

LECTURE NOTES
On
Principles of Extractive Metallurgy



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EXTRACTIVE METALLURGY

ORE VS MINERAL

Ore-(i)The minerals from which we can obtain metal profitably and economically is called ore.

(ii)All ores are minerals.

(iii)Ex-Bauxite is an ore of aluminium.

Mineral- (i)The naturally occurring inorganic substances which are present in the earth's crust is called mineral.

(ii)All minerals are not ore.

(iii)Ex-Clay is the mineral of aluminium.

FLUX-The substance which is added to remove impurities or gangue particles is called flux.

It is divided into 3 types i.e Acidic flux(SiO_2), Basic Flux(CaO , MgCO_3) and

Neutral Flux{cryolite(Na_3AlF_6)}

GANGUE-The unwanted particle or rocky which are comes with metal is called gangue.

SLAG-The low melting chemical compound product which is formed by the reaction between flux and gangue is called slag. It is a solution of oxide.

Flux+Gangue \rightarrow Slag

MATTE-It is a mixture of metal sulphide and some metals from which the principle metallic extracted.

SPEISS-An alloy of arsenides and antimonides of iron, cobalt, nickel, copper or other metals formed in the melting of raw materials with a high arsenic(AS) content.

DRYING-Drying is the process of removal of small amount of liquid(water/volatile liq./moisture) by application of heat to obtain dry solid or solid product.

In general drying process involves two operations; 1. Heat transfer

2. Mass transfer

Drying and Evaporation are relatively same term but are distinguish in terms of removal of water.

AGGLOMERATION PROCESS-

BRIQUETTING-

- In this process fine iron ore pressed to a particular shape with addition of water or other Binding material.
- The pressed material is hardened by heating to a suitable temperature.

- Binder like tar, pitch, limestone, bentonite etc. are generally used in briquetting as per requirement.

NODULISING-

- In this method of agglomeration, ore fines along with some carbonaceous binder like tar are passed through a rotary kiln heated by gas or oil.
- The temperature inside the kiln is sufficient enough to soften the fines. So that they get fused with each other.

VACUUM EXTRUSION-

- Moisture ore with or without binder is fed into a chamber. They are extruded to get cylindrical shape and then they are cut down up to desired length.
- The product is dried to remove the moisture content before we ignite it in blast furnace.

SINTERING-

- Sintering is an agglomeration process.
- Sinter is typically a limp mass of size 5-40mm made from ore fines below 10mm in size.
- Increase the size of ore fines, porous and strong agglomerate, remove volatiles.
- To increase the blast furnace output and decrease the coke rate.

PELLETIZING-

- Pelletizing is an agglomeration process.
- Pelletisation essentially consists of formation of small green balls.
- These green balls are of nearly 5-20mm size.
- Then dried, preheated and fired, all under oxidizing condition, to a temperature of around 1250-1300°C.

GREEN BALL FORMATION-

Green ball agglomerates are economically produced in balling drum or discs and rarely in other specialized equipment.

DISC PELLETIZER-

- Disc pelletizers are industrial machines that agglomerate powder materials and form them into uniform round pellets.
- These discs resemble flying saucers and are normally 3.6-5.6m in dia.
- These are inclined at about 45° to the horizontal.
- The material to be pelletised is generally fed directly onto the disc and moisture level is made up with the help of water sprays.
- Scraper is provided to prevent buildup of moisture material on the disc.

- It can also control the material flow pattern on the disc.

PYROMETALLURGICAL PROCESS-

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 expense of some fuel.

For example, $\text{CaCO}_3 (\text{s}) = \text{CaO} (\text{s}) + \text{CO}_2$. This reaction is endothermic and requires high temperature to decompose it in the kiln.

ROASTING

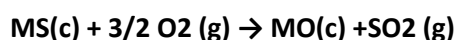
Roasting of an ore or a concentrate is a chemical process in which chemical conversion of ore is taken place by employing oxygen or other element.

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,



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_3 , 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).

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 SiO_2 , Mn to MnO , Fe to FeO , and P to P_2O_5 , 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 walls 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.

Acid oxides: SiO_2 , P_2O_5 etc.

Carbothermic reduction VS 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.

FLASH SMELTING

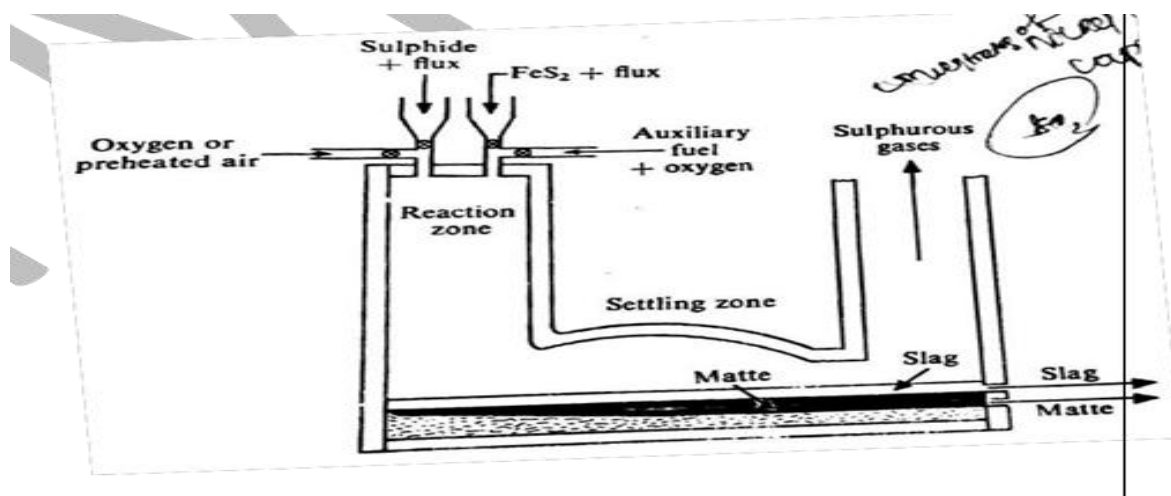
Generally flash smelting is done for the concentrates of nickel sulphide and copper sulphide.

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 FeS₂ 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, Cu₂S or Ni₃S₂ can be avoided by controlling the oxidation of the ore so as to produce only FeO and not Fe₂O₃ and Fe₃O₄. 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.

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.

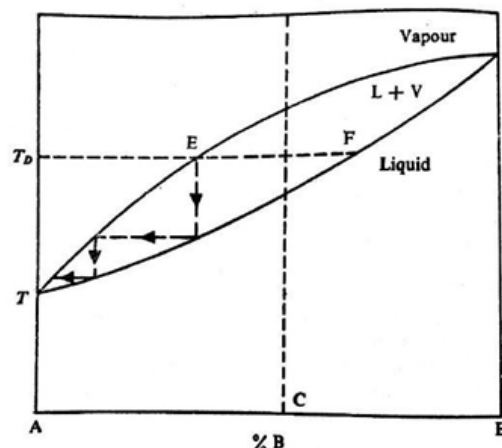
The vapour formed are led off continuously to the condenser where the distillate forms and then drops into a receptable.

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.



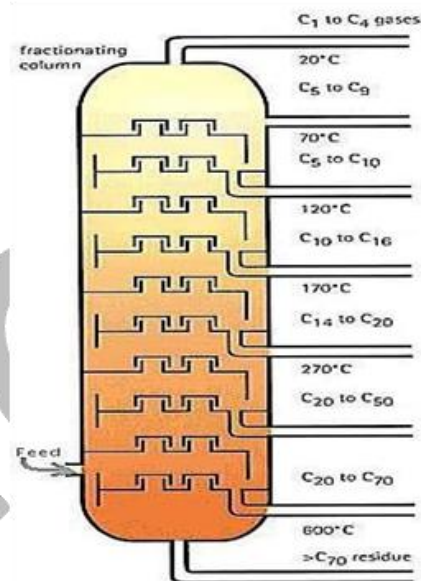
FRACTIONAL DISTILLATION

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.

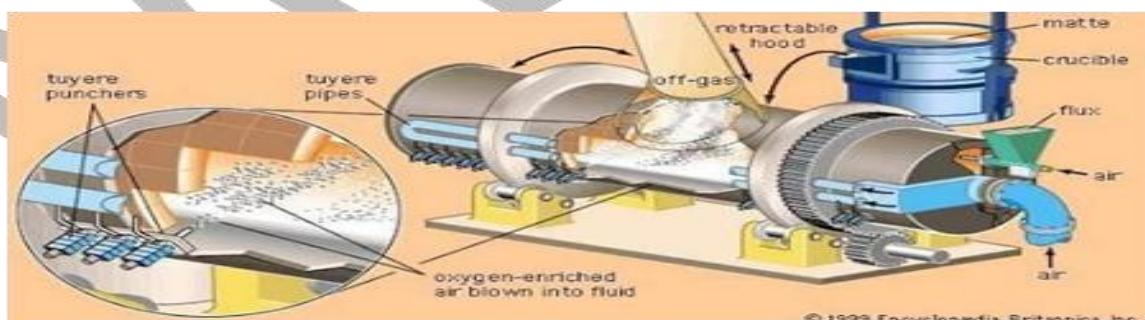
This technique is suitable for refining of iron, lead, tin and copper.

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.

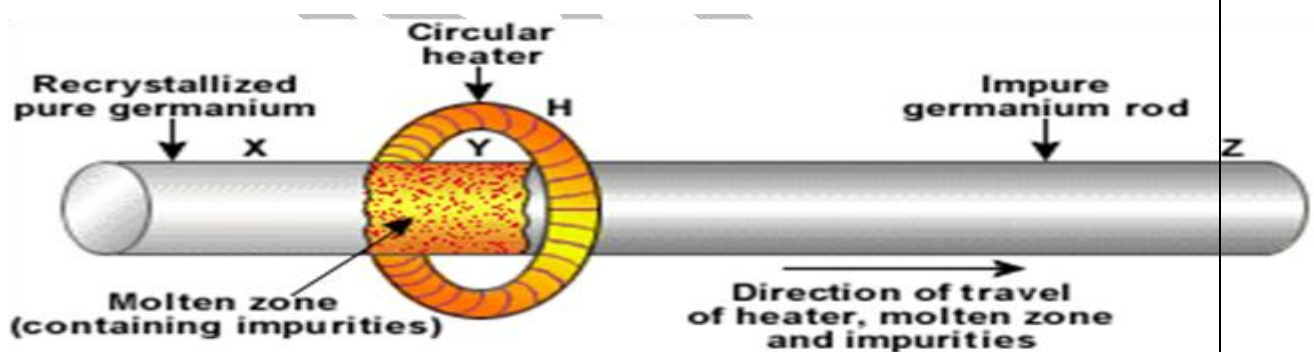
In zone refining, the impure metal is taken in form of rod, and a travelling melting zone (ring) is set up in the rod.

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.

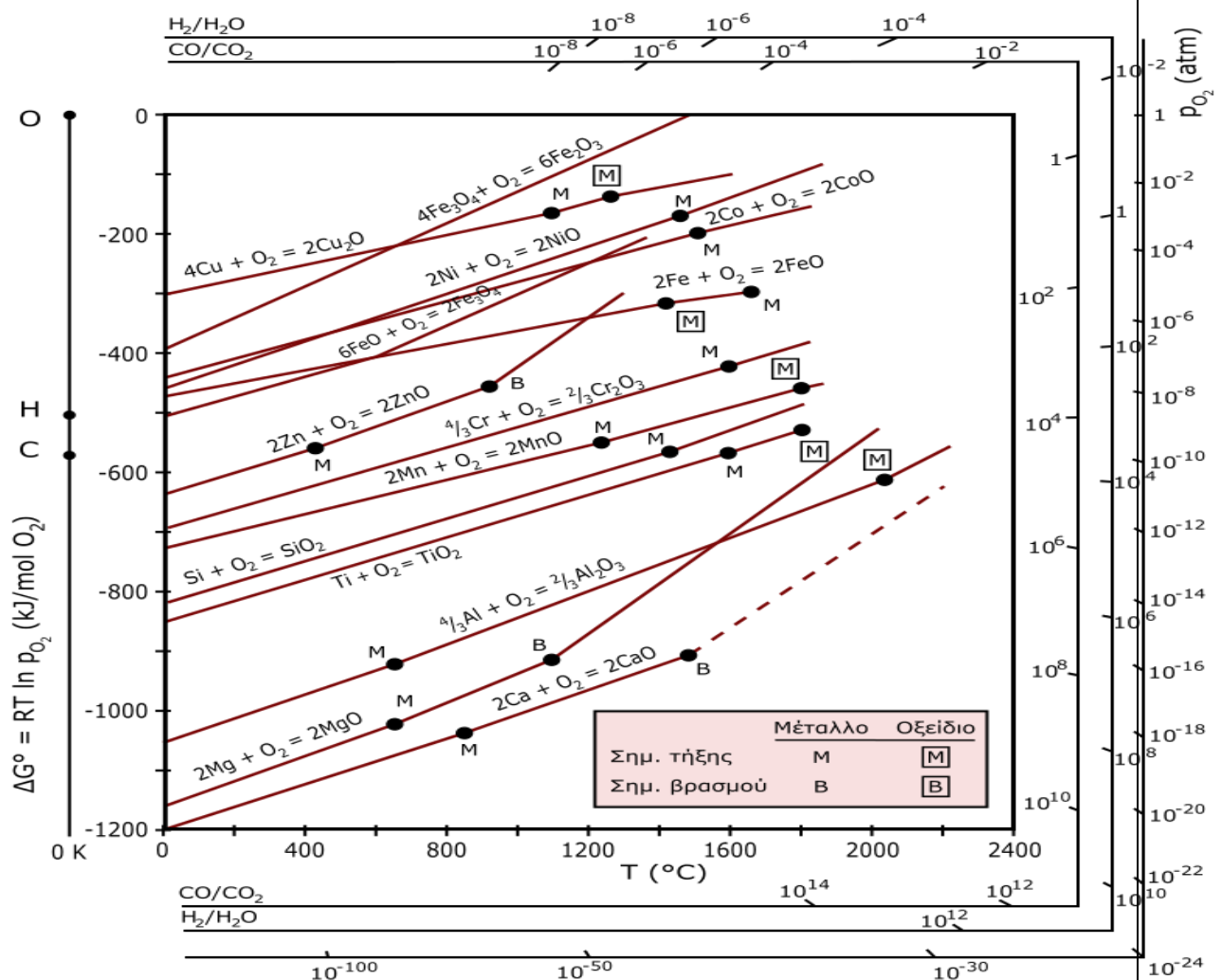
As we know that solute atom is more soluble in the liquid state than in the solid state. So when continuous movement of the zone occurs the previous part of that zone will be solidified and the impurity atom will be segregated into the molten zone created by the travelling melting zone.

When this zone moves down continuously the impurity atom also moves down and settles 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.



ELLINGHAM DIAGRAM(OXIDES)



In metallurgy, the Ellingham diagram is used to predict the equilibrium temperature between a metal, its oxide, and oxygen — and by extension, reactions of a metal with sulfur, nitrogen, and other non-metals. The diagrams are useful in predicting the conditions under which an ore will be reduced to its metal.

LIMITATIONS

Ellingham diagram is based only on the thermodynamic concepts. It does not explain the kinetics of the reduction process. The graph simply indicates whether a reaction is possible or not but not the kinetics of the reaction. → The interpretation of ΔG° is depends on K [$\Delta G^\circ = -RT \ln K$].

PREDOMINANCE AREA DIAGRAMS(SULPHIDES):

- ❖ 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

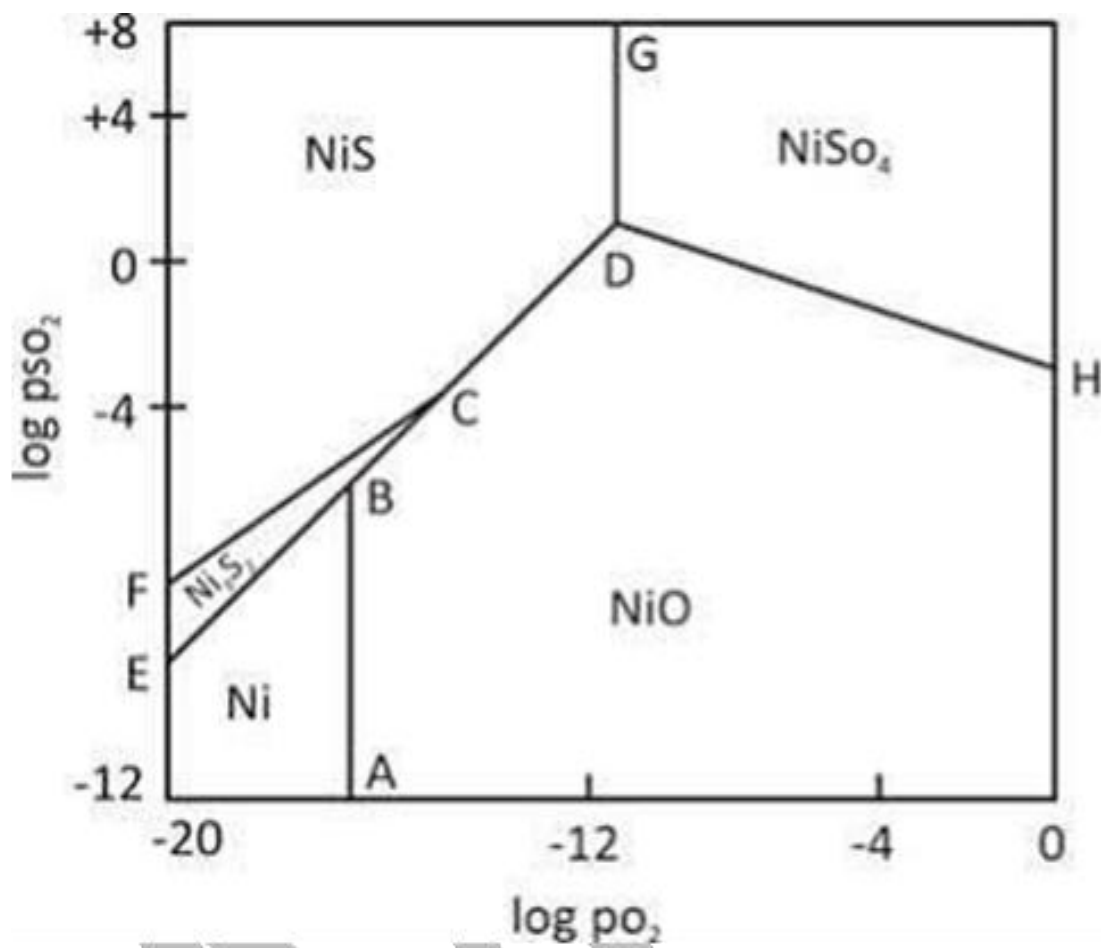
❖ At 1000K this system contains the condensed phases Ni, NiO, NiS, Ni_3S_2 , NiSO_4 .

❖ 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 $\log p_{\text{SO}_2}$ and $\log p_{\text{O}_2}$, 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.



METHOD OF DISTILLATION

Distillation, process involving the conversion of a liquid into vapour that is subsequently condensed back to liquid form. It is exemplified as its simplest when steam from a kettle becomes deposited as drops of distilled water on a cold surface.

The most commonly used techniques are simple distillation, steam distillation, and vacuum distillation.

SUBLIMATION

It is one type of refining process. Here solid doesn't convert into liquid at high temperature instead of that it directly converts into vapour phase.

Sublimation refining is carried out when a high vapour pressure of a particular metal in a compound is available. And this process is advantageous when it is possible at lower temperature.

ADVANTAGES

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

Vapour pressure of chloride increases



ZrCl_2 (High Vapour Pressure)

Guide for manufacturing and making Pig Iron. (Converting of Matte into Pig Iron)

Following three distinct operations are involved in the manufacturing process of pig-iron:

- (1) Dressing
- (2) Calcination and roasting
- (3) Smelting.

(1) Dressing

The iron ores as obtained from mines are crushed into pieces of size of 25 mm diameter. This is achieved in the rock crushers of ordinary type.

The crushing of ores helps in two ways:

- (i) The ore particles of uniform size are obtained.
- (ii) The reducing gases penetrate the ores in a better way.

If ores contain clay, loam and other earthy matter, they are washed in a stream to remove such impurities. The perforated trays may be kept in water to remove pebbles and sand. To work in dry condition, the magnetic separators are used to remove the impurities contained in the iron ores.

Other Methods Of Pig-Iron Manufacture:

In modern age, the attempts are made to modify it or to adopt new methods of manufacturing pig-iron mainly for two reasons: Following are the other alternative methods of pig-iron manufacture:

(1) Electric reduction furnace

(2) Low shaft blast furnace

(3) Sponge iron process.

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-Preparation of ore for leaching

(a)-grinding

(b)-removal of specific impurities by physical methods

(c)-roasting

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

2-Leaching

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.

Rate of leaching depends upon:-

(a)-temperature

(b)-pressure

(c)-volume of leaching liquid

(d)-ore particle size

(e)-the composition and concentration of the reagent

(f)-the pulp density

(g)-duration of 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 poses 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 , MnO_2 , KMnO_4 , FeCl)

✓ reducing agent(SO_2 , H_2)

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.

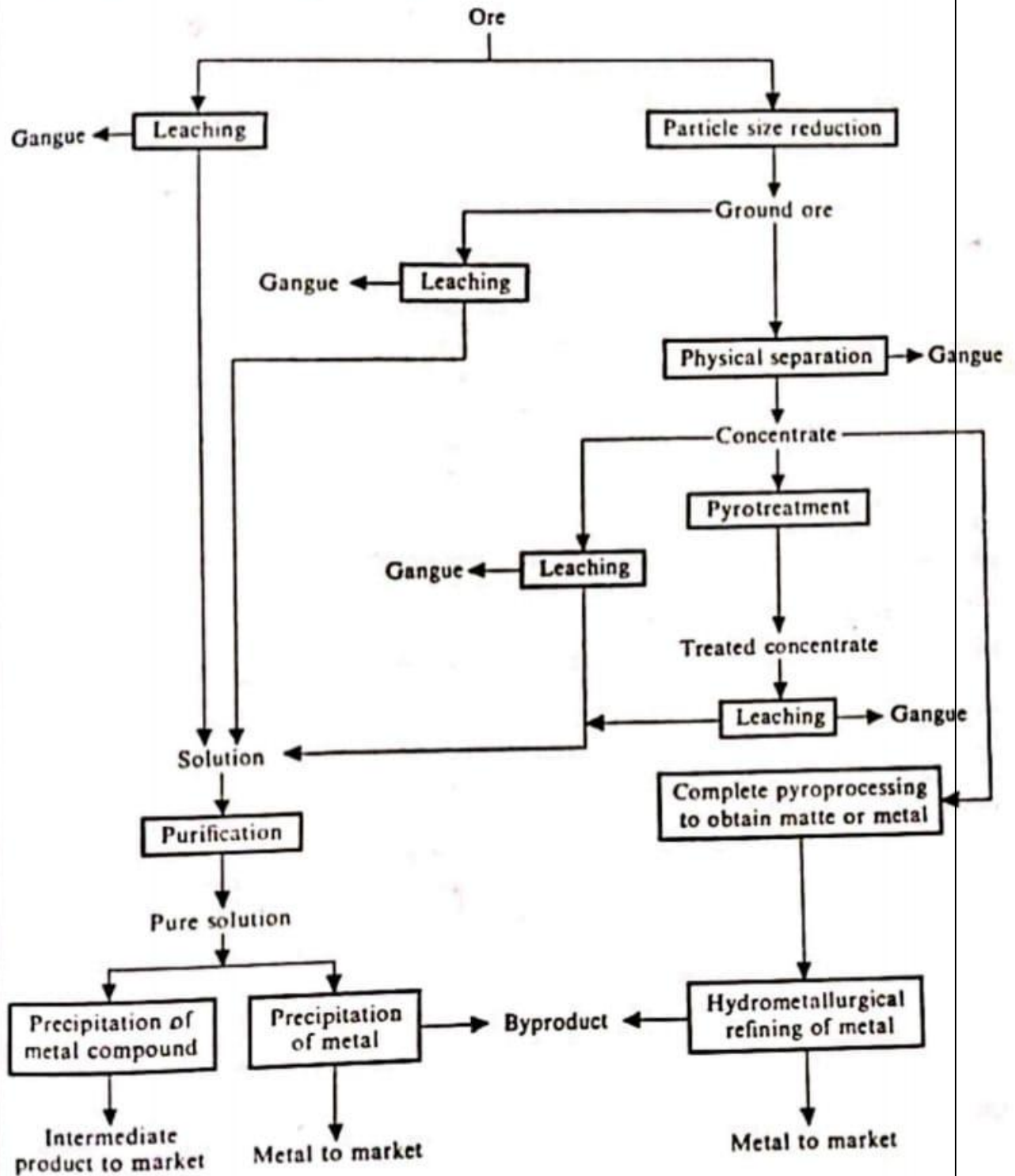


Fig. 4.11 Outline of Various Possible Hydrometallurgical Steps.

BACTERIA LEACHING

- Extraction of metal from low grade ore is usually a thick business, but some bacteria have no problem with heat.
- The metal industry uses these micro to make their extraction.
- Bacteria leaching is the extraction of metals from their ores through the use of living organisms. This is a much cheaper process; it is used to recover Cu, Zn, Ag, Al, As, Sb etc.

ADVANTAGES

1. Enhanced dissolution rate

2. Greater extent of recovery

FACTORS AFFECTING BACTERIAL LEACHING

- Effect of temperature
- Effect of nutrient
- Effect of particle size and bed width
- Effect of radiation
- Effect of acidity and radiation

PRESSURE LEACHING

- This technique is first successfully applied for Zn extraction.
- In this process Zn sulphide ore, bulk Zn concentrate are oxidized under oxygen over pressure 1200 kPa at a temp of 150°C in sulphuric acid to produce Zn sulphate solution and sulphide content is precipitated as elemental Sulphur.



INTRODUCTION TO ELECTROMETALLURGY

PRINCIPLES OF ELECTROMETALLURGY

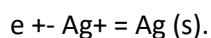
Electrolysis is an electrochemical process involved in the inter conversion of electrical energy and chemical energy—generally in ionically conducting media. Such media include aqueous solutions, molten salts and silicates, and organic liquids.

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 electrode 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



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.

ELECTRODE POTENTIAL

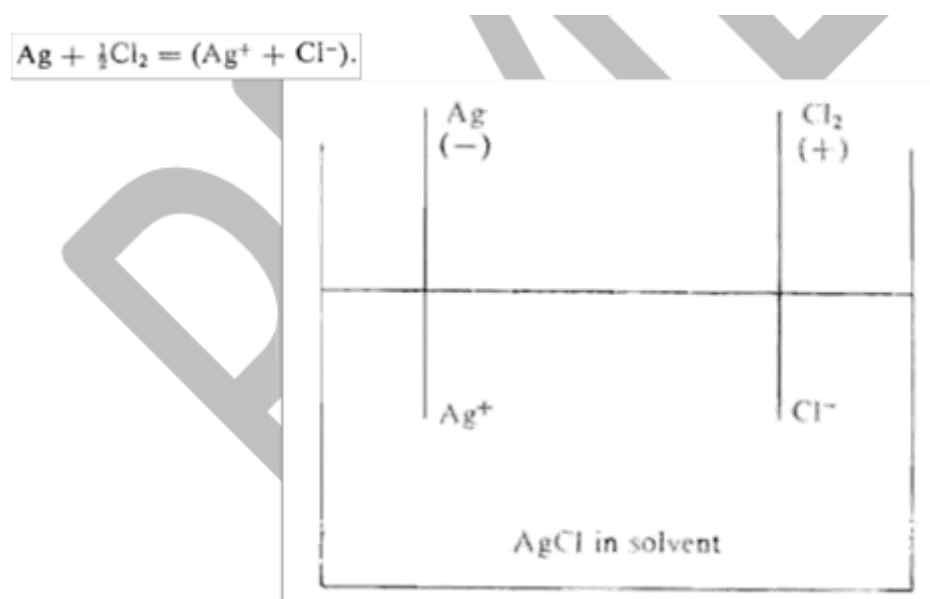
An electrode is immersed in fused salt or aqueous solution having ionic conductivity. A potential difference builds up at the interface between the two phases. This potential difference is called electrode potential, which arises due to the transfer of ions or electrons on breaking their bonds with the 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 consists 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 and the reaction at the anode is

The overall cell reaction in the solution is



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

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.

<u>Electrowinning</u>	<u>Electrorefining</u>
(i) It is the process of producing metals from an aqueous solution.	(i) It is the type of refining process based on electrolytic phenomenon.
(ii) The impure metal is in the leach solution.	(ii) The impure metal is the anode.
(iii) It is the electrodeposition of metals from the ores that have been placed in a solution via leaching.	(iii) It is the electrodeposition of metals from the ores that have been put in solution to remove impurities from the metal ore.
(iv) Difficult to separate heavy metals using this process.	(iv) Can separate heavy metals like plutonium, cesium and strontium from the less-toxic bulk of Uranium.
(v) Ex: Lead (Pb), Copper (Cu), gold (Au), Silver (Ag), Zinc (Zn), aluminium (Al), Chromium (Cr) etc.	(v) Ex: Radium, Electrolyte, Purity, Cathode, Anode, solvent extraction, H_2SO_4

METALLURGICAL THERMODYNAMICS

Metallurgical thermodynamics deals with the study of following.

Inter conversion of energy from one form to another be established of equilibrium during metallurgical process.

SYSTEM

- a. Open system (both energy and mass exchange between system and surrounding)
- b. Close system (only energy exchange)
- c. Isolated system (Neither energy nor mass exchange)

1ST LAW OF THERMODYNAMICS

Energy can neither be created nor be destroyed one form of energy is transferred into another form. The total energy of system and surrounding is constant.

$$E_{\text{SYST}} + E_{\text{SURROUNDING}} = \text{Constant}$$

This gives an idea about laws of conservation energy.

MATHEMATICATION

$$D_u = \delta q - \delta w$$

D_u = change in internal energy

Δq = heat change

Δw = work done on/by system

Which work done is by the system it is positive when work done is on the system it is negative.

$$D_u = \delta q - p dv$$

2nd Law of thermodynamics

The 1st law of thermodynamics gives an idea about the conservation of energy and its change of forces during any thermodynamics process but it gives no information, whether the reaction is likely to occur or not the second law of thermodynamics gives an idea about the direction of propagation of thermodynamics process.

MATHEMATICAL FORM

$$D_s = \delta q / T$$

S = ENTROPY (RANDOMNESS)

3rd Law of thermodynamics

It states that entropy of a perfectly crystalline/homogenous material is 0 at 0 Kelvin.

ENTHALPHY

Enthalpy is nothing but, the summation of internal energy of system and capacity to do work.

$$H = U + PV$$

ENTROPY

Entropy is a measure of degree of disorder in the system.

INTERNAL ENERGY

The energy of a thermodynamic system that is NOT either the kinetic energy or gravitational potential energy of the system as a whole is known as Internal Energy. The internal energy is associated with the internal degrees of freedom of the system

FREE ENERGY OF A CHEMICAL REACTION

The standard free energy change (ΔG°) of a chemical reaction is the amount of energy released in the conversion of reactants to products under standard conditions.

STUDY ABOUT HENRY'S LAW

Henry's law is a thermodynamics law that explains the dissolution of a gas in a liquid medium.

It states that the amount of a gas that dissolves in a liquid is directly proportional to the partial pressure of that gas i.e. in equilibrium with the liquid.

$$[A]_{\text{equilibrium}} = S_A \cdot p^A (\text{Partial pressure})$$

The proportionality constant in Henry's law is Henry's law constant.

SIVERT'S LAW

This law states that the solubility of a gas in a liquid is proportional to the square root of the gas pressure and increases with increasing temperature.

$$[\text{gas}] \propto \sqrt{p_{\text{gas}_2}}$$

$$[\text{gas}] = K \sqrt{p_{\text{gas}_2}}$$

This relationship is known as Siver's law, which is applied to all diatomic gases including $\text{H}_2, \text{N}_2, \text{O}_2$.

FIRST ORDER OF REACTION

When the reaction rate depends on the 1st power of concentration of a single, it is considered to be first order.

Ex: Absorption, Distillation, Microbial death kinetic

Here the rate varies as a first power of the concentration of the reductant.

Consider the reaction

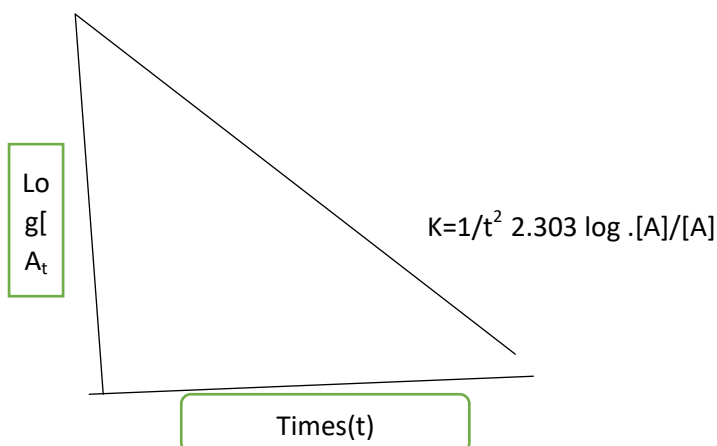
A = product

$[A]_0$ = Initial concentration of A

$[A]_t$ = concentration of A at time

$$K = 1/t \ln [A_0]/[A_t]$$

$$\log_{10} [A_0]/[A] = K / 2.303$$



What is the significance of order of reaction?

The Order of reaction refers to the relationship between the rate of a chemical reaction and the concentration of the species taking part in it. In order to obtain the reaction order, the rate expression (or the rate equation) of the reaction in question must be obtained.

APPLICATION

A first-order reaction is one in which the rate of reaction is proportional to the concentration of the reactant. To put it another way, doubling the concentration doubles the reaction rate. A first-order reaction can have one or two reactants, as in the case of the decomposition reaction.

What is a carbothermic reduction process?

A carbothermic approach, the classical method for reducing (removing oxygen from) metallic oxides, has been for years the subject of intense research. This involves heating the oxide together with carbon to produce carbon monoxide and aluminum

EMF SERIES

The Standard emf Series

Electrode reactions	Standard electrode potential, V° (V)
$Au^{3+} + 3e^{-} \rightarrow Au$	+1.420
$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$	+1.229
$Pt^{2+} + 2e^{-} \rightarrow Pt$	+1.2
$Ag^{+} + e^{-} \rightarrow Ag$	+0.800
$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH)^{-}$	+0.401
$Cu^{2+} + 2e^{-} \rightarrow Cu$	+0.340
$2H^{+} + 2e^{-} \rightarrow H_2$	0.000
$Pb^{2+} + 2e^{-} \rightarrow Pb$	-0.126
$Sn^{2+} + 2e^{-} \rightarrow Sn$	-0.136
$Ni^{2+} + 2e^{-} \rightarrow Ni$	-0.250
$Co^{2+} + 2e^{-} \rightarrow Co$	-0.277
$Cd^{2+} + 2e^{-} \rightarrow Cd$	-0.403
$Fe^{2+} + 2e^{-} \rightarrow Fe$	-0.440
$Cr^{3+} + 3e^{-} \rightarrow Cr$	-0.744
$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.763
$Al^{3+} + 3e^{-} \rightarrow Al$	-1.662
$Mg^{2+} + 2e^{-} \rightarrow Mg$	-2.363
$Na^{+} + e^{-} \rightarrow Na$	-2.714
$K^{+} + e^{-} \rightarrow K$	-2.924

Increasingly inert (Cathodic) ↑

Increasingly active (Anodic) ↓

IONIC CONDUCTIVITY

Ionic conductivity (denoted by λ) is a measure of a substance's tendency towards ionic conduction. Ionic conduction is the movement of ions. The phenomenon is observed in solids and solutions. Ionic conduction is one mechanism of current.

Roasting	Calcination
Ore is heated in excess of air.	Ore is heated in the absence or limited supply of air.
This is used for sulphide ores.	This is used for carbonate ores.
SO ₂ is produced along with metal oxide.	CO ₂ is produced along with metal oxide.
e.g. $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{ZnO} + 2\text{SO}_2$	e.g. $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$

ROASTING VERSUS CALCINATION

Roasting is the heating of a metal ore in the presence of excess air or oxygen	Calcination is the heating of a metal ore in the presence of limited air or oxygen
Requires an excess amount of air or oxygen	Done at limited air or oxygen
Mainly done for sulphide ores	Done for carbonate ores
Releases toxic gases and substances	Releases toxic, volatile compounds
	Visit www.pediaa.com

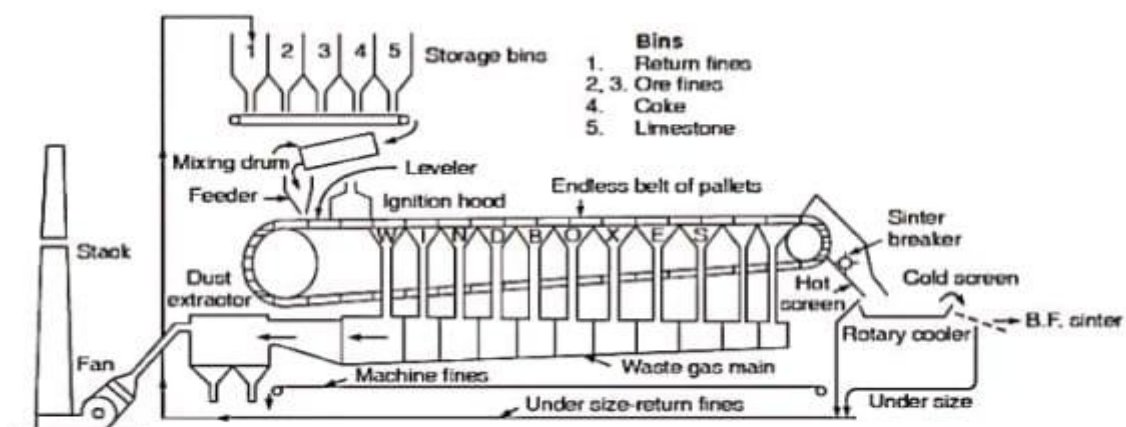
SINTERING

d. Sintering: -

- About 65-75 % of iron ore gets converted into fines (<5mm) during various operations from mining to conversion of blast furnace feed.
- Sintering is the most widely used method for agglomeration of these fines to make them useful for blast furnace.
- *Sintering is essentially a process of heating a mass of fine particles to the stage of incipient fusion for the purpose of agglomerating them into lumps.*
- Sinter is typically a limp mass of size 5-40 mm made from ore fines below 10 mm in size (ideal size of iron ore for sintering is 0.07-10mm).

Objective of sintering: -

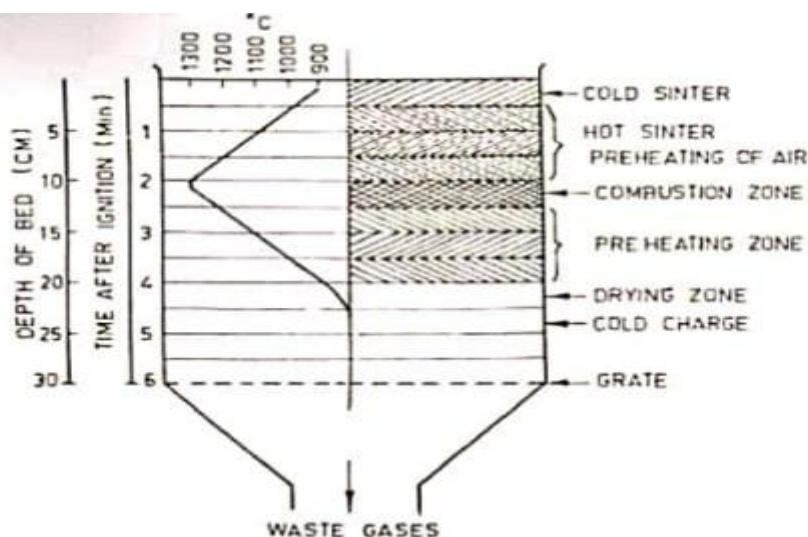
- To increase the size of ore fines to a level acceptable for use in blast furnace.
- To form a porous & strong agglomerate.
- To remove volatiles like CO_2 from carbonates, S from sulphides.
- To incorporate flux into the sinter.
- To increase the blast furnace output & decrease the coke rate.



Schematic of sinter Plant (Dwight-Lloyd technology)

Principle of sintering: -

- A. Iron ore sintering is carried out by putting a mixture of iron bearing fines mixed with solid fuels on a permeable bed. The top layer of sinter bed is heated up to the temperature of 1200-1300°C by a gas or oil burner (external source).
- B. The combustion zone initially develops at the top layer & travel through the bed rising the temperature layer by layer to the sintering level. The cold blast drawn through the bed cools the already sintered layer & get itself heated.
- C. In the combustion zone, bonding takes place between the grains & a strong & porous aggregate is formed. The process is over when the combustion reaches the lower layer of the bed. Then get screened and under sized sinter is recycled & oversized is sent to blast furnace.



Mechanism of sintering: -

2 types of bonds are formed during sintering.

1. *Diffusion / Re-crystalline / solid state bond*
2. *Slag / Glass bond*

1. *Diffusion / Re-crystalline / solid state bond: -*

It is formed as a result of re-crystallisation of the parent phase at the point of two particles in solid state & hence the name.

2. *Slag / Glass bond: -*

It is formed as a result of formation of low melting slag or glass at the point of contact of 2 particles depend upon the material constitution, flux addition etc.

TYPES

Types of Sinter

Depending upon the amount of flux added during sintering, sinter is divided in 3 types:

1. Acid Sinter
2. Fluxed Sinter
3. Super Fluxed Sinter

1. Acid Sinter: The sinter mix doesn't contain flux at all. Flux is added separately in blast furnace.
2. Fluxed Sinter: The amount of flux added in the mix is such that the basicity of the mix is equal to that of slag. If lumpy ore is charged along with this type of sinter then separate flux needs to be added.
3. Super Fluxed Sinter: These are the sinters where sufficient flux is added in the sinter mix for producing slags of desired basicity in blast furnace taking also into account of acidic oxides in other blast furnace burden materials.

PRINCIPLE OF ELECTROMETALLURGY

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

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

FARADAY'S LAW OF ELECTROLYSIS(1ST LAW)

It states, during electrolysis, the amount of chemical reaction which occurs at any electrode under the influence of electrical energy is proportional to the quantity of electricity passed through the electrolyte.

2ND LAW

Faraday's second law of electrolysis states that if the same amount of electricity is passed through different electrolytes, the masses of ions deposited at the electrodes are directly proportional to their chemical equivalents.

What is an Electrolytic Cell?

The electrochemical cell which facilitates a chemical reaction through the induction of electrical energy is known as an electrolytic cell.