PRINCIPLES OF EXTRACTIVE METALLURGY

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LECTURES NOTE

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Extractive metallurgy-

It is a practice of removing valuable metals from ore & refining the extractive raw metal into purer form.

Here you will able to know different extraction processes like pyrometallurgy, hydrometallurgy, electrometallurgy etc, refining operation of the extracted metal & different applications of thermodynamics & kinetics.

CHAPTER -1

Definition of Metallurgical Terms:

Ores:

- Ore is natural occurring aggregate or a combination of minerals from which one or more metals /minerals may be economically extracted.
- It is a natural rock that contain valuable minerals
- It is divided into high grade ore and low grade ore
- It is a mass of mineralization within the earth surface which can be mined.
- Ore can be oxide, sulphide, silicates found in nature.

Minerals:

- It is naturally occurring inorganic compound of one or more metals in association with non metals such as oxygen, sulphur & halogen.
- Minerals has fixed composition and well defined chemical and physical structure.
- All ore can be minerals but not all minerals can be ore.

Gangue:

- The valueless and worthless portion of mineral is gangue.
- It is a waste rock or material overlying on an ore or mineral body.
- The impurities present in the ore such as sand, mud, dirt etc other component present in ore.

Flux:

- It is a chemical cleaning agent or purifying agent.
- Flux is used to lower both the liquidus temperature and the viscosity of the slag.
- Flux is classified into oxidizing flux. Reducing flux and neutral flux.

Slag:

- Slag collect unreduced gangue minerals so as to form separate layer in metal extraction process
- Flux + Gangue=Slag
- Slag is usually a mixture of metal oxide and silicon dioxide.
- It is a stony waste matter separated from metals during the smelting or refining of ore.

Matte:

- A matte is a molten metallic sulphide solution that contains mainly copper sulphide andiron sulphide.
- Mattes have high electrical conductivity and make a density between metal and slag phase.
- It is insoluble with metal and slag phase.

- Its form during smelting operation of copper, nickel etc.

Speiss:

- Speiss is a molten phase consisting primarily of iron arsenide commonly encountered in lead smelting operation.
- It is a combination of metallic arsenide or antimonide formed in the smelting operation.
- The impurities make a strong chemical bond with the slag & also toxic in nature which cannot be resmelted. This compound is called speiss.

Metals:

- Metals have distinctive properties like electrical conductivities, good thermal conductivity, strength, malleability etc.
- E.g. such as gold, silver, platinum ,aluminium etc

Alloys:

- An alloy is a combination of metals or metals combined with one or more other elements
- E .g brass, bronze, steel etc

CHAPTER -2

PRINCIPLE OF PRE TREATMENT OF ORES FOR METAL EXTRACTIONS

Drying

- It usually means the removal of physically bound water or moisture from concentrate, ore, flux, or other solid materials.

- Water has a high heat of vaporization and drying is a expensive operation.
- In drying process moist material can be used directly in roasters or smelting furnaces.
- Drying is commonly done in a drying furnace or kiln where the wet material is brought into contact with hot gas or air.

Agglomeration processes-
The phenomenon of converting fines to lumps is called agglomeration. Here the fines ores are converted into coarse lumps. It renders them for proper roasting, smelting and other such processes during extraction of metals.

Why agglomeration is required?

Use of fines iron ore in iron making, since during communiation of iron ore some of the ores are converted into fines. So these fines cannot be feed into furnace directly so it is first converted into lumps.

Why we cannot charge fines into blast furnace?

1- If we charge fines into furnace it will reduces Permeability of the burden.
2- Heavy dust loss occurs from the top in the b/f .

The basics techniques of agglomeration are:

- *Sintering*
- *Palletizing*
- *Briquetting*
- *Nodulizing*
- *Vacuum extrusion*

*Here sintering and palletizing are most widely used from others.

Sintering:

Sintering principle:

- Here the iron ore fines or iron bearing fines are mixed with solid fuel(coke) and put on a permeable grate.
- Top layer of this sinter bed is heated to the sintering temperature (12-1300) by a gas or oil burner and air is drawn downwards, through the grate , with the help of exhaust blower connected from underneath to the grate.

- A narrow combustion zone is formed on the top and this combustion travels downwards layer by layer up to sintering level.
- The cold blast drawn through the bed cools the already sintered layer and thereby gets itself heated.
- The heat contained in the blast is utilized in the drying and preheating the lower layers in the bed that is in advance of combustion of each layer.
- In the combustion zone bonding of grains takes place and a strong and porous aggregate is formed.
- The process is over when the combustion zone has reached the lowest layer of the bed.
- The sinter formed is dropped after partial cooling it is then broken, screened, and cooled to produce desired fraction.
- The undersized is recycled and over is send to b/f .
- Up draught sintering {for ferrous ore) here the air is suck downwards through the ore bed, or grate Down draught sintering [for non ferrous ore] here the air is suck upward through the ore bed, grate.

Mechanism of sintering:

Two types of bond formed during sintering:

1-solid state bond or recrystallisation bond: Here a bond is formed due to recrystallization of parent particles at the point of contact in solid state.

2-slag bond or glass bond: bond is formed due to formation of slag or glass at the point of contact of two particle , which depend upon the mineral and flux.

*More is the slag bond stronger is the sinter but with less reducibility and more is the diffusion bond more is the reducibility but less is the strength.

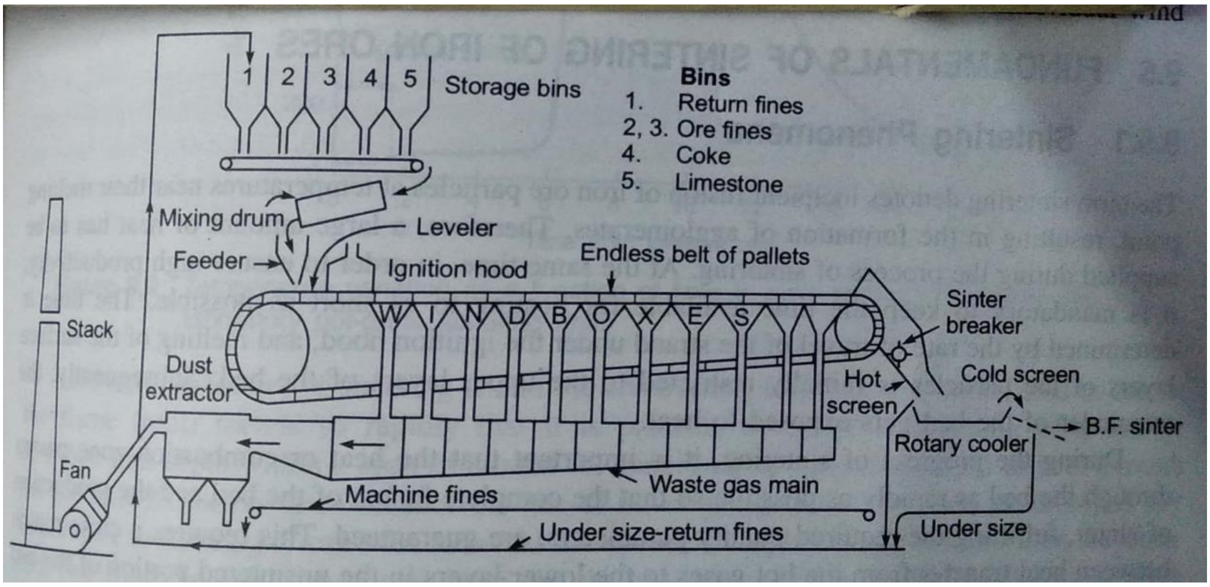
Sinter types:

Acid sinter:
The sinter mix does not contains flux at all. Flux is added in the furnace separately. Now days it is eliminated.

Fluxed sinter:
The amount of flux added in the mix in such that the basicity of the mix is equal to that of slag to be produced.

Super flux :
The amount of flux added in the mix is such that the basicity of the mix is greater than that of slag to be produced.

Equipment for sintering [DWILIGHT LLYOED SINTERING MACHINE]



(Dwight Llyod sintering machine)

Pelletizing:

- Here the very fine iron ore or iron bearing materials(100 mess size) are rolled into balls with addition of binders and additives .
- Raw materials may be flue dust collected from b/g steel making shop, fines produced during up gradation of lean ores of pyrite residue.

Process of palletisation

- In this process the fine iron ores are rolled in the presence of additives and binders into green ball and to get the desired strength these green balls are dried preheated and fired at a high temperature of(1250)degree centigrade.
- So on heating this at high temperature sufficient strength is produced between the particles. And here the sensible heat of out going gas is recovered which is feed back in the indurations period.
- This process is carried out in oxidising atmosphere.

Bonding theory

- Moisture is very much essential for pelletisation process and it must be in less quantity.

- Excess moisture is also detrimental .
- oxidizing atmosphere-T=1250-1350

How this moisture helps in binding the particles ?

- Surface tension of the moisture present in between the particles help in binding.
- Rolling of moist particles lead to formation of high density balls .
- The particles are rolled into balls depend upon the grain finess that is surface area.
- More surfaces more will be tendency of balling.

Three water particle system

1-pendular state:
In this type of water particle system water is present at the point of contact between the particles and the surface tension hold the particles.

2-funnicular state:
In this type of system all the pores are fully occupied by water in an aggregate system.

3-capillary state:
In this system all the pores are fully occupied by water but there in no coherent film of water covering the entire surface of particle. So strength of the ball depends upon the surface tension and mechanical interlocking.

Mechanism of ball formation

Mechanism behind this ball formation is the nucleation and growth mechanism .

Stages:

1-Nucleation of ball
2-Growth of this ball

- But the entire process depend upon the critical amount of moisture (water) present in the feed.
- If the amount of water is less then critical amount then there is nonunifom water distribution in the system, the major amount or water will be present in granulate material leaving non granulated material dry.
- If the amount is more then critical amount then growth will be more where as strength will be reduced due to increase in plastic behavior.

Nucleation formation region:-

• A bond is formed immediately between particles when one wet particle comes in contact with another dry or wet particle .in this way other particles are also attached with it and a highly porous loosely held aggregate is formed.

- Due to rearrangement and partial packing in short duration to from small spherical stable nuclei.
- Transition period: after nuclei are formed they pass through a transition period. In this period rearrangement of particles occurs which lead to removal of pores and voids. System goes from pendular –funicular- to capillary.
- This wet granulates grows if they are favourable oriented.
- In this process some granules may even break because of impacts, abrasion etc.

Growth occurs by two alternative methods.

1. Growth by assimilation: is possible when balling proceeds without the addition of fresh feed material.[during rolling some small particles breaks due to rolling action and these particles attached with bigger one and bigger will grow more big. Here there is no addition of fresh materials.
2. Growth by layering: growth occurs by addition of fresh materials. [Here the ball pick up new materials while rolling the amount of materials picked up by the balls is directly proportional to its exposed surface.

Equipment or industrial practice

• Two type of pelletiser are there:
• 1- disc
• 2-drum

Disc pelletiser:

- It consists of a disc with outward sloping peripheral wall .resemble like flying saucers. Which rotates around its own centre, in an inclined position to horizontal?
- Dia of disc -3.6-5.6 m .Inclination is 45 degree to the horizontal.
- The material to be pelletized is generally fed directly onto the disc and moisture level is made up with the help of moist material on the disc.
- It can also control the material flow pattern on the disc. In the reason where water is added seeds are easily formed.
- With the growth of these seeds their fractional drag against the disc decreases and the centrifugal force acquired by them increases and consequently they move out of nucleation zone.

- They also tend to rise on the inclined surface of the pelletiser in the direction of rotation and fall down against the toe section of the disc.
- The height and the width of trajectory of the ball movement increases with the size of the ball until eventually the balls are deflector downwards by the scraper.
- During this movements the ball encounter fresh feed and growth takes place more by layering while compaction assimilation plays a relatively minor role.

The rate of production of balls on a disc is a function of the following variables:
1- Diameter of the disc
2-height of the peripheral wall
3- Angle of inclination of disc
4-place on the disc where mix is fed
5-speeed of rotation
6-place where water is sprayed
7-rate of feed
8-rate of moisture addition
9-rate of withdrawal of the product
10- Nature of size of feed.
11-desired size range of pellets and percentage recycled
12- Binders and flux.

Drum pelletiser:

- This type of pelletiser is a steel drum which is having both end open with a length to diameter ratio of 2.5-3.5 rotating around its own axis in a slightly inclined position to the horizontal.
- Length-6-9 m,Dia-2-3m
- Here the charge is fed from that side of the drum which is at higher level. Water is also sprayed there the material rolls over the surface of the rotating drum and slides downward due to inclination of the drum in a cascading motion. And finally it comes out at other end.

Briquetting:

The simplest and earliest process for agglomerating fine grained raw material is briquetting.

Fined grained ores are pressed into briquettes with the addition of some water or another binder under high mechanical pressure.

These briquettes may undergo direct further treatment or thermal processing before their use.

Briquetting is the method used to convert loose biomass into high density solid blocks.

Nodulizing:

Nodulising is a process of size enlargement by fusion in which strongest nodules or small rounded lumps are formed.

Iron ore fines+ Tar+ Rotary kiln furnace=Nodules

In nodulising ore concentrate along with tar pass through a fired rotary kiln, the material begins to soften at high temperature and the rotation of the material causes the sticky material to roll into lumps.

The temperature inside the kiln is just sufficient to soften the ore but not enough to fuse the ore.

It is process like sintering as it does not need a binder agent.

Briquetting is mainly used for the recycling of iron waste in steel plant.

Vacuum Extrusion:

It is a process widely used in the ceramic industry.

CHAPTER-3

General methods of Extraction:

Metals are extracted from their ore via three different routes namely, pyrometallurgy, electrometallurgy and hydrometallurgy.

In extraction process specific amount of energy is required to reduce or release a metal ion present in compound into elemental form.

$Fe_2O_3 \rightarrow$ Fe(ion form)

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.

- Practically all iron and steel, nickel, tin, most copper and a large proportion of zinc, gold, as well as many of the minor metals are won from their ores and concentrates by pyrometallurgical methods.

- It deals with chemical reactions at high temperatures.
- It is the principal means of metal extraction.
- It occurs at high temperature at 500-2000 degree C.
- Only pyrometallurgy is used to extract some highly reactive metals like Zr, Ti etc

***A high temperature process is advantageous because*:**

- A high temperature process is often cheaper and more versatile than other method.
- At high temperature the reaction rate is accelerated and production increased
- A high temperature process use inexpensive agents or raw material.
- The reaction rate doubles in each 10ºC rise of temperature which requires small activation energy. It helps in fast reaction.
- A high temperature process has the ability to treat large tonnage of ore in a compact space.

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

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

Calcinations

• Calcinations 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.
• For example, $CaCO_3$ (c) = CaO (c) + CO_2. This reaction is endothermic and requires high temperature to decompose it in the kiln.

Roasting

All process share the first step called 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 (by heating sulphide ore) or other elements such as arsenic and tellurium in the form of a volatile oxide.

- It is a metallurgical process involving gas –solid reaction.

Different types of roasting are there such as:

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 catalyser.

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).

ROASTING PRACTICE/METHODS (TYPES OF ROASTER)

A roasting practice is chosen based on two major criteria:

- The required physical condition
- The Required chemical composition of the product

The required physical condition of the product:

- ➢ If blast furnace is used –The product should be coarser and cellular
- ➢ If reverberatory/retort furnace is used—the product should be fine particles.
- ➢ If leaching—the product should be porous in nature.

The Required chemical composition of the product:

- ➢ If lead is prime metal to recover from sulphide ore, it is required to eliminate the entire sulphur before entering in B/F.
- ➢ For copper the entire sulphur content need not to be eliminated.
- ➢ Formation of zinc ferrite should be avoided when zinc is extracted by leaching.
- ➢ If presence of precious metals is there, it may lose in excessive temperature so a low temp operation is required.

INDUSTRIAL ROASTING UNITS:

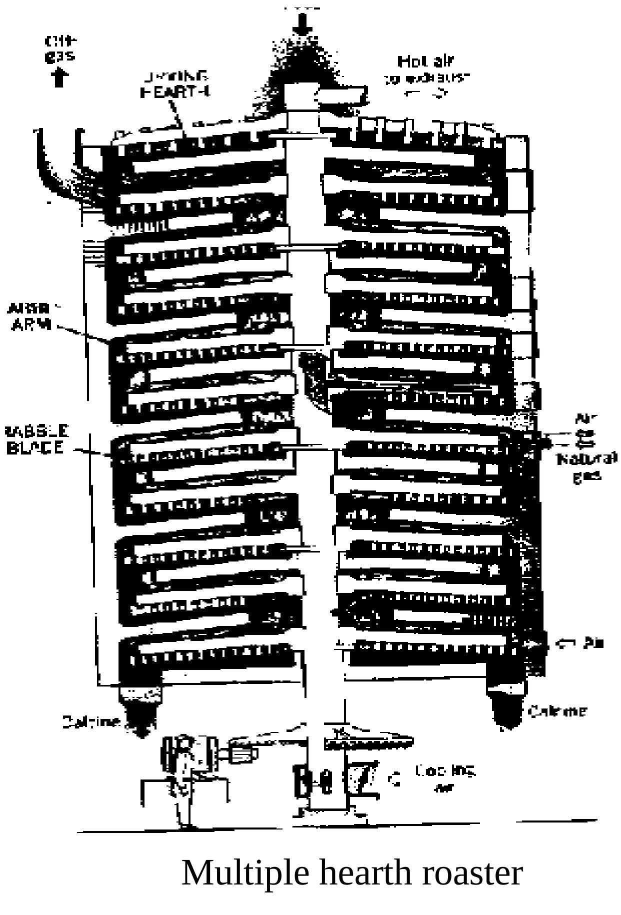
The most widely accepted metallurgical roaster was first designed by MacDougall in England towards the end of the nineteenth century. Its gives the basic principle of counter current flow of the solid ore and the oxidizing gases.

There are mainly 4 types of roasting process:

- Multiple hearth roasting
- Flash roasting
- Fluosolid roasting(Fluidized bed roasting)
- Sinter roasting(Blast roasting)

Multiple Hearth Roasting:

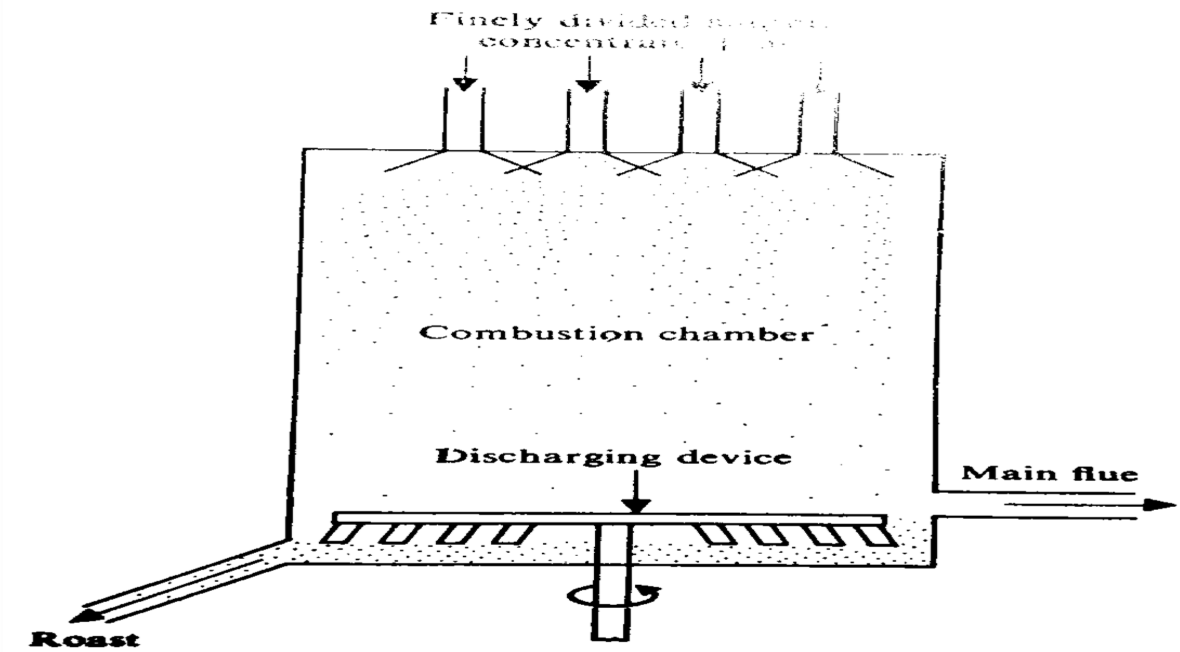
- ✓ A typical MacDougall type roaster consists of several (about 10) circular brick hearths superimposed on each other.
- ✓ The structure is enclosed in a cylindrical brick lined steel shell.
- ✓ Revolving mechanical rabbles attached to arms move over the surface of each hearth to shift the ore.
- ✓ The arms are attached to a rotating central shaft that passes through the centre
- ✓ Ore automatically discharged at top and moves downward and emerges at the bottom.
- ✓ Oxidizing gas flow upward i.e. counter current to descending charge.
- ✓ The hearth at the top dry and heat the charge
- ✓ Ignition & oxidation are occurs at lower portion.
- ✓ Drawbacks-Roasting is slow & sulphur gas evolved is unsuitable for production of sulphuric acid.



Multiple hearth roaster

Flash roasting:

- ✓ In flash roasting preheated ore particles are made to fall through a body of hot air having instantaneous oxidation or 'flashing' of the combustible constituents of the ore, mainly sulphur.
- ✓ A flash roaster was constructed by removing intermediate hearths in a multiple hearth type reactor and creating a large combustible zone.



Flash roaster

Fluosolid roasting (fluidized bed roasting):

- ✓ In fluosolid roasting, the ore particles are roasted while suspended in an upward stream of gas.
- ✓ When a gas is passed upwards through a bed of solid particles- small and preferably regular size over the range 0,005-0.05 cm in diameter the behaviour of the bed depends on the velocity of the gas.
- ✓ Different stages are observed of the porous bed that resr on perforated grate through which gas is forced upward.

Stage-1

- Here the gas flow rate is slow and bed is porous.
- Here the gas permeates the bed without disturbing the ore particle smoothly.
- Here the pressure drop across the bed is proportional to flow rate.

Stage-2

- Here gas velocity increases and bed expands upward due to drag force by gas stream.
- Here the pressure drop across the bed depends on the gas velocity.

Stage-3

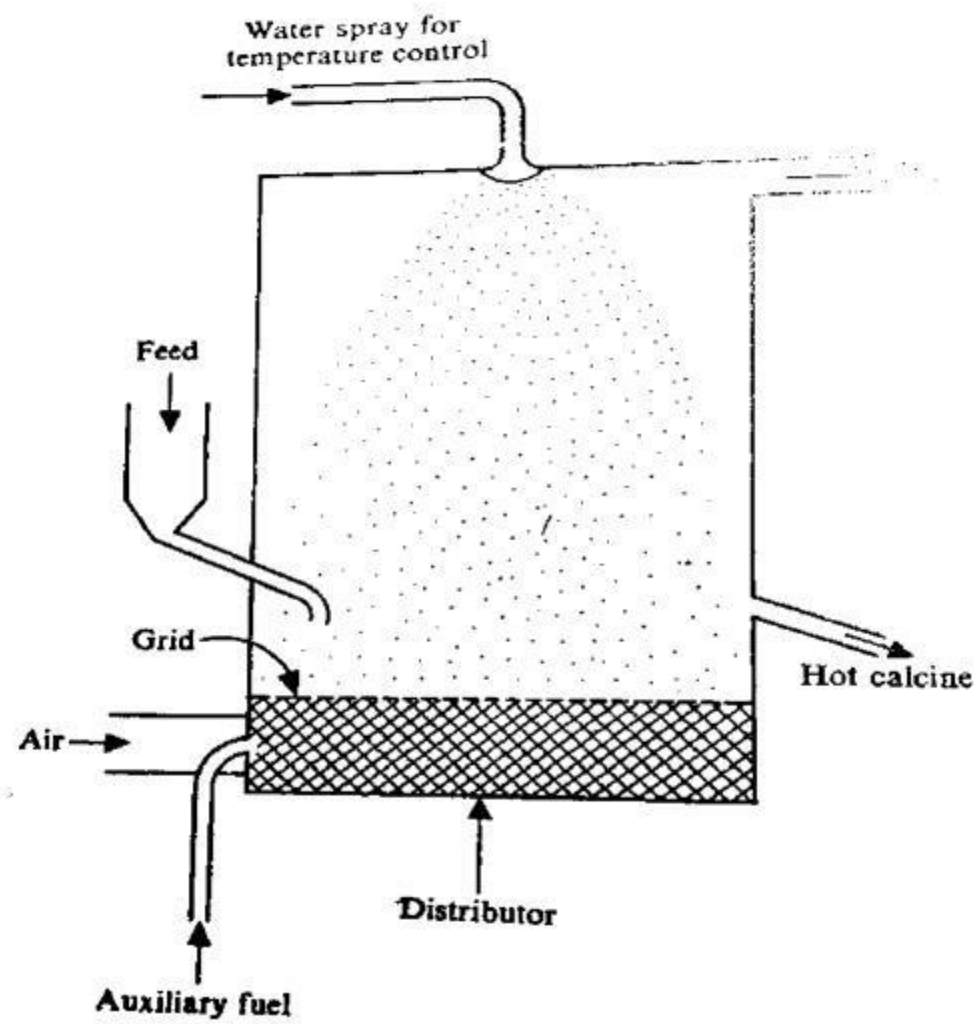
- When gas velocity further increased stage formed where the pressure drop across the bed is equal to the weight of the particles.

Stage-4

- Further increase in gas velocity expands the bed & expansion results in increase the interparticle distance.
- Pressure drop across the bed continue to decreases as the gas velocity increases.

Stage-5

- In final stage expansion of bed became independent of gas velocity.
- Out coming gas stream forms & appear in form of bubbles bursting on surface of bed.
- Its looks like boiling liquid.
- The bed is said to be fluidized & high degree of mixing of solid particles takes place.
- The solid fluid is called pseudo-fluid placed in fluidized bed reactor.
- The fluidization behaviour of a bed can be graphically represented by plotting the pressure drop.



Sinter roasting (blast roasting)

- Heavy dust loss if agglomeration is not done.
- Fine ore have to be agglomerate before they charged into blast furnace.
- It is done for sulphide ore in a sintering machine where sintering and agglomeration take place simultaneously.
- Sintering is carried out in Dwight-Lloyd sintering machine.

Steps in sinter roasting:

- The fine concentrate is discharged 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 are 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 acts as a fuel.
- But for an oxide or fuel is required. Ex- iron ore.

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, and then roasting continues to proceed even in the absence of any external heat such a reaction is termed as autogenously.

ELLINGHAM DIAGRAM:

- It is a free energy data that graphically plot ΔG^O vs T for compound (oxide & sulphides).
- In E.D highly stable oxides are found at the bottom & less stable oxide occupy higher position.
- An element occupying a lower position in the diagram can always reduce the oxide of another metal lying above.
- Where phase transformation does not occurs the plots are almost straight lines.
- An Ellingham diagram shows the relation between temperature and the stability of a compound. It is basically a graphical representation of Gibbs Energy Flow.

*In metallurgy, we make use of the Ellingham diagram to plot the reduction process equations. This helps us to find the most suitable reducing agent when we reduce oxides to give us pure metals.

- Here ΔG is plotted in relation to the temperature.
- The slope of the curve is the entropy and the intercept represents the enthalpy.
- As ΔH (enthalpy) is not affected by the temperature
- Even ΔS that is the entropy is unaffected by the temperature. However, there is a condition here, that a phase change should not occur.

- We will plot the temperature on the Y-axis and the ΔG on the X axis in the given figure below.
- Metals that have curves at the bottom of the diagram reduce the metals found more towards the top.

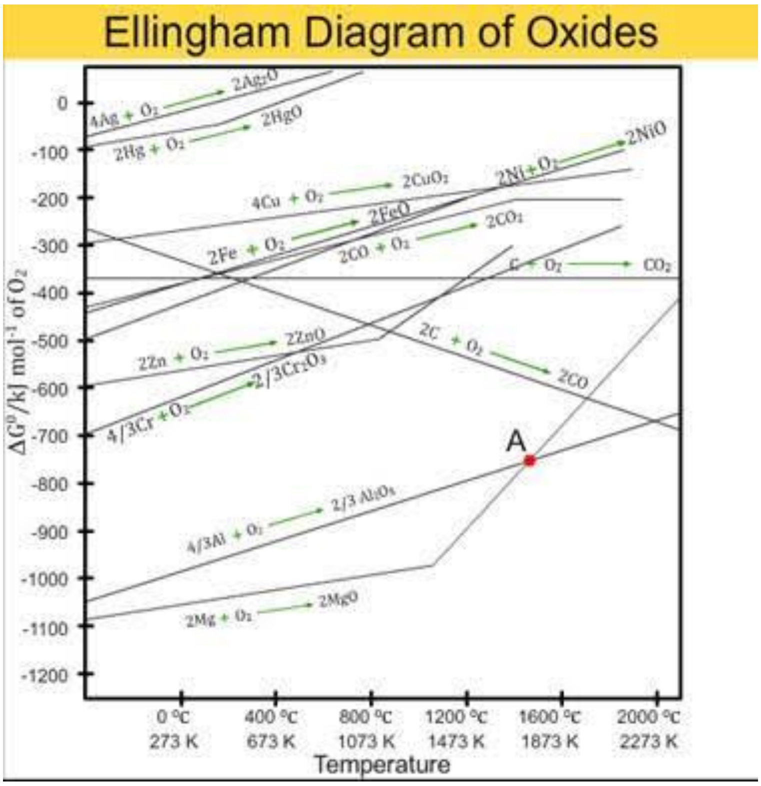
*The reaction of metal with air can be generally represented as

M (s) + O2 (g) → MO (s)

Uses of Ellingham Diagram:

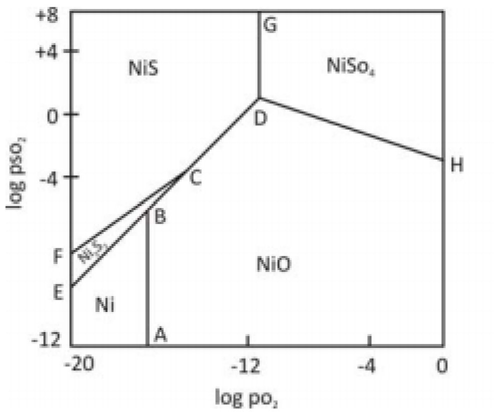
The main application of E.D is in extractive metallurgy industries.
The free energy change at equilibrium of formation of metal oxide from metal & O2 at any temperature can be directly determined from diagram.
1) Alumino Thermic Process
2) Extraction of Iron

<u>Ellingham diagram for Reduction of Oxides</u>:



PREDOMINANCE AREA DIAGRAM(SULPHIDES)

- The isothermal behaviour 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 SO2 gas obtains.
- In order to describe this diagram, let us consider Ni-S-O system at 1000K.



(Predominance area diagram for Ni-S- O system at constant temperature)

- At 1000K this system contains the condensed phases Ni, NiO, NiS, Ni3S2,NiSO4.
- The gas phase contains SO2 and O2 but some amount of SO3 and S2 may also be present inside the roaster.
- It is a two dimensional diagram drawn between log pso2 and log po2, 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.) is the invariant point's and at these points three phases coexist.

Utility of predominance – area diagram (PAD)

1. PAD shows the stable phase under different conditions(gas pressure)
2. PAD predicts possible processing routes.
3. One can predict the conditions for formation of a particular phase. In dead roasting of PbS, PbO can form several compounds like PbSO4. 4PbO, PbSO4. 2PbO and PbSO4. PbO.
4. It is possible thermodynamically to produce metal from sulphide by controlling PO2.

*(For more information follow the Extraction of NonFferrous metals H.S Ray pg no-134-135)

Smelting

- It is a heating process of production of metal or matte.
- Main Reducing agent used is C/S/sulphide.
- Furnace used is 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
- In matte smelting no reducing agent is used because sulphide itself acts as reducing agent

Blast furnace- reduction smelting
Reverberatory furnace- matte smelting
Electric arc furnace- reduction smelting and matte smelting

Characteristics of smelting operation-

I. Material to be smelted are charged in solid state
II. Products of smelting furnace are in liquid state.

SMELTING FURNACES:

- Blast furnace smelting of iron ore is best example of S/F.
- We can smelt in electric arc furnace temp around 2000degree C.
- *Types*

1. Flash smelting
2. Hearth smelting
3. Matte smelting

Flash smelting:

- It is used for concentrated of nickel sulphide and cupper sulphide
- F/S combines the operation of flash roasting+smelting.
- The concentrate burns with oxygen in combustion chamber & sufficient heat is generated in form of matte and slag and get settle.
- Here preheated air is used to increase combustion rate & form autogeneous smelting
- Gas comes out from the furnace are very rich in sulphur dioxide.

Matte smelting:

- Here sulphide ore is fused with a flux to produce a molten mixture of sulphide called as matte.
- Gangue material goes into slag & immiscible with matte & form a separate layer.
- Matte have high electrical conductivity & a density between metal and that of slag
- Mattes are insoluble in metal and slag phase.
- M/S is carried out in reverberatory furnace followed by roasting operation
- M/S is done for Cu, Ni, Sb extraction.
- Copper is recovered from matte smelting by a machine called Converting.

Hearth smelting:

- H/S is carried out in hearth furnace like blast furnace.
- It is carried out for oxide ore.
- C & CO is used as Reducing agent.
- There is no requirement of prior roasting before smelting in H/S.
- It is not a autogeneous process, extra amount of fuel is required for smelting.
- By product gas contains CO that is used for reheating the other material.

TYPES OF REDUCTION:

- Carbothermic reduction
- Metallothermic reduction

Carbothermic reduction:

Carbon is most unique reducing agent because it is expensive & widely available.

$MO + C = M + CO$ e.g

$Fe2O3 + C = 2Fe + 3CO$

According to ellighnam diagram C can reduce all the oxide at different temperature.

These reaction takes place between 2 solids in the form of solid state diffusion & rate is slow.

Metallothermic reduction:

When a oxide is reduced by the metal the reduction reaction is called metallothermic reduction.

It is carried out in an open container or closed container called bomb avoiding C contact.

It is used in small scale.

e.g Thermit reduction-
$Fe_2O_3 + 2Al = Al_2O_3 + Fe$ (product are in liquid state)

METHODS OF DISTILLATION AND SUBLIMATION(PROCESS OF PURIFICATION)

DISTILLATION(chemical process)

- The action of purifying a liquid by a process of heating & cooling at suitable temperature .
- It is the process of separating the components or substances from a liquid mixture by selective boiling & condensation.
- Liquid having different boiling points can be separated from each other & the vapours is then fed into a condenser for purification.
- E,g pure Zn (B.p =907 degree C) can be distilled from brass at 800degree C.

Pb (B.p =1740 degree C) refining by removing Zn by Vacuum distillation.

Mg & Al can be separated from each other .

SUBLIMATION

- It is the phase transition of a substance directly from solid to gas without passing intermediate liquid phase.
- It is an endothermic process.
- E,g snow & ice sublime
  Dry ice sublime
  Naphthalene
  Camphor
  - It is also a purification process to purify compound in sublimation apparatus.
  - Sublimation is done on metal having high vapour pressure.
  - It is advantageous if occurs at low temperature .
  - After sublimation non volatile particles are left.
  -

PROCESS OF CONVERTING:

- CONVERTING OF MATTE
- CONVERTING OF PIG IRON

CONVERTING OF MATTE:(Cu converter)

- Generally converting is carried out for matte.
- The purpose of converting is to remove Fe,S & other impurities from Cu matte.
- For converting the matte is charged into a converter where O2 is supplied to the liquid matte at high pressure
- The converter is lined with chrome magnesite refractory.

- In the converter the atmosphere is oxidising compare to other atmosphere.
- Air or O2 enriched air is injected to molten matte.
- The O2 is directly reacting with the impurities present in the matte i.e Fe,mainly Fe & S
- The impurities are form its oxide & make a slag.
- After oxidation of all the impurities it come to the slag living behind approximately pure Cu.
- The process is autogeneous because all the oxidation reaction is exothermic in nature.

CONVERTING OF PIGIRON:(Fe converter-steel making process)

- Pig iron formed from blast furnace are in liquid state and having high heat content.
- Pig iron charged into the converter for removing impurities.
- The vessel is lined with the magnesite refractory.
- Pure oxygen is lanced into the hot metal .
- This is a autogeneous process & exothermic in nature.
- Flux is charged into the converter for stabilizing the acidic impurities & give protection to the vessel refractory.
- After formation of slag it float over the metal which is removes after oxidation of all impurities.

HYDROMETALLURGICAL PROCESS

- ❖ It involved the use of aqueous chemistry for recovery of metal from ore.
- ❖ It is done to low grade ore.

Stages of hydrometallurgy :
Preparation of ore for leaching
Leaching
Separation of leach liquor
Recovery of metallic value from leach liquor
Recycling of leach liquor

Preparation of ore for leaching:

- Its include crushing,grinding,concentrating of metallic value to remove impurities.
- The impurities are removed by physical methods like roasting.

Leaching:

- Metallic value of ore is selectively dissolved by using a suitable liquid reagent.
- The selectivity in dissolution depends on the nature of the reagengt
- Rate of leaching depends on various factors like temp,pressure,volume of leaching,ore particle size etc.

Separating of leach liquor:
The leach liquor is separated from residue lleft behind after the leaching,settling,thickening,filtration and washing.

Recovery of metallic value from leach liquor;

The metallic value from leach liquor is separated by precipitation,cementation,electrolysis,ion exchange & solvent extraction.

Recycling of leach liquor:

Leach liquor is recycled after it has been purified & its composition is readjusted.

Objectives of hydrometallurgy:

1. To produce high degree of purity
2. To produce metal from crude metal or metal compound which has already been prepared by other method.
3. To produce a metal directly from an ore.

Advantages of hydrometallurgy:

1. Suitable for lean & complex ore
2. This operation ensure greater control than other & resulting in the recovery of valuble by product.
3. It is enviormental friendly & obey enviorment protection law.
4. Due to rapid increase in cost of metallurgical coak an aqueous media is more preferable.
5. Here metals of different variety form such as powders & nodules.
6. This operation is carried out in room temperature.
7. Here waste liquor is recycled.

Disadvantages of hydrometallurgy:

1. Large volumes of dilute solution input involves to obtain relatively small output.
2. Handling of chemicals is difficult.
3. Large amount of space is required
4. Corrosion is often formed as well as erosion of tanks & ducts.
5. Cost of reagent & equipment may be high.
6. The disposal of effluents is a serious problem.

Leaching reagent:

- The leaching reagent include all chemicals & water based.
- In some cases plain water itself can be used as a solvent.
- Acid or alkalis of varying degree are employed.
  Acids-H_2SO_4,HCl
  Alkalies-NaoH,Na_2CO_3,NH_4OH
- Leaching reagent must be selective & as rapid
- It should be possible to dissolve the reagent in order to prepare a strong leaching solution.
- The reagent should not corrode the equipment.
- The reagent should be economical & allow regeneration.

leaching techniques/operation:

types:

1. Insitu leaching
2. Dump leaching
3. Heap leaching

4. Percolation leaching
5. Agitation leaching

First 3 process are traditional technique treat the ore body at the mine site itself with minimum use of equipment.

Insitu leaching:

Here the leaching of the shattered rock residue left behind in a mine after the majour mining operation or in ore deposit.

Dump leaching:

Application of leach solution to dumps consist of off grade ore rejected during normal mining operation.

Heap leaching:

When higher grade of ore are leached in a pre determined manner dumps is heap leaching.

Percolation leaching:

Here the leach solution is percolated upward or downward through an crushed ore bedded into tanks (coarse & fine ore).

Agitation leaching:

In agitation leaching stirring is used to aid the dissolution process.

Pressure leaching:

- Many leaching reactions are carried out in autoclave under high pressures.
- At pressures higher than atmospheric, the boiling point of water increases and temperatures higher than 100°C become available. Leaching is therefore accelerated.
- With increase in pressure the rate of solubility or dissolution increases.
- Pressure would influence if a gaseous reactant such as oxygen or ammonia is present.
- The concentration of these gases in solution will increase with increase in pressure thus enhancing the leaching rate.

Bacterial leaching/Microbial leaching:

- Done for mainly sulphide minerals.
- Accidentally discovered in the early part of twentieth century that certain type of bacteria speed up the natural process.
- Natural process are slow and takes year to produce solution.
- The mincral sulphides that leach faster in the presence of Suitable type of bacteria are -arsenopyrite ($FeS2$. $FeAs$), bornite ($CuFeS$.), chalcopyrite

(CuFeS), enargite (3Cu,S, As2S5,), galena (PbS), marcasite (FeS), millerite (NiS), orpiment (As2S3,), pyrite (FeS) etc.

- Bacterial leaching not only leads to an enhanced dissolution rate but also to an effectively greater extent of recovery.
- The three most important types of bacteria of leaching are

Thiobacillus thiooxidans,

Thiobacillus ferrooxidans,

Ferrobacillus ferrooxidans.

- They are capable of growing in purely inorganic media, obtaining their energy by oxidizing inorganic substances such as –
  i. şulphur and thiosulphate.to sulphate
  ii. and ferrous iron to ferric jon.

- A biological catalyst, called enzyme, is synthesized by the bacteria and helps in acclerating the rate of oxidation reaction.

The oxidation of sulphide minerals can be expressed by the reactions

$S + O_2 + H_2O = H_2SO_4$

$Cus + 2O, = Cu^{+2} + SO_4^{-2}$

EFFECT OF VARIOUS FACTORS ON BACTERIA

Elfect of Temperature

30°C and 35°C is the most required temperature.
As the temperature increases above 50°C, the activity almost stops.
Temperature higher than 70°C, the bacterial microrganisms become sterile and destroyed
As the temperature decreases below 30°C. activity also decreases.
At a temperature below 18°C, it is negligible from a commercial point of view.

Effect of Nutrients

Bacterial nutrients such as $FeSO_4$, FeS_2, $(NH_4)_2,SO_4$, to the leaching solution increases the concentration.
Here the rate and the extent of extraction are increased.

Effect of Particle Size and Bed Depth

The bacterial oxidation rate depends on the surface of the solid material present because the bacteria concentrate at the solid surface contact with the solution and build up colonies there.
Finely ground particles can cover a great surface area, leading to an increased leaching rate.
Very finely ground particles inhibit leaching because both the permeability of the solution and the air supply are reduced.

Shallow bed enhances the leaching rate.

Effect of Radiation

When exposed to direct sunlight, a bacterial culture becomes inactive, but is not destroyed. Bacteria are sensitive to ultravioletlight, so it completely sterilizes it.

Effect of Acidity and Aeration

Oxidizing bacteria are active only in acid media having a pH value between 2.0 and 3.5.
Both above and below these pH values, the rate of bacterial ozidation decreases.
PH having 6, the oxidation is almost completely inhibited.
Bacteria are destroyed in an alkaline medium.
Oxygen is supplied by aerating a portion of the bacterial solution and transferring the aerated solution to the site of bacterial activity.

SEPARATING OF LEACH LIQUOR

After separating leach liquor 2 product formed

1. Liquor having metallic value
2. Solid residue(gangue)

   Reduction of metals from a solution is a complex process & the reducible ions may be present as hydrated cations or complex ions.

So separating of leach liquor from residue achieved by various technique like

- Cementation
- Gaseous reduction
- Electrolysis

Cementation:
It is precipitatation of a metal from an aqueous solution of its salt by another metal.
The basic mechanism is electrochemical in nature.
Here a more reactive metal dissolve in a solution to precipited a less reactive metal.
Emf series can be used to determined the reactivity of a metal.
e.g-Al or Zn can be added to gold cyanide solution to precipited gold.
Precipitation of Cu from $CuSO_4$ by Fe.

Gaseous reduction:
A million tons of pure powders of Cu,Ni,Co metals are produced.
The product of gaseous reduction i.e metallic powders find application in powders metallurgy.
In gaseous reduction gases such as SO_2,CO & H_2 under pressure to effect the final precipitation of metals directly from their solution.

Electrolysis;
Will discuss in the electrometallurgy.

ELECTROMETALLURICAL PROCESS

It includes all the metallurgical process which utilizes e;ectricity & electrical effects.
It includes all the process like electrowinning,electrorefining,electrodeposition,electrolysis etc.

Electrolysis:

- This is a chemical change by using electricity.
- It is a technique that uses a direct electric current.
- It is used for separating of elements from ores using electrolytic cell ,electrolytic cell-it breakup an ionic compound to forms elements.
- Voltage is needed for electrolysis to occurs called decomposition potential.

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.

Components:

1. An electrolyte(molten in nature that will carry electric current)
2. A DC current electrical supply. Electric current is carried by electrons in external circuits.
3. Two electrode-metal /graphite & semiconductors

At cathode—ve charge electrode attract the

EMF series:

- It is the classification of metals in order of their electropositivity i.e their tendency to loose electrons.
- For simplicity all the potential are reffered against the hydrogen electrode H2-H+ which E 0 is zero.
- In these series the reactive metals are at top of the list with large –ve potential i.e these metal dissolve readily.
- Lithium is the most active metal.
- Nobel metal are at the top of the list with large +ve potential i.e these metals are not dissolved easily but are deposited.
- Gold at the top of the list is most nobel metal.
- Only pure metals are their in EMF series.
- Metals are ranked in respect to inherent reactivity.

Application of emf series:

1. Emf series is helpful in determine the tendency of a metal to release energy & corrode.
2. For choosing element as oxidising agent.
3. For choosing element as reducing agent.
4. For studying displacement reaction.
5. To predict which metal will displace another from it salt solution.
6. For corrosion treartment.
7. For construction of a cell.

FARADAYS LAW OF ELECTROLYSIS:

Faraday-F –It is a unit quantity of electricity
1 F =6.02 x 10 23 e- or 96493 coloumb = 96500 C
The relationship between the quantity of electricity passed & the amount of substance formed at the electrode is Faraday Law.
It is of 2 types-

1. 1st law of Faraday
2. 2nd law of faraday

1st law of Faraday:

The amount of electrolytically liberated substance is directly proportional to the quantity of electricity passes through the solution.
$W \alpha It$
$W = Zit$
W =weight of substance formed at an electrode by the passage of current I amp for It second.
So I x t is the total charged passed.
Z=electrochemical equilavent
Z=Electrochemical equivalent of a substance which liberated during electrolysis by the passage of a steady current of 1 amp for one second i.e by 1 C of electricity.

2nd law of electrolysis:

The weight of various substances deposited on or dissolved at several electrode by the same quantity of electricity are directly proportional to their respective equivalent weight.
$W \alpha E$
W=weight of the substances deposited.
E=equivalent weight=atomic wt/electrochemical valency

Faradays laws are applicable to both aqueous & fused electrolytes for discharge of ion at electrode.

ELECTROWINNING & ELECTROREFINING:

Both are electrolytic process
Electrowinning-

It is a process in electrometallurgy that produce a metal by electrolysis of an aqueous solution or a fused salt.

In electrowinning current is passed from anode through a liquid leach silution of metal and the metal is extracted as it deposited in an electroplating process onto the cathode.

In electrowinning the anode is an insoluble conductor while in electrorfining it is impure metal itself.

Electrorefining:

It is also a process of electrometallurgy based on refining process.

It is a process to remove impurities from a metal.

Here the anode consists of unrefined impure metal & as current passed through electyrolyte the anode get corroded into the solution so that the refined pure metal get deposited onto the cathode.

The cathode may be pure metal of pure starting sheet or some times blank of another metal.

REFINING PROCESS

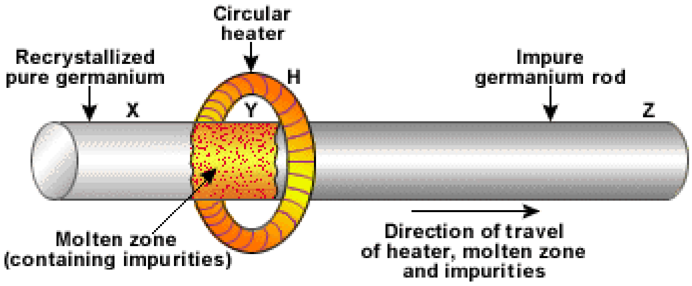
Zone refining

Fire refining

Zone refining:

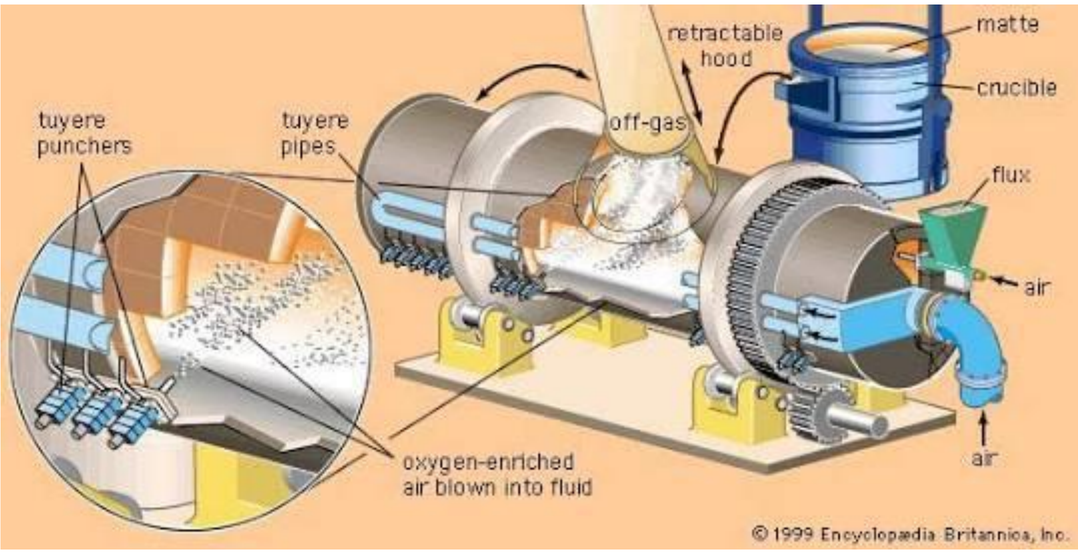
- This method of refining is based on the principle of fractional crystallization. In this technique ultra-refined pure metal is obtained with a restriction that the starting material has low concentration of impurities.
- The impurities have high solubility in the molten metal as compared in the solid 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.

e.g A high purity 99.99% (tantalum single crystal) made by zone refining.



Fire refining:

- This technique is used to remove more reactive elements from a molten metal bypreferential 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.



PRINCIPLE OF METAL EXTRACTIONS—THERMODYNAMICS

It is branch of physical science that deals with the relation between heat & other forms of energy (mech,elect,chemical)

It concerned & give relation between heat & temperature & their relation between heat and temperature.
It deals with heat =work=energy.

LAW OF THERMODYNAMICS
There are basically 4 laws of thermodynamics to define fundamentals physical quantity like (temperature,Energy ,entropy)

Zeroth law of thermodynamics

- If two system are in thermal equilibrium with a third system,then they are in thermal equilibrium with each other.
- This law helps to define the concept of temperature i .e temperature is a important property in thermal equilibrium.
- It's shows equality of temperature & it preceeds the other laws.

e.g If system B is thermal equilibrium with both A & C .,then system A is in thermal equilibrium with system C.

1st law of thermodynamics

- It's shows heat is work ,work is heat.
- This is law of conservation of energy.
- Energy can neither be created nor be destroyed,but it can change from one place to another.
- Heat is a form of energy.
- The 1st law of thermodynamics is a version of law of conservation of energy adapted for a thermodynamics system.
- 1st law suggest that increase in Internal energy of a closed system is equal to the heat supplied to the system minus work done by it.
  i.e del E =q-w
  Del E = E2-E2
  E2-E1=q-w
  q=heat absorbed
  -w=work done by the system
  - When the system loses energy as a result of doing some form of work w may be different kinds.

  W= W volume+W elect+W magnetic+W surface+....
  We always take only volume work i.e workdone against pressure.
  The work is Pdv ,where P=pressure,V=volume
  So del E = q-Pdv---------------(this is the 1st law of thermodynamics)

Condition:

- If q is +be ,then system gain energy in the form of heat.
- If q is -ve , energy is loss(release).
- W=+ve,workdone on the system.
- W=-ve ,workdone by the system.

Application of 1st law :

- Changes of heat depends on the initial and final state ,from this application the amount of fuel required for the metallurgical process can be calculated.
- From 1st law we can calculate the enthalpy change for a reaction.

Internal energy:

- The internal energy of a system is the energy within the system.
- Every system has within itself a definite quantity of energy called internal energy.
- The internal energy of a system can be changed by transfer of matter or heat or by doing work.
- e.g Gas has internal energy as measured by its temperature.
- If heat is added internal energy increases.
- When a system change from state A to state B ,then it's internal energy will also change.
- It is denoted as (E or U)

For state A the internal energy is Dell E A
For state B the internal energy is Dell E B

Change in Internal energy is Dell EA-dell E B

- Internal energy are in several forms like molecular transistional ,vibrational,magnetic,nuclear binding,electric dipole moments.

ENTHALPY:
It is denoted as H.
The total heat content in a body/system is called enthalpy designated by the symbol H.
Thermodynamically it is represented as H=E+PV
E=Internal energy,P=pressure,H=enthalpy,V=volume.
Or total kinetic energy +potential energy of a system at constant pressure.
Change in enthalpy ΔH = change in heat of a system
$\Delta H = \Delta H\text{final} - \Delta H\text{initial}$
Unit of enthalpy is J or KJ per mol

Gibbs free energy

It is the energy that is available to do useful work.
Dell G0 =Dell H -T Dell S
G=H-TS at constant temperature
Gibbs free energy is used for spontaneity check.
If Dell G is more -ve ,the reaction will be more spontaneous.
If Dell G is more +ve,the reaction will be non spontaneous.
G=Gibbs free energy
H=enthalpy
T= temperature

S=entropy

Second law of thermodynamics

- The second law of thermodynamics tells that processes occur in a certain direction and that the energy has quality as well as quantity.
- The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus we need another general principle (second law) to identify whether a process can occur or not.
- A process can occur when and only when it satisfies both the first and the second laws of thermodynamics
- The second law is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators etc.
- Its has 3 forms
    1. Kelvin –plank statements
    2. Clasius statement
    3. Concept of entropy

: Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.
No heat engine can have a thermal efficiency of 100%.
Something will definitely loss in the form of heat to atmosphere.
W =Q1-Q2
Q≠W

- E.g A heat engine ,steam engine ,power plant, jet engine ,I/C engine that violates the Kelvin-Planck statement of the second law cannot be built.

Clacius statement

It is impossible to make a engine that transfer heat from a cold body to hot body by itself spontaneously.
Eg-refrigerator,heatpump
It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body.
e.g a refrigerator will not operate unless its compressor is driven by an external power source.
Kelvin-Planck and Clausius statements of the second law are negative statements, and a negative statement cannot be proved.

Concept of entropy

A measurement of the degree of randomness of energy in a system.
The lower the entropy the more ordered & less random & vice versa.
The entropy of the universe is always increases.
e.g-gallon of gas,preapared food

It is a new concept in thermodynamics & a conceptual property .
For reversible process entropy function is—
dS =Dq==
dS =change in entropy
T=temperature
dQrev=heat absorbed during reversible process
Entropy of the isolated system can never decreases always tends to maximum value

dQ is +ve when added
dQ is -ve when removed
high randomness means high entropy in the system.
The 2nd law of thermodynamics states that the entropy of an isolated system can never spontaneously decreases .
S .I unit = J/K Joules per degree Kelvin
It always measure ΔS not S.
The formulation of second law in terms of entropy is great interest to metallurgist & chemist.

3rd law of thermodynamics

The entropy of a pure crystalline/perfect crystal substance at absolute zero is 0.
At absolute zero all motion stops (no vibration ,no rotation).
Movement of atoms in this temperature is not possible(No entropy)
0^0K =-273.15^0 C =-495^0
Absolute zero temp is = -273.15^0 C

Henrys law

Invent by William Henry
This law state that by using pressure we can dissolve gas in liquid.
The amount of gas dissolved in a liquid is directly proportional to the external pressure applied on it.

Application:
Mixing of O2 ,CO2 in blood
Dissolution of CO2 in soft drinks
Addition of N2 ,in O2 cylinder of mountaineers to increase pressure.

Sivert's law

It is for diatomic gas
It is a rule to predict the solubility of gases in metals.
It state that the solubility of a diatomic gas in metal is proportional to the square root of the partial pressure of the gas in thermodynamic equation.

e.g H_2,O_2 & N_2 dissolved diatomic gases.

Invent by Adolf sivert
In general SA =kpA
SA =solubility of gas A
K'=a constant
PA = partial pressure of diatomic gas A
PN2=partial pressure of gas N2 at the interface

REACTION KINETICS

First order reaction:

Reaction is said to be 1st order if its rate is determined by the change of one concentration term only.

Rate varies as 1st power of the concentration of the reactant.i.e the rate increases as number of times the concentration of reactant is increased.

Unit of rate constant for1 st order is $K=min^{-1}$ or S^{-1}.

Rate constant of a 1st order reaction has only time unit. It has no concentration unit.

It is used to know what is occurring on a molecular level during a reaction & integrated rate laws are used for determining the reaction order & value of rate constant.

1st order reaction changes exponentially.

A---------→P (product) coefficient is 1
(Reactant)

$$\frac{-d[A]}{dt} \propto [A]^1 \Rightarrow$$

$$\Rightarrow \boxed{-\frac{d[A]}{dt} = K[A]^1} \quad (n=1)$$

↳ general rate law

$$\frac{d[A]}{[A]} = -k\,dt \quad (k = \text{rate constant})$$

Integrating between the limit (We will integrate from '0' concentration to initial time i.e t)

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_0^t dt \qquad (A = \text{reactant})$$

$$\left[\ln [A]\right]_{[A_0]}^{[A_t]} = -kdt$$

$$\boxed{\ln [A_t] = \ln [A_0] = -kt}$$

logarithmic form
This is called integrated law for 1st order rx^n.

($\ln$ = natural log)

From this equation we can calculate the Rate constant & the value of k. (k = rate constant)

$$k = \frac{1}{t} \ln \frac{[A_0]\ (\text{initial})}{[A_t]\ (\text{final})}$$

t = time taken to complete the rx^n.

$$kt = \ln \frac{[A_0]}{[A_t]} = \ln \frac{[A_0]}{[A_t]} = kt \qquad \left(-\ln x = \ln \frac{1}{x}\right)$$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A_t]}$$

$$\left[\frac{[A_0]}{[A_t]}\right] = e^{kt}$$

$$[A]_t = [A_0]e^{-kt}$$

It is used for calculation purpose for a rx^n

It is used for calculation purpose of a reaction.