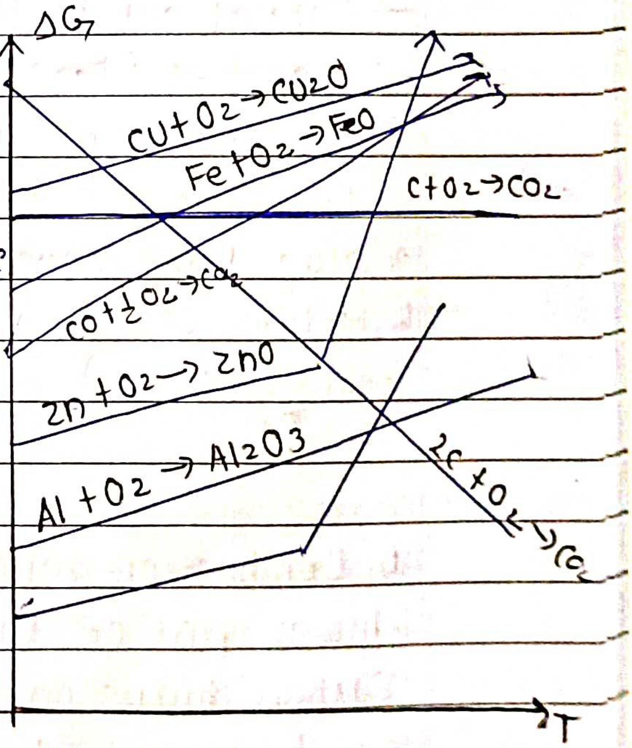
$CO(g) + \frac{1}{2} O_2 \rightarrow CO_2(g)$ $\Delta S = -ve$

$Zn + O_2 \rightarrow ZnO(s)$ $\Delta S = -ve$

$C + O_2 \rightarrow 2CO(s)$ $\Delta S = +ve$

$\frac{4}{3} Al + O_2 \rightarrow \frac{2}{3} Al_2O_3$ $\Delta S = -ve$

$Mg + O_2 \rightarrow MgO$ $\Delta S = -ve$



Imp point

→ Lower line metal reduces upper line metal oxides
(metal having more negative ΔG) (having less negative ΔG)

→ Sharp turn in Ellingham diagram → melting point of metal

In Ellingham diagram

Below 1073 k

'CO' is reducing agent for $Fe + O_2 \rightarrow FeO$

$C + \frac{1}{2} O_2 \rightarrow CO$ → line above

$CO + \frac{1}{2} O_2 \rightarrow CO_2$ → line below.

After 1073 k

C is a good reducing agent

(Coke)

* Smelting of Iron.

→ Carried out in blast Furnace

→ Charge → $[Fe_2O_3 + C] - CaCO_3$

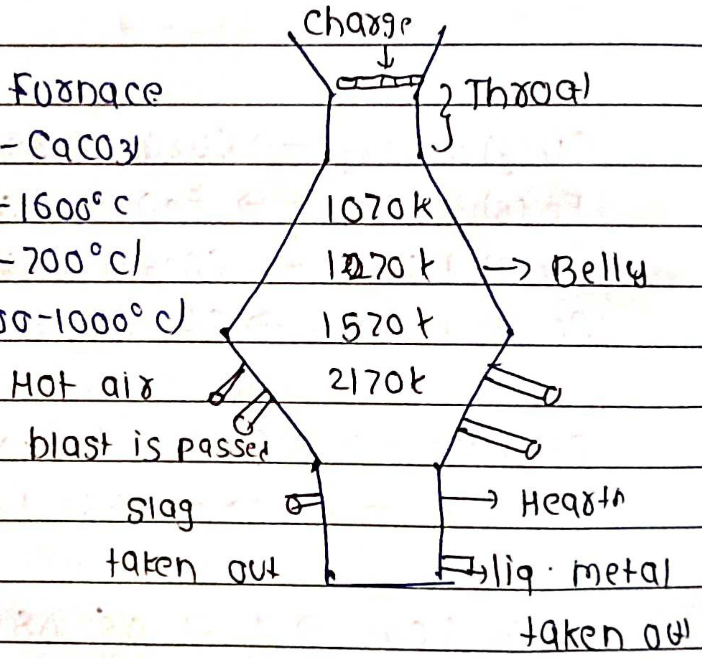
1) Combustion zone- 1500-1600°c

2) Reduction zone (250-700°c)

3) slag formn zone (800-1000°c)

4) Melting zone

(1200-1500°c)



1) Combustion zone

lower part of furnace

carbon burns in presence of hot air

$C + O_2 \longrightarrow CO_2$ heat

CO_2 rises in furnace & it is reduced to CO with red hot coke

$CO_2 + C \Rightarrow CO$

2) Reduction zone- uppermost part in furnace

metaloxide → metal

$Fe_2O_3 + CO \longrightarrow Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \longrightarrow FeO + CO_2$

$FeO + CO \longrightarrow Fe + CO_2 \longrightarrow$ below 1073 K

$FeO + C \longrightarrow Fe + CO \longrightarrow$ above 1073 K

→ Iron formed is spongy iron

3) Slag formation zone- central part of furnace

$CaCO_3 \xrightarrow{\Delta} \underset{\text{basic}}{CaO} + CO_2$

$CaO + SiO_2 \longrightarrow CaSiO_3$

4) Melting zone- above combustion zone.

spongy iron → 1300°C → molten iron

Iron obtained → Pig Iron → 4% carbon

↳ impurities → S, P, Si, Mn

↳ not of any industrial use

↓

Cast Iron — melting pig iron with scrap iron

carbon 3%

↓ Oxidizing impurities in Reverbaratory Furnace

Lining with Fe_2O_3

↓

$Fe_2O_3 + C \rightarrow Fe + CO$

wrought iron

(purest form of iron

Extraction of Cu from copper oxide.

$Cu + O_2 \longrightarrow Cu_2O$ (Top of Ellingham diagram)

So, oxides of copper can easily reduced by heating with C.

$\left.\begin{array}{l} C \rightarrow CO \\ CO \rightarrow CO_2 \end{array}\right\}$ Lines are below $Cu + O_2 \rightarrow Cu_2O$ line So, easily reduce

Copper → mainore → $CuFeS_2$

Concentration → Froth floatation

Step 2 → Roasting (Reverberatory Furnace)

$$CuFeS_2 \longrightarrow \underbrace{\boxed{Cu_2S + FeS}}_{\text{Copper matte}} + \overset{\curvearrowright \text{Basic} + SiO_2 \rightarrow \underset{(\text{slag})}{FeSiO_3}}{FeO} + SO_2$$

copper matter is transferred in bessemer convertor

↳ (Silica is added & blast of air)

Partial Roasting

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

$Cu_2S + Cu_2O \longrightarrow Cu + SO_2\uparrow$

Blister copper

98% pure

Extraction of zinc from zinc blend (ZnS)

① Froth floatation

② Roasting $ZnS + O_2 \longrightarrow ZnO + SO_2\uparrow$

This 'ZnO' is mixed with coke & clay & brickets are formed

heat ↓ $\boxed{Zn}$

$ZnO + C \xrightarrow{1673K} Zn + CO\uparrow$

Electrochemical principles of metallurgy

→ Electrolysis → molten salt

→ cations are collected at cathode

$\underset{(\text{molten})}{NaCl} \longrightarrow \underset{\text{cathode}}{Na} + Cl_2$

Extraction of Aluminium from Alumina

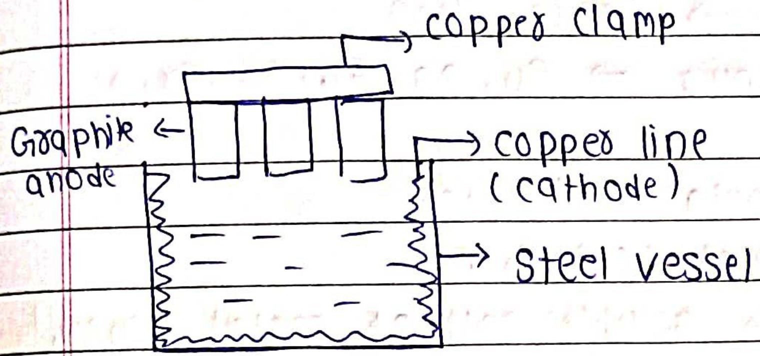
→ Al_2O_3 is mixed with $\underbrace{Na_3AlF_6,\ CaF_2}$ & heated.

→ ↓ MP of mixture (2000°c - 900°c)

↑ conductivity

↗ cathode

molten Al_2O_3 is taken in steel vessel lined with carbon and graphite rod act as anode



$Al_2O_3 + C \rightarrow Al + CO_2$ ↓ Hall Heroult process

During Reduction of Al_2O_3 → carbon forms CO & CO_2 (graphite rod burns out)

Cathode → $Al^{+3} + 3e^- \rightarrow Al\ (s)$

Anode → $C + O \rightarrow CO$

$C + O \rightarrow CO_2$

Extraction of Cu from low grade ore

→ Hydrometallurgy

→ Leaching - bacteria & acid.

Oxidation / Reduction

→ Some metallurgy also involves oxidation

eg- chlorine gas from Brine soln

Molten NaC $\xrightarrow{\text{electrolysis}}$ $Na + Cl_2$

eg. $Au^{0} + NaCN + O_2 + H_2O \longrightarrow Na[Au^{+1}(CN)_2]$

$Ag + NaCN + O_2 + H_2O \longrightarrow Na[Ag^{+1}(CN)_2]$

Refining

1) Distillation → low B.P → Cd, Zn, Hg

2) Liquation → impurity - High MP → Sn, Pb, Bi

3) Cupellation → Noble metals → Ag, Au, Pt

4) Polling → Cu, Sn → from SnO_2

→ from Cu_2O

5) Electrolytic Refining → Cu, Ag, Au, Ni, Cr, Al

Anode → impure metal (Cu) thick

Cathode → pure metal (Cu) thin

Electrolyte soln → soluble salt of metal ($CuSO_4$)

Cathode - $Cu^{+2} + 2e^- \rightarrow Cu$

Anode - $Cu \rightarrow Cu^{+2} + 2e^-$

Electric current pass → metal ion from electrolyte is deposited at cathode

→ Some amount of metal breaks from anode & goes into

→ After some time → anode - gets finished

impurities → collected as $\boxed{\text{anode mud}}$

antimony
selenium
tellurium
Silver
Gold
Platinum

Zone Refining - diff in solubility of impurity in molten state & solid state

↓

Highly pure metal is required → Semiconductor - Si, Ge, B, Ga, In

Vapour phase Refining

Van-Arkel method → Ultra pure metal (Ti, Zr)

$$Zr + 2I_2 \longrightarrow ZrI_4 \xrightarrow{Heat} Zr + 2I_2$$

Mond's process - MO · Ni, CO

$$Ni + 4CO \longrightarrow \underset{Volatile}{Ni(CO)_4} \xrightarrow{\Delta} Ni + 4CO$$

Chromatography principle.
different component of a mixture are differently adsorbed on adsorbent.

Column chromatography - used for elements present in minute quantity.

Lanthanides - purity - ion exchange as adsorbent.