Principles of Extractive Metallurgy

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Learning objectives of the course

➢ **Knowledge of various techniques, unit process and operations used in metal extraction and refining.**

➢ **To apply the fundamental knowledge for design of a reactor and process flow sheets.**

➢ **To develop computational and mathematical abilities to be applied for process design and control. It may be C++, MATLAB, Excel-Solver, FlowBal, FactSage or any other language of interest.**

➢ **To be able to select the correct process routes, reactors and be able to optimize and control them.**

➢ **To develop the leaders for coming future who are able to bring new and economic technologies for metal extraction.**

➢ **Text books:**
1. **Principles of Extractive Metallurgy, Terkel Rosenqvist, McGraw-Hill Book Company**
2. **Principles of Extractive Metallurgy, H. S. Ray and A. Ghosh, WEL Publishing**
3. **Extractive Metallurgy of Copper, W.G. Davenport, A.K. Biswas, PERGAMON publishing company**
4. **Handbook of Extractive Metallurgy: Fathi Habashi; Wiley-VCH**

➢ **Marks distribution (All exam problems will be computational in nature)**
1. **Quiz 1: 10%**
2. **Quiz 2: 10%**
3. **Assignments: 20%**
4. **Term project: 10%**
5. **Final Exam: 50%**

➢ **Assignments**

One every week. Students may use computer coding/techniques to solve them. It is advised to solve the assignment problems by their own if want to perform well in exams.

➢ **Attendance**

**There is no weightage for the attendance.**

Since the course involves a lot of computational work and fundamental understanding about various principles which would be difficult to understand for those who miss the classes. It would be in the interest of the all the students to attend all the classes if they want to score enough to pass the course.

What is Extractive Metallurgy ?

➢ **Deals with extraction of metals from its naturally existing ore/minerals and refining them**

➢ **Minerals: Inorganic compounds with more than one metal in association with non-metals like S,O,N etc.**

➢ **Naturally existing minerals are sulphides, oxides, halides like: Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Chalcopyrite ($CuFeS_2$), Dolomite ($CaCO_3.MgCO_3$) ..list is endless.**

➢ **What are the sources of metals ?**

➢ **Earth Crust (Aluminum: 8.1%, Iron 5.1%, Calcium: 3.6%, Sodium: 2.8%, Potassium: 2.6%, Magnesium: 2.1%, Titanium: 2.1%, Manganese: 0.10%)**

➢ **Ocean water: (Na: 10500 g/ton, Mg: 1270 g/ton, Ca: 400 g/ton, K: 380 g/ton) ; Ocean nodules (Mn: 23.86%, Mg 1.66%, Al 2.86%, Fe 13.80%..)**

➢ **Recycled scrap (at the end of metals' life)**

Resources of metal containing minerals in India

- **Abundant**: Al, Be, Cr, Fe, Mn, Mg, Ti, Zr, Th, Pb and Zn, raw earth metals

- **Very small**: Co, Ni,Cu,Sn, Au, V, Ni, Cd and U.

- **Poor or not found**: Sb, Bi, Co, Hg, Mo, Nb, Ta, Sr, Se, Ag, W, Pt
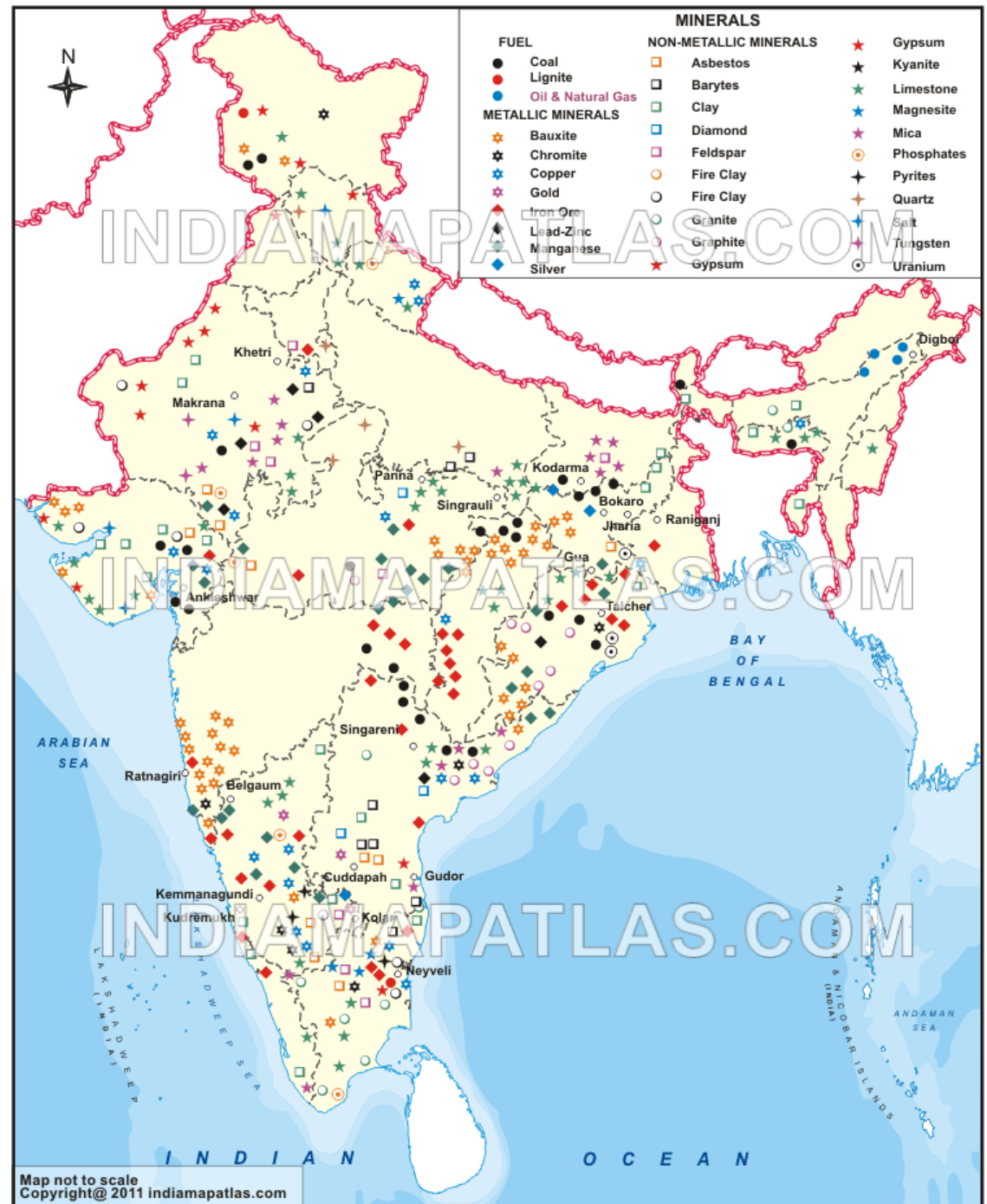
Mineral Map of
THE WORLD

N

LEGEND

⋰	Uranium
●	Silver
▣	Oil
▲	Lead & Zinc
○	Iron
◆	Diamond
✳	Bauxite
◎	Coal
⊢•	Copper
$	Gold

0   1800km

Types of ores

- Oxide ores: Examples: Fe2O3, Fe3O4

  Apart from Fe, other heavy metals which are produced from oxide ores are:

  Manganese, Chromium, Titanium, Tungston, uranium and Tin.

- Sulphide ores: Copper ore (CuFeS2, Chalcopyrite), sphalerite (Zn,Fe)S, Galena PbS, Pyrite FeS2.

  Others: Nickel, Zinc,Mercury and Molybdenum

- Halide ores: Rock salts of Sodium, Magnesium chloride in sea water

Commercial production of metals

- Availability of ore deposits
- Concentration of metal in the ore
- Availability of technology of extraction and refining of that metal
- Physical and chemical properties of the metal
- Market demand of that metal

- **Economy of the process:** Readily available, Easily produced and available at low processing cost with desired properties

Some interesting facts…

- The first metal produced was copper and bronze, produced by smelting copper and tin ores in charcoal fire.
- World production (yearly) Steel: 1400 MT, Aluminum: 40 MT, Copper: 17 MT, Lead: 8 MT, Ni: 2 MT, Magnesium: 1 MT, Ti: 0.15 MT
- Steel is the highly consumed material and its per capita consumption is the index of economic prosperity of any nation.
- Growth rate of metal production was highest during 1950-1970.
- China exhibited very high growth rate in last ten years (182 MT in 2002 to 700 MT in 2011)

Unit processes and Unit operations

- Any metal extraction process is the combination of similar and unique kind of steps known as Unit processes/unit operations.
- Unit operations: Physical operations like crushing, grinding, sizing, mixing through agitation, filteration, distillation, comminution
- Unit processes: Chemical processes like leaching, smelting, roasting,Electrolysis, decarburization, Dephosphorization, Degassing, Deoxidation etc.
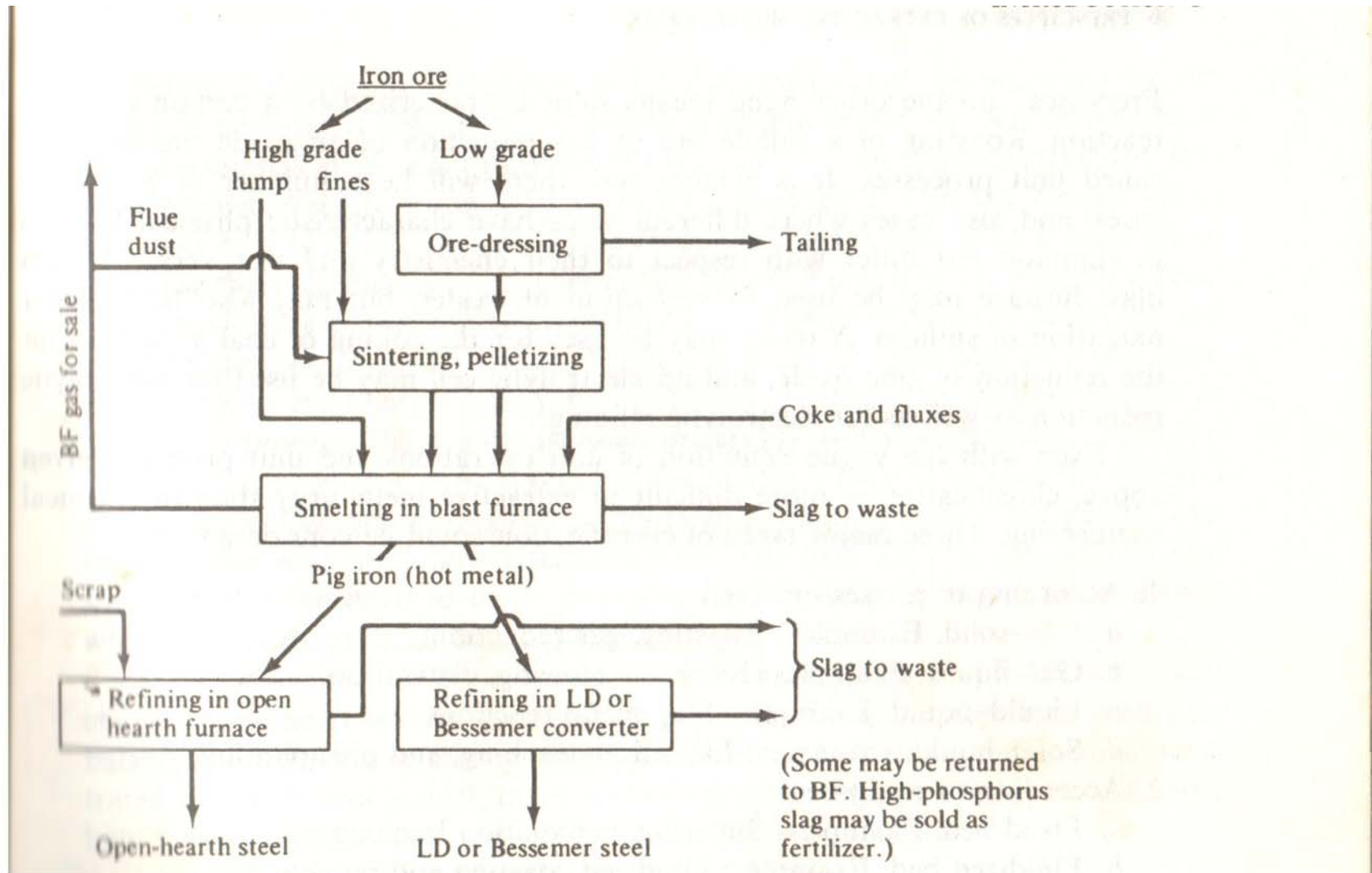
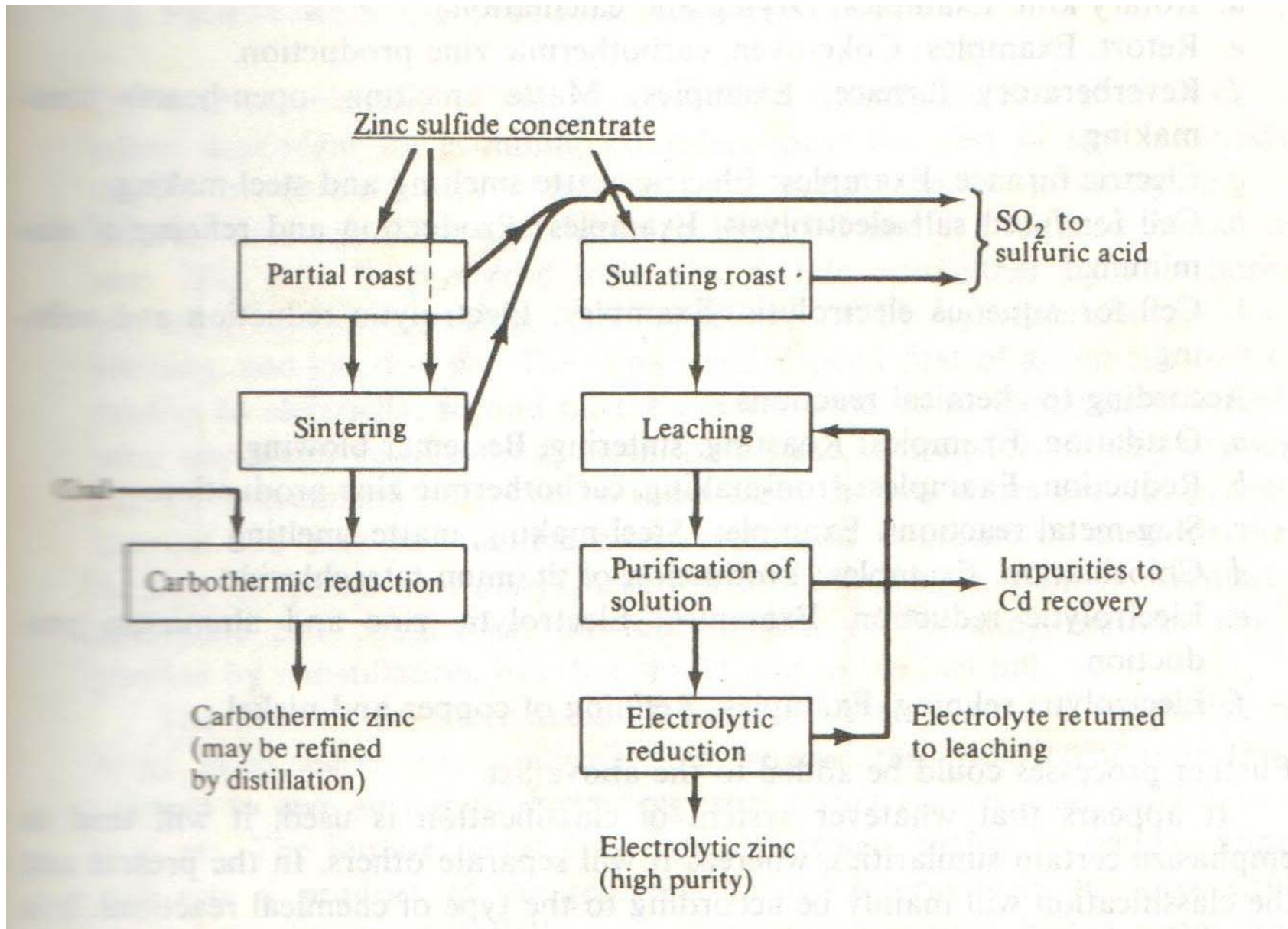**Combination of all unit steps/processes are resulting in Flow-Sheets**
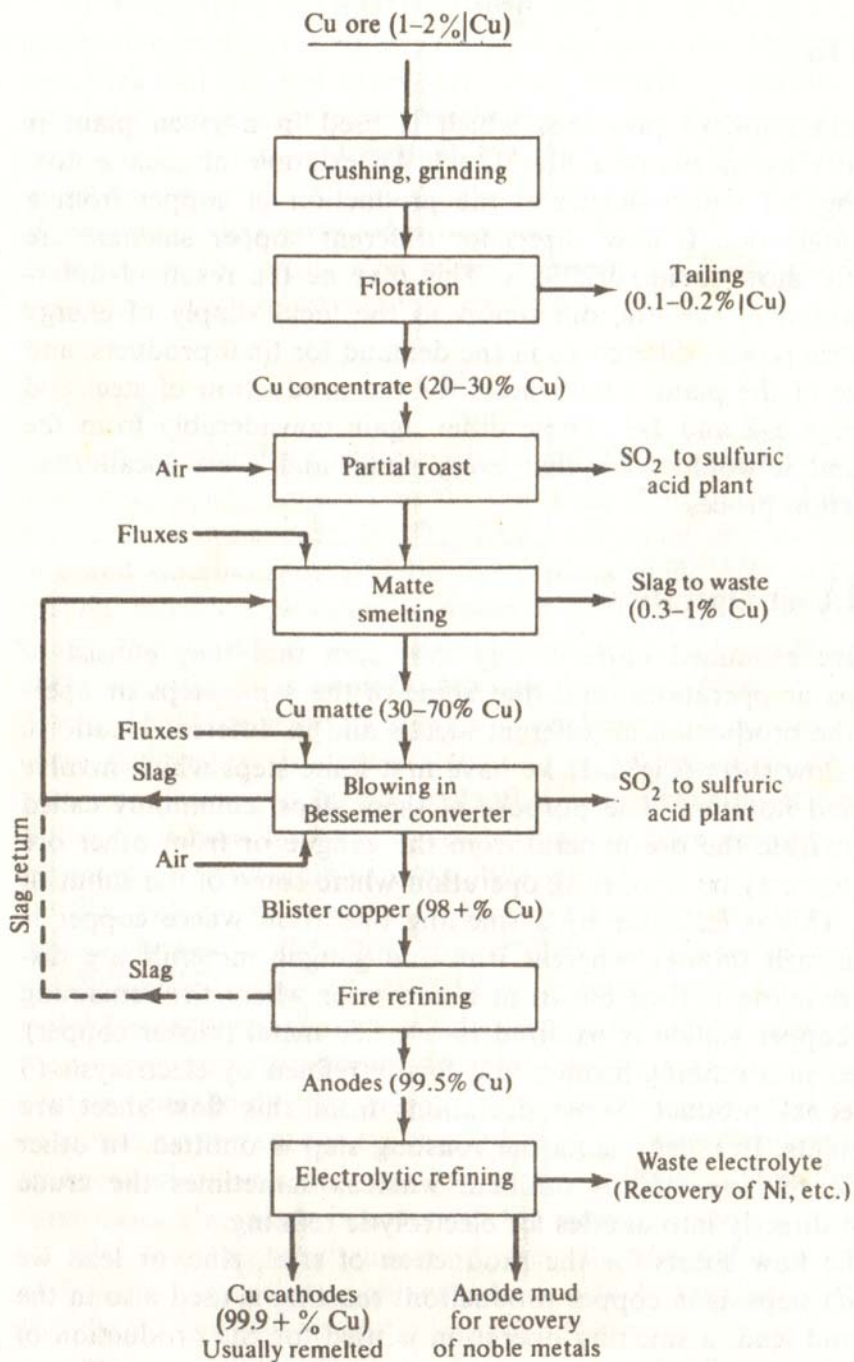
Flow sheet for copper extraction process

➢ Crushing, Grinding, Floatation are unit processes

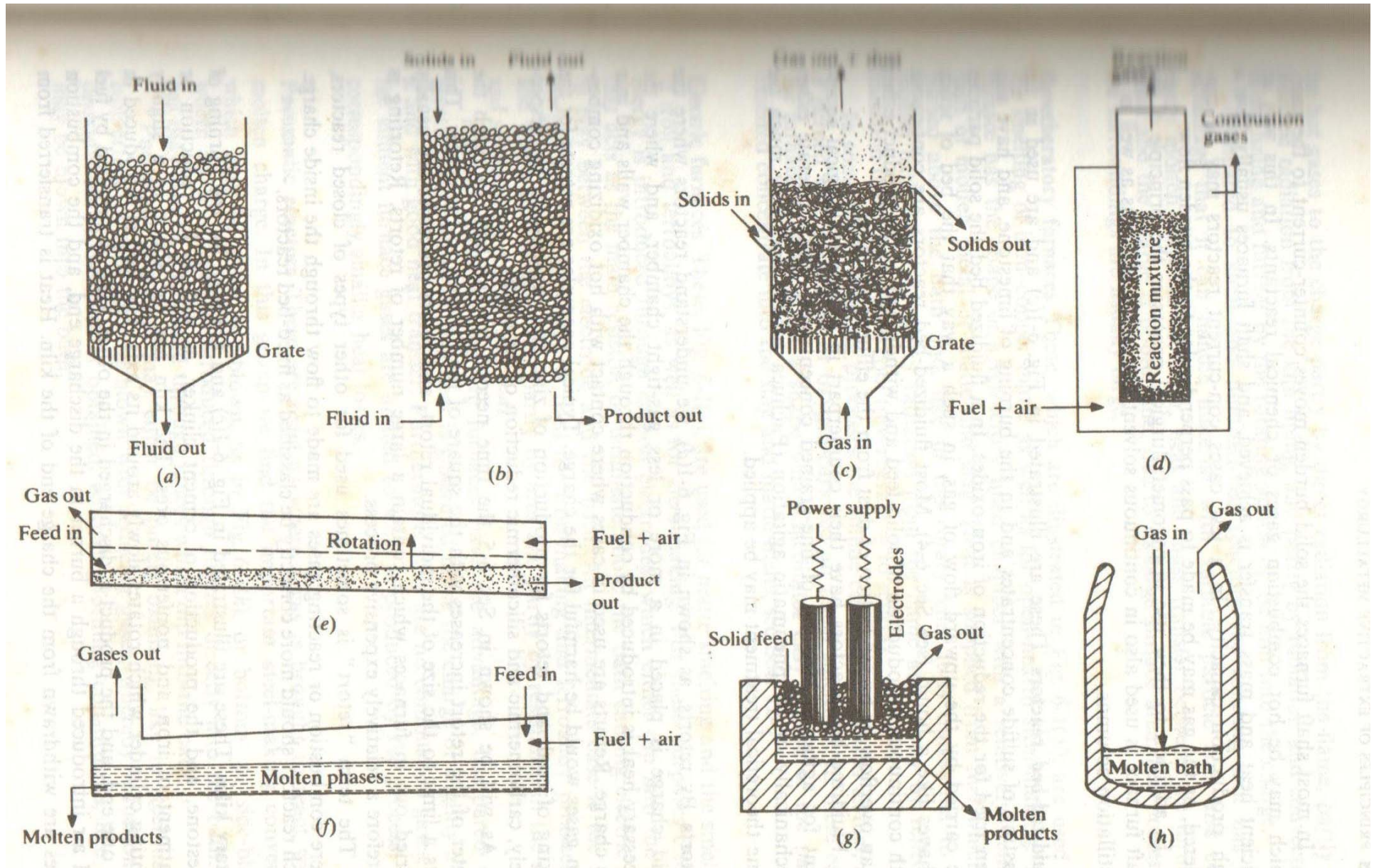➢ Roasting, smelting, Blowing, Refining, Electrolysis are Unit processes

Flow sheet for iron and steel extraction process

Flow sheet for Zinc extraction process

Various reactors: a) Fixed bed reactor b) Shaft furnace c) Fluidized bed d) Retort e) Rotary kiln f) Reverberatory furnace g) Electric arc furnace h) Pneumatic/top blown converter

(a) Fluid in, Grate, Fluid out

(b) Solids in, Fluid out, Fluid in, Product out

(c) Hot out, Solids in, Solids out, Grate, Gas in

(d) Reaction mixture, Combustion gases, Fuel + air

(e) Gas out, Feed in, Rotation, Fuel + air, Product out

(f) Gases out, Feed in, Fuel + air, Molten phases, Molten products

(g) Power supply, Electrodes, Solid feed, Gas out, Molten products

(h) Gas out, Gas in, Molten bath

Classification of unit processes/ operation by different criteria

➤ **According to phases involved:**
- **Gas-Solid:** Roasting, Gas reduction
- **Gas-liquid:** steelmaking blowing/refining, Distillation
- **Liquid-Liquid:** Slag metal reactions
- **Solid-solid:** Leaching, precipitation etc.

➤ **According to equipments involved:**
- **Fixed bed:** Sintering, percolation leaching
- **Fluidized bed:** Fluidized roasting and reduction
- **Shaft furnace:** Iron blast furnace, lime calcination kiln
- **Rotary kiln:** Drying and calcination
- **Ritort:** Coke open, carbothermic zinc production, Mg production by pidgeon
- **Reverberatory furnace:** Matte smelting (Cu etc.), open hearth steelmaking
- **Electric arc furnace:** Steelmaking, matte smelting, ferro alloy production
- **Cell for salt fuse electrolysis:** Production and refining of aluminium
- **Cell for aqueous electrolysis:** Electrolytic reduction and refining

➢ **Classification according to chemical reactions:**

- Oxidation: Roasting, sintering, LD steelmaking
- Reduction: Blast furnace ironmaking
- Slag metal reactions: Steelmaking, matte smelting
- Chlorination: Titanium (converting to tetrachloride)
- Electrolytic reduction: Zinc and Aluminum production
- Electrolyte refining: Refining of Copper and Nickel

Classification based upon methods of metal extraction

➢ **Physical seperation/Mineral processing**

    The objective is to concentrate the metallic content in the ore, achieved by a series of comminition (crushing and grinding), screening and seperation process

➢ **Pyrometallurgy**

    It involves the smelting, converting and refining of metal concentrate.

➢ **Hydrometallurgy**

    It involoves the precipitation of metal in an aqueous solution.

➢ **Electrometallurgy**

    Electrolysis process to extract metal. Electrowinning: Extraction of the metal from electrolyte; Electrorefining: Refining of impure metals in the form of an anode.

Majority of metals are extracted by pyrometallurgical route because it is fast, easily adaptable and cheaper

Principles you must know ?

- **Heat and mass balance** : to know the material requirement

- **Thermodynamics** : Feasibility criteria

- **Kinetics and rate of process**: How long it take to complete the process

- **Heat transfer**: For improving the thermal efficiency of the process

- **Fluid dynamics**: To know the mixing of the reactor

- **High temperature properties of metals/slag**: To know the physical properties of various phases, their mobility and role in metal refining processes.

- **Electrochemistry**: To estimate, overpotential, current efficiency

- **Hydrometallurgy**: Eh-pH diagram, rate estmation of leaching process

Physical separation/ mineral processing

Comminution process:

Size reduction of mineral

By crushing/grinding

a)Jaw crusher
b)Roll crusher
c)Gyratory crusher
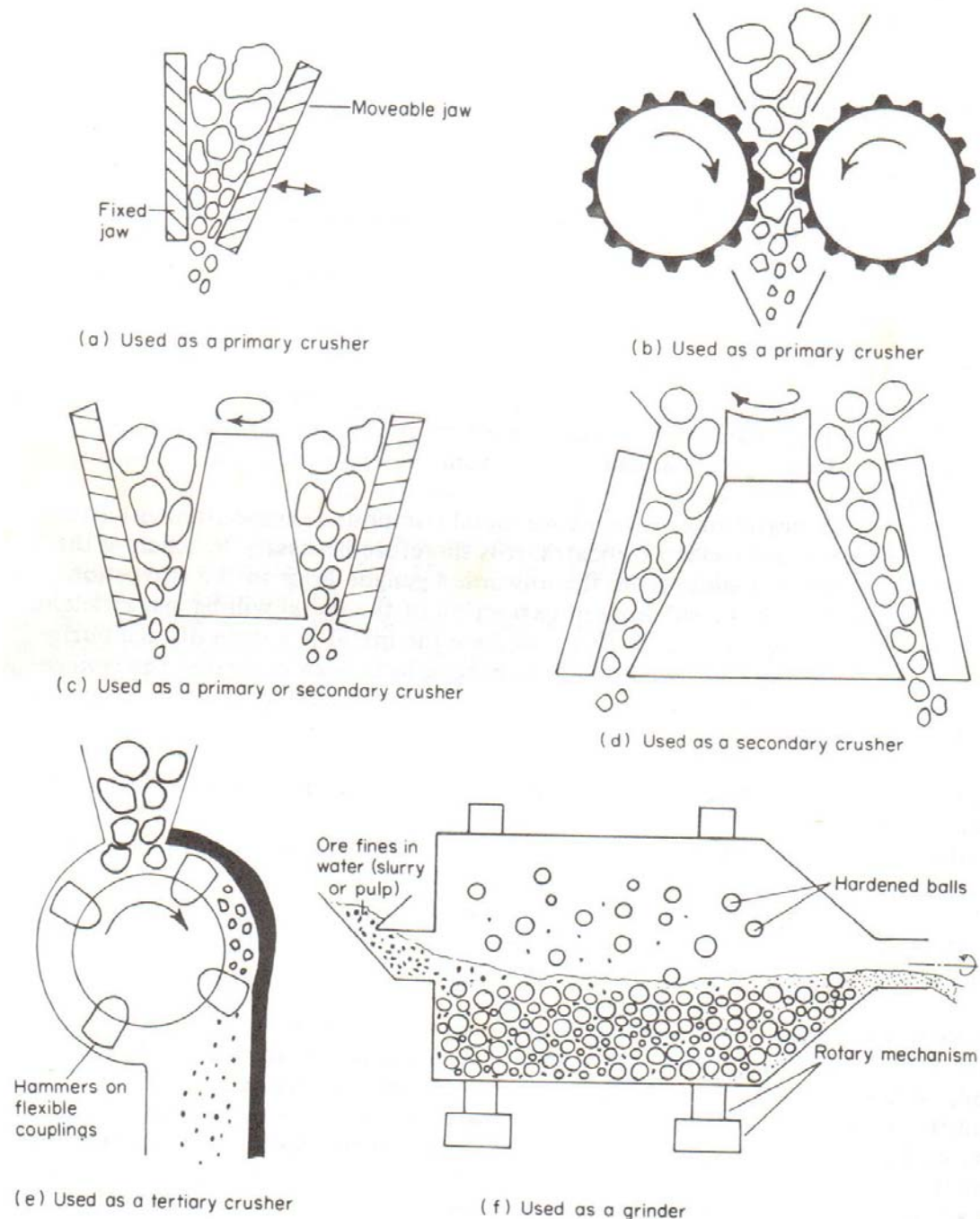**d)Cone crusher**
e)Hammer mill
f)Ball mill

(a) Used as a primary crusher

(b) Used as a primary crusher

(c) Used as a primary or secondary crusher

(d) Used as a secondary crusher

(e) Used as a tertiary crusher

(f) Used as a grinder

Figure 7.1 Diagrams of various comminution

Screening: Sieve analysis

Finer particles are collected in lower boxes

- **Classification process**: Due to different size, shape and densities, materials are classified in fluids/water. It depends upon following factors:
1. Smaller particles fall more slowly in fluids than do larger ones (stokes law)
2. In cyclonic movement (hydrocyclone), centrifugal force have larger influence on larger size particles than smaller ones.
3. Small particles having low intertia behaves like suspended medium.
4. Larger particles require higher velocity for seperation.
Classifiers: 1. simple Box Classifier
2. Bowl/rake clasifier
3. Hydro cyclones

Slurry of ore fines in water

Overflow cointaining the very fine particles and gangue (tailings)

Water pressure control

Coarse particles   Fine particles

(a)

Baffles

Rotating rake ──── Slurry of ore fines in water

Overflow containing fine gange particles (tailings)

Coarse, dense metal-bearing particles

(b)
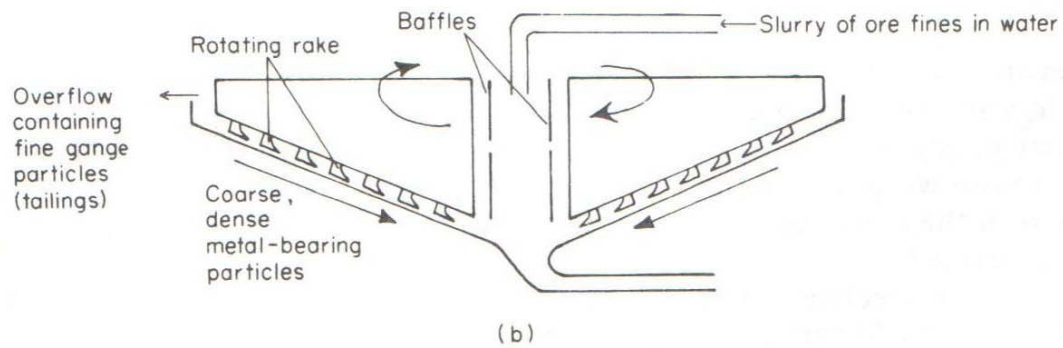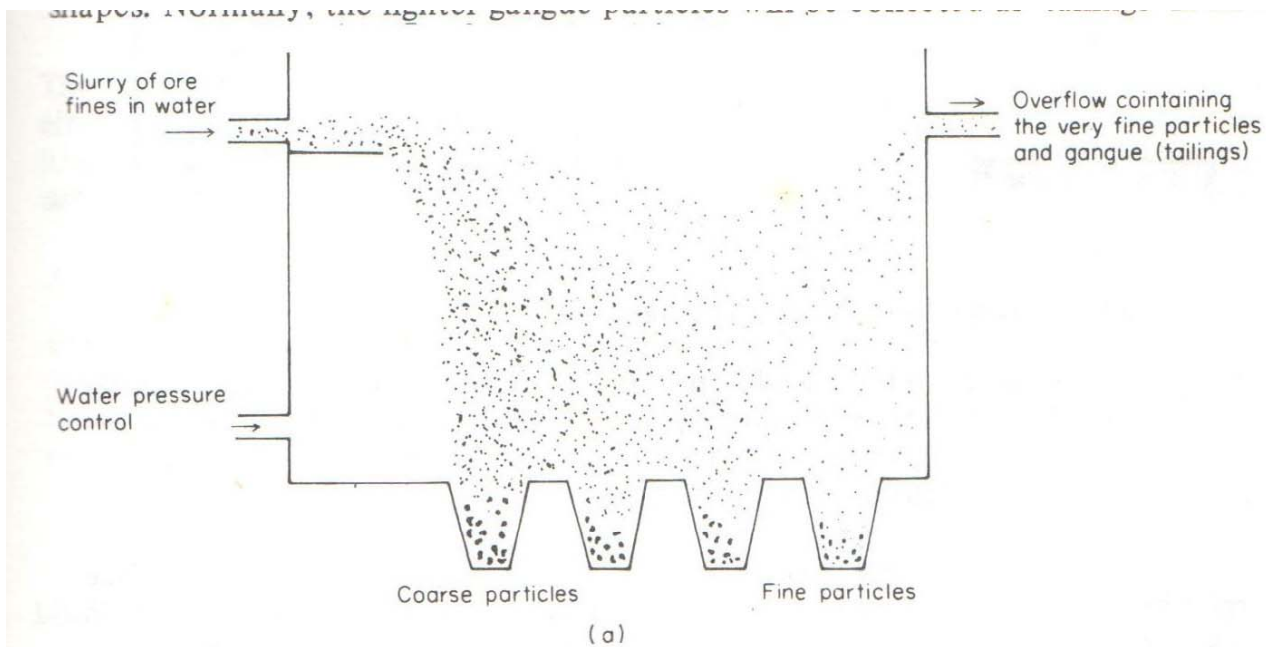
a) Simple sluice box classifier
b) Bowl/rake classifier

Overflow

Feed

Vortex finder

Primary vortex

Secondary vortex

Spigot

Underflow
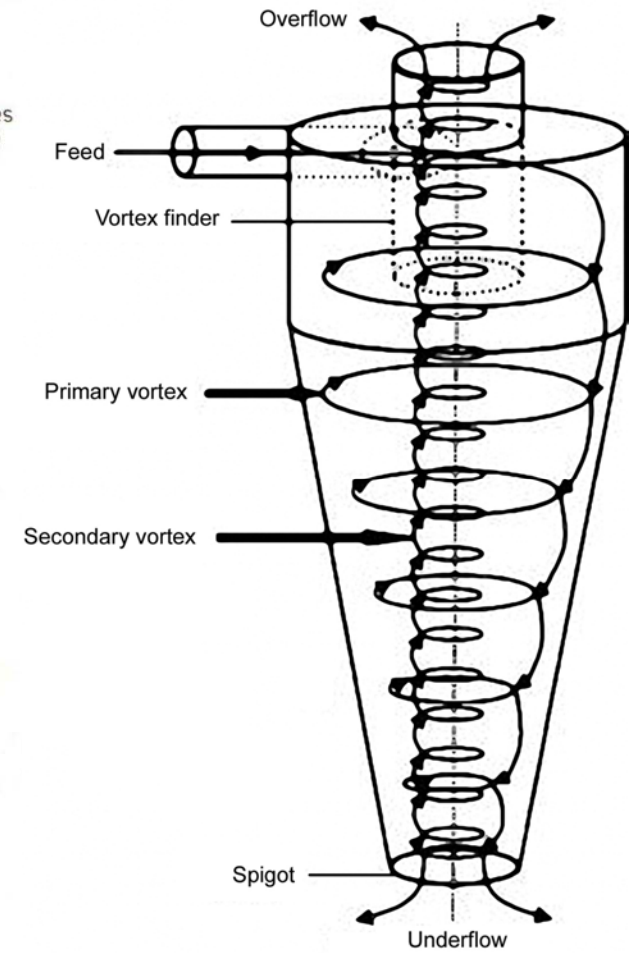
Hydrocyclone

- **Separation process (Froth Floatation)**

  Due to different surface free energies of the different minerals, there is selective adsorption on to the air bubbles

- **Frothers:** To stabilize the air bubbles
- **Collectors:** Selective adsorption by lowering interfacial enegies.
- **Modifying agents:** Intensify the collector performnce

Froth with adhering
metal–bearing particles

Previous cell

Air

Next cell

Scoop

Baffle

Air

Middlings returned
to cell

Middlings (containing metal
fines and gangue fines)

Concentrate

Stirrer

(a)

a) front view b) side view (b)
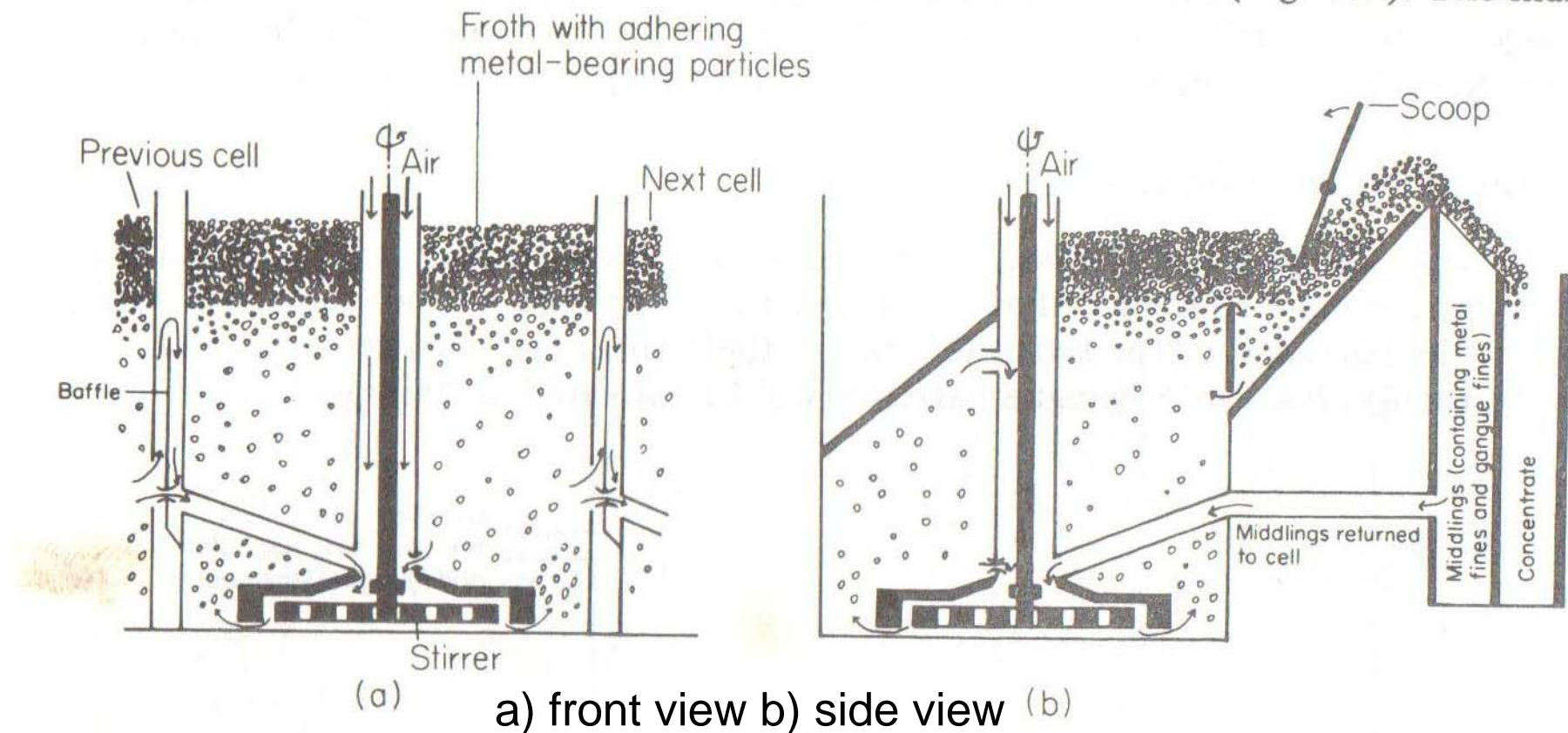
- **Agglomeration process:** Example : Sintering of iron ores)
Moving bed of fine iron ore (<6 mm), mixed with coal fines (5-6%, as a fuel and water (10-12%, for permeability) is ignited for agglomeration of oxide and sulphide fines.

Sinter breaker

Unsintered material

Sintered material

Ignition front

Ignition hood

Ore fines, coal dust and moisture

Roll feeder

Traveling gate

Wind (suction) boxes
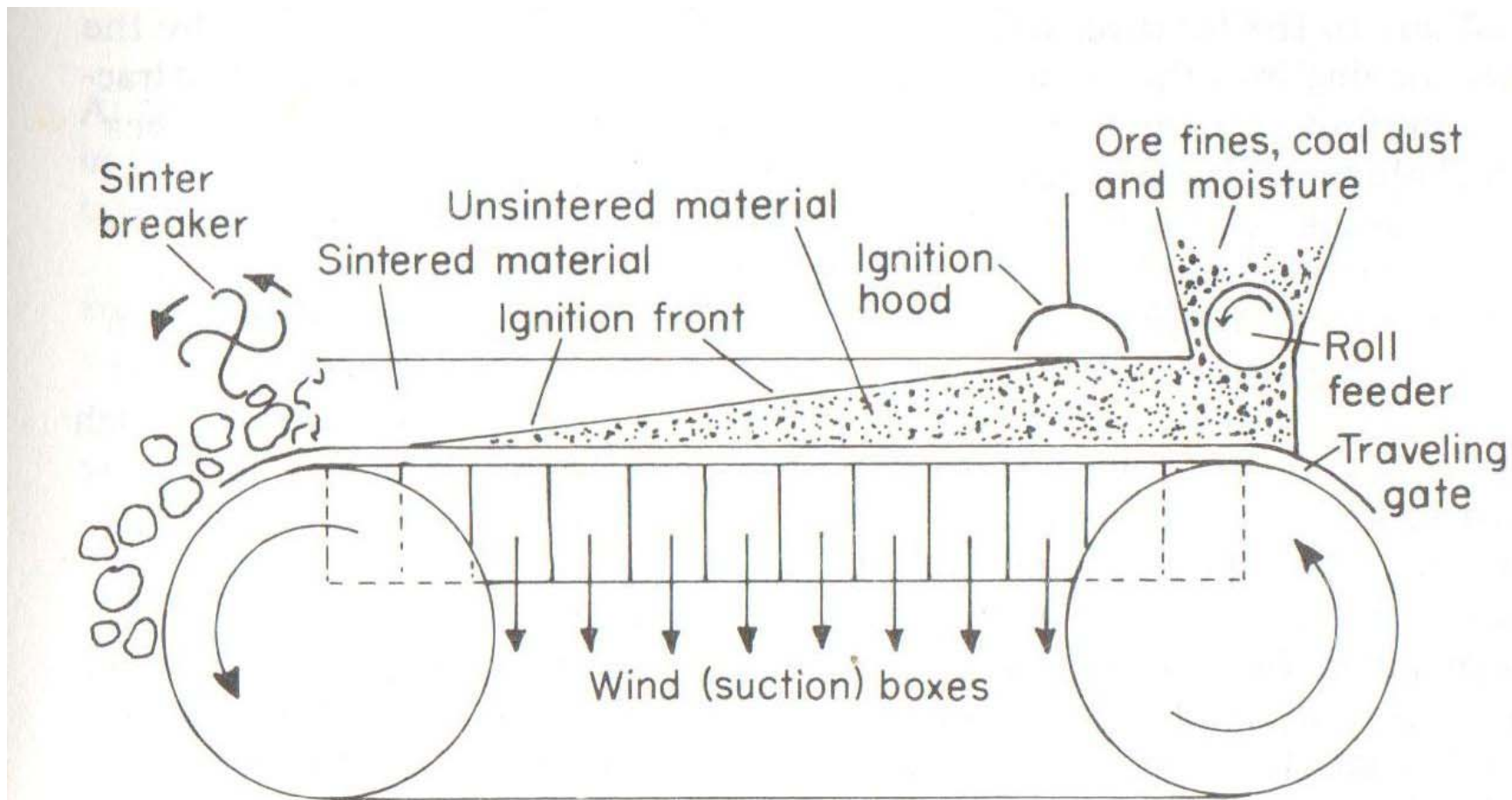
Pyrometallurgy: High temperature processes

- **Calcination:** Thermal treatment of an ore to decompose and eleminate the volatile products (like CO_2, water)

Example: $CaCO_3(s) = CaO\ (s) + CO_2\ (g)$

Feasible tempearture for above reaction is 910 C (at partial pressure of 1 atm.)

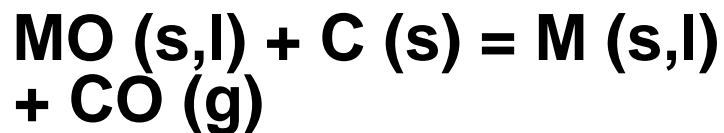Calination temperatures for others:

$MgCO_3$: 417 C, $MnCO_3$: 377 C, $FeCO_3$: 400 C

- **Roasting:** Involves heating of ores below fusion point to in excess of air

- **It is of three types:**

- **Oxidizing roast: to oxidise sulphur in sulphide ores:**

$$PbS + 1.5 O_2 = PbO + SO_2$$
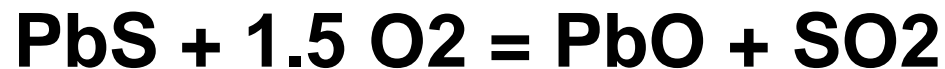
- **Volatilizing roast: To remove volatile oxides like ZnO, As$_2$O$_3$, Sb$_2$O$_3$ etc.**

- **Chloridizing roast: To convert metal compounds to chlorides to be reduced later:**

$$2NaCl (s) + PbS (s) + 2O_2(g) = Na_2SO_4(s) + PbCl_2$$
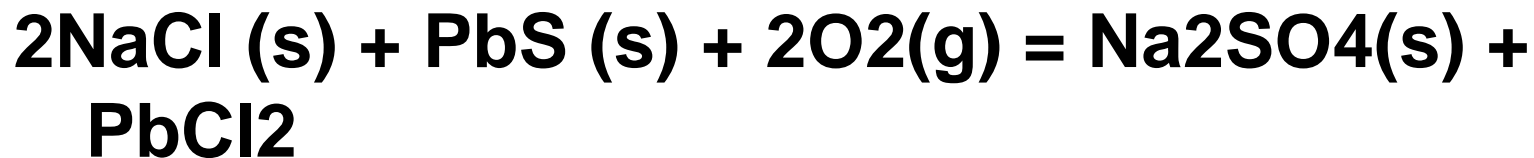
- **Smelting: It is a process for the production of metal/metal rich phase known as 'matte' along with gangue known as 'slag'**

- Reduction of metal oxide ore is done by smelting process:

  MO (s,l) + C (s) = M (s,l) + CO (g)

  MO (s,l) + CO (g) = M (s,l) + CO2 (g)
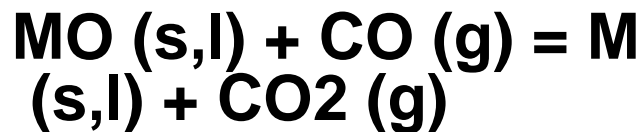
  Example: Blast furnace for ironmaking

Skip car (in dumping position)
Receiving hopper
Revolving distributor
Small bell
Gas seal
Top of lip ring-large bell hopper
Top platform
Uptakes
Skip bridge
Large bell
Throat section
Stock line
Working height and volume
Bend line
Hearth line
Furnace
Inwall
Shell
Belt
Bosh
Hearth
Inwall batter
Bottom inwall line
Bosh line
Bustle pipe
Bosh jacket
Tuyere jacket
Tuyeres
Hearth dia.
Lower hearth wall (Anthracite base Carbon)
Slag notch
Iron notch
Furnace support
Hearth stave
Hearth bottom blocks
Hearth foundation
Hearth jacket
Total volume
Total height

# Carbothermic reduction: Examples: Fe,Sn,Pb,Zn,Ferroalloys

- Carbothermic reduction of iron ore (Hametite) in blast furnace is a well known process. Overall process is written as:

- **Ironore oxide mineral + gangue + Reducer (C) + flux + hot blast oxygen enriched air = Pig iron (liquid) + Slag (liquid) + waste gas (CO,CO2,N2)**

- **Iron ore contains Fe2O3, along with gangue materials such as SiO2, Al2O3.**

- **Charge materials are: Iron ore + limestone (flux) + Coke**

- **Output is**

  pig iron (1300 C), 4.5% C, 0.4-0.6% Si, 0.1-0.2% P, 0.040-0.050% S, 0.1-0.5% Mn

  Slag: CaO/SiO2 = 1.1; CaO = 30-40%; Al2O3 = 10-23%; FeO <1%; MgO <8%

  Waste Gas: CO = 20-25%, CO2 = 20-25%, rest N2
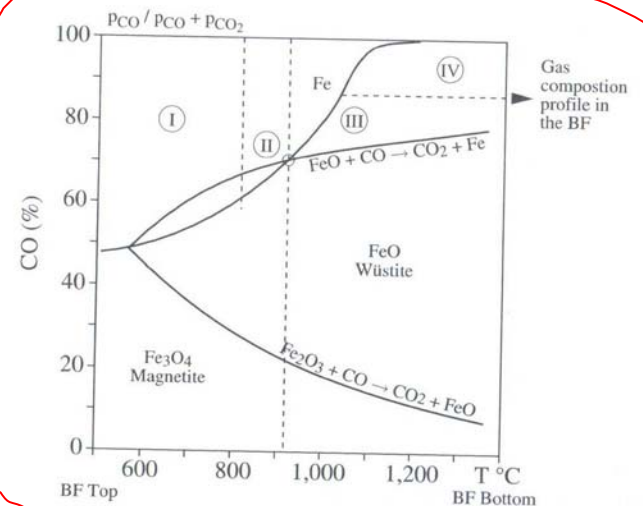
Blast furnace layout with auxillary equipments
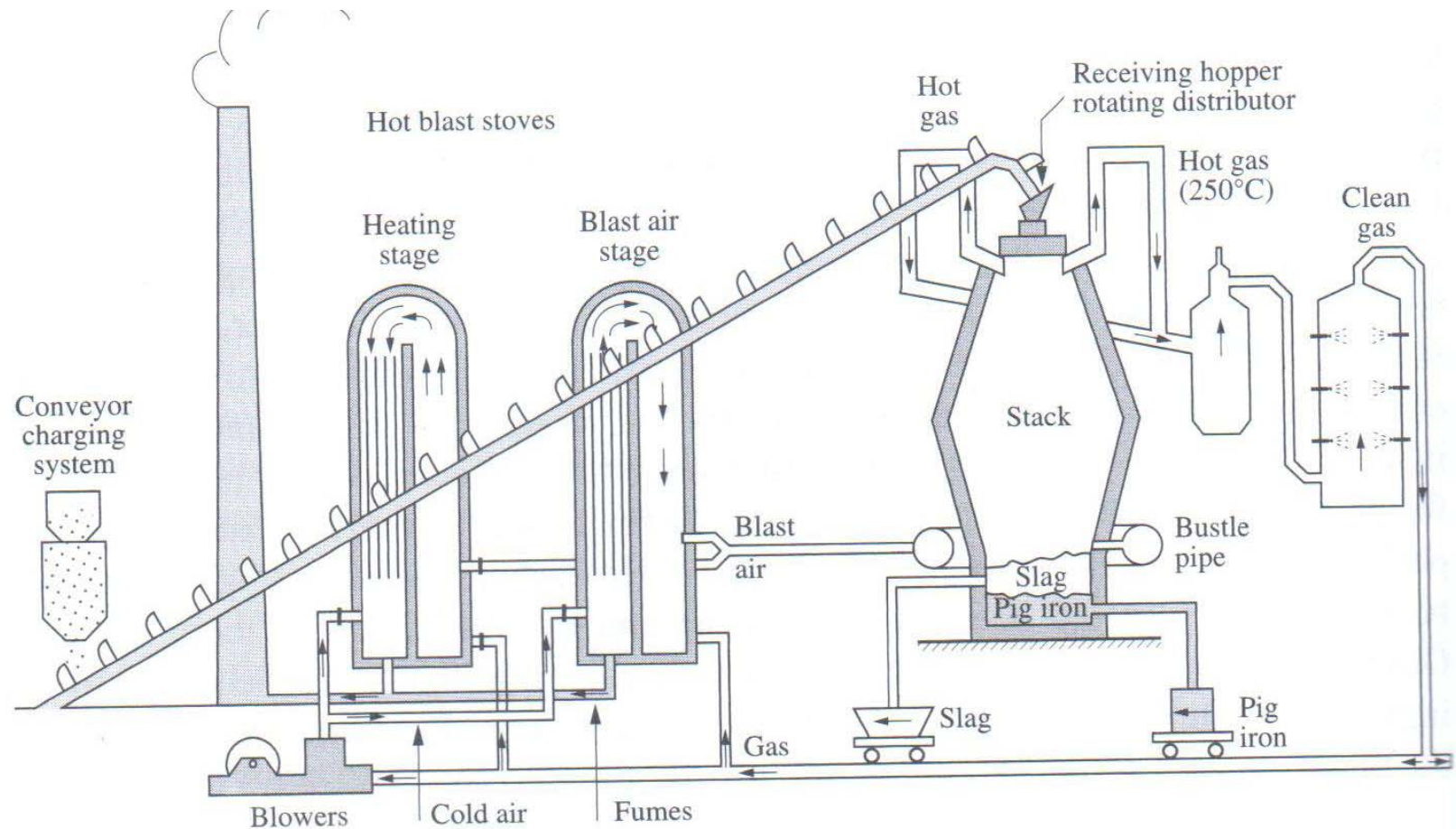
Reaction zones in a blast furnace
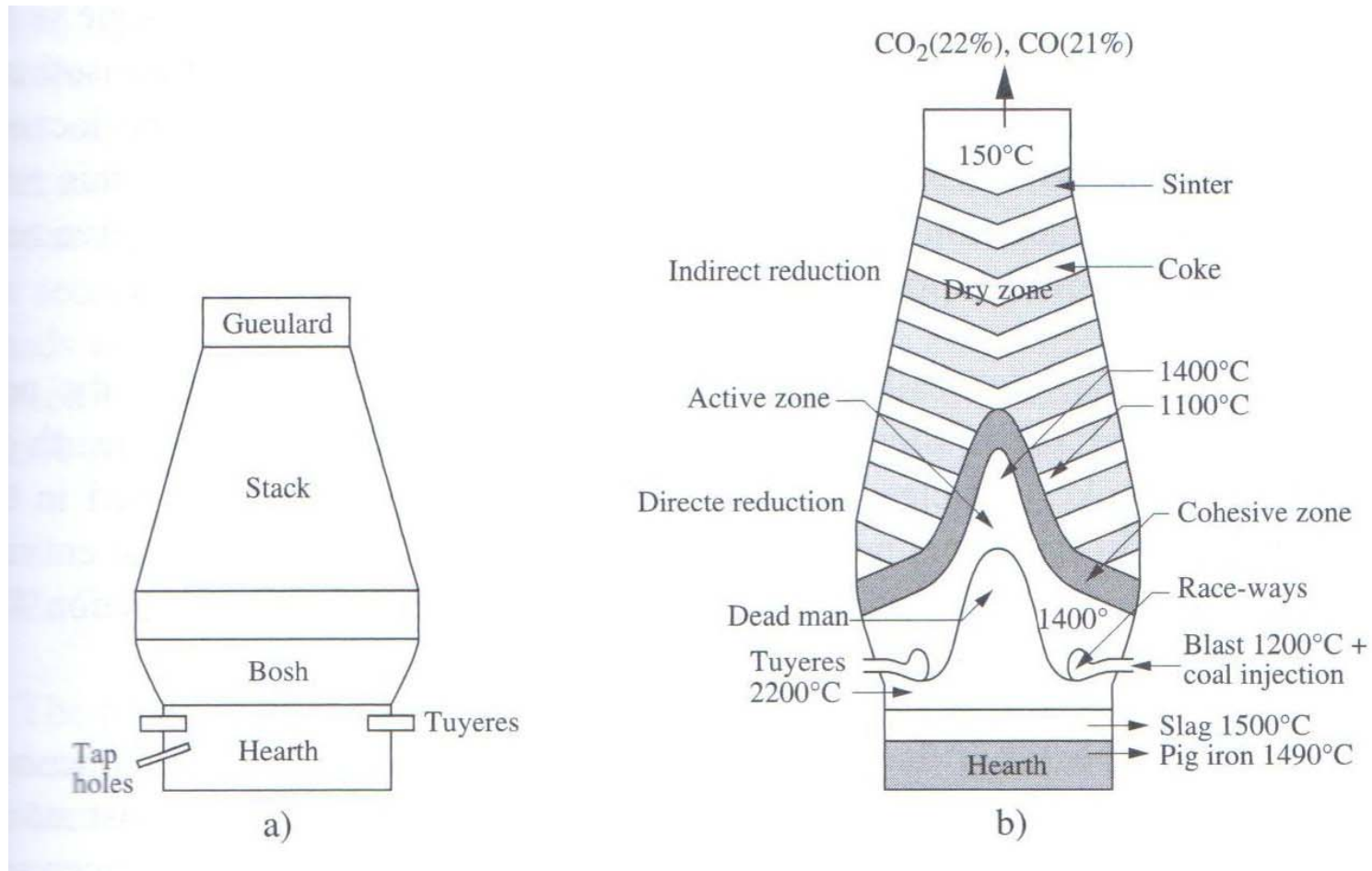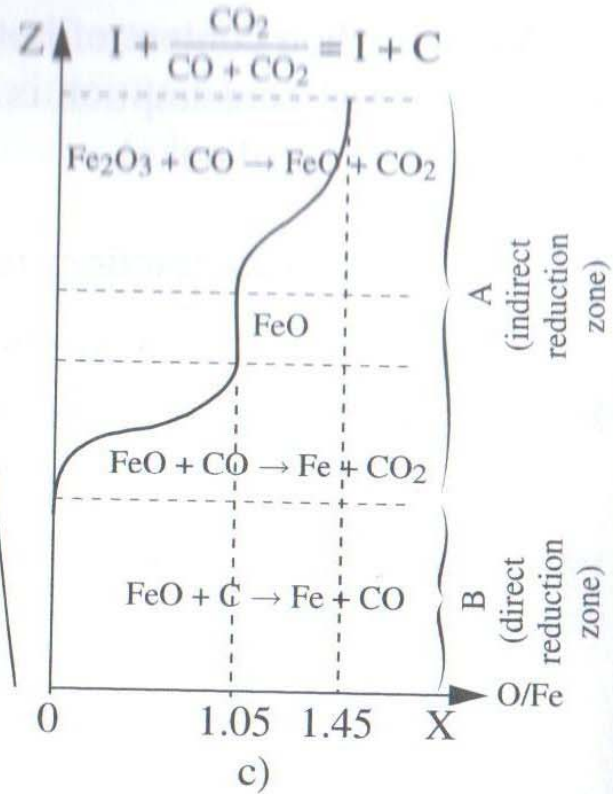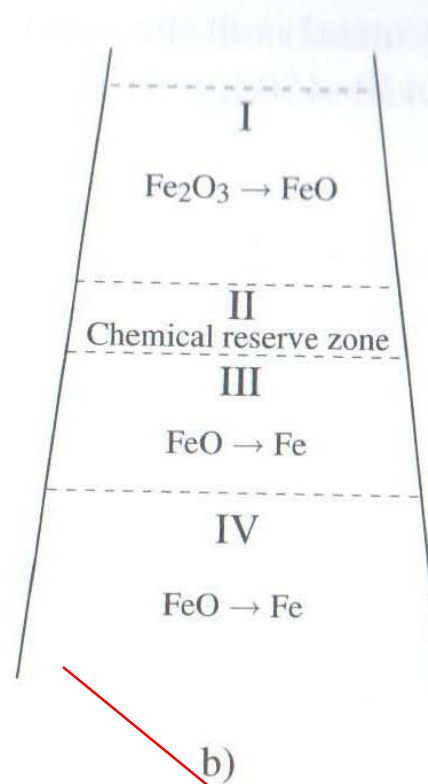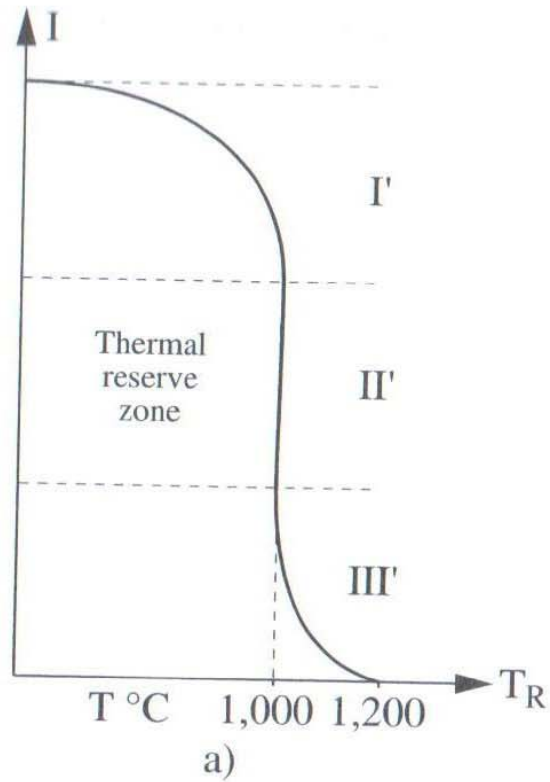
a) Gas temperature along stack along stack
b) Reduction zones along stack
c) Carbon reduction degree (O/Fe) with stack height

Figure a) — Gas temperature along stack:

Thermal reserve zone

I'
II'
III'

T °C   1,000 1,200 T_R

Figure b) — Reduction zones along stack:

I $Fe_2O_3 \rightarrow FeO$

II   Chemical reserve zone
III $FeO \rightarrow Fe$

IV $FeO \rightarrow Fe$

Figure c) — Carbon reduction degree:

$$Z \quad I + \frac{CO_2}{CO + CO_2} = I + C$$

$Fe_2O_3 + CO \rightarrow FeO + CO_2$

FeO

$FeO + CO \rightarrow Fe + CO_2$

$FeO + C \rightarrow Fe + CO$

A (indirect reduction zone)

B (direct reduction zone)

0   1.05 1.45   X   O/Fe

Gas composition profile in the BF:

$P_{CO} / P_{CO} + P_{CO_2}$

100

Fe   (IV)

80   (I)   (II)   (III)

$FeO + CO \rightarrow CO_2 + Fe$

60

FeO Wüstite

40

20   Fe_3O_4 Magnetite $Fe_2O_3 + CO \rightarrow CO_2 + FeO$

0

CO (%)

600   800   1,000   1,200   T °C
BF Top   BF Bottom

Gas compostion profile in the BF

Chemical reactions in a blast furnace

➢ **Zone 1 (<950 C),upper zone of stack, reduction of Fe2O3,Fe3O3 takes place:**
  3Fe2O3(s) + CO → 2Fe3O4(s) + CO2
  Fe3O4(s)+CO → 3FeO(s) + CO2

➢ **Zone 2 (950-1000 C), chemical reserve zone, FeO is in equilibrium with gaseous phase:**
  FeO(s) + CO = Fe(s) + CO2
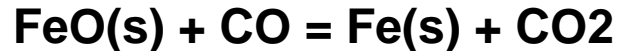
➢ **Zone 3: (950<T<1050 C), the reduction of FeO by rising CO gas takes place:**
  FeO(s)+CO→Fe + CO2
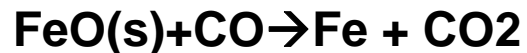
➢ **Zone 4: (>1000-1050C), direct reduction of FeO to carbon takes place.**
➢ **Reaction in raceway zone: C+ O2 → CO2**
  followed by   CO2 + C→ 2CO   (Boudward reaction)
  Overall   C + O2 = 2CO
Boudward reaction is thermodynamically feasible at T >1050 (below zone 4). It supports the conversion of CO2 to CO in raceway and bosh region where T>1050 C.
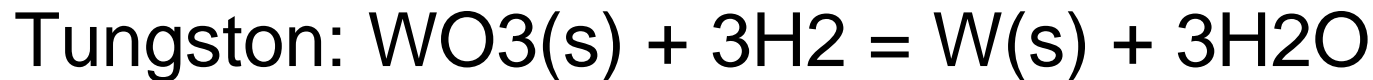
➤ **Metallothermic reduction**

- Thermite welding:

  $Fe_2O_3(s) + 2Al = Al_2O_3(l) + 2Fe(l)$

- Ferroalloy production:

$Cr_2O_3 + 2Al = 2Cr(l) + Al_2O_3(l)$
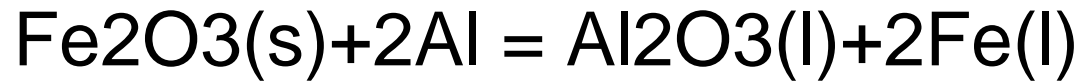
- Titanium production by Kroll's process:

$TiCl_4(l) + 2Mg = 2MgCl_2(l) + Ti(s)$
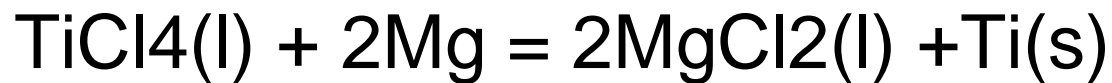
➤ **Solid state reduction of oxides:**

Tungston: $WO_3(s) + 3H_2 = W(s) + 3H_2O$

Iron: $Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$
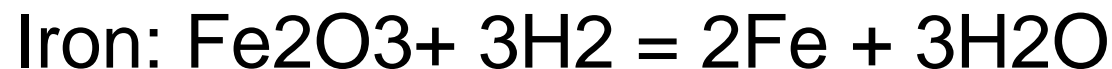
Low pressure/high pressure pyrometallurgical processes

➤ **Low pressure process**
- Magnesium extraction process:
- $2MgO.CaO(s) + Si$ (as Fe-Si)$(s) = 2Mg(g) +2.CaO.SiO2 +Fe$

  This reaction moves in right direction at low pressures.

Vacuum degassing of steels:

$[C] + [O] = \{CO\}$

➤ **High pressure process**

$ZrO2(s) + 2Ca(g) = Zr(s) +2CaO (s)$
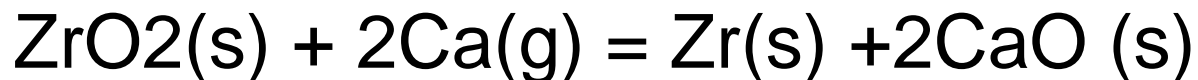
Extraction of metals from sulphide ores (Examples: Cu,Ni,Zn,Pb)

➤ **Extraction of lead**

- Lead ore consists of PbS (galena) along with Sphalerite (ZnS),Pyrite(FeS2),Cu2S and some precious metals like gold and silver as gangue.
- First of all lead ore (3-10% lead) is concentrated to 60-70% by froth floation, then roasted to remove sulpher and form oxides, followed by reduction in blast furnace using coke.

➤ **Extraction of Zinc**
- Zinc ore consists of Sphalerite (ZnS) along with sulphides of copper, lead and cadmium with some precious metals as gangue.
- First of all sulphide is converted to oxide by roasting process, followe by carbothermic reduction:

  $ZnO(s) + C(s) = Zn(g) + CO(g)$..vacuum needed to push reaction if forward direction.

Extraction of copper

- The copper ore is known as Chalcopyrite (CuFeS2). Copper is less than 2%, which is concentrated by froth floatation.

- Roasting of chalcopyrite is done to remove iron sulphide in the form of FeO.

  $2CuFeS2(s) + O2(g) = Cu2S + 2FeS +SO2(g)$

  $FeS+1.5.O2(g) = FeO(s) + SO2(g)$

- Roasted ore is charged into a reverberatory furnce/flash smelting unit along with Silica (SiO2) as a flux.

- Output of the furnace is matte (Cu rich liquid melt) along with FeO.SiO2 slag. Matte and slag are easily seperable.
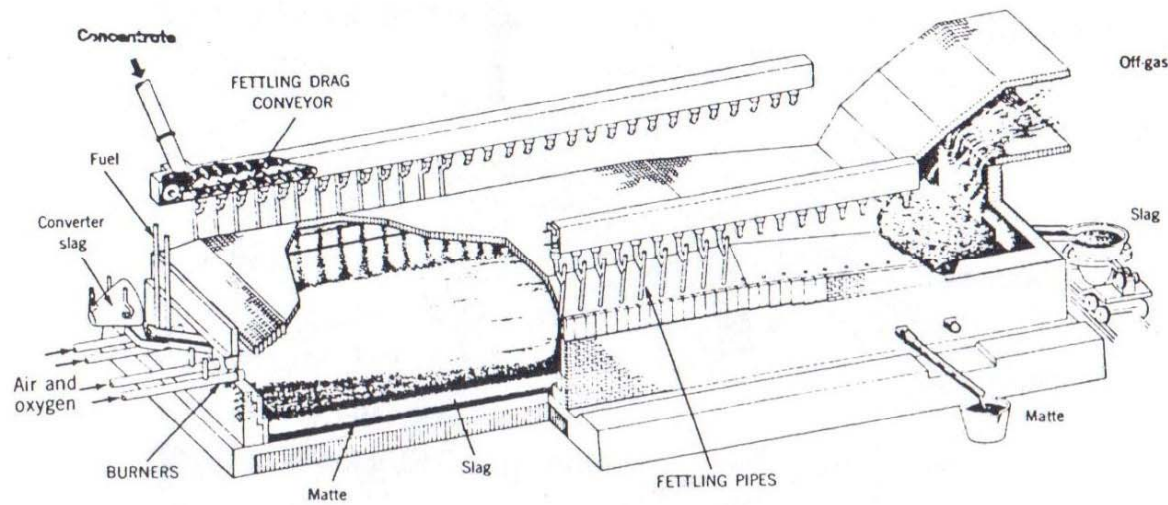
Reverberatory Furnace for Producing Molten Cu-Fe-S Matte
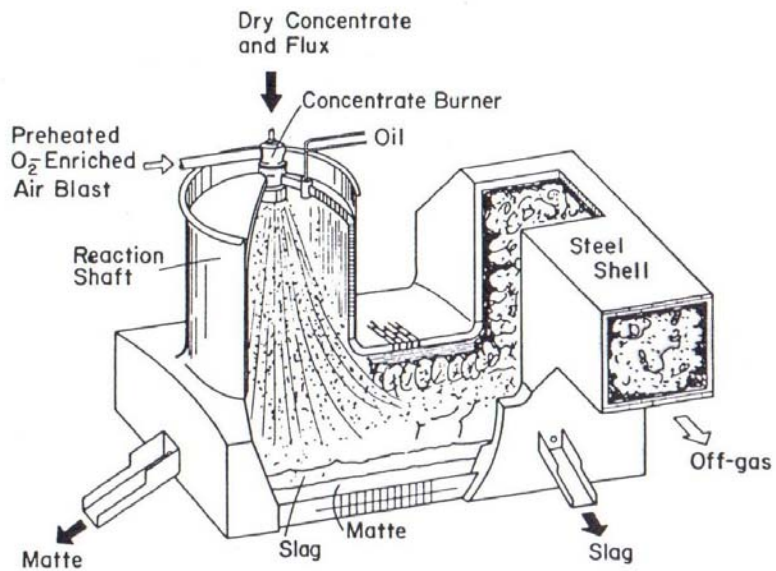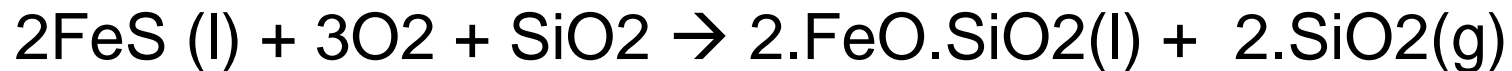

(a) Outokumpu O₂-enriched air flash furnace
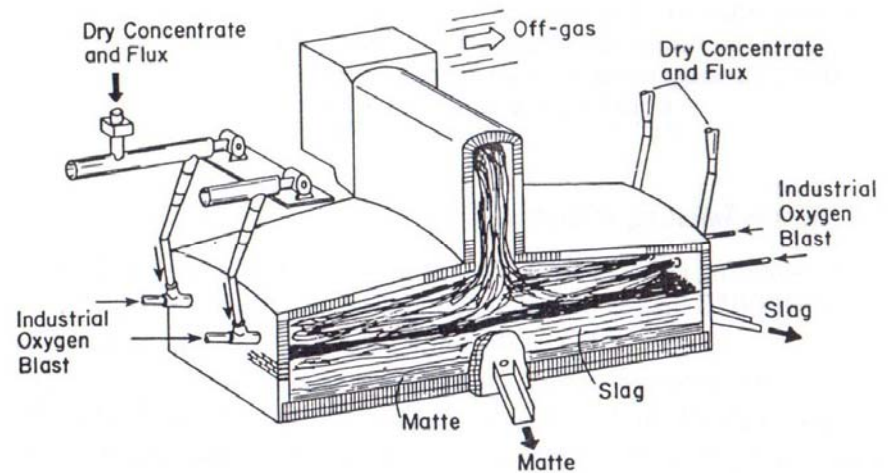
(b) Inco oxygen flash furnace

Converting of Cu-matte in Pierce-Smith converter

- It involves air oxidation of molten matte received from smelting. It involves two step process:
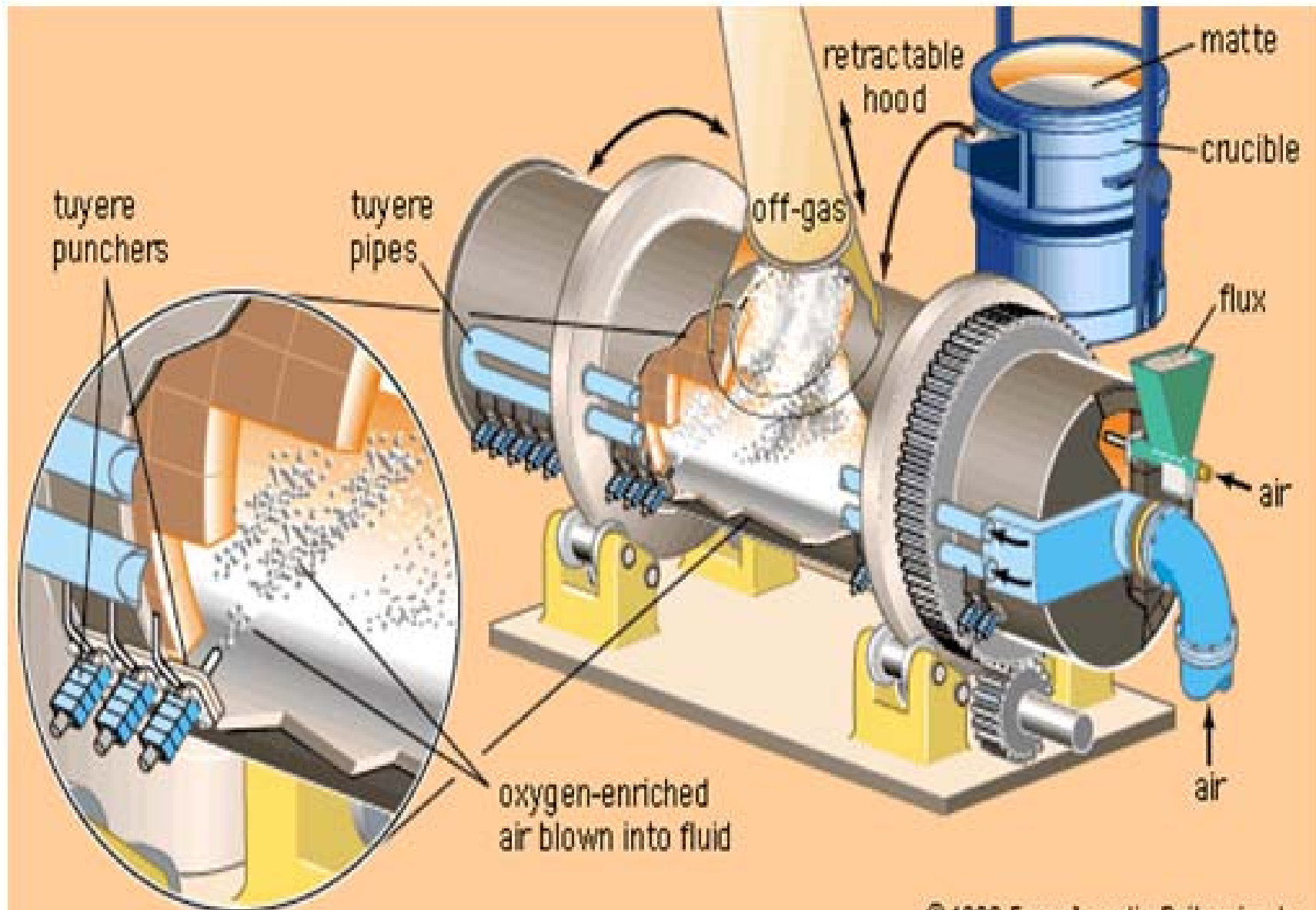
  (a) FeS removal and slag formation:

  $2FeS (l) + 3O_2 + SiO_2 \rightarrow 2.FeO.SiO_2(l) + 2.SiO_2(g)$

  Process temperature: 1200 C

  (b) Blister copper (>99% Cu) formation stage:

  $Cu_2S + O_2 \rightarrow 2Cu + SO_2 (g)$

Point to be noted: Cu loss in slag starts after sulpher in matte falls below 0.02%

**Copper conversion does not start till Fe in matte is below 1%.**

Pierce-Smith Converter

# Extraction of reactive metal by halide route

➢ Extraction of Titanium

• Titanium ore exists in the form of oxide (Rutile, TiO_2) or Ilmenite ($FeO.TiO_2$).

• As a first step TiO_2 is chlorinated at 900 C:

$$TiO_2 (s) + C(s) + 2Cl_2(g) = TiCl_4 (g) + CO_2 (g)$$

• $TiCl_4$ is removed by selective distillation, followed by reduction of $TiCl_4$ by Magnesium, known as Kroll's process.

$$TiCl_4(l) + 2Mg(l) = 2MgCl_2(l) + Ti (s)$$
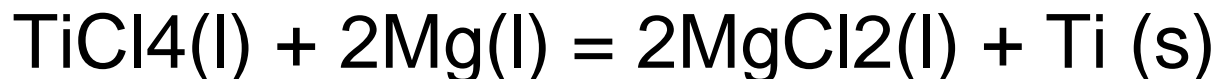
Refining process

- Oxidation to remove C,Si,P,Mn etc (steelmaking)
- Sulphidation to remove :Cu,Ni.Co from lead; Cu from tin etc.
- Chlorination to remove Zn from lead; Zn,Cu and Pb from bismuth
- Electrochemical method by cathodic deposition; examples: Cu,Ag,Au,Ni,Co,Pb,Sb,Bi etc.

Oxygen Steelmaking process for refining of pig iron
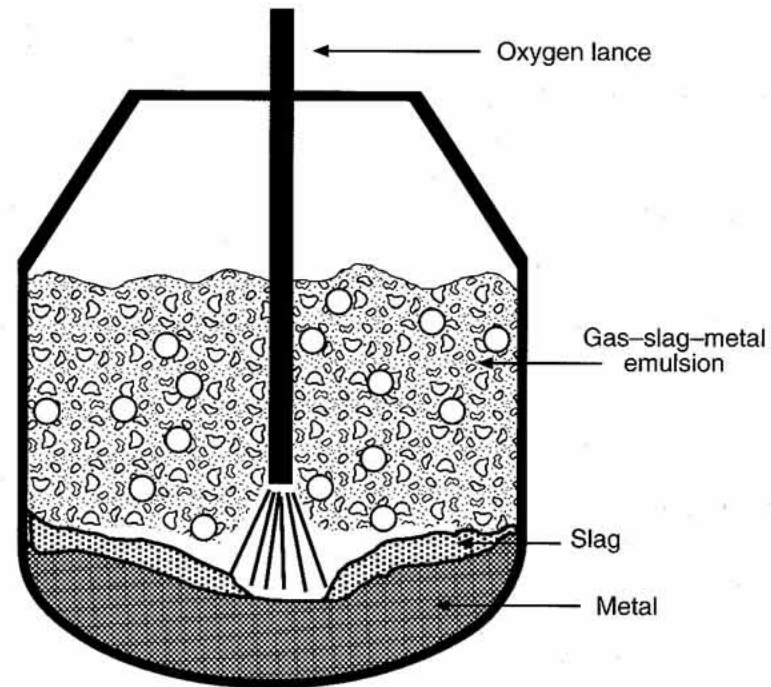
Selective oxidation of C,Si,Mn,P,Fe with the help of high speed oxygen blow. Process done in a basic lined vessel and Lime added as slag former to combine SiO2. Oxidizing and enough volume of slag is formed to promote phosphorous removal. Process generates a lot of heat of oxidation which is compensated by iron ore/scrap additions as a coolant.

Next Class task:

- Material and heat balance of processes.

- Come prepared with Solver model applying MS-Excel

- Flow-Bal software will be introduced and student groups will be formed.