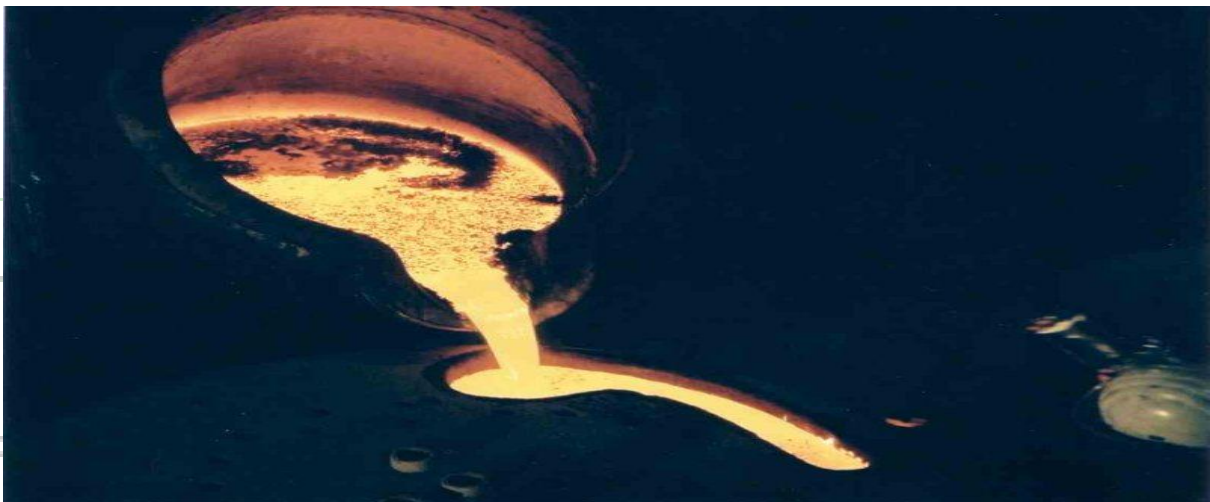


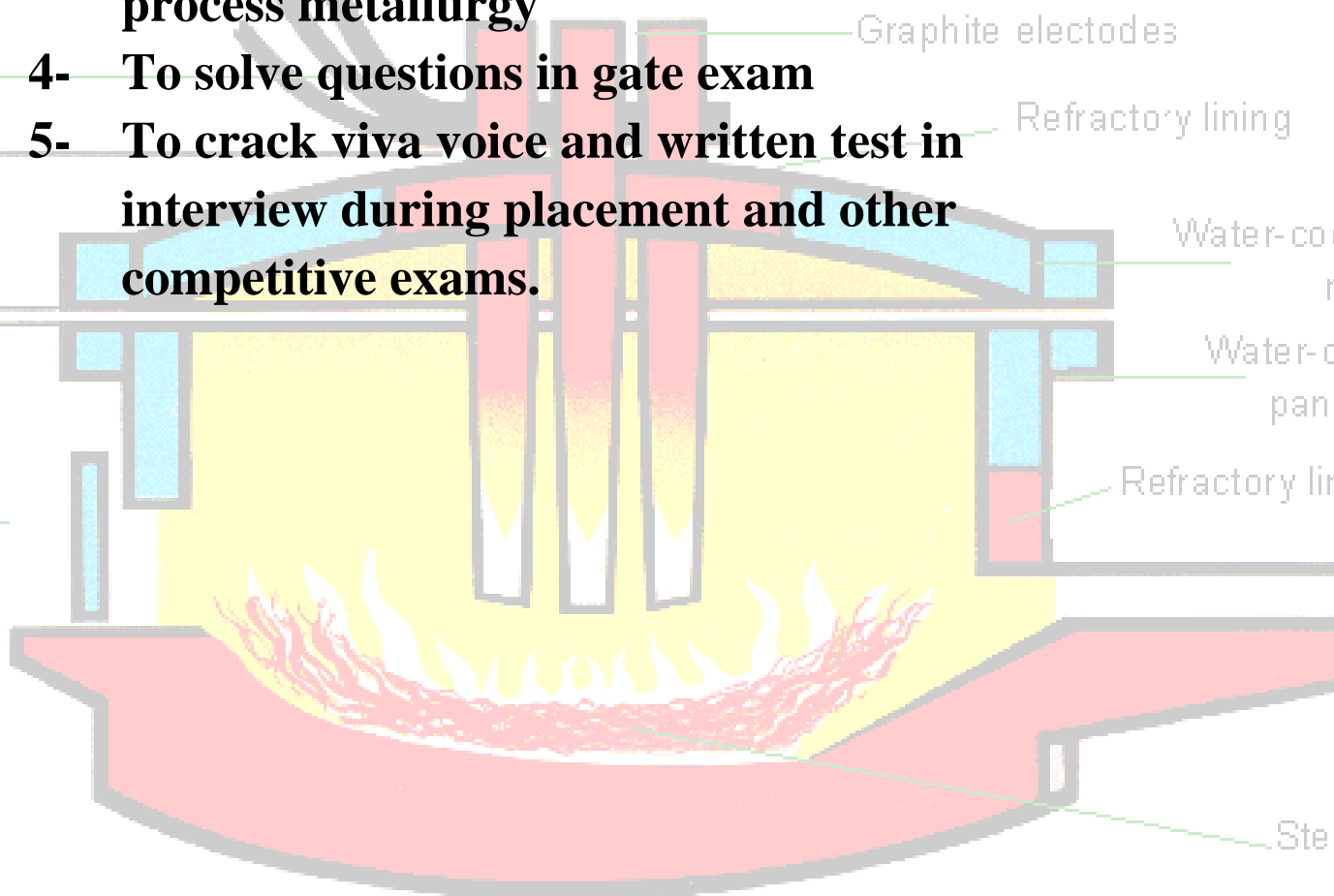
UNIT PROCESS OF EXTRACTION
MM-15052
4TH SEM B. TECH
DEPARTMENT OF METALLURGY AND MATERIAL
ENGINEERING
V.S.S.U.T, BURLA , SAMBALPUR



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GOAL OF THIS SUBJECT

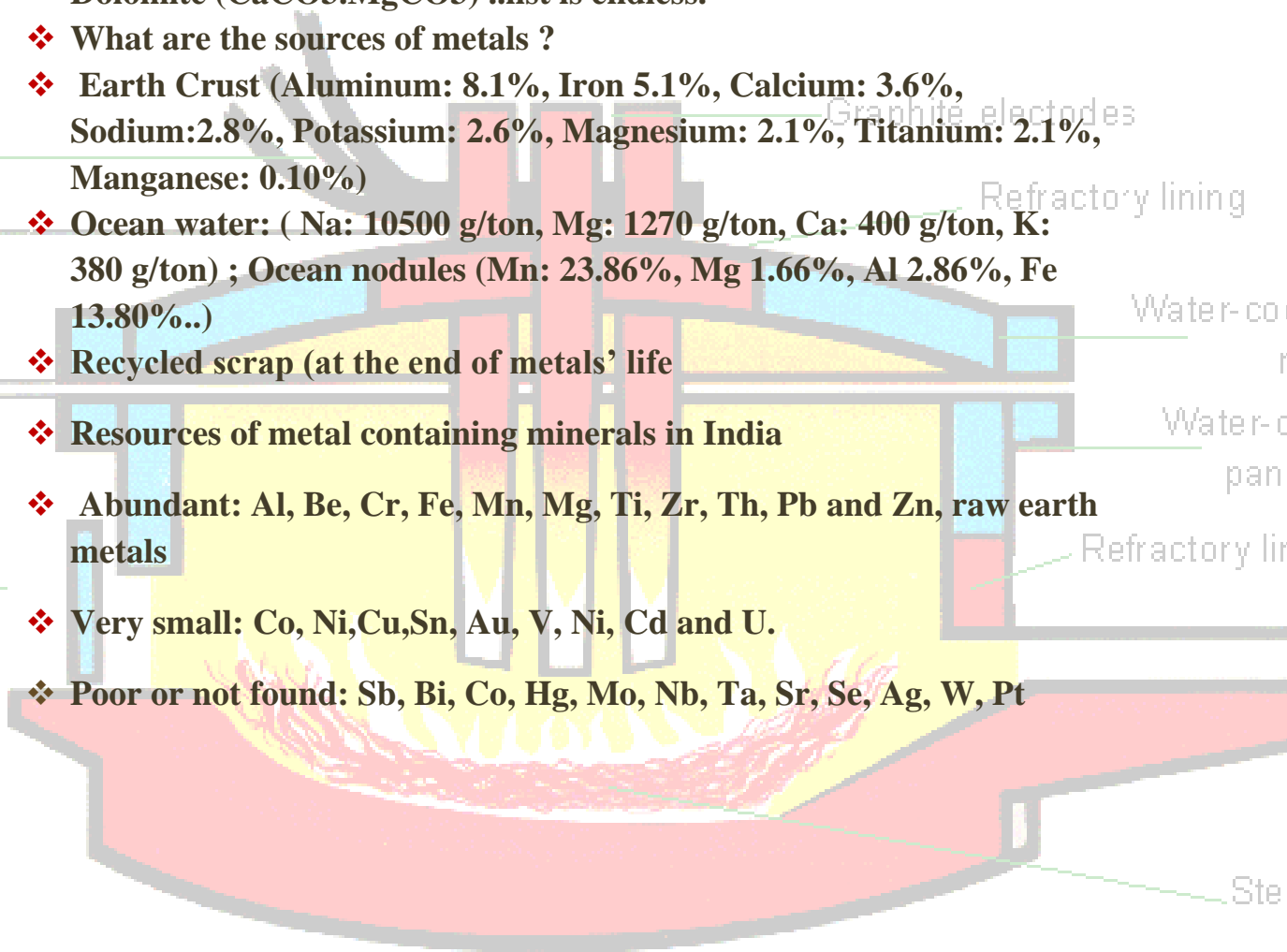
- 1- To impart knowledge about extractive metallurgy which can be implemented while working in any smelter or refinery
- 2- To teach you to think rather than cook.
- 3- To encourage you to consider career path in process metallurgy
- 4- To solve questions in gate exam
- 5- To crack viva voice and written test in interview during placement and other competitive exams.

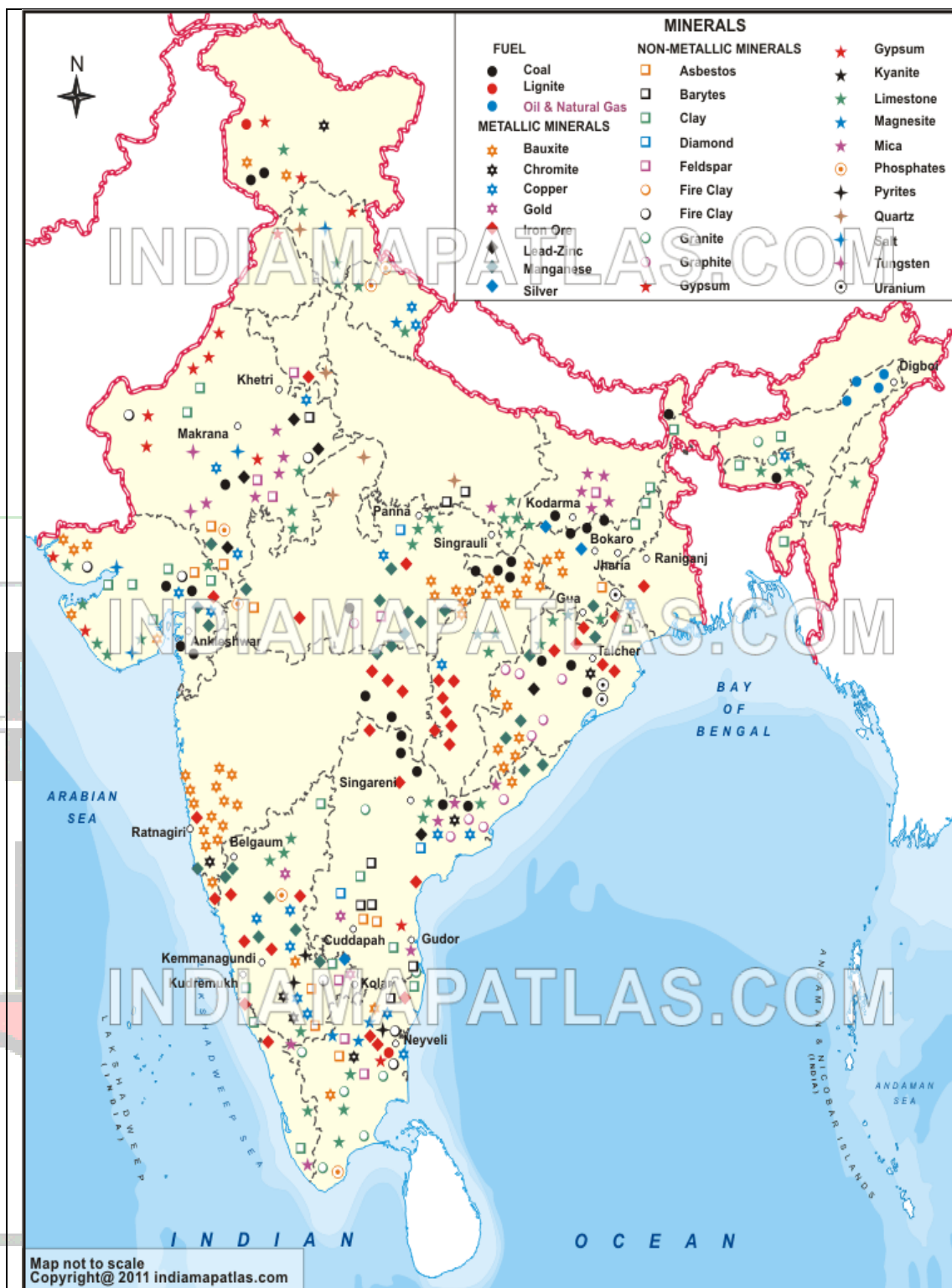


MODULE-1

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 ($\text{CaCO}_3 \cdot \text{MgCO}_3$) ..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 reservoirs in india

Mineral Map of THE WORLD



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Water-co

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TYPES OF ORES

- ❖ Oxide ores: Examples: Fe_2O_3 , Fe_3O_4
- ❖ Apart from Fe, other heavy metals which are produced from oxide ores are: Manganese, Chromium, Titanium, Tungsten, uranium and Tin.
- ❖ Sulphide ores: Copper ore (CuFeS_2 , Chalcopyrite), sphalerite (Zn,FeS), Galena PbS , Pyrite FeS_2 . Others: Nickel, Zinc, Mercury and Molybdenum
- ❖ Halide ores: Rock salts of Sodium, Magnesium chloride in sea water.
- ❖ Others ore are very rare like carbonate ore (zinc carbonate), hydroxide ore and silicate ores.

COMMERCIAL PRODUCTION OF METALS

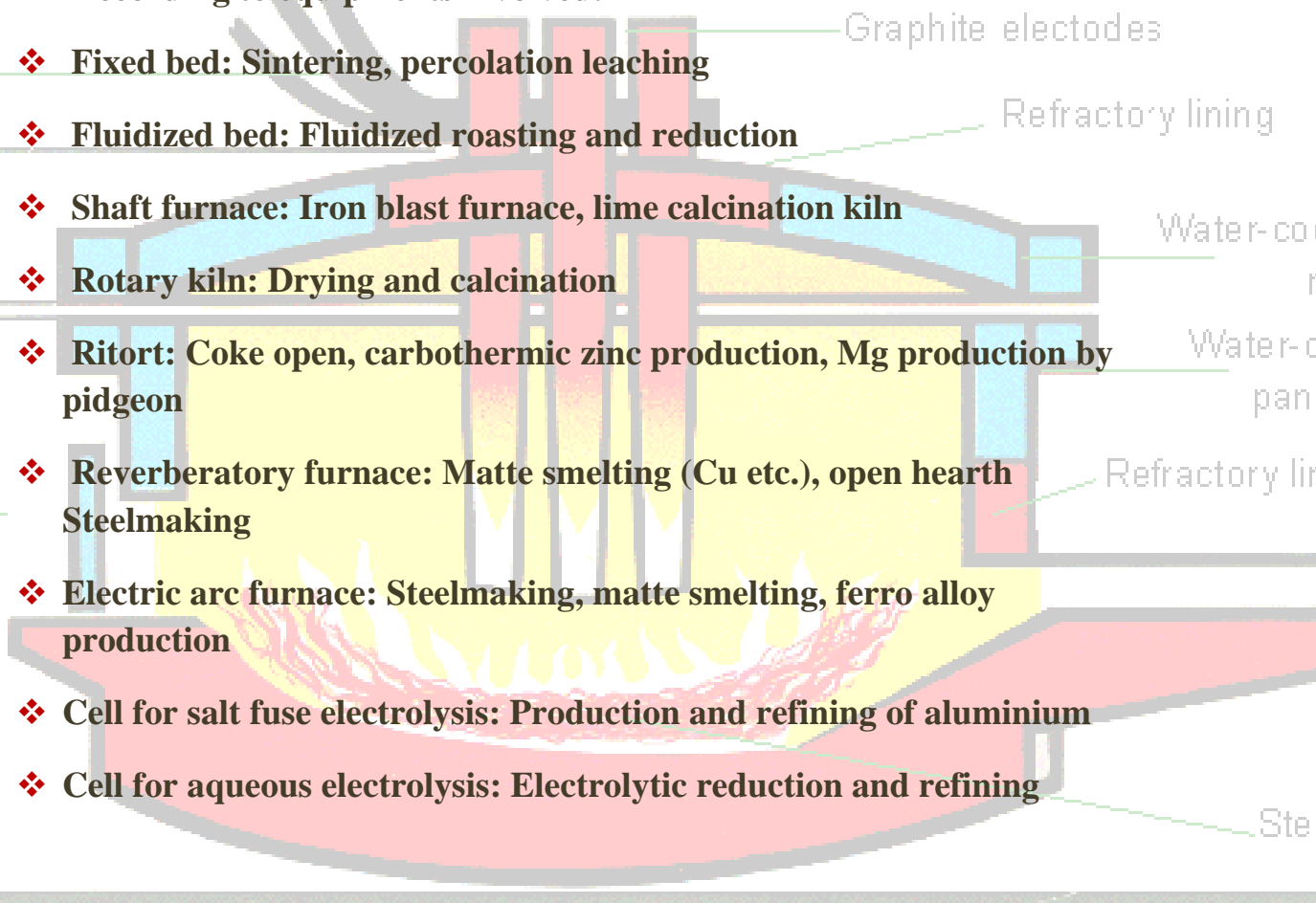
- ❖ Availability of ore deposits
- ❖ Concentration of metal in the ore
- ❖ Availability of technology of extraction and refining of that metal
- ❖ Physical and chemical properties of the metal
- ❖ Market demand of that metal
- ❖ **Economy of the process: Readily available, Easily produced** and available at low processing cost with desired properties

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, filtration, distillation, comminution
- ❖ Unit processes: Chemical processes like leaching, smelting, roasting, Electrolysis, decarburization, Dephosphorization, Degassing, Deoxidation etc.

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
 - ❖ Retort: 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

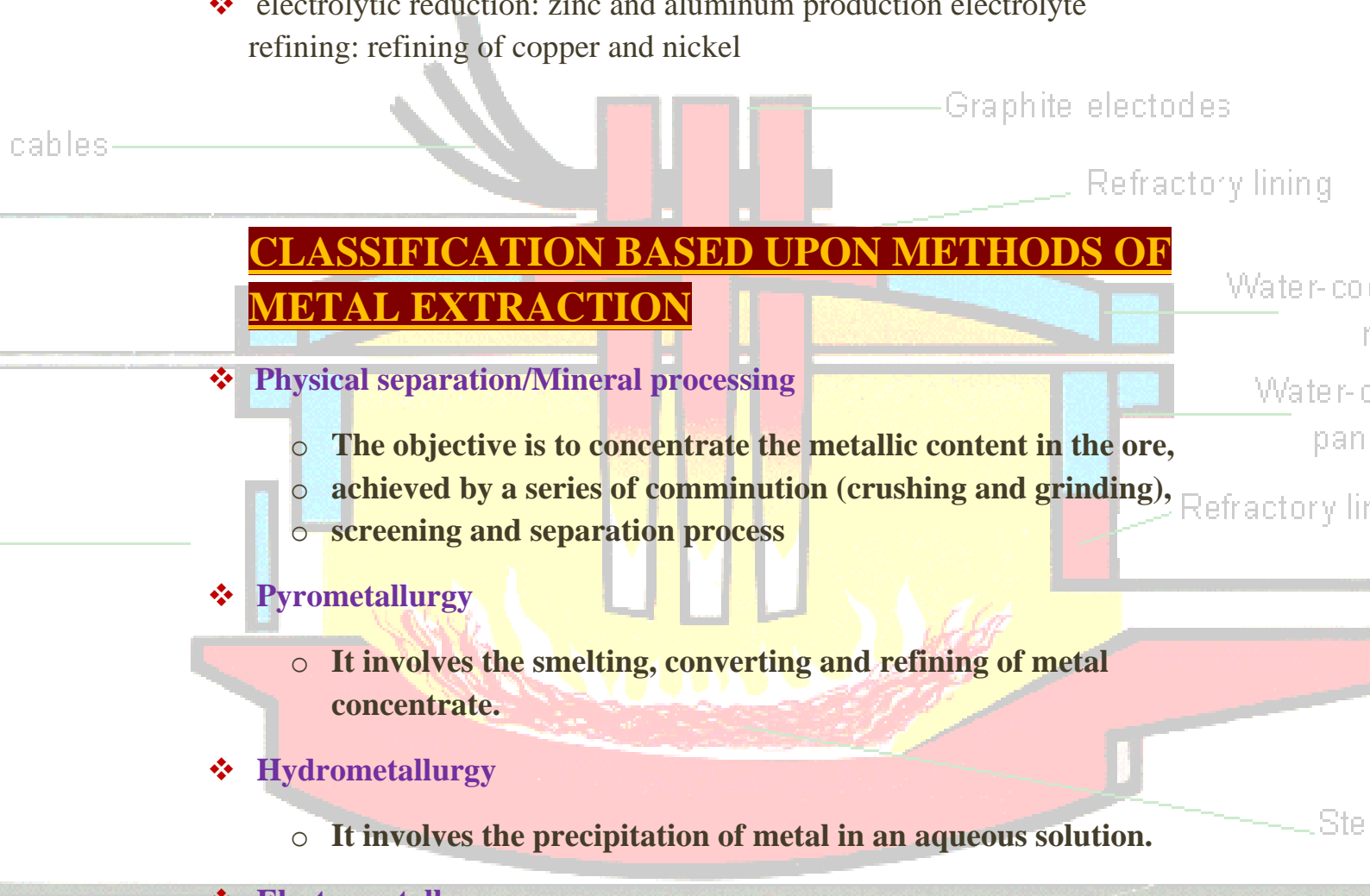


CLASSIFICATION ACCORDING TO CHEMICAL REACTIONS

- ❖ Oxidation: roasting, sintering, ld steelmaking
- ❖ reduction: blast furnace iron making
- ❖ slag metal reactions: steelmaking, matte smelting
- ❖ chlorination: titanium (converting to tetrachloride)
- ❖ electrolytic reduction: zinc and aluminum production electrolyte refining: refining of copper and nickel

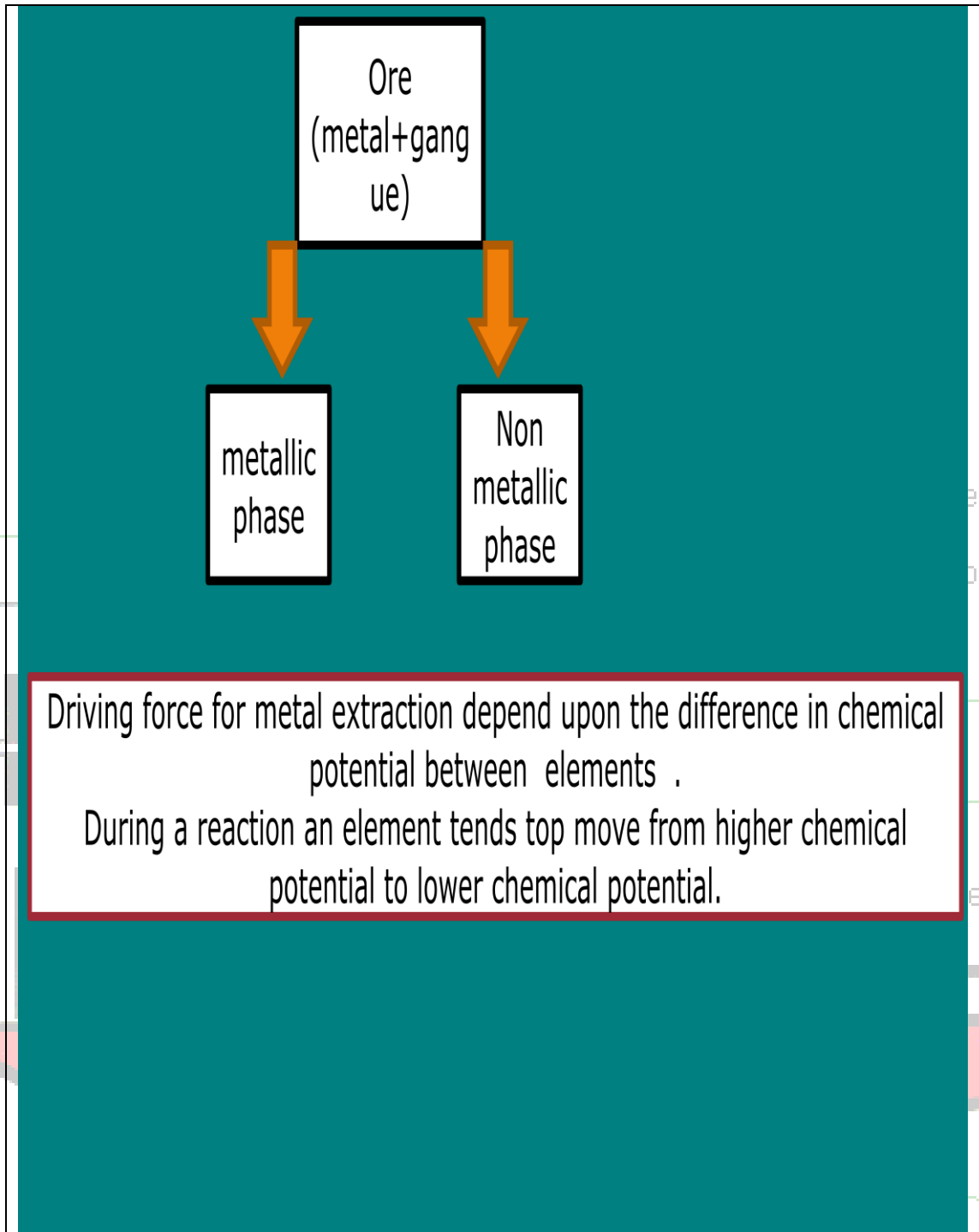
CLASSIFICATION BASED UPON METHODS OF METAL EXTRACTION

- ❖ **Physical separation/Mineral processing**
 - The objective is to concentrate the metallic content in the ore,
 - achieved by a series of comminution (crushing and grinding),
 - screening and separation process
- ❖ **Pyrometallurgy**
 - It involves the smelting, converting and refining of metal concentrate.
- ❖ **Hydrometallurgy**
 - It involves the precipitation of metal in an aqueous solution.
- ❖ **Electrometallurgy**
 - Electrolysis process to extract metal. Electro winning: Extraction of the metal from electrolyte; Electro refining:
 -

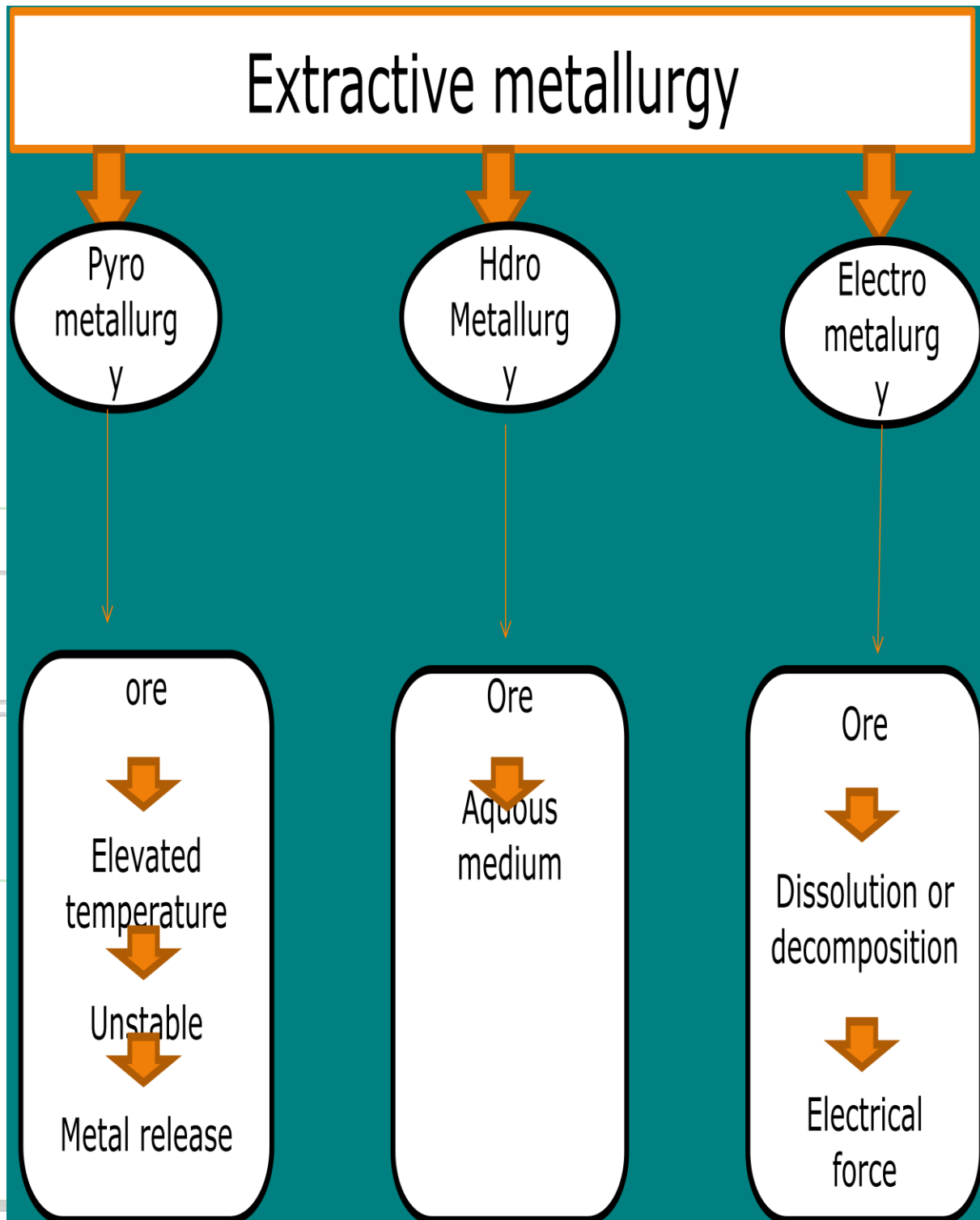


Element	minerals	
Aluminium	Bauxite (gibbsite, diaspore)	
Copper	Chalcopyrite ,chlcocite,bornite	
Gold	Calaverite, sylvanite	
Iron	Hematite ,megnetite,	
Lead	Galena, anglesite, cerussite	
magnesium	Dolomite, magnesite,carnallite	
Mangenes	Pyrolusite braunite, manganite	
Murcury	cinnabar	
Nickel	pentlandite	
Silicon	quartz	
silver	Argentite ,pyrargyrite	
Thorium	Monazite	
Tin	Cassiterite	
Uranium	Pitchblend ,uraninite	
Zinc	Sphalerite	
Zirconium	Zircon	
Elements and their respective minerals		

GENERAL METHODS OF EXTRACTION



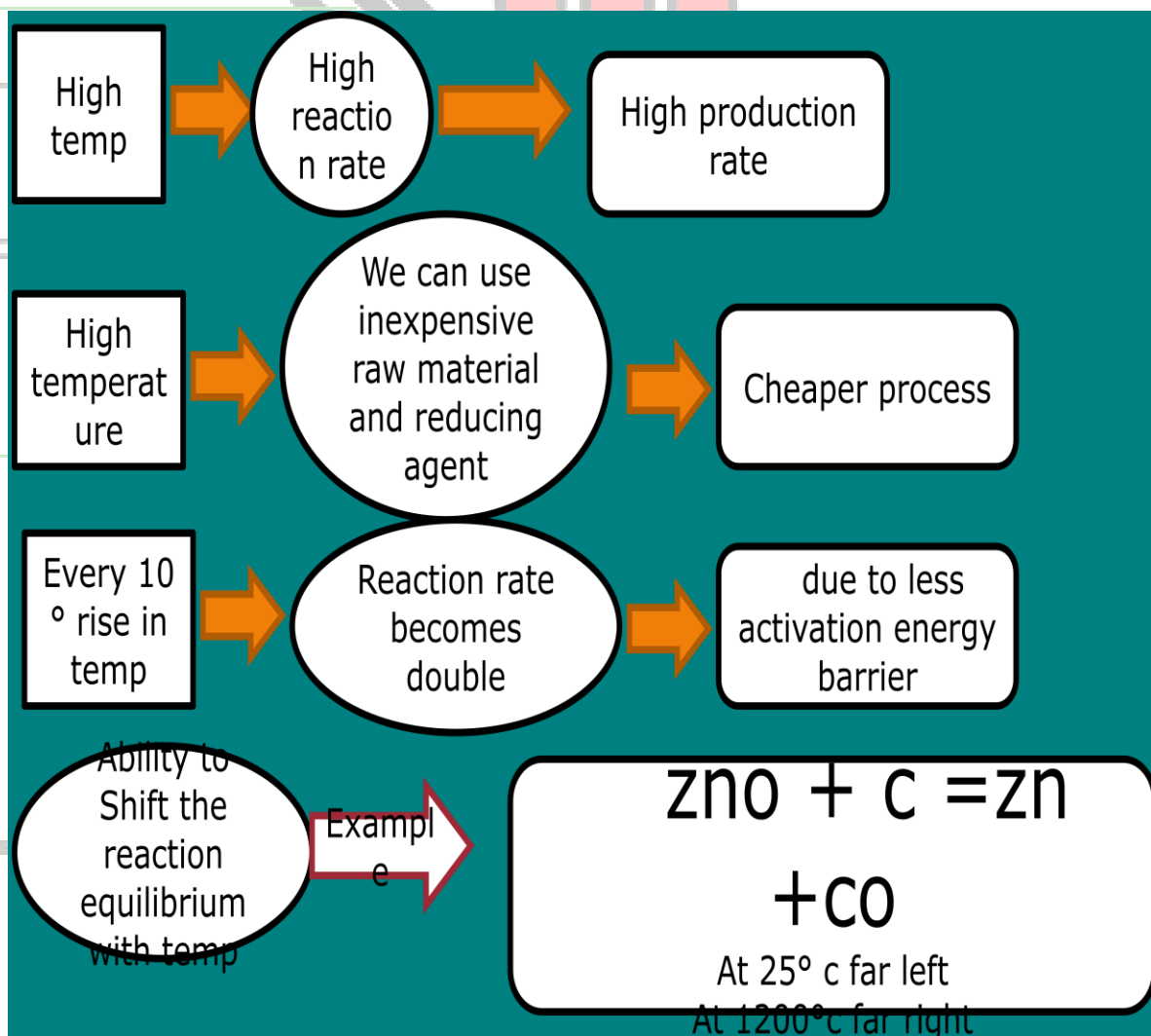
DIVISION OF EXTRACTIVE METALLURGY



PYROMETALLURGY

- ❖ Principle means of metal extraction despite of rapid development in hydro and electro metallurgy.
- ❖ Extraction and refining carried at elevated temperature where physical and chemical changes occurs at 500- 2000 ° c.
- ❖ Significance of pyrometallurgy over hydro and electro metallurgy :
- ❖ Since it is a high temperature process so it is cheaper and more versatile .

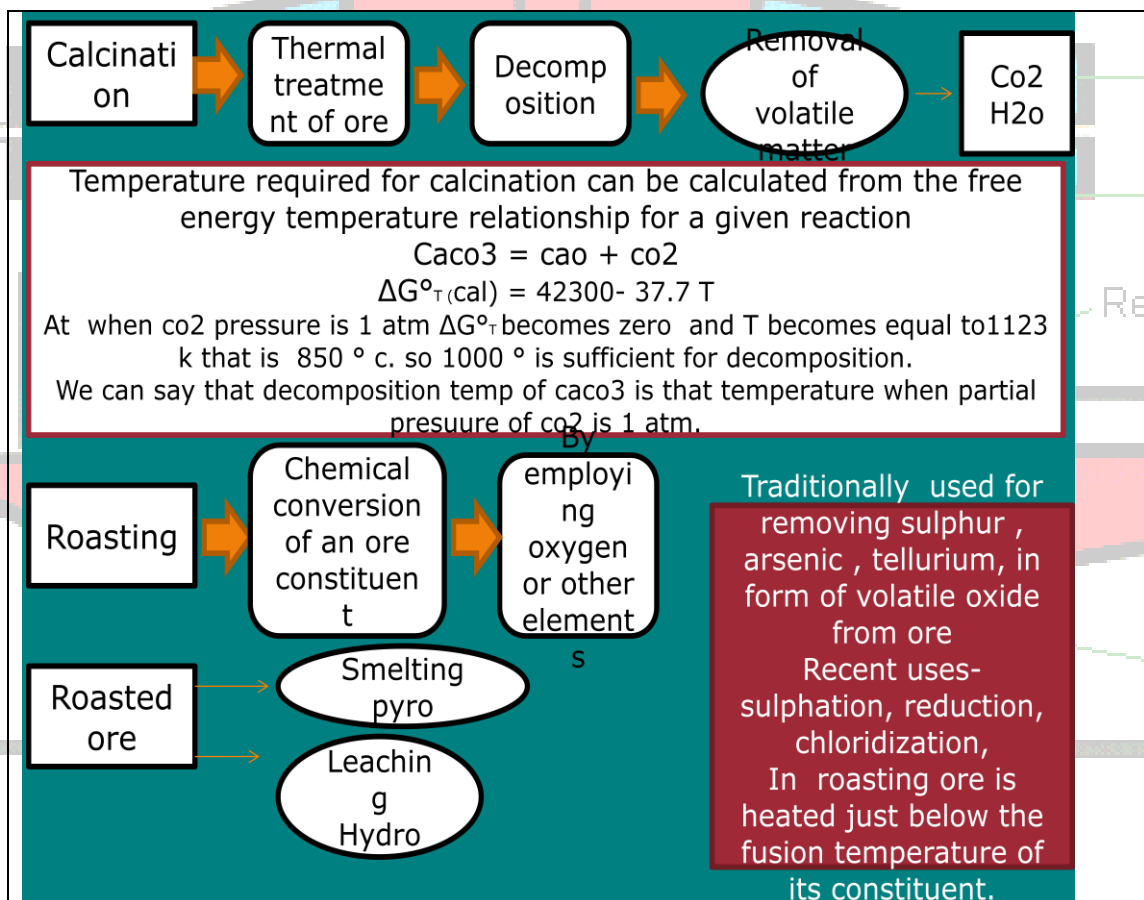
HOW IT IS CHEAPER AND VERSATILE



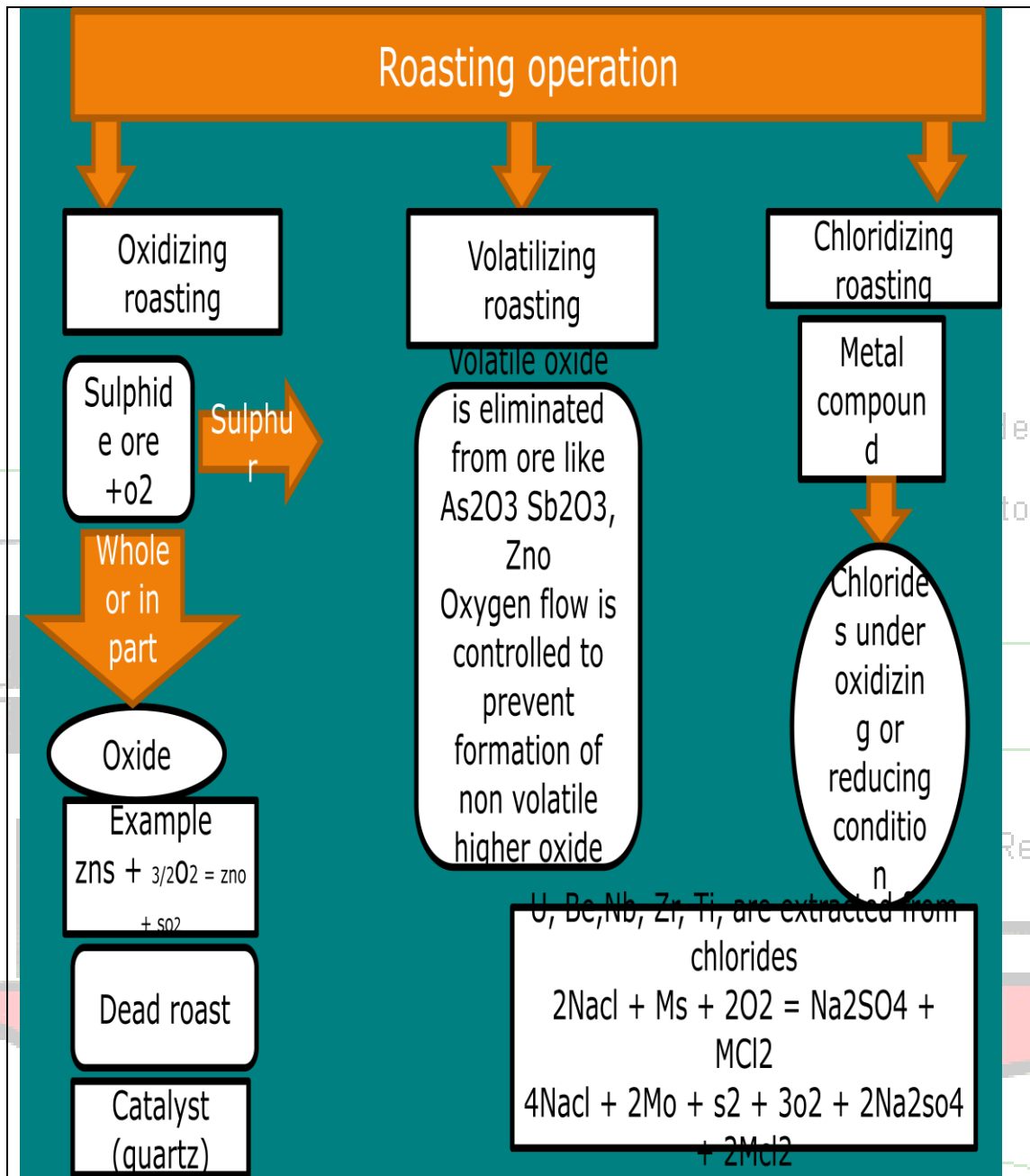
- ❖ Brings about a reduction which cannot take place in presence of water.
- ❖ Only pyrometallurgy and fused salt electrolysis can extract reactive metals namely the alkaline earth metals zirconium and titanium.
- ❖ Ability to treat a large tonnage of ore in a compact space, which leads to a saving in capital cost.

PYROMETALLURGICAL PROCESS (HIGH TEMPERATURE PROCESS)

- ❖ Calcination
- ❖ Roasting
- ❖ smelting
- ❖ Refining



MODULE -2



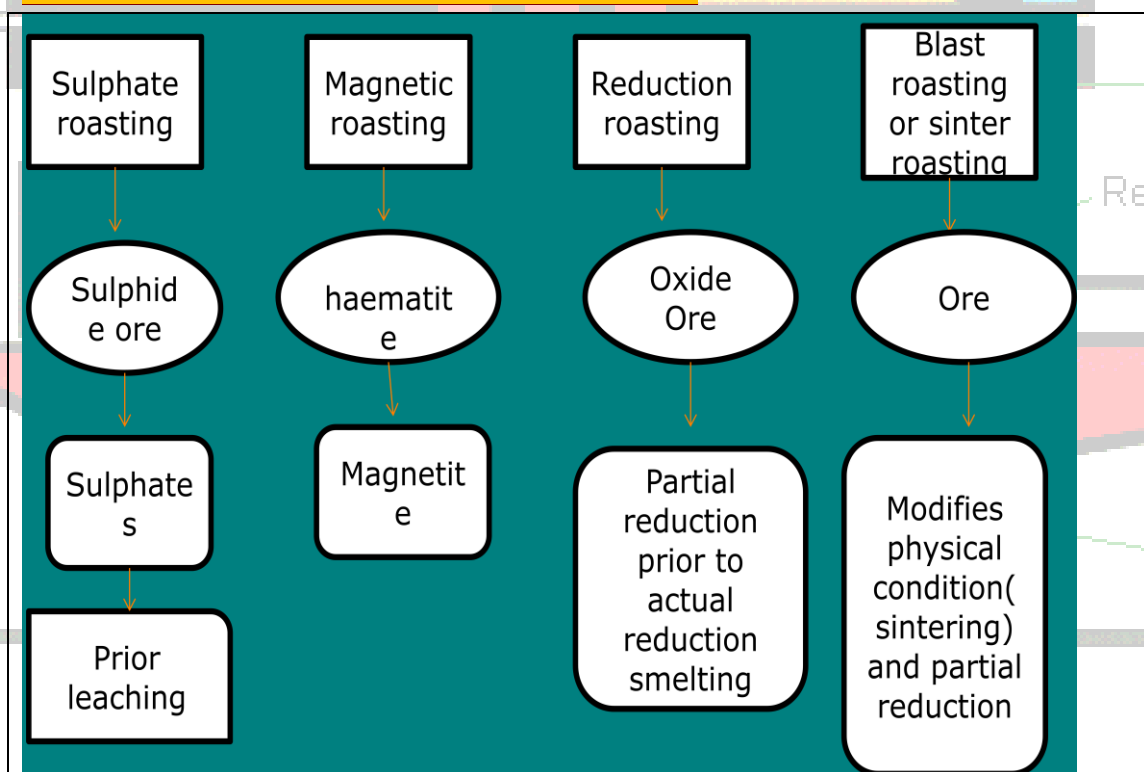
ROASTING DEPEND UPON FOLLOWING FACTOR

- ❖ Time(duration)
- ❖ Availability of oxygen or air
- ❖ Temperature
- ❖ physical condition of the ore
- ❖ Nature of the mechanical device used

DURATION OF ROASTING PROCESS VARIES GREATLY

- ❖ Blast roasting is done in a mere flash of time
- ❖ Hearth roasting takes hour.
- ❖ Heap roasting months
- ❖ Weather roasting year.

OTHER ROASTING PROCESS

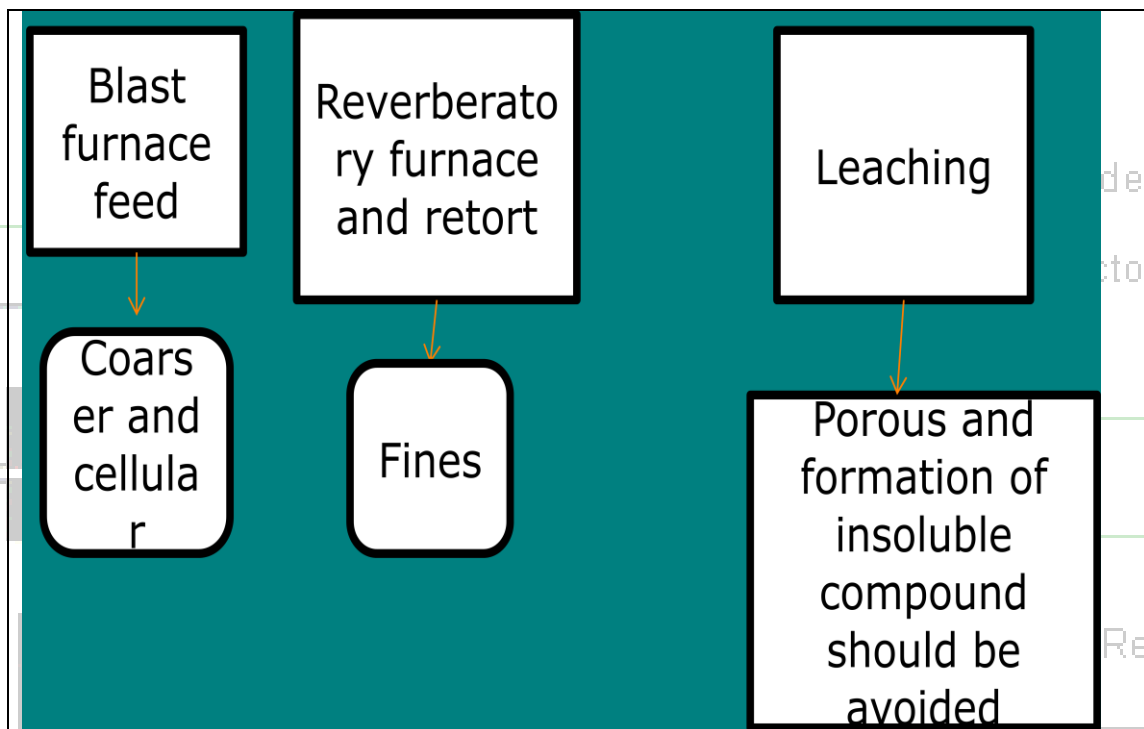


ROASTING PRACTICE

CRITERIA OF CHOOSING A ROASTING PROCESS?

- ❖ Required physical condition of product
- ❖ Required chemical composition of the product.

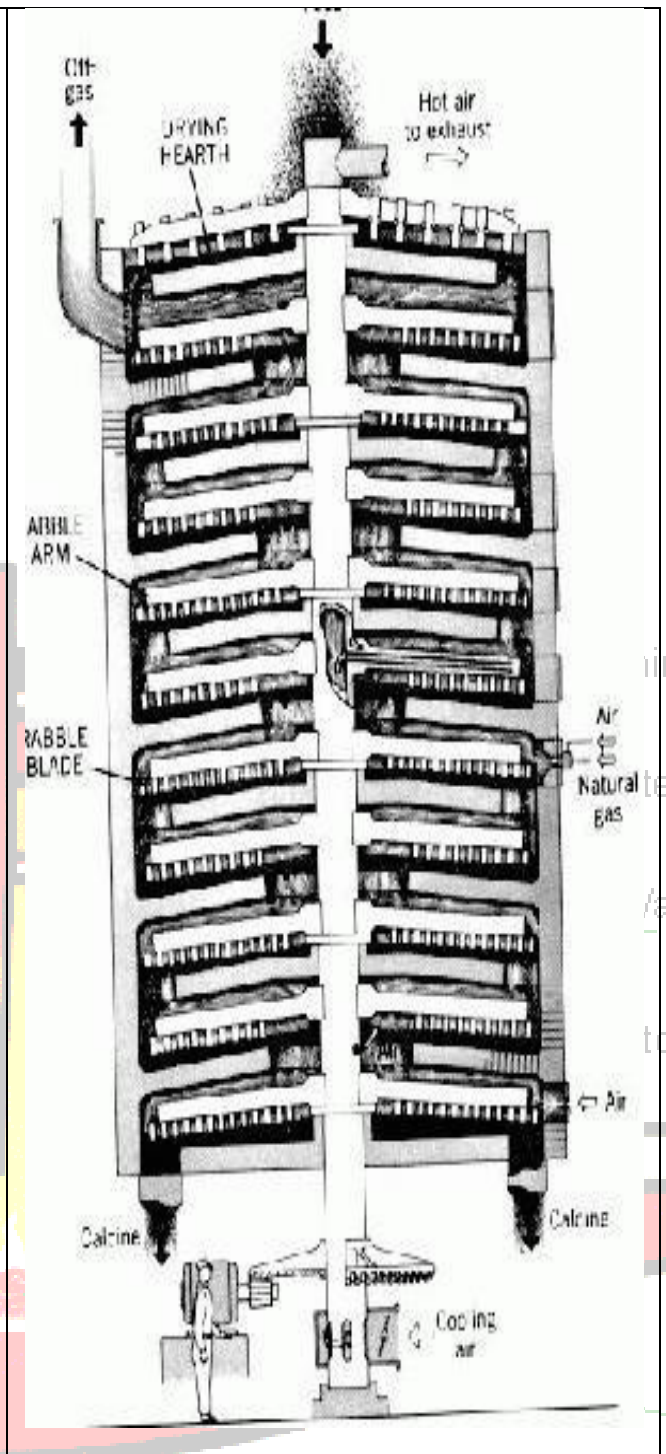
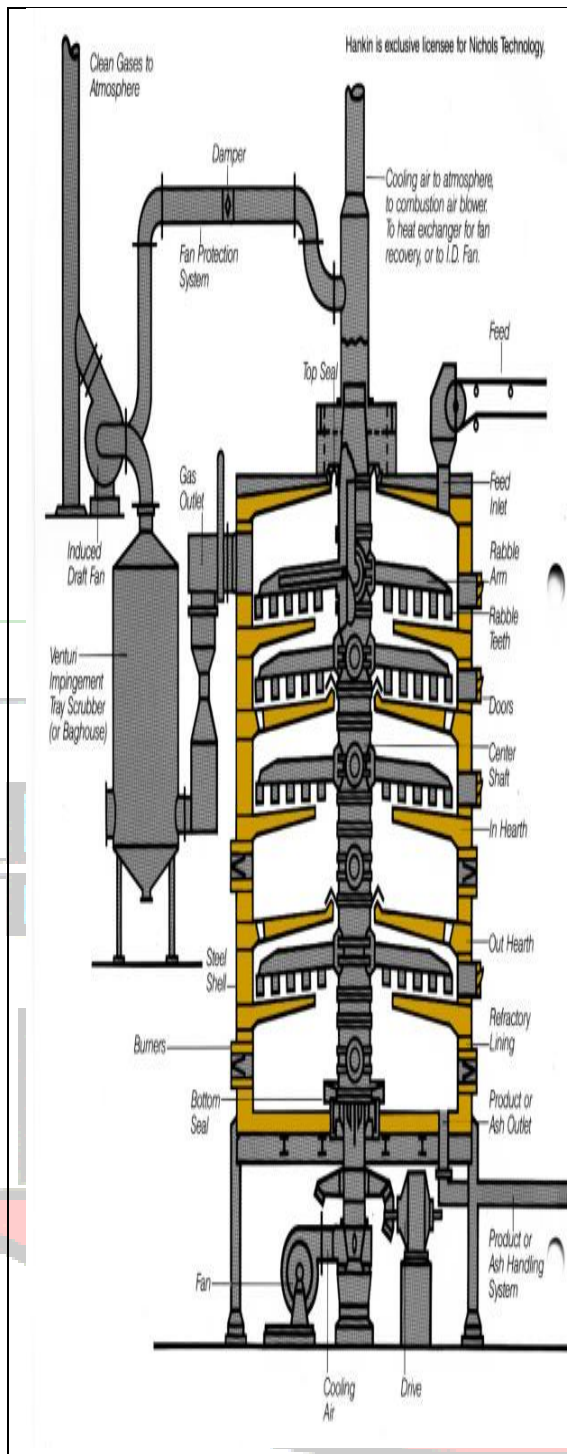
WHAT ARE THE REQUIRED PHYSICAL CONDITION:



WHAT ARE THE REQUIRED CHEMICAL COMPOSITION

- ❖ Lead should be totally free from sulphur before smelting it in BF.
- ❖ In Cu the sulphur content should not be totally removed it should be present in excess amount so as to produce a matte which is mainly the mixture of iron sulphide and copper sulphide of desired grade.
- ❖ For Zn total sulphur content should be removed.
- ❖ Formation of zinc ferrite should be avoided when zinc is extracted by leaching because it is difficult to leach the ferrite.

INDUSTRIAL ROASTING UNITS DIAGRAM



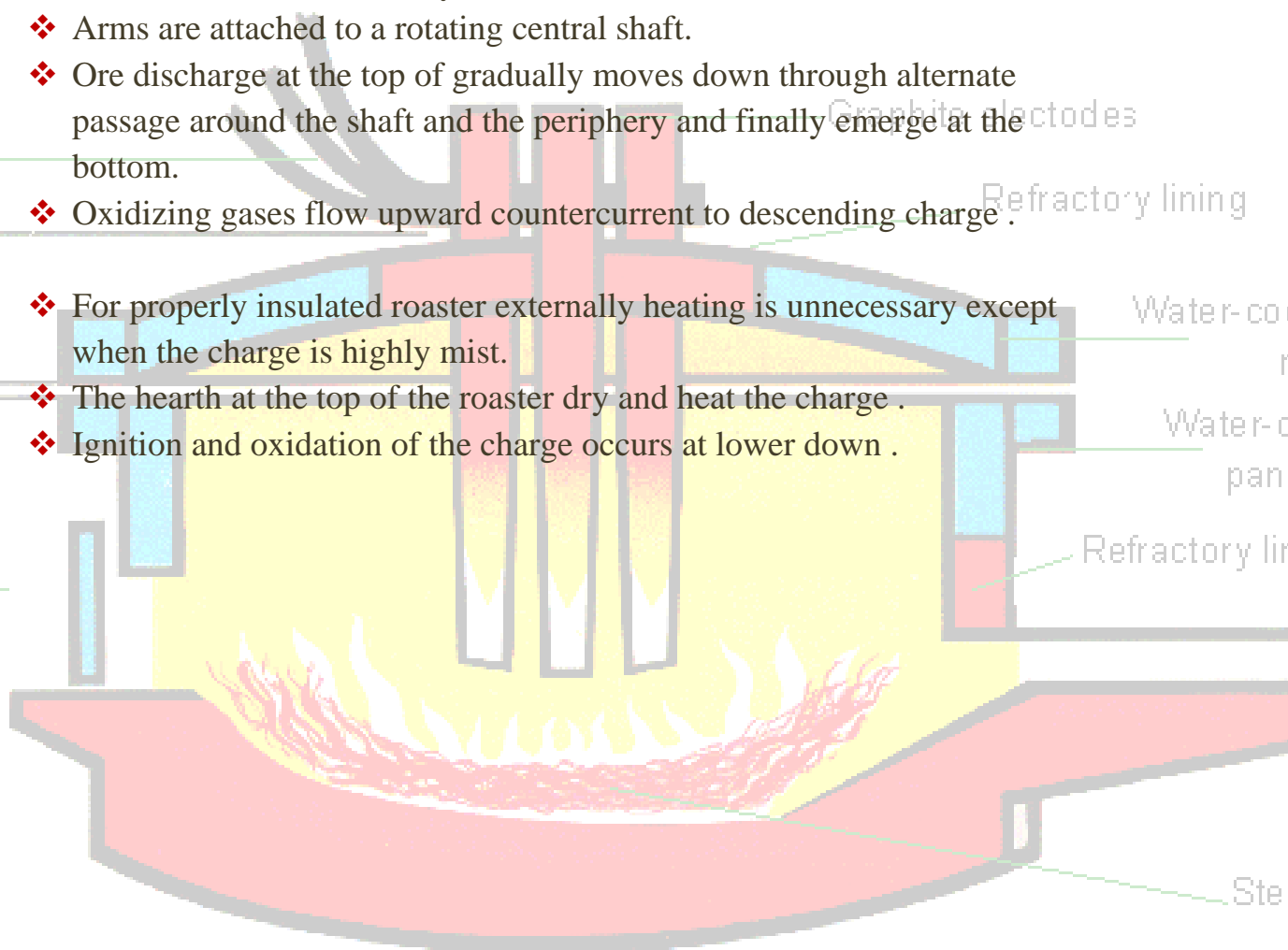
MCDUGALL HEARTH ROASTER OR MULTIPLE HEARTH ROASTER

FIRST DESIGNED BY – Macdougall in England

Basic principle: counter current flow of solid ore and oxidizing gases.

Construction of Macdougall roaster:

- ❖ Consists of several (about 10) circular brick hearth superimposed on each other.
- ❖ Entire structure is enclosed in a cylinder bricks lined steel shell.
- ❖ Revolving mechanical rabblers attached to arm move over the surface of each hearth to continuously shift ore
- ❖ Arms are attached to a rotating central shaft.
- ❖ Ore discharge at the top of gradually moves down through alternate passage around the shaft and the periphery and finally emerge at the bottom.
- ❖ Oxidizing gases flow upward countercurrent to descending charge .
- ❖ For properly insulated roaster externally heating is unnecessary except when the charge is highly moist.
- ❖ The hearth at the top of the roaster dry and heat the charge .
- ❖ Ignition and oxidation of the charge occurs at lower down .

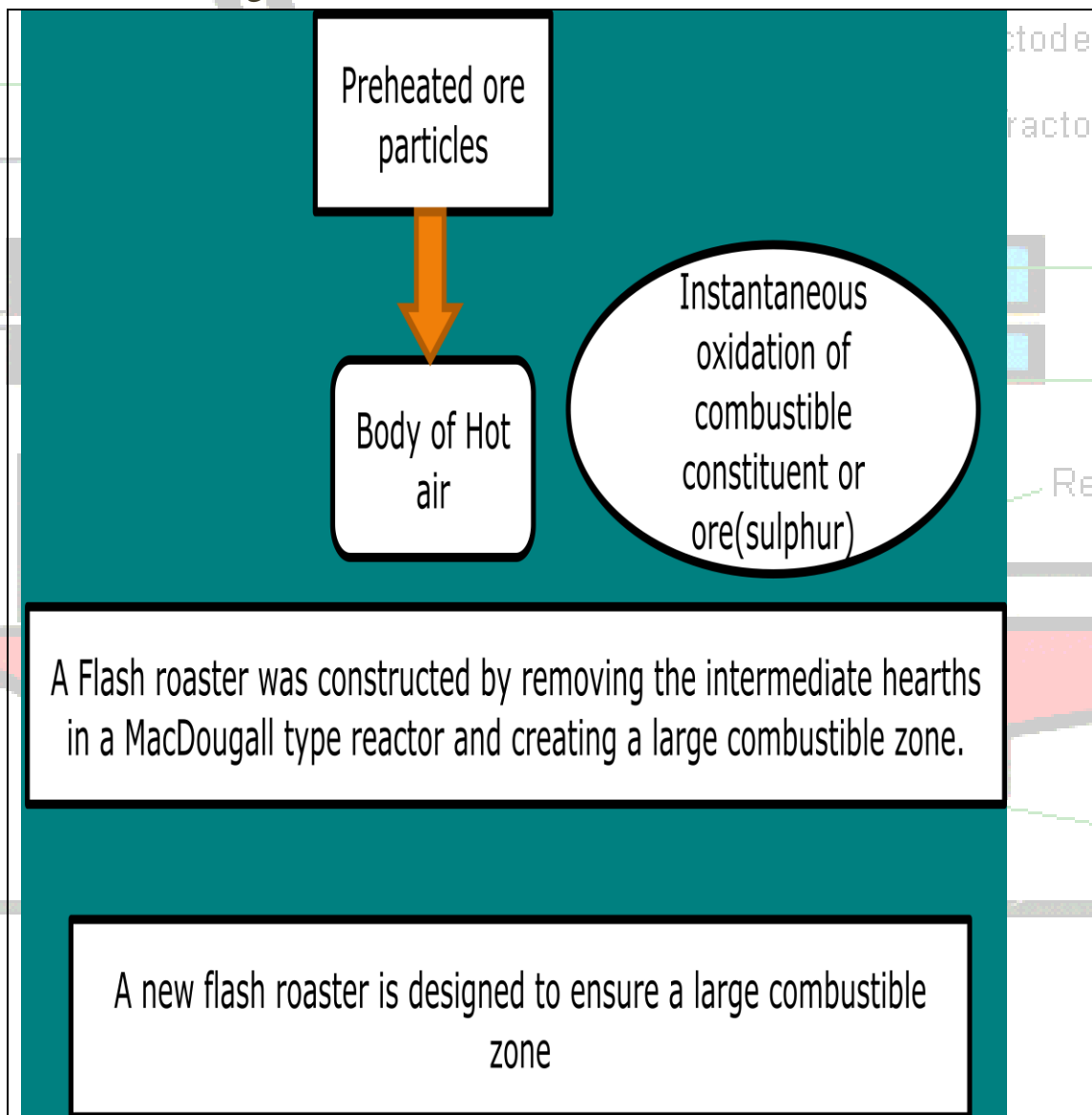


DRAW BACK OF MULTIPLE HEARTH ROASTER

The roasting process is slow and the sulphur gases evolved when a sulphide is roasted are unsuitable for the production of sulphuric acid because they do not contain sufficient SO_2 and SO_3 .

FLASH ROASTER

- ❖ The preheated sulphide ore particles are made to fall through a body of hot air, resulting in the instantaneous oxidation



FLUIDIZED BED ROASTING FLUOSOLID ROASTING

- ❖ The ore particles are roasted while suspended in air
- ❖ Here gas is passed at high velocity through a bed of solid ore particles (small and preferably regular in size over the range of 0.005-0.05 cm in dia .
- ❖ The behavior of bed depends upon velocity of gas .

FIVE STAGE OF FLUOSOLID ROASTING

1-When the gas flow rate is very low and since the bed is porous, the gas permeates the bed without disturbing the ore particles.

In this stage the pressure drop is proportional to the flow rate.

Other factors influencing the pressure drop are

A- Void fraction

B- the particle size

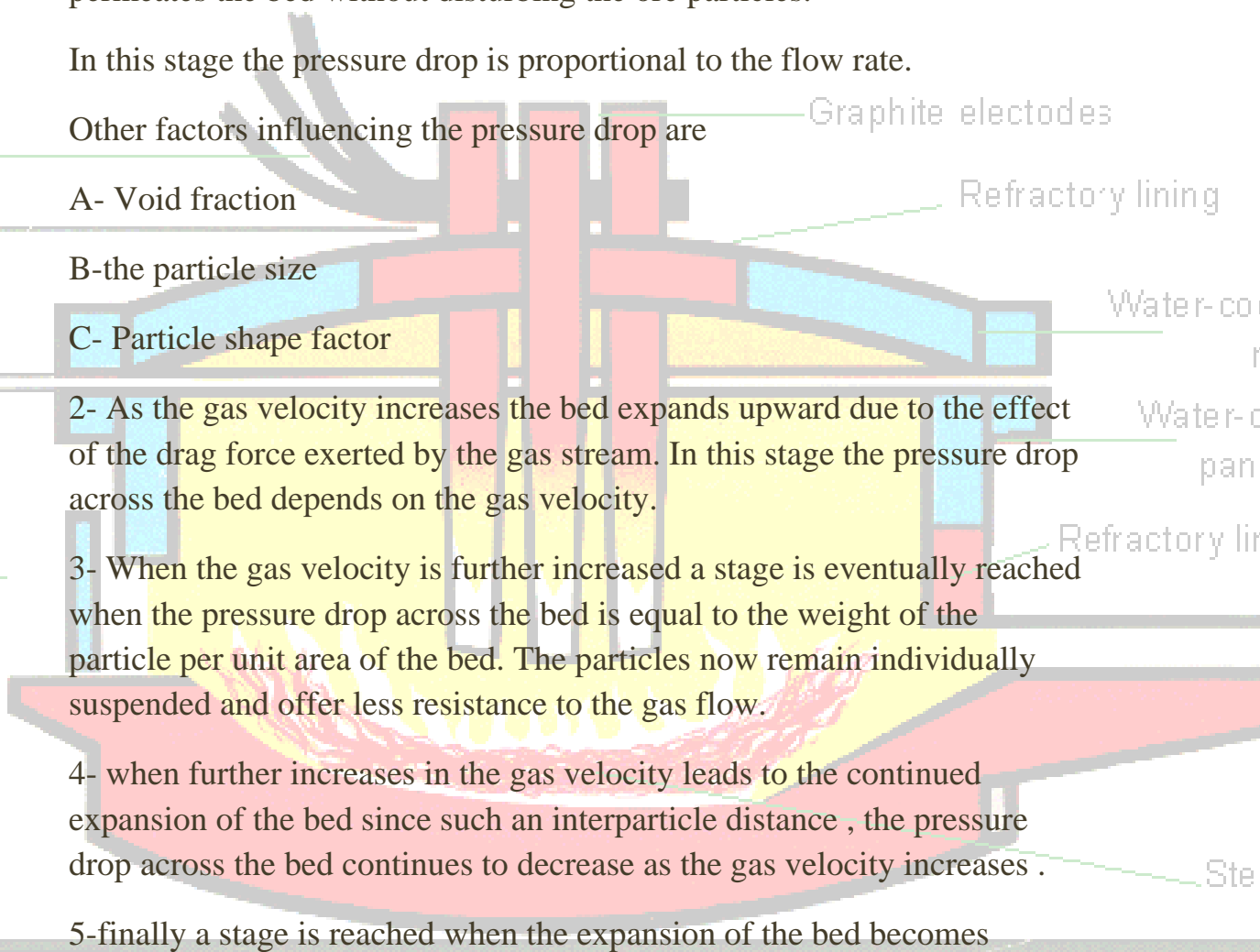
C- Particle shape factor

2- As the gas velocity increases the bed expands upward due to the effect of the drag force exerted by the gas stream. In this stage the pressure drop across the bed depends on the gas velocity.

3- When the gas velocity is further increased a stage is eventually reached when the pressure drop across the bed is equal to the weight of the particle per unit area of the bed. The particles now remain individually suspended and offer less resistance to the gas flow.

4- when further increases in the gas velocity leads to the continued expansion of the bed since such an interparticle distance , the pressure drop across the bed continues to decrease as the gas velocity increases .

5- finally a stage is reached when the expansion of the bed becomes independent of the gas velocity.



Advantage of fluidized bed roasting
It is an autogenous process so it has high energy efficiency .

DIAGRAM OF FLUIDIZED BED ROSTER

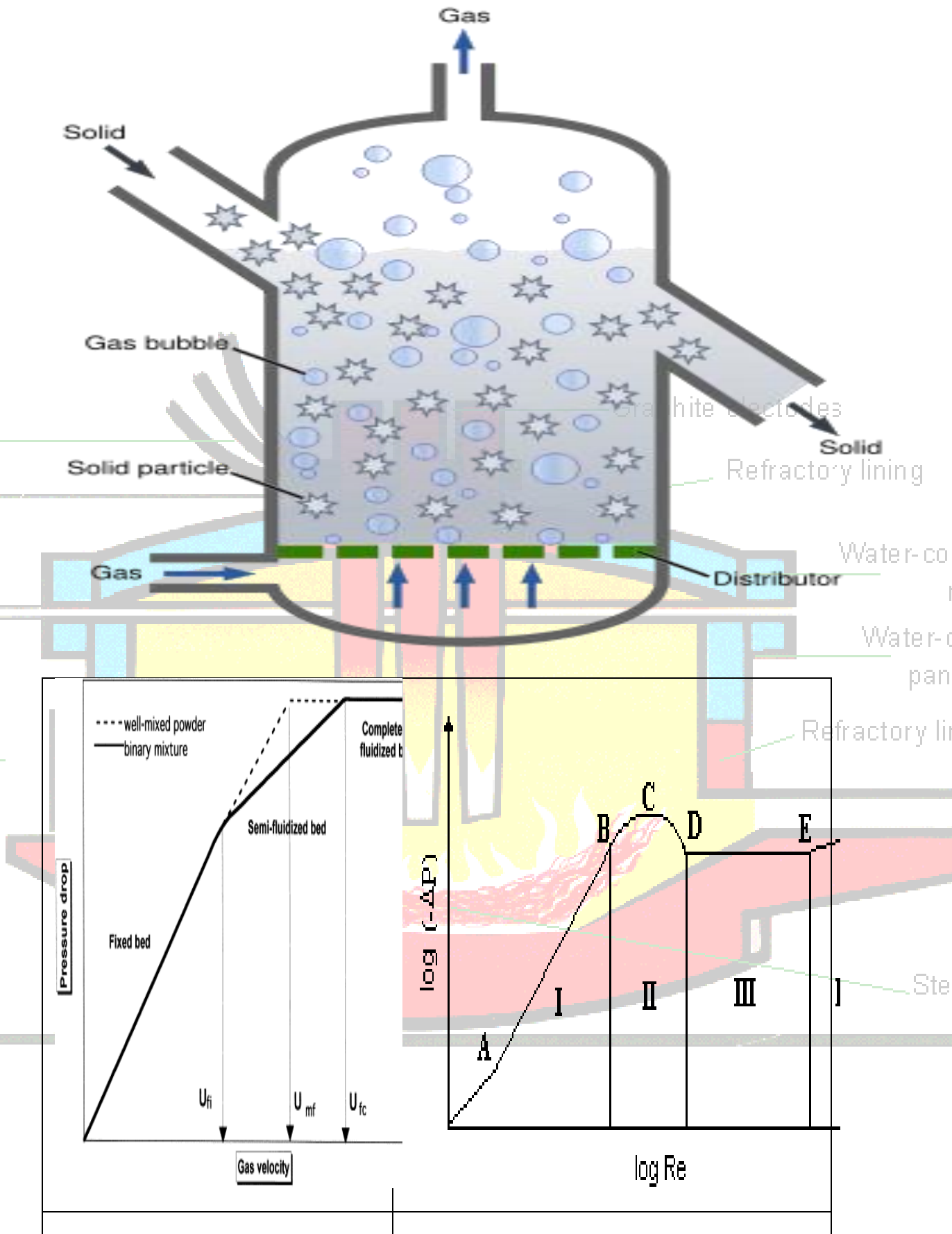


DIAGRAM OF TYPICAL FLUIDIZATION CURVE

- ❖ AB represent the pressure drop for the stationary bed , before fluidization occurs .
- ❖ BC indicates the bed is rearranged to provide minimum resistance to the gas flow.
- ❖ Point C represent or correspond to both maximum voidage of the packed bed or voidage corresponding to minimum fluidization , and the minimum gas velocity required for fluidization.
- ❖ Beyond C the pressure drop become independent of the gas velocity.
- ❖ For fluidized bed design minimum fluidization velocity is one of the most important factors.

AUTOGENOUS ROASTING

- ❖ When an ore particle is initially maintained at the minimum temperature in a stream of air and the roasting is initiated by an ignition device, then roasting continues to proceed even in the absence of any external heat such a reaction is termed as autogenously.

FACTORS ON WHICH IGNITION TEMPERATURE DEPENDS FOR FLUIDIZED BED ROASTING

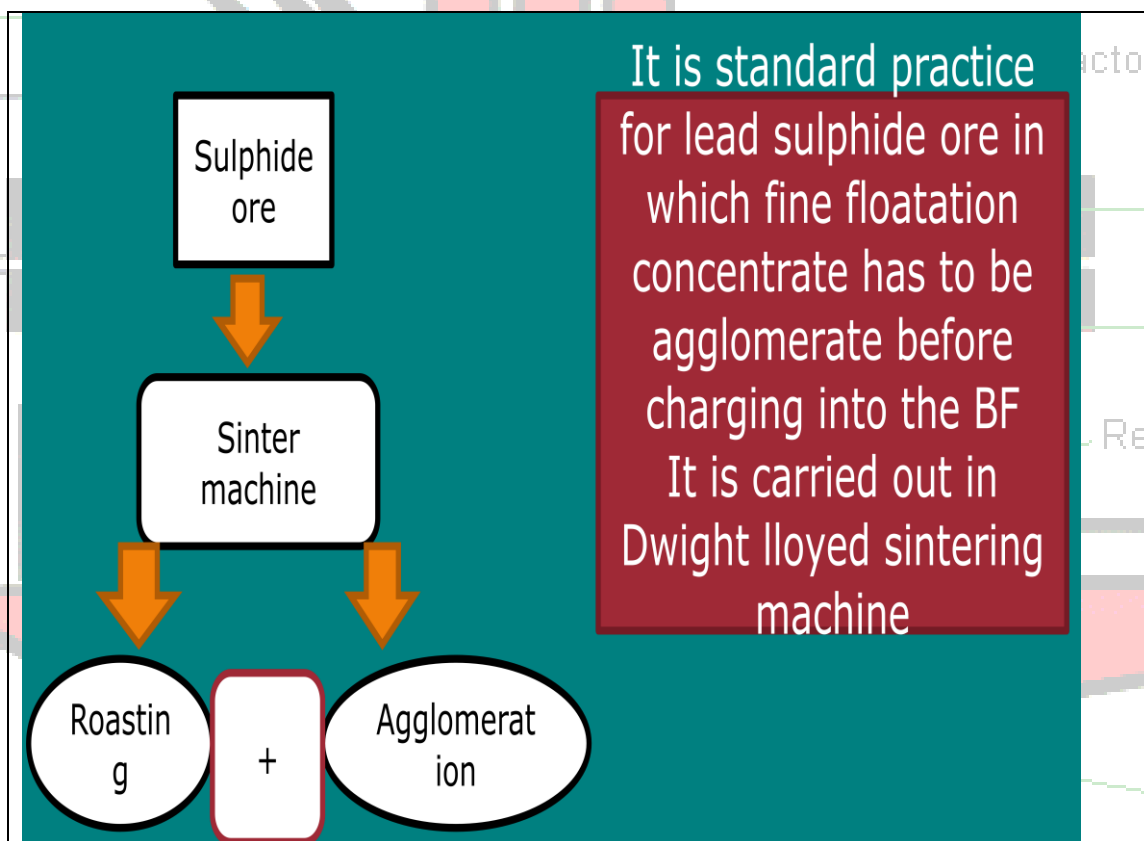
- ❖ Fluid flow
- ❖ Geometry of a reactor
- ❖ Characteristic of ore

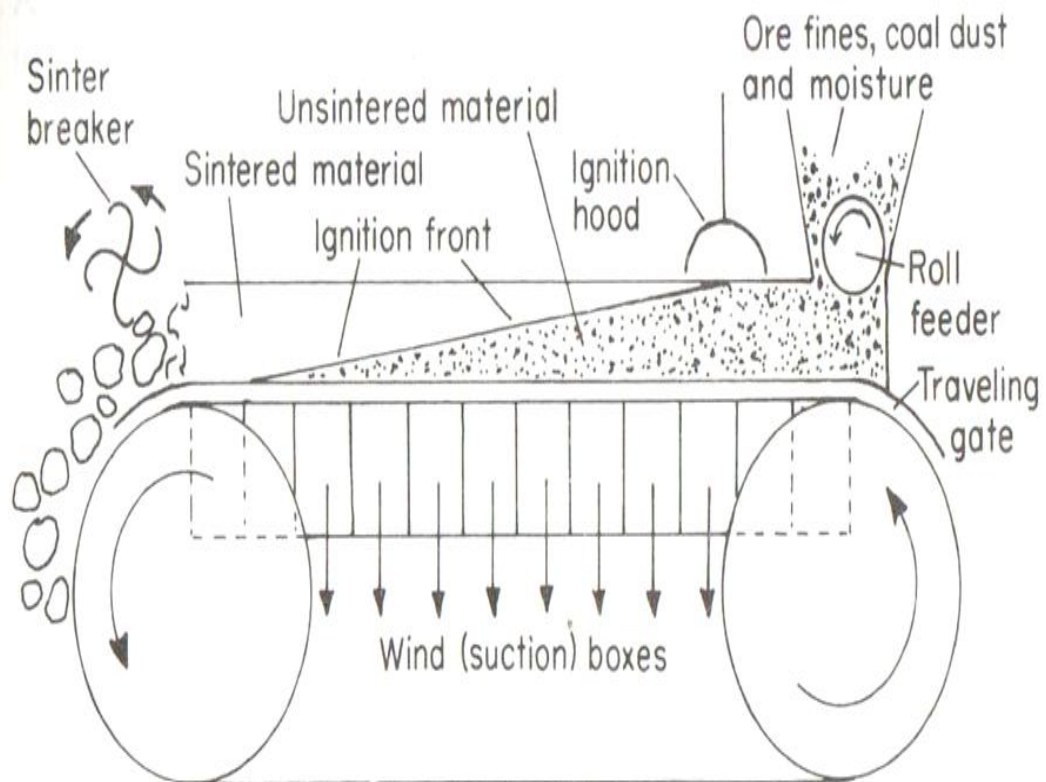
The ignition temperature roughly indicates the temperature required for fluidized bed roasting.

IGNITION TEMPERATURE : minimum temperature at which a mineral particle oxidized fast enough to maintain or increase the temperature of the roaster.

SINTER ROASTING OR BLAST ROASTING

- ❖ Heavy dust loss
- ❖ Permeability reduced it jam the furnace





STEPS IN SINTER ROASTING

1- The fine concentrate is charged as a layer 15-50 cm thick on to the endless revolving belt or grate or pallets which moves over wind boxes at regular speed.

2- Burners under the ignition hood is used to start the combustion of the bed surface. This combustion is propagated through the mass or charge by a current of air drawn through the charge into the wind box below which is connected a suction fan sufficient high temperature are develop in the material to cause partial or incipient fusion which produces a pores cinder like material called sinter.

3- When the sinter reaches the end of the machine it is discharged and cooled.

4-The cooled sinter is sized to give a uniform product.

The sinter roasting of sulphide ore does not require

Addition of any fuel to the charge because the sulphur in the charge itself act as a fuel.

But for an oxide or fuel is required ex- iron ore

WINNING OF METALS FROM SULPHIDES

1- Thermal decomposition (hgs), platinum and iridium sulphide)

2- Roasting and subsequent reduction.(ZnS)

3- Controlled roasting followed by smelting to produce matte and converting the matte to metal.(CuS)

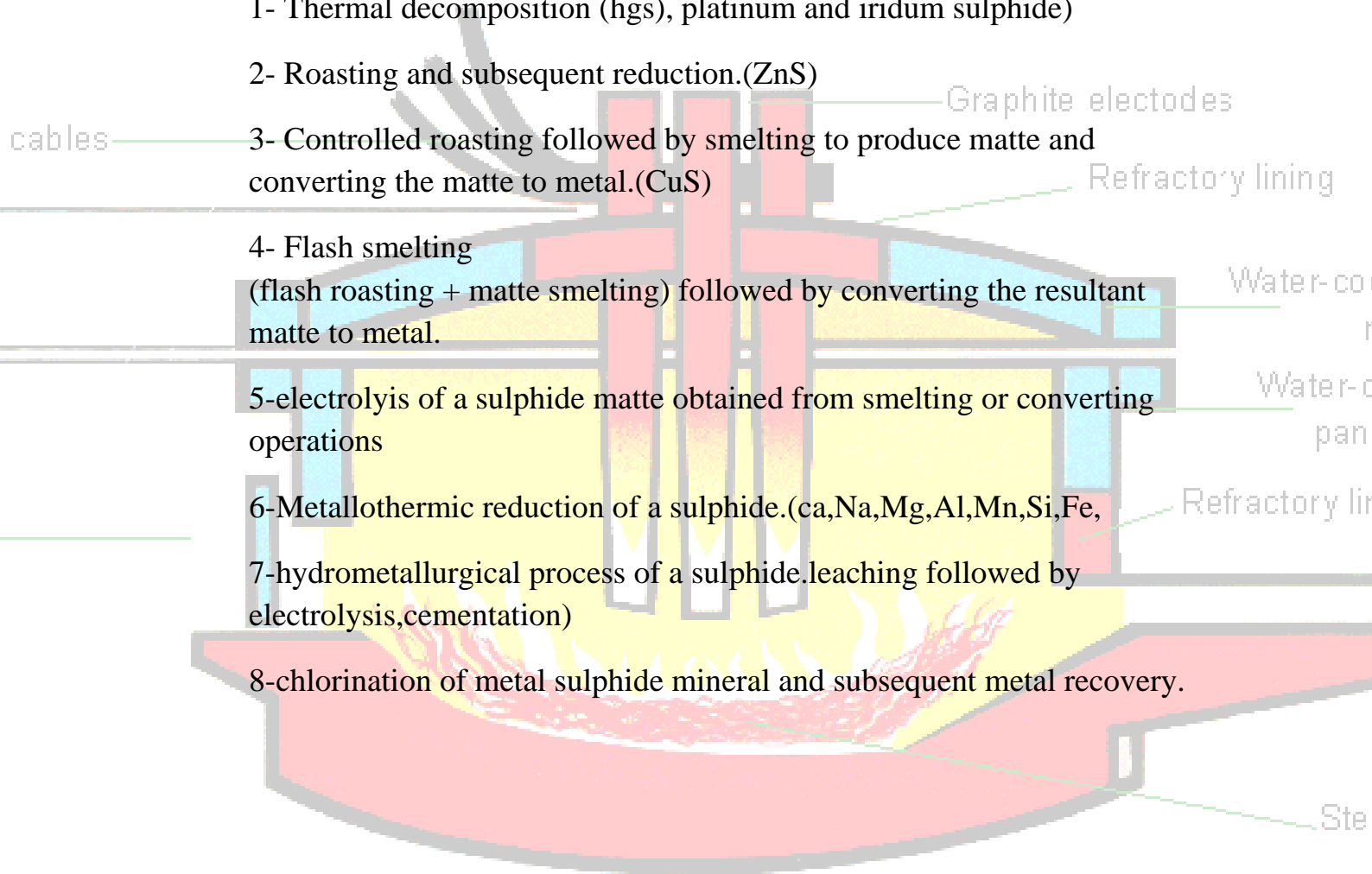
4- Flash smelting (flash roasting + matte smelting) followed by converting the resultant matte to metal.

5-electrolysis of a sulphide matte obtained from smelting or converting operations

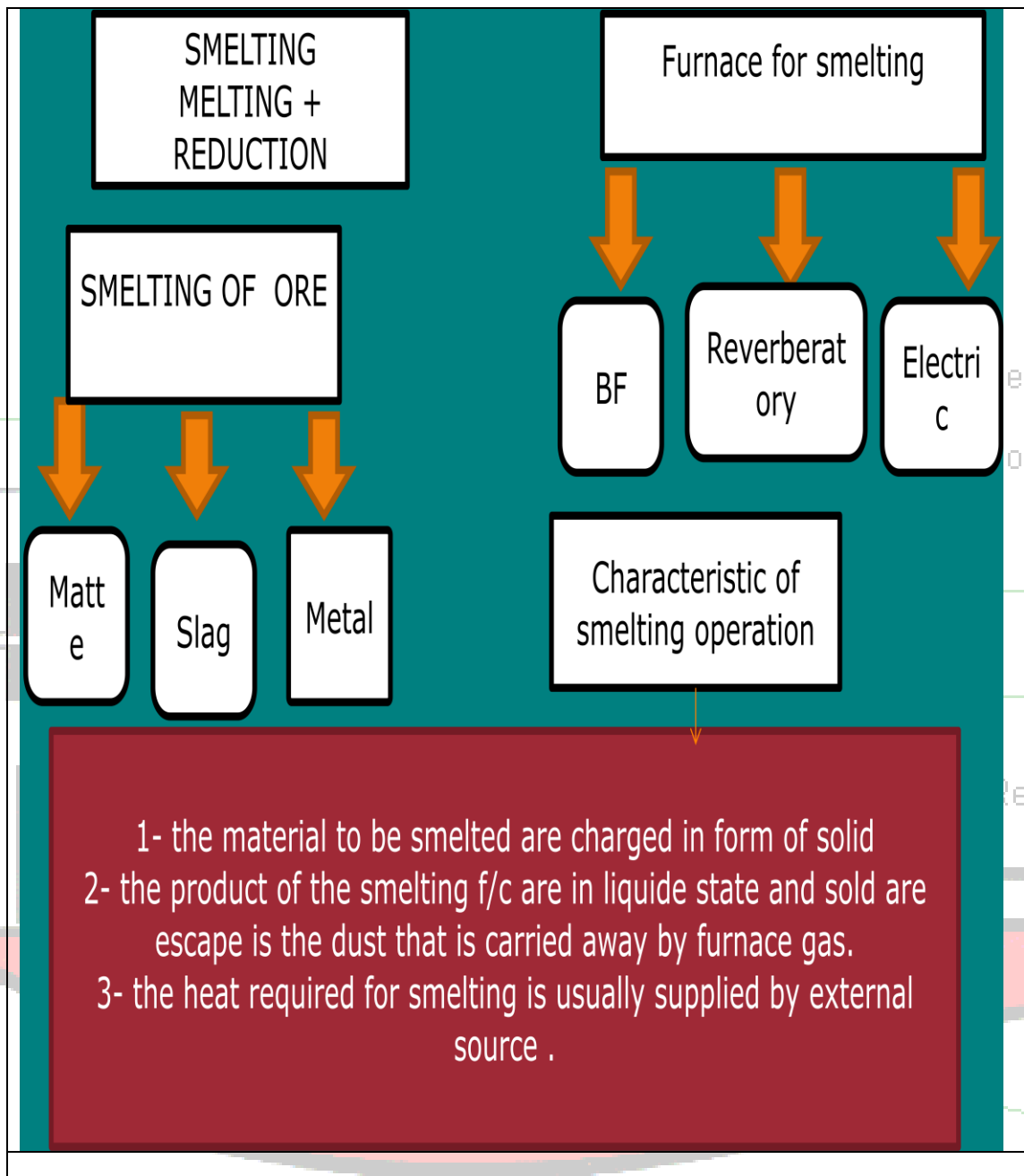
6-Metallothermic reduction of a sulphide.(Ca,Na,Mg,Al,Mn,Si,Fe,

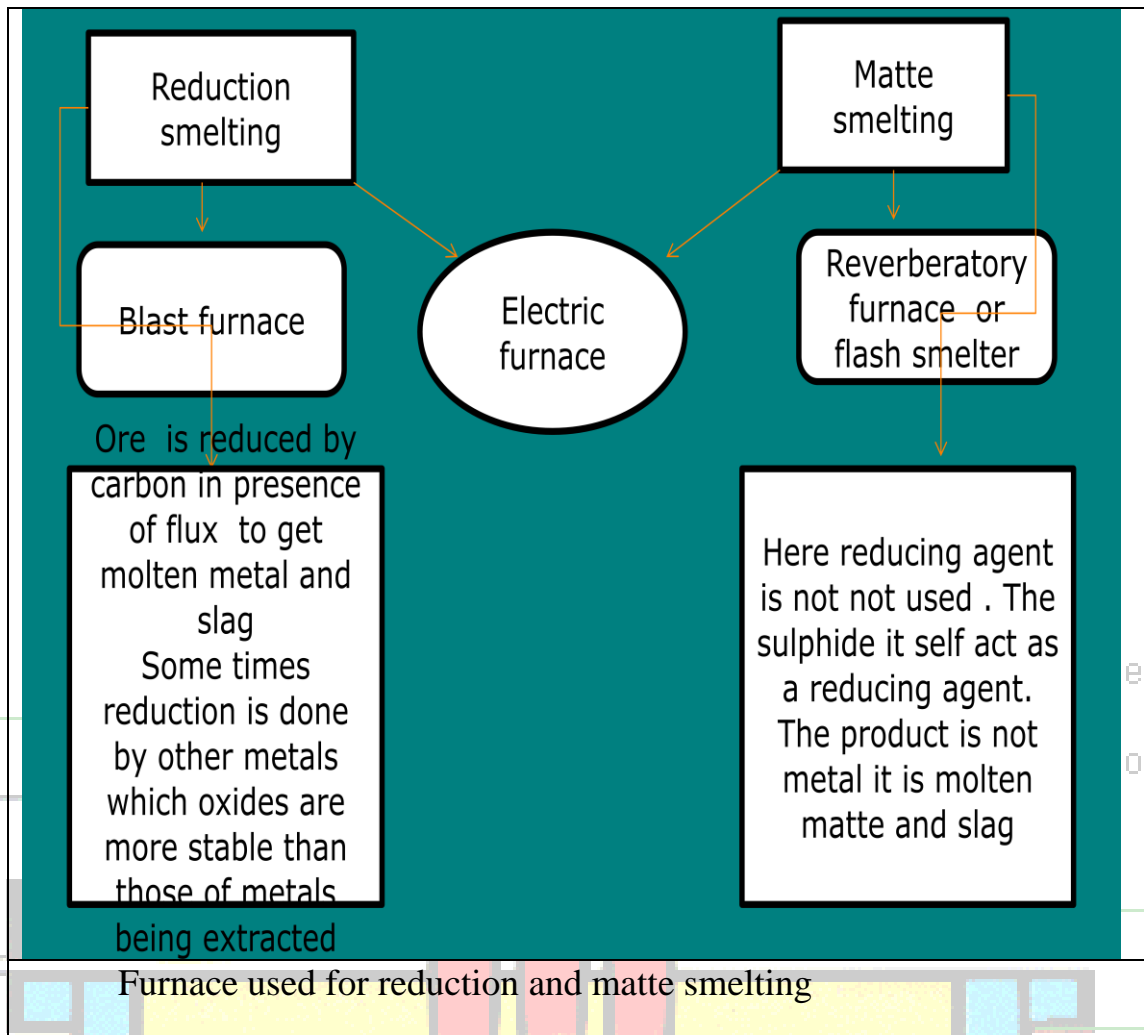
7-hydrometallurgical process of a sulphide.leaching followed by electrolysis,cementation)

8-chlorination of metal sulphide mineral and subsequent metal recovery.



MODULE -3





FLUXES

REASON OF USING FLUXES:

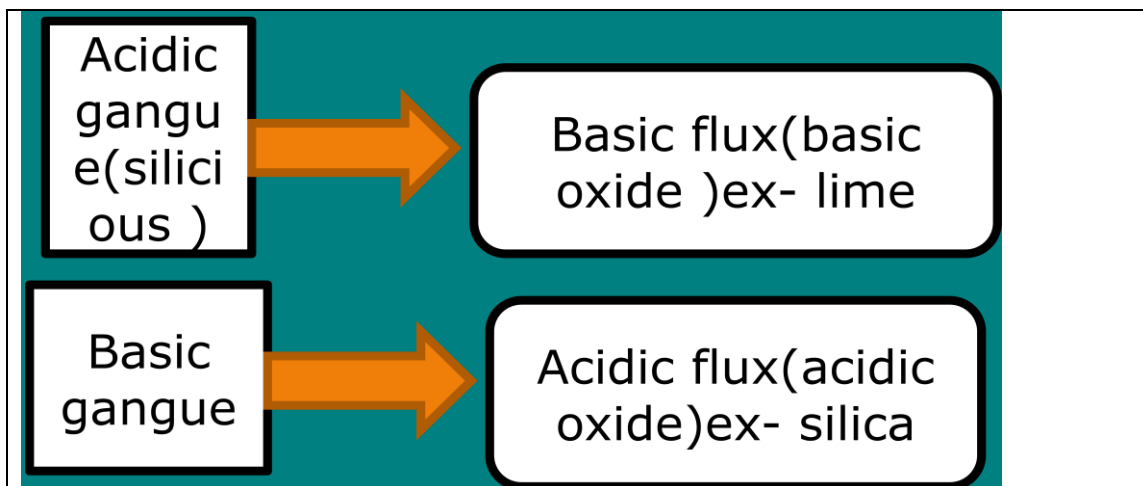
- i. Used to lower the liquidus temperature.
- ii. Lowers the viscosity of slag (increase the fluidity).

FLUX ARE CLASSIFIED ACCORDING TO THEIR CHEMICAL TYPE.

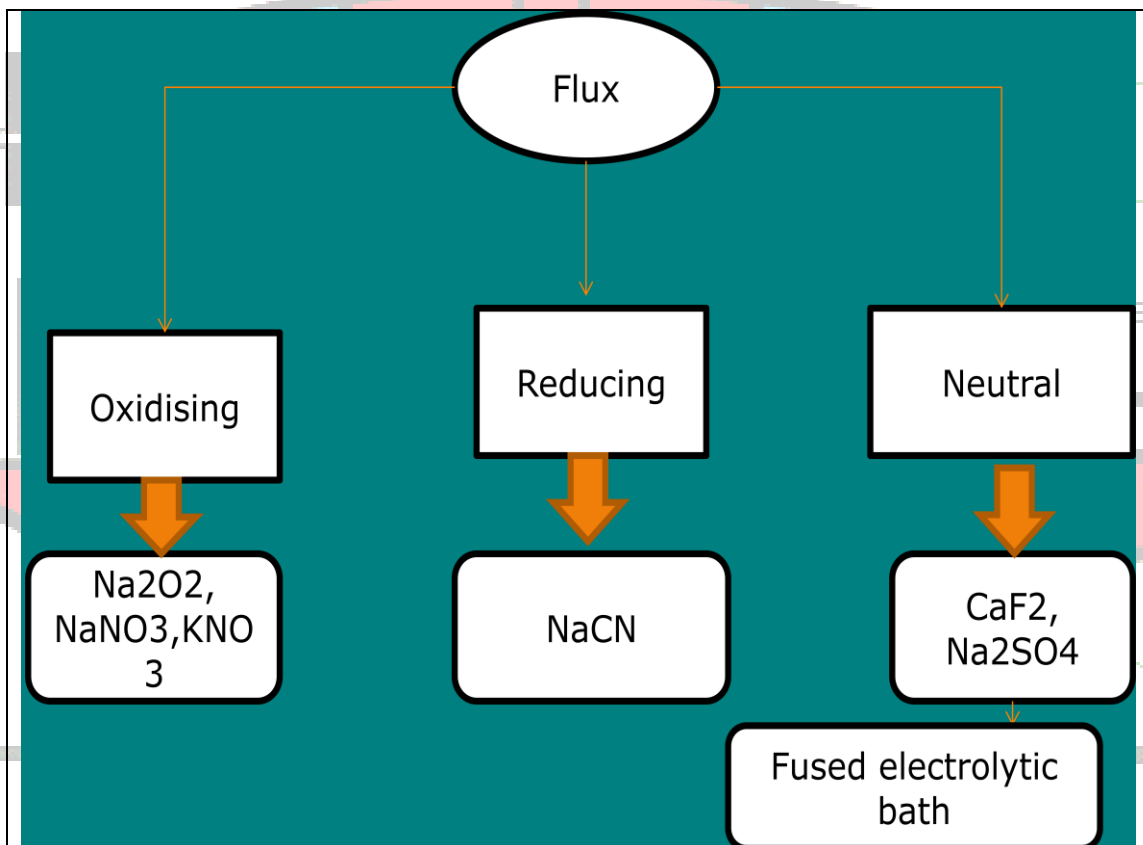
CRITERIA FOR CHOOSING FLUX :

- i. Chemical nature of gangue .
- ii. Properties desired in the slag as density and viscosity

Example :



FLUX TYPES



SLAGS

MAIN FUNCTION OF SLAGS

- i. To collect the unreduced gangue mineral as to form a separate layer in a metal extraction process.
- ii. Slag provides medium in which the impurities in a metal can collect during refining process.

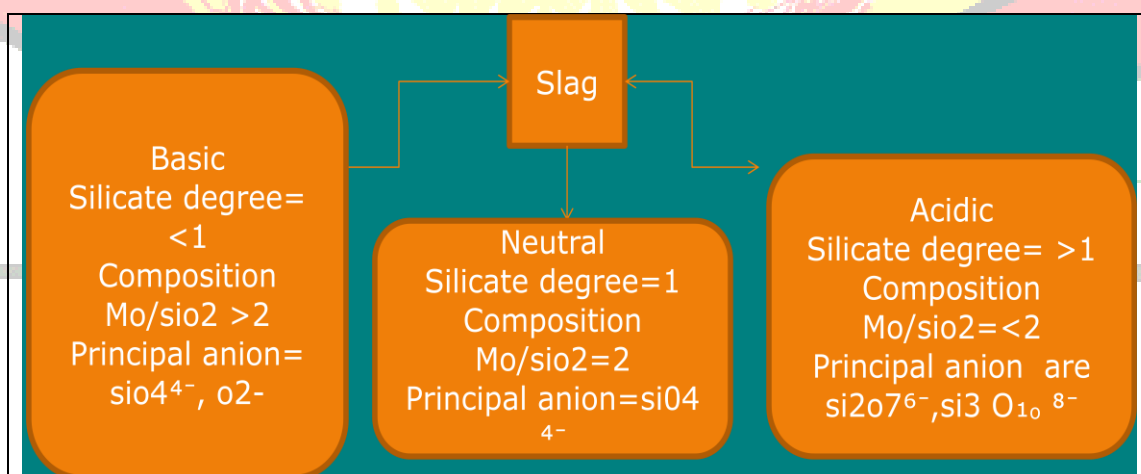
PROPERTIES OF SLAG

- i. Difference between specific gravity of slag and metal should be sufficiently high so that one can be easily separated from the other.
- ii. Slag must be fluid enough to permits its easy separation from the metal and also bring about mass transfer of the reaction and product species.
- iii. 3- The slag have a chemical composition which ensure that the activities of the impurities and of the dissolved gangue mineral are low.

CLASSIFICATION OF SLAG

In smelting slag are classified according to silicate degree.

Silicate degree = moles of acidic oxygen from SiO_2 / moles of basic oxygen from CaO , MgO , FeO .



- ❖ In melt there exist an equilibrium among the various types of anions.

Some free oxygen ions in very small quantity can be present in a neutral slag and even in the acidic slag.

BASICITY OF SLAG

In industrial practice basicity of slag is expressed as basicity number called 'V' ratio and defined by percentage ratio.

EXPRESSION OF BASICITY OF SLAG

- ❖ **Basicity = $\frac{CaO}{SiO_2}$, $\frac{CaO+MgO}{SiO_2+Al_2O_3}$, $\frac{CaO-4P_2O_5}{SiO_2}$**

- ❖ Basic slag contains higher proportion of lime

- ❖ Acidic slag contains higher proportion of silica.

METAL LOSES IN SLAG

- ❖ A serious problem sometimes occurs if the reactant and product oxides themselves form compounds during smelting this occurs for an oxide ore than can form a stable silicate form. Some times this is advantageous in producing slag with low melting point, it indicates a part of reactant raw material would be lost due to dissolution in the slag along with the gangue and flux.

- ❖ Example- during the blast f/c smelting of lead ore a significant lead oxide (PbO) may combines with silica to enter the slag as silicate.

- ❖ PbO loss can be minimised by adding scrap iron to the charge. Function of scrap in extraction of Pb . A- it reduces PbO to Pb, B- it help recover the lead from the silicate slag .

- ❖ $PbO + Fe = FeO + Pb$,

- ❖ $Pb \cdot SiO_2 + Fe = FeO \cdot SiO_2$

REASON FOR LOWERING OF VISCOSITY OF SLAG BY ADDITION OF BASIC OXIDE.

Addition of basic oxide lower the viscosity of slag because it leads to depolymerization and creates smaller flow unit , which are more mobile . Another way to increase fluidity and decrease the viscosity . Its by rising the temperature which leads to depolymerization as bonds break at high temperature occurs.

FORMATION OF SLAG

The formation of slag is facilitates by adding fluxing agent to ore such as quartz and lime , which together with the gangue forms multicomponent silicates slag with a relative low melting point .

All silicates melts are viscous.

To facilitate the removal of silicates the viscosity should be decrease either by two means :

- 1- adding suitable basic oxide
- 2- increasing the temperature.

SILICATE MELTS

Silicate melts are ionic in nature .

Composition of silicate melts : there could be

- 1- metallic ion
- 2-free oxygen ions
- 3-Complex silicates of varying size
- 4- How ever there could not be a silicon ion.

REASON OF HIGH VISCOSITY OF SLAG

Bulky less mobile silicate ions, which decrease the overall fluidity. Structure of silicate slag :structure of pure crystalline slag is a three dimensional network , consisting of silicon and oxygen atoms .

(Where each silicon atom is tetrahedrally attached to four atoms of oxygen . Possessing both long range order and short range order. But in molten silica how ever some si---o—si bonds reatures due to the effect of thermal energy and some depolymerization takes place, the short range order PERSISTS , even the long range order is lost. In such a situation viscosity is very high.

- ❖ When a basic metal oxide is added to molten silica the three dimensional network starts breaking . Here silica (acidic oxide) accept an oxygen ion and mo (basic oxide) donates an oxygen ions.
- ❖ The depolymerization reaction shows that as the quantity of the metal oxide added increases the silicates network is broken down into smaller and smaller unit.

Adding metal oxide to silicate slag at a concentration of 12 mole % the silicate networks break down in random manner, this means the three dimensional bonding would still be present through melt. Further addition leads to complete breakdown of silicates to gives discrete globular anions of the types $Si_3O_9^{6-}$, $Si_4O_{12}^{8-}$, etc. Further addition of metals oxide leads to break down of oxygen bridge and at a composition of $MO: SiO_2 = 2:1$ The smallest unit SiO_4^{4-} is obtained. On adding further metal oxide free oxygen ions (O^{2-}) becomes available in the melt.

REASON FOR LOWERING OF VISCOSITY OF SLAG BY ADDITION OF BASIC OXIDE.

Addition of basic oxide lower the viscosity of slag because it leads to depolymerization and creates smaller flow unit , which are more mobile .

Another way to increase fluidity and decrease the viscosity . Its by rising the temperature which leads to depolymerization as bonds break at high temperature occurs.

REDUCTION SMELTING USING CARBON

- Why carbon occupies unique position as a reducing agent :

- ❖ Easily available abundant .
- ❖ It is inexpensive .
- ❖ According to theory all metal oxide be reduced by carbon provided the temperature is high.

Metal oxide reduction by carbon at high temp :



We observe that temperature required for reduction of oxide by carbon in number of case are beyond practical limit.

SOLID AND GAS REDUCTION

- ❖ $\text{MO} + \text{CO} = \text{M} + \text{CO}_2$
- ❖ $\text{CO}_2 + \text{C} = 2\text{CO}$
- ❖ COMBINING THESE TWO REACTION
- ❖ $\text{MO} + \text{C} = \text{CO} + \text{M}$

It is just possible to produce manganese or at least an alloy of manganese (fe-mn) in a blast furnace ,

Metal lying above mn in the emf series from oxides having higher negative free energy of formation and may be reduced by carbon but not in blast furnace.

So for reduction of these more stable oxides we required electric furnace as it attain much higher temperature.

During cooling (from the reaction temperature) a back reaction may occur especially when the reduced metal is in the form of a vapour as in the case of magnesium.

- Back reaction in the case of magnesium has to be restricted by shock cooling but the resulting powder however is pyrophoric.

Some alkali metals form carbides ex-cac₂.

PROBLEM AT HIGH TEMPERATURE :

A- at high temperature a new stable phase namely the metallic carbides may appear, this occurs when metal reacts with carbon itself.

Formation of carbide is suppressed if the metal were produced in the presence of another solvent.

The solvent metal in which metal M is dissolved reduces the chemical potential of M and pushes the reduction reaction to the right, making reduction possible at lower temperature.

Greater the dilution the lower the temperature required for reduction. For some reason carbide formation is discouraged if M is in the form of alloy.

The production of ferroalloys also makes use of the advantage gained by alloying ferro vanadium, ferrotitanium, ferro silicon, ferro niobium, and other ferro alloys are produced by the reduction of corresponding oxide by carbon in the presence of iron.

Even alloying does not always ensure a carbide free product. Ex- ferro chrome normally contains a high proportion of carbon, the composition approaching Cr₄C(Fe).

METALLOTHERMIC REDUCTION OF OXIDE

- ❖ An oxide is reduced by a metal that forms stable oxides.
- ❖ Metallothermic reaction, carried out in an open container or a closed container (bomb) completely avoids carbon contamination.

- ❖ Metallothermic reduction principle is same as carbon reduction.
- ❖ Metallothermic reduction is usually carried out on a small scale and rarely referred as smelting .
- ❖ Principle : a metal that forms a stable oxide would replace metals from a less stable oxides.

FACTORS ON WHICH METALLOTHERMIC REDUCTION DEPENDS

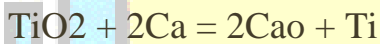
- ❖ reaction rate
- ❖ physical properties of the reactants and products ex- in thermite reduction



The product is in liquid state at the reaction temperature, and all the constituent are relatively non volatile.

Al_2O_3 can be slagged more easily by using another as a flux.

the reduction Of TiO_2 by calcium



In this case clean separation between metal and slag is difficult.

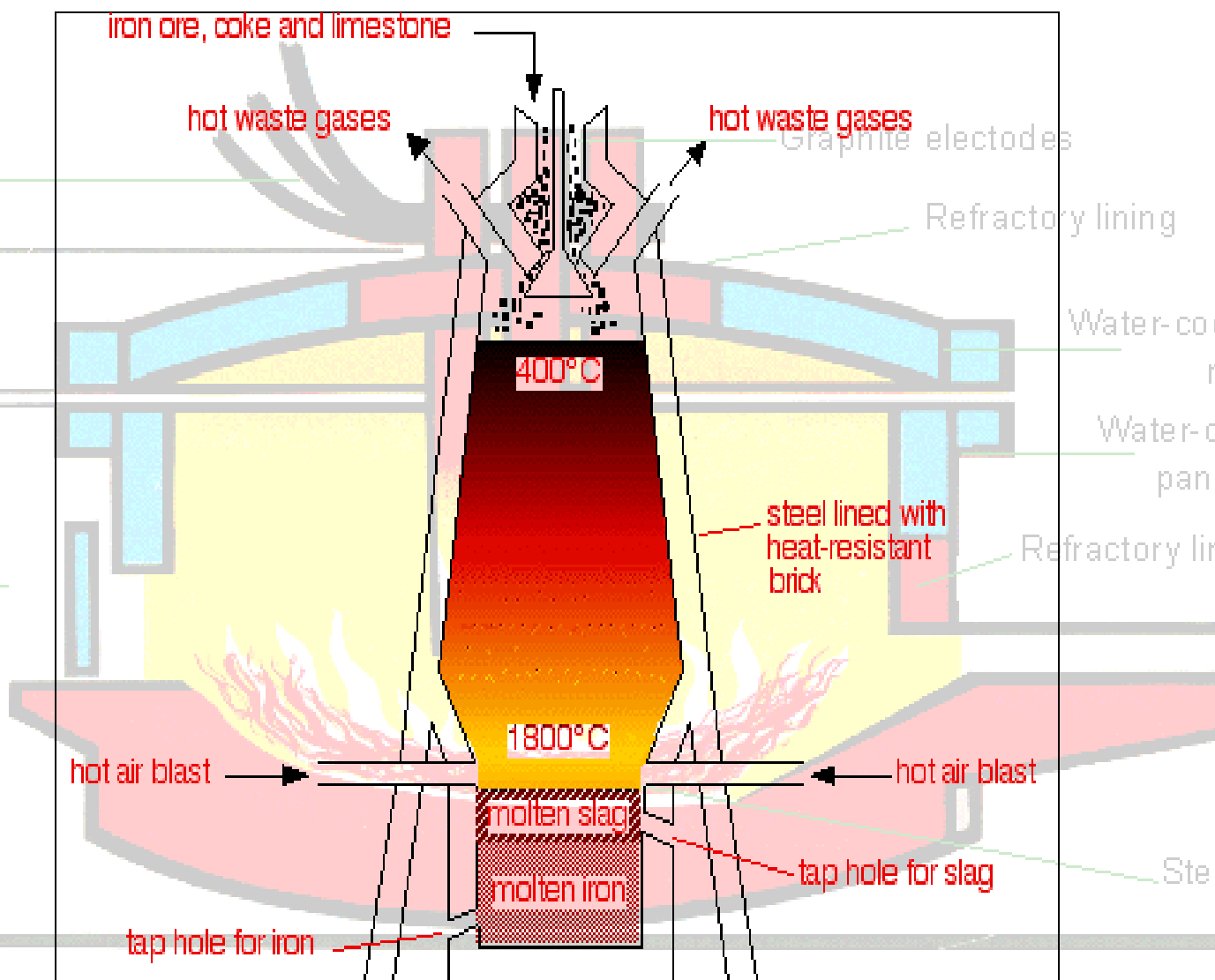
DIFFERENCE BETWEEN CARBOTHERMIC REDUCTION AND METALLO THERMIC REDUCTION

Carbothermic reduction	Metallothermic reduction
Carbon contamination	No carbon contamination
Cheaper process	Expensive process
Carried out in a large scale	Carried out in a small scale
Formation of carbide may takes place at high temperature	Formation of carbides is avoided.

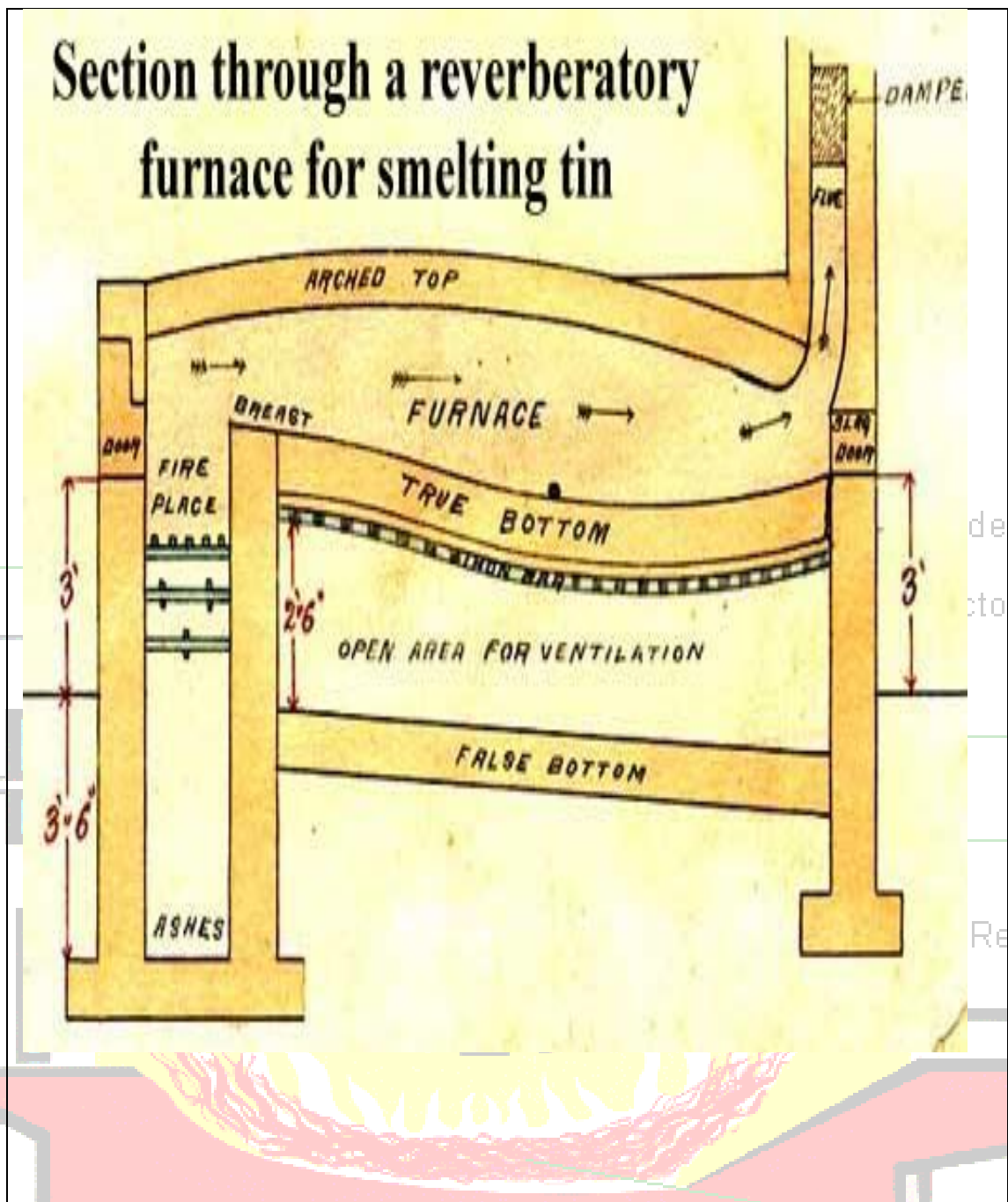
SMELTING FURNACE

- ❖ Blast furnace- for strong reducing condition(1600)
- ❖ Reverberatory f/c- mild reducing condition
- ❖ Electric furnace- for high temperature (2000) to reduce strong oxide to metal .

❖ **DIAGRAM OF BLAST FURNACE**



❖ **DIAGRAM OF REVERBERATORY FURNACE**



cables

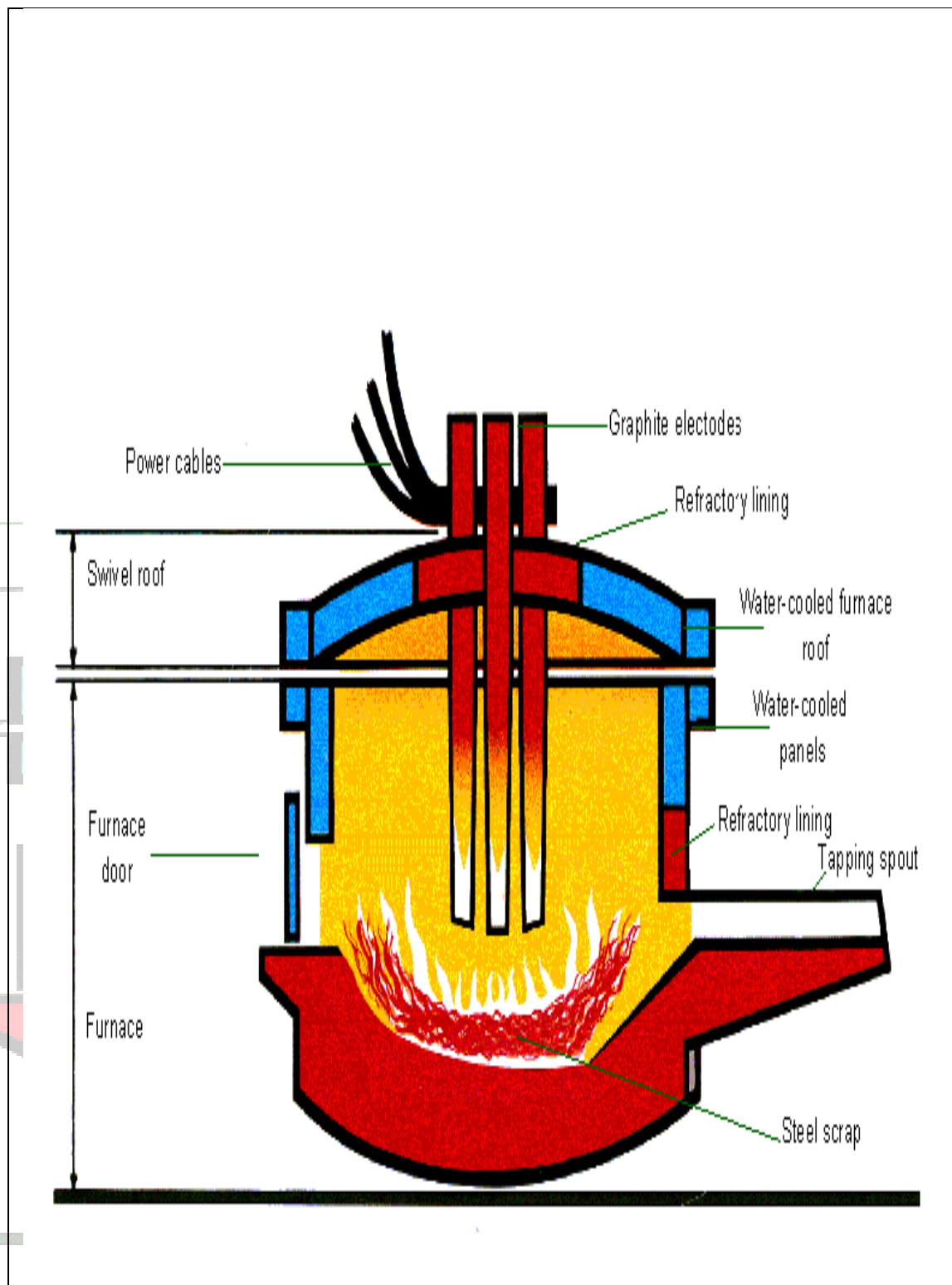
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❖ **Diagram of electric furnace.**



FLASH SMELTING

Flash roasting + smelting

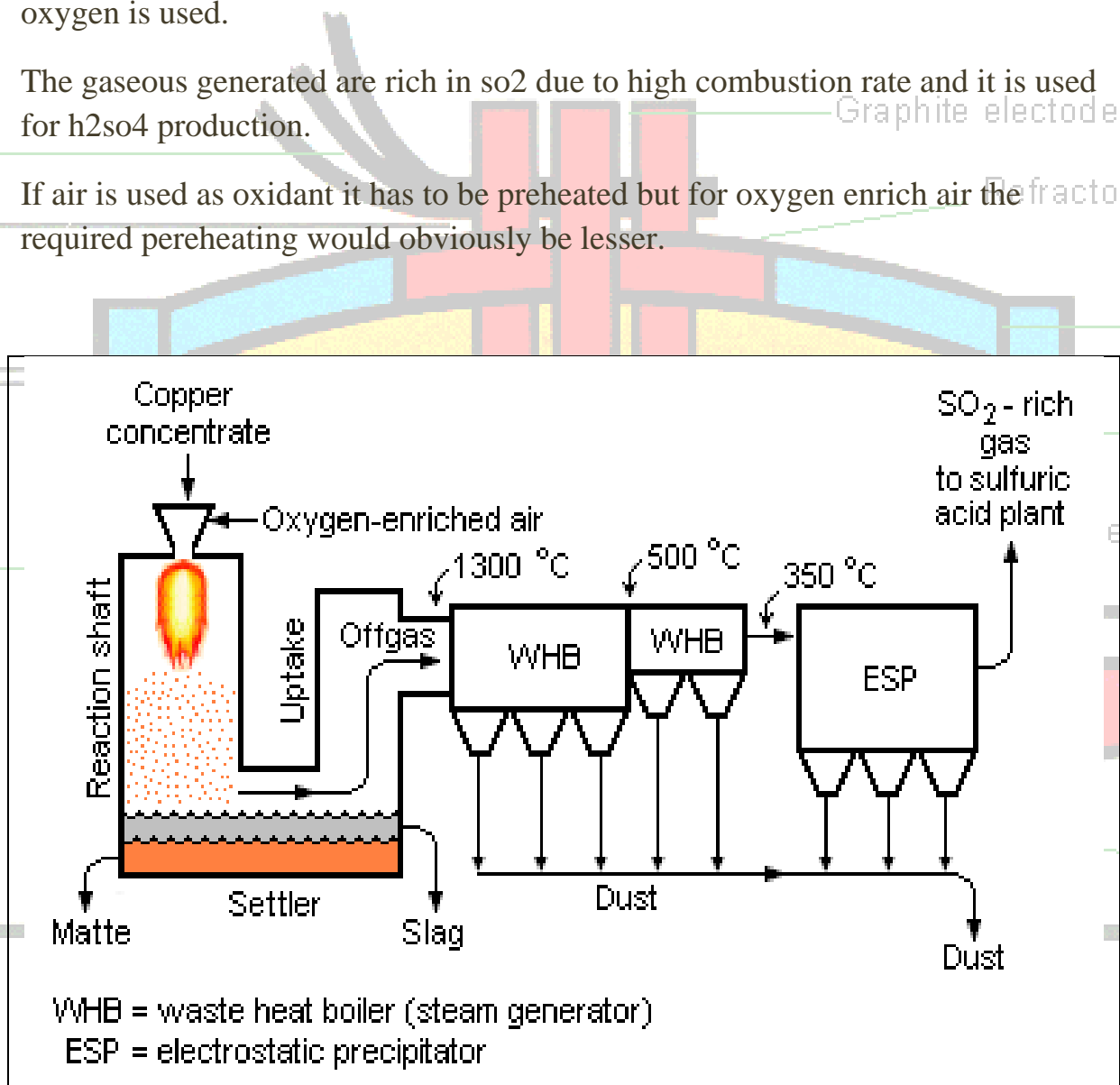
Carried out for sulphide concentrate.(NI & CU sulphide).

In flash smelting the sulphide concentrate is burn with oxygen or preheated air . During this a large amount of heat is generated which melt the concentrate to matte and slag which settle into the hearth.

To maintain autogeneous smelting instead of air enriched preheated air with oxygen is used.

The gaseous generated are rich in so2 due to high combustion rate and it is used for h2so4 production.

If air is used as oxidant it has to be preheated but for oxygen enrich air the required pereheating would obviously be lesser.



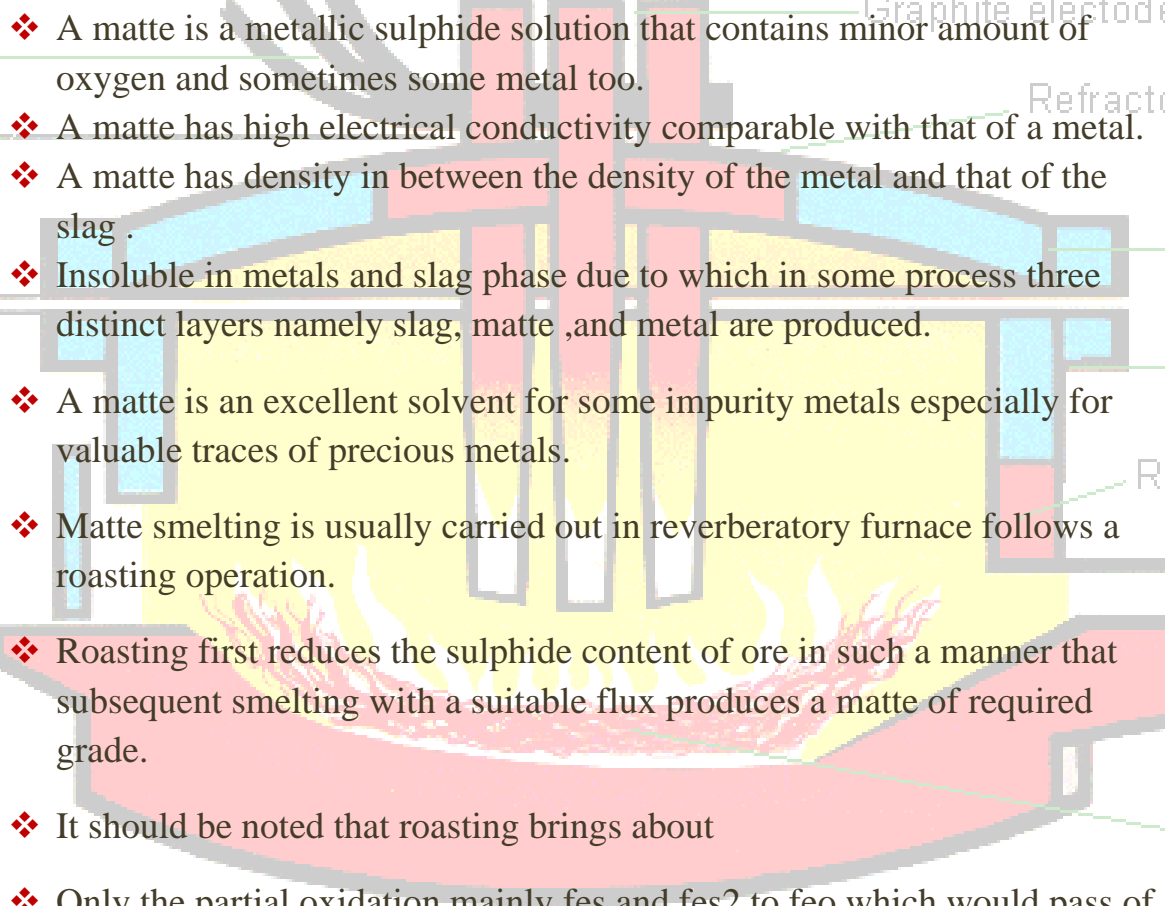
MATTE SMELTING

Type of smelting practice which produces matte and slag as a product .

Matte smelting practice is carried out for sulphide concentrate.

In the extraction of metal from a sulphide ore an important method used involves the production of a liquid matte from the ore and its subsequent conversion to metal .

CHARACTERISTIC OF MATTE.

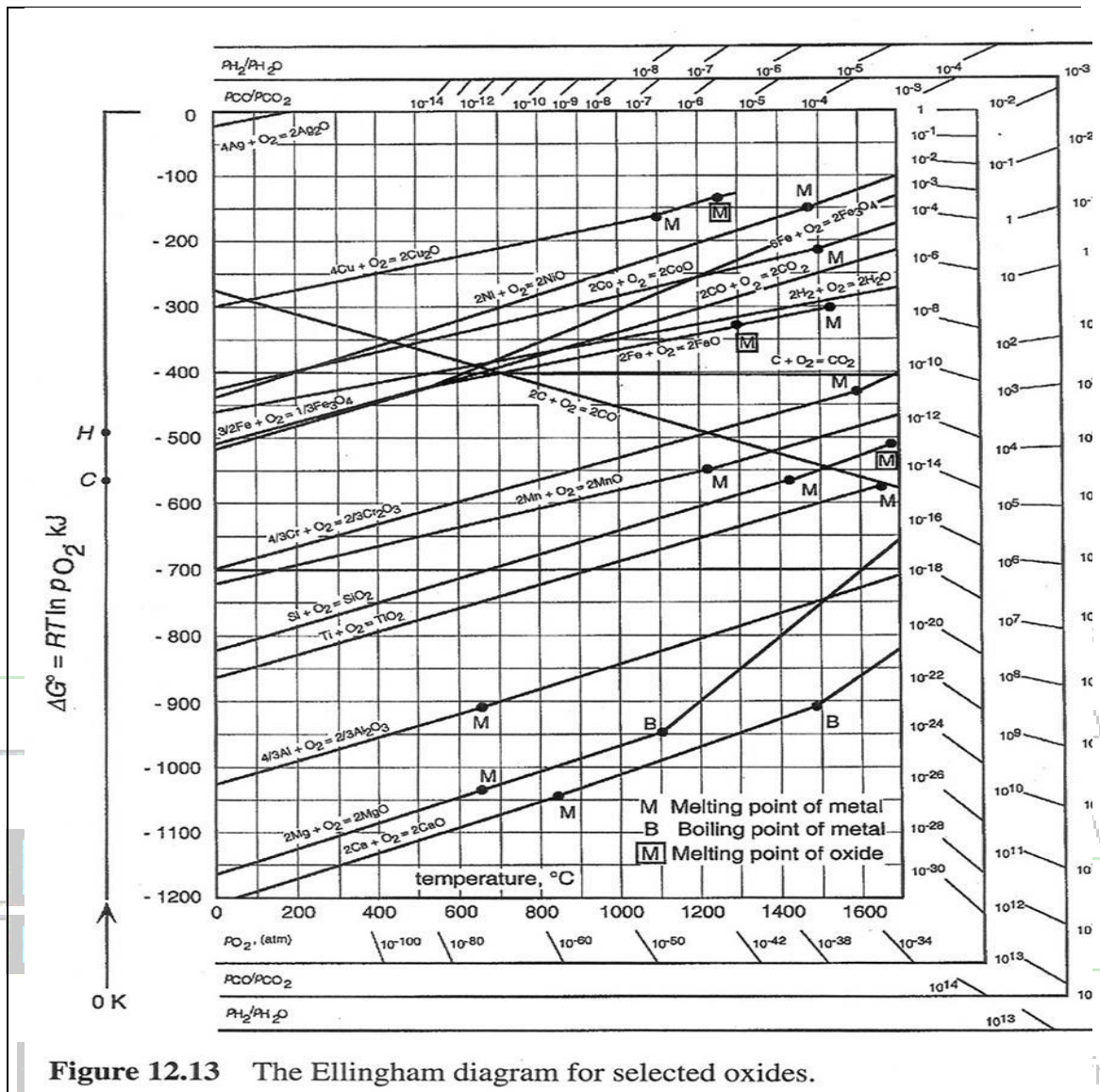
- 
- ❖ A matte is a metallic sulphide solution that contains minor amount of oxygen and sometimes some metal too.
 - ❖ A matte has high electrical conductivity comparable with that of a metal.
 - ❖ A matte has density in between the density of the metal and that of the slag .
 - ❖ Insoluble in metals and slag phase due to which in some process three distinct layers namely slag, matte ,and metal are produced.
 - ❖ A matte is an excellent solvent for some impurity metals especially for valuable traces of precious metals.
 - ❖ Matte smelting is usually carried out in reverberatory furnace follows a roasting operation.
 - ❖ Roasting first reduces the sulphide content of ore in such a manner that subsequent smelting with a suitable flux produces a matte of required grade.
 - ❖ It should be noted that roasting brings about
 - ❖ Only the partial oxidation mainly FeS and FeS_2 to FeO which would pass of into slag phase .
 - ❖ Matte smelting is carried out for extraction of Cu, Ni, and sometimes antimony.
 - ❖ Common ore of this material contains sulphide mineral including FeS .

- ❖ Copper is recovered from the matte by a process known as converting. In which air is blown through a side blown converter,

ELLINGHAM DIAGRAM

Salient features

- ❖ 1. Curves in the Ellingham diagrams for the formation of metallic oxides are straight lines with a positive slope.
- ❖ 2. The lower the position of a metal in the Ellingham diagram, the greater is the stability of its oxide. For example, the Ellingham diagram for Al is found to be below Fe₂O₃.
- ❖ 3. The greater the gap between any two lines, the greater the efficiency of the reducing agent.
- ❖ 4. Stability of metallic oxides decrease with increase in temperature. Highly unstable oxides like Ag₂O and HgO easily undergo thermal decomposition.
- ❖ 5. The formation enthalpy of carbon dioxide (CO₂) is almost a temperature-independent constant, while that of carbon monoxide (CO) has negative slope. According to Boudouard reaction, carbon monoxide is the dominant compound in higher temperatures, and the higher the temperature, the more efficient reductant carbon monoxide also is.
- ❖ 6. A substance whose Gibbs free energy of formation is lower (ΔG line lower on diagram) at given temperature, will reduce one whose free energy of formation is higher on the diagram. Hence metallic aluminum can reduce iron from iron oxide into metallic iron, aluminum itself oxidizing into aluminum oxide. (This reaction is employed in thermite.)
- ❖ 7. The intersection of two lines imply the equilibrium of oxidation and reduction reaction between two substances. Reduction with using a certain reductant is possible at the intersection point and higher temperatures where the ΔG line of the reductant is lower on diagram than the metallic oxide to be reduced. At the point of intersection the Gibbs energy is 0 (zero), below this point the Gibbs energy is <0 and the oxides are stable, while above the point of intersection the Gibbs energy is >0 and so, the oxides are unstable.
- ❖ $MO(s) \rightarrow M(s) + O(g)$



- ❖ Solution loss reaction is an endothermic reaction .
- ❖ And when the change in entropy is positive(due to increases in miles of gas) then change in gibbs free energy is negative .and vice versa . In case of number of moles only gases moles are consider .

PREDOMINANCE AREA DIAGRAM

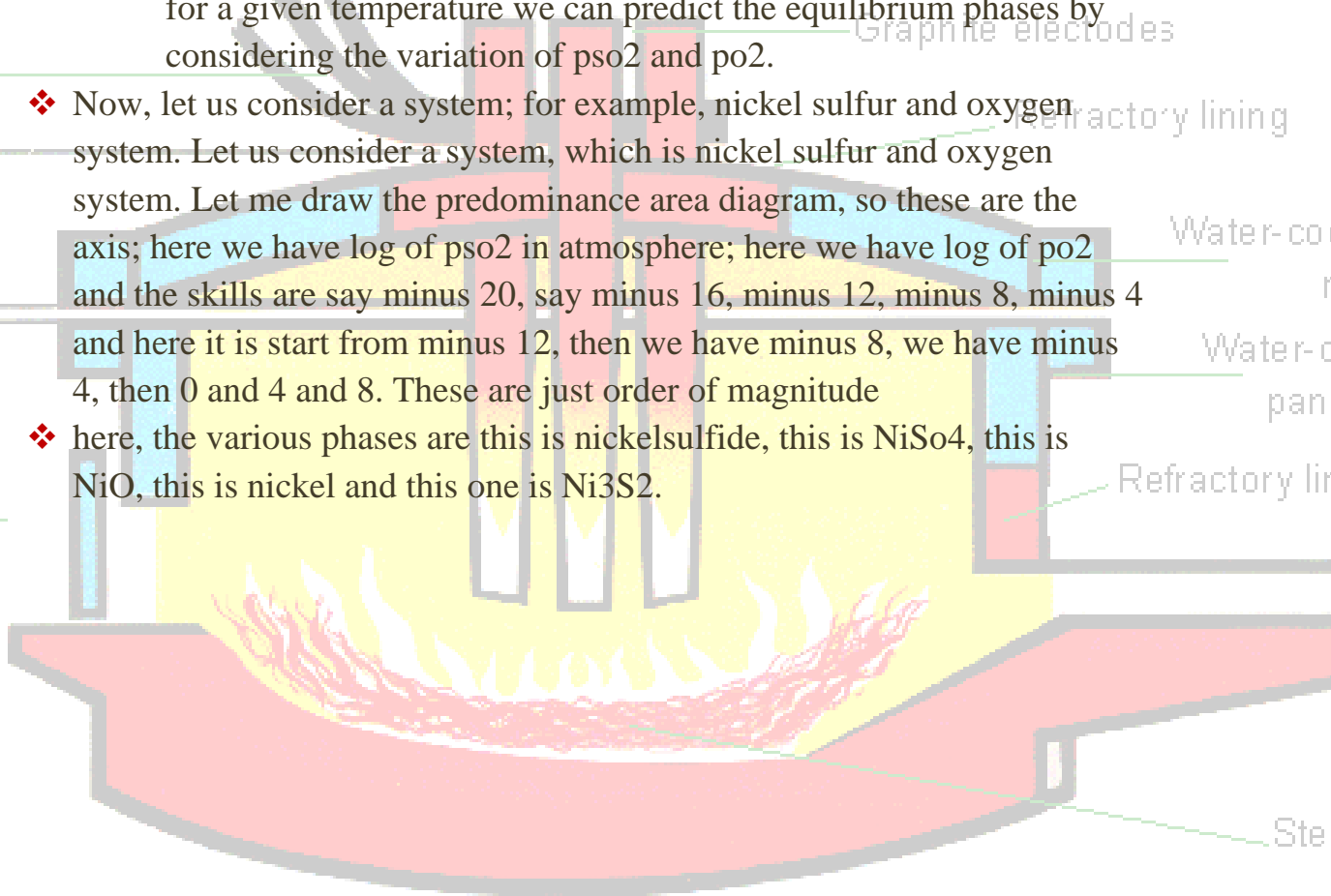
- ❖ Now, one of the important things in case of roasting is to predict the phases or number of phases which can form at a particular temperature. So that information can be derived from the predominance area diagram;

- ❖ the name suggest, this predominance area diagram gives the information about the stability of a phase for a given partial pressures of SO₂ and oxygen.

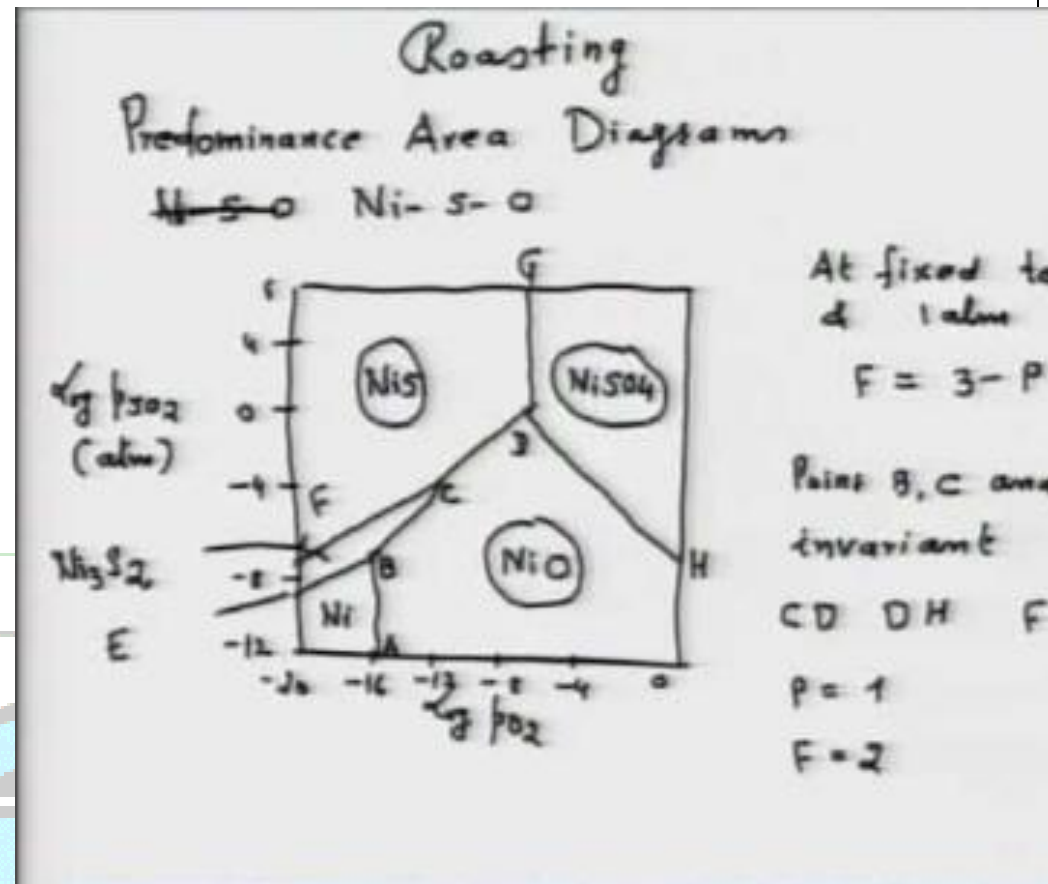
- Remember, this predominance area diagram is constructed at constant temperature and pressure. As I have said that when we apply the phase rule to the equilibrium of the phases, when there is a condensed phase and also temperature is a constant, then the degrees of freedom it becomes equal to 3 minus p. Accordingly, we need a three dimensional diagram if we want to construct a predominance area diagram for MSO system that is metal sulfur and oxygen system, where p_{SO₂}, p_{O₂} and temperature are the variables. But now, if you take temperature also as a constant, then for a given temperature we can predict the equilibrium phases by considering the variation of p_{SO₂} and p_{O₂}.

- ❖ Now, let us consider a system; for example, nickel sulfur and oxygen system. Let us consider a system, which is nickel sulfur and oxygen system. Let me draw the predominance area diagram, so these are the axis; here we have log of p_{SO₂} in atmosphere; here we have log of p_{O₂} and the skills are say minus 20, say minus 16, minus 12, minus 8, minus 4 and here it is start from minus 12, then we have minus 8, we have minus 4, then 0 and 4 and 8. These are just order of magnitude

- ❖ here, the various phases are this is nickelsulfide, this is NiSo₄, this is NiO, this is nickel and this one is Ni₃S₂.



Predominance Diagram for Nickel-Sulfur-Oxygen



PYROMETALLURGY PROCESS USING VACUUM

Vacuum degassing, of steel and purifying certain metals and alloys.

Extraction and refining of metals using vacuum are :

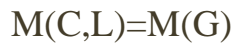
Ti, Ge, Ta, Nb, Zr. Because they possess high affinity to hydrogen and nitrogen.

Others uses are : distillation of metals and alloys, melting, and casting, various heat treatment, sintering of metal powders, deposition of metals in its vapour state, and joining of metals,

REACTIONS THAT ARE FAVORED BY THE APPLICATION OF VACUUM CAN BE CLASSIFIED

AS

- ❖ Thermal reduction : $R(C,L)+MA=RC+M(G,I)$,
- ❖ THERMAL DISSOCIATION : $MA(C,L)=M(G)+A(S,L,G)$
- ❖ SUBLIMATION OR DISTILLATION :



$M(IN SOL)=M(G)$ the equilibrium can be shifted by changing the pressure parameters. The use of vacuum helps in eliminating that reaction products which is volatile, thus driving the reaction toward completion. Pressure changes the free energy tem relationship.

ADVANTAGES OF VACCUM

PYROMETLLURGY

- ❖ Zinc sulphide can directly reduced by iron at 1000 degree centigrade under vacuum of about 1 mm of mercury. In this case roasting and reduction stages are avoided, and metals is produced in a single stage .
- ❖ So its very help full for metallothermic reduction.
- ❖ Vacuum can used for reduction and dissociation of halides, hydrides, nitrides.
- ❖ When vacuum is applied distillation and sublimation occurs at lower temperature.

DEMERITS OF VACCUM PROCESS IS EXPENSIVE

ONE.

Example is vacuum arc re melting :

Application is : refining refractory metals and reactive metals ex- Ti, zr, W, also used for high quality steel and alloys.

here the metal to be refined by vacuum process is first cast , forged or if it in from of powder is pressed by using dies after that its is welded to form a long electrode . Then this metal electrode is melted by creating a ARC between the electrode and metal pad present on crucible. In a copper crucible contain a metal bottom which is water cooled . The electrode is gradually lowered with the help

of the sliding vacuum seal as its tip melts due to the arc power. A constant spacing is maintained between the electrode tip and the surface of metal pool formed. Pure ingot is started forming inside the crucible pressure maintained is 10^{-3} mm Hg

1- Degassing in the arc zone occurs, and volatile impurities are removed depending on the pressure and the temperature prevailing in the arc.

2- Deoxidation of the metal may be brought about if an element with a strong affinity for oxygen is present in the metal, provided the metal oxide is volatile enough. For example if carbon is present in tungsten electrode both carbon and dissolved oxygen are removed in the form of gaseous carbon monoxide because of high temp and vacuum condition.

3- Homogenization of the inclusion occurs if present

4- Ingot is having minimum amount of macro segregation and free from axial soundness.

5- But sulphur and phosphorus are not removed

HALIDE METALLURGY AND HALOGENATION

- ❖ Reactive Chloride and fluorides are most commonly used halides.
- ❖ Chlorides is preferred over fluoride due to less corrosive and easy to handles.
- ❖ Some chlorides are hygroscopic where fluorides are not due to this fluorides are preferred in some case.

**PRINCIPLE OF HALIDE METALLURGY:-
HALIDES ARE HAVING LOW MELTING AND
BOILING POINT.**

OBJECTIVES OF CHLORINATION

- ❖ Opening of relatively complex mineral and the recovery of the metallic value.'

- ❖ Beneficiation of low grade ore to yield the metal halide either in the vapour state or in the condensed state.
- ❖ A chloride can be effectively separated from the gangue materials and processed for the production of metal.
- ❖ Many metallurgical wastes can also be chlorinated for subsequent metal recovery.
- ❖ Production of pure halides of reactive metals from which oxygen free metal can be obtained . reactive metals such as U, Th, Ti, Be, Zr, if produced from oxide may contain appreciable quantity of oxygen which is detrimental to their properties.

A METAL CAN BE PRODUCED FROM HALIDES

BY

- ❖ Metallothermic reduction of chlorides: reactive metals and rare metals are formed by reducing the halides by other metals.
 - Ex- Ti and Zr .
 - In krolls process which is used for reduction of a halides using mg
 - $TiCl_4 + 2mg = 2mgCl_2 + Ti$ here sodium may be used instead of mg
 - the principle of halides reduction can be understood from a chlorine free energy diagram which is similar to that of oxides . in this diagram elements such as Na, K, Li, Ca ,Mg appears at the bottom because their halides are very stable. Therefore these metals are excellent reducing agent.
- ❖ Fused salt electrolysis
- ❖ Vapor transport process.

CHLORINATION PROCESS IS CATEGORISED INTO

- ❖ Chloridising roasting
- ❖ Chloridising volatilizing
- ❖ Chlorination of fused salt.

OLDER CLASSIFICATION OF CHLORINATION PROCESS

- ❖ In chloridising roasting the ore is roasted with common salt and the solid chloride is recovered by leaching. Suited for sulphide ore where roasting reaction is autogenous .

- Ex- $2\text{NaCl} + \text{MS} + 2\text{O}_2 = \text{Na}_2\text{SO}_4 + \text{MCl}_2$
- For oxide ore ore is roasted with elemental sulphur
- Ex- $4\text{NaCl} + 2\text{MO} + \text{S}_2 + 3\text{O}_2 = 2\text{Na}_2\text{SO}_4 + 2\text{MCl}_2$

- ❖ In case of chloridising volatilizing : chlorination is done at high temp and chloride is recovered by volatilizing . For highly volatile chlorides the elimination of reaction products is easier Zr, Ti, Be

Chlorination in a fused salt bath : it is done when the metal chloride is highly hygroscopic and cannot possibly be introduced into an electrolytic cell without considering contamination due to water .

In some cases chlorination of dry oxide in the electrolytic cell render the feed water free and avoid undesirable current loss.

In some electrolytic process a metal chloride is produced by bubbling chlorine through a fused salt bath in which pellets of oxide or carbonates along with carbon are suspended.

NEW CLASSIFICATION OF CHLORINATION

1-direct chlorination: chlorination done by only chlorine



2- Indirect chlorination or reduction chlorination: chlorination involved some reducing agent as well . $\text{MO} + \text{C} + \text{Cl}_2(\text{g}) = \text{MCl}_2(\text{g}) + \text{CO}(\text{g})$

Example : for MgO, Cr₂O₃, Al₂O₃ direct chlorination is not fusible.

Reducing agent for chlorination are c, s, co, H₂ best one is c .

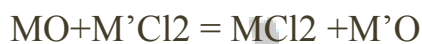
Other reducing agents higher valency chloride compound. Such as FeCl₃, CrCl₃, CuCl₂, VCl₄, TaCl₅, TiCl₄. in association with co, h₂s. here these metal compound are reduced to lower chloride and release the chlorine for chlorination.

Where direct chlorination is not possible due to low affinity of metal oxide toward the chlorine then oxygen at a high temperature 700- 1000 degree centigrade then we go for indirect chlorination. Where we use a reducing agent such as carbon which would lower the chemical potential of oxygen .

So for more production of chlorides we need to pump out the reaction products as there are in gaseous phase or use a strong reducing agent.

in industries chlorination is carried out at 500-1000 degree centigrade.

Chlorination with HCL and MCL₂



The extent of chlorination at equilibrium and magnitude of free energy change for these reaction depend upon difference between the standard free energy of formation of oxide /chloride pair. It is easy to chlorinate the sulphide then oxide because former takes place at lower temperature.

REFINING BY CHLORINATION

1- Gold bullion which contains Ag, Pb, Cu, antimony, can be refined by chlorination of gold bullion. In this case gold is unaffected where is the other impurities get chlorinated.

2- Gold Schmidt process for deleading tin.

Which use fused tin chloride (SnCl₂) employes selective chlorination of lead in Pb-Sn alloy. At 250-260 degreecentigrade.sncl₂ can be reduced to Sn by lead .

3- Refining lead : lead can be seperated from zinc by selective chlorination of of main impurites zinc at about 350-400 degree . Using PbCl₂ or chlorine.

VAPOUR TRANSPORT PROCESS OF REFINING: METALS FROM INTERNEDIATE HALIDES

This process is an example of purification by indirect distillation: purification by forming intermediate gas phase.

There are two type of metals one which is having low m.p and b.p (volatile metals) such as zinc and mercury and other is having high b.p and m.p (less volatile) . So hg, and zn can be purified by distillation technique. Vapor pressure of most metals are however too low to allow distillation at ordinary temp even at reduced pressure. For examples it is practically impossible to distill refractory metals such as Ti, and Zr because of low m.p and b.p more over at high temp they pick up additional impurities from the container material.

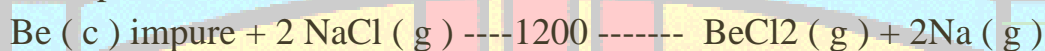
For those metals which cannot be distilled at ordinary temp , there are indirect methods for producing a vapour species from impure metal and then pure metals is recover by cooling this species. The impurities are eliminated during the formation of the vapor species and the metal liberated subsequently very pure. These reaction usually also liberate the original vapour forming reagents which can be recycled.

Two stage of reaction:

1- impure metals + vapour 1 ----- vapour 2

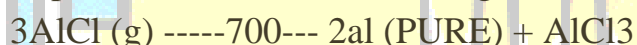
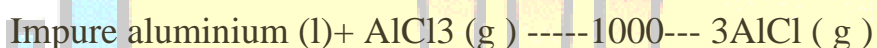
Vapour 2 ----- pure metal + vapour 1

Example of metals from intermediate halides :



Ti can be similiary purified.

Purification of Al



IODIDE PROCESS OF REFINING

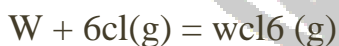
- ❖ Iodide process of refining (hot filament process or hot wire process): here heated filament is used for decomposition of vapors.
- ❖ Process used to purify the metals such as Be, Cr , Cu , Hf Ni, Pa , SI, Th Ti,U ,V ,Zr .
- ❖ In this process formation of volatile halides of metals at low temperature by reaction with halogen and its subsequent decomposition to produce very pure crystalline metals. A thermodynamics analysis shows that this process works better in the case of metals halides having high oxidation state because this

ensure the necessary . Large entropy change for the decomposition reaction.

a necessary precondition for this process is that the volatile halides must be capable of decomposing at a temperature lower than the m.p of the metals.

- ❖ Moreover this halides should be capable of being synthesized from its element under the prevailing condition s. the halides vapour are decomposed by hot filament on which crystal of the metal grows.
- ❖ If the filament temp is high than the m.p of the metal , then the build up of crystal would not takes place . More over the liquid metal attack the filament itself.

THERMODYNAMICS OF VAN ARKELPROCESS



The thermodynamics of this reaction is of course governed by the entropy and heat content change . Here we can see that a large volume change occurs leading to the large change in entropy of the system . Now since change in entropy is large then change in free energy is also large and there fore the process itslef is sensitive to change in temperature. Thus the free energy which is positive at room temperature rapidly becomes negative with increasing temperature and the decomposition of hexachloride occurs.

Consider w, Ta, Hf in the periodic table. Ta and Hf, are placed just after the W. which form chlorides is that TaCl₅, HfCl₄ respectively. For these compound the number of chlorine atom set free is smaller than in the case of tungsten and so is the entropy change . The M.p of Hf is lower than that of Ta and the m.p of Ta is lower than that of W. therefore , as we move across the transition series in the direction W to Ta to Hf , the melting point and covelency with respect to chlorine decreases , and the probability of achieving decomposition at a temperature below m.p of the metal under consideration also decreases .

KINETICS OF IODIDE PROCESS

1- Diffusion of the iodide vapour (halide vapour) to the filament, the chemical decomposition reaction at the filament, and outward diffusion of the gaseous decomposition product (iodine in this case)

Effect of ambient temperature:

As the filament temperature increases at a constant ambient temperature, the equilibrium dissociation pressure of iodine at the filament increases.

The pressure value at different filament temperature and ambient temperature can be calculated from thermodynamic data.

In general deposition rate increases with filament temperature. At very high temperature however. There may be an apparent drop in this rate because of loss of metal due to evaporation. This is specially true if the m.p of the metal is not very much high than the filament temperature.

Below a minimum filament temp the rate becomes immeasurably small.

BENEFICIATION OF LOW GRADE ORE BY HALOGENATION

- ❖ Beneficiation of low grade ore by halogenations is done by :
 - Removal of undesirable constituent in the form of volatile chlorides by selective chlorination
 - Recovery of metallic values also in the form of volatile chlorides.
- ❖ Beneficiation of minerals such as ilmenite and chromite is brought about by the selective chlorination and volatilization of the iron oxide impurities. Beneficiation by chlorination is necessary because in these minerals iron is present in chemical combination with the desired metals and cannot be eliminated by the conventional ore dressing methods.
- ❖ In the chlorination of these ore main aim is to eliminate iron oxide by producing FeCl_3 only (b.p-319 degree) chlorination may produce FeCl_2 (b.p-1026 degree) which tends to choke the

chlorinator . Chlorination carried out with slight excess of chlorine markedly decrease the production of $FeCl_2$.

- ❖ Generally chlorination is carried for the beneficiation of ilmenite and chromite ore may be direct or indirect chlorination by using CO , C , H_2 as reducing agent and CCl_4 and HCl as reducing agent.
- ❖ Manganese can be recovered from slag and low grade ore through chlorination :

Chlorination in this case yield chloride vapour which contains both Mn , Fe for removing iron selective condensation of the chloride vapours based on the wide difference in the b.p of $MnCl_2$ and $FeCl_2$ which are 190 degree and 319 degree respectively.

HYDROMETALLURGY

Hydrometallurgical treatment was generally confined to low grade ore, but it has been used to extract metals from concentrate , matte , speiss and scrap.

STEPS IN HYDROMETALLURGICAL EXTRACTION PROCESS

1-preparation of ore for leaching

- A- grinding,
- B- removal of specific impurities by physical methods
- C-roasting

D-special chemical treatment to render these values soluble to the subsequent leaching operation or to prevent the leaching reagent from being consumed by impurities.

2- leaching : by using a suitable liquid reagent the metallic values in an ore are selectively dissolved.

The selective dissolution depends upon the nature of reagent .

Rate of leaching depend upon:

- a- temperature
- B-pressure
- C- volume of leaching liquid

- D- ore particle size
- E- the composition and concentration of the reagent.
- F-The pulp density
- G-duration of leaching reaction
- F-Degree of aeration of the leaching reagent.

3- Separation of leach liquor:

Leach liquor is separated from the residue by process such as :

- A- settling
- B-thickening
- C-filtration
- D-washing

4- Recovery of metallic values from leach liquor

- A- precipitation
- B- cementation
- C-electrolysis
- D-ion exchange
- E- solvent extraction

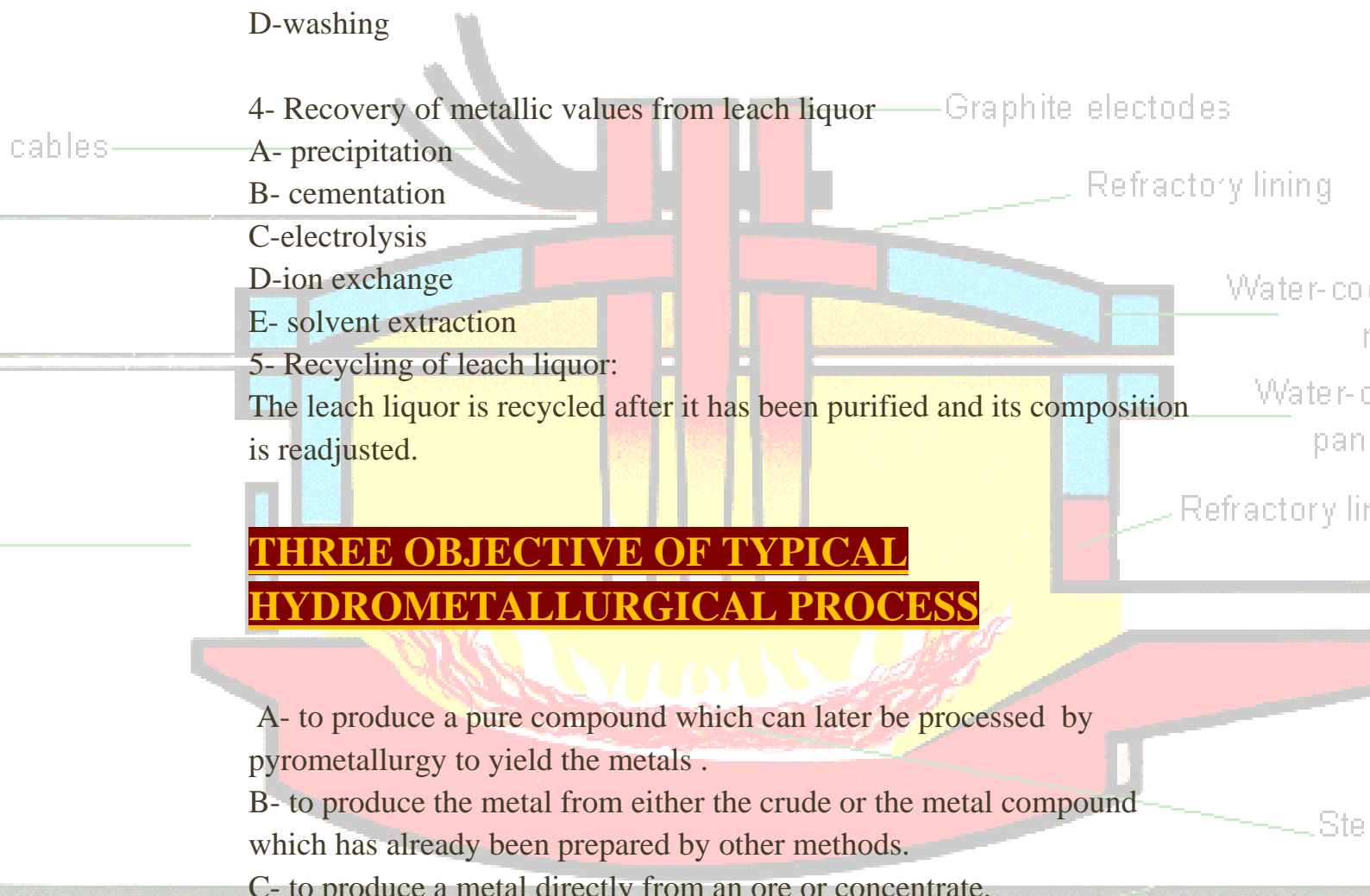
5- Recycling of leach liquor:

The leach liquor is recycled after it has been purified and its composition is readjusted.

THREE OBJECTIVE OF TYPICAL HYDROMETALLURGICAL PROCESS

- A- to produce a pure compound which can later be processed by pyrometallurgy to yield the metals .
- B- to produce the metal from either the crude or the metal compound which has already been prepared by other methods.
- C- to produce a metal directly from an ore or concentrate.

ADVANTAGES OF HYDROMETALLURGICAL PROCESS



A- hydrometallurgical methods are ideally suited for lean and complex ores.

B- hydrometallurgical operation ensure great control than other conventional methods over every step in the processing of ore. Resulting in the recovery of valuable by products .

C- hydrometallurgical process is ecofriendly it does not creates much pollution like pyrometallurgical operation.

D- because of rapid increase cost of metallurgical coke , which is both the main source of energy and the main reluctant in many pyrometallurgical process , an aqueous processing route is favoured.

E- beside meeting the mounting demand for both the quantity and quality of metals hydrometallurgy can produces metal in a variety of physical forms such as powders , nodules, and coherent surface deposits.

F- processs are generally carried out at room temperature or slightly elevated temp.

G- the waste liquor from the final recovery step can be recycled to the initial leaching operation.

DISADVANTAGES OF HYDRO

A- handling of large amount of chemicals becomes difficult and also a large amount of space is required.

B- corrosion and erosion of tanks and ducts used for strong and handling fluids.

C- The coast of the reagent and equipment is high.

D- In hydrometallurgy the disposal of effluent without causing pollution poses a serious problem.

CONCENTRATE FOR LEACHING

Leaching is a process which selectively dissolve the feed material . In leaching metallic values containing the main metal goes into the solution , leaving behind the gangue and solid residue.

But some exception is there where gangues desirable to leach in case of thorium.

To facilities material handling and to minimize the consumption of the leaching reagent an ore is usually concentrate prior to leaching , except when leaching is carried out in situ , as in solution mining , dump leaching , heap leaching or vat leaching.

LEACHING SOLUTION PREPARATION

Leaching solution contains-

- main solvent
- wide variety of reagent (helps in the dissolution because of their chemical effect)

- ❖ Example- these chemicals helps in obtaining an oxidized or reduced state of a metal or a metal compound.
- ❖ Examples of reagents – inorganic salts (ferric chlorides) and acidified sodium chlorides)
- ❖ All solvents are water based . And some isolated case , plain water itself can used as solvent.
- ❖ In most cases acids and alkalies in varying concentration in varying degree of concentration are employed .
- ❖ Acid is much stronger solvent then alkali.
So acidic solution do not required fine grounding of the ore or concentrate but alkali required this.

Some specific cases requires alkalies to obtained a particularly type of solution for subsequent treatment or in retaining some ore constituent which may be destroyed by acid leaching.

Examples of reagents are

- ❖ acids(H_2SO_4 , HCl)
- ❖ alkalies ($NaOH$, Na_2CO_3 , NH_4OH)
- ❖ oxidising agent ($NaClO_3$, MnO_2 , $KMnO_4$, $FeCl_3$)
- ❖ Reducing agent(SO_2 , H_2)

CRITERIA OF SELECTING A LEACHING REAGENT

- 1- Leaching by a reagent must be selective and rapid as possible.
(Depends on nature of ore and reagent)
- 2- It should be possible to dissolve the reagent in order to prepare a sufficient strong leaching solution which can ensure a fast rate of leaching.
- 3- The reagent should not corrode the equipment
- 4- The reagent should be economical and should preferably allow regeneration.

LEACHING OPERATION CLASSIFICATION

Traditional leaching technique (3 types)

- A- In situ (leaching of shattered rock residue left behind in a mines after the major mining operations have been carried out or the direct leaching of ore deposit.
- B- Dump (leaching of off grade ores rejected during mining operation
- C- Heap leaching (when higher grades of ore are leached in a predetermined manner using dumps, the process is known as heap leaching.

HOW TO INCREASE THE LEACHING (DISSOLUTION PROCESS)

- By recirculation the solvent and by continuously agitating the solution.
- Percolation leaching : in this leaching solution is percolated upward or downward through an ore which has been crushed and bedded into tanks .
- To get permeability mixture of coarse and fines ores are used .
- Agitation leaching : stirring is used to aid the dissolution process.

Advantages of percolation leaching :

- 1- It is operated in batches each batch is separated or distinct operation flexibility is greater.
- 2- A percolation leaching circuit is more versatile and can be employed in case of ores for which the leaching rate is very slow.

THEORY OF LEACHING

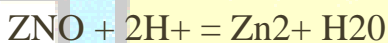
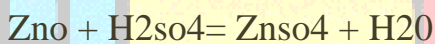
In leaching a mineral decompose in an aqueous environment , the mineral may simply dissolves completely , leaving behind the gangue as a solid residue . Some times , only some constituent of the mineral may dissolve.

Simple leaching:

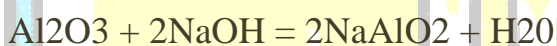
Some times pyrometallurgical treatment yields salts for example chlorodising roasting and sulphating roasting that can be easily leached with water.



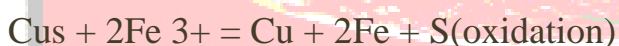
Acid leaching :



Alkali digestion:



leaching with oxidation



leaching with reduction



KINETICS OF LEACHING

Concentration profile when a mineral surface dissolve in a leaching medium.

During leaching two situations can occur

A- complete dissolution (situation is simple)

B- partial dissolution and product is formed and further dissolution occurs.

1- when the mineral decomposes and dissolves only partially then a new solid residue appears.

2-leaching would continue if this new phase is porous .

i- residue

II- residue solution interface

THE KINETIC STEP THAT DETERMINES THE RATE OF LEACHING COULD BE ONE OR COMBINATION OF FOLLOWING

1-The diffusion of the reagent R from the bulk of the solution to the solid surface [II]

2- The diffusion of the reagent R through the porous reaction product layer.

3- The reaction of the reagent with the mineral surface I to form a soluble metal species.

4- The diffusion of product metal species m or other reaction product p through the porous reaction product layer in the outward direction.

5- The diffusion of the product metal species M (or other product) away from the surface. When there is no porous reaction product layer, then step (2) and (4) would of course be absent.

- If we know the rate determining step then the appropriate technique required for speeding up the leaching reaction can be adopted.

If diffusion step 1 and diffusion step 5 is rate controlling then leaching can be speeded up by stirring the aqueous medium.

If the chemical reaction step (3) is rate controlling agitation would have no effect

IN THIS PROCESS AS THE TEMPERATURE INCREASES ALL THE FORGOING STEPS WOULD ACCELERATED.

DIFFERENCE BETWEEN ELECTROCHEMICAL AND CHEMICAL REACTION.

In electrochemical reaction the electron travels much larger distance that is many atomic dimensions but in case of chemical reaction electron travels few atomic dimension.

Some leaching operation is generally electrochemical in nature.

During the electrochemical reaction of metal compound (leaching) which is a dissolution process or oxidation process the electron produces are not restricted to any particular location but are free to move through the solid.

So a specific number of electron may be released to the oxidizing medium anywhere on the surface. When this happened the element would oxidized at some particular area (anodic area) and at other area electron would transfer to oxidising agents likewise in galvanic corrosion.



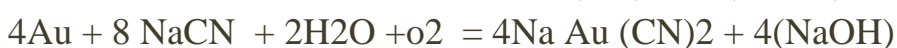
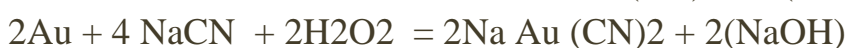
EXAMPLES OF LEACHING BY AN ELECTROCHEMICAL MECHANISM

- ❖ Cyanidation of Gold and silver
- ❖ Coper in ammonia solution
- ❖ Oxides in acid
- ❖ Sulphides in acids.

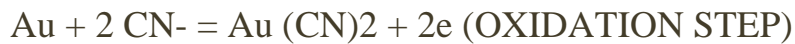
What is cyanidation: process in which metals (gold ,silver) are dissolved(leached) into the solution of cyanide is called cyanidation

Various types of cyanides are used sodium , potassium , calcium .

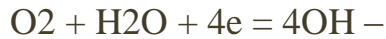
In general case NaCN is used for cyanidation of gold:



CYANIDATION IS A COMBINATION OF TWO STEP AN OXIDATION STEP AND A REDUCTION STEP.



REDUCTION STEP



Dissolution of copper in ammonia solution.

Role of oxygen in leaching operation

- ❖ It is directly involved as a reactant for example is cyanidation process for dissolution of gold and silver. This reaction will not occur if oxygen will be absent.
- ❖ The equilibrium of the reaction depends upon the partial pressure of oxygen.
- ❖ The kinetics of the leaching also depends upon the oxygen pressure if the rate controlling mechanism were to involve the diffusion of oxygen either in gaseous phase or in the aqueous solution.
- ❖ Oxygen pressure would also influence the diffusion process in an aqueous solution. by controlling the concentration of dissolved oxygen.
- ❖ Indirect role of oxygen.
- ❖ In bacterial leaching. Here microorganism serves as catalyst. Since these organisms necessarily need oxygen for survival, all catalytic would cease in the absence of oxygen.

PRESSURE LEACHING

When a solid is dissolved in a leaching reagent, the change in the total volume of the mixture, from a thermodynamic point of view, is negligible. Thus an increase in the pressure hardly affects the leaching process. Pressure would however, become an influential parameter if a gaseous substance is introduced simultaneously along with the solid so as to take part in the dissolution reactions, it should be noted that an increase in the pressure necessarily shift the equilibrium in favour of better dissolution. However it is not necessary that the actual rate of the dissolution changes. This rate would become dependent on the pressure

only if oxygen transport, either in the gas phase or in the liquid, were rate determining.

Others reason are :

- ❖ In many leaching process, an increased pressure is advantageous for entirely different reason. We know that the rate of dissolution is increased by leaching at high temperature. Some leaching processes are carried out at a temperature as high as 200 degree centigrade. And the operator has to use a high pressure in autoclaves to prevent the water from becoming steam. Thus in many instances a high pressure is applied only so that a high temperature can be attained and boiling away of the solvent can be suppressed, for example the leaching of highly volatile and gaseous reagent are used in leaching.
- ❖ By increasing the partial pressure of such reagents, their concentration in aqueous solution can be maintained. At sufficient high level to ensure their efficient utilization. Boiling point is directly proportional to pressure its means higher the pressure higher is the boiling point.

BACTERIAL LEACHING

Natural process are however very slow and takes years to produces a solution suitable for commercial exploitation.

There are certain bacteria that considerably speed up the natural conversion process.

Mineral sulphide that leach faster in the presence of a suitable type of bacteria are.

Arsenopyrite, bornite, chalcopyrite, covellite, enargite, galena, marcasite, sphalerite, tetrahydrite, molybdenite, orpiment.

ADVANTAGES OF BACTERIAL LEACHING

- 1- Enhanced dissolution rate
- 2- Greater extent of recovery

Three important types of bacteria for leaching are:

- 1- thiobacillus thiooxidans
- 2- thiobacillus ferrooxidans
- 3- ferrobacillus ferrooxidans

These bacteria are capable of growing in purely inorganic media.

These bacteria obtain energy by oxidising inorganic substance such as sulphur and thiosulphate, to sulphate and ferrous iron to ferric iron.

Rate of oxidation reaction is accelerated by a biological catalyst called enzyme produced or synthesized by the bacteria.

Oxidation of sulphide mineral.



Iron oxidation is given by :



Iron sulphide is a common impurity in many sulphide mineral. During leaching ferric iron acts as a good oxidant and attacks the mineral sulphide



Here the function of bacteria is to rapidly reoxidise the ferrous ion to ferric ion.

thiobacillus ferrooxidans oxidise ferrous ion. Where the thiobacillus thiooxidans do not.

thiobacillus ferrooxidans thiobacillus thiooxidans both oxidise sulphur and thiosulphate.

FACTORS AFFECTING BACTERIAL LEACHING

- ❖ effect of temperature
- ❖ effect of nutrient
- ❖ effect of particle size and bed width
- ❖ effect of radiation
- ❖ effect of acidity and radiation
- ❖

Effect of temperature:

- ❖ bacterial activity is highest at temp range of 30-35 degree . And above 50 degree activity stops.
- ❖ below 30 degree the activity decreases, and at temperature below 20 degree activity activity once again stop.
- ❖ above 70 degree microorganism becomes sterile and are destroyed.

Effect of nutrient

- ❖ the addition of bacterial nutrients such as FeSO_4 , FeS_2 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Fe}_2(\text{SO}_4)_3$ to leaching solution increases the concentration of ferrous ions present . Consequently the bacterial activity becomes more so that both rate and extent of extraction are increased.
- ❖ Effect of particle size and bed depth:
- ❖ Bacterial oxidation rate depends on the surface of the solid material present because the bacter concentrate at the solid surface that in te contact with the solution and build of colonies there.
- ❖ Finely grounded particles can cover a great surface area leading to an increased leaching rate.
- ❖ However very finely grounded partilces inhibit leaching because both the premeability of the solution and the air supply are reduced.
- ❖ Generally if the bed is shallow then leaching rate is enhanced,

Effect of radiation

When the bacterial cultural is exposed to sunlight directly they becomes in active not destroyed.

bacterial cultural is extremely sensitive to ultraviolet light , even a short exposure completely sterilize it.

Effect of acidity and aeration:

oxidising bacteria are active only in acidic media.

bacterial oxidation is highly pronounced in a medium having a pH value between 2.0 to 3.5.

Both above and below the pH value the rate of bacterial oxidation decreases. at pH value of 6 the oxidation is completely inhibited.

Oxidising bacteria are destroyed in alkaline medium,

Supply of oxygen to living organism is vital generally oxygen is supplied by aeration a portion of the bacterial solution and subsequently transferring the aerated solution to the site of bacterial activity.

Scope of bacterial leaching in india.

CONTACT REDUCTION OF METALS IN AQUEOUS SOLUTION (CEMENTATION)

LEACHING OF AN ORE RESULT IN TWO DISTINCT PRODUCT

- 1- Solid residue containing gangue
- 2- Leach liquor containing metallic value

The reduction of metallic ions to elemental form of the metal is generally accomplished by three methods :

- 1- Cementation or contact reduction
- 2- Gaseous reduction
- 3- electrolysis

WHAT IS CEMENTATION PROCESS:

In cementation process a more reactive metals dissolve in a solution to precipitate a less reactive metal from the solution. Here the electrochemical series can be used to determine the reactivity of a metal.

1- Example aluminum or zinc can be added to gold cyanide solution to precipitate gold. It shows that aluminium and zinc are placed high in the electrochemical series having greater oxidation potential .

Gold is placed toward the bottom having low oxidation potential. It shows that more reactive metals are having high oxidation potential as compared to less reactive metals.

Aluminium or zinc dissolve because the conversion of the metals to metal ion involves a greater free energy decrease than that is the case of gold.

PRECIPITATION OF CU FROM CUSO4 SOL BY IRON

Since the oxidation potential of iron (Fe arrow mark Fe^{2+}) is 0.44 volt while the Cu (cu arrow mark Cu^{2+} is -0.344 volt iron would normally be expected to reduce Cu^{2+} according to overall reaction.



However the oxidation potential taken from the standard electrochemical series are valid only for unit ion concentration.

The actual M/M^{2+} potential depends among other factors on the actual concentration of M^{2+} .

This if the $CuSO_4$ solution is sufficient dilute the Cu/Cu^{2+} potential may become higher.

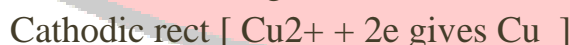
When iron is immersed in $cuSO_4$ the initial Fe/Fe^{2+} potential is high because of the absence of $FeSO_4$.

As the reaction proceed the $feso_4$ conc. builds up and the $Cuso_4$ in the soln get depleted.

According Fe/Fe^{2+} potential decreases from an initial high value and Cu/Cu^{2+} potential increases from an initial low value. After a certain period two potential becomes equal and the reaction attains equilibrium.

Obviously the reaction never proceed to completion unless some means is devised to continuously remove $Feso_4$ and Cu as they are formed.

So precipitate of Cu from $CuSO_4$ solution by Fe is an electrochemical reaction.



HOW TO INCREASE THE DRIVING FORCE FOR CEMENTATION

Higher driving force for the cementation reaction is obtained by using a reactive metal which would give an anode potential as high as possible.

Factors affecting cementation process:

- 1- Degree of agitation
- 2- Diffusion process.

CHEMICAL METHODS OF PURIFICATION

ION EXCHANGE METHOD

In the preparation of pure compound by ion exchange methods, the solid phase is made to initially absorb a suitable ion of the desired metal through an ion exchange reaction.

The absorbed ion is subsequently taken into solution by once again employing an ion exchange reaction. This is called elution.

The metal is finally recovered from the solution by precipitation through further treatment of the leaching solution.

So there are three steps in preparation of pure compound by ion exchange methods.

- 1- Absorption of suitable ions of desired metal by a solid phase through ion exchange.
- 2- Bringing back the metal ions into solution employing ions exchange mechanism.
- 3- To get the pure metal –recovery through ppt of pure leach solution.

Example of ions exchange

Ammonium sulphate solution when percolated through a layer of solid the resulting effluent is found to contain numerous calcium ion but no ammonium salt.

Medium of ion exchange:

An ion exchange medium generally consists of synthesis resins which are small but hard porous beads so that they can be easily packed in columns.

What are resins:

- 1-Resins are complex organic acids or base
- 2- which are insoluble in water.
- 3-Salt of resins are also insoluble in water
- 4- basically resins are large molecule that comprise interconnected and cross linked chains .
- 5- resins structure contains a large number of basic and acidic group which are capable of ionization and exchange .

Types of resins :

1- cationic resins

2- anionic resins

cationic resins :

1- structure of cationic resins is written as RX

R- polymeric back bone CH₂, OH and benzene .

X- ION EXCHANGE SITE example SO₃H (sulphonic group)

2- when a cation exchange resin react with solution containing suitable cation the H in the sulphonic group is replaced by the cation.

Example : $\text{CuSO}_4 + 2 \text{RSO}_3\text{H} = 2(\text{RSO}_3)_2\text{Cu} + \text{H}_2\text{SO}_4$

anionic resins :

Formula of resins may be RNO₃ or RCl. Depending on whether the ions exchange site contain NO₃ or Cl-

When anionic – exchange resins reacts with a solution containing suitable anions NO₃ and Cl can be replaced by anions.

Application of ion exchange resins.

1- uranium recovery

2-Recovery of gold and silver from cyanide leach liquor.

A clear filtrate containing the metallic values is passed through a column of suitable anionic exchange in the form of chlorides which absorbs the cyanide complex of the metal.

These absorbed complex are later removed by selective elution.

Gold and silver are finally recovered by distillation off the acid organic mixture.

Degree of extent of ion exchange phenomenon depend upon several factors.

- 1- Size and valence of ion taking part in the exchange
- 2-The concentration of ions in water
- 3-The physical and chemical nature of the ion exchange resins
- 4- The temperature

Condition under which ions exchange render more effective

1- at low concentration of the aqueous solution the extent of ions exchange increases as the valence of exchanging ions increases.

$\text{Na}^{2+} < \text{Ca}^{2+} < \text{Al}^{3+} < \text{Th}^{4+}$

2- at lower concentraion and for the element having the same valency the efficiency of ions exchange increases as the atomic no. increases.

$\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{mg} < \text{cA} < \text{Sr} < \text{Ba}$.

3- the difference in the efficiecnyn of ion exchange process seems to be disappears at high solution concentration at high temperature.

4- organic ions having high molecular weight and complex metallic anions complex are usually better suited to ion exchange.

ION EXCHANGE KINETICS

1- during ion exchange reaction an ion must migrate from the solution to the interior of the ion exchanger and another ion must must move in the opposite direction in a stoichiometric equivalent

2- Various steps in ion exchange reaction:

1- The transport of ion from the solution across a liquid film boundary surrounding a resin which is in the form of bead.

2- The diffusion of the ion to the interior of the resin.

3- The main chemical exchange reaction occurs

4- The diffusion of the outgoing ion to the surface of the resin bead.

5- The diffusion of outgoing ion across the liquid film boundary.

Diagram of ion exchange plant:

A,B,C

SOLVENT EXTRACTION

- 1- solvent extraction is also called liquid liquid extraction
- 2- solvent extraction is the separation of one or more components from liquid by preferentially dissolution in an extracting solvent.
- 3- application of solvent extraction :
 - A- processing of nuclear fuels which demanded a high degree of purity.

Commercial application of solvent extraction: separation of

- A- Tantalum from niobium
- B- Zirconium from hafnium
- C- vanadium from uranium
- D- Cobalt from nickel
- E- Fission product from irradiated material
- F- Purifying compound of copper, uranium, thorium, and rare earth metals.

DIFFERENT STAGES IN SOLVENT EXTRACTION:

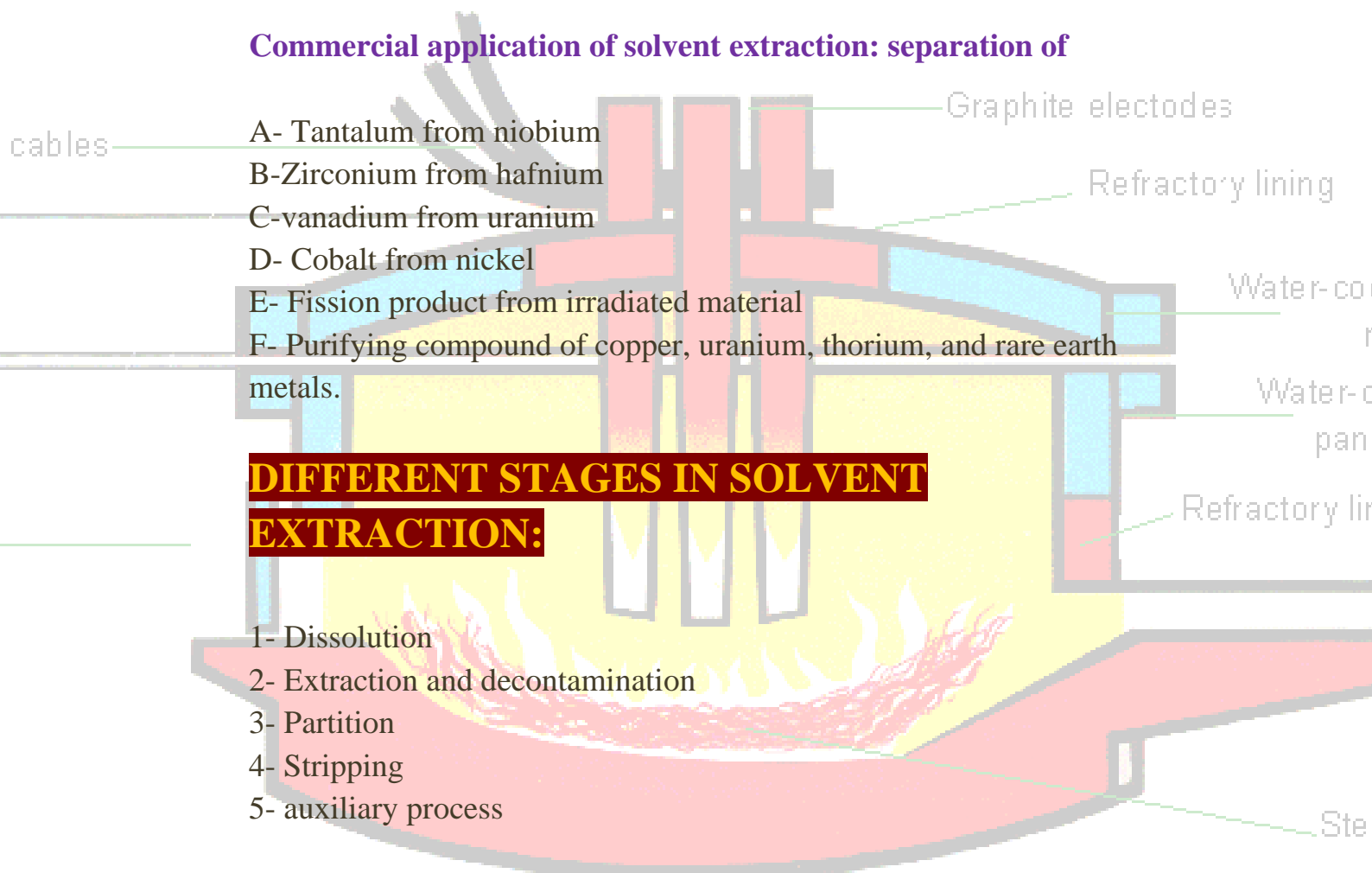
- 1- Dissolution
- 2- Extraction and decontamination
- 3- Partition
- 4- Stripping
- 5- auxiliary process

1- dissolution:

In dissolution the impure compound or the ore is dissolved in a suitable acid or alkali aqueous medium.

2- extraction and decontamination:

In extraction and decontamination the extractant usually an organic liquid is brought into contact with an aqueous solution containing the desired



metal ions as well as impurity ions . The metal ions enter the organic phase preferentially.

3- partition :

In partition the organic and aqueous layers are separated by employing suitable techniques.

4- stripping :

The loaded solvent containing the product is introduced into another extracting unit where the values are removed by contacting with another aqueous phase.

5- auxiliary proces :

A number of auxiliary process e;g –

- ❖ Solvent purification and recirculation are used in solvent extraction
- ❖ Multistage contacting and the countercurrent principle are usually used for better selective and recovery of the metallic values as well for the better utilization ,

Example of solvent extraction :

Recovery of uranium .

- 1- The uranium ore is first leached with sulphuric acid to form the sulphate ion $UO_2(SO_4)_3$ in the solution
- 2- Next the organic extracted by R_3N in the organic phase is allowed to react with the sulphate ion in the presence of an acid . The reaction are :
- 3- In the 3rd step the loaded organic phase is scrubbed by a sodium carbonate solution . This reaction:
- 4- In the fourth step , uranium is ppt frm the aquous solution by adding sodium hydroxide . The reaction is :

We must use an organic phase which is almost immiscible with water.

Example of organic phases

- 1- diethyl ether, methyl isobutyl ketone, and higher alkyl amines.

Example of aquous phase –

The metal salt in the aquous phase is usually a halide , sulphate , or nitrate with an excess of corresponding acids.

FACTORS AFFECTING THE SOLVENT EXTRACTION METHODS.

Major factor is the PH value of the aqueous phase . So by reversing the pH value the metallic values are stripped by using a second phase at different PH.

So stripping is inversely related to extraction.

If extraction is easy then stripping is difficult.

If two metals are extracted simultaneously (Ta, Nb, Zr, Hf) selective stripping is possible.

If not possible the separation of one metals from the other can be carried out by selective ppt from the strip solution.

CHOICE OF EXTRACTANT (ORGANIC PHASE)

- 1- Cost of solvent
 - 2- Selectivity – ability to dissolve one metals preference to other.
 - 3- Solvent power:
 - 4- Adaptability: adaptable to feed composition and desire product.
- Easy of recovery: it is very expensive it is necessary to recover them as completely as possible.
 - 5- Density – low density as much as possible of solvent for clear and quick separation

Extraction coefficient: ratio of concentration of solute in two phases at equilibrium

$F_o/a = y/x$. Concentration of solute in organic / concentration of solute in aqueous.

MODULE -4

ELECTROCHEMISTRY

Here electrical energy is converted into chemical energy or vice versa.

Example: galvanic cell, electrochemical cells.

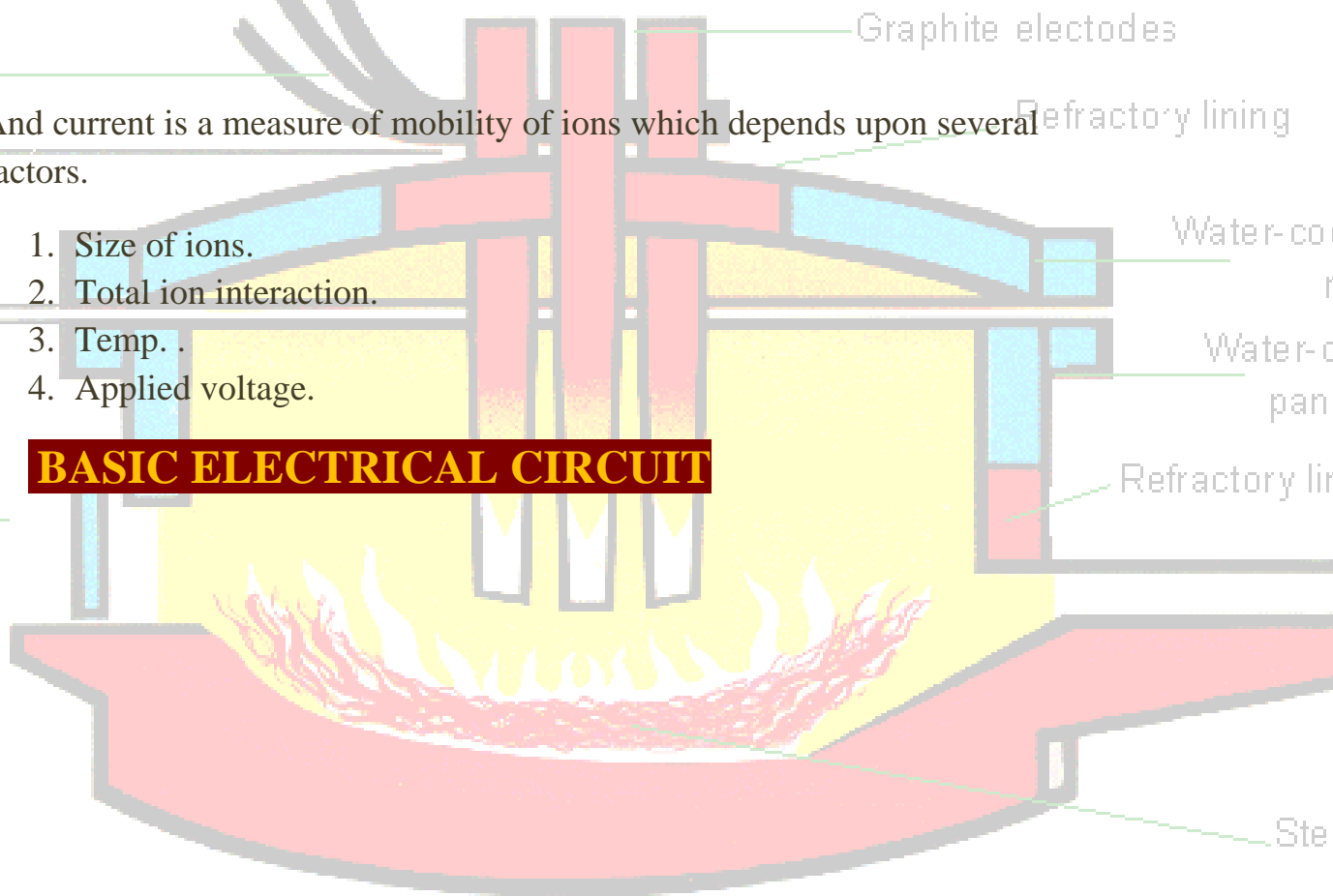
Electrolyte:-it is a medium which gives ions. Ex of ion conducting medium are,

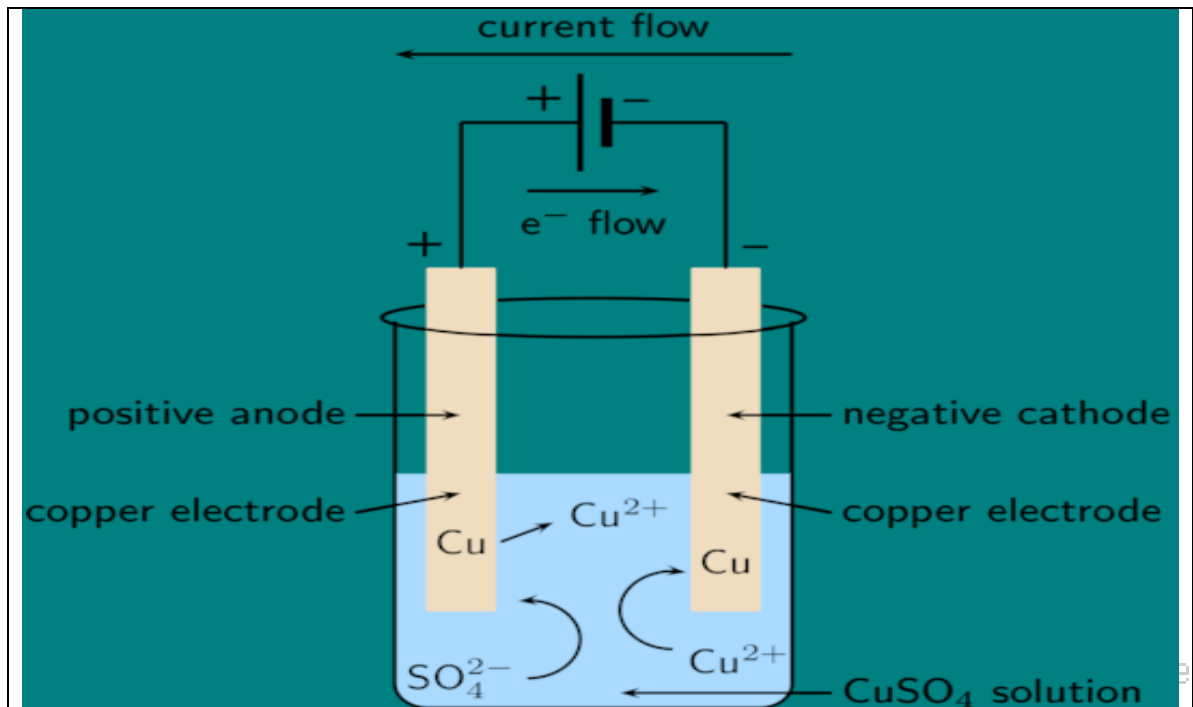
1. Aq. Salt:- CuSO_4 ,
2. Molten salt:-molten silicates.
3. Organic liquids.

And current is a measure of mobility of ions which depends upon several factors.

1. Size of ions.
2. Total ion interaction.
3. Temp. .
4. Applied voltage.

BASIC ELECTRICAL CIRCUIT





PRINCIPLE OF ELECTROLYSIS DEPENDS ON FOLLOWING

Faradays law of electricity: 1st law

It states that, quantity of metal deposited or released at any electrode is directly proportional to the electricity passing through the electrode.

2nd law:-.....

It states that, when same quantity of electricity is passed through the different electrodes connected in series, the amount of metal deposited or released is directly proportional to their chemical equivalent.

Electrochemical equivalent:-

1 faraday = 96491/96500 coulomb .

No. of grams of substance released when one coulomb of electricity is passed .Or 1 Amp. Of current in one sec. deposits the no. of grams of substance is called as chemical equivalent.

ELECTRODE POTENTIAL

Definition of electrode potential

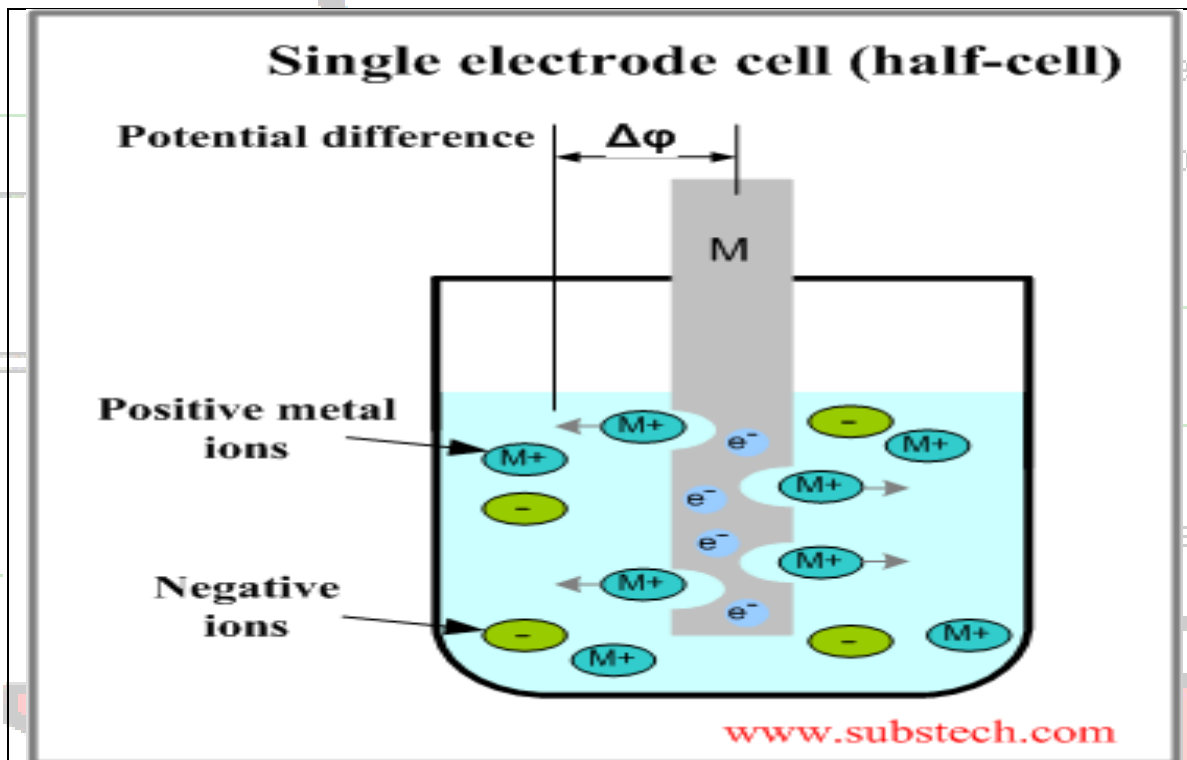
Factors on which magnitude of electrode potential depend:

1- nature of chemical activity of metal itself

For pure metals activity is 1.

2-concentration of its ion in liquid

Electrode potential cannot be measure but the potential difference between two electrode (emf of cell)can be measured that is between the electrode undergoing decomposition and reference electrode(potential taken as zero) present in electrolytic cell. She is mostly used as reference electrode.



APPLICATION OF ELECTRODE POTENTIAL

- ❖ Purification of zinc from nickel and other impurities which are more noble than zinc
- ❖ Purification of mercury from impurities like cadmium
- ❖ Protection of iron by zinc or cadmium coating
- ❖ Plating of copper on iron

PRINCIPLE OF ELECTROMETALLURGY

- Electricity is used for electrolysis and heating.
- What is electro winning : process of extraction of metals using electrolysis .
- Electro refining : process of purification of metals using electrolysis.
- Metals produced by electrolytic reduction :
- Al, Na, Li Mg, Cr, Co, Cd, Zn Cu, Ni ,

More reactive metals are extracted using fused salt electrolysis, and less reactive using aqueous electrolysis.

ELECTRO WINNING AND ELECTRO REFINING

Electro winning is a metal extraction process where as electro refining is purification process.

Difference is that anode is either an insoluble conductor or an electrical conductor such as copper matte or nickel matte.

In the electro winning the anode is either an insoluble conductor or an electrical conductor such as copper matte or nickel matte.

In electro refining the anode is impure metal itself.

Electrolyte in both electro winning and electro refining is a solution with a sufficient high electrical conductivity and reasonable high metal ion concentration.

Cathode- is a pure metal built up as a pure starting sheet or sometimes, it could be built up on a blank of another metal

CONDITION OF USING AN ELECTROLYTE

- ❖ They decompose or break down to give large number of ions, which conduct electricity.
- ❖ They should be chemically inert toward the electrode. And inert towards the container material.

CURRENT EFFICIENCY

- ❖ In industrial practice one usually obtained less yields than what the law predicts.
- ❖ The effective utilization of current is expressed as current efficiency.

ARRANGEMENT OF ELECTRODES IN ELECTROLYTIC CELL

Limiting current in an electrolytic cell depends upon the surface area of the electrodes, so by increasing the surface area we can increase the amount of current and thereby we can increase the production. So we can say rate of production is limited by surface area of the electrodes. Since it is not convenient to use very large electrodes, the surface area is increased by incorporating into the cell a large number of electrodes of convenient size. For example for copper extraction by electrometallurgy route we use a rectangular electrolytic cell having 20-40 number of cathodes and anodes, size of tank is nearly 4m x 1m x 1m.

TWO MAIN TYPES OF ARRANGEMENTS OF ELECTRODES IN CELL

1- Series arrangements: here only the first and last electrode of the electrolytic cell is connected to external

circuit. And other electrodes plates are arrange between them.

Side of each plate facing the anode serves as cathode and receive the metal deposit. The side which faces the cathode serves as anode. Excepting the first and last plate other electrodes are bipolar in nature.

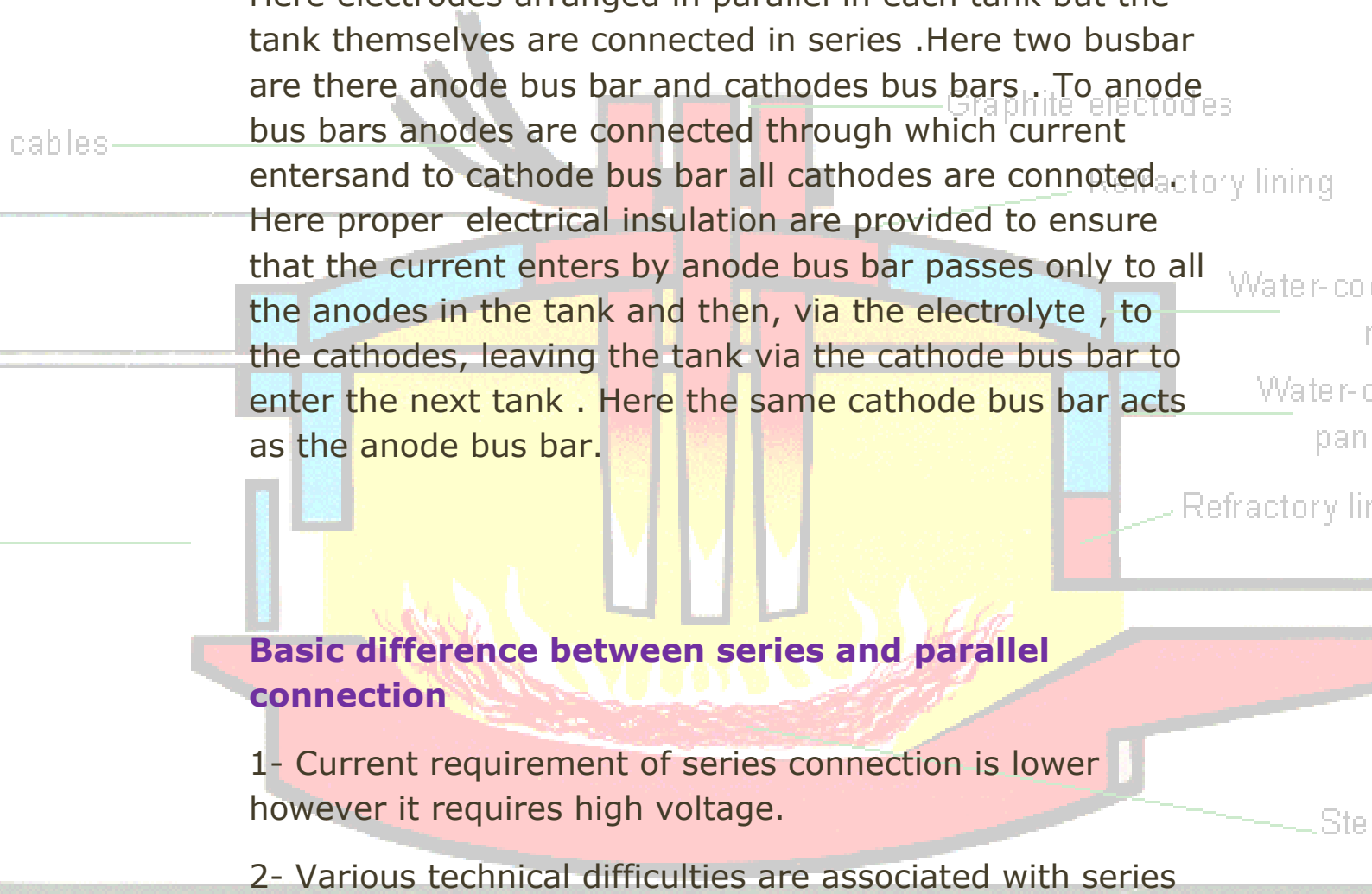
PARALLEL ARRANGEMENTS

Parallel arrangement is also called multiple arrangements. Here electrodes arranged in parallel in each tank but the tank themselves are connected in series .Here two busbar are there anode bus bar and cathodes bus bars . To anode bus bars anodes are connected through which current enters and to cathode bus bar all cathodes are connoted. Here proper electrical insulation are provided to ensure that the current enters by anode bus bar passes only to all the anodes in the tank and then, via the electrolyte , to the cathodes, leaving the tank via the cathode bus bar to enter the next tank . Here the same cathode bus bar acts as the anode bus bar.

Basic difference between series and parallel connection

- 1- Current requirement of series connection is lower however it requires high voltage.
- 2- Various technical difficulties are associated with series and it is less flexible.
- 3- Power requirement is the same in either case.

What is the Function of adding acids in aqueous electrolyte.



Ans- to increase the electrical conductivity of the solution.

Prevent the hydrolysis of the metal salts.

STRUCTURE OF ELECTROLYTIC MEDIA

Nature of Dissociation of electrolyte depends upon its ionic structure. Two types of electrolytic are there one is aqueous and another is non aqueous electrolyte. Under non aqueous electrolyte we consider only molten salt electrolyte.

Silent features of ionic melts (molten salt electrolyte) (halide salt)

1- They form system some of which remain liquid even at very high temperature

2- Some melt at very low temperature

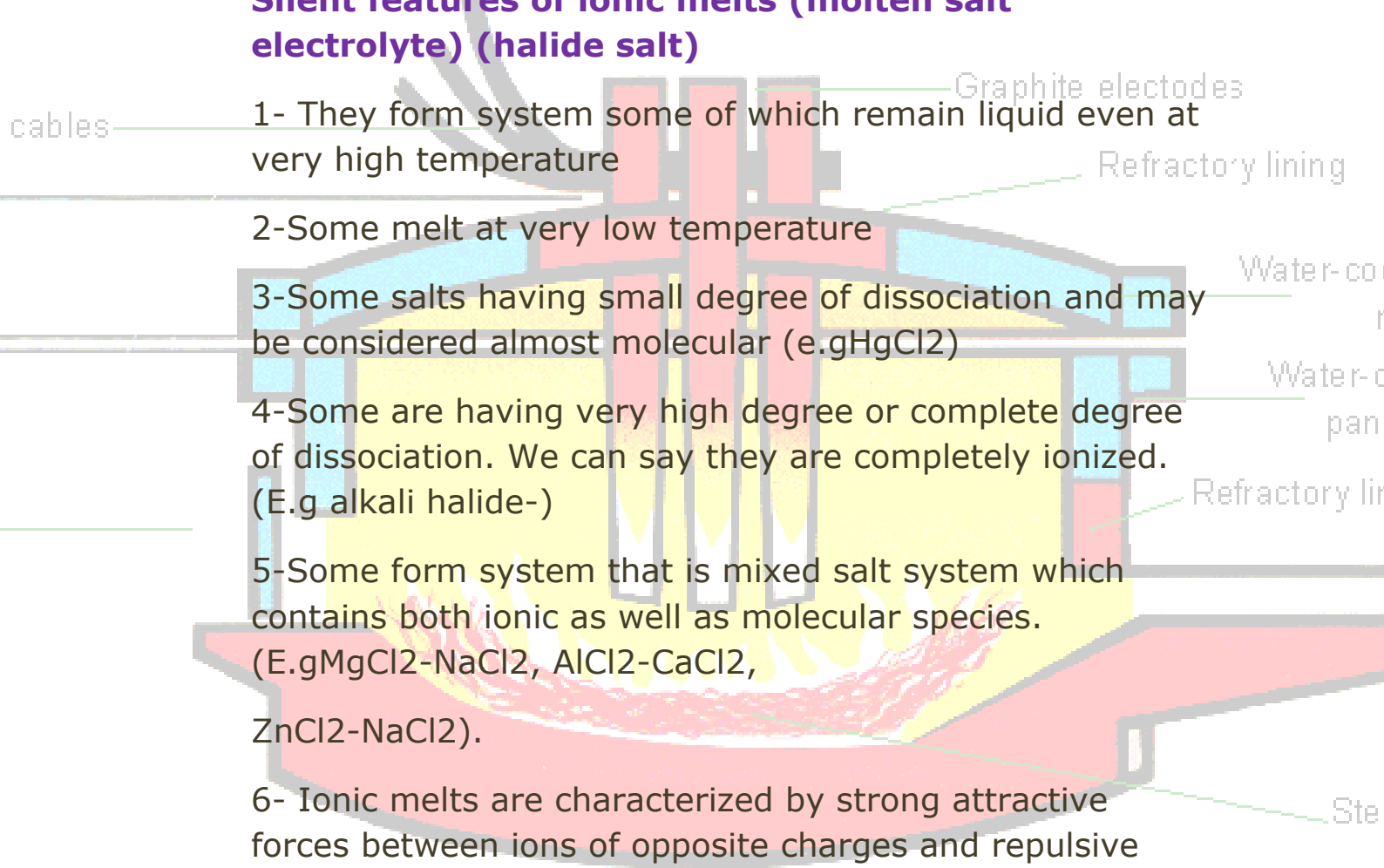
3- Some salts having small degree of dissociation and may be considered almost molecular (e.g. HgCl_2)

4- Some are having very high degree or complete degree of dissociation. We can say they are completely ionized. (E.g. alkali halide-)

5- Some form system that is mixed salt system which contains both ionic as well as molecular species. (E.g. $\text{MgCl}_2\text{-NaCl}_2$, $\text{AlCl}_3\text{-CaCl}_2$,

$\text{ZnCl}_2\text{-NaCl}_2$).

6- Ionic melts are characterized by strong attractive forces between ions of opposite charges and repulsive forces between ions of similar charge. Because of this cation is surrounded by anions as closest neighbor and vice versa. It has been seen that energy required to transfer a cation in NaCl melt from a position surrounded by anions to one surrounded by cation is exceedingly large.

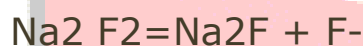


Heat of fusion and evaporation are very small ($1/30^{\text{th}}$ and $1/5^{\text{th}}$) as compared to this. So we can say that there can be no significant mix up of positive and negative ions. Each kind has a sub lattice of its own. Thus where as all anions are free to occupy any configuration in the anion sub lattice. So as cation in cation sublattice the anion and cation owever can be freed from mutual interaction under an applied potential. Which causes ionic dissociation, migration, and electrolysis. Ionic melts have high electrical conductivity due to mobility of ions. Ionic melts have high electrical conductivity due to mobility of ions.

$$K = A \exp(E_{\chi}/RT)$$

$K = \chi$

which is specific conductance and E_{χ} is the activation energy for specific conductance, similar equation applies for metals also. Ionic melts such as alkali halides generally are highly conducting, an exception is the fluorides of Na and K. It is believed that these form dimers such as Na_2F_2 which dissociates according to the reaction:



NaF^+ ions are having high weight they are bulky as compare to other ions so the conductivity decreases.

When the salt have molecular lattice where the element of salt structure have few ions, then the fused salt conducts little current (e.g. HgCl_2) where there is incomplete

dissociation (e.g MgCl_2), the conductivity value occupies an intermediates position.

Like other liquid, molten salts are also characterize by an expression in volume and a positive entropy change upon melting .

During melting of alkali halides , the nearest neighbor distance between anion and cation decreases considerably . The expansion in volume is therefore accounted for not by an expansion of the lattice by introduction of holes.

Molten salts are missibles in all proportion provided the temperature is sufficiently high. At lower temperature there may be incomplete miscibility.

STRUCTURE OF WATER SOLUBLE SALT ELECTROLYTE

It is known that some compound such as alkali chlorides readily dissociates in water to give rise to ionic solution.

This is commonly attributed to high dielectric constant of water. Water comprises of associated molecules because of the polar nature of the latter. In the state of association, the asymmetric molecules cling to each other through hydrogen bond. The hydrogen bonds are formed between slightly negatively charged oxygen atom of one molecule and slightly positively charge hydrogen atom of the others.

The nature of association of molecules in water results in a liquid of high dielectric constant which helps in the breakdown of the crystal lattice of ionic compound. The unlike charge in the compound are no longer strongly bound because the attractive force between the unlike charges is inversely proportional to the dielectric constant of the medium between them. In addition to its ability to

break up ionic compounds, water also forms complex ions with metal cations. Such complex ions are known as hydrated complex.

Example hydrated copper ion- the arrow representing coordinate covalent bonds formed when each oxygen donates a pair of electron to the cupric ions to stabilize the configuration.

In general most aqueous solution of metals compounds contains metal ions complexes with water molecules or with other reagents such as NH_3 , Cl^- , CN^- , OH^- , $\text{P}_2\text{O}_7^{4-}$.



MATERIAL AND HEAT BALANCE

Aim of material and heat balance is estimating inflow and out flow of mass of mass and energy respectively.

These are essential plant record and routine calculation for plant operation.

The first thing before material and heat balance is that we have to obtain a clear picture of that process.

So get the clear picture of any metallurgical process we have to draw a flow sheet or flow diagram

FLOW DIAGRAM: diagram showing successive steps of a process by indicating the piece of equipment in which they occurs and the material stream entering and leaving each piece of equipment.

Advantage of using a flow diagram is it is time saving and it prevents any mistakes.

- Flow diagram should show the unit operation and process by simply rectangles.

In a flow diagram each arrow should represent an actual stream of material in a single phase.

For example a gaseous mixture is coming out of a furnace it is shown by one arrow line not by different arrow lines (CO_2 , CO , N_2 , H_2O).

And for example slag and metal is produced by b/f then it is shown by two different arrows not by single arrow.

Material balance is based on the Law of conservation of mass.

General material balance is given by equation: for batch process (process which involves treatment of a given mass of material in a process after which the product is taken out.

[Accumulation of mass within the system] = [input through system boundaries] - [output through system boundaries]

This can be written as :

[Accumulation of mass within the system] = [input - output]

If there is no accumulation then input = output

For continuous process:

Here we have to consider the rate of input and rate of output for continuous process if runs as steady state the chemical composition of the input material and output material remain unchanged and there can be no accumulation within the system either.

Mass balance equation:

Rate of input of material into the system = rate of output of material from the system.

It should be noted that material balance holds on the total mass of material but not on moles.

STEPS OR PROCEDURE IN MATERIAL BALANCE CALCULATION

1- Write complete flow diagram, represent each process by a rectangle and indicate each feed or product material by an arrow.

2-gather all known data in a table accompanying the sketch or, if there are not too many data put the data on the flow diagram itself.

3- Make suitable assumption if it is necessary.

4- Choose a convenient basis for calculation

5- Write the overall chemical reaction that take place in the process.

6-write the element balance equation

7- Solve the equation

8-mak up the material balance table

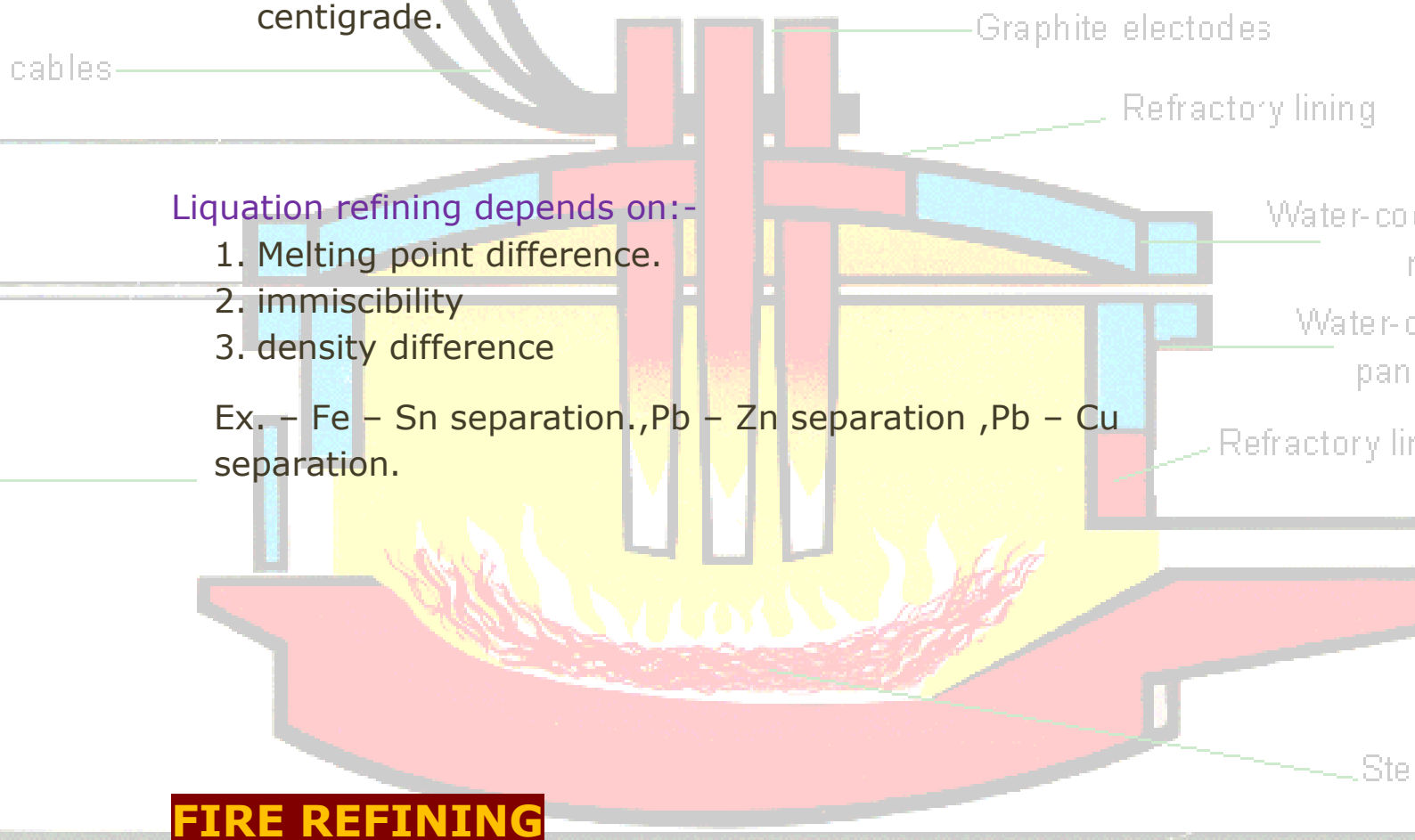
Check by an independency method that the calculation is correct

REFINING METHODS

LIQUATION REFINING

- ❖ It is also called selective melting of a component in an alloy. .
- ❖ Principle of refining is : difference in melting point of the alloy component.,

- ❖ Immiscibility of phases, and the difference in density of the alloy component which lead to the separation of alloy into two or more layers.
- ❖ Example of separation of lead and zinc. This is done by slow cooling of the alloy in reverberatory furnace over a period of two or three days. Here the lead separates out and accumulates at the bottom of the furnace.
- ❖ Separation of copper and lead. By cooling the molten alloy to 370- 380 degree centigrade the copper crystallizes and floats at the surface.
- ❖ Refining of tin and iron. Cooling to 550 degree.
- ❖ Refining of zinc and iron.. Slow cooling to 780 degree centigrade.



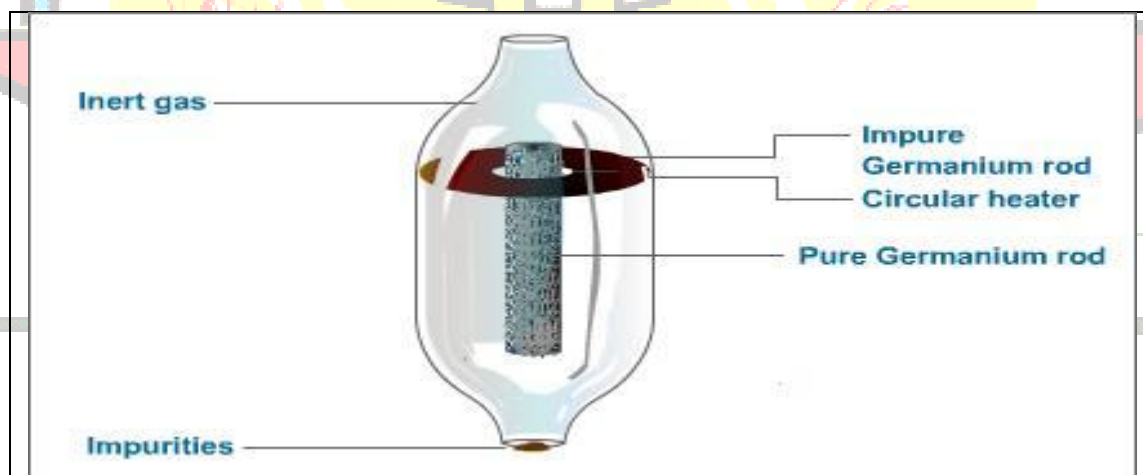
FIRE REFINING

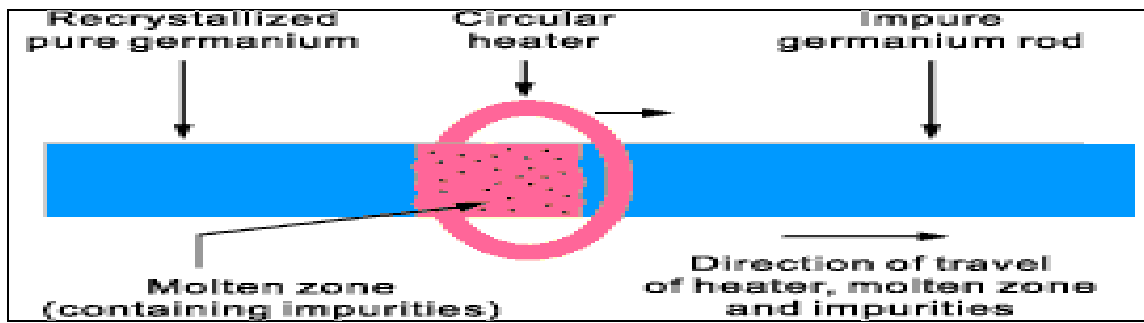
- ❖ It is same process as steel making .in fire refining impurities are selectively oxidized by blowing air or oxygen.

- ❖ In steel making the product is alloy but in fire refining the product is pure metal. And this is only the common difference between them.
- ❖ Ex.: -refining of Cu, Zn , Fe.

ZONE REFINING

- ❖ This is also called as zone melting. In process we melt specific zone of metal and product we got is ultra pure.
- ❖ Principle of zone refining is based on segregation coefficient. When we heat the metal at specific zone the impurities present around that zone move to liquid phase and we heat the metal from one end to another end by moving the heating zone or by moving the heater through the heater. by this all impurities of metal get collected in heated zone and this part is removed . Segregation coefficient = $\frac{\text{solute in solid}}{\text{solute in liq.}}$





SUBLIMATION

- ❖ It is one type of refining process. Here solid doesn't convert into liquid at high temp instead of that it directly converted into vapour phase.
- ❖ Sublimation refining is carried out when a high vapour pressure of a particular metal in a compound is available. And this process is advantageous when it is possible at lower temp.

Advantages:-

1. At higher temp corrosion rate is higher hence low temp is beneficial.
2. Lower temp. Prevents the decomposition of heat sensitive impurities.
3. After sublimation we get pure metal in gaseous form and impurities in solid form.
4. Ex:-we convert sulphide ore into chloride form hence vapour pressure of chloride increases.



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CRYSTALLISATION

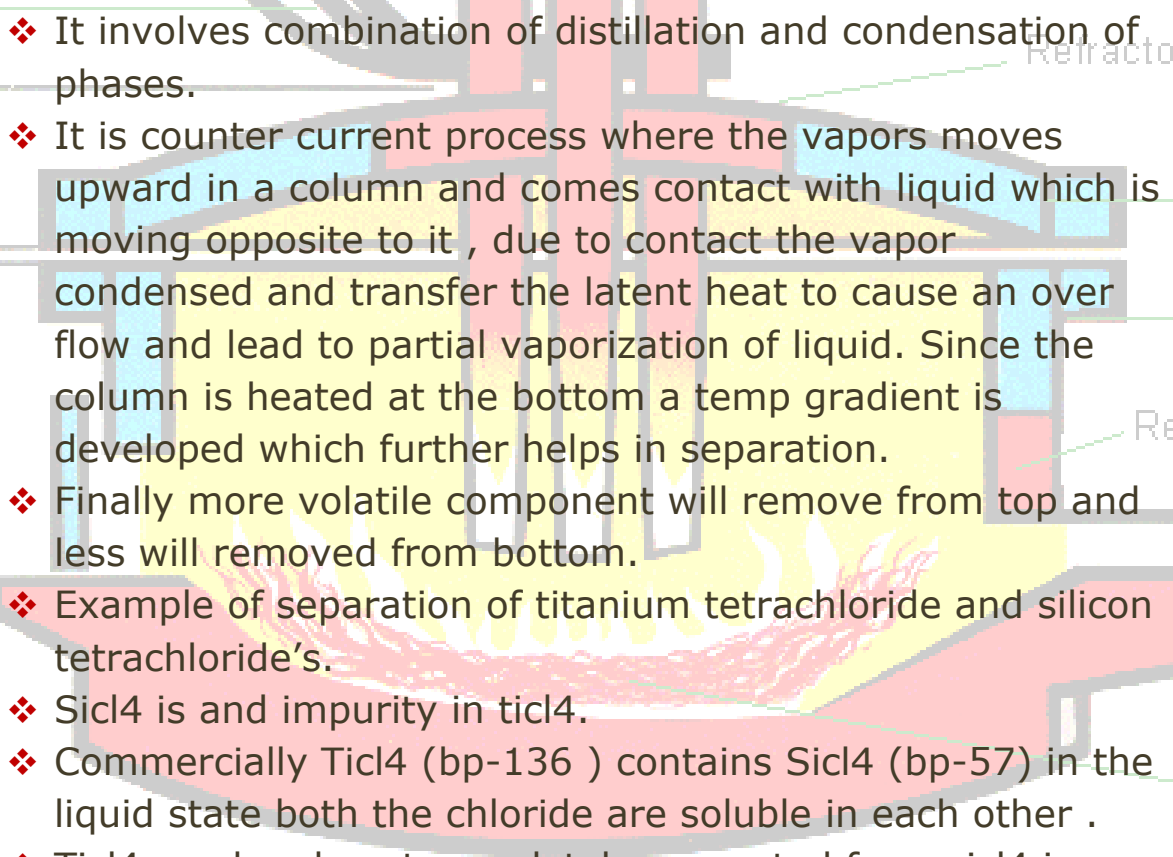
- ❖ In case of crystallization we are separating a solid phase from liquid phase.
- ❖ Here the solid phase may be impurities or the metallic values.
- ❖ Principle of crystallization is based on the difference between the solubility values various compound dissolved in a solvent usually water .
- ❖ Crystallization is nearly same as ppt A solute is ppt from a solution when its concentration exceed the solubility limit.
- ❖ crystallization is carried out in two process :
 - either evaporating the solution to increase the concentration .
 - by lowering the temperature so that the values of the solubility limits is decreased below the actual concentration.

REFINING BY DISTILLATION

- ❖ Principle is relative volatility of the components present in solution.
- ❖ Suppose we are having a solution containing two different substances A and B with different volatility. And we want to separate this two. Separation is done by partial vaporization followed by the recovery of the vapor and residue.
- ❖ So efficiency of separation depend upon the relatively volatility(α).

- ❖ relative volatility (α) = $\frac{P_A/X}{P_B/XB}$
 - $\frac{Y_A \cdot P^*A}{Y_B \cdot P^*A}$
- ❖ So we can say that relative volatility is a direct measure of the ease with which the component can be separated by distillation process.
- ❖ relative volatility do not vary with temperature.
- ❖ But it is influenced by the relative values of activity coefficient of A and b.
- ❖ Separation by distillation would be particularly effective when the relative volatility has a large value.

PURIFICATION BY RECTIFICATION OR FRACTIONAL DISTILLATION/RECTIFICATION

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- ❖ It involves combination of distillation and condensation of phases.
 - ❖ It is counter current process where the vapors moves upward in a column and comes contact with liquid which is moving opposite to it , due to contact the vapor condensed and transfer the latent heat to cause an overflow and lead to partial vaporization of liquid. Since the column is heated at the bottom a temp gradient is developed which further helps in separation.
 - ❖ Finally more volatile component will remove from top and less will removed from bottom.
 - ❖ Example of separation of titanium tetrachloride and silicon tetrachloride's.
 - ❖ SiCl_4 is an impurity in TiCl_4 .
 - ❖ Commercially TiCl_4 (bp-136) contains SiCl_4 (bp-57) in the liquid state both the chloride are soluble in each other .
 - ❖ TiCl_4 can be almost completely separated from SiCl_4 in a stainless steel fractionating column.

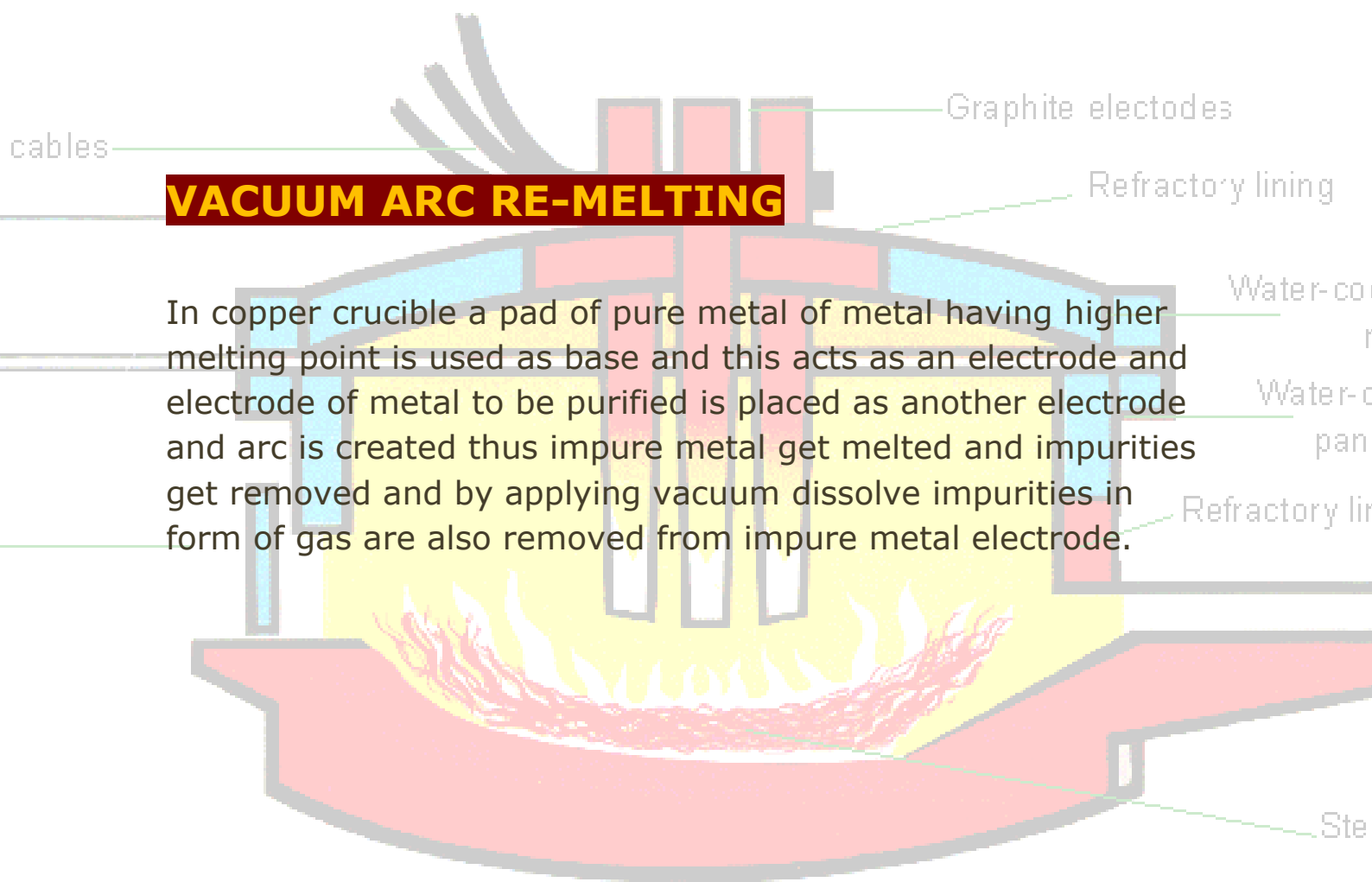
PURIFICATION BY CHEMICAL TRANSPORT REACTION

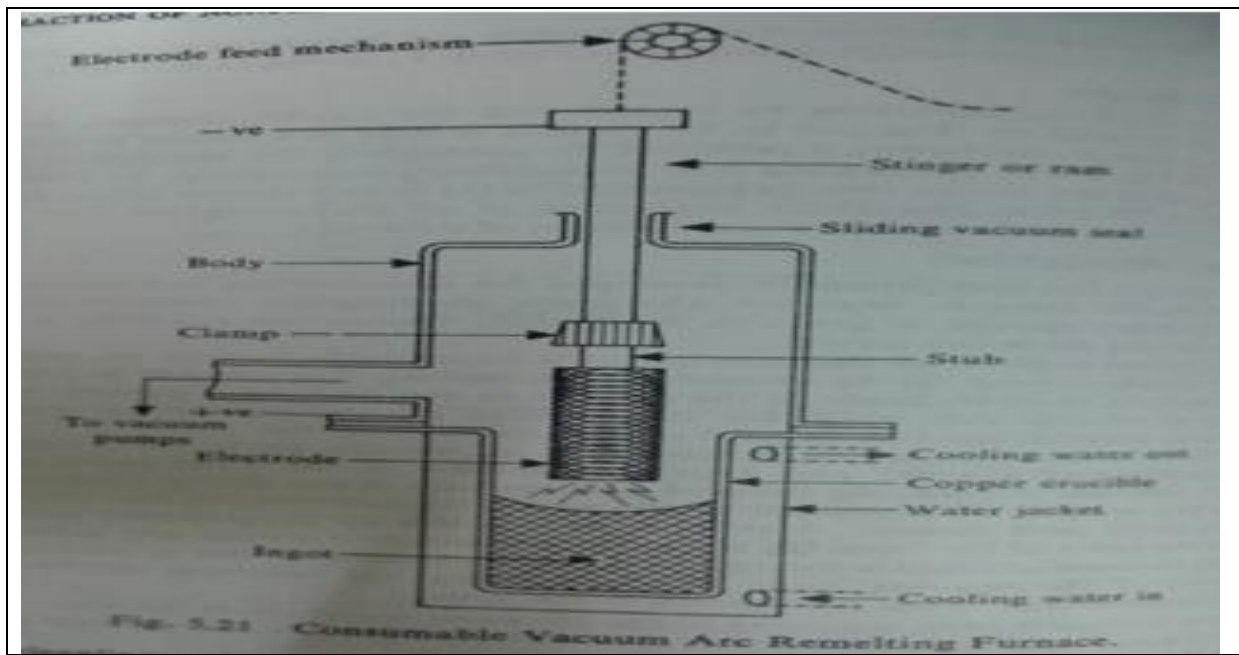
In this method we add another chemical which reacts with the impurities and forms insoluble compound and by addition of flux to this we can separate slag.

Ex:-in extraction of Pb , Cu is present as impurity .so we add sulphur which reacts with copper and forms CuS which present in solid phase and starts floating on soln.

VACUUM ARC RE-MELTING

In copper crucible a pad of pure metal of metal having higher melting point is used as base and this acts as an electrode and electrode of metal to be purified is placed as another electrode and arc is created thus impure metal get melted and impurities get removed and by applying vacuum dissolve impurities in form of gas are also removed from impure metal electrode.

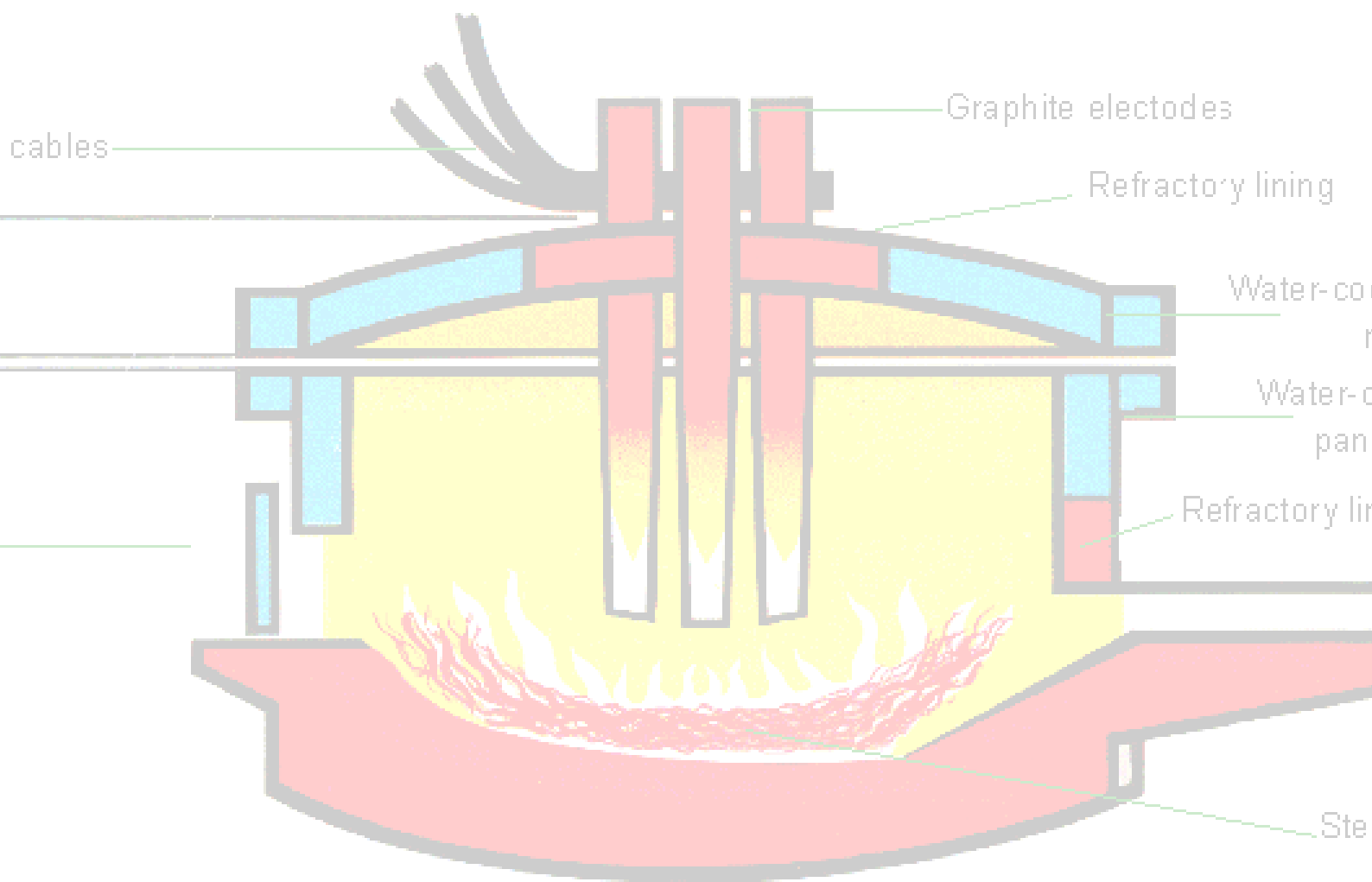




IODIDE PROCESS OR VAN ARKEL PROCESS

- ❖ It is also called hot filament or hot wire process. Due to the use of a heated filament for the decomposition of vapors.
- ❖ This process aims at the formation of volatile halides of a metal at a low temperature by reacting it with a halogen and its subsequent decomposition to produce very pure crystalline metals. A necessary precondition of this process is that the volatile halides must be capable of decomposing at a temperature lower than the m.p. of the metal. Moreover, these halides should be capable of being synthesized from their elements under the prevailing conditions. These metal halide vapors are decomposed by a hot filament on which the crystal grows. If the filament temperature is higher than the m.p. of the metal, then the buildup

of crystal would not take place more over the liquid may attack the filament itself.



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