PRINCIPLES OF EXTRACTIVE METALLURGY

4TH SEMESTER

COURSE CODE:- Th 3

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BPUT SYLLABUS

PRINCIPLES OF EXTRACTIVE METALLURGY (3-1-0)

MODULE I (14 HOURS)

Unit processes in Pyro metallurgy: Calcination and roasting, sintering, smelting, converting, reduction, smelting-reduction, Metallothermic and hydrogen reduction; distillation and other physical and chemical refining methods: Fire refining, Zone refining, Liquation and Cupellation. Small problems related to pyro metallurgy.

MODULE II (14 HOURS)

Unit processes in Hydrometallurgy: Leaching practice: In situ leaching, Dump and heap leaching, Percolation leaching, Agitation leaching, Purification of leach liquor, Kinetics of Leaching; Bio-leaching: Recovery of metals from Leach liquor by Solvent Extraction, Ion exchange , Precipitation and Cementation process. Importance of potential-pH diagram. Some process flow sheet: recovery of Au from leach liquors, recovery of Nickel and Cobalt. Small problems relate to hydrometallurgy

MODULE III (12 HOURS)

Unit Process in Electrometallurgy: Faraday’s Laws of Electrolysis, concept of overvoltage, limiting current density, total cell voltage, series and parallel electrical circuits in refining, aqueous and fused salt electrolysis, electro refining of common metals like Cu, Zn, Au, Ni, Al, Mg etc. Electroplating. Small related problems to Electrometallurgy

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INTRODUCTION TO PYROMETALLURGY

CHAPTER 1

UNIT PROCESSES IN PYROMETALLURGY

- **MINERAL:** It is a naturally occurring inorganic compound of one or more metals in association with nonmetals such as oxygen, Sulphur and the halogens. A mineral has fixed composition and well defined physical and chemical properties.
- **ORE:** It is the naturally occurring aggregate or combination of minerals from which one or more metals or minerals may be extracted economically (profitably).
- **UNIT OPERATIONS:** The physical processes like crushing, grinding, classification, concentration etc. are called unit operations.
- **UNIT PROCESSES:** The chemical processes like calcination, smelting, roasting, leaching etc. are called unit processes.

UNIT PROCESS

PYROMETALLURGY **HYDROMETALLURGY** **ELECTROMETALLURGY**

PYROMETALLURGY:

- Pyrometallurgy deals with the methods of extraction of metals from their ores and their refining and is based on physical and chemical changes occurring at high temperatures.

WHAT ARE THE ADVANTAGES OF HIGH TEMPERATURE?

- As at high temperature, the reaction rate is accelerated which leads to more metal production.
- Also at high temperature the inexpensive reducing agent can be used and cheaper raw material can be used.
- As we know that the reaction rate doubles in each 10°C rise of temperature which requires small activation energy. It helps in fast reaction.
  - Shift of reaction is possible.

- Brings about a reduction which cannot takes 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.

There are 4 processes that are included in pyrometallurgical treatment. i.e.

1. Calcination
2. Roasting
3. Smelting
4. Refining

CALCINATION:

- Calcination is the thermal treatment of an ore that brings about its decomposition and elimination of volatile products i.e. carbon dioxide and water.
- Temperature required for this process can be calculated from free energy temperature relationship for the reaction under consideration.
- As the most decomposition reaction is endothermic, so the temperature of calcination is generally depends on the transfer of heat into the particle. This result in even high temperature of the furnace (kiln) at the expanse of some fuel.
- For example, $CaCO_3$ (c) = CaO (c) + CO_2. This reaction is endothermic and requires high temperature to decompose it in the kiln.

CHAPTER-2

ROASTING

- Roasting of an ore or a concentrate is a chemical process in which chemical conversion of ore is taken place by employing oxygen or other element.
- This process was used to remove Sulphur or other elements such as arsenic and tellurium in the form of a volatile oxide from an ore.
- Different types of roasting are,
    1. OXIDIZING ROASTING:
        - ☞ It is the important roasting process in which Sulphur burns out from the sulphide ore by supplied oxygen and oxygen replaces the burnt Sulphur. The roasting reaction will be,

          $$MS(c) + 3/2\ O_2\,(g) \rightarrow MO(c) + SO_2\,(g)$$
        - ☞ When complete removal of Sulphur from the sulphide ore occurs then the residue called DEAD ROAST.
        - ☞ Quartz and other gangue material acts as catalyzer.
    2. VOLATILIZING ROASTING:
        - ☞ In this roasting process volatile oxides such as As_2O_2, Sb_2O_3 and ZnO from an ore.
    3. CHLORIDIZING ROASTING
        - ☞ In this roasting process the ores are converted to chlorides either in oxidizing or reducing condition.
        - ☞ Metals like uranium, beryllium, niobium, zirconium and titanium are extracted from their chlorides.
- There are also other kind of roasting methods like sulphating roasting (sulphide ore to sulphate ore), magnetic roasting (hematite to magnetite), reduction roasting (partial reduction of oxide prior to reduction smelting), blast or sinter roasting (modification of physical property of ore as well as partial oxidation of ore).
- **PREDOMINANCE AREA DIAGRAMS:**
    - ❖ The isothermal behavior of some M-S-O systems with respect to their relative stability can be represented by predominance area diagram.
    - ❖ These diagrams indicate those solids which are in equilibrium with the gas having certain partial pressure of oxygen and Sulphur dioxide.

- Hence this diagram helps to predict the type of solid present that would be in equilibrium with the roaster gas of a known composition.
- Sulphur dioxide gas is taken into account because during roasting of sulphide ore SO_2 gas obtains.
- In order to describe this diagram, let us consider Ni-S-O system at 1000K

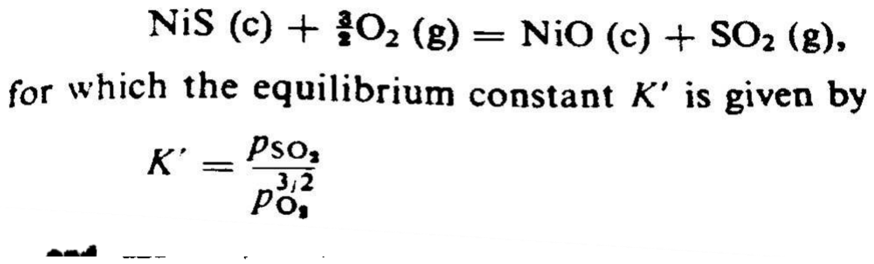
Ni-S-O system at 1000K

- At 1000K this system contains the condensed phases Ni, NiO, NiS, Ni_3S_2, $NiSO_4$.
- The gas phase contains SO_2 and O_2 but some amount of SO_3 and S_2 may also be present inside the roaster.
- It is a two dimensional diagram drawn between log p_{so2} and log p_{o2}, in which each region represents a specific two dimensional area and these are has 2 degree of freedom.

Each line (AB, BC etc.) represents transition line between two phases and has 1 degree of freedom.

- And each point on the diagram (A, B, C etc.) are the invariant points and at these points three phases coexist.

- Let us consider the reaction along the line CD,

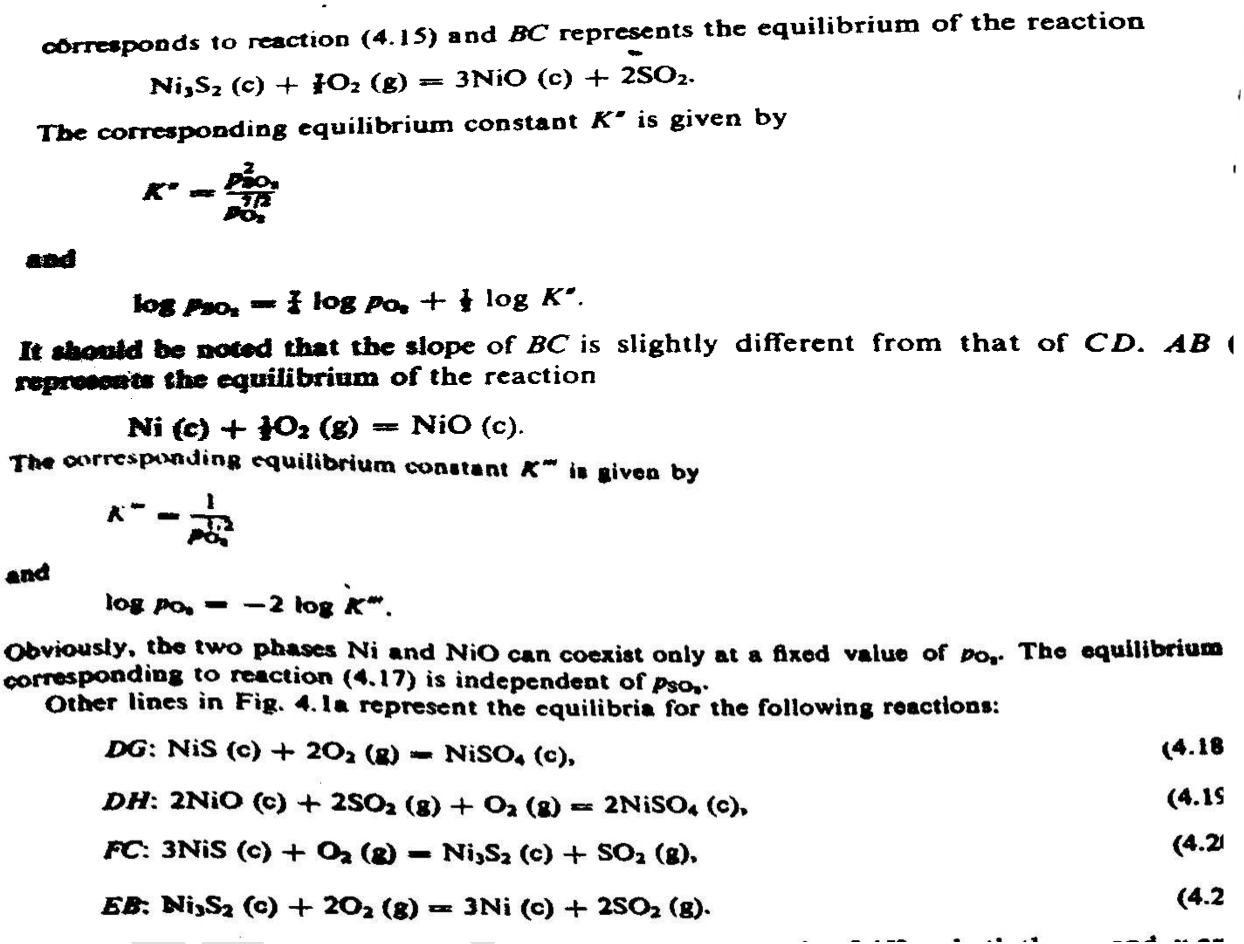


$$NiS\ (c) + \tfrac{3}{2}O_2\ (g) = NiO\ (c) + SO_2\ (g),$$

for which the equilibrium constant K' is given by

$$K' = \frac{p_{SO_2}}{p_{O_2}^{3/2}}$$

and



corresponds to reaction (4.15) and BC represents the equilibrium of the reaction

$$Ni_3S_2\ (c) + \tfrac{7}{2}O_2\ (g) = 3NiO\ (c) + 2SO_2.$$

The corresponding equilibrium constant K'' is given by

$$K'' = \frac{p_{SO_2}^2}{p_{O_2}^{7/2}}$$

and

$$\log p_{SO_2} = \tfrac{7}{4} \log p_{O_2} + \tfrac{1}{2} \log K''.$$

It should be noted that the slope of BC is slightly different from that of CD. AB (

represents the equilibrium of the reaction

$$Ni\ (c) + \tfrac{1}{2}O_2\ (g) = NiO\ (c).$$

The corresponding equilibrium constant K''' is given by

$$K''' = \frac{1}{p_{O_2}^{1/2}}$$

and

$$\log p_{O_2} = -2 \log K'''.$$

Obviously, the two phases Ni and NiO can coexist only at a fixed value of p_{O_2}. The equilibrium corresponding to reaction (4.17) is independent of p_{SO_2}.

Other lines in Fig. 4.1a represent the equilibria for the following reactions:

DG: $NiS\ (c) + 2O_2\ (g) = NiSO_4\ (c),$ (4.18

DH: $2NiO\ (c) + 2SO_2\ (g) + O_2\ (g) = 2NiSO_4\ (c),$ (4.1

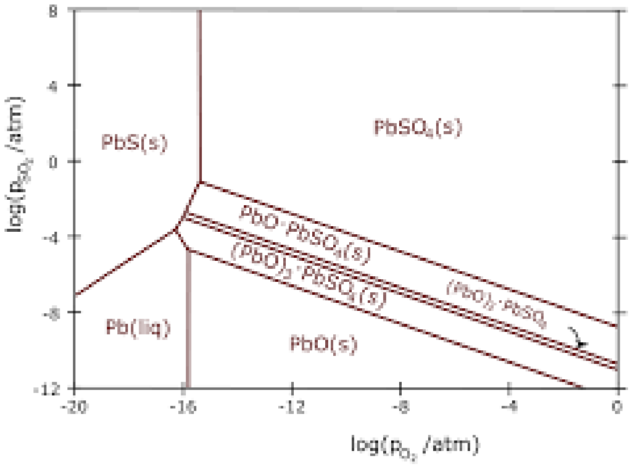
FC: $3NiS\ (c) + O_2\ (g) = Ni_3S_2\ (c) + SO_2\ (g),$ (4.2

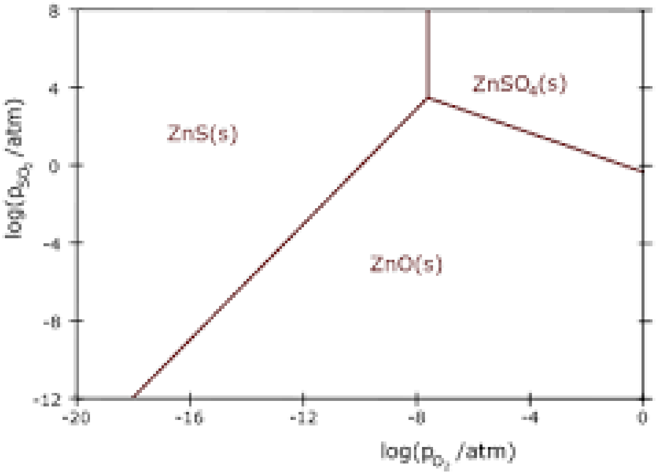
EB: $Ni_3S_2\ (c) + 2O_2\ (g) = 3Ni\ (c) + 2SO_2\ (g).$ (4.2

- Again consider the reaction along the line BC,

(Refer pg. 134, 135; extraction of nonferrous metals by h s ray, r Sridhar and k p Abraham)

Other predominance area diagrams are,





FACTORS AFFECTING ROASTING:

- 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.

ROASTING PRACTICES:

CRITERIA OF CHOOSING A ROASTING PROCESS-

- Required physical condition of product
  - Blast furnace- coarse and cellular feed
  - Reverberatory furnace or retort- fines
  - Leaching- porous

- Required chemical composition of the product.
  - Lead should be totally free from Sulphur before smelting it in BF.

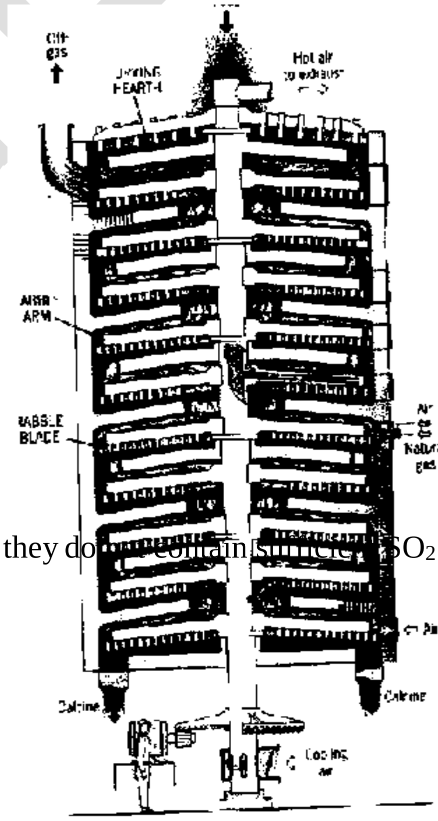
- In Cu the Sulphur content should not be totally removed it should be present in excess amount so as to produce a matte which is mainly the mixture of iron sulphide and coper sulphide of desire grade.
- For Zn total Sulphur content should be removed.
- Formation of zinc ferrite should be avoided when zinc is extracted by leaching because it is difficult to leach the ferrite.

INDUSTRIAL ROASTING UNITS:

MULTIPLE HEARTH ROASTER

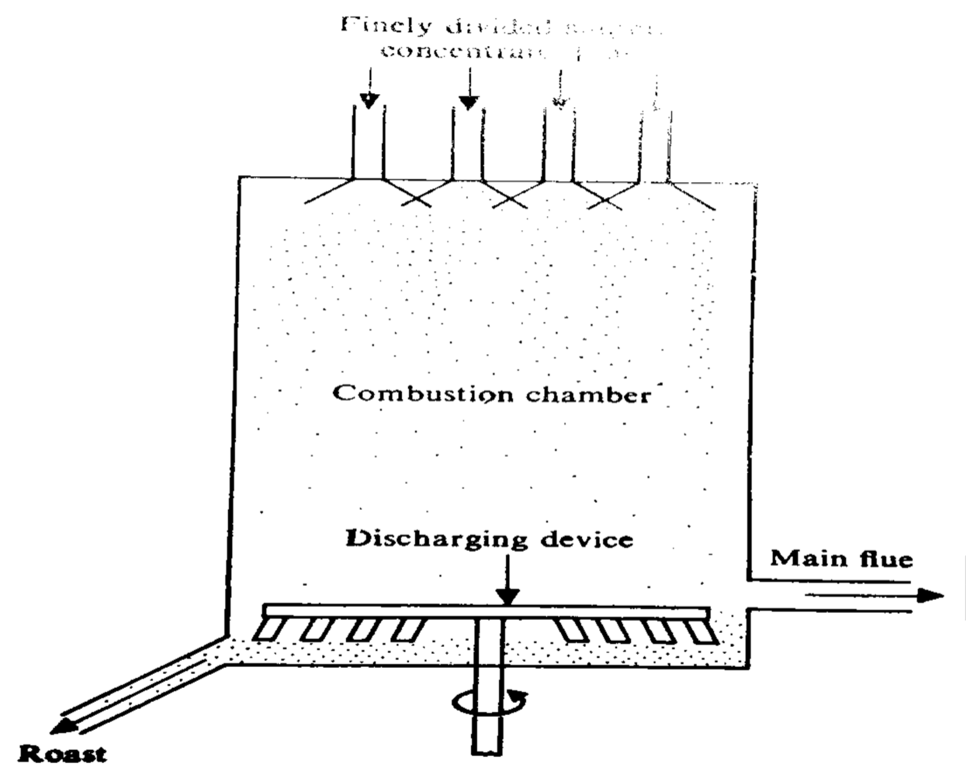
- Consists of circular bricks superimposed on each other.
- The entire structure is enclosed in a circular brick lined steel shell.
- Rabbles are attached to arms.
- Arms are attached to rotating central shaft.
- Ore is fed at the top.
- Oxygen is blown at bottom.
- Due to the countercurrent flow of gas and feed, roosting occurs and the roasted products are collected at bottom of roaster.

Drawback:-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 ROASTING:

- Instantaneous oxidation(flashing)
- Large combustion zone.

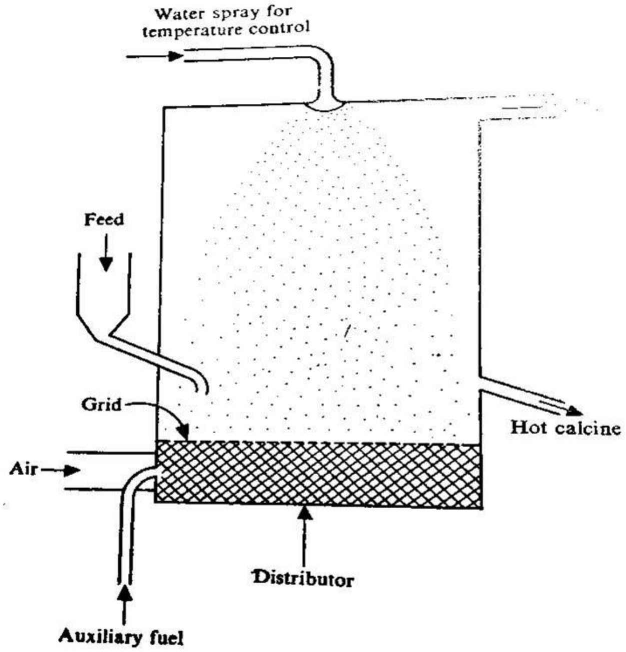


FLUIDIZED BED ROASTING:

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

Five stage of fluo-solid roasting

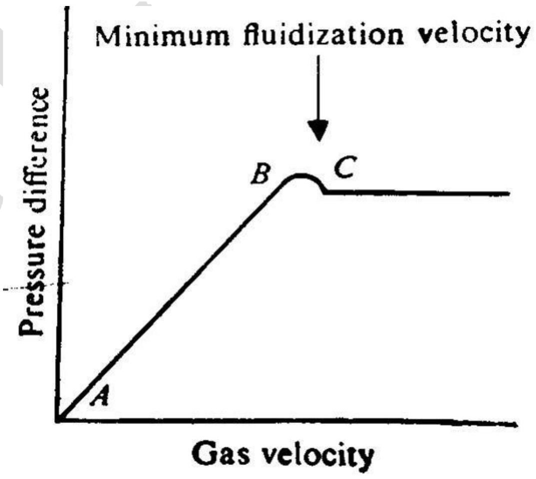
- ☞ When the gas flow rate is very low and since the bed is porous, the gas permeates the bed without disturbing the ore particles. In this stage the pressure drop is proportional to the flow rate. Other factors influencing the pressure drop are



A- Void fraction
B-the particle size
C- Particle shape factor

- 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.
- 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.
- 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 .
- Finally a stage is reached when the expansion of the bed becomes independent of the gas velocity.
- Fluidized bed roasting is autogenous so its efficiency is more.

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 and 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

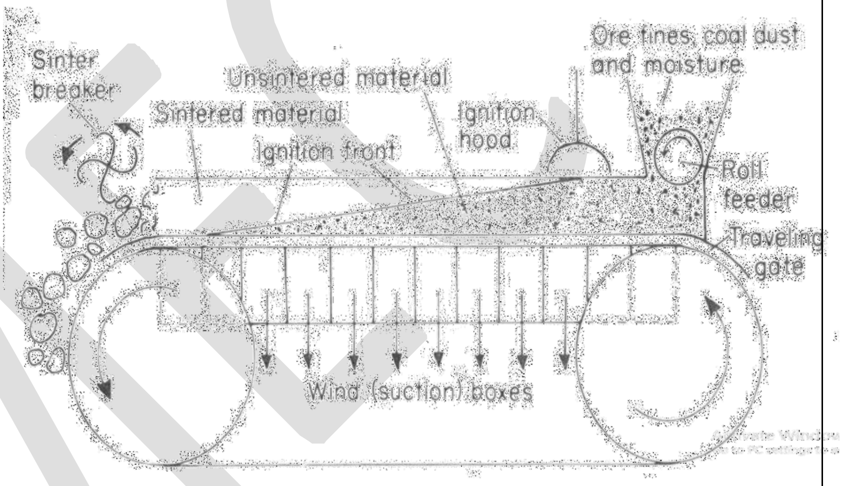
The ignition temperature roughly indicates the temperature required for fluidized bed roasting.

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

SINTER ROASTING (SINTERING):

- Heavy dust loss if agglomeration is not done.
- Permeability reduced it jam the furnace.

Steps in sinter roasting



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

CHAPTER- 3

SMELTING

- Heating process of production of metal or matte**.**
- Reducing agent- C/S/sulphide
- Furnace used- reverberatory furnace, blast furnace, electric arc furnace
- As gangue is less fusible than metal so flux must be added to form slag which is easily fusible.

Mineral + gangue+ reducing agent+ flux = metal/matte + slag + gas

Blast furnace- reduction smelting

Reverberatory furnace- matte smelting

Electric arc furnace- reduction smelting and matte smelting

In matte smelting no reducing agent is used because sulphide itself acts as reducing agent.

FLUXES

REASON OF USING FLUXES:

1. Used to lower the liquidus temperature.
2. Lowers the viscosity of slag (increase the fluidity).

Flux are classified according to their chemical type.

CRITERIA FOR CHOOSING FLUX:

1. Chemical nature of gangue.
2. Properties desired in the slag as density and viscosity.

For acidic slag- basic oxide such as lime is used as flux

For basic slag- acidic oxide such as silica is used as flux

SLAGS:

A solution of molten oxides is called “Slag”. The purpose of slag in metal extraction and refining is to collect all the “gangue” waste products in the form of oxides (or sulphide in small quantities) and eliminate the impurities into a separate phase. Thus refining reactions are often studied in terms of the relevant “metal-slag equilibrium”. The thermodynamics of the refining behavior of a slag phase with respect to a liquid metal is a function of temperature and of the composition of the two phases. Slag plays a very important role in steelmaking to the extent that it is said that “take care of slag and metal will take care of itself”. Slag is a generic name and in steelmaking it is mostly a solution of oxides and sulphides in the molten state and the multicrystalline phases in the solid state.

Slag is a separate phase because:

- It is lighter than molten metal and
- It is immiscible in metal

Slag is formed during refining of hot metal in which Si oxidizes to SiO2, Mn to MnO, Fe to FeO, and P to P2O5, and addition of oxides such as CaO, MgO, iron oxide, and others. The addition of oxides is done to obtain desired physico-chemical properties of slag like melting point, basicity, viscosity etc. All these oxides float on the surface of the molten metal. Synthetic slag is also used to absorb inclusions to produce clean steel for certain applications.

The role of slag:

- It acts as a sink for impurities during refining of metal.
- It controls oxidizing and reducing potential during refining through FeO content. Higher FeO makes the slag oxidizing and lower FeO reducing.
- It prevents passage of nitrogen and hydrogen from atmosphere to the molten steel.
- It absorbs oxide/sulphide inclusions.
- It acts as a thermal barrier to prevent heat transfer from molten steel to the surrounding.
- It protects metal against re-oxidation.
- It emulsifies hot metal and promotes carbon oxidation.
- In electric melting, slag prevents the radiation of heat of arc to the wails of the furnace and roof.

The above functions require that slag should possess certain physical (density, melting point, viscosity) and chemical properties (basicity, oxidation potential). Both physical and chemical properties are controlled by composition and structure of slag. In smelting, slag is predominantly a mixture of oxides with small amounts of sulphides and phosphides. The oxides are either acidic or basic in nature. We will first consider the structure of pure oxides and then we discuss what happens on addition of one type of oxide to the other.

Basic oxides: FeO, MnO, CaO, MgO. Na_2O etc.

Acid oxides: SiO_2, P_2O_5 etc.

$Slag\ Basicity B = \Sigma(wt\%\ All\ Basic\ oxides)\ \Sigma(wt\%\ All\ Acid\ oxides)$

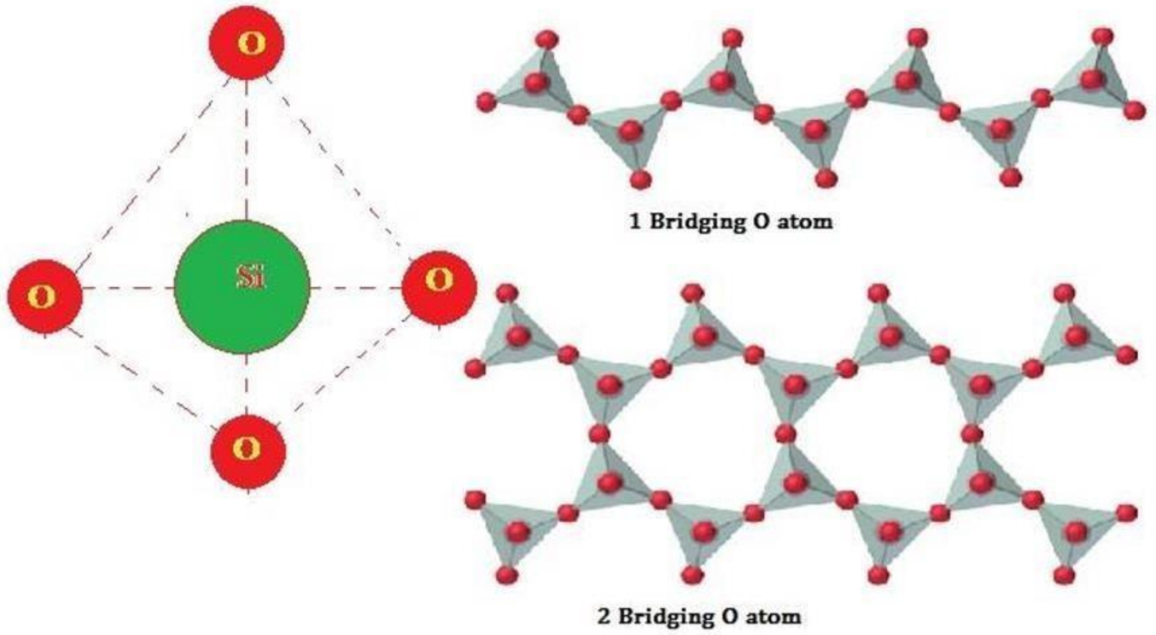
$V\ ratio = wt\%\ CaO /\ wt\%\ SiO_2$

$Modified\ V\ ratio = wt\%\ CaO / [\ (wt\%\ SiO_2) + (wt\% Al_2O_3) + (wt\% P_2O_5)\ ]$

The basic oxides have octahedral and acidic oxides tetrahedral structure.

STRUCTURE OF PURE SILICA

In silica, each atom of silicon is bonded with four oxygen atoms and each atom of oxygen is bonded with two silicon atoms. The elemental tetrahedral of silica are joined at the vertices to give the hexagonal network in three dimensions.



As seen in the figure each tetrahedron is joined at the vertex so as to obtain the three dimensional hexagonal network.

NETWORK FORMER AND BREAKER OXIDES

It must also be understood that the bonding between cations and anions in acidic oxides like $SiO2$ and $P2O5$ is strong, and these simple ions group to form complex ions as $(SiO4)4-$ and $(PO4)3-$. In slags, these tend to form hexagonal network. These oxides are, therefore, called network formers or acids. These acidic oxides can accept one or several oxygen ions.

Basic oxides like CaO, MgO, $Na2O$, FeO dissociate and form simple ions like $Ca2+$ and$O2-$. All basic oxides are donors of oxygen ions. These oxides are called network breakers, since they destroy the hexagonal network of silica by reacting with it.

STRUCTURE OF SLAG

Most slags are silicates. Pure silica has very high viscosity at the melting point. Addition of basic oxides decreases the viscosity by breaking the hexagonal network of silica. Consider the addition of CaO to molten silica. Calcium oxide dissociates to

$CaO = Ca2+ + O2-$

Each mole of CaO introduces one mole of oxygen ions in the hexagonal network of silica and can break two vertices of the hexagonal structure of silica. By adding 2 moles of $O2$-for every mole of silica all the four vertices are broken and we simply have $Ca2+$ and $(SiO4)4-$ as shown below

Note that $Ca2+$ can combine with two tetrahedrons

The reaction between alkaline base oxides, e.g. $Na2O$ and $SiO2$ is as follows:

$Na2O + 2Na+ O2-$ and

Since Na has one charge, each tetrahedron of silica will have Na ion attached to oxygen ion. As a result one should expect more decrease in viscosity of silica on addition of alkaline base oxides as compared with basic oxides.

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. Sometimes 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 minimize 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.
- $PbO + Fe = FeO + Pb$,
- $Pb.SiO_2 + Fe = FeO.SiO_2$

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. It causes by rising the temperature which leads to depolymerization as bonds break at high temperature occurs.

FORMATION OF SLAG

The formation of slag is facilities 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 however some si---o—si bonds ruptures 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 stage 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^- is obtained. On adding further metal oxide free oxygen ions (o2-) becomes available in the melt.

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

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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 :
      MO + C = CO + M
      2MO + C = 2M +CO2
      We observe that temperature required for reduction of oxide by carbon in number of case are beyond practical limit.

SOLID AND GAS REDUCTION

- MO + CO = M + CO2

- $CO_2 + C = 2CO$

COMBINING THESE TWO REACTION

- $MO + C = CO + M$

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 occurs especially when the reduced metal is inform of a vapor as in case of magnesium.
- Back reaction in case of magnesium has to be restricted by shock cooling but resulting powder however is pyrophoric. Some alkali metals form carbides ex-CaC_2.

PROBLEMS AT HIGH TEMPERATURE:

- At high temperature a new stable phase namely the metallic carbides may appears, this occurs when metal react 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 are discoursed if M in the form of alloy.
- The production of ferroalloy also makes uses 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 $Cr_4C(Fe)$.

METALLOTHERMIC REDUCTION OF OXIDE

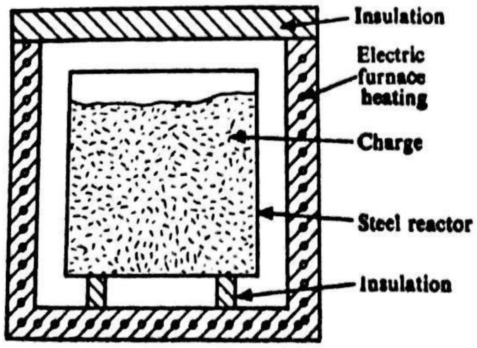


Fig. 4.8 Unit for Metallothermic Reduction.

- 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 avoid 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

$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$

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

$Al2O3$ can be slagged more easily by using another as a flux.

The reduction Of $TiO2$ by calcium

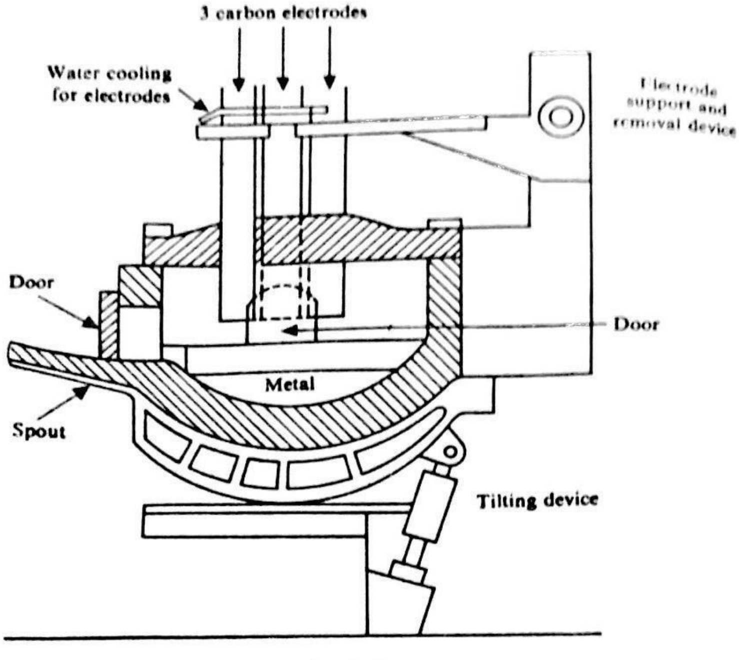
$TiO2 + 2Ca = 2Cao + Ti$

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

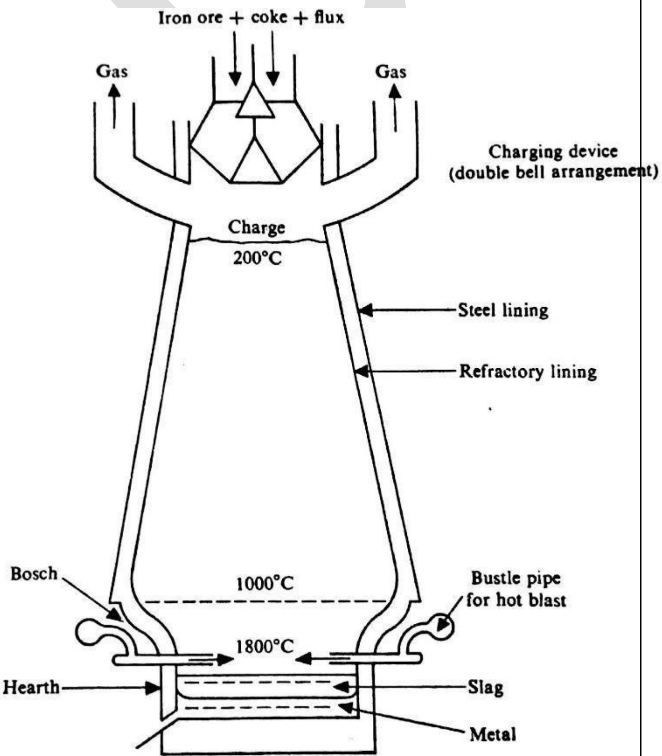
DIFFRENCE BETWEEN CARBOTHERMIC REDUCTION AND METALLO THERMIC REDUCTION

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.

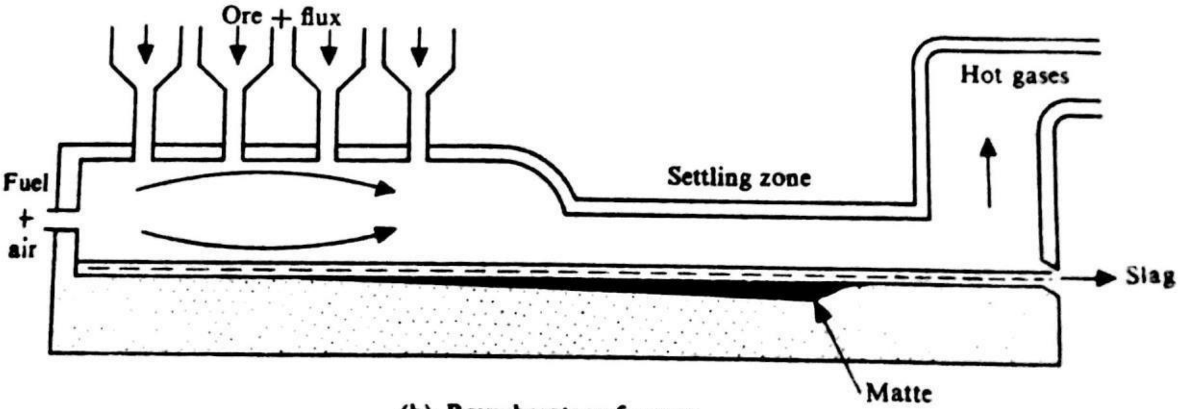
SMELTING FURNACES



(c) Direct arc electric furnace



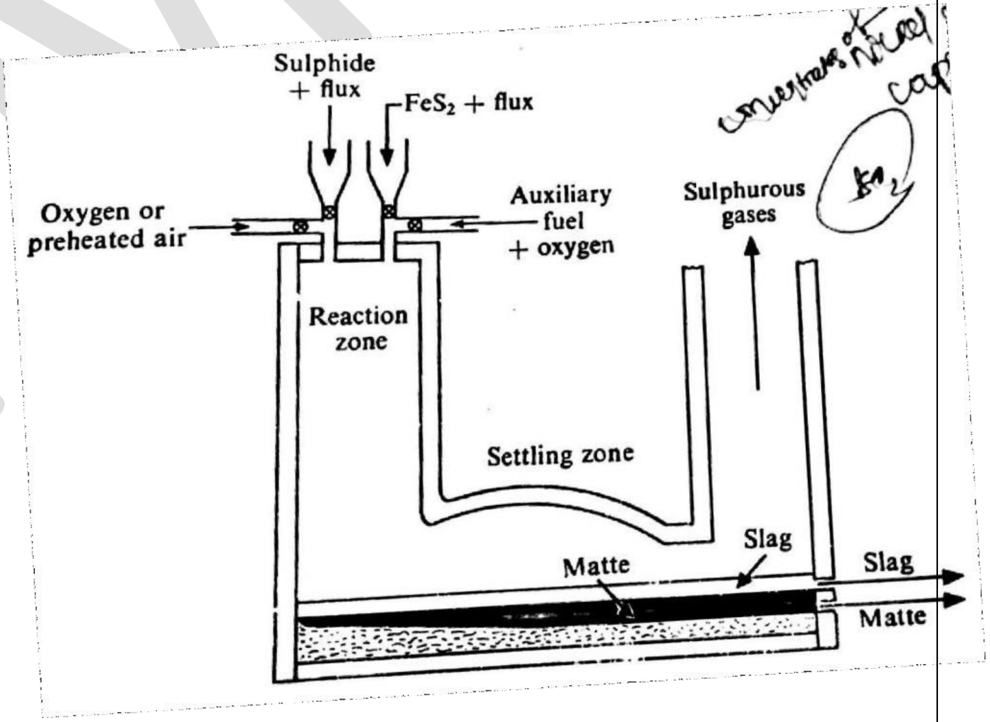
Iron blast furnace



(b) Reverberatory furnace

FLASH SMELTING

- Generally flash smelting is done for the concentrates of nickel sulphide and copper sulphide.
- This process combines the process of flash roasting and smelting.
- The flash smelting roaster consists of a reaction chamber in which flash roasting is carried out and a settling chamber (or smelting chamber) in which the roasted products, which is obtained from the reaction chamber, are smelted in order to separate slag from the metal.



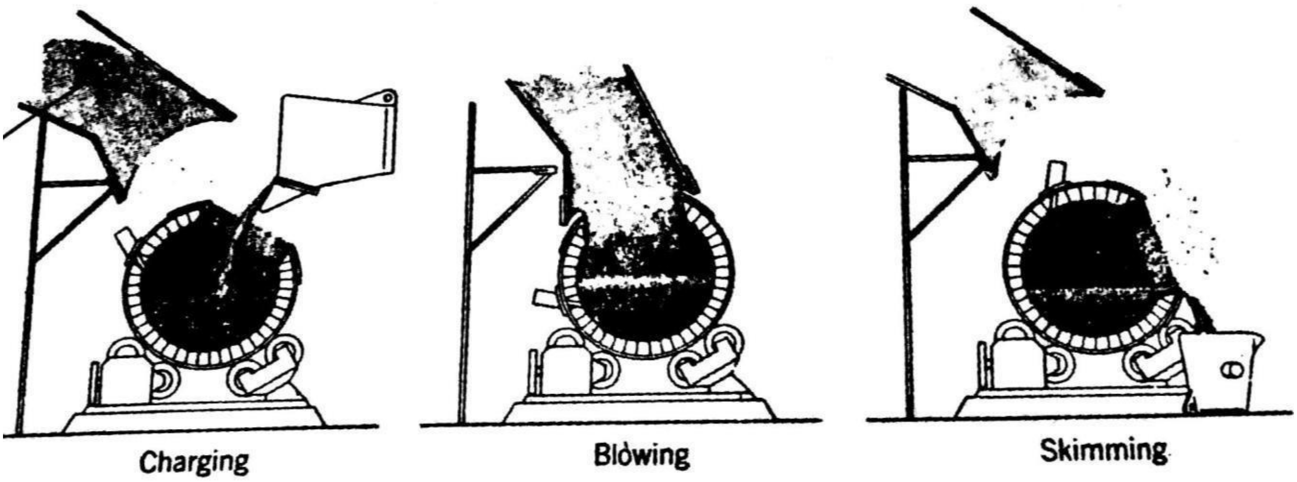
- In this smelting process, enriched preheated air or pure oxygen is usually used instead of air to increase the combustion rate and to maintain autogenous smelting.
- The gases coming out of the furnace is rich in SO_2 or SO_3 which is further used for the manufacturing of sulphuric acid.

MATTE SMELTING

- In matte smelting, the sulphide ore is fused with a flux to produce a molten mixture of sulphides known as a matte.
- The gangue materials pass off into the slag, which is immiscible with the matte, i.e., it forms a separate layer. Some Sulphur is lost in the furnace gases as SO_2 or SO_3. In this sense for a sulphide ore, matte smelting is a thermal concentrating process.
- A matte is a metallic sulphide solution that contains minor amounts of oxygen and, sometimes, some metals too. A matte exhibits a high electrical conductivity comparable with that of a metal and has a density in between the density of the metal and that of the slag.
- Mattes, in general, are insoluble in the metal and slag phases. Thus, in some processes three distinct layers, namely, slag, matte, and metals are produced.
- Matte smelting, which is usually carried out in a reverberatory furnace, follows a roasting operation. Roasting first reduces the sulphide content of an ore in such a manner that subsequent smelting with a suitable flux produces a matte of the required grade. It should be noted that roasting brings about only the partial oxidation mainly of FeS and FeS_2 to FeO, which would pass off into the slag phase.
- Matte smelting is adopted in the extraction of copper, nickel, and, sometimes, antimony. The common ores of these metals contain sulphide minerals including FeS. During roasting, prior to matte smelting, the sulphides of iron are oxidized more easily than those of copper and nickel. The oxidation of say, Cu_2S or Ni_3S_2 can be avoided by controlling the oxidation of the ore so as to produce only FeO and not Fe_2O_3 and Fe_3O_4. This is necessary because the higher oxides of iron do not pass off into the slag easily and are thus difficult to remove. Copper is subsequently recovered from the matte by a process known as '*converting*' in which air is blown through a side-blown converter.

CONVERTING

- The purpose of converting is to remove iron ore, Sulphur and other impurities from matte.
- For the process, the molten matte produced as a result of smelting, is fed into the side blown converter which is a cylindrical vessel with a capacity of 100-200 tons of matte.
- A typical vessel is 4m in diameter and 9m in length and lined with a layer of chrome-magnesite refractory.
- Inside the converter the atmosphere is highly oxidizing.
- Air or oxygen enriched air (up to a maximum limit of 32 vol% oxygen in the blast) is injected into the molten bath through tuyeres.
- The products of converting process are slag and metal.



HYDROGEN REDUCTION

- Generally reduction of ore by hydrogen is an exothermic process so no extra heat is required for the reduction except the ignition temperature.
- As the by-product of this process is water gas so negligible pollution is taking place.
- One of the important hydrogen reduction reaction is reduction of iron ore (Fe_2O_3).
- $3Fe_2O_3 + H_2 \longrightarrow 2Fe_3O_4 + H_2O_{(g)}$

  $Fe_3O_4 + H_2 \longrightarrow 3FeO + H_2O_{(g)}$

  $FeO + H_2 \longrightarrow Fe + H_2O_{(g)}$

In each reaction high heat will be evolved which helps in reduction process.

CHAPTER-4

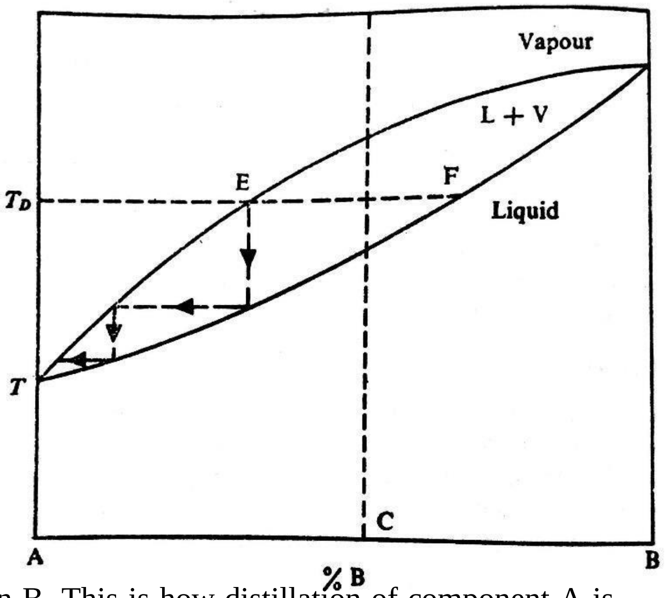
REFINING

DISTILLATION

- It is a process of separation of one component from a liquid mixture according to their difference in boiling point.
- Different methods of distillation are used, depending upon the physical properties of the components in the liquid mixtures.

SIMPLE DISTILLATION

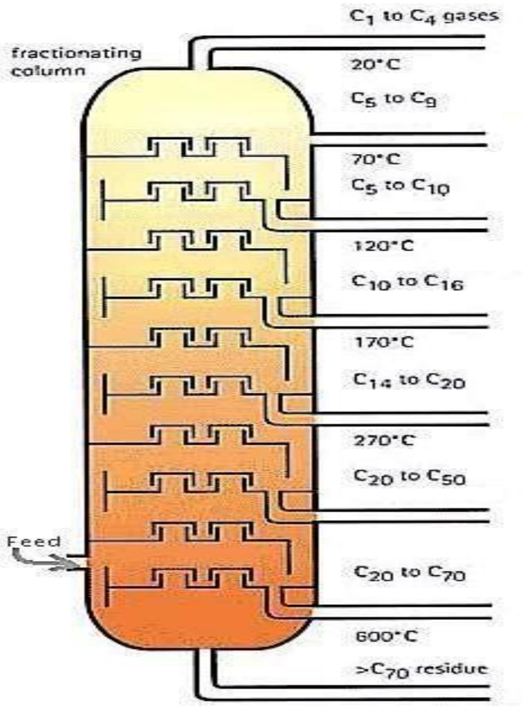
- In this process partial vaporization of liquid mixture occurs with continuous removal of vapour and subsequent condensation of vapour formed.
- Since the vapour above the boiling liquid mixture contains more amount of low boiling point component, so the condensate (distillate) is enriched and unevaporated liquid is lack in them.
- The vapour formed are led off continuously to the condenser where the distillate forms and then drops into a receptable.
- This simple distillation process is a function of time because as time passed, continuous drop of low boiling point component in the liquid mixture and the vapour as well.
- Let us consider an A-B binary phase diagram, in which A has lower boiling point than B. So A is more amenable/prone to distillation. Suppose a liquid having composition C is being distilled at distillation temperature T_D. At this temperature we obtain an equilibrium mix of A rich vapour (composition E) and B rich liquid (composition F). When vapour is removed and condensed, the resulting liquid phase is richer in A than in B. This is how distillation of component A is done.



PROBLEM: - This process suffers from the inherent problem that enhanced purity must necessarily be achieved at the cost of reduced recovery.

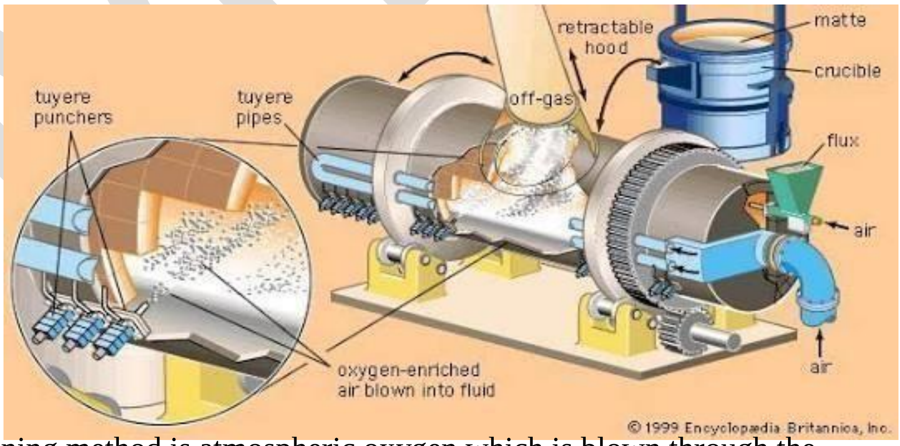
FRACTIONAL DISTILLATION

- This process is based on the principle of intimate countercurrent flow and repetitive liquid vapour contact.
- This process gives high degree of purification and large amount of recovery.
- In this process long column is used in which a large number of trays are there.
- Each tray has a hole at bottom through which vapour/liquid may pass.



FIRE REFINING

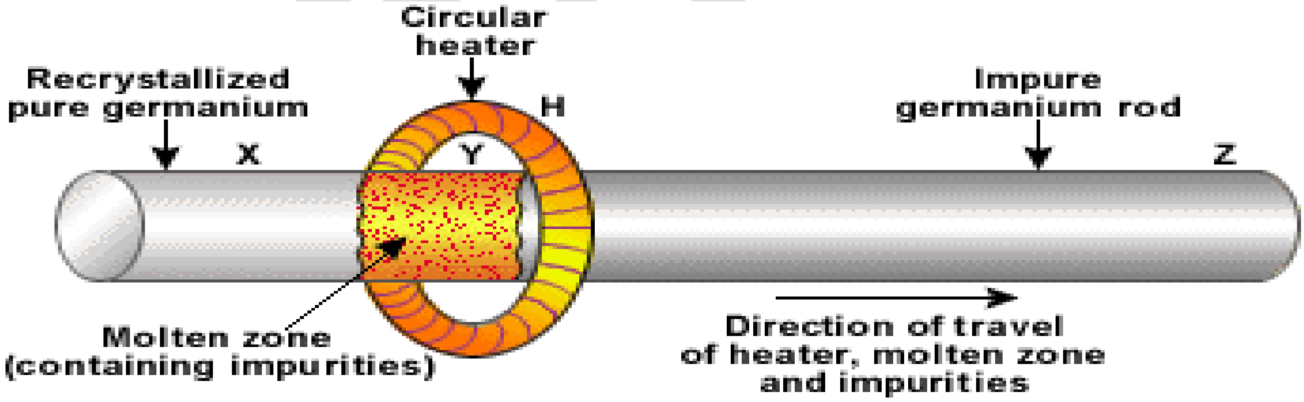
- This technique is used to remove more reactive elements from a molten metal by preferential oxidation.
- This technique is suitable for refining of iron, lead, tin and copper.



- The reagent used for this refining method is atmospheric oxygen which is blown through the metal.
- Flux is added in order to remove impurity oxide but not as solid, but dissolved in a mixture of liquid oxides.
- The oxygen is transferred through gas-metal transfer, through slag layer or through a combination of both.
- In some cases, instead of atmospheric oxygen, oxygen is supplied from a salt such as $NaNO_3$, Which is added to the melt. The nitrate decomposed to give nascent oxygen.

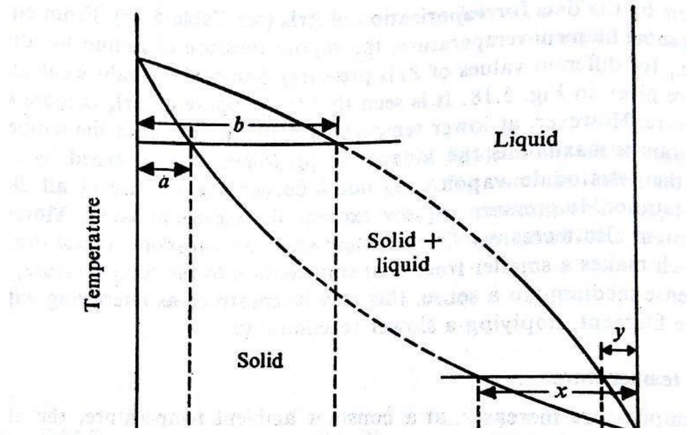
ZONE REFINING

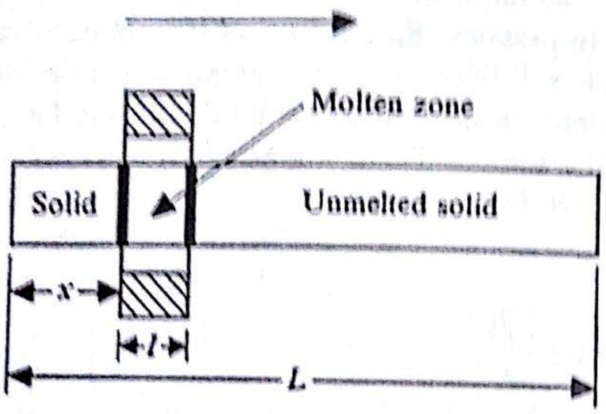
- This method of refining is based on the principle of fractional crystallization. In this technique ultra-refined pure metal is obtained with a restriction that the starting material has low concentration of impurities.
- The impurities have high solubility in the molten metal as compared in the solid metal.
- Generally Silicon (Si), Gallium (Ga), Germanium (Ge) are required in purest metal for their application.
- In zone refining, the impure metal is taken in form of rod, and a travelling melting zone (ring) is set up in the rod.
- A narrow zone near one end of the rod is first melted and then moved slowly to the other end of the rod. This is achieved by the slow movement of the rod or the heating unit.
- As we know that solute atom is more soluble in the liquid state than in the solid state. So when continuous movement of the zone occurs the previous part of that zone will be solidified and the impurity atom will be segregate into the molten zone created by the travelling melting zone.
- When this zone move down continuously the impurity atom also move down and settle at the bottom of the rod.



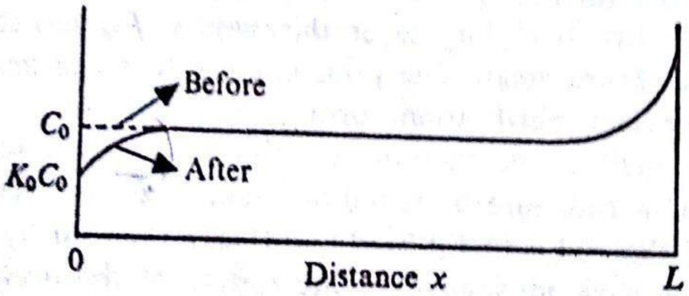
- The zone passage is repeated several times in the same direction. After repeated passages, the impure end is removed, leaving behind a zone-refined pure material.

- Let us consider the zone refining of a rod of element A which contains element B as an impurity having a composition P. Let us take the length of the rod as L and the width of the zone as *l*.
- The distribution of B along the length of the rod after one zone passage is shown in the second figure.
- Before the zone passage, the concentration of B throughout the material is C_0. Assuming that the diffusion in the solid is slow, the first liquid is formed at temperature T with composition P.
- In the zone at left extremity, which solidifies first, the concentration of B changes to K_0C_0 corresponding to Q.
- This concentration increases as the distance from the end increases because the concentration of B in the molten zone gradually increases due to rejection from the solid.
- After a certain distance from the end, a point is reached where the concentration C_0 remains unchanged, showing that the solidified material and the freshly melting material have the same concentration of B.
- At the other end, the concentration of B is increased. After each zone passage, the left extremity of the rod becomes purer, and the impurity accumulates at the right extremity.





(a) Zone refining

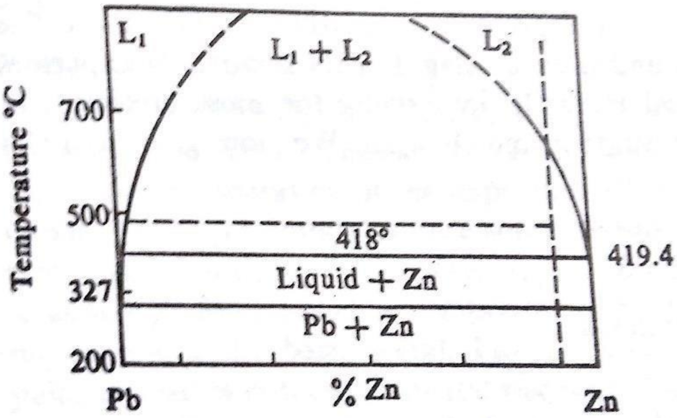


(b) Approximate concentration distribution of B after one zone passage

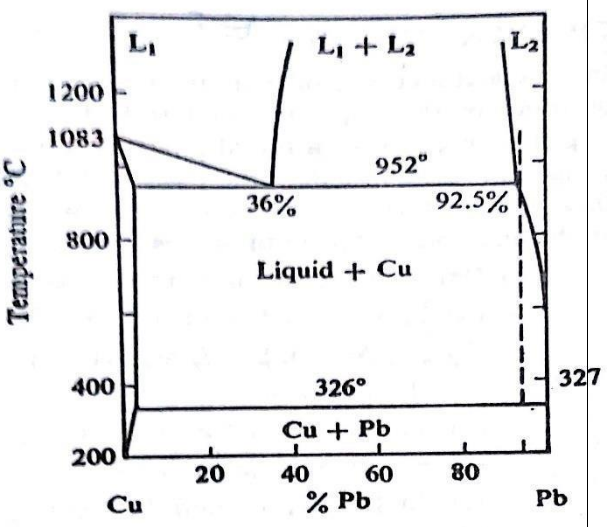
LIQUATION

(Refer pg. 254; extraction of nonferrous metals by h s ray, r Sridhar and k p Abraham)

- Liquation implies the selective melting of a component in an alloy.
- Liquation refining is a technique for removing impurities from metals based on factors such as the difference in the melting points of the alloy components, the immiscibility of phases and the difference in densities of the alloy components which causes the alloy to separate into two or more layers.
- The phenomenon of immiscibility is governed by the phase diagram of the alloy system.
- Crude zinc containing about 5% lead can be refined in a reverberatory furnace by slowly cooling the molten metal i.e., over a period of two to three days.
- Eventually lead separates out and accumulates at the bottom of the furnace. Solid lead dissolves about 0.05% zinc at 318 degree centigrade, whereas the solubility of lead in solid zinc is very small i.e. about 0.001% or less.



- From figure which shows the zinc rich portion of the Pb-Zn system, it is evident that on cooling the molten metal below a certain temperature, it separates into two layers, one rich in zinc and other rich in lead.
- Below 417.8ºC, almost pure solid zinc separates out, leaving behind a lead rich liquid. At 418ºC, the zinc phase contains about 0.5% lead and the lead phase about 2% zinc.
- Although the foregoing process seems theoretically easy, there are some practical limitations. For example it is desirable to have zinc in liquid form.
- This would necessitate temperature of at least 420ºC.At this temperature, however, there would be three phases in the system.



- Because of this problem and other problems, liquation of lead finds little application in the industries.
- Liquation refining of crude lead containing copper is conducted either as an independent or a complementary process. This process can be understood with the help of the figure.
- As lead is cooled down to 370-380ºC, a copper rich scum crystallizes out and floats to the surface.
- This scum is usually a mixture of oxides of copper and lead.
- Theoretically, liquation allows the refining of lead up to 0.06% copper but in practice, it is difficult to proceed beyond 0.1%.

CUPELLATION

- It is a refining process where ore or alloyed metals are treated under high temperature and have controlled operations to separate noble metals or precious metals like gold and silver from base metals like Lead, Copper, Zinc, Arsenic, Antimony or Bismuth present in the ore.
- This process is based on the principle that the precious metals do not oxidize or react chemically, unlike the base metals.
- So when they are heated to high temperature, the precious metals remain apart and others react to form slags or other compounds.

INTRODUCTION TO HYDROMETALLURGY

Hydrometallurgy refers to production of metal or pure compounds with the help of reaction in aqueous and organic solution. It is a process of beneficiation as well as extraction. Hydrometallurgical treatment is generally confined to low grade ore, but it has been used to extract metals from concentrate, matte, species and scrap.

Steps in hydrometallurgical extraction process

1-Prepration 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

In 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.

<u>Rate of leaching depends upon:-</u>

(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 the leaching reaction

(h)-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)-filtrations

(d)-washing

4-Recovery of metallic values from leach liquor

(a)-precipitation

(b)-cementation

(c)-electrolysis

(d)-ion exchange

(e)-solvent extraction

(f)-recycling of leach liquor

The leach liquor is recycled after it has been purified and its composition is re-adjusted.

THREE OBJECTIVES OF TYPICAL HYDROMETALLURGICAL PROCESS:-

1. To produce a pure compound which can later be processed by pyrometallurgy to yield the metal.

2. To produce the metal either the crude or the metal compound which has already been prepared by other method.

3. To produce a metal directly from an ore or concentrate.

ADVANTAGES OF HYDROMETALLURGICAL PROCESS:-

1-Hydrometallurgical methods are ideally suited for lean and complex ores.

2-Hydrometallurgical operation ensures great control than other conventional method over every step in the processing of ore. Resulting in the recovery of valuable by products.

3-It is ecofriendly, it does not create much pollution like pyro metallurgical operation.

4-Process are generally carried out at room temperature or slightly elevated temperature.

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

6- Besides meeting the mounting demand for both the quantity and quality of metals hydrometallurgy can produce metal in a variety of physical form such as powders, nodules, and coherent surface deposit.

DISADVANTAGES:-

1- Handling of large amount of chemicals become difficult and also a large amount of space is required.

2- The cost of the reagent and equipment is high.

3- Corrosion and erosion of tanks and ducts used for strong and handling fluids.

4- In hydrometallurgy, the disposal of effluent without causing pollution posses a serious problem.

CONCENTRATE FOR LEACHING:-

- Leaching is a process which selectively dissolves 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 gangue desirable to leach in case of Thorium.
- To facilitate 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 effects)

- For example-these chemicals help in obtaining an oxidized or reduced state of a metal or a metal compound.
- Example of reagent-Inorganic salts (ferric chlorides) and acidified sodium chlorides can be used.
- All the solvents are water based. In some isolated case, plain water itself can be used as a solvent.
- In most cases, acids or alkalis, in varying degree of concentration are employed.

- Acid is much stronger solvent than alkali. So acidic solution do not required fine grounding of the ore or concentrate but alkali required this.

Examples of reagent are:-

- ✓ Acids (H_2SO_4,HCl)
- ✓ alkalies (NaOH,Na_2CO_3,NH_4OH)
- ✓ oxidising agent ($NaClO_3$, MnO2, $KMnO_4$, FeCl)
- ✓ reducing agent(SO2,H2)

CRITERIA OF SELECTING A LEACHING REAGENT: -

1- Leaching by a reagent must be as selective and as 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 fast rate of leaching.

3- The reagent should not corrode the equipment.

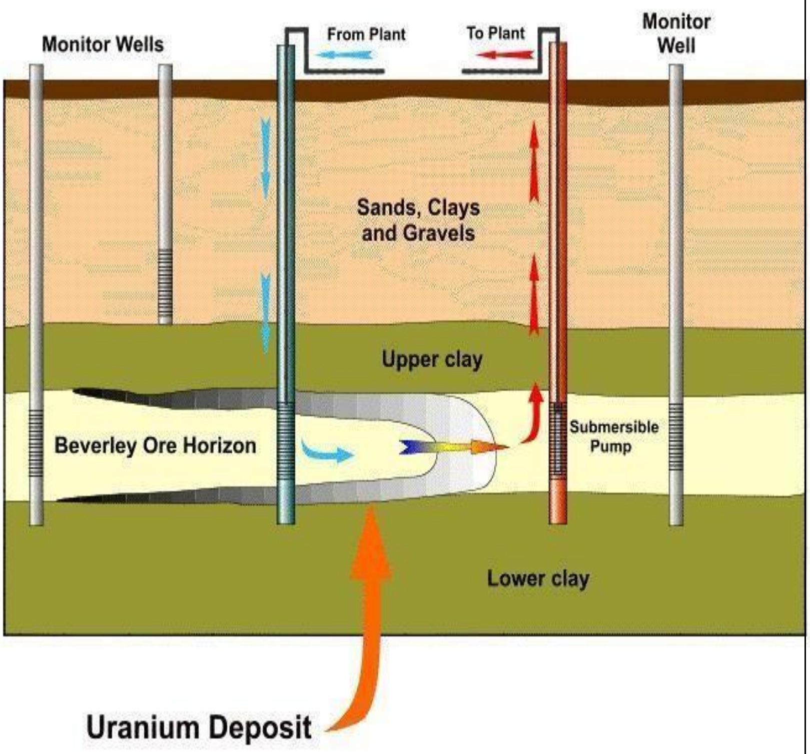
4- The reagent should be economical and should preferably allow regeneration.

LEACHING OPERATION:-

1- In Situ leaching (In Situ Recovery or solution mining):-

- It is a operation in which either the leaching of the shattered rock residues left behind in a mine after the major mining operation have been carried out or the direct leaching of the ore deposited .
- It works by artificially dissolving minerals occurring naturally in a solid state.

- It involves pumping of a lixiviant into the ore body via a bore hole, which circulates through the porous rock dissolving the ore and is extracted via a second bore hole.
- The lixiviant varies according to the ore deposit: For salt deposit the leachate can be fresh water in which salt can readily dissolved. For copper, acids are generally needed to enhance solubility of the ore minerals within the solution. For uranium ore, the lixiviant maybe acid or sodium bicarbonate.



Advantages:-

- Shorter mine development time
- No excavating cost
- Reduces visual and impact of mining operation
- Lower mining and infrastructure cost.

Disadvantages:-

- If ore body is impermeable, it must be cracked by explosions
- Risk of contamination of ground water (compare acid rock generation) because of poor solution controlled.
- Precipitation of secondary minerals might cause permeability problems.

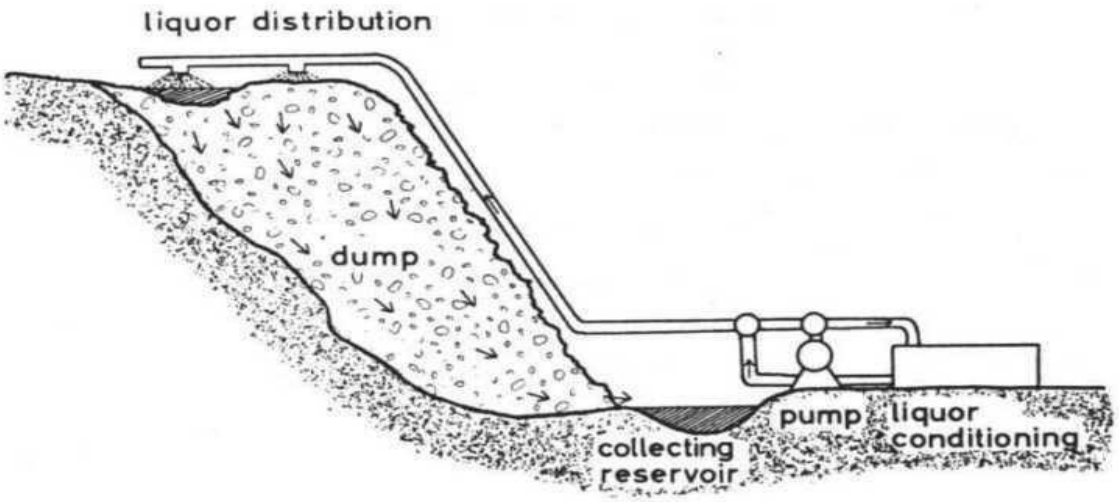
2-**Dump Leaching: -**

- It is the application of the leach solutions to dumps consisting of off-grade ore rejected during the normal mining operation.
- It is similar to heap leaching, however in the case of dump leaching ore is taken directly from the mine and stacked on the leach pad without crushing, where in the case of gold

and silver, the dump is irrigated with a dilute cyanide solution that percolates through the ore to dissolve gold and silver.

- The solution containing gold and silver exists the base of the dump, is collected and precious metal extracted.
- The resultant barren solution is recharged with additional cyanide and returned to the dump.
- This method of leaching is usually suitable for low grade ores because it is very low cost. However, it operates with slow kinetics and make take up about 1 to 2 years to extract 50% of the desired.

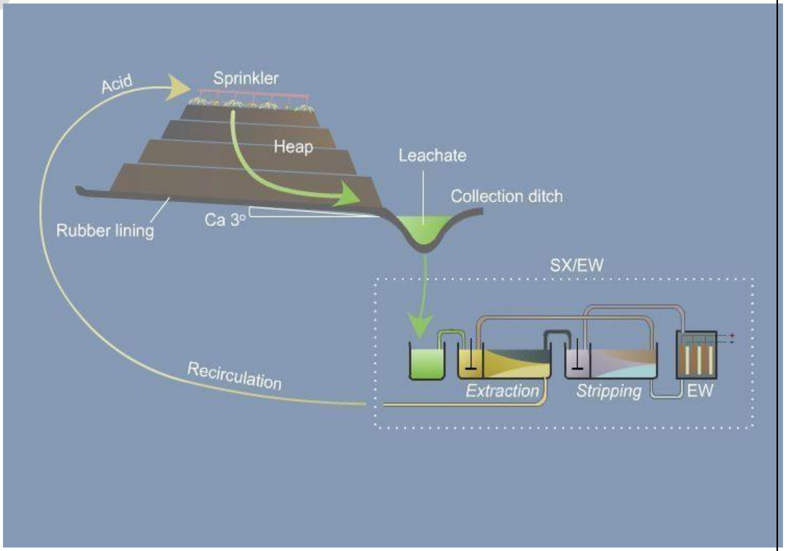
3-



dump ore leaching on a slope

Heap Leaching:-

- It is a technique where run-of-mine crushed(generally>5mm) and agglomerated ores are stacked over an engineered impermeable pad, wetted with lixiviant(solvent)chemicals under atmospheric condition and leachate(metal loaded solution)are collected for metal recovery processes. The mined ore is generally crushed into small chunks and heaped on an impermeable plastic

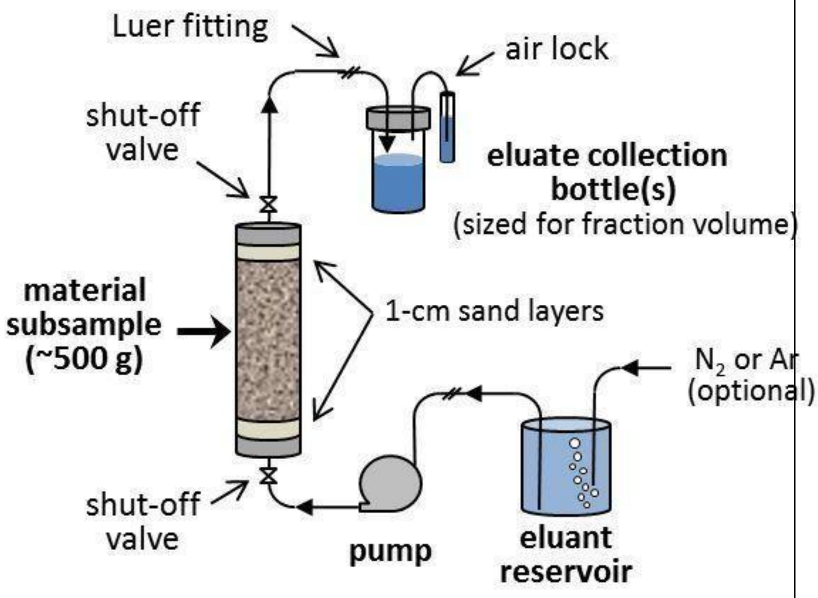


and/or clay lined leach pad where it can be irrigated with leach solution to dissolve the valuable metal.

- While sprinklers are occasionally used for irrigation, more often operation use drips [irrigation to minimize irrigation, provide more uniform distribution of leach solution and avoiding damaging the exposed mineral.
- The solution then percolates through the heap and leaches both the target and other minerals. This process, called the **LEACH CYCLE**, generally takes from one or two months for simple oxide ore (e.g. most gold ores) to two years.
- The leach solution containing the dissolved mineral is then collected, treated in a process called to recover the target minerals and then recycle to the heap after reagent levels are adjusted.
- Ultimate recovery of the target minerals can range from 30% of contained to over 90% for the easiest to leach ores.

4- <u>Percolation Leaching:-</u>

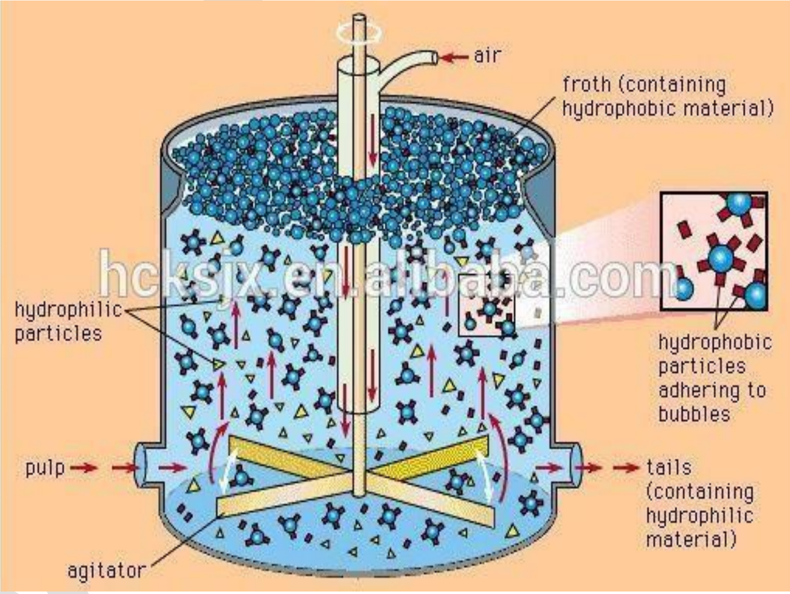
- It is a selective removal of the metal values from a mineral by causing a suitable solvent or leaching agent to seep into and through a mass or pile of material containing the desired material.
- In this process, the leach solution is percolated upward or downward through an ore which has already been crushed and bedded into tanks.
- Usually, a mixture of coarse and fine ores is used so as to ensure permeability.
- By subjecting the ore to 10 or more leach cycle, 80 to 90% of the metal values are recovered.
- Percolation leaching has certain advantage because it is operated in batches. For example, since each batch is separated or distinct, operational flexibility is greater and accidental break down are not that serious.



- A percolation leaching circuit is more versatile and can be employed in the case of ore where the leading rate is very slow.

5- Agitation Leaching:-

- It is a process where the soil slurred with the extraction fluid for a period of time.
- When equilibrium between the metal on the soil surface and the metal contained by the solution is approached, the solubility of the metal in the soil is slowed, and the extraction is said to be complete.
- At equilibrium, additional metal will not be extracted from the soil’s surface unless the soil is subjected to fresh extraction solution.
- Once the process is said to be at equilibrium, the soil is separated from the extraction fluid using sedimentation, thickening or clarification.



- The extraction process may be continued in a separate extraction vat with clean extraction solution to enhance extraction.
- An agitation vat coupled with a solid-liquid separation vessel (sedimentation or clarification) is considered to be a single stage.

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. Sometime, only some constituent of the mineral may dissolve.

Slime leaching:-

Sometimes pyro metallurgical treatment yield salts, for example- chloridizing roasting and sulphating roasting that can be easily leached with water.

Ex-$CuSO_4 + nH_2O = CuSO_4.nH_2O$

Acid leaching:-

$ZnO + H_2SO_4 = ZnSO_4 + H_2O$

$ZnO + 2H = Zn + H_2O$

Alkali digestion:-

$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$

$Al_2O_3 + 2OH = 2AlO_2 + H_2O$

Leaching with oxidation:-

$CuS + 2Fe^{3+} = Cu^{-} + Fe + S$ (oxidation)

Leaching with reduction:-

$MnO_2 + SO_2 = Mn^{2+} + SO^{4-}$

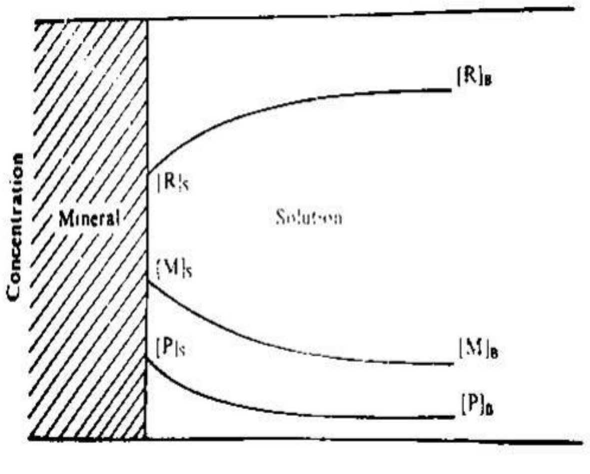
KINETICS OF LEACHING

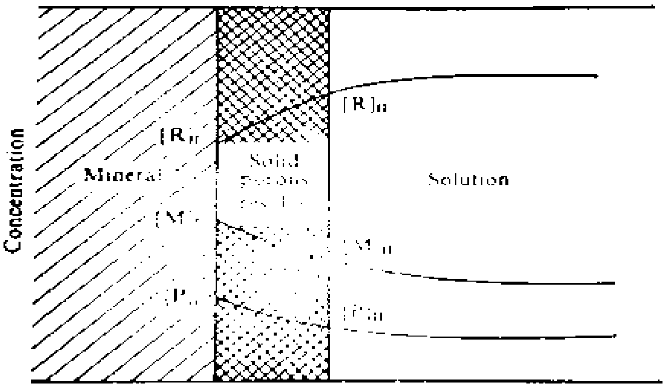
Figure shown below is the concentration profile when a mineral surface dissolves in a leaching medium. Subscript S refers to surface or interface whereas Subscript B refers to bulk.

From the diagram it is noted that;

1. The diffusion from the reagent are from bulk of the solution to the solid surface.
2. The diffusion of the reagent is with the mineral surface.

The diffusion of the product metal(M) or other products(P) from the surface to the bulk.





The above figure explains the detailed dissolution steps. The situation is simple for complete dissolution. However, when the mineral decomposes and dissolves only partially, then a new solid residue appears. Leaching would continue if the new phase is porous. In this figure 4.13, the subscript 1 refers to the mineral residue whereas Subscript 2 refers to the residue solution interfaces respectively. The kinetic step that determines the rate of leaching could be one or a combination of the following:-

1. The diffusion of reagent are from the bulk of the solution to the solid surface 2(S2).
2. The diffusion of the reagent are through the porous layer.
3. The reaction of the reagent are with the solid surface 1(S1).
4. The diffusion of the product metal species (M) or other reaction products (P) through the porous layer is in the outward direction.
5. The diffusion of the metal species (M) or other products (P) from solid surface 2 to the bulk.

- ✓ When there is no porous layer, then step 2 and step 4 will not occur.
- ✓ The techniques required for speeding up the leaching reaction mainly depends upon rate determining steps and surface area exposed to the leaching action.
- ✓ Larger the surface area, faster is the leaching process.
- ✓ Increase in temperature, increases the rate of the leaching process.
- ✓ For e.g.:- If diffusion step 1&5 is rate controlling then leaching can be speeded up by stirring the aqueous medium. However, if the chemical reaction step 3 is rate controlling then agitation would have no effect.

Bioleaching/Microbial leaching

Microbial ore leaching is the process of extracting metals from ores with the use of microorganisms. This method is used to recover many different precious metals like copper, lead, zinc, gold, silver and nickel

3. Bioleaching is cheaper than chemical extraction, safer for the environment, and more efficient in extracting metals with low concentration in ores.

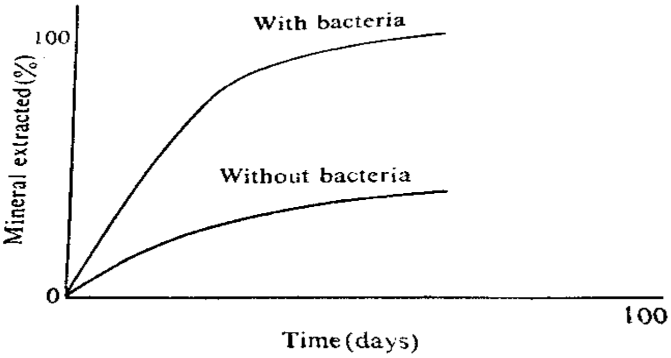
Microorganisms are used because

6. Lower the production costs.
7. Cause less environmental pollution in comparison to the traditional leaching method.
8. Very efficiently extract metals when their concentration in the ore is less.

There are three most important types of bacteria used

- Thiobacillus thiooxidans
- Thiobacillus ferrooxidans
- Ferrobacillus ferrooxidans

These bacterias have capable growing in purely inorganic media, obtaining their energy by oxidizing inorganic substances such as sulphur and thiosulphate to sulphate and Ferrous iron to ferric ion. A biological catalyst, called enzyme, is synthesized by the bacteria and helps in accelerating the rate of oxidation reaction.



Oxidation of sulphide minerals

$S + {}^{3}/{}^{2}O_2 + H_2O = H_2SO_4$

$CuS + 2O_2 = Cu^{2+} + (SO_4)^{2-}$

Iron oxidation

$2Fe^{2} = 2Fe^{3+} + 2e$

$2H^+ + \frac{1}{2}O_2 + 2e = H_2O$

Process

As a general principle, Fe^{3+} ions are used to oxidize the ore . This step is entirely independent of microbes .

The role of the bacteria is the further oxidation of the ore , but also the regeneration of the chemical oxidation of Fe^{3+} fromFe^{2+} .

For ex : bacteria catalyst the breakdown of the mineral pyrite (FeS2) by oxidizing the sulphur and metal (in this case Ferrous iron (Fe^{2+})) using oxygen .

Some important information

It should noted that iron sulphide is a common impurity in many sulphide minerals . During leaching , ferric ions acts as a good oxidant and attacks the metal sulphide as shown by the reaction

$$MS + 2Fe^{3+} = M^{2+} + S + 2\,Fe^{2+}$$

Since iron is found in most leach solution , in practise , both the direct and indirect mechanisms operate simultaneously ; their relative importance being largely dependent on both the type of mineral being Leached and the type of bacteria being employed . Thus , Thiobacillus ferrooxidans oxidize Ferrous ion , Thiobacillus thiooxidans do not .

Factors affecting Bio leaching

- *Effect of temperature*- The temperature range for Bio leaching should be 32 degree Celsius to 35 degree Celsius .Above this temperature I.e. above 50 degree Celsius , the activity almost stops, and at a temperature higher than 70 degree Celsius the bacterial microorganisms becomes destroyed .As the temperature decreases ,I.e. ,below 30 degree Celsius , the activity also decreases , and , at a temperature below 18 degree Celsius , it is not commercial feasible .
- *Effect of Nutrients*- The additional of bacterial nutrients such as $FeSO_4$, FeS_2, $(NH_4)_2SO_4$, and $Fe_2(SO_4)_3$ to the leaching solution increases the concentration of Ferrous ion present in it , due to which bacteria becomes more active .
- *Effect of radiation*- If the bacterias are expose to direct sun light , the activity of bacteria is decreases but not destroy. But when expose to UV ray the bacterias are destroy.
- *Effect of particles size and bed depth-* Fine particles have large surface area and expose to more oxidation. That's why the leaching process accelerate by using fine particles. But very fine particles reduces the permeability of solution, due to which oxygen can't

pass into the solution .So the leaching process is inhibits. Shallow bed is good for the leaching process

- *Effect of acidity and aeration*- Oxidizing bacteria active only in acid media .Generally the bacterias are active in the pH limit between 2- 3.5 . Oxygen is supply in the leaching reaction by aerating a Portion of the bacterial solution and subsequently transferring the aerated solution to the site of bacterial activity

CYANIDATION OF GOLD AND SILVER

Cyanidation:-

4. Cyanidation is a process in which gold and silver are leached by a cyanide solution.

5. The commonly used cyanides are *sodium cyanide*, *potassium cyanide, calcium cyanide.*

- Let us consider the dissolution of gold by *NaCN* is represented by the overall reaction:-

$$\begin{array}{l} 2Au+4NaCN+2H_2O+O_2=2NaAu(CN)_2+2NaOH+H_2O_2 \\ 2Au+4NaCN+H_2O_2=2NaAu(CN)_2+2NaOH \\ \hline \\ 4Au+8NaCN+O_2+2H_2O = 4NaAu(CN)_2+4NaOH \end{array}$$

- The cyanidation of silver can also be expressed as similar to cyanidation of gold.
- A cyanidation reaction can be considered to be a combination of

two steps :- oxidation step, reduction step

- The oxidation step is $\mathbf{Au+2CN^- -=Au(CN)_2^-+2e}$
- The reduction step may be written according to any one of the steps $\mathbf{O_2+2H_2O+4e=4OH^-}$

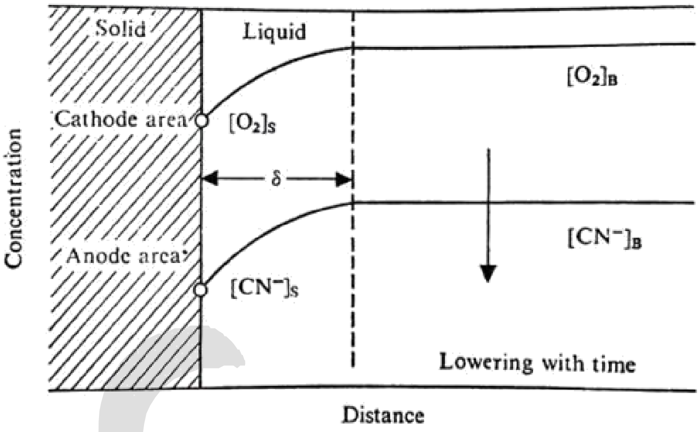
$\mathbf{O_2+2H_2O+2e=H_2O_2+2OH^-}$

$\mathbf{H_2O_2+2e=2OH^-}$

- The surface being leached is divided into 2 areas:-

(i) Anode

(ii) Cathode



- The areas are represented by A1 and A2. Let us assume that a boundary layer thickness at the anode and cathode is delta.

It is assumed that the kinetics of the above reactions are basically determined by the diffusion of both the dissolved O2 and the CN^-ion and not by the chemical reactions at the surface.

Fick's 1st law of diffusion:-

$$dn/dt = -DA\ dc/dx]$$

Where, **dn/dt =** Moles of diffusing species

D = diffusion constant

Dc/dx = concentration gradient

- So the appropriate equation for the diffusion of oxygen from the bulk to the cathode area is

$$d[O_2]/dt = D_{O2}\,A_1\{[O_2]_B - [O_2]_S\}/\delta$$

Where $[O_2]_S$ =concentration of O_2 at the interface.

$[O_2]_B$ = concentration of O_2 in bulk medium.

- So diffusion of CN^- will be

$$d[CN^-]/dt = D_{CN-}\,A_2\{[CN^-]_B - [CN^-]_S\}/\delta$$

Where, $[CN^-]_S$= concentration of CN^- at the interface.

$[CN^-]_B$= concentration of CN^- at the bulk medium.

- Assuming that the surface reaction proceeds very fast so the concentration can be taken as the equilibrium value. As these values must necessarily be very low,**$[O_2]_s$** and **$[CN^-]_s$** can be eliminated from the diffusion reactions.

- Molar rate of dissolution of the metal (R):-

= 2× molar rate of dissolution of oxygen

= ½× molar rate of consumption of cyanide

Hence,

$$R = 2D_{O_2} A_1 [O_2]_B / \delta,$$

i.e,

$$A_1 = R\,.\delta / 2D_{O_2} [O_2]_B$$

Similarly,

$$A_2 = 2R \times \delta / D_{CN^-}[CN^-]_B$$

The total area **A** is given by equation 1 :-

$$A = (A_1 + A_2) = \frac{R\delta\{D_{CN^-}[CN^-]_B + 4D_{O_2}[O_2]_B\}}{2D_{O_2}[O_2]_B D_{CN^-}[CN^-]_B}.$$

From the above equation, we make the following Observations:-

1. If $[CN^-]_B$ is small as compared with $[O_2]_B$, then the equation reduces to

$$R = AD_{CN^-}[CN^-]_B / 2\times\delta$$

This implies that oxygen should have no role to play when $[CN^-]_B$ is too low compared with $[O_2]_B$.

2. If $[CN^-]_B$ is high and $[O_2]_B$ is negligible as compared with $[CN^-]_B$ then the equation reduces to

$$\mathbf{R=2A\ D_{O2}\ [O_2]_B\ /\delta}$$

This implies that when the cyanide concentration is high, oxygen plays an important role in cyanidation kinetics. In this case, the diffusion of CN^- is already fast because of the high concentration gradient of CN^-. Therefore the rate determining factor should be the rate of oxygen diffusion.

3. In intermediate ranges of $[CN^-]_B$ concentration, both $[O_2]_B$ and $[CN^-]_B$ influence cyanidation kinetics, as expressed by equation

(1). When

$\mathbf{D_{CN-}\ [CN^-]_B = 4\ D_{O2}\ [O2]B,}$ Then

$$R = \sqrt{D_{O_2} D_{CN^-}} A[O_2]_B^{1/2}[CN^-]_B^{1/2}/(2\delta).$$

Recovery of metal from leach liquor

1. Solvent extraction

2. Ion exchange

3. Precipitation

4. Cementation.

SOLVENT EXTRACTION

Solvent extraction or liquid- liquid extraction is the separation of one or more components from a liq. by preferential dissolution in an extractive solvent. This method is employed for separate. This method is employed for separate tantalum from niobium and zirconium from hafnium. Vanadium from iridium and cobalt from nickel.

Steps for solvent extraction

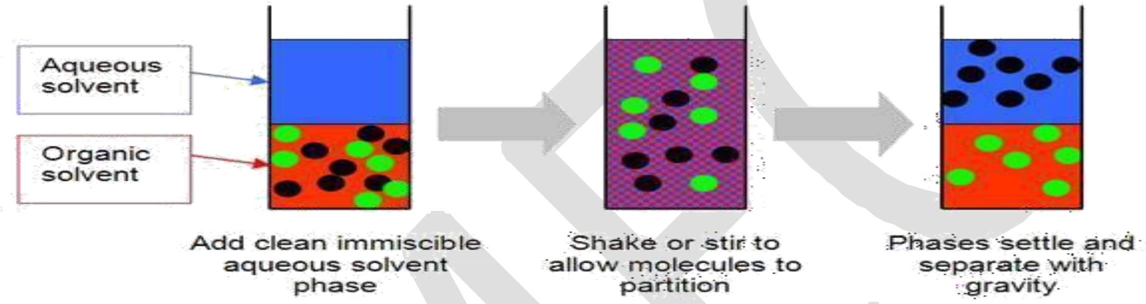
1. **Dissolution**-ion dissolution the impure compound or the ore is dissolved into a alkaline or acid aqueous solution.

2. **Extraction and decontamination**- in this process the extractant usually organic solution is brought into contact with the aqueous solution containing the desired metal ion as well as impurities.

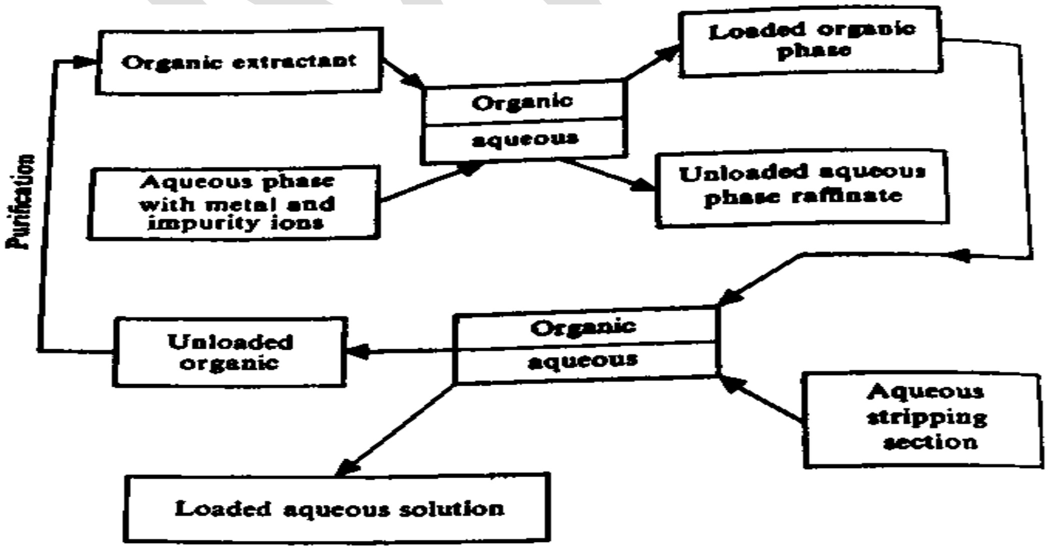
The metal ions enters into the organic solution.

3. **partition**-in this step the organic and aqueous layer are separated by using suitable techniques.

4. **stripping**-in this step the loaded solvent containing the product is introduced into another extracting unit where metallic values are removed by contacting another aqueous phase.



5. **Auxiliary process**-a no of auxiliary process i.e. solvent purification and recirculation are generally used in this solvent extraction process.



Extraction of coefficient

The ratio of concentration of a solute in two phase at equilibrium is called extraction co-efficient E(o/a)=y/x

y= concentration of solute in the organic phase.

x=concentration of solute in the aqueous phase.

1. If equilibrium is established b/w the organic phage and the aqueous phase w.r.t metal ions the chemical potential and the activity of the metal ions ion the complex dissolved in the organic solvent is much lower than the aqueous solution due to which the e(o/a) coefficient is high.
2. The extraction coefficient sometimes independent of concentration of the phases then case the volume of the two phases is more meaningful.so

   E_f= L/H.(y/x)=L/H .E(o/a)

   E_f = Extraction factor

   l=volume of light organic phase

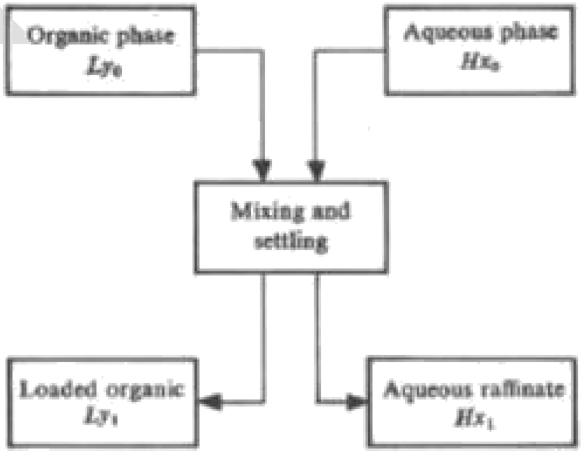
   h=volume of heavy aqueous phase

   If the value of E_f is high then the separation of organic phase from the aqueous phase. E_f value can be increased by increasing the value of E(o/a) since the organic extractant are more expensive so that volume are kept minimum.

PROCESSES

SINGLE STAGE CONTACTING

Here a given volume of the solvent is thoroughly mixed with aqueous feed and then the liquids are separated.



Single stage solvent extraction process

Let L be the volume of the light organic phase, H be the volume of the heavy organic phase.

X_1 is the concentration of the solute in the aqueous phase and y1is the concentration of the solute in the organic phase. Ly_0 and Hx_0 give the total weight of the solute in organic phase and the aqueous phase respectively.

If the initial concentration of the solute in the organic phase is zero, then the material balance across the extraction step gives

$Hx_0 = Hx_1 + Ly_1$

Also we know that

$E_f = L/HE_{(o/a)} = L/H\ (y_1/x_1)$

Hence $x_0/x_1 = 1 + L/H\ (y_1/x_1) = 1 + E_f$

$x_0/x_1 = 1/\ (1 + E_f)$

the contacting step is effectively carried out by agitating the two phases together in a vessel so that one phase is finely dispersed in the other. And when agitation has been stopped one phase is allowed to separate from the other.

It results in high efficiency only if E_f is high.

MULTISTAGE COCURRENT CONTACTING

The single stage contacting can be repeated several times by contacting the raffinate left over with successive batches of fresh solvent. This leads to improved recover of metallic value.if the quantities of solvent used during each contacting are equal in volume then the overall change in concentration of the raffinate after n contacts is

$x_0/x_n = 1/\ (1 + E_f)^n$

Efficiency of multistage operation is greater than that of single stage operation. The recovery is the highest when n is large and the indivisual volumes of the solvent in each stage are small i.e. small volume of solvent are used for extracting a large number of fines.

COUNTERCURRENT EXCHANGE

Concurrent arrangement effectively removes the moisture from the slurry only in the initial stages where the difference in the moisture content in the slurry and the air is high. But in counter current arrangement maintain a uniform driving force for moisture removal over the entire period.

CONTINEOUS COUNTER CURRENT EXTRACTION

It has distinct sections for extraction and stripping. It allows the initial loading of the solvent and then a multistage wash by a suitable aqueous phase which blends with the main aqueous feed. The flow rate of the aqueous stripping solution is adjusted so that it strips the impurities but not the principal solute.

ION EXCHANGE-

1. When a solution of ammonium sulphate is percolated through a layer of soil then the resulting efficient is found to contain calcium ion no ammonium ions.

2. This is because of exchange ions between the solution and the soil.

3. In ion exchange method which can be used in the preparation of pure compound the solid phage is made initially absorbed a suitable ion of desired metal through an ion exchange reaction.
4. The absorbed ion is subsequently taken into solution by once again applying ion exchange reaction tis is called ellution.
5. This solid phase generally a synthetic resin. This resin is a complex organic acids or bases which is insoluble in water.

Cation exchange resin

This structure can be written as Rx. When R=polymer, X=ion exchange side or exchangeable ion. If X is a sulphonic group (SO_3H) THEN (H) in the sulphonic group is replaced by the cation .when the cation exchange resin (RSO_3H) reacts with the leaching solution containing suitable cation .

Anion Exchange resin:-

The formula for this type of resin can be RNO_3 or RCl.

-When ion exchange resin reacts with the leaching solution containing suitable anion the NO3 or Cl group is replaced by the anion.

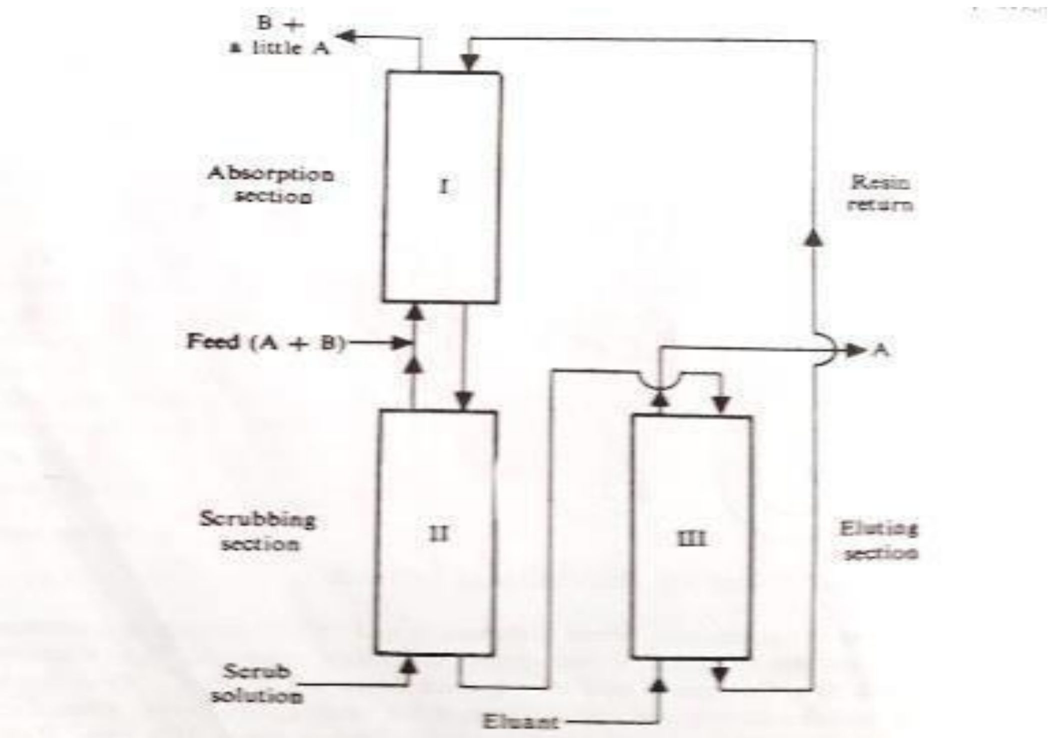
-The degree of extends of ion exchange depends on following factors.

(1) Size and valence of the ion taking part in exchange reaction.
(2)Concentration of ion in the solution.
(3)Physical, chemical characteristic of the ion exchange reaction.
(4)Temperature

Ion exchange kinetics:-

The various steps in this process are:-

(1) The transport of an ion from the solution across a boundary surrounding the region which is in the form of bead.
(2) Diffusion of ion in the inter ion of the region
(3) The main chemical exchange reaction
(4) Diffusion of the outgoing ion to the surface of the resin bead.
(5) Diffusion of the outing ion across the boundary.



Three column continuous counter-current ion exchange

In industries operation, ion exchange plants differ widely in term factor such as the arrangement of columns, the flow of resin and the sequence of operations. Above figure shows a three-column continuous counter current arrangement suitable for separating two components, namely A and B of which A is more selectively absorbed. In this fig the resin passes down column I and then into column II, while the two aqueous solutions are pushed upward. The main feed solution enters at the base of column I and meets the scrub solution coming up through column II. The flow rates of the feed solution and the scrub solution are adjusted so that the resin leaving the base of column II contains virtually only species A. This resin is eluted in column III by a counter current flow of the eluent. The product A is thus transferred to the resin is passed back to column I for reuse.

PRECIPATION:

Precipitation is the hydrometallurgy involves chemical precipitation of either metals and their compounds or the contaminants from the aqueous solution. Precipitation will proceed when any given spaces exceeds its solubility limit through addition of reagent, temperature manipulation, PH change or evaporation or each of these factors influences the cost and the type of treatment.

In theory precipitation process has two steps i.e. nucleation and particle growth.

Nucleation is represented by the appearance of very small particle which are generally composed of 10 to 100 molecules.

Particle growth involves the addition of more atoms and molecules into this particle structure. The rate and extent of this process is dependent upon the temperature and chemical characteristics of leach liquor such as concentration of metal initially present and other ionic species present which can compete with the target metal species or form soluble complexes.

CONTACT REDUCTION (cementation)

In cementation a more active metal dissolves in a solution to precipitate less active metal from the solution.

For example, Aluminum or zinc can be added to a gold cyanide solution to precipitate the gold. In this case Aluminum or zinc are the more active metal as compared with the gold. Due to which Aluminum or zinc replaces the gold from the gold cyanide solution, as a result gold will be precipitated out and can be removed later.

For example, in precipitation of copper from $CuSO_4$ solution by iron, since the oxidation potential of iron (Fe$-$ Fe^{2+}) is 0.44 volts while that of copper (Cu-Cu^{2+}) is -0.344 volts, iron would normally be expected to reduce Cu^{2+} according to the overall equation:

Fe + $CuSO_4 = FeSO_4$ + Cu

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 proceeds, the $FeSO_4$ concentration builds up and the $CuSO_4$ in the solution gets depleted. Accordingly the Fe/Fe^{2+} potential gradually decreases from an initial high value and the Cu/Cu^{2+} potential increases from an initial low value. After a certain period, the two potentials become equal, and the reaction attains equilibrium.

$$Fe \xrightarrow[\text{anodic reaction}]{} Fe^{2+} + 2e$$

$$Cu^{2+} + 2e \xrightarrow[\text{cathodic reaction}]{} Cu$$

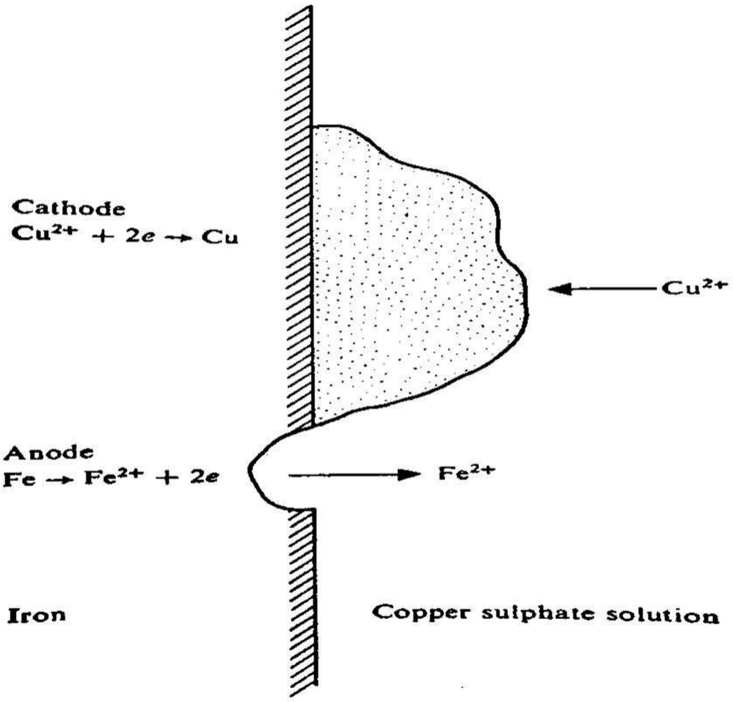
In this iron dissolves at the anode, and each copper ion picks up electrons at the cathode to deposit metallic copper.

The general reaction for the reduction of a metal ion M_1^{Z1+} *by a metal* M_2 *to form* M_2^{Z2+} *ions is written as*:- $M_1^{Z1} + \frac{Z1}{Z_2} M_2 = M_1 + \frac{Z1}{Z_2} M_2^{Z2+}$.

The appropriate equation for the electrode potentials of metals $M_1$and M_2,respectively, are: $E_1 = E_1^0 + \frac{RT}{Z_1F} \ln C_1$,

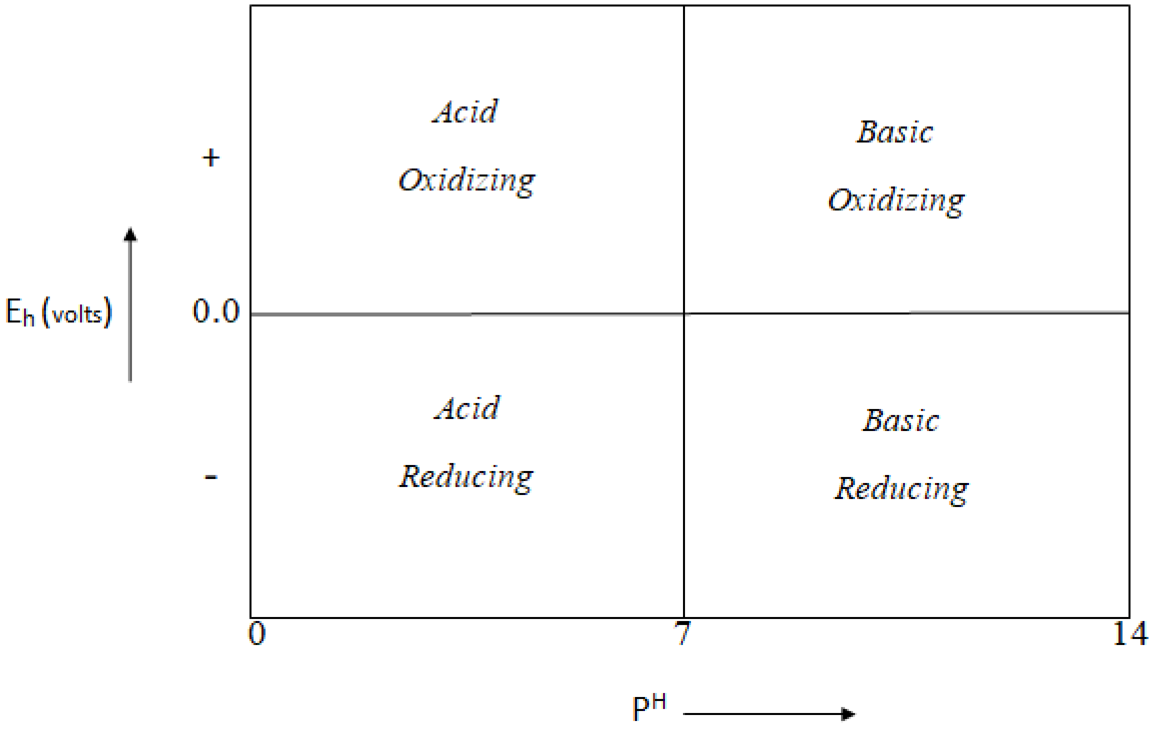
$$E_2 = E_2^0 + \frac{RT}{Z_2F} \ln {}_2 ,$$

Where F is the Faraday constant, E_1^0 andE_2^0 are, respectively, the standard potentials of M_1 $andM_2$. Due to the continuous flow of anode area to the cathode area, this system has a unique electrode potential E-known as the ‘compromise potential’- which is less than the equilibrium potential E_1 of the cathode greater than the equilibrium potential E_2 of the anode. If the slow discharge is controlled by diffusion or reaction at cathode, that is, by a cathodic process, the anode reaction will essentially be at equilibrium. In such a situation, the compromise potential will be equal to the anode equilibrium potentialE_2. This situation implies that the over potential at the anode would be negligible, which is indeed the case in most contact process,



IMPORTANCE OF POTENTIAL PH DIAGRAM

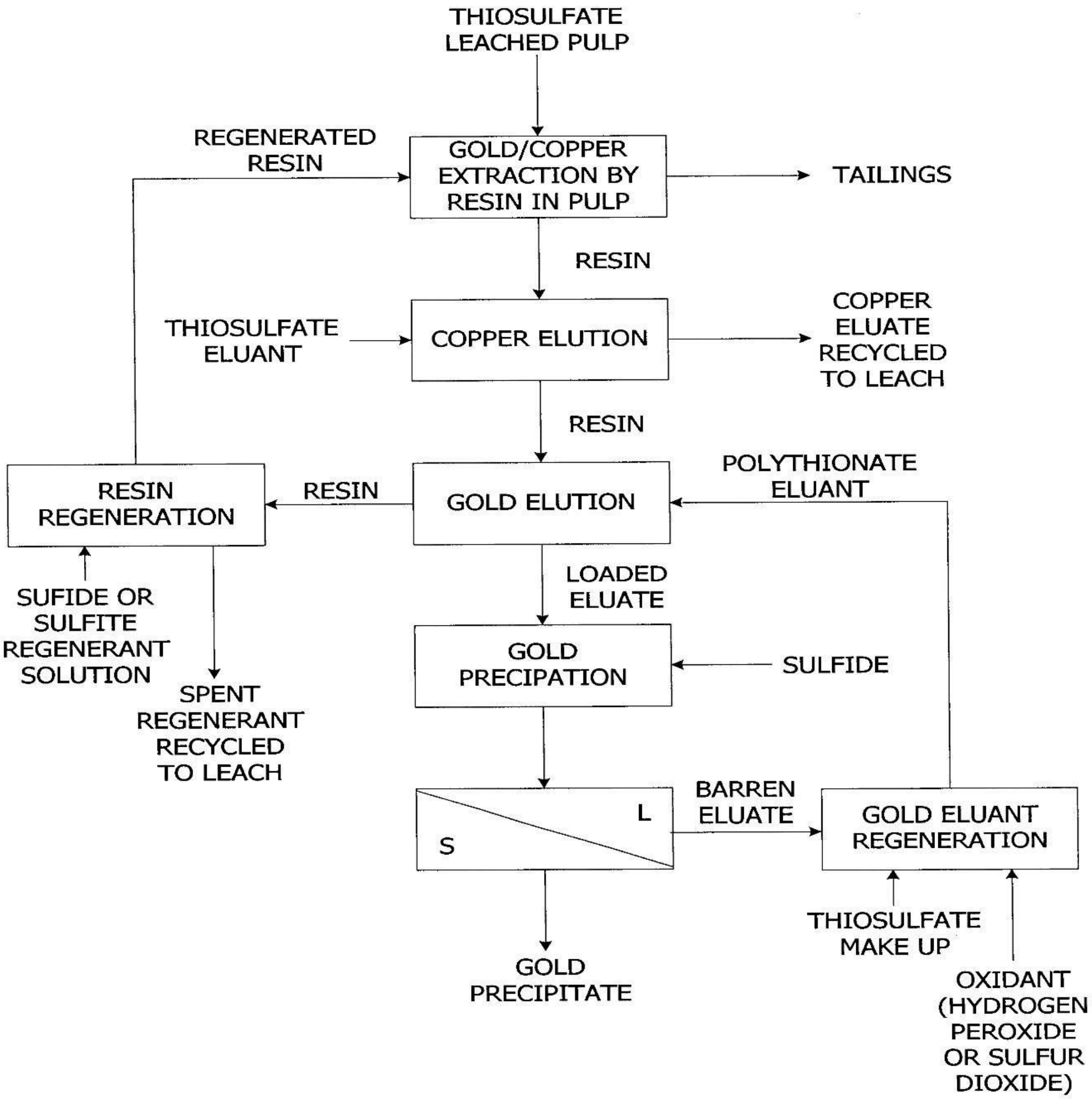
- Leaching may be carried out under different conditions. It may be performed with either acidic or basic solution or under oxidizing, reducing or neutral environment.
- The particular condition for leaching is governed primarily by the nature of material being treated and degree of selectivity required for the leaching process.
- In other word, by using appropriate leaching condition may be possible to dissolve certain metal compounds from a complex feed material and either to leave others on attack or to convert them into insoluble solid pieces which will be rejected in leach residue.
- These conditions are generally obtained from a diagram called potential-pH diagram (Eh-pH). It is also known as **Pourbaix** diagram.
- In this diagram various metal phase are in equilibrium with the aqueous phase. So the co-ordinates of **Pourbaix** diagram or potential-pH diagram, potential volt at Y-axis and pH in solution along X-axis.
- If the diagram is divided into four imaginary quadrants, the conditions prevailing for each quadrants are shown by the diagram given below:



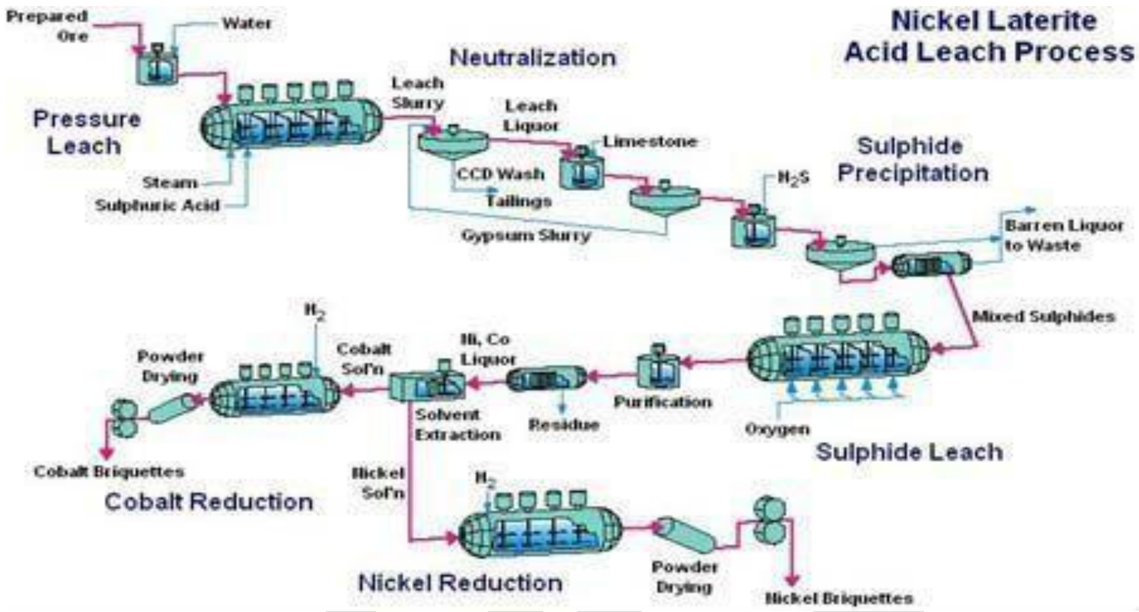
- The potential phase diagram can be constructed for any system in hydrometallurgy if thermodynamic data are given.
- It can be of great value in selecting the solution conditions necessary not only for the dissolution of solid pieces but equally for precipitation of solid phase from the process liquor or leach liquor.

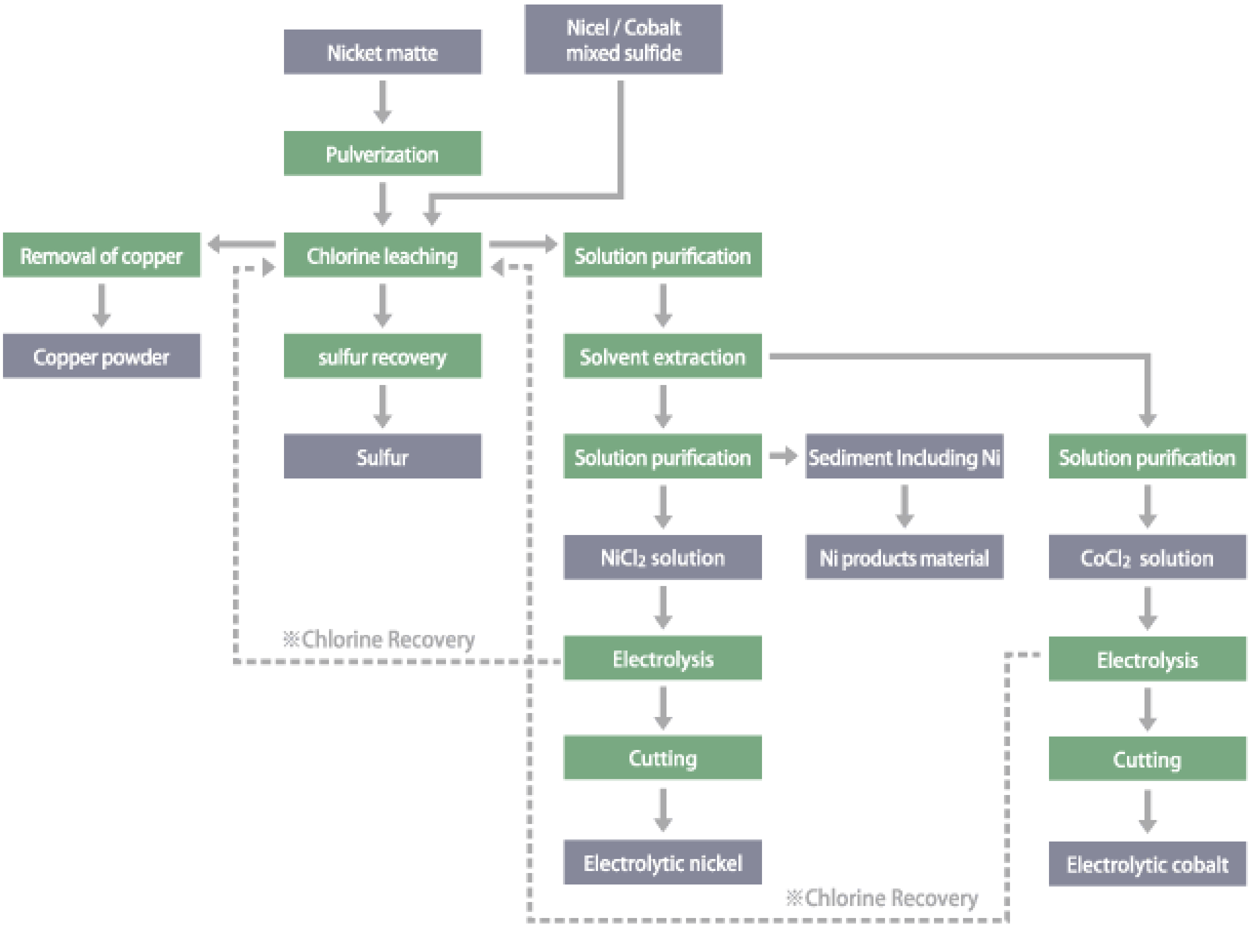
SOME IMPORTANT PROCESS FLOW SHEETS

✓ Recovery of Au from leach liquors



✓ Recovery of Nickel and Cobalt

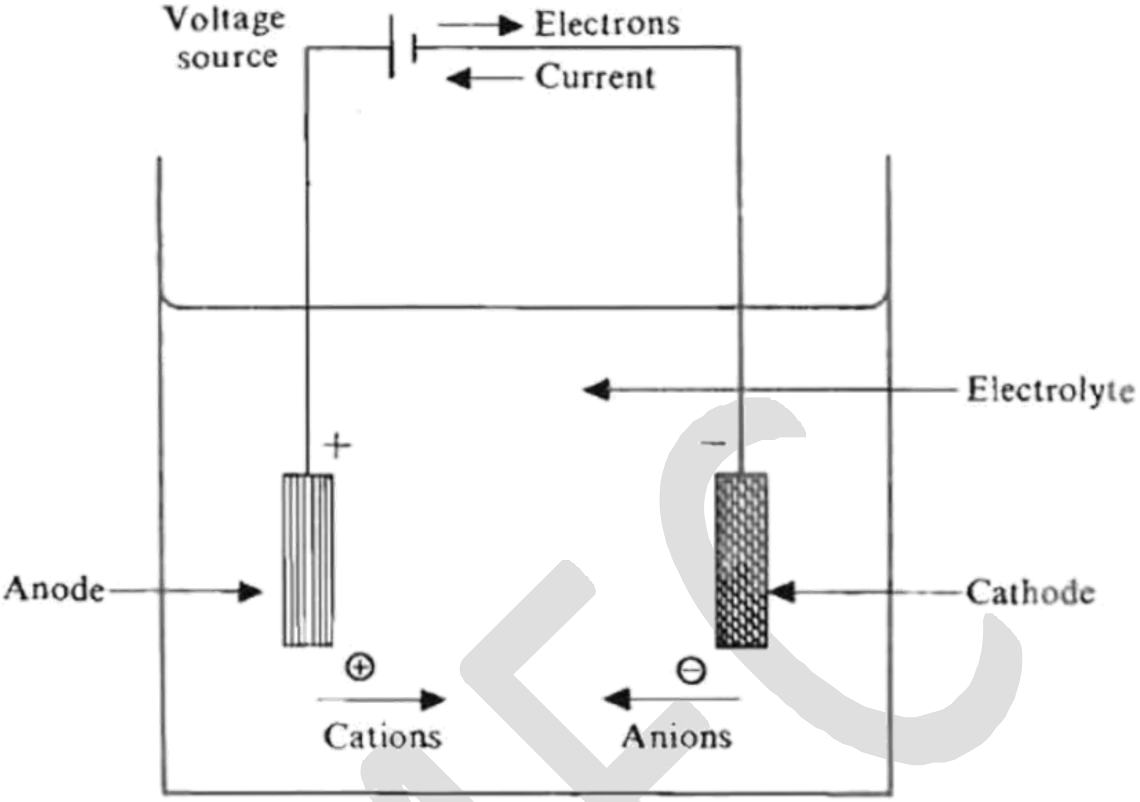




INTRODUCTION TO ELECTROMETALLURGY

PRINCIPLES OF ELECTROMETALLURGY

Electrolysis is an electrochemical processes involved in the inter conversion of *electrical energy* and *chemical energy-generally* in ironically conducting media. Such media include aqueous solutions molten salts and silicates, and organic liquids.



FARADAY's LAWS OF ELECTROLYSIS

Faraday‘s first law states that during electrolysis, the chemical action produced by a current at an electrode is proportional to the quantity of electricity passed, and

Faraday's second law states that the masses of substances deposited on or dissolved at an electrodes by the passage of same quantity of electricity which are directly proportional to their chemical equivalent weights.

For example, in an electrolytic cell, the reaction for the deposition of silver on the cathode is

$$e + Ag^{+} = Ag\ (s).$$

The equivalent weight of Ag is here equal to its atomic weight 107.88. Therefore, 96,493.1 coulombs would deposit 107.89 gm of silver.

The quantity of charge that generates I gm equivalent weight of any chemical is called a *faraday.* A faraday is equal to 96,493.1 coulombs.

ELECTRODE POTENTIAL

An electrode is immersed in fused salt or aqueous solution having ionic conductivity. A potential difference builds up at the interface between the two phases. This potential difference is called ***electrode potential***, which arises due to the transfer of ions or electrons on breaking their bonds with the substances in one phase and reacting to form new bonds with substances in the other phase. Such charge transfer reactions are electrochemical in nature. The metal electrode consist s of metal ions bound together by the attraction of free electrons which enable it to conduct electricity.

Electrode potentials are expressed with respect to a reference electrode. For an aqueous solution, the standard hydrogen electrode is conventionally used as the reference electrode.

ELECTROLYTIC CELL

An electrolytic cell consists of two electrodes. The negative electrode (cathode) is made of silver and the positive electrode (anode) of graphite bathed in chlorine under one atm. The electrolyte is AgCl dissolved in a solvent. The reaction at the cathode is

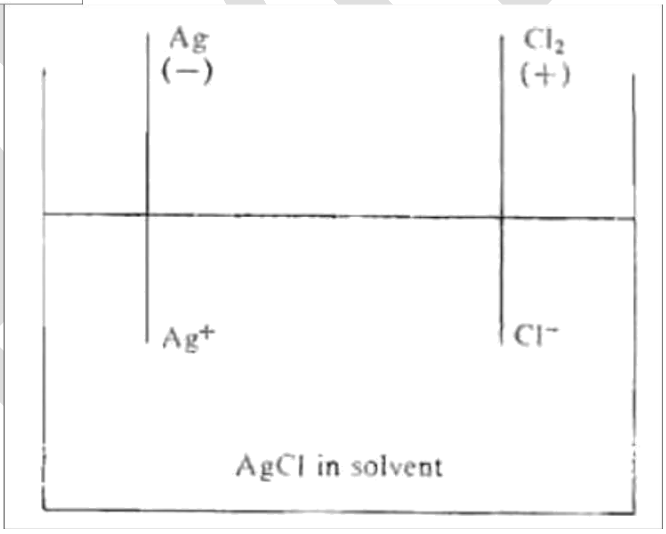
$$\mathrm{Ag} = \mathrm{Ag}^+ + e,$$

and the reaction at the anode is

$$\tfrac{1}{2}\mathrm{Cl}_2 = \mathrm{Cl}^- - e.$$

The overall cell reaction in the solution is

$$\mathrm{Ag} + \tfrac{1}{2}\mathrm{Cl}_2 = (\mathrm{Ag}^+ + \mathrm{Cl}^-).$$



The emf measured between the two electrodes is the difference between the two electrode potentials. If an external potential source is connected. Under these conditions, the reversible free energy change *dG is* related to the emf generated.

For a cell reaction involving stoichiometric quantities of reactants and products, the quantity of electricity required is *ZF*, where Z is the number of electrons required for the cell reaction to occur and *F* is Faraday‘s constant. The amount of electrical work done when Z electrons are involved in the cell reaction is *ZFE* joules, where *E* is the emf of the cell in volts. Therefore,

$$\Delta G = -ZFE.$$

The standard value of electrode potential, E_O is measured if AgCl is pure. Such a standard value is the standard forma t ion potential and the standard free energy of formation of AgCl is given by

$$\Delta G^0 = -ZFE^0 = -RT \ln K.$$

In general, the electrode potential of electrolytic is given by in terms of the standard potential (E_i) and of the activities of the species *i* involved in the electrode reaction. The standard potential obviously, is the potential of the electrode when all the species are at unit activity , i.e., they are in their standard states.

$$E_i = E_i^0 - \frac{RT}{ZF} \Sigma \ln a_i^{\nu_i}$$

KINETICS OF ELECTRODE PROCESSES

Consider a metal M in contact with its metal ions M^{Z+} in solution. The tendency of the metal ions from t he elect rode to go in to solution is opposed by the ions in solution which try to get themselves discharged on to the metal. The rates of transfer of metal ions can be expressed in terms of the absolute reaction rate theory,

The rate of transfer of ions from the metal to the solution V_1 is given by

$$V_1 = K_1 \exp\left(-\frac{\Delta G_a^*}{RT}\right),$$

The rate of discharge of ions on the metal V_2 is given by

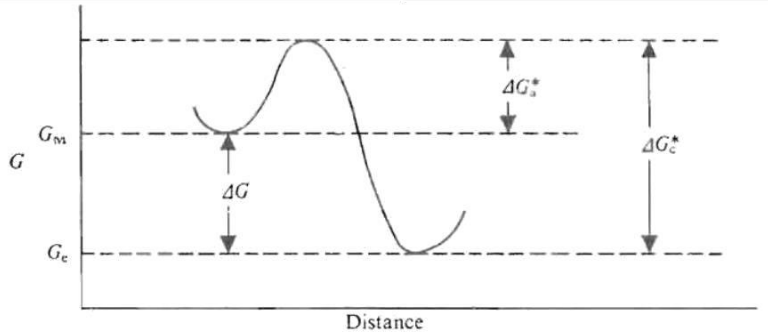
$$V_2 = K_2 \exp\left(-\frac{\Delta G_c^*}{RT}\right),$$

Since the system operates under conditions of reversible equilibrium, $V_1 = V2$

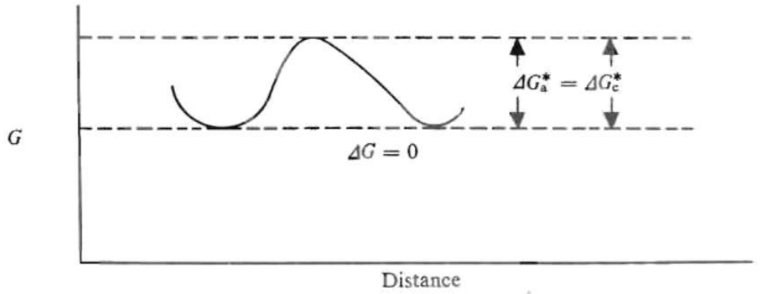
Now, assume that the metal electrode forms a part of a system where a net reaction takes place and the ions leave the metal at a rate faster than that of the ion discharge at the electrode. Under these conditions, the system loses thermodynamic reversibility and the reversible electrode potential changes its value by an amount η (overpotential). The activation energies for the forward anodic reaction and the backward cathodic reaction are shown as ΔG^* and ΔG^* respectively.

The rates of reaction are related to the current density *i.* for an anodic or a cathodic process

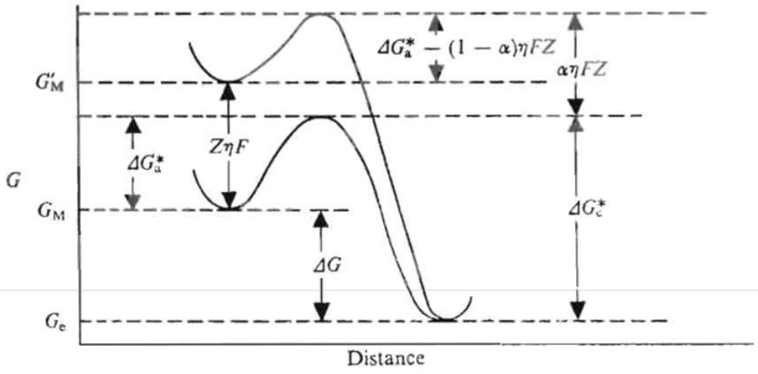
$$i = i_0 \exp\left[\frac{\alpha\eta FZ}{RT}\right] - i_0 \exp\left[-\frac{(1-\alpha)\eta FZ}{RT}\right].$$



(a) General condition



(b) Equilibrium condition



(c) Activation polarization

ACTIVATION POLARIZATION

The polarization of the electrodes just described is referred to as *activation polarization.* Activation polarization is dependent on the current density, and η is called the activation overpotential.

The overpotential at an electrode is the difference between the reversible electrode potential and the polarized electrode potential.

CONCENTRATION POLARIZATION

The polarization also results from the concentration gradients in a solution. Ions that are discharged at an electrode must be replaced by other ions in the vicinity of the electrode. Such a replacement is brought about by ionic migration, agitation, and diffusion. If migration and agitation cannot provide ions rapidly enough to replace those discharged, the concentration at the electrode surface falls below that in the bulk solution. In such a situation, ions are transported by diffusion across the thin film surrounding the electrode and a concentration gradient is built up across this film. Therefore, we see that the electrode kinetics is controlled by the rate of diffusion. This control causes a change in the reversible electrode .potential. Such a change is known as *concentration overpotential* or *concentration polarization.* It should be noted that concentration polarization arises from concentration gradients within the solution. So, concentration polarization of the type just described can be minimized by stirring the solution vigorously. An increase in the temperature also tends to decrease the concentration polarization by accelerating the diffusion of ions.

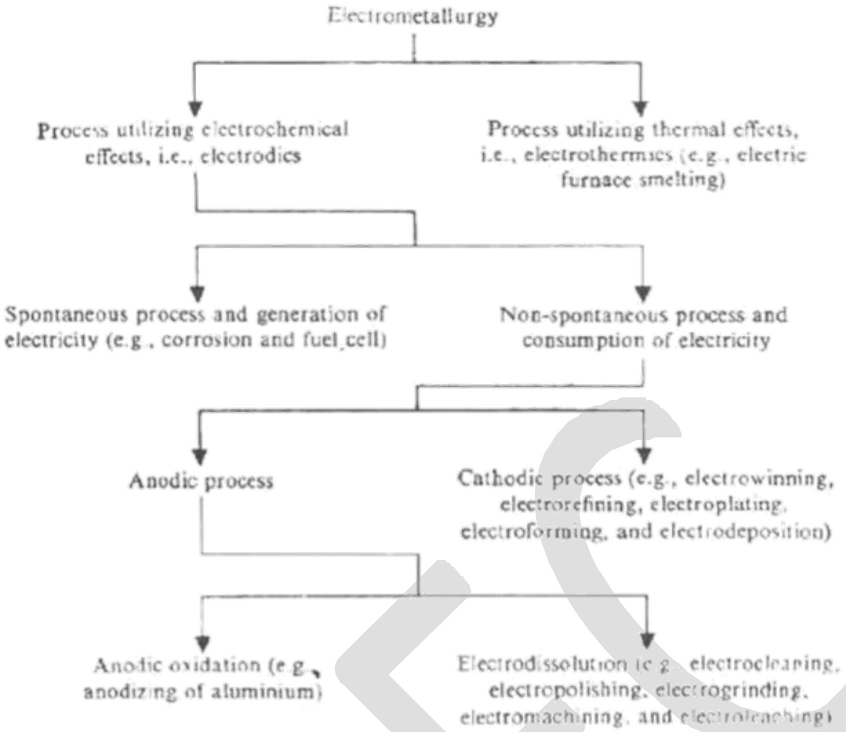
GENERAL METHODS OF ELECTROMETALLURGY

Electrometallurgy includes all metallurgical processes which _utilize electricity and electrical effects. Under the scope of process metallurgy, there are larger numbers of processes as shown figure below but only a limited number of processes that use electricity supplied from external sources are considered as, *electrowinning, electrorefining,* and *electrodeposition*

Electrowinning refers to a process that produces a metal by the electrolysis of an aqueous solution or a fused salt.

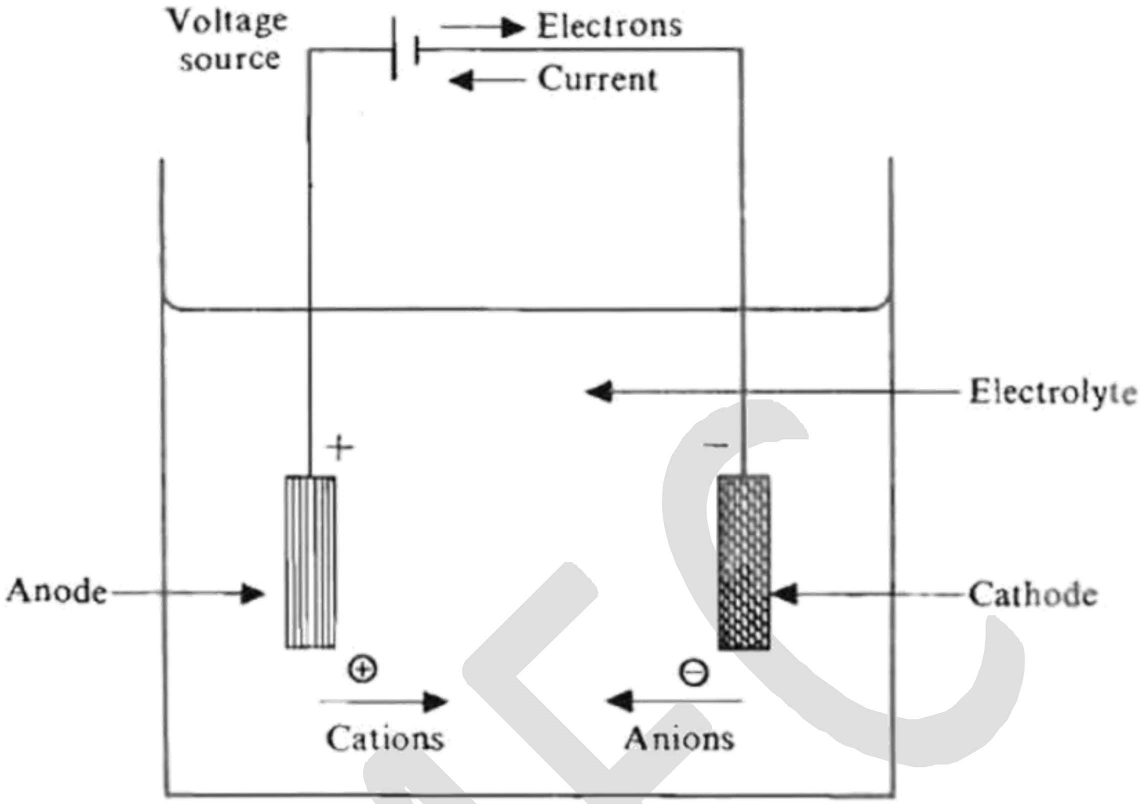
Electrorefining is a refining process based on electrolytic phenomena.

Electrode position refers to the technique of depositing one metal on another at the cathode.



PRINCIPLES OF ELECTROMETALLURGY

Electrolysis is an electrochemical processes involved in the interconversion of *electrical energy* and*chemical energy-generally* in ironically conducting media. Such media include aqueous solutions molten salts and silicates, and organic liquids.



FA RAD AY's LAWS OF ELECTROLYSIS

Faraday‘s first law states that during electrolysis, the chemical action produced by a current at an electrode is proportional to the quantity of electricity passed, and

Faraday's second law states that the masses of substances deposited on or dissolved at an electrodes by the passage of same quantity of electricity which are directly proportional to their chemical equivalent weights.

For example, inan electrolytic cell, the reaction for the deposition of silver on the cathode is

$$e + Ag^{+} = Ag\ (s).$$

The equivalent weight of Ag is here equal to its atomic weight 107.88. Therefore, 96,493.1 coulombs would deposit 107.89 gm of silver.

The quantity of charge that generates Igm equivalent weight of any chemical is call ed a *faraday*. A faraday is equal to 96,493.1 coulombs.

ELECTRODE POTENTIAL

An electrode is immersed in fused salt or aqueous solution having ionic conductivity.A potential difference builds up at the interface between the two phases. This potential difference is called ***electrode potential***, whicharises due to the transfer of ions or electrons on breaking their bonds with the substances in one phase and reacting to form new bonds with substances in the other phase. Such charge transfer reactions are electrochemical in nature. The metal electrode consist s of metal ions bound together by the attraction of free electrons which enable it to conduct electricity.

Electrode potentials are expressed with respect to a reference electrode. For an aqueous solution, the standard hydrogen electrode is conventionally used as the reference electrode.

ELECTROLYTIC CELL

An electrolytic cell consists of two electrodes. The negative electrode (cathode) is made of silver and the positive electrode (anode) of graphite bathed in chlorine under oneatm. The electrolyte is AgCl dissolved in a solvent. The reaction at the cathode is

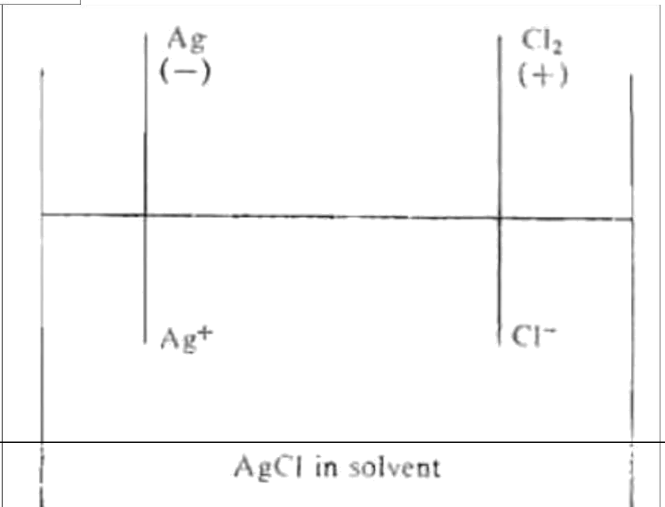
$$\mathrm{Ag} = \mathrm{Ag}^+ + e,$$

and the reaction at the anode is

$$\tfrac{1}{2}\mathrm{Cl}_2 = \mathrm{Cl}^- - e.$$

The overall cell reaction in the solution is

$$\mathrm{Ag} + \tfrac{1}{2}\mathrm{Cl}_2 = (\mathrm{Ag}^+ + \mathrm{Cl}^-).$$



The emf measured between the two electrodes is the difference between the two electrode potentials. If an external potential source is connected. Under these conditions, the reversible free energy change *dG is* related to the emf generated.

For a cell reaction involving stoichiometric quantities of reactants and products, the quantity of electricity required is *ZF*, where Z is the number of electrons required for the cell reaction to occur and *F* is Faraday‘s constant. The amount of electrical work done when Z electrons are involved in the cell reaction is *ZFE* joules, where *E* is the emf of the cell in volts. Therefore,

$$\Delta G = -ZFE.$$

The standard value of electrode potential, E_O is measured if AgCl is pure. Such a standard value isthe standard formation potential and the standard free energy of formation of AgCl is given by

$$\Delta G^0 = -ZFE^0 = -RT \ln K.$$

In general, the electrode potential of electrolytic is given by in terms of the standard potential (E_i) and of the activities of the species *i* involved in the electrode reaction. The standard potential obviously, is the potential of the electrode when all the species are at unit activity , i.e., they are in their standard states.

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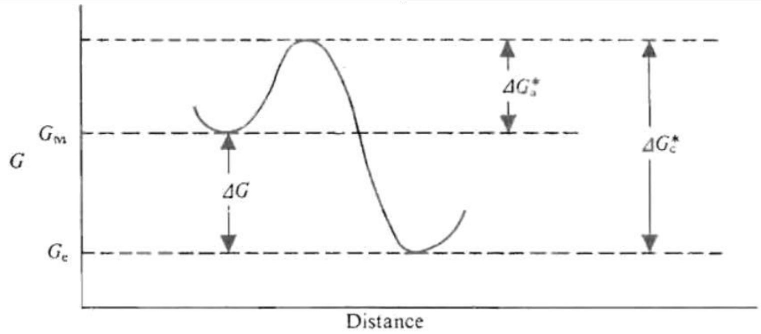

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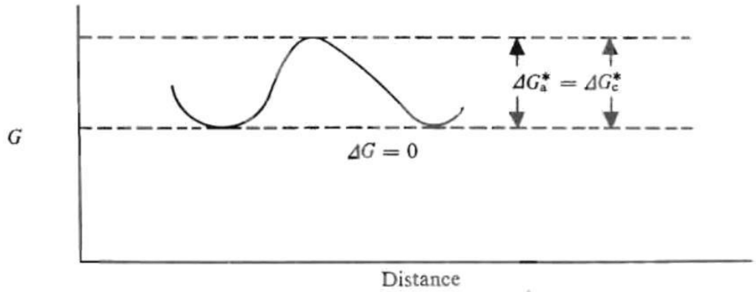

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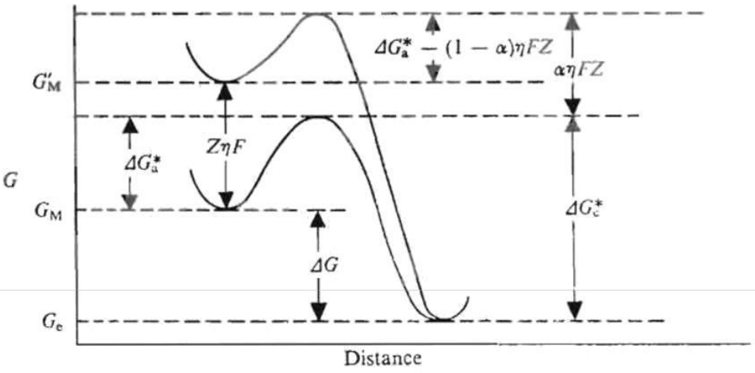

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ELECTROLYTIC DECOMPOSITION

Electrolytic decomposition is used in both the extraction and the refining of metals. In both processes, the electrolyte is an aqueous solution or a mixture of fused salts.

In this process, the anode is either an insoluble conductor or an electrical conductor such as copper matte or nickel matte.While, in electrorefining, it is the impure metal itself. The electrolyte in both cases is a solution with a sufficiently high electrical conductivity and a reasonably high metal ion concentration. The cathode could be the pure metal built up as a pure starting sheet' or, sometimes, it could be built up on a blank of another metal. The selection of the electrolytic is important in electrode position process. The basic conditions that an electrolyte must satisfy are:

(I) It must have a sufficiently high ionic conductivity, and conduction must be entirely due to ions.

(2) It must be chemically inert towards the electrodes, the container material, and theelectrolysis products.

(3) It must be stable at the temperature of operation.

(4) When a solution containing the metal to be extracted is being used, then it must be chemically more stable than the solute.

Common metals such as Cu, Zn, Sn, Au, and Mn can be produced by aqueous electrolysis; whereas reactive metals such as Ti, Zr, Th, Na, K, Mg, and Al cannot. To obtain reactive metals, their fused salts must be electrolyzed at a high temperature.

ELECTROLYTES

The electrolytic phenomena depend on the structure of the solvent media. There are two types of electrolytic such as aqueous salts and molten salts electrolytes.

Aqueous salts electrolytes: Water is made up of associated molecules because of the polar nature of its molecule. In 'association', the asymmetric molecules cling to each other by means of hydrogen bonds and result of such association which causes the breakdown of the crystal lattice of ionic compounds to form aqueous solution. In general, most aqueous solutions of metal compounds contain complexes metal ions .Complexes may be formed by NH_3 CI^-, OH^-, and P_2O_4.

Molten salt electrolytes: Molten salts are ionic melts, some of which are liquids at temperatures up to 3000°C at 1 atm. They form the largest class of nonaqueous inorganic solvents. Ionic melts consist of charged particles, namely, anions and cations, in intimate contact. The attractive forces between particles having opposite charges and the repulsive forces between similarly charged particles are very strong. Therefore, a cation has anions as its closest neighbours and vice versa. To determine energy change required to form thisarrangement of the ions, we estimate the energy needed to break up the arrangement of ions.

ELECTROLYSIS OF AQUEOUS SOLUTIONS

The fact that water can dissolve relatively high concentrations of salt renders it suitable for electrolysis. It may be noted that aqueous solutions have a high conductivity at ambient temperatures, especially when acidic.

The stages involved in the overall extraction process leading to the electrowinning of metals from aqueous solutions are:

(1) Leaching of a rosted ore (e.g., an oxide) to a form soluble in an aci

(2) Purification and concentration of the leaching liquor.

(3) Anode and cathode reactions during electrolysis

$$xH_2O \rightarrow \tfrac{1}{2}xO_2 + 2xH^+ + 2xe \text{ [anode (in acid solutions)]},$$

$$M^{2x+} + 2xe \rightarrow M \text{ (cathode)}.$$

(4) Recirculation of the acid liberated at the anode for leaching purposes

The overall reaction for the conversion of the oxide roast to the metal is written simply as

$$MO_x \rightarrow M + \tfrac{1}{2}xO_2.$$

During electrolysis, the reactions take place at two distinct regions, namely, at the cathode and at the anode. At the cathode, the metal ion is discharged and the metal deposited. At the anode, the reactions depend on the nature of the electrolyte.

For example, the reactions in acidic and alkaline aqueous solutions, respectively, are

.

$$2H_2O = O_2 + 4H^+ + 4e, \qquad E_0 = -1.23 \text{ V (acidic solution)},$$

$$4OH^- = O_2 + 2H_2O + 4e, \qquad E_0 = -0.40 \text{ V (alkaline solution)}.$$

Table 2: Electrolysis of aqueous salt solutions.

ELECTROLYSIS OF FUSED SALTS

The emf series-in which the electrode potentials are arranged with respect to the potential of the standard hydrogen electrode-indicates that the metals placed above manganese are too reactive to be produced from aqueous solutions, and are also produced by electrolyzing water-free fused salt mixtures.Theoretically, any metal can be obtained by the direct electrolysis of one of its salts.

Molten salts have some distinct advantages over aqueous salt solution.

(1) The conditions are favourable for attaining a more complete heterogeneous equilibrium because all the reactions are accelerated.

(2) The metal produced, if molten, may be easily removed.

(3) Overvoltages on molten metals are often small enough to allow high current densities and, therefore, greater throughput.

(4) Further, at high temperatures, diffusion rates are high andtherefore, during electrorefining processes, impurities can be transferred from the anode to the cathode so as to purify the metal.

Disadvantages

(1) The efficiency is lowered due to the increased possibility of side reactions taking place in high temperature.

(2) In most molten salt electrolytic processes, the anode material is graphite, which leads to formation of CO and CO_2, unless inert gases are used.

(3) In most fused salt electrolytic processes, several side reactions may take place apart from the desired decomposition reaction.

(4) Consequently, the current efficiency is far below the optimum value of 100 per cent due to apparent deviation from Faraday's laws.

The factors lead to a lower current efficiency. Howthese can be avoided.

(1) Mechanical losses (handling losses) of the substances formed at the electrodes.
These losses can be minimized by using improved operational techniques.

(2) The evaporation of the metal from the cathode. This may take place during the electrolytic liberation of sodium from fused sodium chloride because the operating temperature wouldbe close to the boiling point of the metal.

The problem can be solved by dissolving the sodium chloride in a suitable medium to form a low melting mixture, thus lowering the operating temperature.

(3) Chemical side reactions.

The unwanted side reactions can be controlled by choosing the proper electrolyte and using a lower operating temperature.

(4) The formation of lower valency compounds at the cathode. For example, in the electrolysis of SnCI4, in the initial stages, tin reacts with the electrolyte to form SnCl2, and the cathode current efficiency is zero. In most instances, the melt is soon saturated with the lower valency compounds, and after a while, the metal starts depositing on the cathode.

(5) The formation of higher valency compounds at the anode. This reduces to zero the anode current efficiency in the initial stages of electrolysis. For example, during the electrolysis of SnCl4 in the initial stages, the chlorine liberated at the anode reacts to produce SnCl4 However, after some time, the melt becomes saturated with SnCI4, and further reaction would cease.

(6) The dissolution of the metal in the fused salt.

This drawback can be eliminated to a great extent by dissolving the metal sait in a more stable salt to form a relatively dilute solution.

(7) The recombination of the electrolysis products with the original salt.

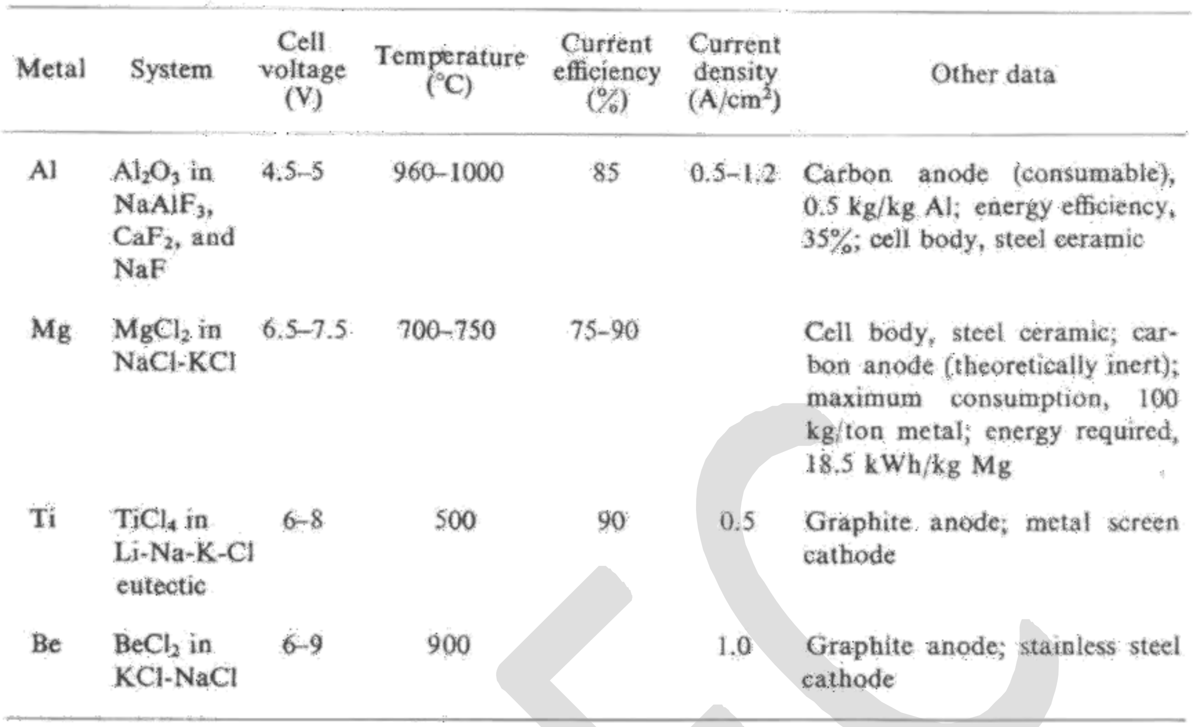
Recombination can be eliminated by the immediate and complete isolation of the electrolysis products by employing an electrolytic cell with a special design.

(8) Current losses due to the presence of moisture.

This problem is not serious in the case of fluorides because they can be prepared and stored in a dry state without much difficulty.

MOLTEN SALT PROCESSES

Electrowinning is presently being used for extracting a large number of metals from their molten salts. The most outstanding example is the electrolysis of alumina that has been dissolved in a cryolite bath.



Metal	System	Cell voltage (V)	Temperature (°C)	Current efficiency (%)	Current density (A/cm²)	Other data
Al	Al_2O_3 in $NaAlF_3$, CaF_2, and NaF	4.5–5	960–1000	85	0.5–1.2	Carbon anode (consumable), 0.5 kg/kg Al; energy efficiency, 35%; cell body, steel ceramic
Mg	$MgCl_2$ in NaCl-KCl	6.5–7.5	700–750	75–90		Cell body, steel ceramic; carbon anode (theoretically inert); maximum consumption, 100 kg/ton metal; energy required, 18.5 kWh/kg Mg
Ti	$TiCl_4$ in Li-Na-K-Cl eutectic	6–8	500	90	0.5	Graphite anode; metal screen cathode
Be	$BeCl_2$ in KCl-NaCl	6–9	900		1.0	Graphite anode; stainless steel cathode

For the extraction of aluminium from bauxite

For a cathode of aluminium and an anode of oxygen, the decomposition reaction may be

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) = Al\ (l) + 0.75O_2\ (g),$$

In otherwords, the above reaction is split into

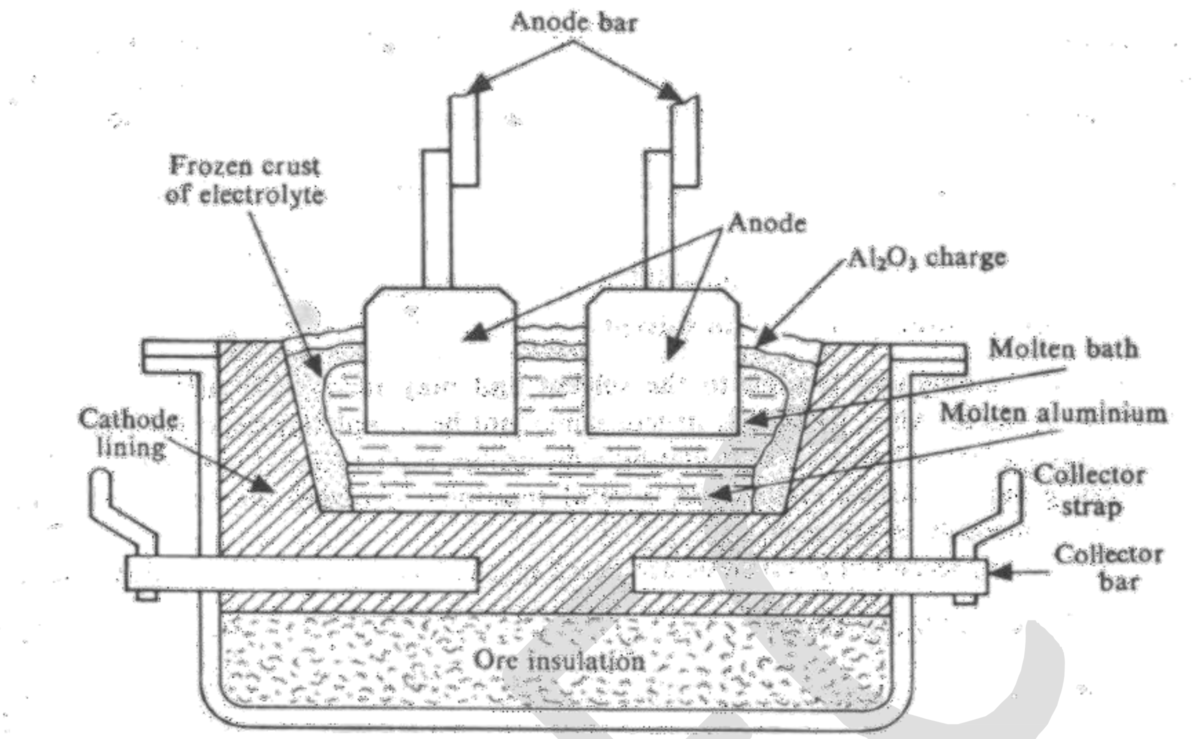
$$Al\ (l) + 0.75O_2\ (g) = 0.5Al_2O_3\ (c),$$

$$0.5Al_2O_3\ (c) = 0.5Al_2O_3\ (l),$$

$$0.5Al_2O_3\ (l) + Na_3AlF_6\ (l) = 0.5Al_2O_3 \text{ (solution in } Na_3AlF_6),$$

At 1000°C, for the reaction

$$\tfrac{4}{3}Al\ (l) + O_2\ (g) = \tfrac{2}{3}Al_2O_3\ (c),$$



Electrolytic cell for aluminium extraction

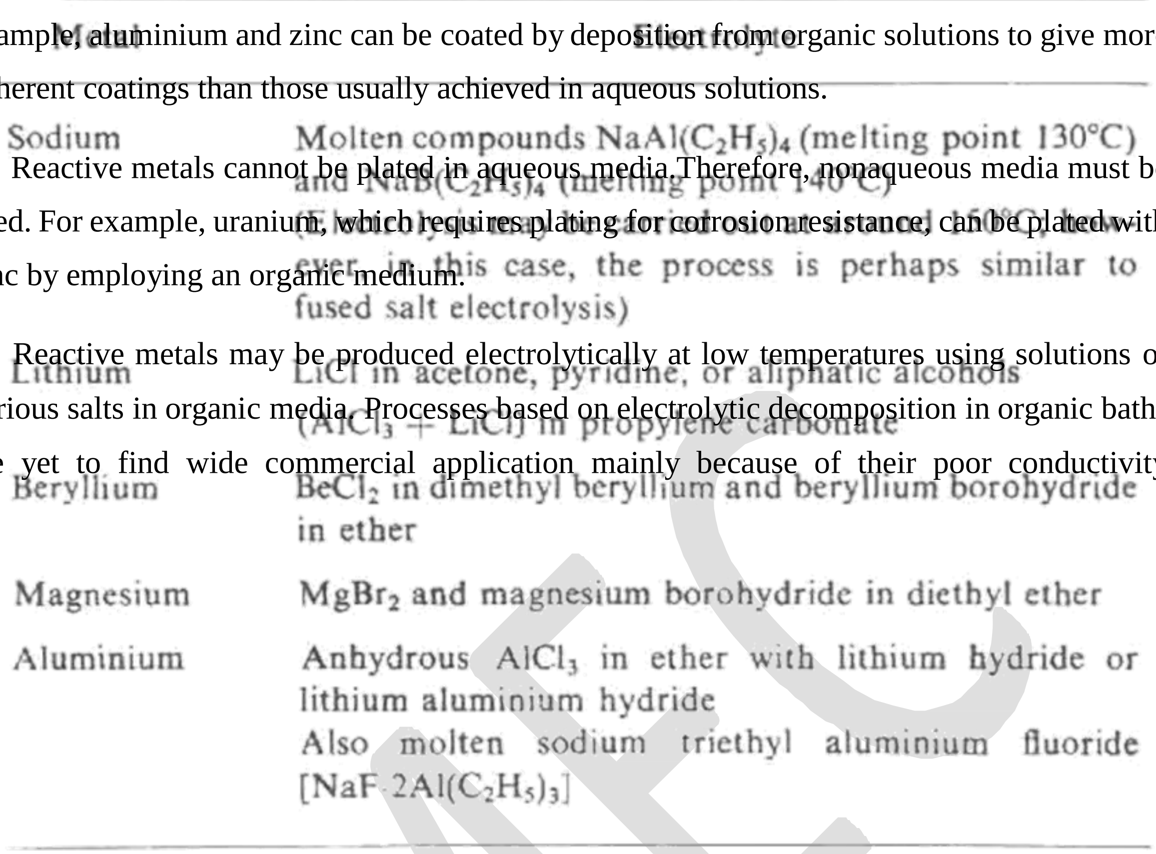
ELECTROLYSIS OF LOW-TEMPERATURE NONAQUEOUS SYSTEMS

Nonaqueous systems refer to organic solutions in which metals can be deposited and dissolved at the anode. We now list the general advantages of such systems:

(1) In some instances, the organic medium is better suited than other media for plating For example, aluminium and zinc can be coated by deposition from organic solutions to give more coherent coatings than those usually achieved in aqueous solutions.

(2) Reactive metals cannot be plated in aqueous media.Therefore, nonaqueous media must be used. For example, uranium, which requires plating for corrosion resistance, can be plated with zinc by employing an organic medium.

(3) Reactive metals may be produced electrolytically at low temperatures using solutions of various salts in organic media. Processes based on electrolytic decomposition in organic baths are yet to find wide commercial application mainly because of their poor conductivity



Metal	Electrolyte
Sodium	Molten compounds $NaAl(C_2H_5)_4$ (melting point 130°C) and $NaB(C_2H_5)_4$ (melting point 140°C) (E[illegible] 150°C, however, in this case, the process is perhaps similar to fused salt electrolysis)
Lithium	LiCl in acetone, pyridine, or aliphatic alcohols ($AlCl_3$ + LiCl) in propylene carbonate
Beryllium	$BeCl_2$ in dimethyl beryllium and beryllium borohydride in ether
Magnesium	$MgBr_2$ and magnesium borohydride in diethyl ether
Aluminium	Anhydrous $AlCl_3$ in ether with lithium hydride or lithium aluminium hydride Also molten sodium triethyl aluminium fluoride [$NaF \cdot 2Al(C_2H_5)_3$]

ELECTROPLATING

Electroplating is a process in which an object, usually metallic, is coated with one or more relatively thin but adherent layers of some other metal or alloy. This process is used to impart better surface characteristics and protection against corrosion.

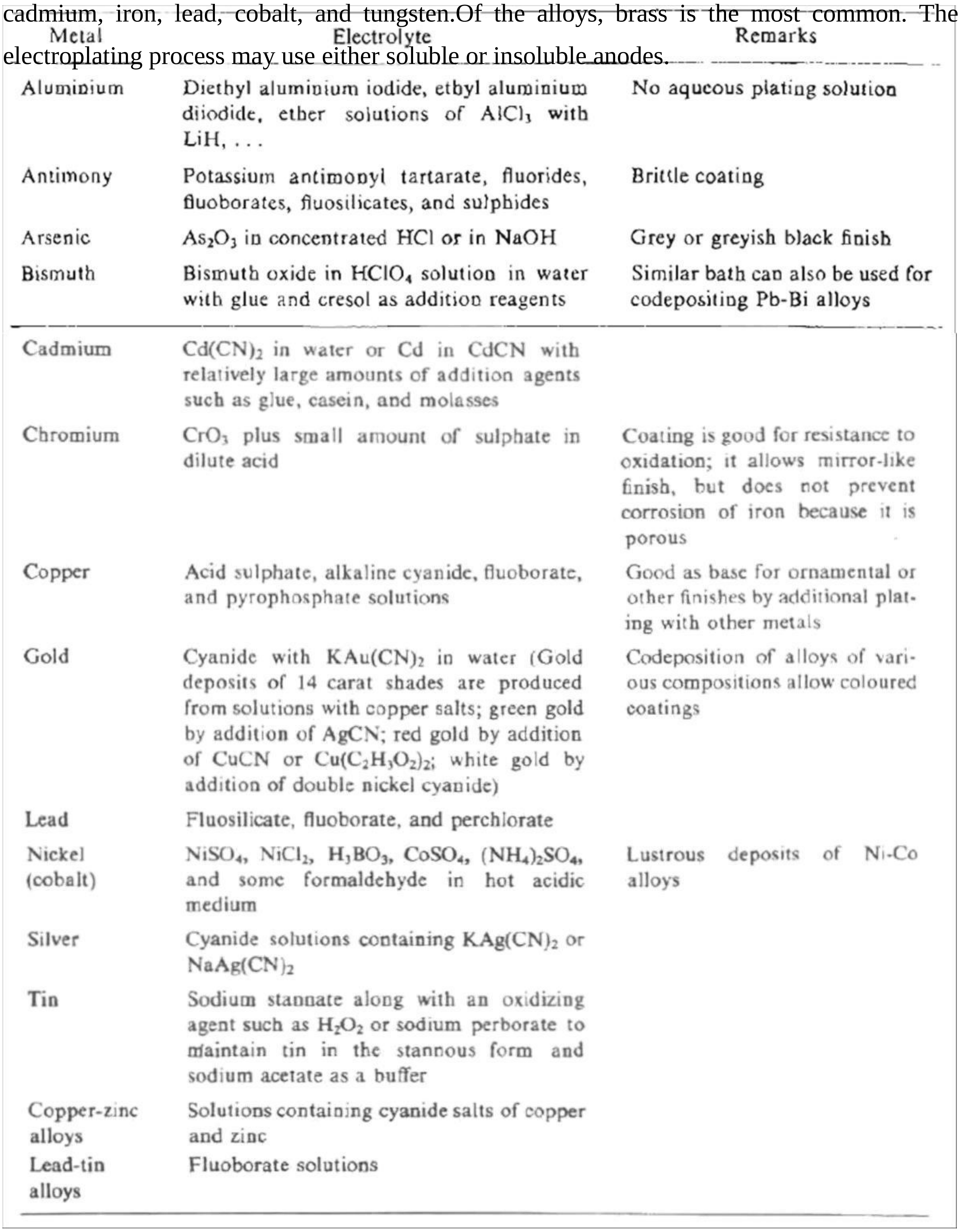
Since the aim of electroplating is to produce only a thin coating layer, the characteristics of the surface to be coated must be taken into account. For example, in chromium plating, if the underlying metal has already been polished, then, the chrome will retain this polish if a thin layer is deposited.

The potential *(Ed)* required for the electrodeposition of a metal is given by a modified form of the Nernst equation as

$$E_d = E_0 - \frac{RT}{ZF} \ln a + P,$$

Where E_0 is the decomposition potential, *a* the activity of the depositing cation on the cathode film, and *P* a rate factor expressed as the additional potential that must be provided to maintain a uniform rate of deposition. It is possible to achieve codeposition of two metals by adjusting values of *a* and *P*.

The principal metals used in electroplating are nickel, silver, chromium, copper, zinc, gold, cadmium, iron, lead, cobalt, and tungsten.Of the alloys, brass is the most common. The electroplating process may use either soluble or insoluble anodes.



Metal	Electrolyte	Remarks
Aluminium	Diethyl aluminium iodide, ethyl aluminium diiodide, ether solutions of $AlCl_3$ with LiH, . . .	No aqueous plating solution
Antimony	Potassium antimonyl tartarate, fluorides, fluoborates, fluosilicates, and sulphides	Brittle coating
Arsenic	As_2O_3 in concentrated HCl or in NaOH	Grey or greyish black finish
Bismuth	Bismuth oxide in $HClO_4$ solution in water with glue and cresol as addition reagents	Similar bath can also be used for codepositing Pb-Bi alloys
Cadmium	$Cd(CN)_2$ in water or Cd in CdCN with relatively large amounts of addition agents such as glue, casein, and molasses	
Chromium	CrO_3 plus small amount of sulphate in dilute acid	Coating is good for resistance to oxidation; it allows mirror-like finish, but does not prevent corrosion of iron because it is porous
Copper	Acid sulphate, alkaline cyanide, fluoborate, and pyrophosphate solutions	Good as base for ornamental or other finishes by additional plating with other metals
Gold	Cyanide with $KAu(CN)_2$ in water (Gold deposits of 14 carat shades are produced from solutions with copper salts; green gold by addition of AgCN; red gold by addition of CuCN or $Cu(C_2H_3O_2)_2$; white gold by addition of double nickel cyanide)	Codeposition of alloys of various compositions allow coloured coatings
Lead	Fluosilicate, fluoborate, and perchlorate	
Nickel (cobalt)	$NiSO_4$, $NiCl_2$, H_3BO_3, $CoSO_4$, $(NH_4)_2SO_4$, and some formaldehyde in hot acidic medium	Lustrous deposits of Ni-Co alloys
Silver	Cyanide solutions containing $KAg(CN)_2$ or $NaAg(CN)_2$	
Tin	Sodium stannate along with an oxidizing agent such as H_2O_2 or sodium perborate to maintain tin in the stannous form and sodium acetate as a buffer	
Copper-zinc alloys	Solutions containing cyanide salts of copper and zinc	
Lead-tin alloys	Fluoborate solutions	