

DATE \_\_\_\_\_

1

A mineral is a naturally occurring compound. These are mostly inorganic in nature. It consists of one or more metals in association with non-metals.

An ore is a naturally occurring aggregate of minerals from which one or more metals or minerals can be extracted economically. Some minerals in the ores are not useful from the point of view of metal extraction. These are known as gangue minerals. The useful minerals are called ore minerals.

Ques Extractive Metallurgy - A process of separation. Justify. 5 or 7

Extraction as a refining process consists of individual sequential steps i.e. unit steps. These unit steps can be further classified into unit process/unit operations.

Unit Step Eg: Filtration, Distillation and Commendation (size reduction)

Unit process Eg: Leaching, Smelting, Melting, etc.  
Production of desired purity metal from natural ores is mainly a separation process. It can be classified into 2 stages -

Separation of the compound containing the desired metal from other constituent. This is known as concentration & comes under the discipline of mineral engineering.

(2) Separation of desired metal from other metallic compound and its purification to the pure metal. It comes under the subject-matter of extractive metallurgy.

Eg: for Aluminium extraction, there 2 stages are distinct. Initially the bauxite is converted into anhydrous alumina through Bayer's process. In the subsequent stage, it is dissolved into cryolite and pure aluminium metal is extracted through electrolysis.

From Chemistry and chemical engineering point of view, extraction process can be classified into 2 steps -

① Mechanical separation process - Eg: Gravity separation, Filtration, Magnetic separation. Here, separation takes place as aggregates of molecules, more specifically in form of particles.

(2) Diffusion or separation process - Eg: Distillation, precipitation, extraction, etc. Here, separation takes place by movement of individual atoms and molecules by diffusion aided by other mass transfer process.

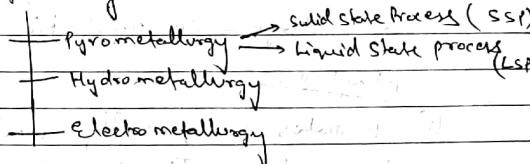
Distillation over

Some of these processes are accompanied by chemical reaction. Eg: leaching, smelting, etc. whereas others are purely physical separation. Eg- distillation, zone refining, etc. The diffusional process again can be subdivided into 2 categories -

① Separation method based on phase equilibria & kinetics - Here, the separation unit is determined by chemical or phase equilibria. Eg: Distillation, solvent extraction, slag-metal Rxn, etc.

② Separation Method based on Rate process - Eg: Electrophoresis, gaseous diffusion, etc.

#### Classification of Extraction Process



SSP - It does not involve melting, typically carried out in the temp. range of 800-1200°C, so products of solid state processing is either pure or a mechanical mixture.

DATE \_\_\_\_\_

(4)

DATE \_\_\_\_\_

(5)

Cg - Roasting of sulphides, calcination, solid state reduction of metal oxide by hydrogen or CO, etc.

LSP - It involves melting of atleast the metal containing phase. Appreciable compositional changes in the liquid state is possible due to immiscibility, rapid diffusion and mixing. Eg - Blast furnace melting, steel making, distillation refining of Zn from impure lead.

Pyrometallurgy - Pyrometallurgical extraction methods are usually cheaper & suited for large scale production.

Advantages-

- R<sup>x</sup> rates are generally accelerated at high temperatures. The R<sup>x</sup> rate approximately doubles for every 10°C rise in temp. & the activation energy barrier also becomes smaller. Hence, small unit can achieve high production rate.

② High temp. process permits the use of inexpensive reducing agents and raw materials.

③ Some R<sup>x</sup>'s are only feasible at high temp. carbon can reduce ZnO under 1 atmospheric pressure when the min. temp. is 900°C

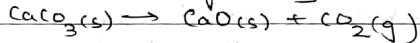
④ There is a greater ease of physical separation of metal and gangue if the products can be melted or vapourised. Eg-(i) Due to the density diff. b/w liquid metal & slag they can be easily separated in blast furnace. (ii) Zn vapour is collected upon blast furnace reduction of Zn ore.

⑤ Pyrometallurgy or fused salt electrolysis is used to extract highly reactive metals say, the alkaline earth metals. Eg - Zr & Ti

DATE \_\_\_\_\_

(6)

Calcination - It is the thermal treatment of an ore that brings about its decomposition & eliminates the volatile products, normally  $\text{CO}_2$  and/or  $\text{H}_2\text{O}$ .  
e.g. decomposition of  $\text{CaCO}_3$



$$\Delta G_0 = 42,300 - 37.7 T$$

When  $\text{CO}_2$  pressure is 1 atmosphere, then  $T_0$  becomes zero and provided the temp. is 1123 K or about  $850^\circ\text{C}$ .

This is often known as decomposition or calcination temperature.

Most other carbonates have lower decomposition temp. e.g.  $\text{MgCO}_3 \sim 417^\circ\text{C}$   
 $\text{FeCO}_3 \sim 400^\circ\text{C}$

It can be used for differential calcination.  
e.g. Mg ore that contains both  $\text{MgCO}_3$  and  $\text{CaCO}_3$  are calcined around the decomposition temp. of  $\text{MgCO}_3$ . Water is used to leach out the  $\text{MgO}$  and the decomposed  $\text{CaCO}_3$  is left behind.

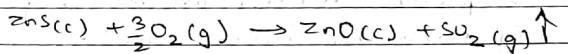
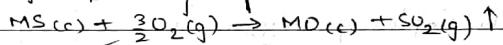
DATE \_\_\_\_\_

(7)

Roasting - Roasting usually involves heating of ores or a concentrate below the fusion point normally in excess air. It brings about chemical conversion and renders the raw material suitable for subsequent reduction.

The major application of roasting is removal of elements like sulphur, Arsenic, Tellurium, etc. as a volatile oxide.

Oxidizing Roasting - This process burns out sulphur from a sulphide ore and replace it fully or partially by oxide.



During Roasting, metal sulphates may also form. A high temp. is required to break up the sulphates specially the Zn sulphate.

When a sulphide ore is roasted to the point/temp. where almost the entire sulphur content is eliminated. The residue is called "alead roast".

DATE \_\_\_\_\_

(8)

A catalytic agent often speeds up the roasting process. Eg: quartz and other gangue materials.

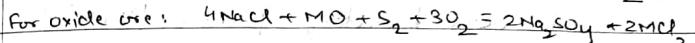
Roasting essentially depends on time, temp., availability of oxygen or air, physical condition of the ore & the nature of mechanical device used. Eg:- blast roasting is done in very short time, Hearth roasting takes hours, Heap roasting takes months & weather roasting takes years.

Volatileizing Roasting - This process eliminates volatile oxides like  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{ZnO}$ , etc. The inflow of oxygen is carefully controlled to prevent excessive oxidation & formation of non-volatile higher oxides.

Chlorinating Roasting - This is carried out to convert the metal compounds to chloride form which metal can be subsequently obtained by reduction. Metals like uranium, Niobium, Titanium, Zirconium, Beryllium are extracted from their chlorides.

DATE \_\_\_\_\_

(9)



Sulphating Roasting - SR converts certain sulphide ores to sulphate, prior to leaching.

Magnetic Roasting - MR is controlled reduction of Haematite to magnetite.

Reduction Roasting is partial red. of oxides, prior to reduction smelting.

Blast Roasting or Sinter Roasting modifies the physical condition and partially oxidizes the charged ore.

**Roasting Practices** Roasting process is chosen based on 2 major criteria-

- ① Required physical condition of the product
- ② Required chemical composition of the product.

- ① Required Physical Condition of the Product - for blast furnace roasting, the product should be

DATE \_\_\_\_\_

(10)

coarse and cellular.

~~porous and collector like~~

For reverberatory furnace, the product should be fine. For leaching, porosity is the prime factor & composition of the product should be such that formation of insoluble compounds can be avoided.

## ② Required Chemical Composition of the Product

- For the extraction of lead from sulphide ore, it is required to eliminate entire sulphur content before blast furnace melting.
- for copper extraction, a sufficient quantity of sulphur should be retained to produce the matte.
- For Zn extraction, almost entire sulphur content should be eliminated. It should be noted that formation of zinc ferrite should be avoided when Zn is extracted by leaching bcoz it is difficult to leach out the ferrite.

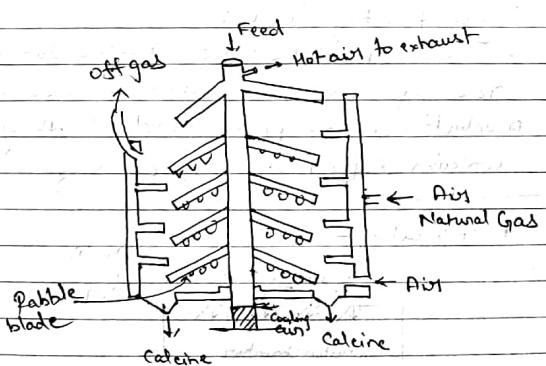
DATE \_\_\_\_\_

(11)

(iv) If precious metals or other valuable recoverable metals are present which may melt at high temp., the low temp. operation was adopted.

(v) The most desirable combination of roasting operation is one that is commercially most satisfactory in long run.

**Multiple Hearth Roasting** - It consists of ~~several~~ (about 10) ~~circular~~ brick hearth superimposed on each other



The entire str. is closed in a cylindrical brick line ~~at~~ steel plate.

DATE \_\_\_\_\_

(12)

DATE \_\_\_\_\_

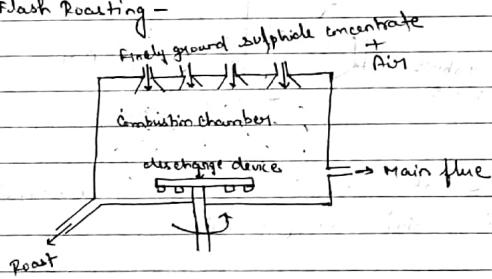
(13)

- Revolving mechanical grilles continuously shift the ore.
- The ore gradually moves downward & the oxidizing gas is moving upward.
- In oil insulated roaster, external heating is unnecessary except the charge is highly moist.

### Drawbacks

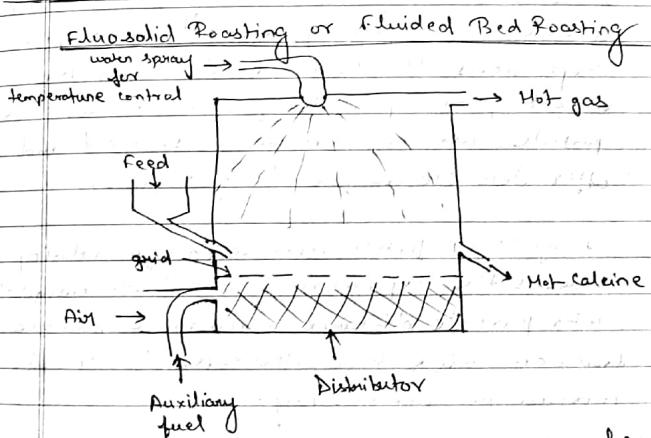
- (i) Slow Roasting Process
- (ii) The sulphurous gases evolve during the roasting are not suitable for the production of sulphuric acid as they do not contain sufficient  $\text{SO}_2$  or  $\text{SO}_3$ .

### Flash Roasting -



Pre-heated ore particles ~~fall~~ through hot air resulting in almost instantaneous oxidation that's or "flashing" of the combustible constituents of the ore mainly sulphur.

Flash Roaster has a large combustion zone.



In this process, ore particles are mounted ~~when~~ suspended in an upward stream of gas.

Stages: Gas flow rate is very low. The pressure drop across the bed is proportional to the flow rate. Pressure drop is mainly influenced by void fraction, particle size & particle shape.

DATE \_\_\_\_\_

14

Stage 2: As gas velocity increases, the bed expands upwards due to the drag force exerted by the gas. In this stage, pressure drop across the bed depends on gas velocity.

Stage 3: When the gas velocity further increases, a stage is eventually reached when pressure drop across the bed equals with the weight of the particle per unit area. The particles are now remains suspended and offer less resistance to gas flow.

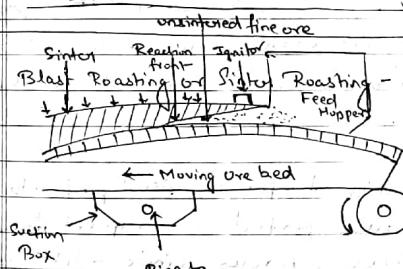
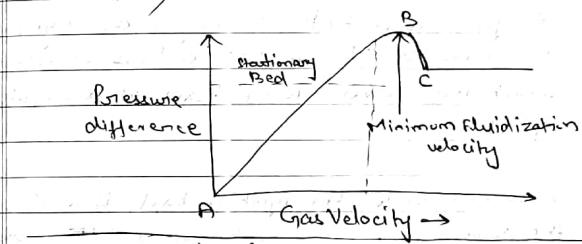
Stage 4: A further increase in gas velocity causes the expansion of the bed. Consequently, inter-particle distance increases & pressure drop across the bed decreases due to the increase in gas velocity.

Stage 5: Finally, a stage reached when the expansion of the bed becomes independent of gas velocity. The major portion of the outgoing gas appears in the form of bubbles bursting on the surface of the bed. In this condition, the bed is said to be fluidized.

DATE \_\_\_\_\_

15

(Note:- A high degree of intermixing provides an ease for maintaining uniform bed temp. The thermal conductivity of some fluidized bed are about 100 times higher than the conductivity of best known metallic conductor (say silver).)



① Sinter Roasting is the treatment of sulphide ore where Roasting and ~~agglomeration~~ takes place simultaneously.

DATE \_\_\_\_\_

(16)

DATE \_\_\_\_\_

(17)

- (2) Sinter Roasting of sulphide ore does not require addition of any fuel in the charge because sulphur content in the charge itself acts as fuel. In case of oxide ore (eg: iron ore), fuel addition is required.
- (3) The fine concentrate is charged as layer of 15-50 cm. thick on the endless revolving bed which moves over wind boxes at a regulated speed.
- (4) A burner under the ignition hood is used to start the combustion. This combustion is then propagated through by the air content drawn through the charge into the ~~wind~~ box which is connected to the suction fan.
- (5) Sufficiently high temp. is developed into the charge to cause partial or incipient fusion, which produces a porous cinder-like material called sinter. A certain amt. of moisture is necessary to render the ~~sintered~~ porous.

- (6) When sinter reaches the end of the machine it is discharged & cooled.

Ignition Temperature and Autogeneous Roasting  
 The Fluidized Bed Roasting is ideal for sulphide ores because the oxidizing reactions that takes place during the roasting are highly exothermic - For any exothermic  $R^x$ , there is a minimum temp. above which the  $R^x$  is sustained by the heat liberated by itself. When an ore particle is maintained at this min. temp. in a stream of air and the roasting is initiated by the ~~the~~ ignition device ~~device~~, then the  $R^x$  proceeds even in the absence of any external heat. Such  $R^x$  is called Autogeneous.

In a Fluidized Bed Roaster, the min. temp. or the ignition temperature required depends on the characteristics of the ore and condition of ignition i.e. the geometry of the reactor. Since the ignition temp. is the min. temp. at which a mineral particle oxidize first to maintain or increase the temp. of the roaster, its value roughly indicates the temp. required for fluidized Bed Roasting.

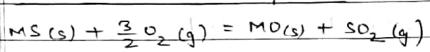
DATE \_\_\_\_\_



DATE \_\_\_\_\_



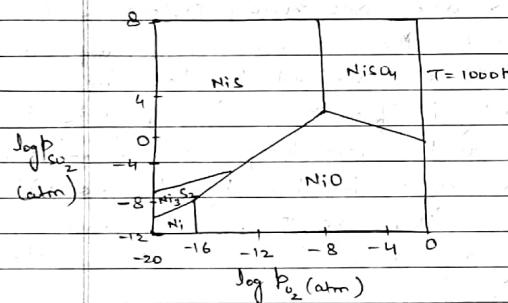
### Predominance Area Diagram -



Graphical Representation  
of a chemical RP

$$K = \frac{P_{\text{SO}_2} \alpha_{\text{NiO}}}{P_{\text{O}_2}^{3/2} \alpha_{\text{NiS}}} = \begin{bmatrix} P_{\text{SO}_2} \\ P_{\text{O}_2}^{3/2} \end{bmatrix}$$

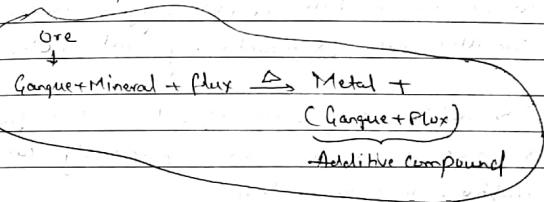
with partial press.  
of O<sub>2</sub> and partial  
press. of SO<sub>2</sub> is  
called PA Diagram.



NiS will form under high partial pres. of SO<sub>2</sub>.

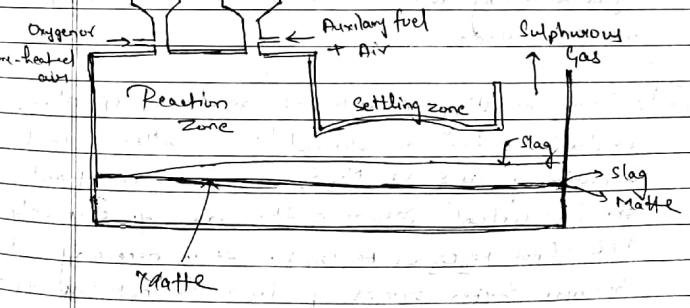
NiS can be directly converted to NiSO<sub>4</sub> at high  
partial pres. of SO<sub>2</sub>. However, it is more convenient to  
do this through intermediate formation of Ni<sub>3</sub>S<sub>2</sub> and  
NiO

### SMELTING



### Flash Smelting -

Sulphide + FeS<sub>2</sub> + flux



(1) where both P<sub>SO<sub>2</sub></sub> & P<sub>O<sub>2</sub></sub> can be varied, the system has 2 DOF.

(2) Along the line, the system has 1 DOF.

(3) when 3 condensed phases are present, there will be  
DOF is zero i.e. the system is invariant.

(4) At 1000K, if the roaster gas contains 10% SO<sub>2</sub> and  
10% O<sub>2</sub>, the NiSO<sub>4</sub> is thermodynamically stable.

If the gas contains only 1% SO<sub>2</sub> & 1% O<sub>2</sub>, the  
final product is NiO.

DATE \_\_\_\_\_



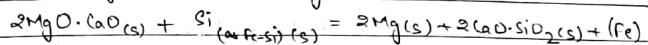
DATE \_\_\_\_\_



- (1) It is used for smelting of concentrates of Ni and copper sulphide. Flash smelting process combines both roasting and melting. This process burns out the concentrate falling through the combustion chamber with oxygen or pre-heated air blown with the concentrate.
- (2) Use of pre-heated air or pure oxygen increases the combustion rate for maintaining autogenous melting.
- (3) The sulphurous gas coming out of the furnace is very rich in  $\text{SO}_2$  and can be profitably used for sulphuric acid production.
- (4) Matte is the molten mix of sulphides produced after smelting and the gangue materials pass off into the slag.
- (5) During roasting, prior to the smelting operation, oxidation of the ore should be controlled so that oxidation of  $\text{Cu}_2\text{S}$  or  $\text{Ni}_3\text{S}_2$  can be avoided and the iron content present in the ore produce only  $\text{FeO}$  (not  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ). It is necessary because higher oxides of iron do not pass off into the slag.

- (6) Copper is subsequently recovered from matte by the process known as "converting" into a side blown converter.

#### Pyrometallurgical Process using Vacuum-



- (1) — Pidgeon's Process  
(Ferro-silicon Reduction of calcined dolomite.)

The reduction is carried out under vacuum ( $0.1 \text{ mm Hg}$ ) at  $1100 - 1200^\circ\text{C}$ . In presence of  $\text{CaO}$ , free energy change of the  $R^{\ddagger}$  decreases.

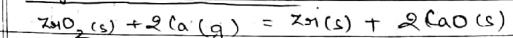
$$\Delta G^\ddagger = 52 \text{ kcal (without CaO)}$$

$$\Delta G^\ddagger = 19 \text{ kcal (with CaO)}$$

At  $1200^\circ\text{C}$ , equilibrium press. of  $\text{Mg}$  is  $15 \text{ mm Hg}$  and to attain 1 atm Hg above  $1700^\circ\text{C}$  is required. Since such high temp. is not practicable with external heating, vacuum is employed to drive the  $R^{\ddagger}$ .

(2)

#### High Pressure Process



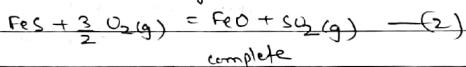
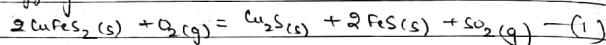
Equilibrium partial press. of  $\text{Ca}$  is very high therefore, high press. is essential. These processes are mainly employed for extraction of rare earth metals.

DATE \_\_\_\_\_



### Matte Smelting & Extraction of Copper -

The principle mineral of copper is  $\text{CuFeS}_2$  usually containing 1 to 2% copper. These ores are upgraded by grinding and flotation followed by roasting under controlled condition. During roasting, iron sulphide is partially converted to  $\text{FeO}$  and subsequently removed by slagging.



It is not allowed to add oxygen to ensure the absence of higher oxides because these higher oxides are not at all suitable for slag formation.

The roasted solids are charged into a ~~blast~~ smelter along with quartz ( $\text{SiO}_2$ ) as flux. The charge is heated up in a temp. range of  $1200-1300^\circ\text{C}$ . The iron oxide is removed as  $\text{FeO}\text{SiO}_2$  into the slag and the remaining sulphides form matte.

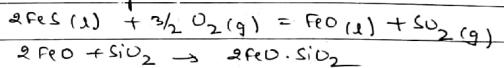
Since matte is heavier than the slag, it gets settled down and provides ease for slag-metal separation.

The liquid matte is then charged into a ~~blast~~ - blown converter where preparation of metal occurs by 2 distinct stages:

### Slagging Stage

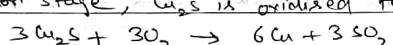
### Stage 2: Blister formation Stage

Slagging Stage - In the slagging stage, iron sulphide present in the matte is oxidized & slagged out by the addition of silicious flux.

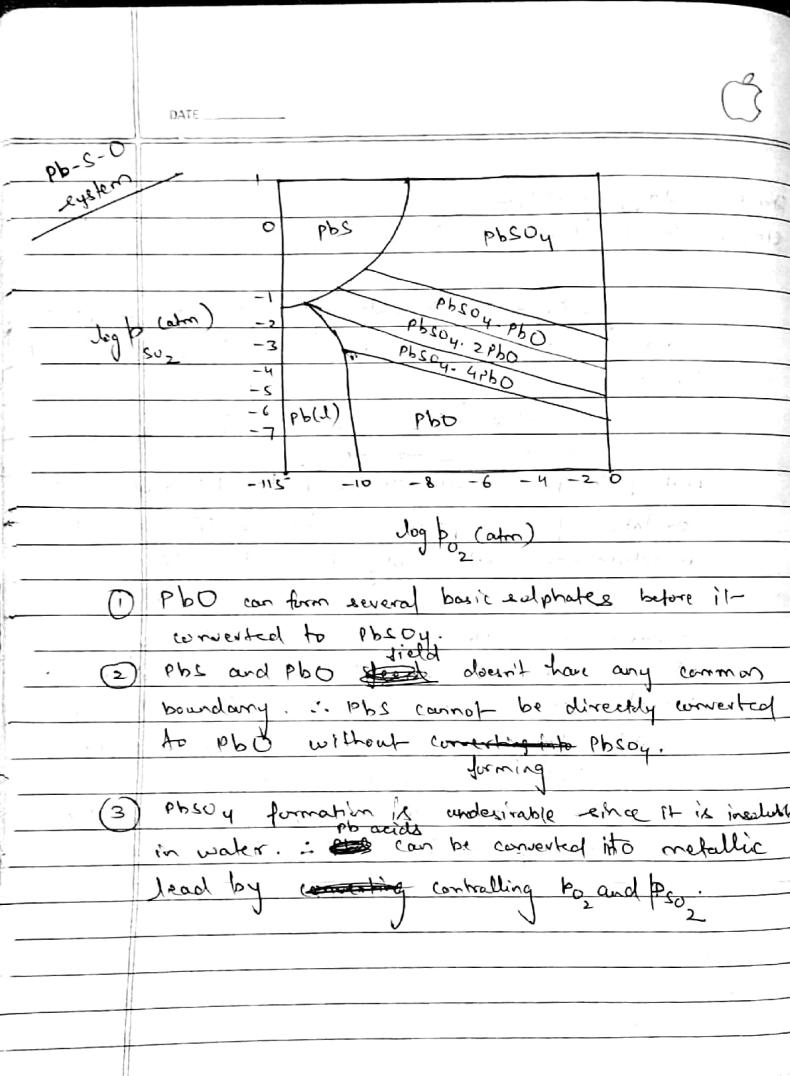


Part of the  $\text{FeO}$  is also oxidized to Magnetite. The oxidation of iron sulphide generates sufficient heat and maintains the matte & slag in liquid state.

Blister formation Stage - After the completion of slagging, the converter contains  $\text{Cu}_2\text{S}$  which is called White Metal because of its appearance. In the Blister formation Stage,  $\text{Cu}_2\text{S}$  is oxidized to form copper.



This copper is known as Blister copper (so called due to its appearance).

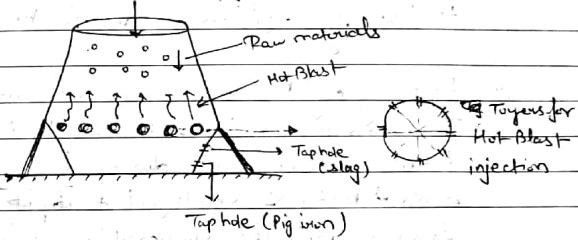


- (1)  $PbO$  can form several basic sulphates before it is converted to  $PbSO_4$ .
- (2)  $PbS$  and  $PbO$  ~~field~~ doesn't have any common boundary.  $\therefore$   $PbS$  cannot be directly converted to  $PbO$  without converting into  $PbSO_4$ . forming
- (3)  $PbSO_4$  formation is undesirable since it is insoluble in water.  $\therefore$  ~~Pb acids~~ can be converted into metallic lead by controlling  $P_{O_2}$  and  $P_{SO_2}$ .

### DATE \_\_\_\_\_ Counter current heat exchange operation

#### Blast Furnace Smelting Reduction

- (1) Fundamental principles.
- (2) Role of coke in BF smelting
- (3) Aerodynamics
- (4) Problems - Operational problems frequently encountered.  
ore, coke, flux, Mn



### Hydro-Metallurgy

Operational Steps:- Hydro-metallurgical process normally involves following steps-

- (i) Leaching - In leaching, the metallic values in an ore are selectively dissolved by using suitable liquid reagent. The selectivity in dissolution depends on the nature of the reagent and the state of the leaching depends on factors like temperature, pressure, volume of the leaching liquid, ore particle size, composition & concentration of the reagent, pulp density, duration

DATE \_\_\_\_\_



of Leaching  $R^x$  and the degree of ~~extraction~~ avitation of the Leaching Reagent.

(ii) Separation of Leach Liquor - The leach liquor is separated from the residue left behind after processes such as leaching, settling, thickening, filtration and washing.

(iii) Recovery of Metallic values from Leach liquor - The desired solute or the metal in elemental form is obtained during the recovery stage. Methods employed to treat the leach liquor includes evaporation, distillation, precipitation, cementation, electrolysis, ion exchange, solvent extraction, etc.

(iv) Recycling of Leach Liquor - The leach liquor is purified & its composition is re-adjusted for further utilisation.

Advantages of Hydro-Metallurgy -

1) Hydrometallurgical Methods are ideally suited for lean and complex ore with gradual depletion of which ~~ore~~ deposit, it become difficult to

DATE \_\_\_\_\_



adapt conventional pyrometallurgical route for extraction. Processing of ~~lean~~ grade ore at high temp. causes energy wastage as well as problem of slag disposal.

The ~~siliceous~~ gangue minerals must be slag down in the pyrometallurgical process whereas it remains unaffected during the leaching operation.

2) Hydrometallurgical process allows greater control over processing steps resulting in the recovery of valuable by-product. Metals can be directly obtained from leach liquor.

3) Hydrometallurgical operations are often preferable for reducing environmental pollution. The pyrometallurgical processing of sulphide ore produces  $SO_2$ , which is often not suitable for sulphuric acid production. Even if the  $SO_2$  used for acid production, there is still escape of  $SO_2$  in air unless stringent anti-pollution measures are taken. Leaching on the other hand keeps sulphur in the soln. phase.

4) The cost of metallurgical grade coke is increasing rapidly & it is the main source of energy

DATE \_\_\_\_\_



DATE \_\_\_\_\_



and reducing agent in pyrometallurgical processes.  
∴ the aqueous processing route is favoured.

- 3) Hydrometallurgical route can produce metal in variety of physical form such as powder, nodules and coherent surface deposits-
- 4) Leaching operations are generally carried out at room temp. or at slightly elevated temp.
- 5) In hydrometallurgy, the waste liquor from the final recovery step can be recycled to the initial leaching operation.

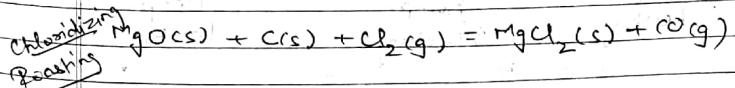
Disadvantages of Hydrometallurgy -

- 1) Aqueous soln. employed are generally dilute- Thus, a large vol. of soln. are to be handled for relatively smaller metal output. This requires considerable amt. of handling as well as space.
- 2) Some reagents are expensive and must be recycled or regenerated for economy.

(3) Rx rates are lower at room temp. hence the tonnage capacity of the plant is lower as compared to pyrometallurgical process.

Leaching - Leaching is the selective dissolution of feed material. In most of the cases, the metal to be extracted goes into the soln. However in some cases, it is desirable to leach away the gangue materials. Eg- Leaching of complex ore of Thorium.

Before leaching the ore is crushed & ground to suitable size range. It increases the specific surface area of particles, in turn the rate of the Rx. In some cases, primary chemical treatment makes the ore suitable for dissolution. for eg- Sulphide ores are subjected to oxidizing & chlorinating pasting.  $ZnS(s) + \frac{3}{2}O_2(g) = ZnO(s) + SO_2(g)$   
 $ZnS(s) + 2O_2(g) = ZnSO_4(s) + SO_2(g)$   
Both  $ZnO$  and  $ZnSO_4$  can be easily dissolved in  $H_2SO_4$ .



DATE \_\_\_\_\_



DATE \_\_\_\_\_



#### Selection Criteria Leaching Reagent -

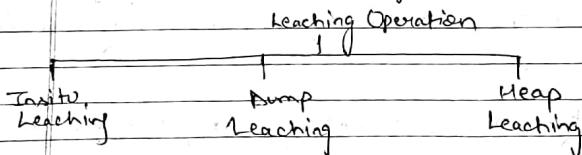
- (1) Chemical & physical character of the material to be leached.
- (2) Cost of the reagent.
- (3) Corroding action of the reagent & the material for construction.
- (4) Selectivity of Leaching Agent for the desired constituent to be leached.
- (5) Ability to be regenerated.

#### Common Reagents -

- (i) Acid -  $H_2SO_4$ ,  $HCl$
- (ii) Alkali -  $NaOH$ ,  $Na_2CO_3$ ,  $NH_4OH$
- (iii) Oxidizing Agent -  $NaClO_3$ ,  $MnO_2$ ,  $KMnO_4$ ,  $FeCl_3$
- (iv) Reducing Agent -  $SO_2$  and  $H_2$

#### Classification of Leaching Operation -

Type (A) Methods based on treating the ore at mine site



In-situ Leaching - Leaching of the shattered rock left after major mining operation or direct leaching of the ore deposit.

Dump Leaching - In this method, the leaching soln. ~~is~~ is applied to the dump consisting of off-grade ore that are rejected during mining.

Heap Leaching - Leaching of high-grade ore in a pre-determined manner using dump.

Type (B) Methods based on types of ~~soln~~ solvent - re-circulated -

#### Leaching Operation

##### Percolation Leaching

Percolation Leaching -

- (1) Leach soln. is percolated upward & downward through the crust ore into a tank.
- (2) A mixture of coarse & fine particles are used to ensure sufficient permeability.

##### Agitation Leaching

(3) Operates in batches hence it has much higher operational flexibility & less accidental breakdown.

#### Agitation Leaching -

(1) Stirring is used to aid the dissolution process.

(2) There could be variations Eg - (i) atmospheric or high press operation, (ii) continuous concurrent or continuous countercurrent operation, (iii) single stage or multi-stage operation.

Pressure Leaching - Mainly leaching reactions are carried out in autoclave under high press. At high press, a high temp can be obtained & the boiling away of the solvent can be suppressed.

Eg - leaching of Bauxite by sodium hydroxide A high press. becomes necessary when highly volatile & gaseous reagents are used in leaching. By increasing the partial press. of such reagents, their conc. in aq. soln. can be maintained at sufficiently high level. Eg All Leaching

operations involving ammonia are aided by high press.

When a liquid absorbs a gas, the rx proceeds very rapidly. Such rx could be rate-determining if a large rx vessel is used because as the size of the reactor increases the ratio of gas-liquid interface to the volume of liquid decreased. The rate of gas absorption can be accelerated by -

- 1) By increasing the partial press. of the gas
- 2) By " " area of gas-liquid interface relative to the volume of the liquid.
- 3) By increasing the efficiency of agitation.

#### Applications -

- 1) Leaching of oxides of metals like Al, V, Ti, and Uranium.
- 2) Sulphide minerals such as  $ZnS$ ,  $PbS$ ,  $MoS_2$ ,  $FeS_2$ ,  $FeS$  and the mix constituent of these minerals are rapidly oxidized under high press. at elevated temp. in aq. soln. of  $H_2SO_4$ , ammonia or sodium hydroxide.

DATE \_\_\_\_\_

F(As) Fe-As mixture

(3) B.F smelting of lead yields "Speiss". About 98% of Arsenite can be recovered at high partial press. by leaching by NaOH solution.

(4) Complex low grade sulphide concentrate of lead and zinc produced by flotation is press-leached in autoclave using sulphuric acid solution. This yields ZnSO<sub>4</sub> soln. and a residue containing PbSO<sub>4</sub>, elemental sulphur, and pyrite. To separate the pyrite, sulphur & PbSO<sub>4</sub>, the slurry is heated above the melting point of elemental sulphur. As a result, pellets of elemental sulphur & pyrite are formed which can be separated out from PbSO<sub>4</sub> by screening.

The advantages of such process are -

- (1) Zn is not lost in form of zinc ferrite.
- (2) Elemental sulphur can be recovered.

(5) During the matte smelting of Ni ore, a matte containing 60-75% Ni along with Cu and Fe is produced.

As and Sb can also present in some cases. Cu, Ni & As can be extracted by leaching finely ground matte at 120-125°C under 1.5-7 atm (P<sub>O<sub>2</sub></sub>) in acid medium (pH = 4.5-5).

(6) Complex ore of zinc is leached in conc. H<sub>2</sub>SO<sub>4</sub> at 110°C and 6 atm (P<sub>O<sub>2</sub></sub>). About 98% Zn can be recovered by this technique.

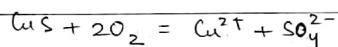
~~Many~~ Microbial or Bacteria Leaching - ~~sulfide~~ minerals form water soluble sulphates.

However the natural dissolution process is very slow. It has been ~~found~~ that ~~certain~~ certain types of bacteria speeds up the natural conversion process. Bacteria leaching not only leads to an enhanced dissolution rate but also effectively improves metal recovery.

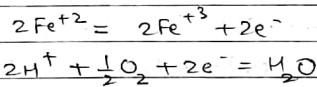
3. Most important types of bacteria from leaching viewpoint are -

- (1) Thiobacillus thiooxidans  
 (2) Thiobacillus ferrooxidans  
 (3) Ferrobacillus ferrooxidans

They are capable of growing in purely inorganic medium & obtain their energy by oxidizing the inorganic substances like sulphur, thiosulphate and ferrous <sup>iron</sup>. The enzyme synthesized by the bacteria accelerates the rate of oxidation p/x. Eg - Oxidation of sulphide minerals  $S + \frac{3}{2}O_2 + H_2O = H_2SO_4$



#### Iron Oxidation



Iron sulphide is the common impurity for sulphide minerals. During leaching, ferric ion acts as oxidant and ~~attack~~ attacks the metal sulphide and dissolves the metal sulphide.

(#) Factors affecting bacteria leaching -  
 (1) Effect of temp. - Temp. has marked effect on bacterial conversion of  $Fe^{2+}$  to  $Fe^{3+}$ . Maximum bacterial activity occurs b/w  $30-35^\circ C$ . As temp. increases beyond  $50^\circ C$ , their activity almost stops & above  $70^\circ C$ , microorganisms become sterile and are destroyed. Below  $30^\circ C$ , their activity also decreases and below  $18^\circ C$ , it is negligible from commercial view point.

(2) Effect of Nutrients - Addition of nutrients such as  $FeSO_4$ ,  $FeS_2$ ,  $Fe(SO_4)_3$  to the leaching soln. increases the ~~the~~ ferric ion concentration. Consequently, the bacteria become more active and the extent of extraction increased.

(3) Effect of particle size & bed depth - The bacterial oxidation rate depends on the available surface area of the solid feed material because the bacteria concentrate at the solid surface & build up colonies. Finely ground particles

DATE \_\_\_\_\_



DATE \_\_\_\_\_



therefore, leads to increase in leaching rate. However, very fine particles reduces bed permeability & degree of aeration, thereby inhibits leaching. Leaching rate enhances for shallow bed height.

(4) Effect of Radiation - When exposed to direct sunlight, a bacterial culture becomes inactive but not destroyed. This culture is extremely sensitive to UV light. Even a short exposure completely sterilizes it.

(5) Effect of Acidity & Aeration - Bacterial oxidation is highly pronounced in a medium having pH value 2-3.5. Above & below this pH level, oxidation rate decreases. At pH value 6, the oxidation is completely inhibited. These bacteria are destroyed in alkali medium.

The oxygen supply to the living microorganisms is vital.

Generally oxygen is supplied by circulating a portion of bacterial soln. & subsequently transferring flat soln. to the site of bacterial activity.

Cementation or Contact Reduction of Metal in aqueous solution - Leaching of an ore results in 2 distinct products -

- (1) A leach liquor containing metallic values.
- (2) A solid residue containing the gangue.

The reduction of metallic ion from soln. to the elemental form is generally accomplished by 3 methods -

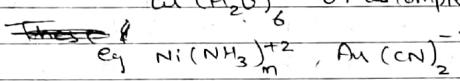
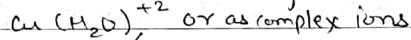
- (1) Cementation or contact reduction
- (2) electrolysis
- (3) Gaseous Reduction

In cementation, precipitation of metallic values occurs on the surface of the added metal. The basic mechanism is electrochemical in nature. The metal with more +ve oxidation potential in EMF series will pass into the soln. & displace a metal with a less +ve potential.

DATE \_\_\_\_\_

~~Electro-~~However, the ~~and~~ overall phenomenoncomprise several steps including  
non-electrochemical phenomenon such  
as diffusing process and sequential  
chemical rxn.

The reduction of metal  
from soln. Is a complex process  
~~with~~ when the ~~the~~ overall stoichiometry  
is concerned becoz the reducible  
ion may 'present as' hydrated condition  
or as complex ion. Eg -



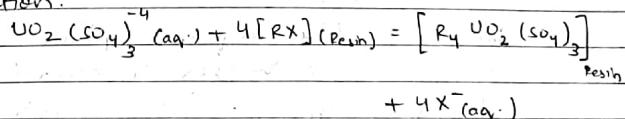
These ions are involved in electrolysis  
of Cu, hydrogen reduction of Ni  
ammine & zinc-precipitation of gold  
from cyanide solution

Precipitation - The impurities in the leach liquor  
that is the undesirable solute can be eliminated  
through precipitation under controlled pH,  
concentration as well as with the help of  
special additive.

DATE \_\_\_\_\_



Ion Exchange - During ion-exchange,  
the leach liquor is brought into contact with  
an organic resin containing an active compound  
(RX). This active compound exchanges a  
~~radical~~ radical with the anion in  
the solution. Eg - Leaching of uranium  
with sulphuric acid produces a complex  
anion in aqueous solution  $\text{UO}_2(\text{SO}_4)_4^{4-}$   
The impurity metal are mostly present as  
cation.



This resin is now called loaded with uranium.  
This is now separated and brought into  
contact with a strong solution of X-ions  
and the reverse rx takes place. The  
resin is regenerated and a strong and  
pure soln. of uranium can be obtained.

Solvent Exchange - It is also known as Liquid-Liquid  
separation.

In this process, the leach liquor is brought  
into contact with an organic liquid.  
One typical solvent is kerosene

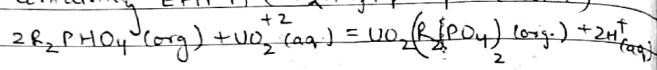
DATE \_\_\_\_\_



DATE \_\_\_\_\_



containing EHPA (diethyl phosphoric Acid)



R = 2 ethylene

This RF involves cation exchange. The loaded organic is separated and the uranium is recovered by reacting with sodium carbonate solution which regenerates the organic reagents & extracts uranium back into the aqueous phase but in a much more higher concentration than the pure form. Solvent extraction involves 2 liquids which can be agitated together to enhance the transfer of metallic value from one place to another.

### Electrometallurgy

Faraday's law -

- ① The quantity of material deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

Q) The quantity of material deposited at an electrode is proportional to the equivalent weight of the same.

$$m \propto It$$

$m = \frac{w}{nF} It$        $m = \text{mass of the substance discharged (g)}$

$w = \text{atomic mass}$

$I = \text{current (A)}$

$t = \text{time (s)}$        $F = \text{Faraday constant}$

$$\frac{w}{n} = Z = \text{chemical equivalent}$$

$$\text{current efficiency} = \frac{\text{Actual amt. of metal deposited}}{\text{Amt. of metal expected to be deposited acc. to Faraday law}} \times 100$$

Q) Determine the current efficiency of a chromium plating cell in which a current of 10A flowing for 60min. deposits 0.9gm of Cr from chromic acid electrolyte containing  $Cr^{+6}$  ion. Given the relative atomic mass of Cr is 52

$$m = \frac{wIt}{nF} = \frac{52 \times 10 \times 3600}{6 \times 96500} = 3.233$$

$$\text{current efficiency} = \frac{0.9}{3.233} \times 100 = 27.84\%$$

DATE \_\_\_\_\_

Decomposition Voltage -

$$V_A = V_D + V_R + V_O + V_E$$

sum of the overpotential  
of cathode & anode

voltage drop due  
to electronic  
resistance of  
the circuit

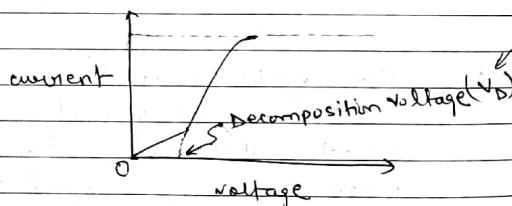
voltage applied  
across the cell.

decomposition  
voltage is  
the thermodynamic  
voltage measurement  
for overall cell Rx

chmic  
voltage drop  
due to the  
resistance  
of electrolyte

With the increase in the value of current,  
the value of  $V_R$ ,  $V_O$  &  $V_E$  increases -

Current-voltage relationship during decomposition  
of an electrolyte -



- ① voltage across the electrode increases from initial zero
- ② very small current that flows through the circuit until a critical value is reached

DATE \_\_\_\_\_

③

This current is called residual current and it is generally larger for fused-salt electrolysis than the aqueous soln.

④

The minimum voltage at which appreciable current starts flowing is called Decomposition Voltage. This voltage indicates the onset of decomposition of electrolyte.

⑤

Beyond the  $V_D$ , the current increases sharply with the increase in applied voltage & reaches a constant value known as limiting current -

⑥

The max. current that can be drawn per unit area of the electrode is known as limiting current density of that electrode.

Efficient Recovery of Cu from waste Printed Circuit Boards - The "urban ore" are getting greater attention as a secondary resource for recovery of valuable metals. The WPCBs are one of the major urban ore

DATE \_\_\_\_\_



having 10-250 times more content of precious metals and copper. Conventionally the recovery of Cu from WPCB's are carried out by -

- (1) Crushing of boards
- (2) Fine grinding for efficient liberation of metals.
- (3) Separation of metal & non-metal to enrich grain of the metal.
- (4) Leaching & recovering of copper.

Using this route, the max. recovery is limited to 75-80% because of the inefficient liberation, losses in form of fine dust and ~~coarse~~ poor separation of metal & non-metal.

for efficient recovery, the clean WPCB's are chopped into smaller sizes  $1\text{ cm}^2$  & then it is treated by DMA-dimethyl acetamide under 433 K temp. for 240 minutes. After the  $\text{P}_x$  layers of PCB's were separated, the solvent treated circuit boards were then subjected to leaching in a pressurized vessel under

DATE \_\_\_\_\_



433 K temp. in 6N sulphuric acid soln. with 15 volume % Hydrogen peroxide at a pulp density of 50 g/l for 45 minutes. Under this condition, about 93.5-95% Cu has been leached out from the printed circuit boards (PCB's)

#### Bayer Process for Alumina Production

flowchart - Book (RSA)  
only

#### factors affecting Bayer Process

- (1) Dissolution of alumina is better for finely ground bauxite.
- (2) Wet grinding is more efficient than dry grinding. It also reduces the time required for subsequent digestion.
- (3) Dissolution is accelerated at high temp. however at a temp. above about  $100^\circ\text{C}$ , the water is evaporated. Hence to attain a temp. of  $220^\circ\text{C}$ , 25 atm. pressure has been employed.
- (4) There is a lower limit of temp. at which the leaching & subsequent processing can be carried out. At a temp.

Below this limit, aluminium hydroxide may precipitate which causes loss of alumina.

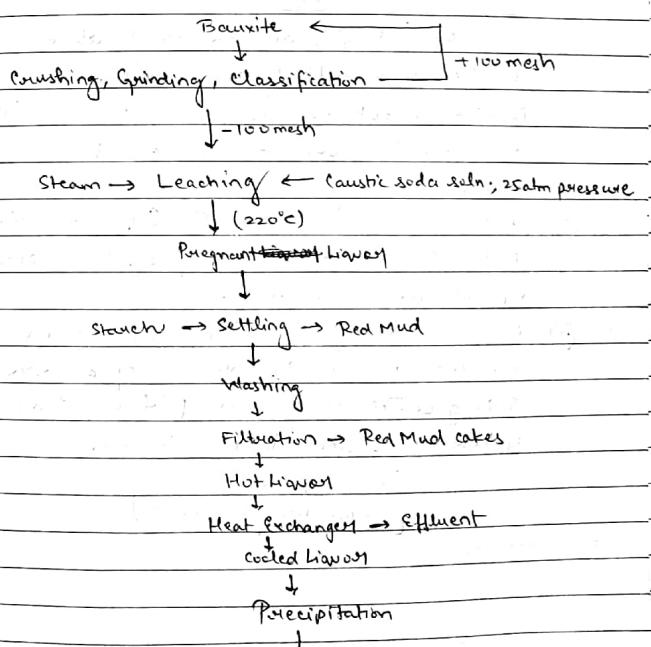
- (c) The sensible heat of hot-pregnant liquor ~~is lost~~ after filtration is recovered by heat-exchanger. This heat is further used for steam production.

- (d) In the precipitation stage, the entire amount of alumina in the soln. is not allowed to precipitate because it may lead to simultaneous precipitation of silica & the product becomes unsuitable for electrolysis.  
 $\therefore$  The precipitation is deliberately kept incomplete & the residual soln. is re-circulated.

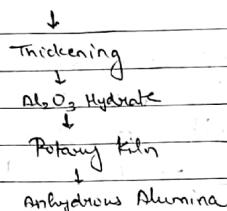
- (e) For the efficient calcination of alumina more than  $1400^{\circ}\text{C}$  is required.  
 Decomposition of  $\text{Al}(\text{OH})_3$  produces monohydrates & trihydrates i.e.  
 $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

The min. temp. for dehydration of monohydrate & trihydrate are  $1200^{\circ}\text{C}$  &  $800^{\circ}\text{C}$  resp. The addition of smaller quantity of  $\text{CaF}_2$  helps in the dehydration.

#### Bayer Process of Alumina Production



DATE \_\_\_\_\_



#### Hall-Heroult Process -

- (1) It is the electrolytic decomposition of alumina dissolved in the liquid bath of cryolite.
- (2) Alumina is not ionic compound, cryolite ( $\text{NaF} \cdot 3\text{NaF}$ ) is a naturally occurring mineral & dissociates it upto 15% at  $1000^\circ\text{C}$ .
- (3) Addition of small amount of  $\text{CaF}_2$  and sodium fluoride ( $\text{NaF}$ ) enhance the conductivity of the electrolyte & improves metal recovery.
- (4) At  $1000^\circ\text{C}$ , density of the molten cryolite is around  $2.1\text{ g/cc}$  whereas the density of alumina is around  $3.96\text{ g/cc}$ . The liberated metal having density of  $2.3\text{ g/cc}$  is heavier & sinks to the bottom.

[ Iron Bar - Anode  
Carbon lining - Cathode ]

DATE \_\_\_\_\_

$$j = \frac{i}{A}$$



#### Factors affecting Electrolysis/Electrolytic Production in Hall-Heroult

- (1) Bath temp. is an important factor. An increase in temp. decreases current efficiency due to the increase in side reactions. Decrease in temp. improves the current efficiency depending on the bath composition.
- (2) Higher the current density, better will be the current efficiency. Therefore, the current density is maintained to a higher value.
- (3) The lower the density of the bath, higher will be the rate of separation. The density can be lowered by using a high  $\text{AlF}_3/\text{NaF}$  ratio. However, a higher quantity of  $\text{AlF}_3$  ~~has~~ certain drawbacks. For instance, the conductivity of the bath decreased, the solubility of the alumina reduces and a large volume of ~~excess~~ fluorine is produced. On the other hand, higher NaF content reduces the current efficiency due to an increase in sodium ion concentration & deposition of sodium at the cathode and  $\text{NaF}/\text{AlF}_3$  ratio slightly less than 3 is considered to be optimum.
- (4) The current efficiency is also affected by

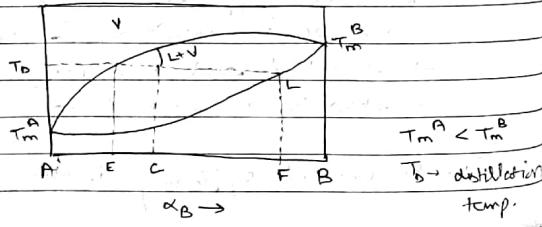
DATE: 21/10/2023

the distance from the bottom of the anode to the top of metal bath. The current efficiency increases with inter-polar distance to a maximum of 90% when the height is about 65 cm.

- (v) The cell efficiency can be improved by controlling the addition of alumina. The current efficiency is minimum when the alumina content in the bath is about 4%. When the alumina content is either higher or lower, the efficiency increases. However, to maintain a higher current efficiency, the cell should be operated at higher alumina content.

### Methods of Refining

#### (i) Purification by Distillation



DATE: \_\_\_\_\_

### Fractional distillation

$$\alpha_A = \frac{P_A}{P_A^0}, \quad \alpha_B = \frac{P_B}{P_B^0}$$

$$\frac{P_A}{P_B} = \frac{\alpha_A P_B^0}{\alpha_B P_A^0} = \frac{\gamma_A X_A P_A^0}{\gamma_B X_B P_B^0}$$

$$\frac{P_A}{P_B} = \left[ \frac{\gamma_A P_A^0}{\gamma_B P_B^0} \right] = \alpha \text{ (separation efficiency)}$$

### Application -

- (i) Separation of Zn from liquid lead.
- (ii) Removal of As and Sb from Fe.
- (iii) Removal of volatile impurity from reactive metals like Ti, Mo, etc.

### Zone Refining

- (i) It is based on fractional crystallization. In this technique, ultra refined pure metal is obtained with a restriction that the starting material has low concentration of impurities.

(ii) The impurities ~~have~~ have <sup>have</sup> higher solubility in the molten metal as compared to the cold metal.

DATE \_\_\_\_\_



DATE \_\_\_\_\_



(3) In zone refining, the impure metal is taken in form of a rod and a travelling melting zone is set-up in the rod.

(4) A narrow zone near the end of the rod is melted & then move slowly to the inner end of the rod.

(5) With a continuous movement of molten zone, impurities atom move down to settle at the ~~end~~ end of the rod.

(6) The zone passage is repeated several times in the same direction. After repeated passage, the impure end is removed, leaving behind the zone refined pure metal.

### (iii) Fire Refining

(1) It is used to remove more active elements from molten metal by preferential oxidation.

(2) It is suitable for refining Fe, Pb, Sn and Cu.

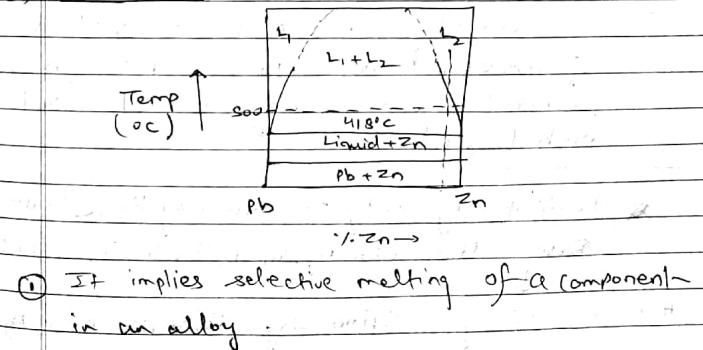
(3) Reagent used for refining method is the atmospheric oxygen blown through the molten metal.

(4) Flux is added to remove impure oxide in form of a mixture of liquid oxides.

(5) The oxygen is transferred ~~through~~ to gas-metal interface or through the slag layer or a combination of both.

(6) In some cases, instead of oxygen, oxygen is supplied from a salt like  $\text{NaNO}_3$  which is added to the melt. The nitrate decomposes to give nascent oxygen.

### (iv) Liquidation



(1) It implies selective melting of a component in an alloy.

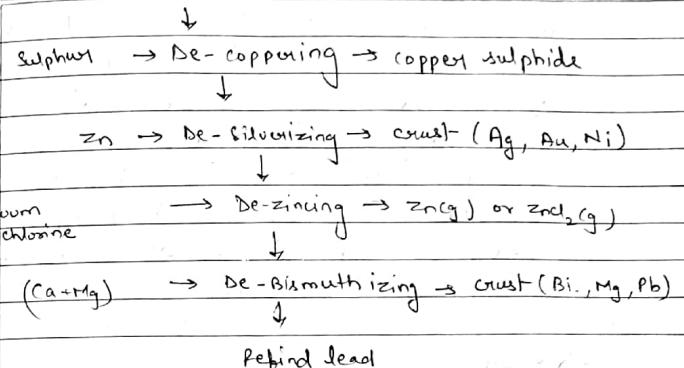
(1) It is based on factors such as diff. in m.p. of the alloy component, the immiscibility of the phases at the diff. in densities of the alloy component which causes the alloy to separate into 2 or more layers.

(2) The phenomenon of immiscibility is governed by phase diagram. Eg - Claude Zn containing 5% lead can be refined in a furnace by slowly cooling it from the molten state over a period of  $\approx 3$  days.

(3) Eventually lead separates out & accumulates at the bottom of the furnace. Below  $418^\circ\text{C}$ , pure Zn is separated out leaving behind lead rich liquid.

~~#~~ Purification of Lead / Treatment of Base Bullion  
Base Bullion (Pb, Ag, Cu, Sb, Bi, Sn, Se, Te, As, Ni)

Ag → Dressing → Softner slag (Sb, Sn, As, Te, Se, Ag)



~~Dressing~~  
Dressing is a combination of liquation & oxidation & usually carried out in a reverberatory furnace. The base bullion is subjected to dressing at  $350^\circ\text{C}$ . At this temp, many metals get oxidized and are ~~skinned off~~ skinned off.

Subsequently, the temp. is raised to  $500-550^\circ\text{C}$  & sulphur is added to remove Cu in form of copper sulphide.

~~Desilverization of lead~~ / Parkes Process -  
Dressing & De-coppering are followed by a treatment of removal of precious



DATE \_\_\_\_\_

metals mainly the silver. In Parkes process, Zn is added to the molten metal for de-silverization of lead. The mutual solubility of lead and zinc is very low & Ag can readily dissolve in Zn than Pb. The Ag absorbed by the Zn layer is subsequently recovered by distillation of Zn.

#### De-zincing

In a Parkes process, some Zn is inadvertently carried over into the lead, the lead containing Zn are subjected to Cupellation where Zn is primarily removed by oxidation. Zn can also be separated by application of vacuum or by preferential chlorination.

#### De-Bismuthizing

If the base bullion containing large quantity of Bi, it can be separated by addition of an alloy of Ca and Mg which forms an insoluble intermetallic compound with Bi.

DATE \_\_\_\_\_



#### Production of Uranium - Only flow chart