ELEMENTS OF PROCESS METALLURGY

B.TECH, 3rd SEMESTER

LECTURES NOTE

BY

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Disclaimer

MTPC2003 ELEMENTS OF PROCESS METALLURGY (3-0-0)

MODULE-I (08 hrs)

Overview of Extractive Metallurgy processes; Pyro-metallurgy, Hydrometallurgy and Electrometallurgy; Thermodynamic and Kinetic Principles of metal extraction; Ellingham diagrams, Calcinations; Roasting; Predominance Area Diagram, Roasting Practices, Smelting, Formation and function of slag and their calculations,

MODULE-II (08 hrs)

Metallo-thremic and carbothermic reduction of oxides, Smelting Furnaces, Matte Smelting, Pyro metallurgical processes using vacuum Hydrometallurgy: Leaching; Theory of Leaching; Role of oxygen in leaching operation; Bacterial and microbial leaching; Contact reduction of metals in aqueous solutions;

MODULE-III (08 hrs)

Gaseous reduction of metals in aqueous solutions; Ion exchange, Solvent Extraction and Electrolysis, Electrometallurgy: laws of electrolysis, electrolyte Structure of solvent media; Electrolysis of aqueous solution; Electrolysis of fused salts; Cell design; Electro refining

MODULE-IV (08 hrs)

Halide Metallurgy and Halogenation., Basic approaches of refining, preparation of pure compounds; Purification of crude metals produced in bulk

MODULE-V (08 hrs)

Concept of activity, chemical potential, fugacity, real and idle solution, and the significance in metal extraction, Numerical problems relevant to Pyro, Hydro and Electrometallurgical processes

Books:

[1] Principles of Extractive Metallurgy: A. Ghosh & H.S. Ray, IIN Publications, Kolkata 1984

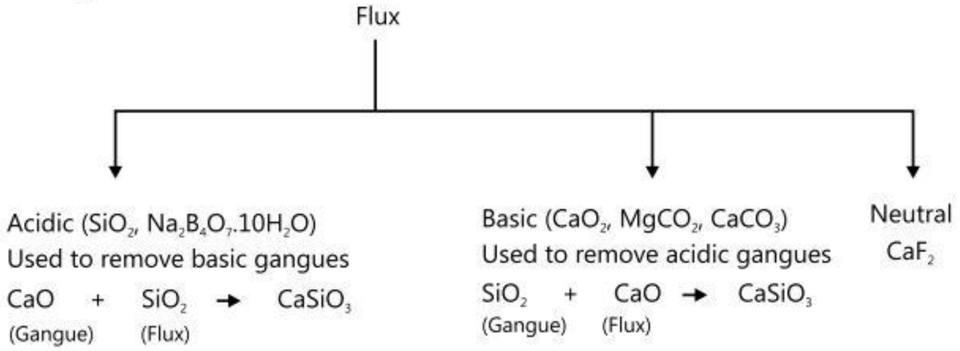
[2] Principles of Extractive Metallurgy: Rosenquist, T., McGrawhill - Kogakusha International – 1983 [3] Mineral Processing and Extractive Metallurgy by Corby G. Anderson (Editor), Robert C. Dunne (Editor), John L. Uhrie (Editor)

[4] Metallurgy a Brief Outline of the Modern Processes for Extracting the More Important Metals by W. Borchers

Elements of process metallurgy deals with processes of extraction and refining of metals.

BASIC TERMINOLOGY

- **UNIT OPERATIONS:** The physical processes like crushing, grinding, classification, concentration of ore etc., are called unit operations.
- **UNIT PROCESSES:** The chemical processes used to extract the metal from their ores are called as unit processes.
- **Flux**: Flux are chemical substances which are generally added to an ore in order to remove the impurities or gangue. E.g., CaO, SiO2 etc

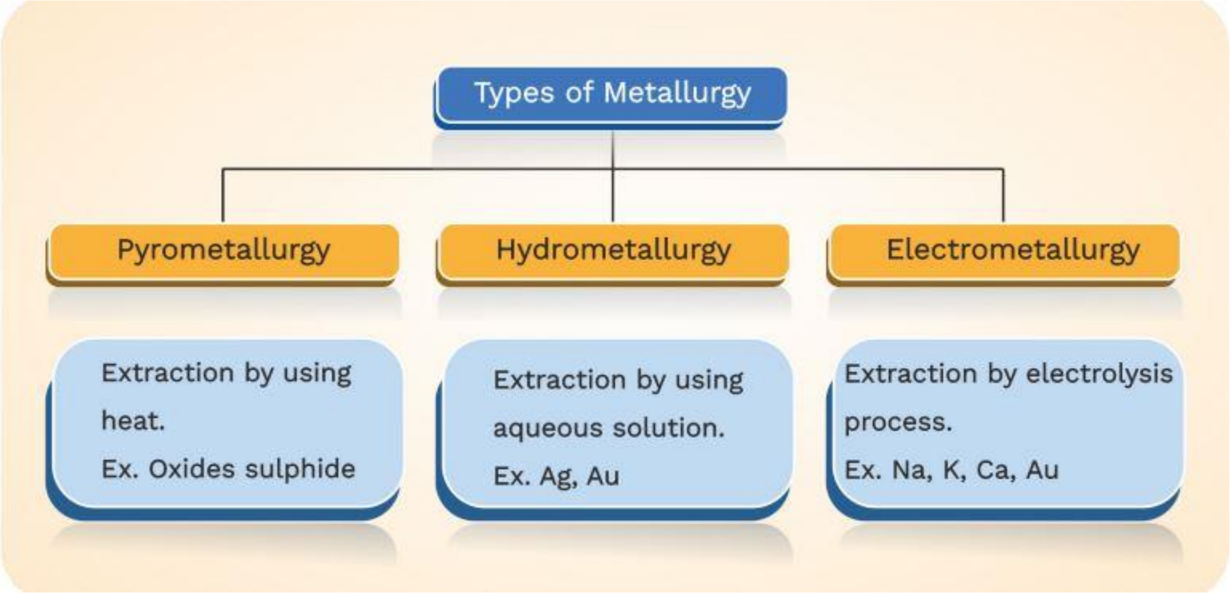


- **Gangue:** Gangue is the non-metallic impurities present in the ore. Which are removed with the addition of flux, while extracting the metal from ore minerals.

Extraction Process

It is the process of removing impurities or undesired materials from the ore, leaving behind the required materials.

Classification of Unit/Extraction Processes



PYRO-METALLURGY

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

WHAT ARE THE ADVANTAGES OF HIGH TEMPERATURE?

- As at high temperature, the reaction rate is accelerated which leads to more metal production.
- As we know that the reaction rate doubles in each 10ºC rise of temperature which requires small activation energy. It helps in fast reaction.
- Shift of reaction is possible.
- Only pyrometallurgy and fused salt electrolysis can extract reactive metals namely the alkaline earth metals zirconium and titanium.
- Ability to treat a large tonnage of ore in a compact space, which leads to a saving in capital cost.

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

1. Calcination

2. Roasting

3. Smelting

4. Refining

CALCINATION:

- Calcination is the thermal treatment of an ore that brings about its decomposition and elimination of volatile products i.e. carbon dioxide and water.

- Temperature required for this process can be calculated from free energy temperature relationship for the reaction under consideration.

- As the most decomposition reaction is endothermic, so the temperature of calcination is generally depending on the transfer of heat into the particle. This result in even high temperature of the furnace (kiln) at the expanse of some fuel.

  For example, $CaCO3 (s) = CaO (s) + CO2(g)$.
- This reaction is endothermic and requires high temperature to decompose it in the kiln. Other examples are as follows

$CaCO_3 \rightarrow CaO + CO_2\uparrow$ ~ 901^{O}C
(Lime stone)
$AI_2O_3.2H_2O \rightarrow AI_2O_3 + 2H_2O\uparrow$ ~700 ^{O}C
(Bauxite)
$MgCO_3 \rightarrow MgO + CO_2\uparrow$ ~417 ^{O}C
(Magnesite)
$2Fe_2O_3.3H_2O \rightarrow 2Fe_2O_3 + 3H_2O\uparrow$ ~400 ^{O}C
(Limonite)

Thermodynamics of Pyrometallurgy

Which involves the Ellingham diagram

Thermodynamics useful to understand the variation in **temperature required for the thermal reduction of oxides** and to **predict which element will suit as the reducing agent for a given metal oxide.**

The oldest, and still the most common smelting process for oxide ores involves heating them in the presence of carbon.

Originally, charcoal was used, but industrial-scale smelting uses coke, a crude form of carbon prepared by pyrolysis (heating) of coal.

- The Gibbs energy is the most important thermodynamic term in metal extraction.
- For a spontaneous reaction the change in the Gibbs energy, ΔG, must be negative
- Only the reactions having a negative value of Gibbs Free Energy are feasible.
- Change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S$$

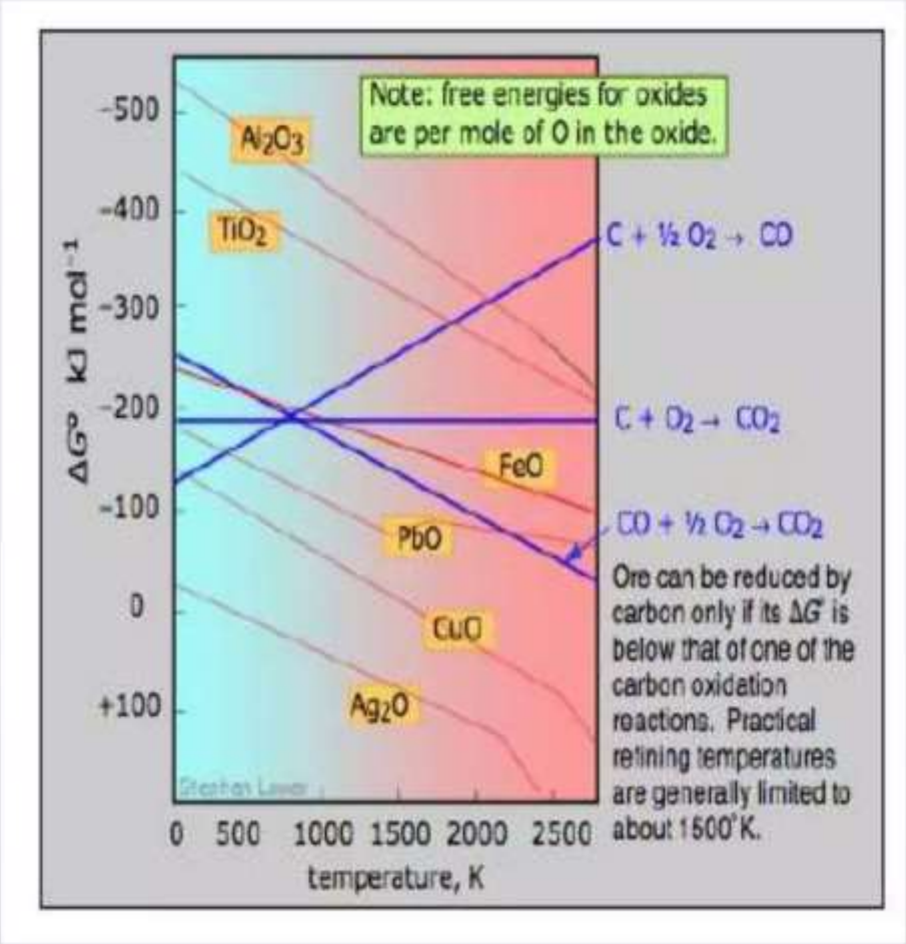
where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become negative

Ellingham diagram

- The change in the Gibbs energy when 1gram molecule of oxygen, Sulphur or halogen is used to form oxides, sulphides or halides of metals plotted against temperature. This graphical representation is called an Ellingham diagram.

- These plots are useful to determine the relative ease of reducing a given metal oxide to the metal and also to predict the feasibility of the thermal reduction of an ore.

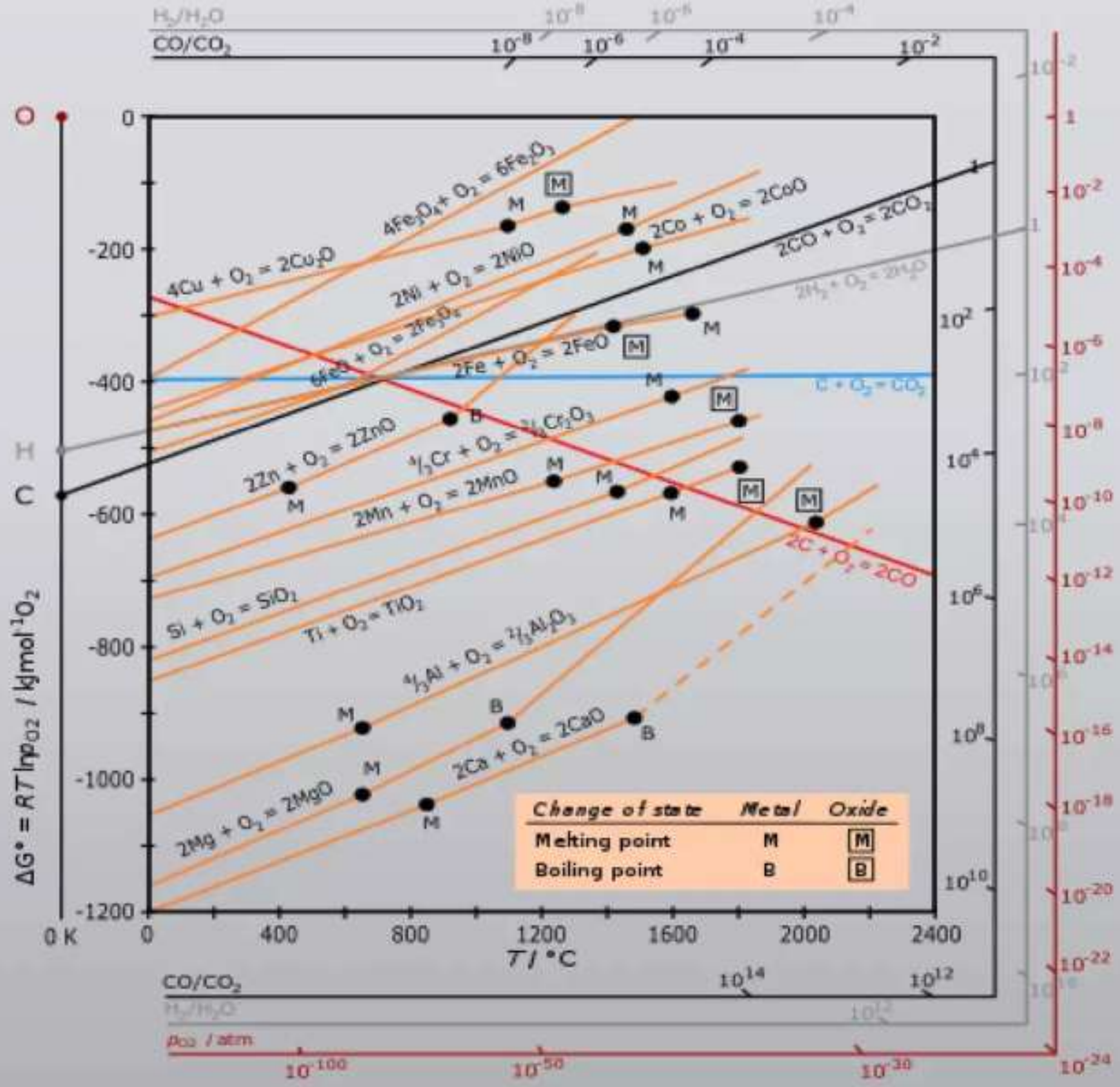


Note: free energies for oxides are per mole of O in the oxide.

Ore can be reduced by carbon only if its ΔG° is below that of one of the carbon oxidation reactions. Practical refining temperatures are generally limited to about 1500°K.

Ellingham diagram. **An ore can be reduced by carbon only if its Gibbs free energy of formation falls below that of one of the carbon reduction reactions** (blue lines.) Practical refining temperatures are generally limited to about1500°K.

- An Ellingham diagram normally consists of plots of change in the Gibbs energy with temperature for the formation of oxides.



There are three main uses of the Ellingham diagram:

- Determine the relative **ease of reducing a given metallic oxide** to metal

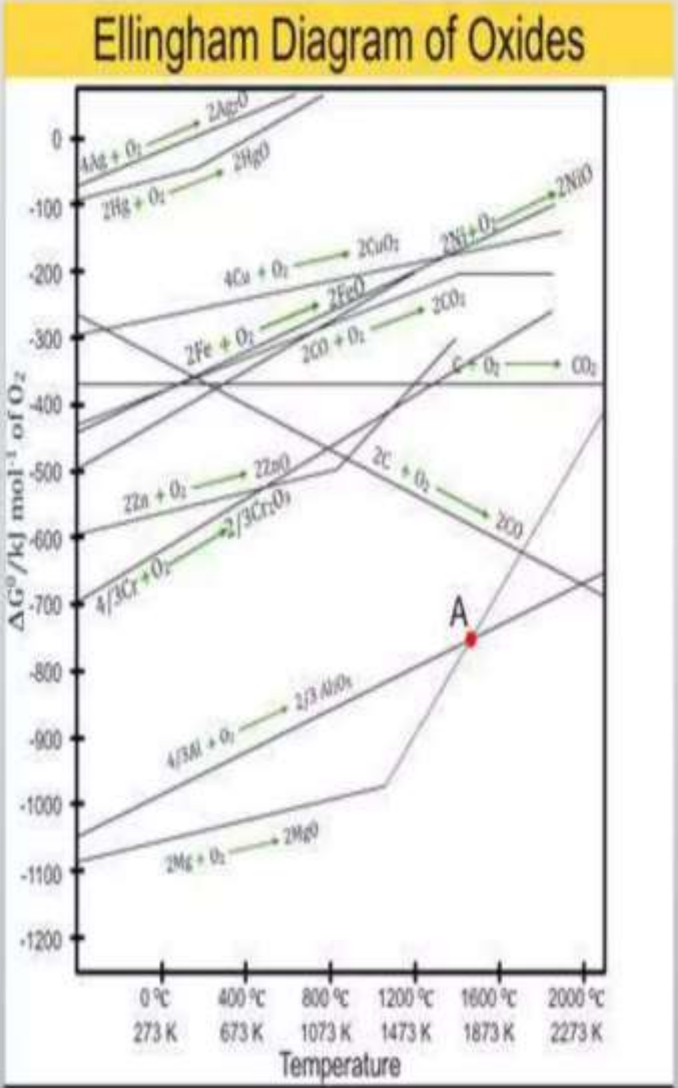
- Determine the **partial pressure of oxygen** that is in equilibrium with a metal oxide at a given temperature and

- Determine the **ratio of carbon monoxide to carbon dioxide** that will be able to reduce the oxide to metal at a given temperature.

An Ellingham diagram for oxides has several important features. **The graphs for most metal to metal oxide reactions show a positive slope.**

Ex: $2M + O_2 \rightarrow 2MO$.

- In this reaction, the entropy (or) randomness decreases from left to right due to the consumption of gases.
- Hence, ΔS becomes negative. If the temperature is raised, then T ΔS becomes more negative. So, ΔG becomes less negative.
- The Gibbs energy changes follow a straight line, unless the materials melt (or) vaporize. The temperature at which such a change occurs is indicated by an increase in the slope on the positive side.

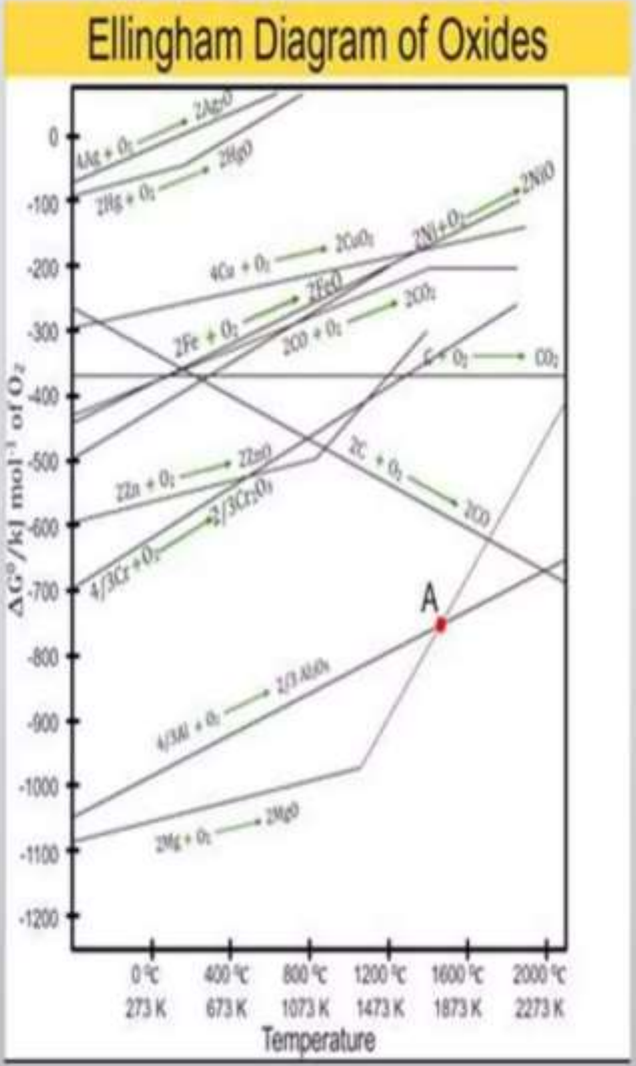


- When the temperature is raised, a point will be reached where the graph crosses the line "ΔG is zero."

- Below this temperature, the free energy of formation of the oxide is negative, so the oxide is stable.

- Above this temperature, the free energy of formation of the oxide is positive the oxide becomes unstable and will decompose into the metal and dioxygen.

- Any metal will reduce an oxide of another metal that lies above it in an Ellingham diagram. Ex: Al reduces FeO, CrO and NiO in termite reaction but Al will not reduce MgO at a temperature below 1500 ⁰C.



Ellingham Diagram of Oxides

Ease of Reduction

- The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature.

- Reactions closer to the top of the diagram are the most “noble” metals (for example, gold and platinum), and their oxides are unstable and easily reduced.

- As we move down toward the bottom of the diagram, the metals become progressively more reactive and their oxides become harder to reduce.

- **A given metal can reduce the oxides of all other metals whose lines lie above theirs** on the diagram. For example, the $2Mg + O_2 \Longrightarrow 2MgO$ line lies below the $Ti + O_2 \Longrightarrow TiO_2$ line, and so magnesium can reduce titanium oxide to metallic titanium.

- Since the $2C + O_2 \Longrightarrow 2CO$ line is downward-sloping, it cuts across the lines for many of the other metals.

- This makes carbon unusually useful as a reducing agent, because as soon as the **carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to metal.**

- So, for example, solid carbon can reduce chromium oxide once the temperature exceeds approximately 1225°C, and can even reduce highly-stable compounds like silicon dioxide and titanium dioxide at temperatures above about 1620°C and 1650°C, respectively.

- **For less stable oxides, carbon monoxide is often an adequate reducing agent.**

Equilibrium Partial Pressure of Oxygen

- The scale on the right side of the diagram labelled "Po_2" is used to determine what partial pressure of oxygen will be in equilibrium with the metal and metal oxide at a given temperature.
- The significance of this is that, **if the oxygen partial pressure is higher than the equilibrium value, the metal will be oxidized, and if it is lower than the equilibrium value then the oxide will be reduced.**

Ratio of CO/CO_2 Needed for Reduction

- When using carbon as a reducing agent, there will be a minimum ratio of CO to CO_2 that will be able to reduce a given oxide.
- **The harder the oxide is to reduce, the greater the proportion of CO needed in the gases**.

Applications of Thermodynamics and Ellingham Diagrams

Extraction of iron from its oxides

- Oxide ores of iron, after concentration through calcination/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a Blast furnace from its top.
- Here, the oxide is reduced to the metal.
- Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is:

$$\mathrm{FeO(s) + C(s) \rightarrow Fe(s/l) + CO\ (g)}$$

It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO

$$\mathrm{FeO(s) \rightarrow Fe(s) + 1\ 2\ O2(g)\ [\Delta G(FeO, Fe)]}$$

$$\mathrm{C(s) + 1\ 2\ O2\ (g) \rightarrow CO\ (g)\ [\Delta G\ (C, CO)]}\ ..$$

- When both the reactions take place the net Gibbs energy change becomes:

$$\Delta G\,(C, CO) + \Delta G\,(FeO, Fe) = \Delta rG$$

- Naturally, the resultant reaction will take place when the right hand side in equation is negative.
- In ΔG vs T plot representing reaction, the plot goes upward and that representing the change $C \rightarrow CO$ (C,CO) goes downward.
- At temperatures above 1073K (approx.), the C,CO line comes below the Fe,FeO line [ΔG (C, CO) < ΔG(Fe, FeO)].
- So in this range, coke will be reducing the FeO and will itself be oxidised to CO.
- In a similar way the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve

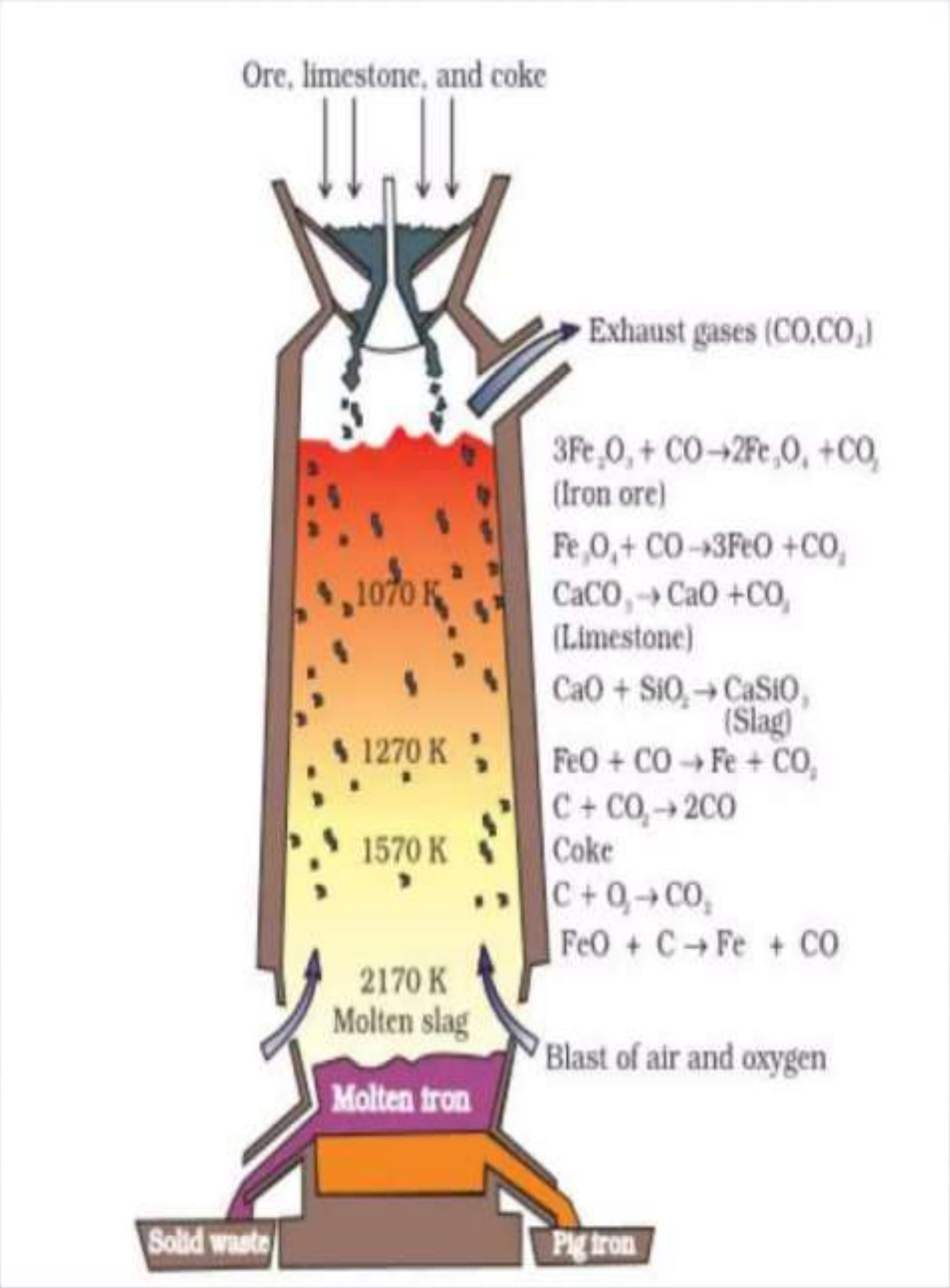
- In the Blast furnace, reduction of iron oxides takes place in different temperature ranges.
- Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself.
- The burning of coke therefore supplies most of the heat required in the process.
- The CO and heat move to upper part of the furnace.
- In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO.
- Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the $\Delta_f G^0$ *vs* T plots.

- These reactions can be summarised as follows:
- At 500 – 800 K (lower temperature range in the blast furnace)–

$3\,Fe_2O_3 + CO \rightarrow 2\,Fe_3O_4 + CO_2$ ....

$Fe_3O_4 + 4\,CO \rightarrow 3Fe + 4\,CO_2$.........

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$ ....



Extraction of copper from cuprous oxide [copper(I) oxide]

- In the graph of $\Delta rG0$ *vs* T for formation of oxides, the Cu_2O line is almost at the top.
- So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500 – 600K).
- However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \text{ ……..}$$

The oxide can then be easily reduced to metallic copper using coke:

$$Cu_2O + C \rightarrow 2\,Cu + CO \text{ ……..}$$

Extraction of zinc from zinc oxide

- The reduction of zinc oxide is done using coke.
- The temperature in this case is higher than that in case of copper.
- For the purpose of heating, the oxide is made into brickettes with coke and clay.
  - $ZnO + C \xrightarrow[673\ K]{} Zn + CO$
- The metal is distilled off and collected by rapid chilling.

Limitations of Ellingham Diagram

- The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. **It does not say about the kinetics of the reduction process**

- The interpretation of $\Delta G0$ is based on K ($\Delta G0 = - RT \ln K$). Thus **it is presumed that the reactants and products are in equilibrium**. This is not always true because the reactant/product may be solid.

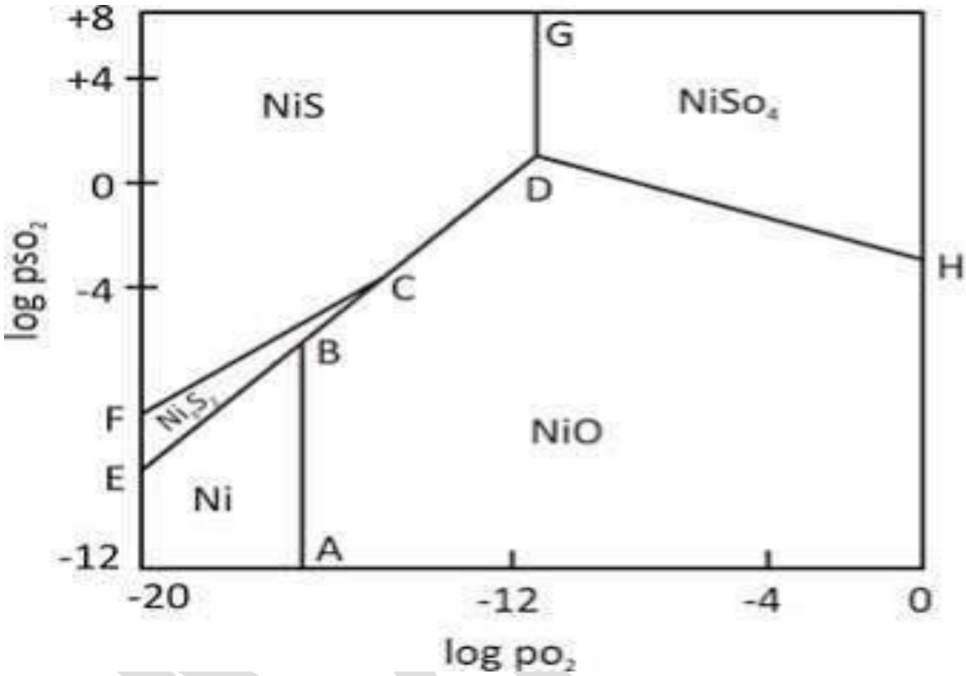
CHAPTER-2

ROASTING

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

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

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



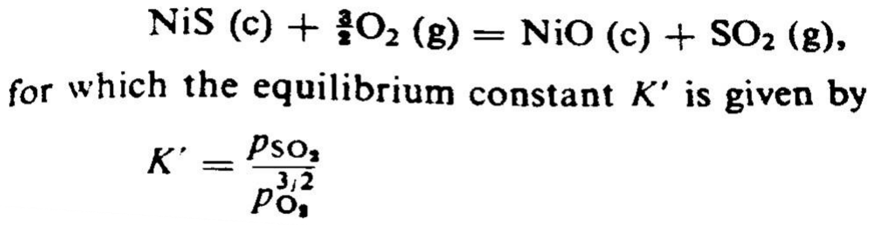
Ni-S-O system at 1000K

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

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

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

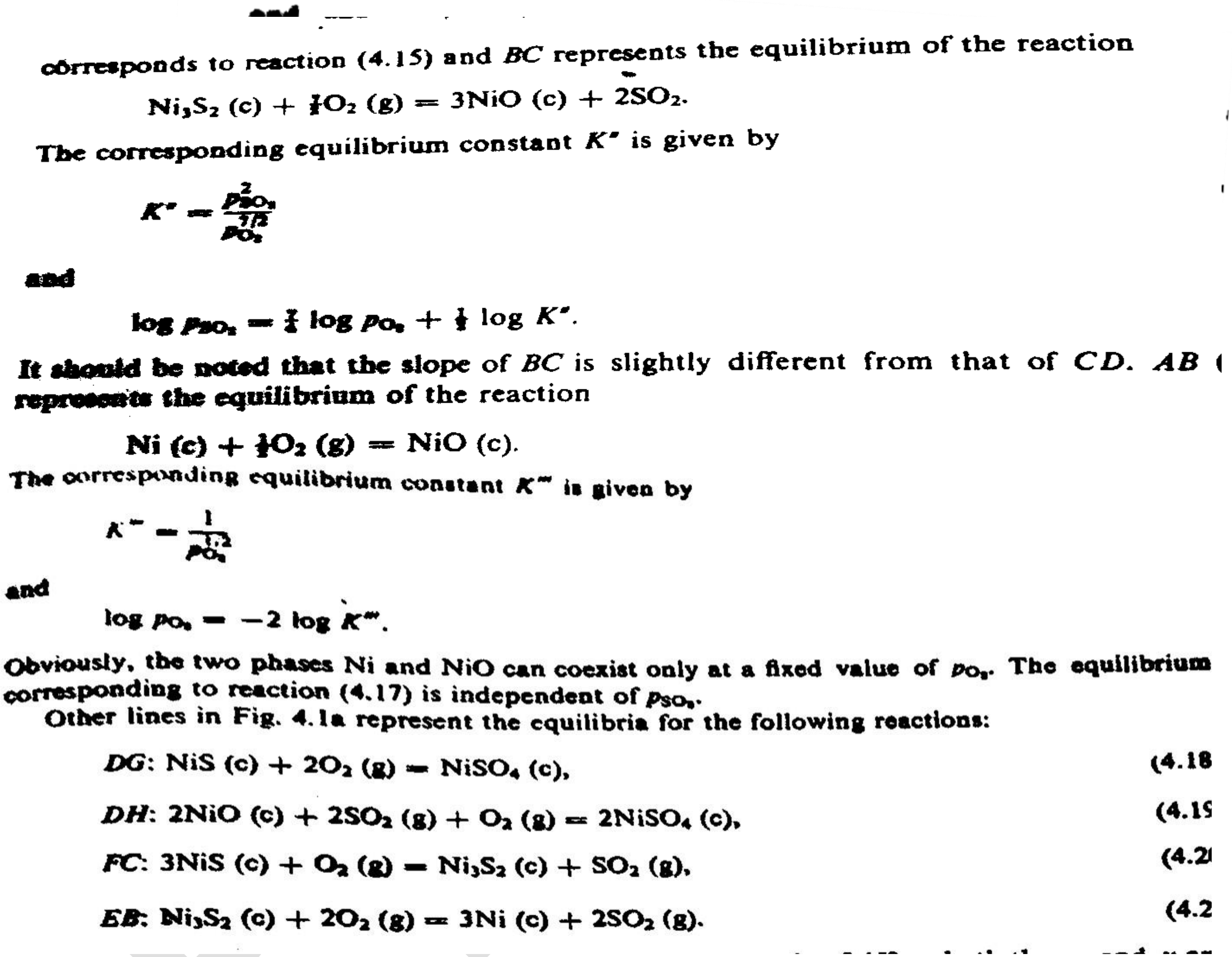
- Let us consider the reaction along the line CD,



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

for which the equilibrium constant K' is given by

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



and

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

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

The corresponding equilibrium constant K'' is given by

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

and

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

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

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

The corresponding equilibrium constant K''' is given by

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

and

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

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

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

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

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

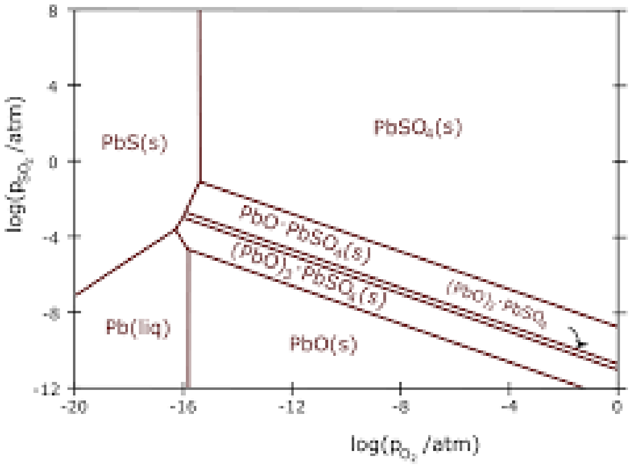
FC: $3NiS\ (c) + O_2\ (g) = Ni_3S_2\ (c) + SO_2\ (g),$ (4.2

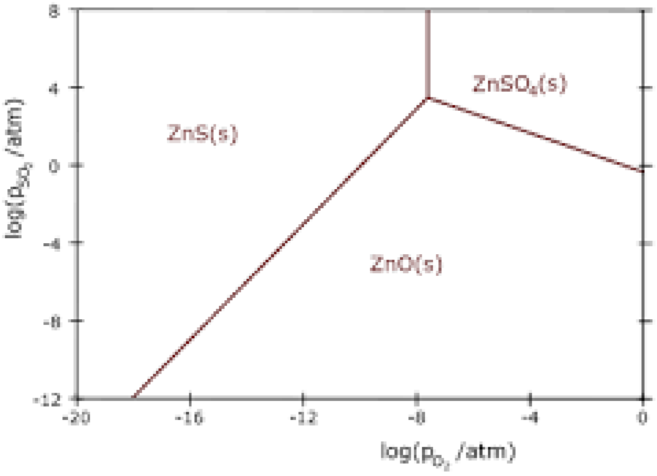
EB: $Ni_3S_2\ (c) + 2O_2\ (g) = 3Ni\ (c) + 2SO_2\ (g).$ (4.2

- Again consider the reaction along the line BC,

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

Other predominance area diagrams are,





FACTORS AFFECTING ROASTING:

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

DURATION OF ROASTING PROCESS VARIES GREATLY:

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

ROASTING PRACTICES:

CRITERIA OF CHOOSING A ROASTING PROCESS-

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

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

Calcination vs. Roasting

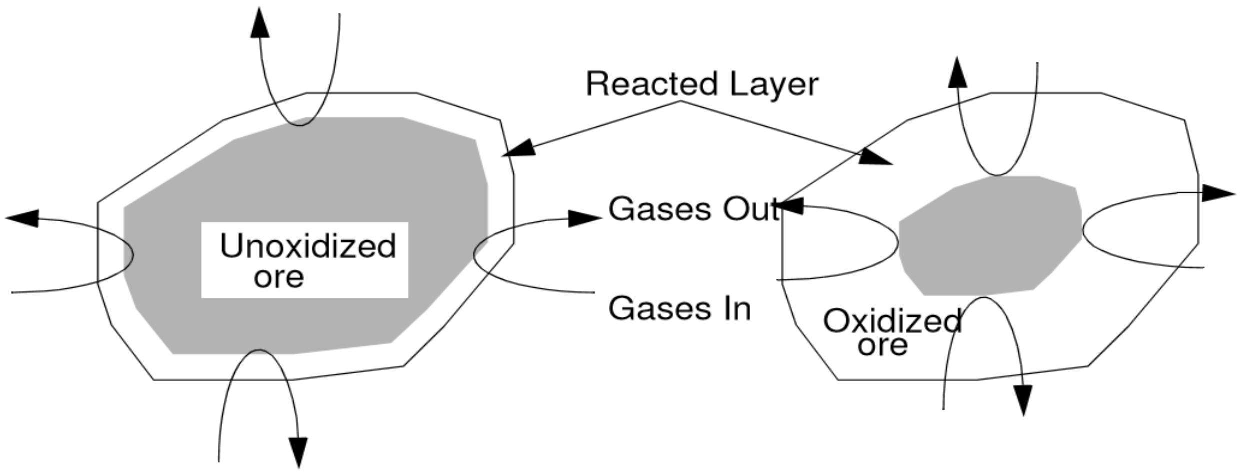
Calcination	Roasting
Used primarily for carbonate ores.	Used primarily for sulphide ores.
Work in absence of air.	Work/done in presence of excess air
CO_2 gas evolved/separated	Sulphur dioxide (SO_2) is a product.

Roasting (continue..)

Basic Steps in Roasting:

- Particles are heated.
- Reactive gas (air, oxygen, chlorine, etc.) contacts the particles.
- Particles react with the gas.
- Gaseous reaction product are carried away.

Since the particles do not melt, the reaction starts on the particle surface and gradually works in to the particle core, as shown in the ***Shrinking-Core*** reaction model.



The Shrinking-Core model. As the shell of oxidized ore becomes thicker, it becomes more difficult for fresh gas to reach the unreacted ore, and so the roasting rate slows down. It is often difficult to react the last bit of material in the center of the particles

Roasting (continue..)

Basic Roasting Terms:

- Dead Roast: the ore is completely reacted, and leaves the process cold.
- Sweet Roast: the ore is completely reacted, but leaves the furnace still hot.
- Sour Roast: the roasting reaction is not run to completion.

Roasting (continue..)

Roasting depends on following factors:

1. Time
2. Temperature
3. Availability of O_2 or air
4. Physical condition
5. Nature of the mechanical device used

Criteria of selection of roasting process

1. **Physical condition of product**

- Blast furnace smelting – product should coarse or cellular.
- Reverberatory furnace – product should be fine.
- Leaching - product should be porous.

2. **Chemical composition of product**

- For copper – retain some Sulphur
- For Lead & Zinc - complete elimination of Sulphur

Multiple Hearth Roasting

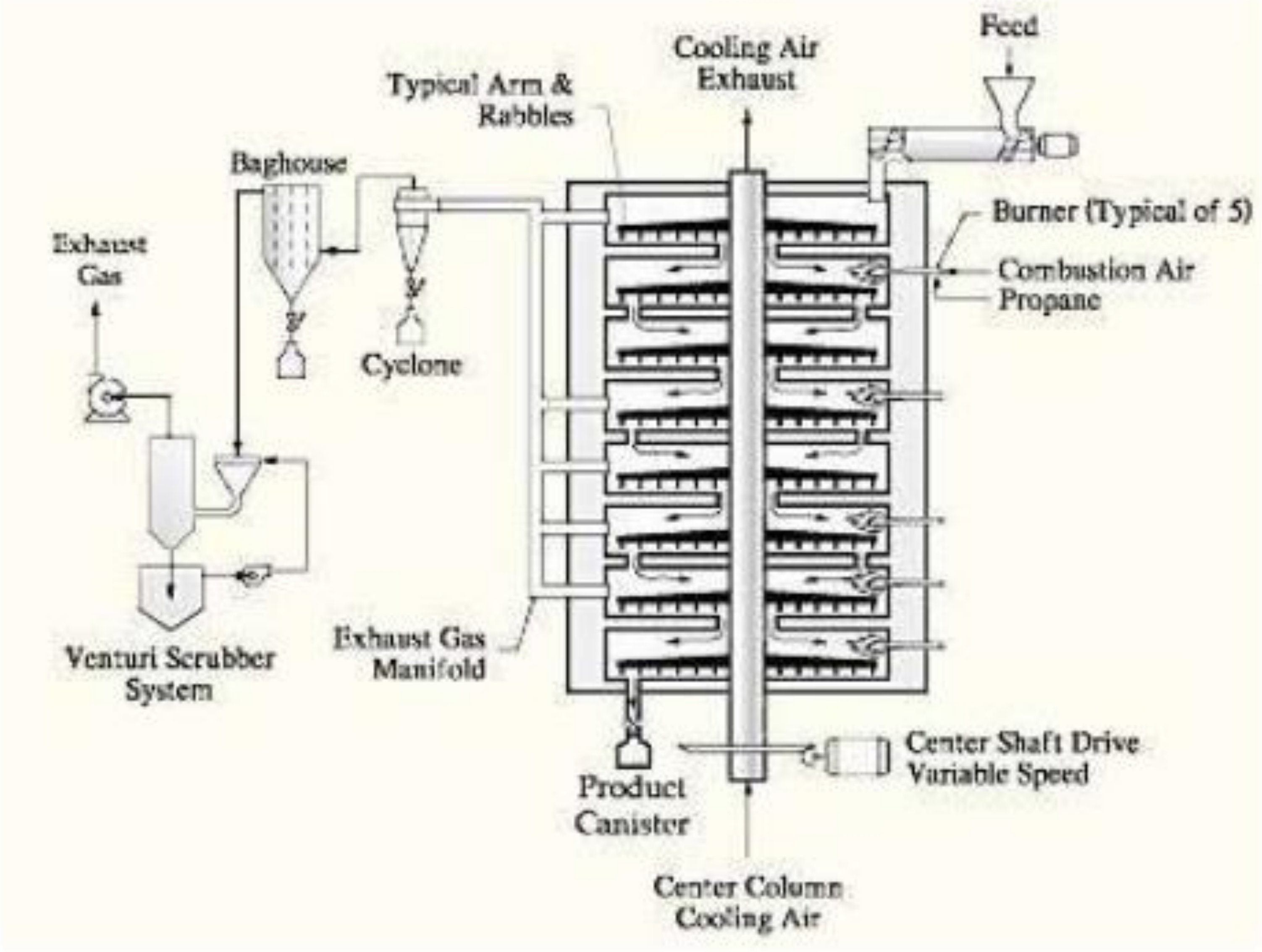
MacDougall in England (19th Century)

Basic principle : Counter current flow of solid ore & the oxidizing gases.

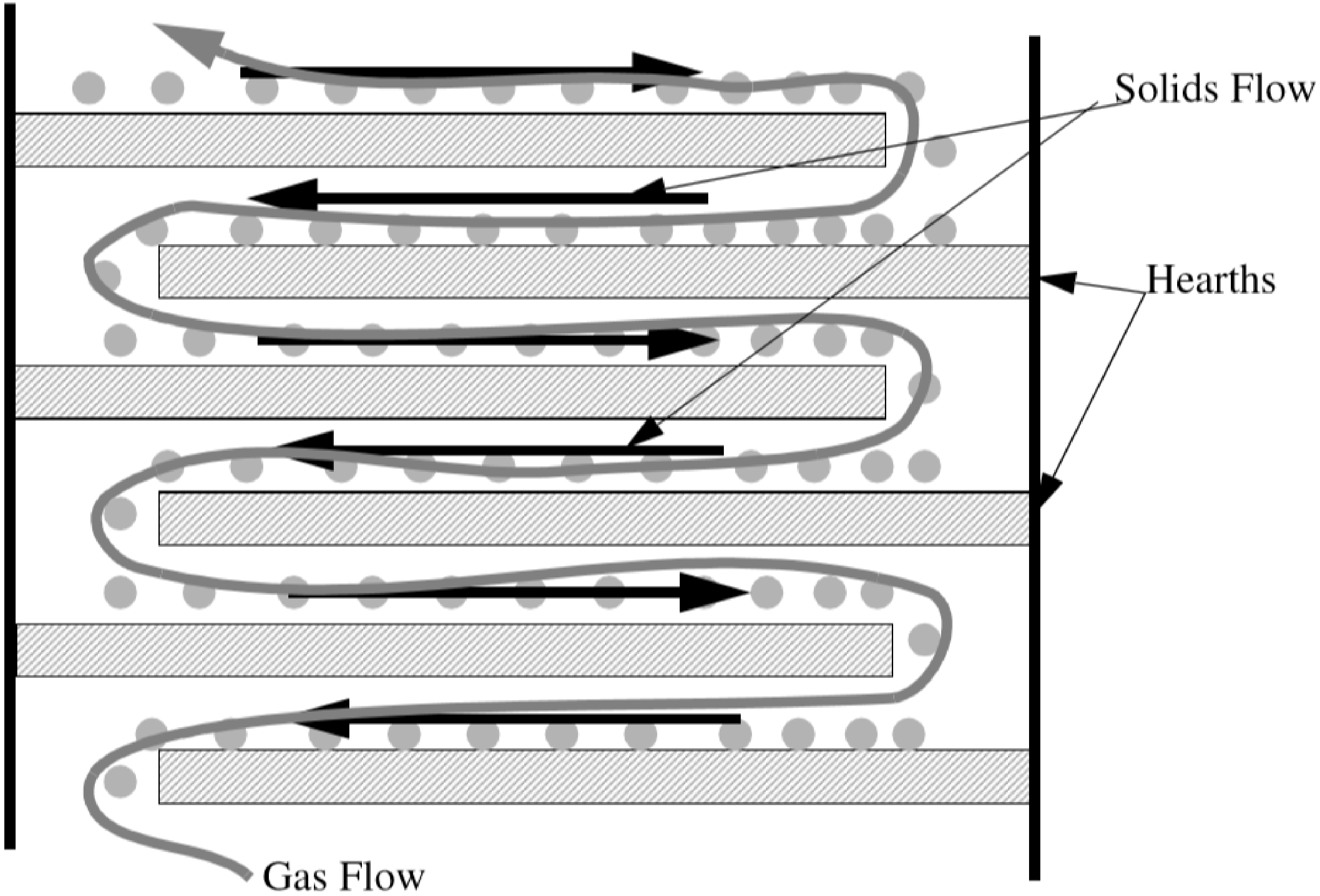
Construction:

- It consists of several (about 10) circular brick hearths superimposed on each other.
- Cylindrical steel shell lined with brick.
- Revolving mechanical rabbles attached to arms move over the surface of each hearth to continuously shift the ore.
- Arms are attached to a rotating central shaft that passes through the center of the roaster.

Multiple Hearth Roasting (continue..)



Multiple Hearth Roasting (continue..)



Multiple Hearth Roasting (continue..)

Working principle:

- The hearth at the top dry and heat the charge.
- Ore is discharged automatically at the top hearth.
- It gradually moves downwards through alternate passages around the shaft and periphery and finally emerges at the bottom.
- The oxidizing gases flow upwards.
- External heating of charge is unnecessary *except* when charge contain moisture.

Drawbacks:

- Roasting is slow.
- Gases are unsuitable for production of H_2SO_4 because they do not contain sufficient SO_2 and SO_3.

Roasting of Zinc sulfide

- Roasting is a high-temperature process that converts zinc sulfide concentrate to an impure zinc oxide called calcine.
- The following reactions occur during roasting:

$2ZnS + 3O_2 \rightarrow 2ZnO + SO_2$

$2SO_2 + O_2 \rightarrow 2SO_3$

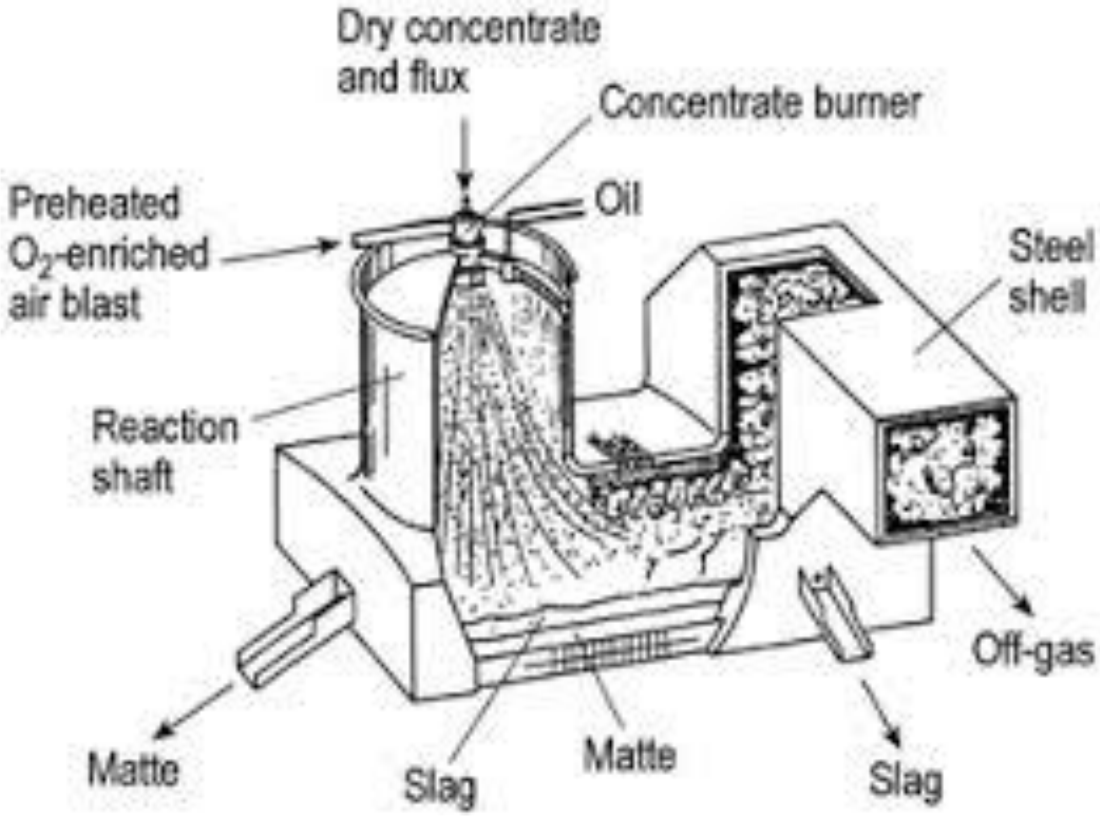
- In a multiple-hearth roaster, the concentrate drops through a series of 9 or more hearths stacked inside a brick-lined cylindrical column.

- As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine.

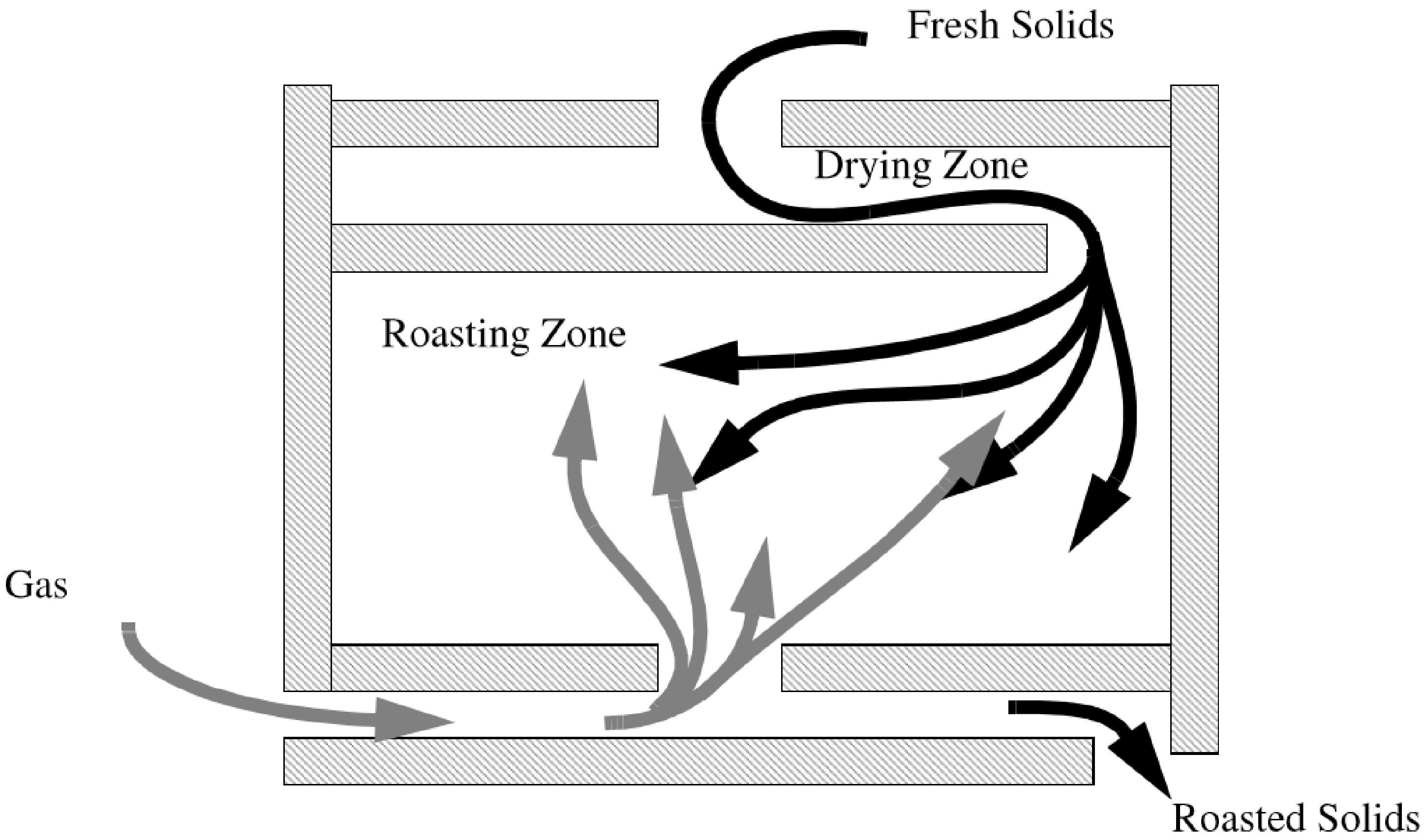
- Multiple hearth roasters are unpressurized and operate at about 690°C (1300°F). Operating time depends upon the composition of concentrate and the amount of the sulfur removal required. Multiple hearth roasters have the capability of producing a high-purity calcine.

Flash Roasting

- Preheated ore particles are made to fall through body of hot air resulting in instantaneous oxidation or '*flashing*' of combustible constituents of the ore, mainly Sulphur. Hence called flash roasting.
- Ore should be of fine size.
- Capacity of flash roaster > hearth roaster.
- Temp. of combustion zone = 900-950 °C



Flash Roasting (continue..)



Flash Smelting. The heat produced by the roasting reaction is used to dry the incoming ore and bring it up to roasting temperature. If the reaction is sufficiently exothermic, the ore can even be melted.

Fluidized bed Roasting

- The ore particles are roasted while suspended in an upward stream of gas.

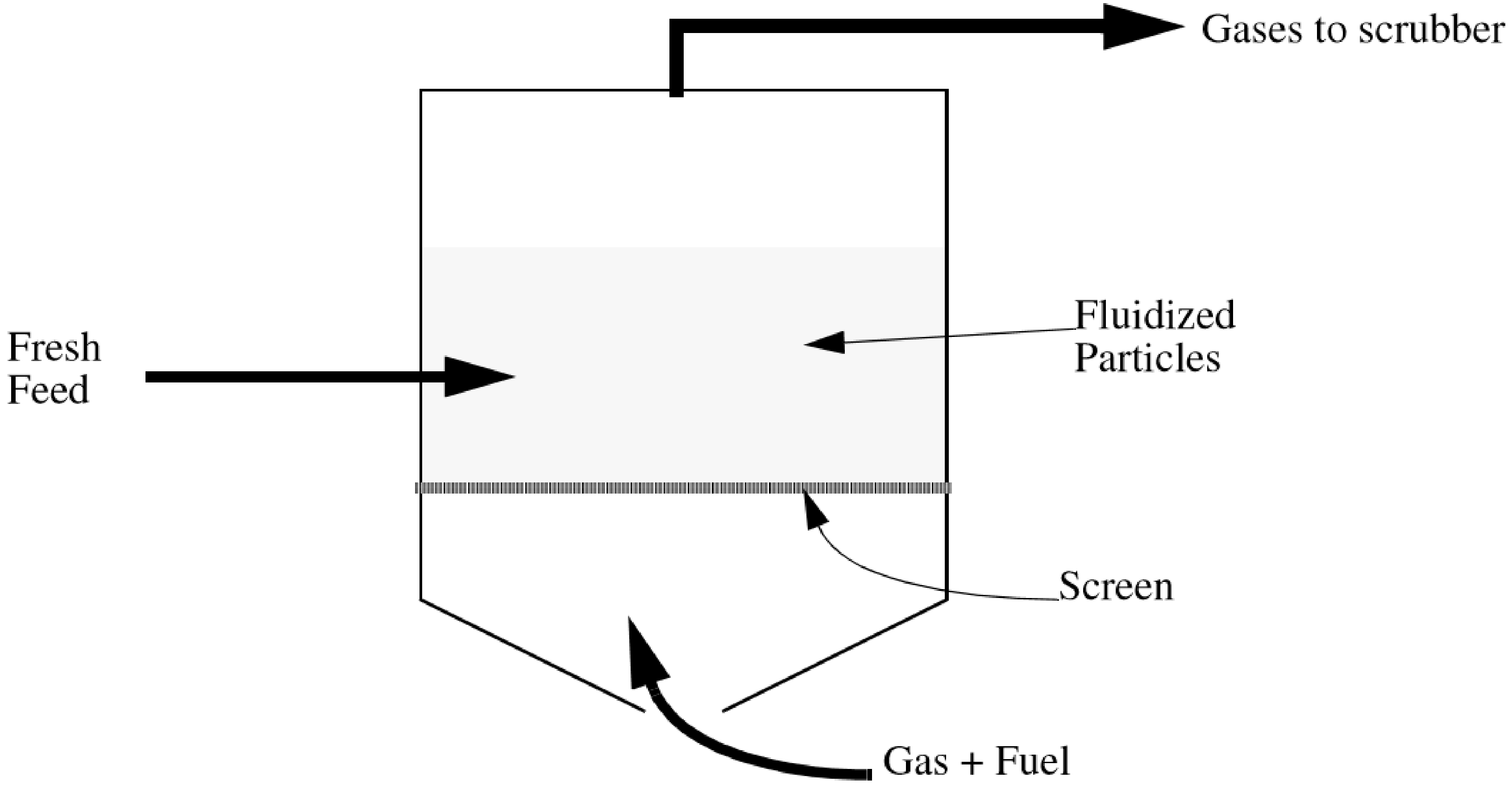
- Finely ground sulfide concentrates in size over the range 0.005 to 0.05 cm in diameter is used.

- As in the suspension roaster, the reaction rates for desulfurization are more rapid than in the older multiple hearth processes.

- Fluidized-bed roasters operate under a pressure slightly lower than atmospheric and at temperatures averaging 1000°C (1800°F).

- In the fluidized-bed process, no additional fuel is required after ignition has been achieved.

Fluidized bed Roasting (continue..)

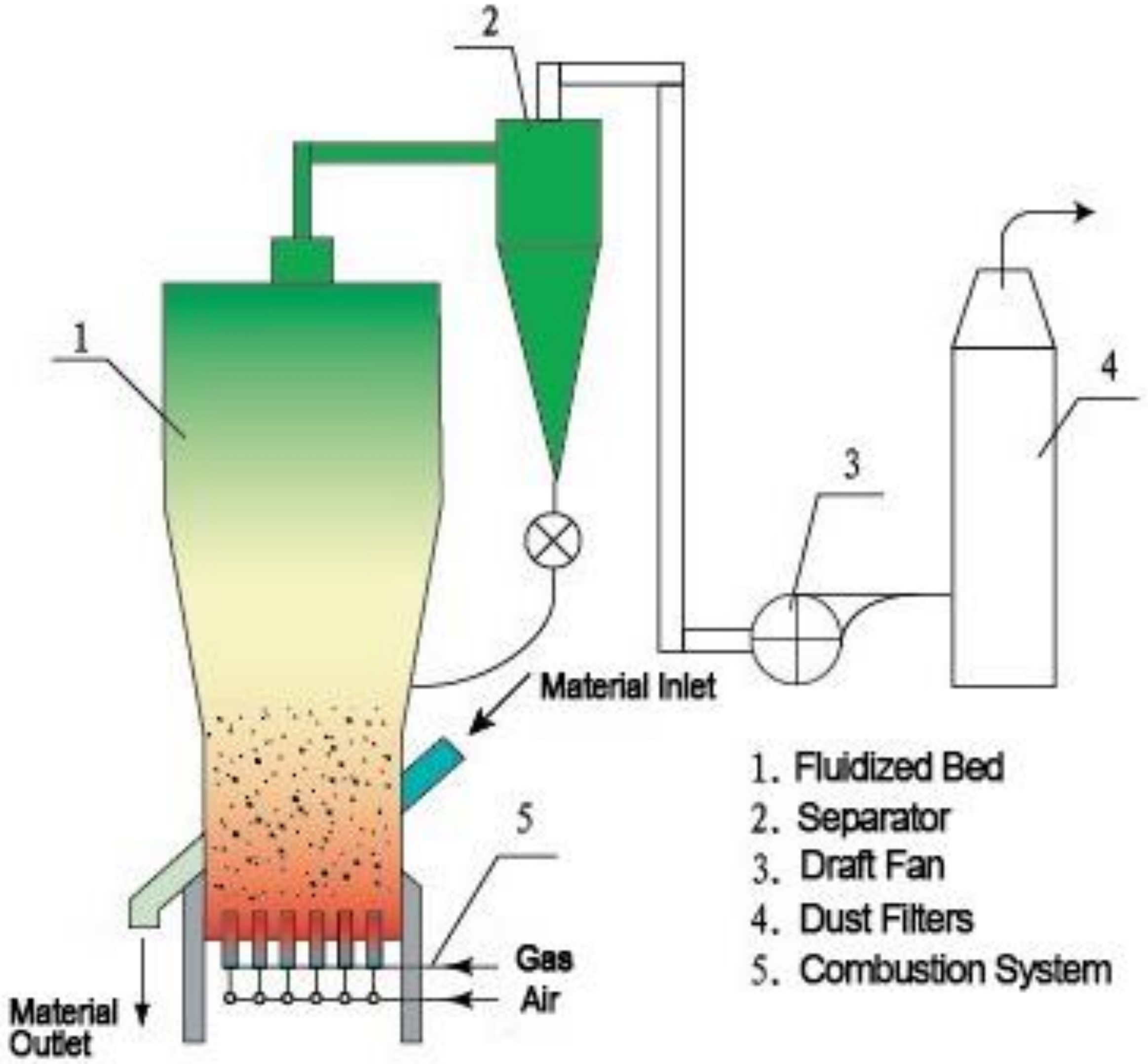


Fluidized Bed Reactor

Fluidized bed Roasting (continue..)

Principle:

- Ore particles are roasted while it is suspended in an upward stream of gases.
- Gas passes through bottom of the bed.
- Behavior of the bed depends on the velocity of gas.



Fluidized bed Roasting (continue..)

Stages observed during roasting process :

Stage-1

- When the gas flow rate is very low, and the ore bed is porous, the gas permeates the bed without disturbing the ore particles.
- Pressure drop across the bed is proportional to flow rate.

Stage-2

- Gas velocity increases, the bed expands upwards due to the effect of the drag forces exerted by gas stream.
- The pressure drop across the bed depends on the gas velocity.

Stage-3

- When gas velocity further increases a stage is reached.
- Pressure drop = wt. of the particle per unit area of the bed.
- Particles remain individually suspended and offer less resistance to gas flow.

Fluidized bed Roasting (continue..)

Stages observed during roasting process :

Stage-4

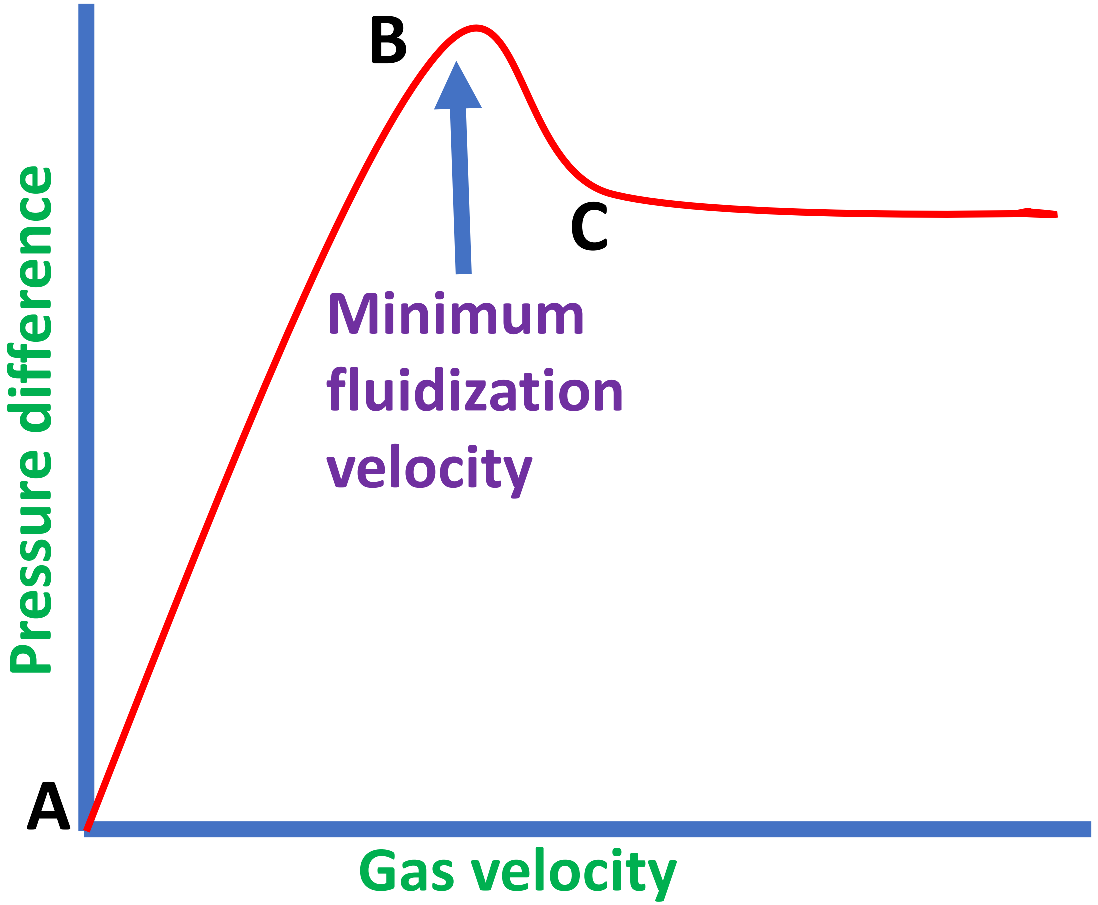
- Further increase in gas velocity lead to continued expansion of the bed.
- Results in increase in interparticle distance.
- Pressure drop across bed continues to decrease as the gas velocity increase.

Stage-5

- Finally, the expansion of the bed is independent of gas velocity.
- Outcoming gas stream appears in the form of bubbles bursting on the surface of the bed which looks like well stirred boiling liquid.
- In this condition the bed is said to be fluidized.
- The fluidized bed has an apparent density distinctly different from the density of the solid and is capable of flowing like a liquid.

Fluidized bed Roasting (continue..)

Stages observed during roasting process :



Typical fluidization curve

AB = Pressure drop across the bed before fluidization.

BC = As pressure drop increases, bed is rearranged and cause minimum resistance to gas flow.

Point C = Maximum voidage of packed bed and minimum gas velocity required for fluidization.

Fluidized bed Roasting (continue..)

Advantages:

- High energy efficiency because it can be autogenously operated.
- Useful in recovery of Sulphur because the gas that it produces has high SO_2 content.
- Ideal for roasting of oxide ores because the oxidizing reactions that take place during roasting is highly exothermic. e.g. Pyrite (FeS_2), Millerite (NiS) etc.

Sinter Roasting / Blast Roasting

- Fine ore & concentrate have to be agglomerated before they can be charged in a blast furnace.
- Treatment of sulphide ore in a sintering machine where roasting and agglomeration take place simultaneously.
- Charge = (fine ore+ moisture) as layer of 15-50 cm thick on revolving belt.
- Combustion is done by burner.
- Speed is adjusted - roasting should be completed before it is discharged.
- Produce porous cinder called sinter.
- Cooled sinter is sized to give uniform product.

Lead Roasting

- PbS lead ore (Galena) is friable, brittle and fuses easily.
- For blast furnace smelting it should be in the form of hard, strong and porous. Hence sinter roasting is carried out in Dwight-Lloyd sintering machine.
- Roasting reacting:

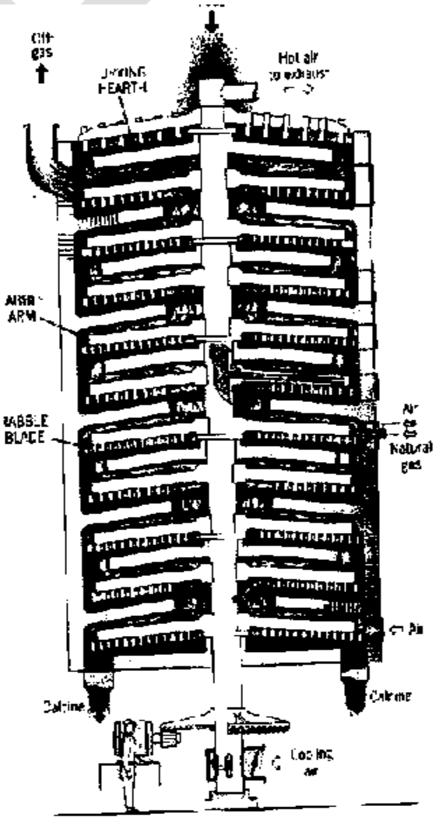
$$PbS + 3/2\ O_2 \rightarrow PbO + SO_2 \text{ at } 800°C$$

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

INDUSTRIAL ROASTING UNITS:

MULTIPLE HEARTH ROASTER

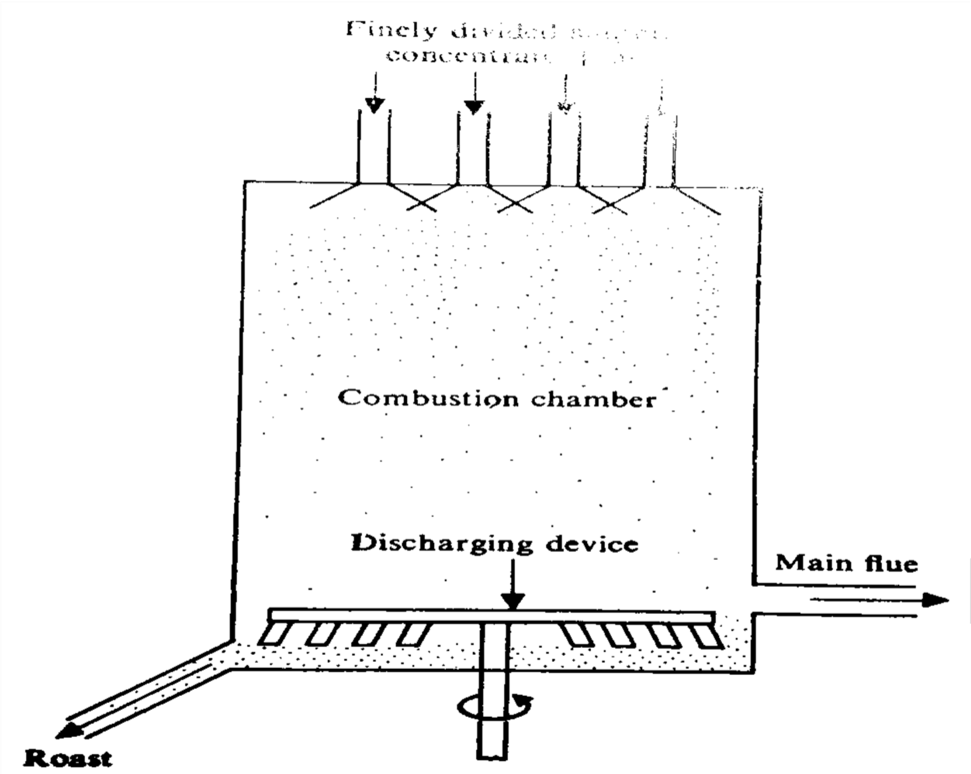
- Consists of circular bricks superimposed on each other.
- The entire structure is enclosed in a circular brick lined steel shell.
- Rabbles are attached to arms.
- Arms are attached to rotating central shaft.
- Ore is fed at the top.
- Oxygen is blown at bottom.
- Due to the countercurrent flow of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



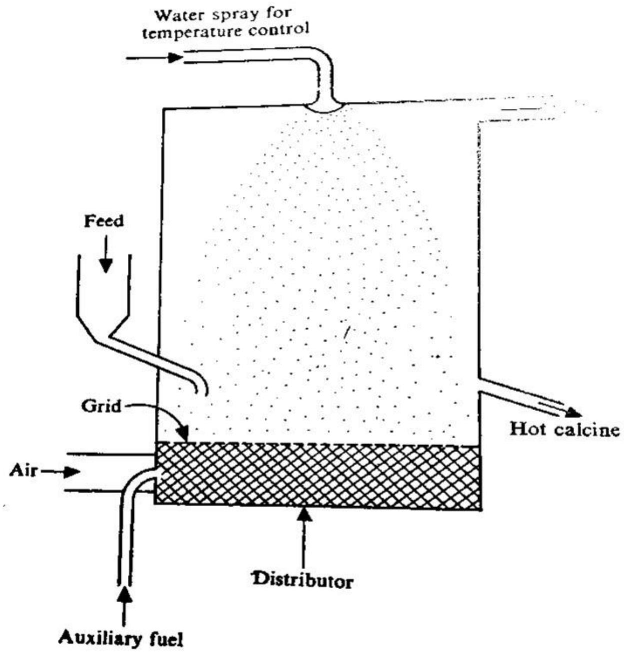
Drawback:-The roasting process is slow and the Sulphur gases evolved when a sulphide is roasted are unsuitable for the production of sulphuric acid because they do not contain sufficient SO_2 and SO_3.

FLASH ROASTING:

- Instantaneous oxidation(flashing)
- Large combustion zone.



FLUIDIZED BED ROASTING:



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

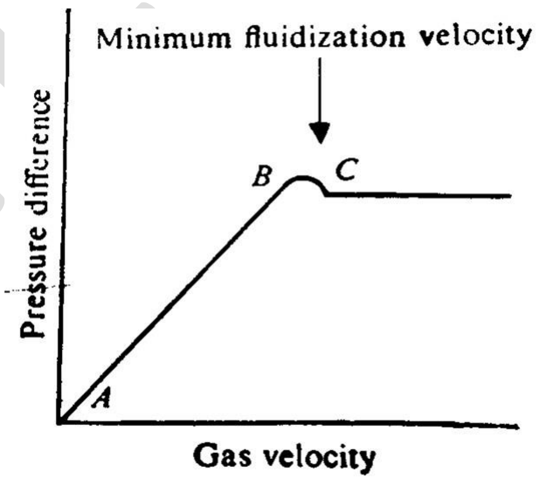
Five stage of fluo-solid roasting

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

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

- As the gas velocity increases the bed expands upward due to the effect of the drag force exerted by the gas stream. In this stage the pressure drop across the bed depends on the gas velocity.
- When the gas velocity is further increased a stage is eventually reached when the pressure drop across the bed is equal to the weight of the particle per unit area of the bed. The particles now remain individually suspended and offer less resistance to the gas flow.
- when further increases in the gas velocity leads to the continued expansion of the bed since such an interparticle distance , the pressure drop across the bed continues to decrease as the gas velocity increases .
- Finally a stage is reached when the expansion of the bed becomes independent of the gas velocity.
- Fluidized bed roasting is autogenous so its efficiency is more.

Diagram of typical fluidization curve



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

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

Factors on which ignition temperature depends for fluidized bed roasting

- Fluid flow
- Geometry of a reactor

- Characteristic of ore

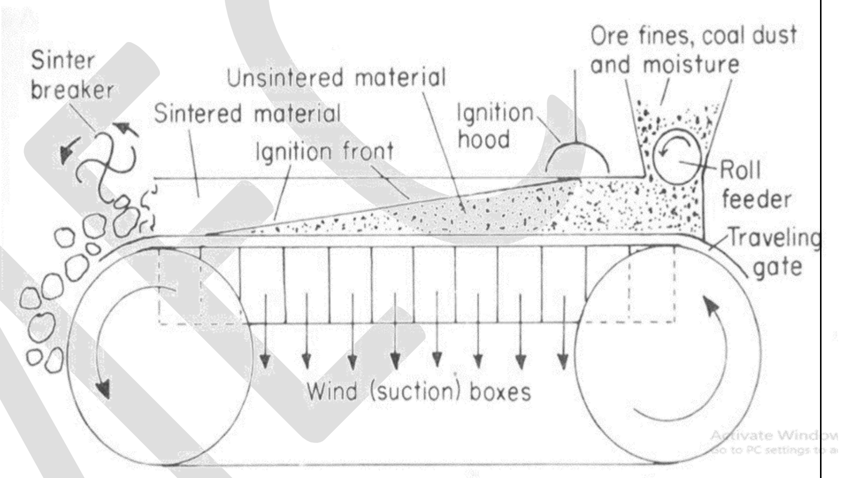
The ignition temperature roughly indicates the temperature required for fluidized bed roasting.

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

SINTER ROASTING (SINTERING):

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

Steps in sinter roasting



- The fine concentrate is charged as a layer 15-50 cm thick on to the endless revolving belt or grate or pallets which moves over wind boxes at regular speed.
- Burners under the ignition hood is used to start the combustion of the bed surface. This combustion is propagated through the mass or charge by a current of air drawn through the charge into the wind box below which is connected a suction fan sufficient high temperature are develop in the material to cause partial or incipient fusion which produces a pores cinder like material called sinter.
- When the sinter reaches the end of the machine it is discharged and cooled.
- The cooled sinter is sized to give a uniform product.

- The sinter roasting of sulphide ore does not require
- Addition of any fuel to the charge because the Sulphur in the charge itself act as a fuel. But for an oxide or fuel is required. Ex- iron ore.

CHAPTER- 3

SMELTING

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

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

Blast furnace- reduction smelting

Reverberatory furnace- matte smelting

Electric arc furnace- reduction smelting and matte smelting

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

FLUXES

REASON OF USING FLUXES:

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

Flux are classified according to their chemical type.

CRITERIA FOR CHOOSING FLUX:

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

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

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

SLAGS:

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

Slag is a separate phase because:

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

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

The role of slag:

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

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

Basic oxides: FeO, MnO, CaO, MgO. Na2O etc.

Acid oxides: SiO2, P2O5 etc.

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

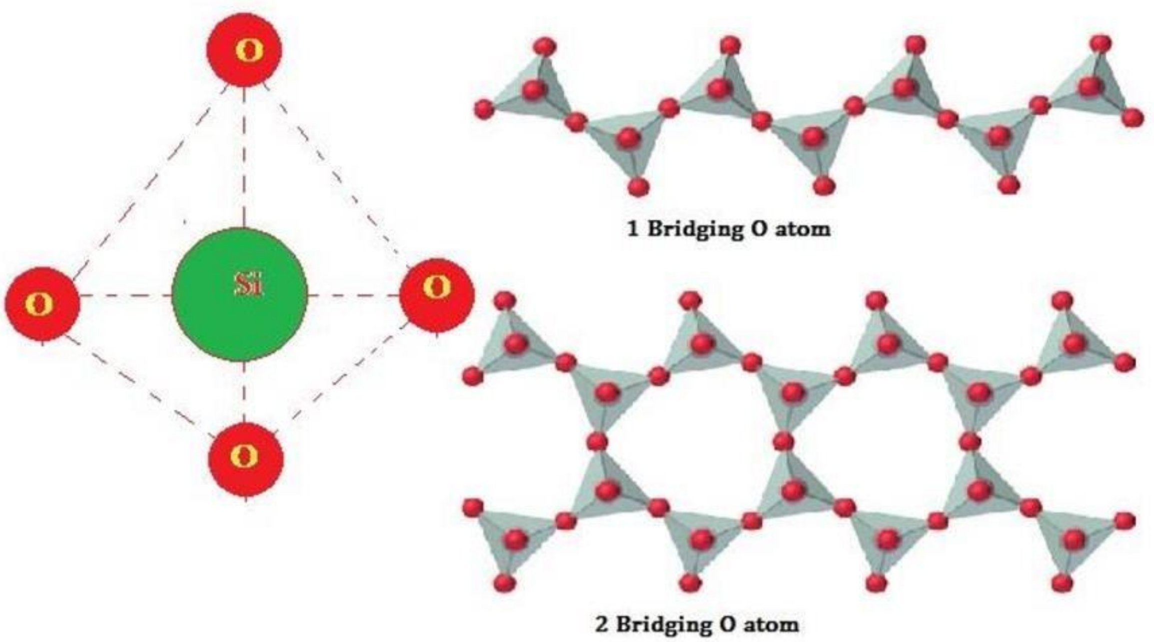
$V\ ratio = wt\%\ CaO/\ wt\%\ SiO2$

$Modified\ V\ ratio = wt\%\ CaO/[\ (wt\%\ SiO2) + (wt\% Al2O3) + (wt\% P2O5)\ ]$

The basic oxides have octahedral and acidic oxides tetrahedral structure.

STRUCTURE OF PURE SILICA

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



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

NETWORK FORMER AND BREAKER OXIDES

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

Basic oxides like CaO, MgO, Na2O, FeO dissociate and form simple ions like Ca2+ andO2−. All basic oxides are donors of oxygen ions. These oxides are called network breakers, since they destroy the hexagonal network of silica by reacting with it.

STRUCTURE OF SLAG

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

CaO = Ca2+ + O2−

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

Note that Ca2+ can combine with two tetrahedrons

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

Na2O + 2Na+ O2− and

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

METAL LOSES IN SLAG

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

- Example- during the blast f/c smelting of lead ore a significant lead oxide (PbO) may combines with silica to enter the slag as silicate.
- PbO loss can be minimize by adding scrap iron to the charge. Function of scrap in extraction of Pb. A- it reduces PbO to Pb, B- it help recover the lead from the silicate slag.
- $PbO + Fe = FeO + Pb$,
- $Pb.SiO2 + Fe = FeO.SiO2$

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

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

FORMATION OF SLAG

The formation of slag is facilities by adding fluxing agent to ore such as quartz and lime, which together with the gangue forms multicomponent silicates slag with a relative low melting point. All silicates melts are viscous. To facilitate the removal of silicates the viscosity should be decrease either by two means:

1- Adding suitable basic oxide

2- Increasing the temperature.

SILICATE MELTS

Silicate melts are ionic in nature. Composition of silicate melts: there could be

1- Metallic ion

2-free oxygen ions

3-Complex silicates of varying size

4- How ever there could not be a silicon ion.

REASON OF HIGH VISCOSITY OF SLAG

Bulky less mobile silicate ions, which decrease the overall fluidity. Structure of silicate slag: structure of pure crystalline slag is a three dimensional network, consisting of silicon and oxygen atoms. (Where each silicon atom is tetrahedrally attached to four atoms of oxygen. Possessing both long range order and short range order. But in molten silica however some si---o—si bonds ruptures due to the effect of thermal energy and some depolymerization takes place, the short range order PERSISTS , even the long range order is lost. In such a situation viscosity is very high. When a basic metal oxide is added to molten silica the three dimensional network starts breaking. Here silica (acidic oxide) accept an oxygen ion and Mo (basic oxide) donates an oxygen ions. The depolymerization reaction shows that as the quantity of the metal oxide added increases the silicates network is broken down into smaller and smaller unit. Adding metal oxide to silicate stage at a concentration of 12 mole % the silicate networks break down in random manner, this means the three dimensional bonding would still be present through melt. Further addition leads to complete breakdown of silicates to gives discrete globular anions of the types $Si_3O_9^{6-}$, $Si_4O_{12}^{8-}$ etc. Further addition of metals oxide leads to break down of oxygen bridge and at a composition of Mo: SiO_2 = 2:1. The smallest unit SiO_4^- is obtained. On adding further metal oxide free oxygen ions (o2-) becomes available in the melt.

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

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

REDUCTION SMELTING USING CARBON

- Why carbon occupies unique position as a reducing agent :
    - Easily available abundant.
    - It is inexpensive.
    - According to theory all metal oxide be reduced by carbon provided the temperature is high. Metal oxide reduction by carbon at high temp :
      $MO + C = CO + M$
      $2MO + C = 2M + CO2$
      We observe that temperature required for reduction of oxide by carbon in number of case are beyond practical limit.

SOLID AND GAS REDUCTION

- $MO + CO = M + CO2$

- CO2 + C = 2CO

COMBINING THESE TWO REACTION

- MO + C = CO + M

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

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

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

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

PROBLEMS AT HIGH TEMPERATURE:

- At high temperature a new stable phase namely the metallic carbides may appears, this occurs when metal react with carbon itself.
- Formation of carbide is suppressed if the metal were produced in the presence of another solvent.
- The solvent metal in which metal M is dissolved reduces the chemical potential of M and pushes the reduction reaction to the right, making reduction possible at lower temperature.
- Greater the dilution the lower the temperature required for reduction. for some reason carbide formation are discoursed if M in the form of alloy.
- The production of ferroalloy also makes uses of the advantage gained by alloying Ferro vanadium, ferrotitanium, Ferro silicon, Ferro niobium, and other Ferro alloys are produced by the reduction of corresponding oxide by carbon in the presence of iron.
- Even alloying does not always ensure a carbide free product. Ex- Ferro chrome normally contains a high proportion of carbon, the composition approaching $Cr_4C(Fe)$.

METALLOTHERMIC REDUCTION OF OXIDE

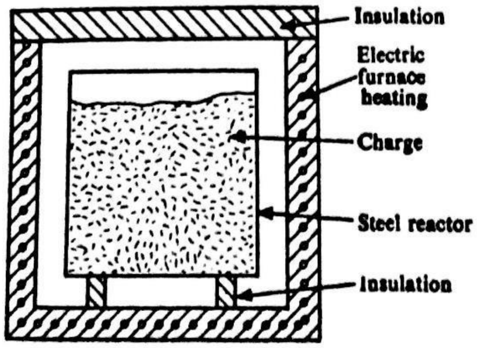


Fig. 4.8 Unit for Metallothermic Reduction.

- An oxide is reduced by a metal that forms stable oxides.
- Metallothermic reaction, carried out in an open container or a closed container (bomb) completely avoid carbon contamination.
- Metallothermic reduction principle is same as carbon reduction.
- Metallothermic reduction is usually carried out on a small scale and rarely referred as smelting.
- Principle: a metal that forms a stable oxide would replace metals from a less stable oxides.

FACTORS ON WHICH METALLOTHERMIC REDUCTION DEPENDS

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

$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$

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

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

The reduction Of $TiO2$ by calcium

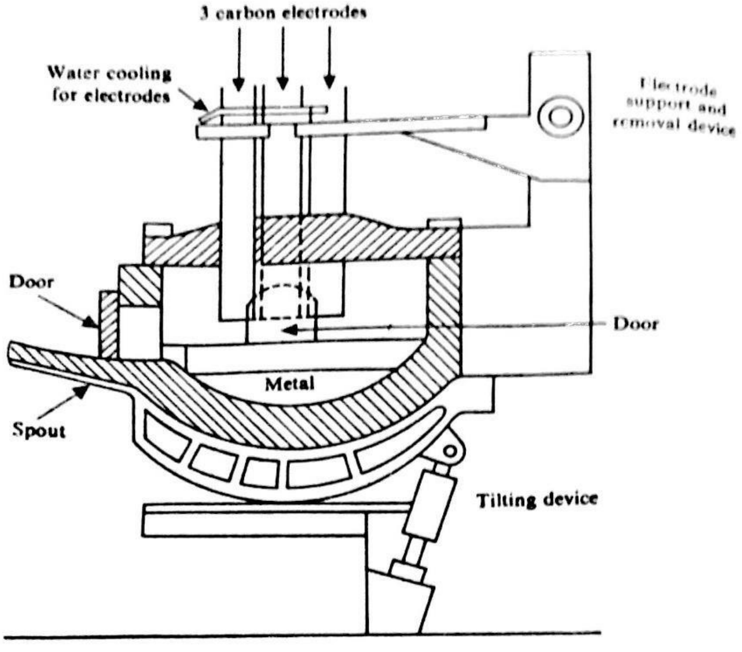
$TiO2 + 2Ca = 2Cao + Ti$

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

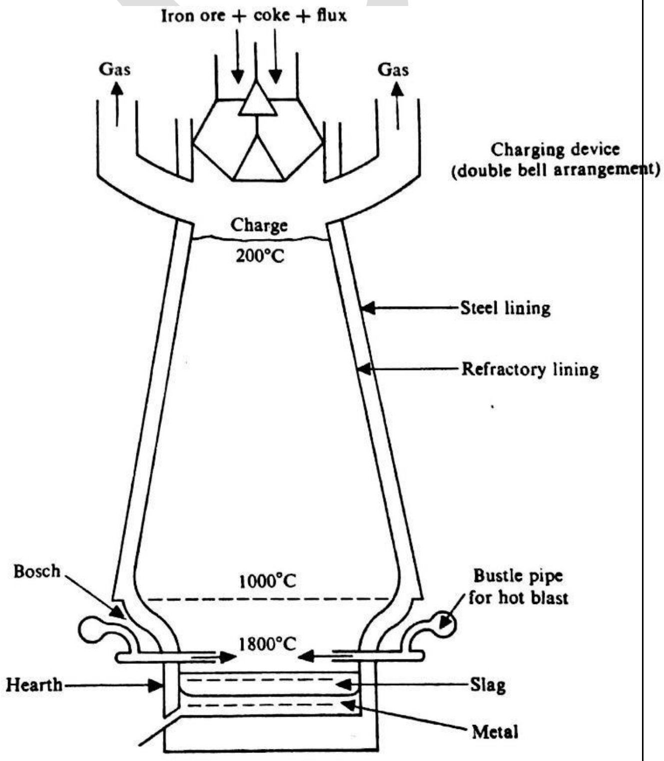
DIFFRENCE BETWEEN CARBOTHERMIC REDUCTION AND METALLO THERMIC REDUCTION

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

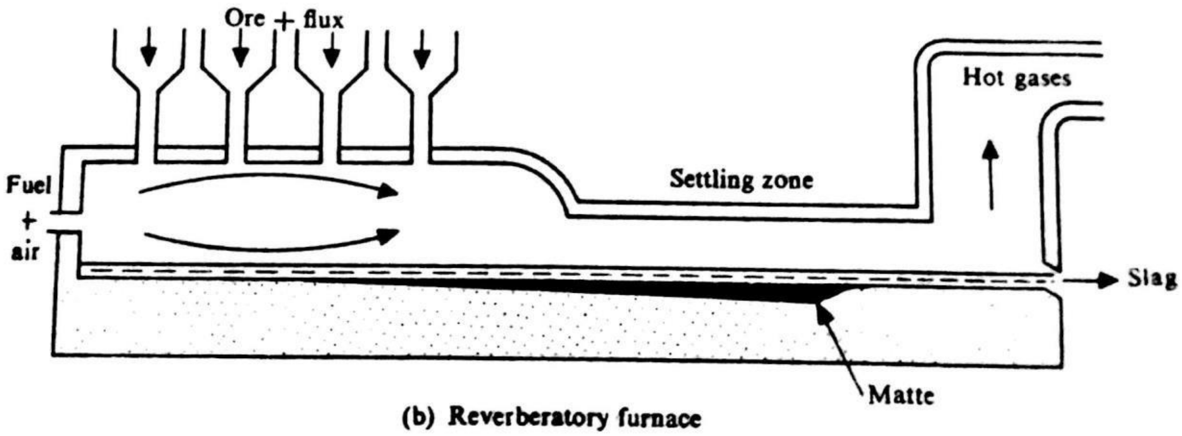
SMELTING FURNACES



(c) Direct arc electric furnace



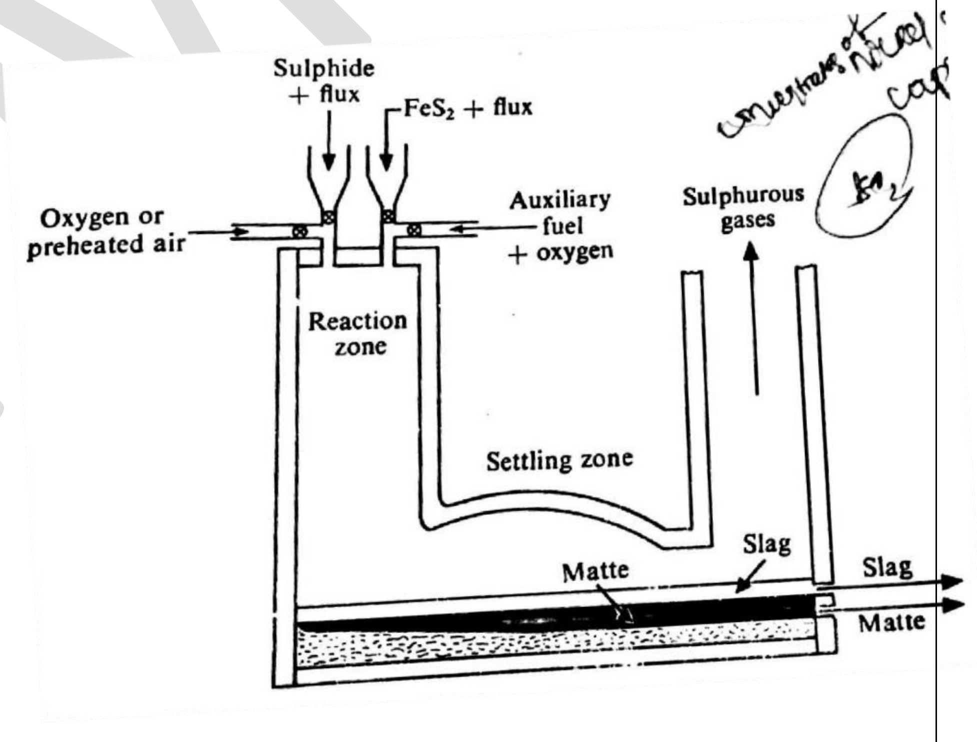
Iron blast furnace



(b) Reverberatory furnace

FLASH SMELTING

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



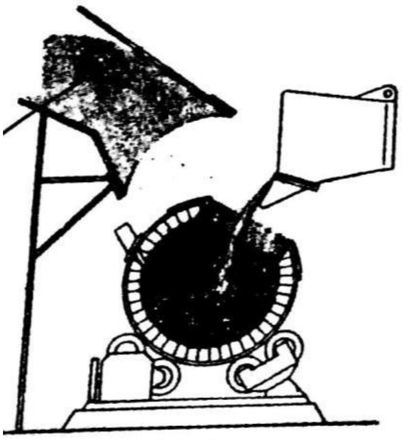
- In this smelting process, enriched preheated air or pure oxygen is usually used instead of air to increase the combustion rate and to maintain autogenous smelting.
- The gases coming out of the furnace is rich in SO_2 or SO_3 which is further used for the manufacturing of sulphuric acid.

MATTE SMELTING

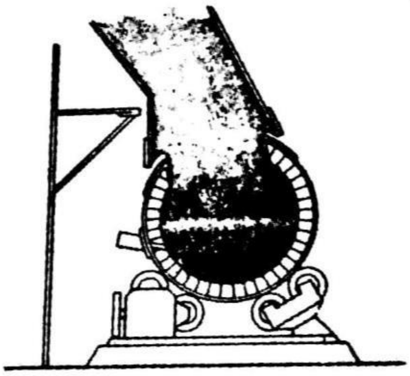
- In matte smelting, the sulphide ore is fused with a flux to produce a molten mixture of sulphides known as a matte.
- The gangue materials pass off into the slag, which is immiscible with the matte, i.e., it forms a separate layer. Some Sulphur is lost in the furnace gases as SO_2 or SO_3. In this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

CONVERTING

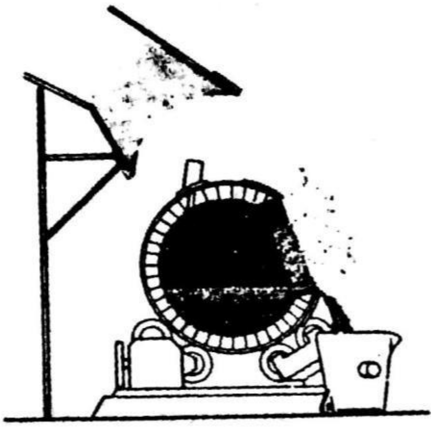
- The purpose of converting is to remove iron ore, Sulphur and other impurities from matte.
- For the process, the molten matte produced as a result of smelting, is fed into the side blown converter which is a cylindrical vessel with a capacity of 100-200 tons of matte.
- A typical vessel is 4m in diameter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



Charging



Blowing



Skimming

HYDROGEN REDUCTION

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

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

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

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

CHAPTER-4

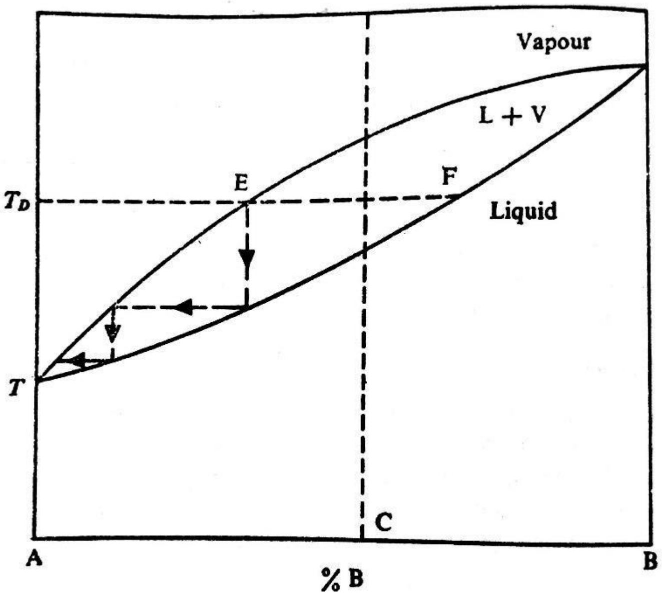
REFINING

DISTILLATION

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

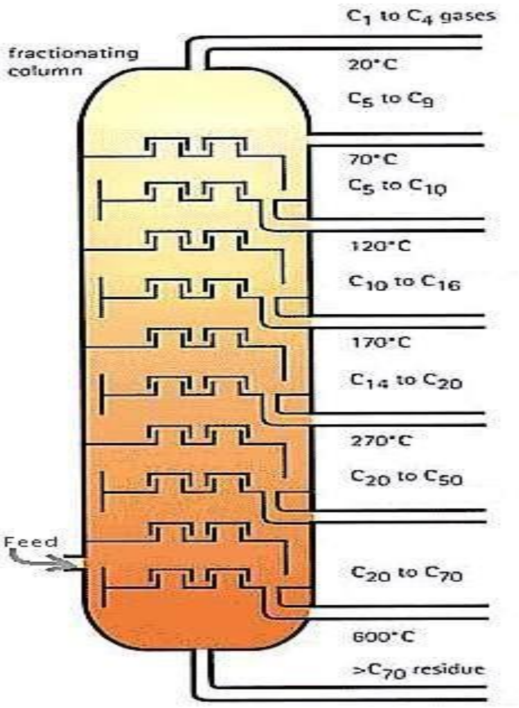
SIMPLE DISTILLATION

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



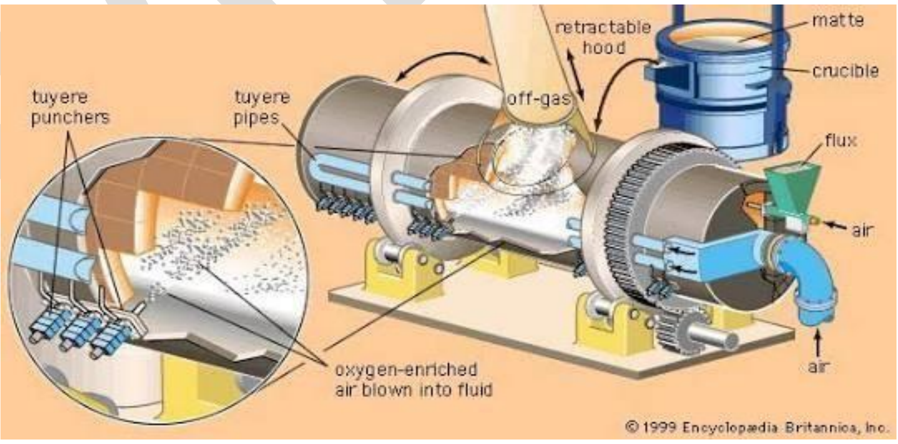
PROBLEM: - This process suffers from the inherent problem that enhanced purity must necessarily be achieved at the cost of reduced recovery.

FRACTIONAL DISTILLATION



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

FIRE REFINING



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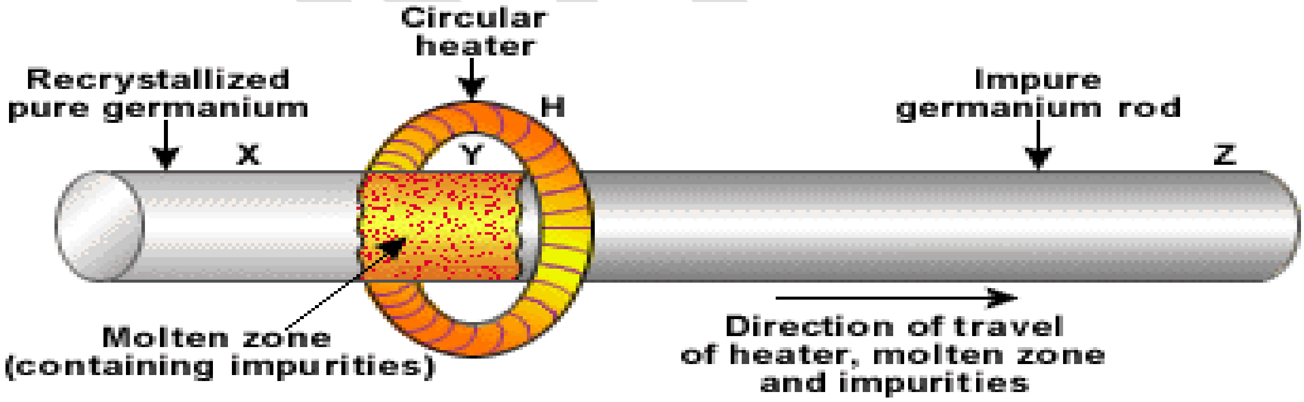
- This technique is used to remove more reactive elements from a molten metal by preferential oxidation.
- This technique is suitable for refining of iron, lead, tin and copper.
- The reagent used for this refining method is atmospheric oxygen which is blown through the metal.
- Flux is added in order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

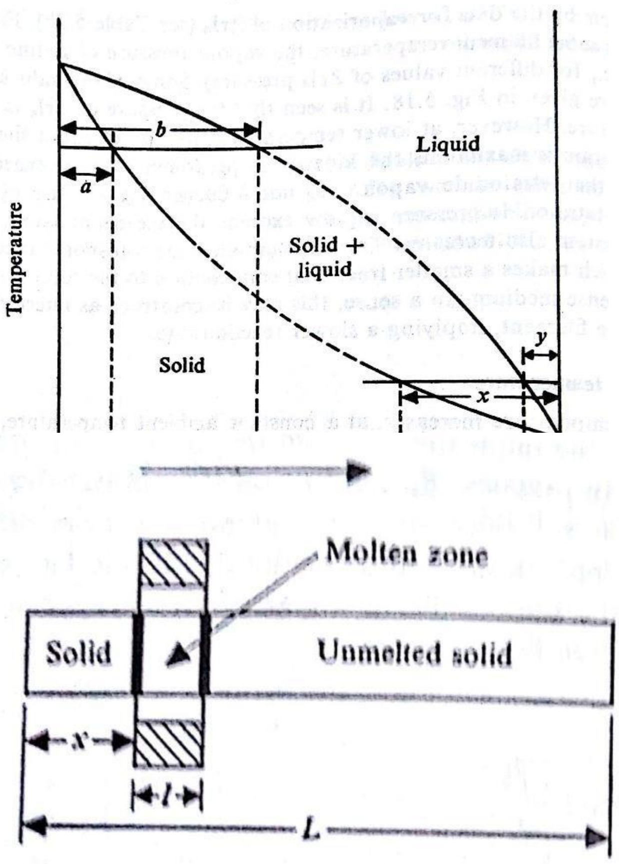
ZONE REFINING

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

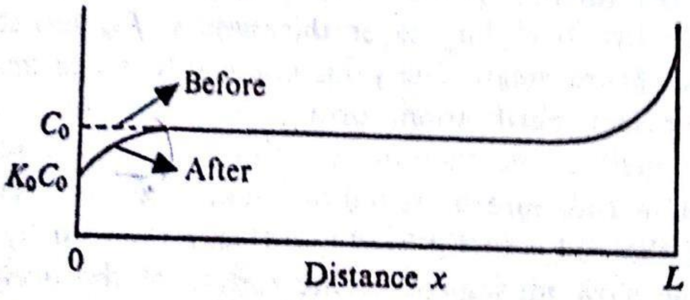


- The zone passage is repeated several times in the same direction. After repeated passages, the impure end is removed, leaving behind a zone-refined pure material.

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



(a) Zone refining



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

INTRODUCTION TO HYDROMETALLURGY

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

Steps in hydrometallurgical extraction process

1-Prepration of ore for leaching

(a)-grinding

(b)-removal of specific impurities by physical methods

(c)-roasting

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

2- Leaching

In leaching, by using a suitable liquid reagent the metallic values in an ore are selectively dissolved.

The selective dissolution depends upon the nature of reagent.

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 posses a serious problem.

CONCENTRATE FOR LEACHING:-

- Leaching is a process which selectively dissolves the feed material. In leaching metallic values containing the main metal goes into the solution leaving behind the gangue and solid residue.
- But some exception is there where gangue desirable to leach in case of Thorium.
- To facilitate material handling and to minimize the consumption of the leaching reagent an ore is usually concentrate prior to leaching, except when leaching is carried out In situ, as in solution mining, dump leaching, heap leaching or vat leaching.

LEACHING SOLUTION PREPARATION:-

- Leaching solution contains:-
- main solvent
- wide variety of reagent (helps in the dissolution because of their chemical effects)

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

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

Examples of reagent are:-

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

CRITERIA OF SELECTING A LEACHING REAGENT: -

1- Leaching by a reagent must be as selective and as rapid as possible (depends on nature of ore and reagent)

2- It should be possible to dissolve the reagent in order to prepare a sufficient strong leaching solution which can ensure fast rate of leaching.

3- The reagent should not corrode the equipment.

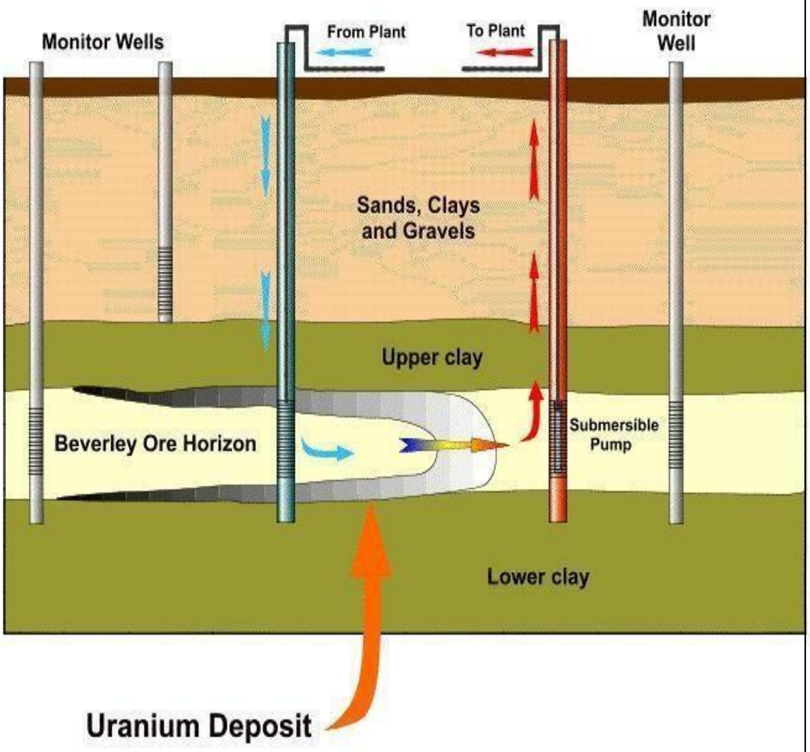
4- The reagent should be economical and should preferably allow regeneration.

LEACHING OPERATION:-

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

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

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



Advantages:-

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

Disadvantages:-

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

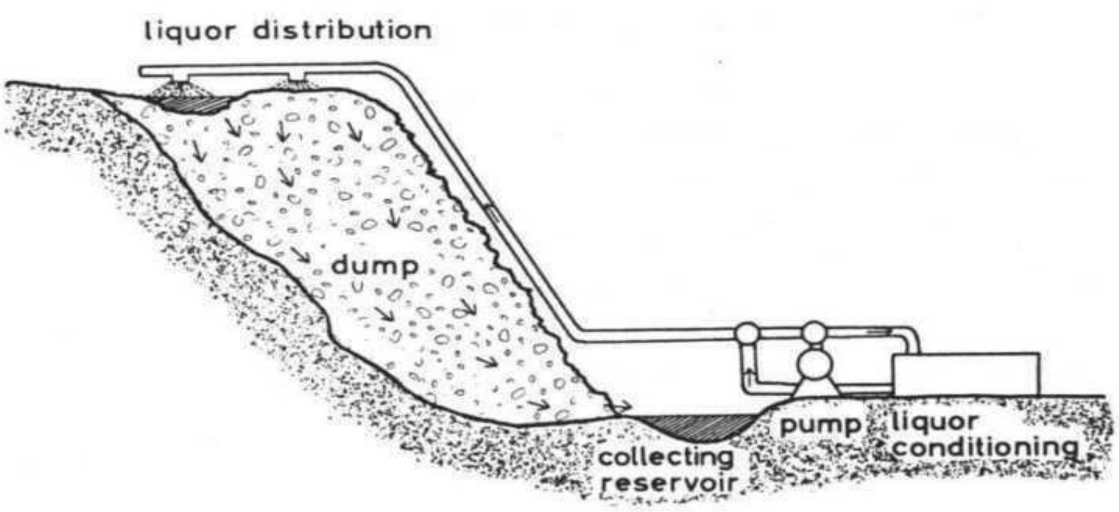
2- **Dump Leaching: -**

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

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

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

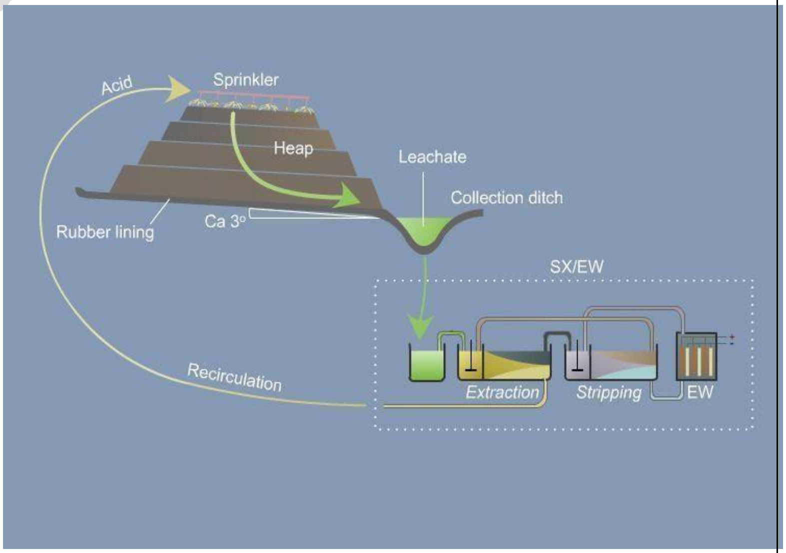
3-



dump ore leaching on a slope

Heap Leaching:-

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

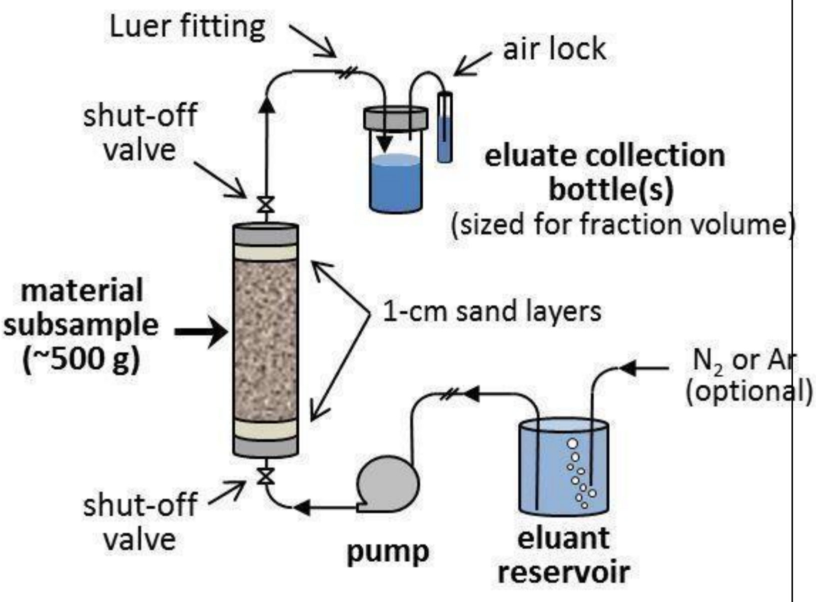


and/or clay lined leach pad where it can be irrigated with leach solution to dissolve the valuable metal.

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

4- Percolation Leaching:-

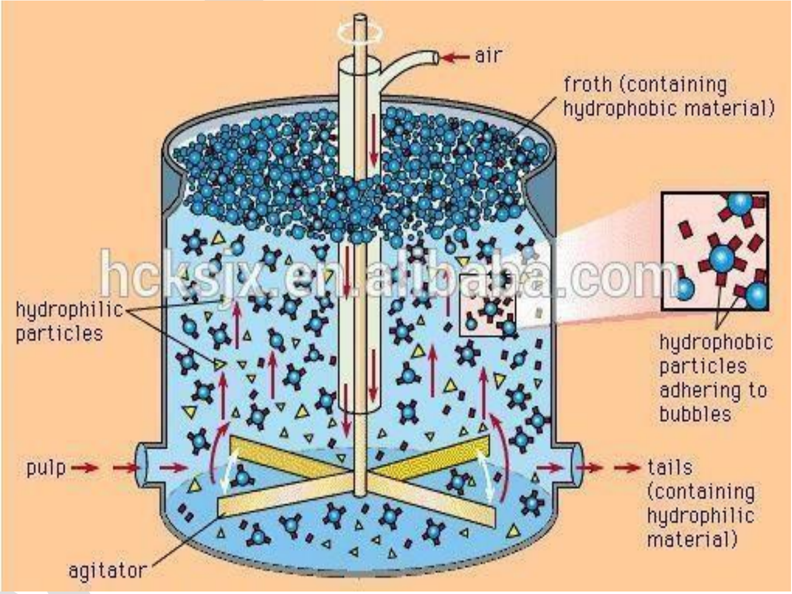
- It is a selective removal of the metal values from a mineral by causing a suitable solvent or leaching agent to seep into and through a mass or pile of material containing the desired material.
- In this process, the leach solution is percolated upward or downward through an ore which has already been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



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

5- **Agitation Leaching:-**

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



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

Theory of Leaching:-

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

Slime leaching:-

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

Ex-$CuSO_4 + nH_2O = CuSO_4.nH_2O$

Acid leaching:-

$ZnO + H_2SO_4 = ZnSO_4 + H_2O$

$ZnO + 2H = Zn + H_2O$

Alkali digestion:-

$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$

$Al_2O_3 + 2OH = 2AlO_2 + H_2O$

Leaching with oxidation:-

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

Leaching with reduction:-

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

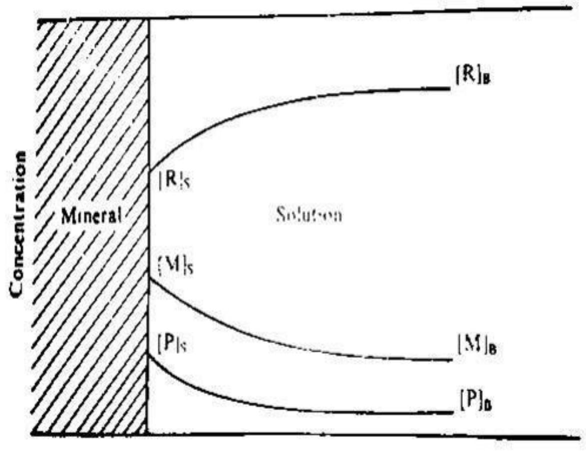
KINETICS OF LEACHING

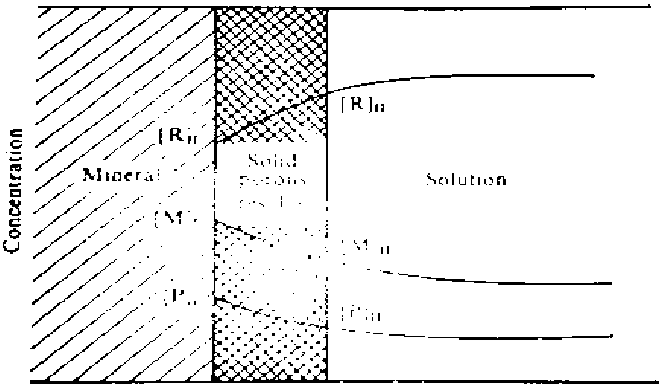
Figure shown below is the concentration profile when a mineral surface dissolves in a leaching medium. Subscript S refers to surface or interface whereas Subscript B refers to bulk.

From the diagram it is noted that;

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

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





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

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

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

Bioleaching/Microbial leaching

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

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

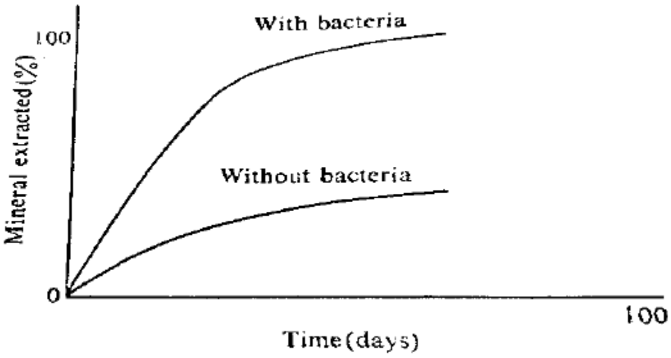
Microorganisms are used because

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

There are three most important types of bacteria used

- Thiobacillus thiooxidans
- Thiobacillus ferrooxidans
- Ferrobacillus ferrooxidans

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



Oxidation of sulphide minerals

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

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

Iron oxidation

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

$2H^+ + ½O_2 + 2e = H_2O$

Process

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

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

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

Some important information

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

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

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

Factors affecting Bio leaching

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

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

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

CYANIDATION OF GOLD AND SILVER

Cyanidation:-

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

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

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

$2Au+4NaCN+2H_2O+O_2=2NaAu(CN)_2+2NaOH+H_2O_2$

$2Au+4NaCN+H_2O_2=2NaAu(CN)_2+2NaOH$

$4Au+8NaCN+O_2+2H_2O = 4NaAu(CN)_2+4NaOH$

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

two steps :- oxidation step, reduction step

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

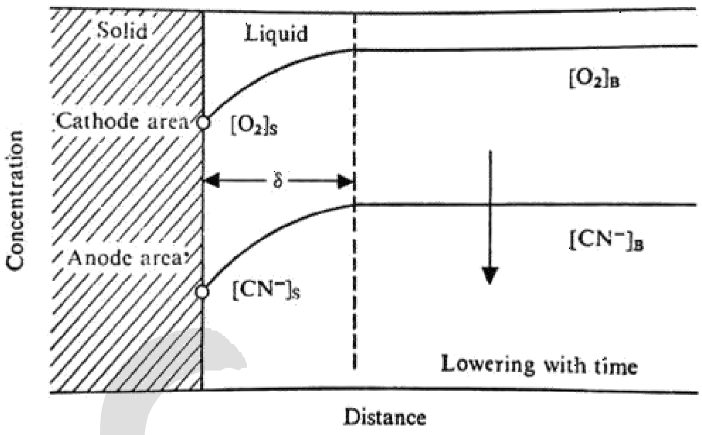
$O_2+2H_2O+2e=H_2O_2+2OH^{-}$

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

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

(i) Anode

(ii) Cathode



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

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

Fick's 1st law of diffusion:-

dn/dt =-DA dc/dx]

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

D = diffusion constant

Dc/dx = concentration gradient

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

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

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

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

- So diffusion of CN^- will be

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

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

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

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

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

= 2× molar rate of dissolution of oxygen

= ½× molar rate of consumption of cyanide

Hence,

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

i.e,

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

Similarly,

$A_2 = 2R \times \delta / D_{CN^-}[CN^-]_B$ The total area **A** is given by equation 1 :-

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

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

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

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

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

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

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

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

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

   (1). When

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

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

Recovery of metal from leach liquor

1. Solvent extraction

2. Ion exchange

3. Precipitation

4. Cementation.

SOLVENT EXTRACTION

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

Steps for solvent extraction

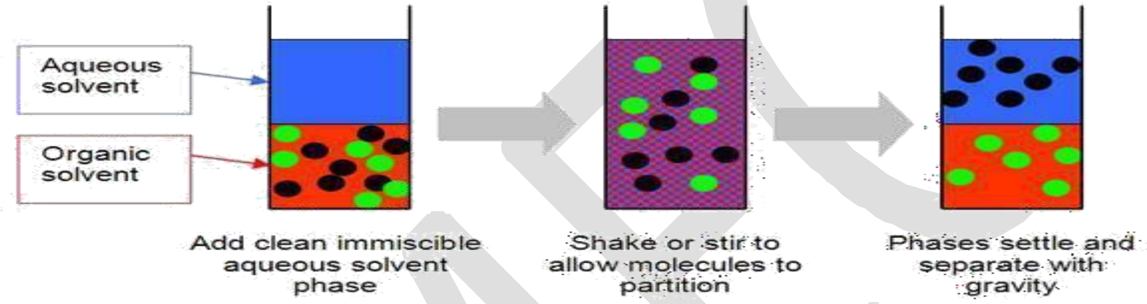
1. **Dissolution**-ion dissolution the impure compound or the ore is dissolved into a alkaline or acid aqueous solution.

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

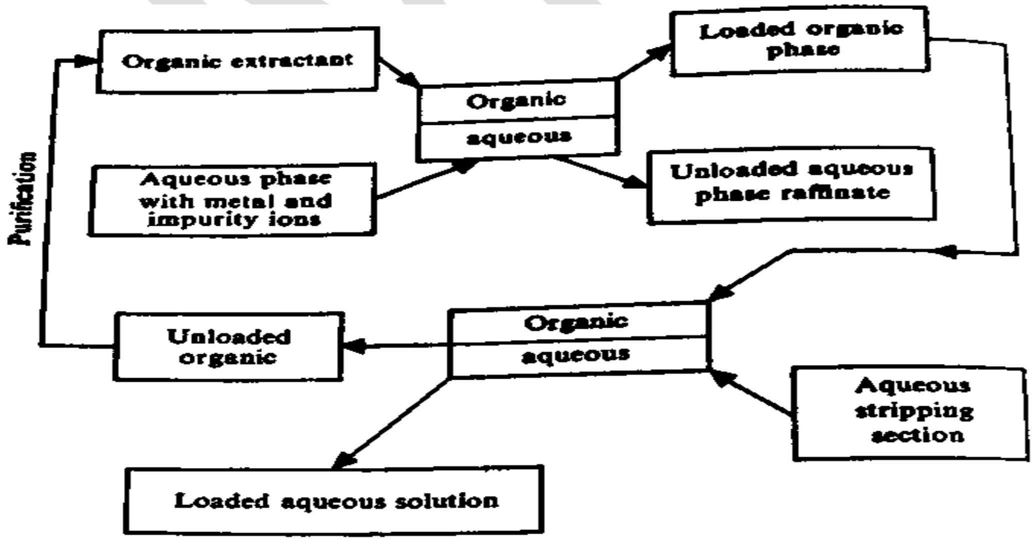
The metal ions enters into the organic solution.

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

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



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



Extraction of coefficient

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

y= concentration of solute in the organic phase.

x=concentration of solute in the aqueous phase.

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

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

   E_f = Extraction factor

   l=volume of light organic phase

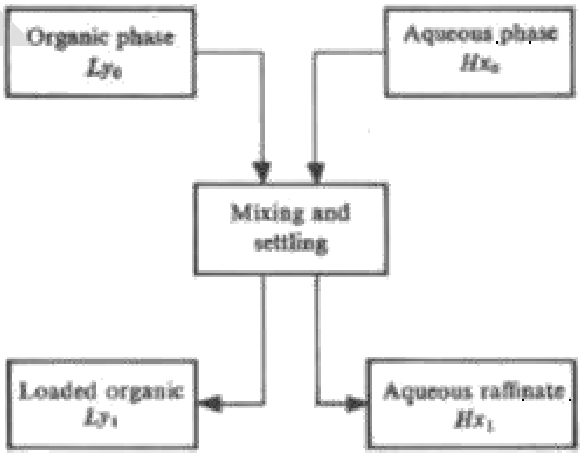
   h=volume of heavy aqueous phase

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

PROCESSES

SINGLE STAGE CONTACTING

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



Single stage solvent extraction process

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

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

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

$Hx_0 = Hx_1 + Ly_1$

Also we know that

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

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

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

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

It results in high efficiency only if E_f is high.

MULTISTAGE COCURRENT CONTACTING

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

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

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

COUNTERCURRENT EXCHANGE

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

CONTINEOUS COUNTER CURRENT EXTRACTION

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

ION EXCHANGE-

1. When a solution of ammonium sulphate is percolated through a layer of soil then the resulting efficient is found to contain calcium ion no ammonium ions.
2. This is because of exchange ions between the solution and the soil.
3. In ion exchange method which can be used in the preparation of pure compound the solid phage is made initially absorbed a suitable ion of desired metal through an ion exchange reaction.
4. The absorbed ion is subsequently taken into solution by once again applying ion exchange reaction tis is called ellution.
5. This solid phase generally a synthetic resin. This resin is a complex organic acids or bases which is insoluble in water.

Cation exchange resin

This structure can be written as Rx. When R=polymer, X=ion exchange side or exchangeable ion. If X is a sulphonic group (SO3H) THEN (H) in the sulphonic group is replaced by the cation .when the cation exchange resin (RSO3H) reacts with the leaching solution containing suitable cation .

Anion Exchange resin:-

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

-When ion exchange resin reacts with the leaching solution containing suitable anion the NO3 or

Cl group is replaced by the anion.

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

(1) Size and valence of the ion taking part in exchange reaction.

(2)Concentration of ion in the solution.

(3)Physical, chemical characteristic of the ion exchange reaction.

(4)Temperature

Ion exchange kinetics:-

The various steps in this process are:-

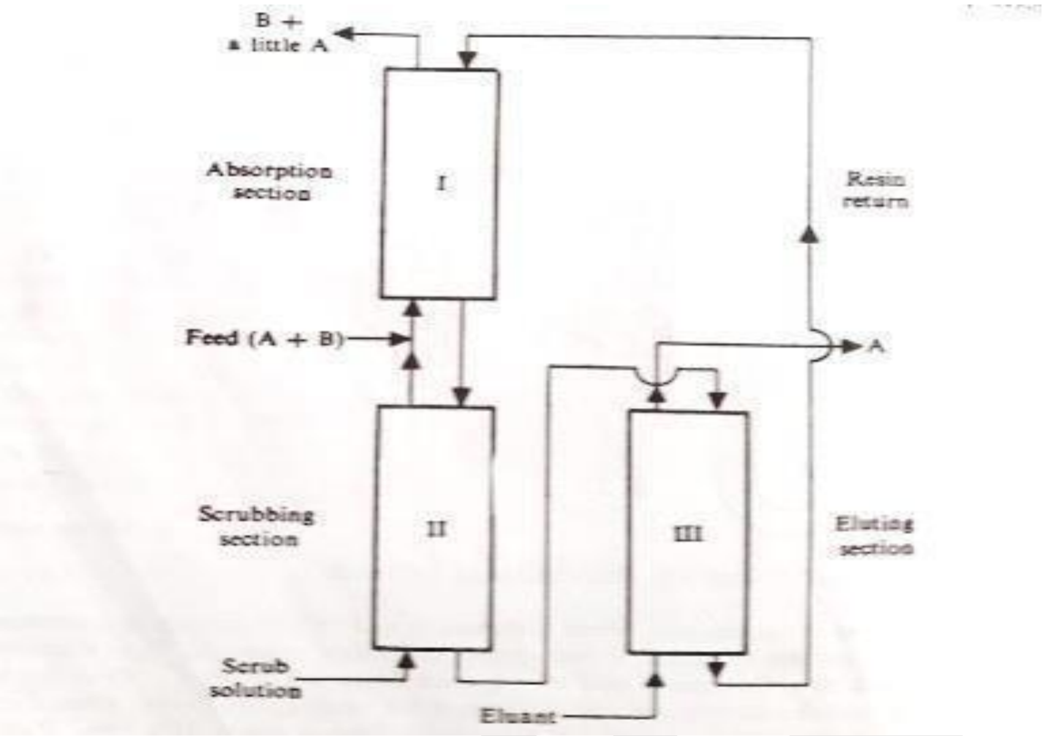
(1) The transport of an ion from the solution across a boundary surrounding the region which is in the form of bead.

(2) Diffusion of ion in the inter ion of the region

(3) The main chemical exchange reaction

(4) Diffusion of the outgoing ion to the surface of the resin bead.

(5) Diffusion of the outing ion across the boundary.



Three column continuous counter-current ion exchange

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

PRECIPATION:

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

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

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

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

CONTACT REDUCTION (cementation)

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

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

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

$Fe + CuSO_4 = FeSO_4 + Cu$

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

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

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

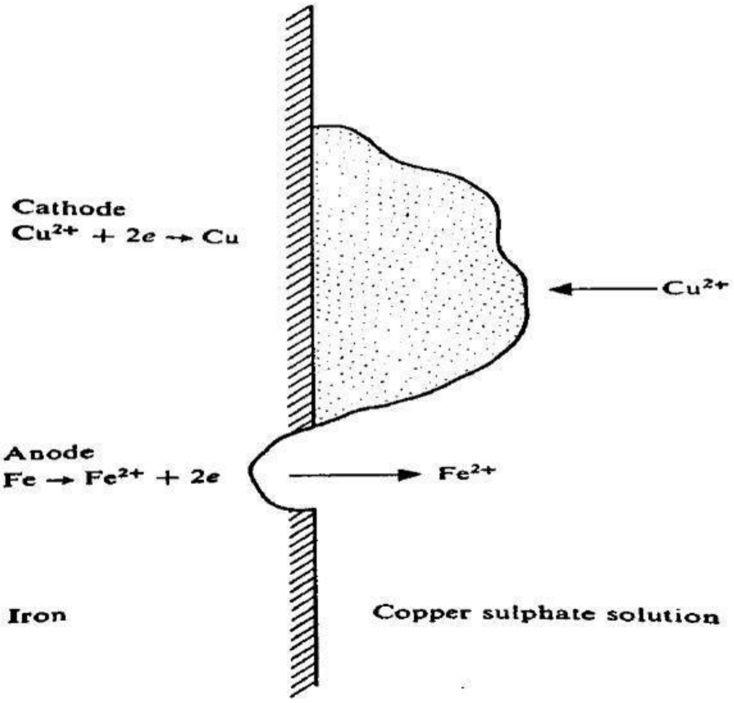
In this iron dissolves at the anode, and each copper ion picks up electrons at the cathode to deposit metallic copper.

The general reaction for the reduction of a metal ion $M_1^{Z_1+}$ by a metal M_2 to form $M_2^{Z_2+}$ ions is written as:- $M_1^{Z_1} + \frac{Z_1}{Z_2} M_2 = M_1 + \frac{Z_1}{Z_2} M_2^{Z_2+}$.

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

$$E_2 = E_2^0 + \frac{RT}{Z_2F}\ln C_2,$$

Where F is the Faraday constant, E_1^0 and E_2^0 are, respectively, the standard potentials of M_1 and M_2. Due to the continuous flow of anode area to the cathode area, this system has a unique electrode potential E-known as the ‘compromise potential’- which is less than the equilibrium potential E_1 of the cathode greater than the equilibrium potential E_2 of the anode. If the slow discharge is controlled by diffusion or reaction at cathode, that is, by a cathodic process, the anode reaction will essentially be at equilibrium. In such a situation, the compromise potential will be equal to the anode equilibrium potential E_2. This situation implies that the over potential at the anode would be negligible, which is indeed the case in most contact process,



Chapter 2

Electrometallurgical Extraction Processes

2.1. Overview of electrometallurgical processes

Electrometallurgy deals with the conversion of metallic salts, oxides or sulfides into metals (electrowinning) or with purification of the metals (electrorefining) by electrolytic processes, i.e. processes where the chemical energy required by the chemical reactions is supplied by electrical energy, involving passage of an electric current through an electrolyte that conducts current between two electrodes

There are two main electrolysis processes:

– *aqueous salt electrolysis*: electrowinning of metals (Cu, Zn, Ni, Co, Cd and Cr) from their salts and electrorefining of impure metals (copper, nickel, lead and tin);

– *fused salt electrolysis*: electrowinning of magnesium from $MgCl_2$, of aluminum from alumina.

The extraction of metals from their salts or oxides by electrolysis requires the electrolyte to be an ionic conductor. An electrolyte possessing electronic conductibility leads to a decrease in current efficiency. Therefore, the electrolyte can only be a salt in an aqueous solution or a mixture of molten salts or oxides.

The extraction of metals by electrolysis of salts (chlorides or sulfates) in an aqueous solution is limited by the discharge of H^+ ions (see section 2.3.3). Metals whose electrode potential is more negative than the hydrogen overvoltage can only be obtained by electrolysis in molten salts. These electrode potentials (see [VIG 11a], Chapter 8, equation [8.2.6]) prohibit the electrolysis of their salts in aqueous media. These potentials are: aluminum: -1.66 V; titanium: -1.75 V; magnesium: -2.03 V; sodium: -2.71 V.

This chapter studies the electrolytic extraction processes in aqueous solution.

2.2. Electrolysis – bases

2.2.1. *The electrolytic cell*

The elementary electrolytic cell (see Figure 2.2.1) is made of a tank that contains the electrolyte and two electrodes, possibly a diaphragm (membrane, see section 2.2.7.3) that separate the cell into two zones, and a generator. Under an applied voltage, a current of ions in the electrolyte, current of electrons in the external circuit and two elementary electrochemical reactions (discharge) on the electrodes occur.

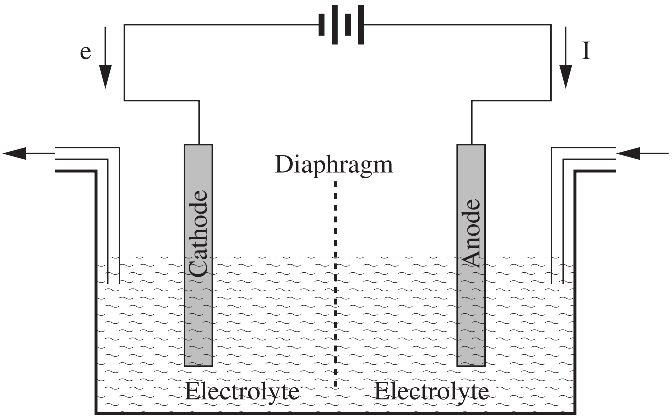


Figure 2.2.1. *Schematic diagram of an elementary electrolytic cell*

At the cathode (negative pole) there is a reduction (discharge of a cation) giving the desired metal, see [VIG 11a], reaction [8.1.2]:

$$M^{z+} + ze \rightarrow M(s \text{ or } l) \qquad [2.2.1]$$

The M^{z+} ion in solution in water or molten salt is reduced by the electrons at the cathode. There is then formation of a deposit on the cathode or a liquid metal layer in contact with the cathode (which in that case is horizontal) depending on whether the metal is solid or liquid at the temperature of the electrolysis.

At the anode (positive pole) there is an oxidation reaction of different nature depending on the electrolytic system considered (see [VIG 11a], reaction [8.1.1]):

$$A^{y-} \rightarrow A + ye \qquad [2.2.2]$$

For instance, there is discharge of the chlorine ion with release of gaseous chlorine at the anode, $2\ Cl^{-} \rightarrow Cl_2(g) + 2\ e$. In the external circuit, a current of electrons flows from anode to cathode.

2.2.2. *Faraday's law*

According to Faraday's law, for reaction [2.2.1], 96,484 coulombs are needed to produce 1 gram-equivalent of metal: M/z. The mass m of metal deposited on or at an electrode is then proportional to the total quantity of electricity I.t supplied[1]:

$$m = (r / 96{,}484) . (M/z) . I.t \qquad [2.2.3]$$

where m is in grams, M is the atomic mass of the element that is deposited at the cathode, z is the valence of the ion involved, I is the current in amperes, t is the time of the operation in seconds and r is the Faraday yield or current efficiency. Only a fraction r of the current is used for the desired deposit. A fraction $(1 - r)$ is consumed by parasite reactions. Industrially, we aim to maximize r.

Industrial electrolyses operate under current control. This is because it is technically easier to control the current than the potential. This is therefore the current I that is flowing through the cell, which thus imposes the production per unit time according to Faraday's law:

$$dm/dt = \alpha\, I \text{ in g/hr} \quad \text{with} \quad \alpha = (37.3 . M/z) . r . 10^{-3} \qquad [2.2.4]$$

In the modern industrial units, the current is increasingly high. This is achieved either by increasing the size of electrodes or number of elementary cells in a "cell tank". The voltage being U, the current is NI for a cell tank with N monopolar cathodes in parallel (see section 2.2.7 and Figure 2.2.4a), the current densities i being 100–1,000 A/m^2 for electrodes of the same surface S:

$$I = i . S \qquad [2.2.5a]$$

---

[1] 1 Faraday = 96,484 coulombs = 96,484 A.sec. = 26.8 A.h. A current of 1 ampere corresponds to 0.01036 mg-eq/sec = 37.3 mg-eq/h. 1 Volt * 1 Faraday: 96,484 (volt.coulomb) Joules = 23,060 calories.

In order for such a current to flow through the electrolyte, a voltage V must be applied at the terminals of the cell.

$$V = E + RI \qquad [2.2.6]$$

where R represents the ohmic resistances of the conductors, electrodes and electrolytic bath and E is the electromotive force (EMF) necessary to ensure both the anodic and cathodic current densities:

$$i = f(E) \qquad [2.2.7]$$

The inter-electrode distance and conductance of the bath, and thus composition of the electrolyte, are fixed in order to minimize the resistance of the electrolytic R_{bath}.

2.2.3. *The electromotive force (EMF)*

In electrolysis, a catholic deposition reaction and an anodic reaction occur, each with its own kinetics and thus its own polarization curve, whose respective positions are shown in Figure 2.2.2. The reversible electrode potential of the anodic reaction needs to be higher than the reversible electrode potential of the cathodic reaction for the electrolysis to occur. The cathodic deposition rate is *a priori* set by the production rate desired, which sets the necessary cathodic current i_c. The EMF, E, for achieving the current, i_a, can be determined by the graphic construction, as shown in the figure. It can be obtained by fulfilling the condition that the cathodic current has to be equal (without considering the sign) to the anodic current and equal to the current that has to flow through the cell. This graphic construction is valid in the case where the surfaces of the two electrodes are equal. We can also fulfill these conditions with anodic and cathodic current densities, such as:

$$I = i_a \,.\, S_a = i_c \,.\, S_c \qquad [2.2.5b]$$

The surfaces of the electrodes are determined to minimize the highest anodic or cathodic overvoltage. The EMF, E, see Figure 2.2.2, is the sum of:

$$E = E^* + \eta_c + \eta_a \text{ with } E^* = E^*_a - E^*_c \qquad [2.2.8]$$

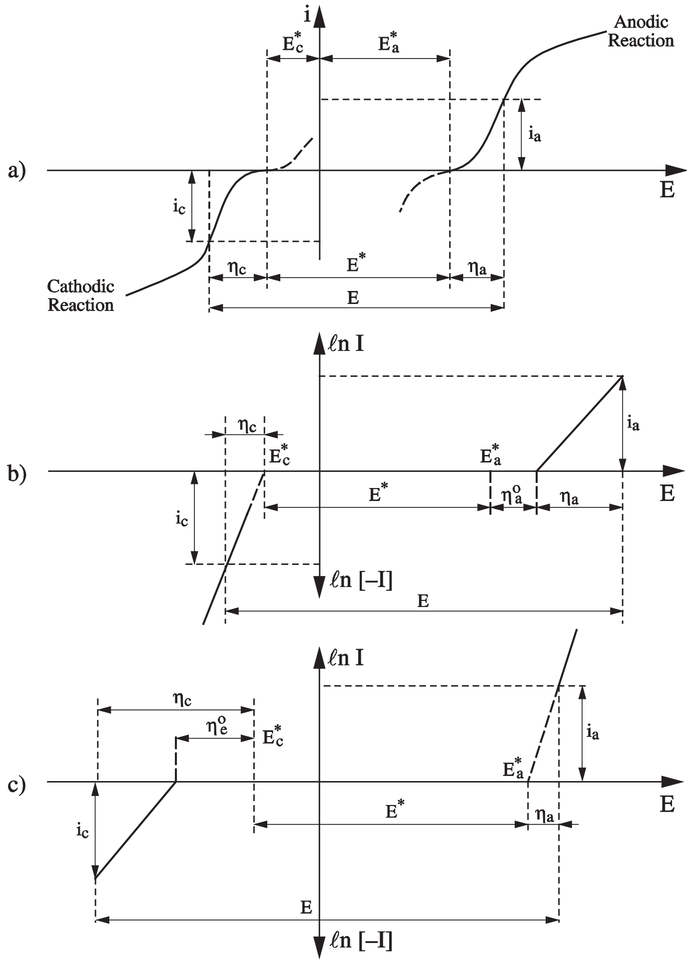


Figure 2.2.2. *Electrolysis: a) graphical determination of the electromotive force $E = E^* + \eta^\circ_a + \eta^\circ_c$ necessary for a current density of $i = i_c = i_a$;b) high initial anodic overvoltage η°_a; and c)high initial cathodic overvoltage η°_c (see Figure 8.4.4 [VIG 11a])*

E^*_a and E^*_c are the reversible electrode potentials (see [VIG 11a], Chapter 8, equation [8.2.6]). η_c and η_a are the cathodic and anodic overvoltages necessary for current I to flow in the cell, which depend on the nature of the electrodes. The electrodes are chosen in order to minimize the highest anodic or cathodic overvoltage. Figures 2.2.2b and c present the cases of high initial anodic overvoltage η°_a and high initial cathodic overvoltage η°_c in its usual form: ln i = f(E), see Figure 8.4.4b [VIG 11a].

2.2.4. *Electrical energy consumption*

The electric power consumed is then:

$$P = V \cdot I = EI + RI^2 \qquad [2.2.9]$$

The energy consumed W to produce one ton of metal can be calculated by the following expression:

$$W(\text{Joule/ton of metal}) = 96{,}484 \cdot 10^6 \cdot V / \{r \cdot (M/z)\} \qquad [2.2.10a]$$

$$W(\text{kWh/ton of metal}) = 96{,}484 \cdot V / \{3.6\ r\ (M/z)\} \qquad [2.2.10b]$$

The aqueous electrolysis of salts of metals such as Cu, Zn, Ni consumes about 2,000–4,000 kWh/ton of metal.

For a desired hourly production, set by the current flowing through a cell, the energy consumed, which has to be minimized, depends on the operating parameters: nature of the electrodes, inter-electrode distance, composition of the electrolyte, and anodic and cathodic over-voltages.

2.2.5. *Decomposition potential of a salt*

When the cathodic and anodic reactions at the (inert) electrodes involve the components (cation and anion) of the salt we want to extract the metal from (e.g. electrolysis of nickel chloride in an aqueous solution, electrolysis of magnesium chloride in molten salts), the reversible potential E* is equal to the decomposition potential of the salt. For example, consider the electrolysis of nickel chloride in aqueous solution:

$$(NiCl_2)_{(\text{dissolved in the electrolyte})} \rightarrow Ni_{(\text{at the cathode})} + Cl_2(g)_{(\text{at the anode})} \qquad [2.2.11]$$

The reversible decomposition potential is related to the affinity (or Gibbs free energy) of the decomposition (see [VIG 11a], equation [8.2.10b]) by:

$$E^*_{(\text{decomposition})} = A_{(\text{decomposition})} / zF = -\Delta G_{(\text{decomposition})} / zF \qquad [2.2.12]$$

where z is the number of electrons flowing from the anode towards the cathode per mole of decomposed salt:

– when $\Delta G < 0$, the decomposition occurs spontaneously and when $E^* > 0$ the reaction produces electrical energy;

– when $\Delta G > 0$ and $E^* < 0$, electrical energy has to be supplied to obtain the decomposition by electrolysis. The voltage to be applied must be $E_{appl} > | E^*|$, where:

$$A_{(decomposition)} = - \Delta G^\circ_{(decomposition)} + RT \ln a_{(NiCL2)} - RT \ln p_{Cl2} \qquad [2.2.13]$$

$$E^*_{(decomposition)} = E^\circ - RT / zF \ln p_{Cl2} / a_{(NiCL2)} \qquad [2.2.14]$$

The standard decomposition potential of the salt is related to the standard affinity (standard free energy) of formation of the compound:

$$E^\circ_{(decomposition)} = -A^\circ_{f(NiCl2)} / zF = + \Delta G^\circ_{f(NiCl2)} / zF \qquad [2.2.15]$$

At 25°C, $\Delta G^\circ_{f(NiCl2)} = -70$ kcal/mol and $E^\circ_{(decomposition)} = -1.5$ volt.

The reaction is the sum of three reactions, with two elementary electrochemical reactions on the electrodes:

– in the electrolyte, a dissociation reaction: $(NiCl_2) \rightarrow Ni^{2+} + 2\ Cl^-$. $NiCl_2$ being entirely dissociated $A_{diss} = 0$;

– at the cathode a reduction (discharge) reaction: $Ni^{2+} + 2\ e \rightarrow Ni$ ($E^\circ_c = -0.25$ V) at 25°C;

– at the anode an oxidation (discharge) reaction: $2\ Cl^- \rightarrow Cl_2 + 2\ e$ ($E^\circ_a = 1.35$ V) at 25°C.

In terms of standard electrode potentials of the reactions at 25°C, we have:

$$E^\circ_{(decom)} = A^\circ_{(decom)} / zF = E^\circ_{c(Ni)} - E^\circ_{a(Cl2)} = -0.25 - 1.35 = -1.6 \text{ V} \qquad [2.2.16]$$

The lower the $NiCl_2$ content in the solution, the higher the voltage to be applied for decomposition to occur (see equation [2.2.14]):

$$E > | E^*| > 1.6 \text{ volts}$$

flow of ionic current by ion migration from one compartment to the other. See, for example, the SOM process ([VIG 11c], Chapter 9 and Figure 9.1.2). It can also be a porous sheet (porous polypropylene) allowing convective flow of the electrolyte from one compartment to the other (see the nickel electrorefining cell in Figure 2.5.1).

2.3. Aqueous electrolysis: bases

2.3.1. *Electrolytic water decomposition*

The decomposition of water by electrolysis occurs:

– at the cathode: hydrogen ion (discharge) reduction (water reduction) with release of hydrogen, see [VIG 11a], reaction [8.2.19]:

$$2\ H^+ + 2\ e \rightarrow H_2(g) \qquad [2.3.1]$$

$$E = -0.0591\ pH - 0.0295\ \log p_{H2}$$

– at the anode: water oxidation with release of oxygen, see reaction [8.3.1]:

$$2\ H_2O \rightarrow O_2(g) + 4\ H^+ + 4\ e \qquad [2.3.2a]$$

which is also written as:

$$2\ OH^- \rightarrow O_2(g) + H_2O + 2\ e \qquad [2.3.2b]$$

As the decomposition of water involves two electrons, the standard reversible decomposition voltage (see equation [2.2.12]) is then equal to:

$$\Delta G_f^\circ = \mu^\circ_{H2O} = -58{,}900 + 13.1\ T\ (\text{cal/mol } H_2O)$$

$$E^\circ_{(\text{decomposition})} = E^\circ_a - E^\circ_c = \Delta G_f^\circ/2\ F = -1.228\ V \text{ at } 25°C \qquad [2.3.3]$$

As by convention the standard hydrogen electrode potential is equal to 0 (see [VIG 11a], Chapter 8, equation [8.2.21]), the standard potential of the oxygen electrode (anodic reaction, see equation [8.3.1b] is:

$$E_a^\circ = (1/2\ \mu^\circ_{O2} - \mu^\circ_{H2O}) / 23{,}060 \times 2$$

$$= +\ 1.228\ V - 0.0591\ pH + 0.0148\ \log p_{O2} \qquad [2.3.4]$$

These two reactions present polarization curves that depend on the nature of the electrode the reaction occurs on (see Figure 8.4.4 [VIG 11a]).

2.3.1.1. *Hydrogen cathodic overvoltage*

The mechanism of hydrogen ion reduction is very complex and the initial cathodic overvoltage $\eta°_c$ required to produce a release of hydrogen at the cathode (the lower the exchange current density i_0, the higher the cathodic overvoltage $\eta°_c$) significantly depends on the nature and characteristics of the metallic surface the cathode is made of (see Figure 8.4.4 and Table 8.4.1 [VIG 11a]).

Both in acidic and alkaline media, on Ni, Pt and Pd metals, the initial hydrogen cathodic overvoltage $\eta°_c$, is low; whereas on metals such as Zn, Cd, and Hg, the hydrogen cathodic overvoltage is high. Table 2.3.1 lists some initial hydrogen cathodic overvoltage values ($i = 5 \times 10^{-5}$ A/cm^2) and for a current of $i = 0.01$ A/cm^2.

Metal	*Initial over-voltage* ($i = 5 \times 10^{-5}$ A/cm^2) $\eta°_c$	*Overvoltage when* ($i = 0{,}01$ A/cm^2) η_c
Platinized platinum	0.005 V	0.055 V
Polished platinum	0.090 V	0.39 V
Copper	0.230 V	0.820 V
Nickel	0.200 V	
Zinc	0.700 V	
Mercury	0.780 V	1.18 V
Lead	1 V	

Table 2.3.1. *Cathodic over-voltage for the release of hydrogen at the cathode for different metals [DEM 99]*

2.3.1.2. *Oxygen anodic overvoltage*

The oxygen anodic overvoltage $\eta°_a$ for reaction [2.3.2] (release of oxygen) also depends on the material the anode is made of, its surface state, the temperature and the nature of the electrolyte. It is about 0.2 V for a platinum anode, 0.4 V for iron and 0.7 V for gold.

2.3.2. *Aqueous salt electrolysis*

The metallic salts that are usually used as electrolytes are chlorides and sulfates. Electrolyses in alkaline media are also carried out (Zimaval process, see section

2.6.3). Sulfate ions SO_4^{2-} are not involved in the electrolysis. Oxidation (discharge) of SO_4^{2-} ions at the anode:

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e$$

does not occur as the Nernst potential of this oxidation is + 2.22 V for $SO_4^{2-} = 1$ and $S_2O_8^{2-} = 10^{-7}$. It is therefore significantly higher than the oxygen electrode potential, even considering the high anodic overvoltage required. For this reason, oxygen is released at the anode.

The release of oxygen leads to the regeneration of sulfuric acid. The overall reaction is:

$$MSO_4(aq) + H_2O \rightarrow 1/2\ O_2(g) + (H_2SO_4) + M(s)(deposit) \qquad [2.3.5]$$

For the electrolysis of chlorides, release of chlorine at the anode usually occurs, the value of the Nernst potential (see [VIG 11a], equation [8.2.14]) at 25°C being:

$$E°_{Cl_2/Cl} = 1.359 + 0.0295 \log\{[p_{Cl2}/[\ Cl^-]^2\} \qquad [2.3.6]$$

The initial anodic over-voltage $\eta°_a$ for the release of chlorine is equal to 0.2 V, compared to 0.8V for O_2.

The cathodic reactions in chloride media are more reversible than in sulfate media. The more reversible the reaction, the lower the overvoltage $\eta = E_C - E^*_C$ needed for a current I (see [VIG 11a], Figure 8.4.4). The EMF, see equation [2.2.8], is then lower for the electrolysis of a chloride salt than a sulfate salt. In addition to this, the conductances of chloride solutions are higher than sulfate solutions, therefore the ohmic resistance of the electrolytic bath is lower. The consumption of energy is thus lower for electrolysis in a chloride medium than in a sulfate one.

Most electrolyses reactions in aqueous media use sulfates, however, due to the formation of complex ions in chloride media (see [VIG 11a], section 4.2.3.1) whose stability is very high and whose electrode potentials (see equation [8.2.23], [VIG 11a]), which depend on the stability constant, are higher in absolute value than the electrode potential of the couple M/M^{z+}. The EMF is then much higher than for electrolysis of the cation.

Nickel chloride, $NiCl_2$, does not form a complex with Cl^- anion in hydrochloric solutions; it is entirely dissociated (see Chapter 4, section 4.2.3.1 [VIG 11a]). For this reason, nickel chloride can easily undergo an electrolysis reaction (see microstructure will be more or less fine. Near the plateau, the microstructure progressively becomes polycrystalline (randomly oriented). At the plateau of the polarization curve where the deposition rate is limited by ion transport in the diffusion layer (see [VIG 11a], Chapter 8, section 8.4.2), the microstructure tends to become a powder with simultaneous formation of hydrogen. The hydrogen content in the deposit increases with the cathodic over-potential (see Figure 2.3.1a)

Cells are normally run at levels well below the plateau to achieve a good, adherent product.

2.3.4.2. *Deposits from salt complexes*

These are microcrystalline. The more stable the complex, the stronger the bonds between the central ion and complexing agent, and the more inhibited the crystalline growth.

2.3.4.3. *Effect of additives*

Many substances, usually organic ones, significantly influence deposit characteristics. Being adsorbed on the surface of the growing crystals, they inhibit crystal growth, making the continuous formation of new crystalline nuclei easier, thus leading to polycrystalline deposits. Increasingly fine deposits that are microcrystalline and smooth are obtained for increasing deposition rates and increasing additive contents.

Gelatin, “glue” and thiourea are additives commonly used as grain refiner for the cathodic deposit of metals. The problem is controlling the “activity” of these additives as they degrade and the need to add more during electrolysis. On the other hand, these additives have a significant effect on the DLC plateau (see [VIG 11a], Figure 8.4.4) and hydrogen content of deposit, which has a harmful effect on the subsequent operations these deposits undergo [CHI 87]. An exhaustive analysis of the problem can be found in [WIN 92].

2.4. Electrowinning of copper

2.4.1. *Copper chloride electrolysis*

There is no industrial production of copper by electrolysis in a chloride medium [LIN 91]. In chloride solutions, as shown by the E-log a_{Cl^-} diagram for the $Cu/Cu^{2+}/Cl^-/H_2O$ system (see [VIg 11a], Chapter 8, Figure 8.3.7), the electrolysis of a cupric chloride solution can lead to contamination of the cathode by the formation of solid CuCl at low ion Cl^- content by the reaction:

$Cu + Cl^{-} \rightarrow CuCl(s) + e$

or to the dissolution of the copper cathode at high Cl^{-} contents by complexation according to the reactions:

$1/2\ Cu + 1/2\ Cu^{2+} + Cl^{-} \rightarrow CuCl_{ads}$, fast reaction

$CuCl_{ads} + Cl \rightarrow CuCl_2^{-}$, slow reaction

The problems encountered in the electrolysis of cuprous and cupric chloride solutions are dealt with by Lin [LIN 91].

2.4.2. *Copper sulfate electrolysis*

In the industrial processing route of oxidized ores, the last step is the electrolysis of concentrated copper sulfate solutions (see sections 1.4.2, 1.4.3.1 and 1.5.3.1 and reaction [5.3.5]).

The problems encountered in the electrolysis of metal salts with several oxidation degrees (for copper: Cu^{+} and Cu^{2+}) do not arise in the electrolysis of copper sulfate solutions. In these solutions, the cuprous ion, Cu^{+}, is present at low concentrations. Its concentration is controlled by the following reaction:

$Cu^{2+} + Cu(s) \rightarrow 2\ Cu^{+}$

whose equilibrium constant at 25°C is very low: $K = [Cu^{+}]^2 / [Cu^{2+}] = 10^{-6}$. For a 0.157 M concentration of copper ions, the concentration in cuprous ions is equal to 37×10^{-4} M.

The electrolyte contains 45–70 g/l copper and 70–150 g/l free H_2SO_4. The bleed electrolyte contains 30 g/l copper and 80–185 g/l H_2SO_4.

The rectangular cells (2–5 m long) are of monopolar cell type with a stack of anodes and cathodes with a surface of about 1 m^2, vertically hung and connected in parallel (see Figure 2.2.4a). The cathodes are made of Cu or titanium sheets. The anodes are made of lead-antimony (6% Sb) or lead-tin (Sn1.2 to 1.5%). The spacing between two cathodes for Cu is in the order of 95 mm.

For a copper concentration of 0.5 mol/L: $a_{Cu2+} = 0.1$ and for SO_4H_2 a concentration of 1 mol/L: $a_{H+} = 1$ (strongly acidic solution) (see [VIG 11a], Chapter 4, Figure 4.28, in the electrolytic bath the reversible EMF: E* is equal to:

$$E^* = E°_{H2O/O2} - E°_{Cu/Cu}{}^{2+} + RT \ln\{a_{Cu}{}^{2+} / (a_{H+})^2\}$$

$$E^* = 1.23 - 0.34 + 0.03 = 0.92 \text{ V at } 30\text{–}35°\text{C}$$

Current densities ranging from 220–320 A/m^2 are applied. The current flowing in each tank line is 16,000–36,000 A, depending on the size of the electrodes and number of cathodes per tank (40–72). For these current densities, the anodic over-voltage is in the order of 0.6 V and the cathodic over-voltage is in the order of 0.2 V (see Figure 2.2.2). With cathodic current densities of about 220 A/m^2 < DLC, a compact microcrystalline deposit is obtained. The voltage drop, RI, in the electrolyte (the conductance of the electrolyte being 0.6–0.7 $\Omega^{-1}.cm^{-1}$ depending on the concentration in SO_4H_2 and iron ions) is also about 0.5–0.6 V.

The cell voltage V is normally in the range of 1.9–2.3V. It is lower for the purer leach-SX-EW operations than for the direct electrowinning operations:

$$V= 0.92 + 0.2 + 0.6 + 0.6 = 2.3 \text{ V}$$

To deposit 1 ton of copper, $8.4 \,.\, 10^5$ A.h are required (1 A.h deposits 1.186 g of copper).

Current efficiency for direct electrowinning operations can be as low as 65%, and for leach-SX-EW operations it can be up to about 93%. It depends on the concentration of iron in the feed solution. Fe^{3+} is reduced at the cathode:

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad E° = + 0.77 \text{ V}$$

and Fe^{2+} is re-oxidized at the anode by the oxygen released there. In addition, the following reaction occurs:

$$2\,Fe^{3+} + Cu(s) \rightarrow 2\,Fe^{2+} + Cu^{2+}$$

which produces some cathode corrosion.

The cathodes are extracted when the deposit reaches a thickness of 5mm after a few days.

Iron has to be removed from the electrolyte. One of the processes used is solvent extraction. The electrolyte purified by this process has a high content in sulfuric acid (150 g/l) due to the stripping operation, see section 1.4.3.1. This is an advantage, as the electric conductance increases with SO_4H_2 concentration. Despite this, the corrosion of the anodes is stronger.

The electrical energy consumed to produce 1 ton of copper for a current efficiency of 90% and average voltage of 2.1 V, is of the order:

$$2.1 \,.\, 8.4 \,.\, 10^5 \,(100/90) \,.\, (1/1{,}000) = 2{,}000 \text{ kWh/ton of copper}$$

A surfactant is added, which makes the formation of foam easier and prevents the oxygen bubbles being ejected. A small amount of glue is added to the electrolyte to obtain dense deposits.

The purity of the Cu cathodes is 99.5–99.8%, which is enough for non-electric uses. For electrical and electronic uses, the purity has to reach 99.9%. This can be obtained by electrorefining.

2.4.3. *Electrolytic copper and blister copper electrorefining*

A high copper purity is required in its uses, such as an electric conductor [CHE 90, CHE 04]. A large number of metallic and metalloid impurities are present in electrolytic copper and blister copper. The purity in copper varies from 98.5–99.8%. The main impurities are oxygen (from 130–4,000 ppm as copper oxide), lead (7–4,300 ppm), nickel (90–6,700ppm), silver (90–7,000 ppm), gold (10–100 ppm), Se, As and Sb whose contents can also reach several thousand ppm. Copper oxide, Cu_2O (containing Pb, As, Sb and Bi), is the main impurity. It occurs as spheroidal particles <1–15 µm in size, as inclusions in a shell of $Cu_2(Se, Te)$ located at the copper grain boundaries.

In the electrorefining operation, the anodes are the copper cathodes from the electrolysis of sulfate solutions or are cast from blister copper. The cathodes are made of thin copper sheets. The electrolyte is a purified copper sulfate solution with concentrations of 40–50 g/l in Cu in and 160–180 g/l in H_2SO_4. At 60–66°C with a current density of 180–300 A/m^2 and a potential of 0.2 V–0.3 V, the electrical energy consumed is in the order of 250 kWh/ton of Cu [CHE 04]. Dissolution of the anodes lasts from 9–23 days. It can be stopped before the anode collapses in the tank. The cathodes are removed twice during this time. An anode of 350 kg therefore gives two cathodes of 140–150 kg.

Passivation of the copper anode is the problem when electrorefining copper. The copper of the anode is dissolved as Cu^+ ions, with formation of a continuous layer of cuprous oxide at the surface due to the following reaction:

$$2\ Cu^+ + H_2O \rightarrow Cu_2O(s) + 2\ H^+$$

The thickness of this layer is 0.5−1 mm.

Some impurities are dissolved in the electrolyte; others are not and form slimes. There is 5−10 kg of slime per ton of anode. Ni, Fe and Co are dissolved in the electrolyte but are not deposited at the cathode below a certain concentration. Metalloids As, Sb and Bi are partially dissolved.

Precious metals, such as gold and platinum, are not dissolved in the electrolytic solution. They form slimes at the surface of the anode and at the bottom of the electrolysis tank. Metalloids S, Se and Te form insoluble compounds with copper and silver and are carried, in this form, into the slimes. These slimes contain 0.2−1 % gold in the form of metallic particles of 1 µm connected to silver selenides. The processing route of these slimes is presented in [VIG 11c], Chapter 10, section 10.3.3.

2.4.4. *Electrorefining of copper matte*

Although the electrorefining of nickel mattes is an industrial process, there is no electrorefining process for the copper mattes that has reached industrial level [MCK 93]. The anode is made of copper matte. The electrochemical dissolution process of a chalcocite Cu_2S matte is similar to the process described in Chapter 1, section 1.2.3.4. Dissolution occurs in two stages (see reactions [1.2.39] and [1.2.40]):

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2\ e$$

$$CuS \rightarrow Cu^{2+} + S°(s) + 2\ e$$

The product of dissolution is the Cu^{2+} ion, which can undergo reduction at the cathode.

The problem comes from the low rate of of covellite (CuS) decomposition, which is not explained. In addition, sulfur forms an external layer that is then oxidized and the voltage of 0.5 V rapidly increases to 1 V.

2.5. Electrowinning of nickel

Electrolytic extraction of nickel is industrially performed by electrolysis of nickel chloride solutions from hydrochloric leaching operations and by electrorefining nickel mattes. Electrorefining of nickel is performed in aqueous solutions of nickel sulfate and chloride.

2.5.1. *Nickel chloride electrolysis*

Nickel chloride is entirely dissociated in hydrochloric solutions, see [VIG 11a], Chapter 4, section 4.2.3.1. As it does not form any complex, nickel chloride can easily be electrolysed (see Chapter 8, section 8.2.2.3 in [VIG 11a]).

After removing iron and cobalt by solvent extraction, the nickel chloride solution is subjected to a succession of final purifications on resins in order to remove all the remaining impurities (Cr, Mg, Al, Cu), see section 1.5 and Figure 1.5.9.

The purified nickel chloride solution (120 g/l, pH 2.5) is sent to a series of tanks at 80°C. The insoluble anodes are made of titanium (Ti+Ru). They are hollow, which allows extraction of the gaseous chlorine by pumping. Nickel is deposited at the cathode on nickel mother-sheets. Air saturated with water steam is blown under each cathode in order to prevent the formation of dendrites, see section 2.3.4. Under a voltage of 3.5 V, current of 800 A per electrode and 7 cm distance between electrodes, after four days the cathodes of pure nickel are thick (12 mm) and extremely low impurity levels are obtained. The cathodes are then annealed in order to eliminate hydrogen, see section 2.3.3 [FUJ 82].

2.5.2. *Electrorefining of nickel*

In some pyrometallurgical processing routes of Ni-Cu sulfide ores, the final product is an alloy with the composition: 76% Ni, 1.5% Co, 17% Cu, 2% Fe and 1.5% S.

This metal is cast into anodes and an electrorefining operation is carried out in a solution of nickel sulfate and chloride in order to produce pure nickel cathodes. The process is shown in Figure 2.5.1. The anolyte resulting from dissolution of the impure anode in the electrolytic solution is sent to the purification tanks. The electrolyte thus purified is sent into the cathodic compartment, where the reverse reaction of cathodic deposition of nickel occurs. In order to avoid contamination of the cathodic solution by the cuprous ion liberated at the anode, a diaphragm separates the anodic and cathodic compartments allowing the electrolyte to flow from the cathodic compartment to the anodic compartment. In this way the cuprous anolyte does not contaminate the cathodic bath.

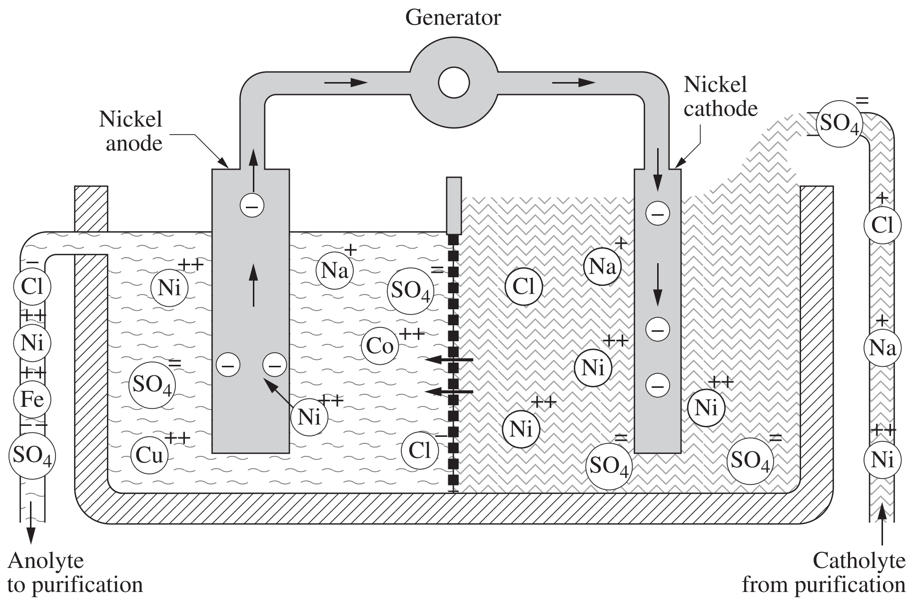


Figure 2.5.1. *Idealized operation of a nickel electrorefining cell*

For a current density in the order of 200 A/m^2, the voltage V (see equation [2.2.6]) is equal to:

$$V = \eta_A + \eta_C + RI = 0.5 + 0.9 = 1.4 \text{ V}$$

The values of the over-voltages respectively are: $\eta_A = + 0.3$ V and $\eta_C = -0.2$ V. Due to the low cathodic over-voltage required, there is almost no production of hydrogen at the cathode. The ohmic voltage drop is equal to 0.9 V.

2.5.3. *Electrorefining of nickel matte*

Impure nickel mattes are cast into anodes that undergo an electrorefining process [JEB 06, STE 86]. The anode is dissolved in the anodic compartment and the sulfuric solution is subjected to an extraction of Cu, Fe, Co etc., by hydrometallurgical treatments. The purified solution is injected into the cathodic compartment, where reduction of the nickel ion and the deposition of nickel occur.

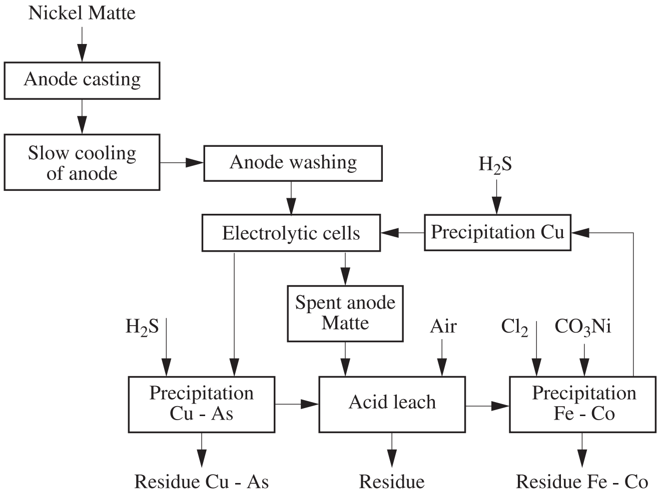


Figure 2.5.2. *Flowsheet of the electrorefining operations of nickel matte [JEB 06]*

The nickel matte, in the solid state with a composition of 73% Ni, 3% Cu, 0.8% Co, 20% S, 0.6% Fe and 0.2% As, contains 50% nickel sulfide, the rest being nickel as an element. In the anodic compartment, the following dissolution reactions occur with formation of elemental sulfur:

$$Ni \rightarrow Ni^{2+} + 2\ e$$

$$Ni_3S_2 \rightarrow 3\ Ni^{2+} + 2\ S°(s) + 6\ e$$

$$Ni_3S_2 \rightarrow 2\ NiS + Ni^{2+} + 2\ e$$

At the anode, oxygen is produced, which consumes 5–7% of the current.

The impurities of the anode are dissolved. The anodes (250 kg) are placed in envelopes made of synthetic fibers in order to store the sulfur slimes that form on the anodes. The slime occupies twice the volume of the original anode. This growing slime layer causes the cell voltage to rise from 3 to 6 V between the start and end of the operation in order to maintain a current density of 240 A/m^2. The dissolution of an anode takes around 20 days. Each liter of the electrolytic bath contains 60 g nickel ions, 90 g sulfate ions, 35 g sodium ions, 60g of chloride ions and 16 g of boric acid. The partially-dissolved anodes are processed to separate the sulfur from the residual matte. They are sent back to the manufacturing factory of the anodes. The cathodes are made of nickel mother-sheets.

The anolyte and the residual matte are sent to the purification tanks where Cu, As, Fe and Co are chemically eliminated. In the first stage, hydrogen sulfide is added to precipitate copper, arsenic and lead (see Chapter 1, section 1.3.2. and reaction [1.3.10]). The second stage is an acid leach, in which the residual matte from the spent anodes (from the electrorefining cells) is leached to recover the nickel. In the third stage, chlorine gas and nickel carbonate (to keep the pH at 3.7) are added to oxidize and precipitate cobalt and iron by reaction [1.3.8], see section 1.3.1.4. In the fourth stage, the copper in solution after the leach stage is precipitated by hydrogen sulfide. The electrolyte, which has then been purified, is sent into the cathodic compartment where the reverse deposition reaction of nickel occurs. The cycle of a cathode is about 12 days. Due to the low cathodic over-voltage required, $\eta_C \approx -0.2$ V, there is almost no hydrogen production at the cathode.

2.6. Electrowinning of zinc

2.6.1. *Zinc sulfate electrolysis*

In the hydrometallurgical processing routes of zinc calcine and zinc sulfide concentrates, the final operation is electrolysis of the zinc sulfate solution [O'K 00], see Figures 1.5.2 and 1.5.3). The electrolysis occurs between an aluminum cathode and a lead anode, according to the overall reaction [2.3.5]. A layer of alumina on the cathodes prevents the adhesion (sticking) of zinc being too strong. This allows the zinc deposit to be easily removed. The composition of the zinc sulfate solution is 175−210 g/l sulfuric acid and 50−60 g/l zinc as $ZnSO_4$. There is only about a 5 g/l drop in the electrolyte zinc content between the feed and bleed in order to maintain a high zinc concentration and minimize hydrogen production (see section 2.3.3). The temperature is kept between 30 and 40°C. Additives, such as gelatin, are introduced in order to improve the quality of the deposits.

The standard electrode potential of zinc $E°_{Zn/Zn^{2+}}$ is -0.76 V; so thermodynamically in an acid zinc bath hydrogen should preferentially evolve before zinc deposits. It should not be possible to obtain dense zinc deposits. A zinc deposit is nevertheless formed. The exchange current density i_O of the H^+/H_2 couple on a zinc electrode is very low (see [VIG 11a], Chapter 8, equation [8.4.9] and Table 8.4.1), so a very high over-voltage $\eta° = 0.7$ V (see Table 2.3.1) is needed for the production of hydrogen on zinc (see Figure 8.4.4b). As a result, on an extremely pure zinc surface, with a high zinc concentration in the electrolyte, the hydrogen polarization curve shifts to a more negative potential allowing zinc to be deposited as a metal with only limited hydrogen gas production.

To keep the cathodic hydrogen over-voltage high, all the impurities within the solution have to be removed beforehand [KRA 93]. The noblest impurities (Cu, Ag, Pt, Ni, Co, Pb and Cd) act as catalysts for the production of hydrogen. They lead to significant drops in current efficiency. Cobalt, for instance, being nobler (E° = -0.28 V) than zinc, is simultaneously deposited on zinc. This reduces the quality of zinc and influences the structure and morphology of the deposit. The hydrogen over-voltage on cobalt is lower than zinc and therefore every co-deposit of cobalt catalyzes the production of hydrogen. Hydrogen production at the cathode creates a local increase in pH, which can lead to the formation of zinc hydroxide.

The reversible EMF is E* = 1.99 V. The over-voltages required to obtain the desired current density of 400 A/m^2 are 0.60 V for the anodic reaction and 0.15 V for the cathodic reaction. The voltage drop due to the electrolytic bath resistance for an inter-electrode distance of 30 mm and current density of 400 A/m^2, is close to 0.5 V. For the other cell resistances (0.25 V), the cell voltage to be applied is 3.44 V. The cathodic current yield is in the order of 90–93%, due to the hydrogen production that still occurs simultaneously with the deposition of zinc. The energy consumption per ton of Zn produced is therefore 3,000–3,300 kWh.

For an annual production of 100,000 t/year of zinc, the zinc cell house in Asturiana, Spain, is made of two lines of 36 tanks . In each tank 110 cathodes with a surface of 3.4 m^2 are immerged. The voltage applied to the cell house terminals is 240 V, for a nominal voltage of 3,290 mV per tank (therefore between the electrodes: 36 × 2 × 3.290 = 237 V). The current flowing in both lines is equal to 155 kA for a nominal current density of 411 A/m^2 (110 × 3.4 × 411 = 154 kA), see Figure 2.6.1.

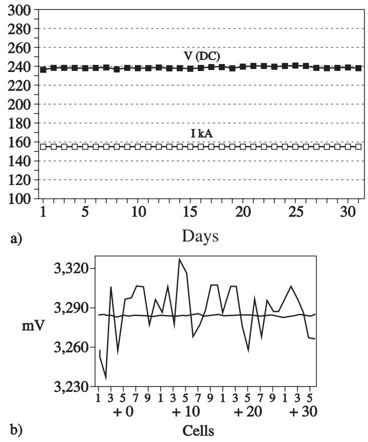


Figure 2.6.1. *Operating conditions of an electrolytic zinc cell house (two rows of 36 cells, each with 110 cathodes): a) cell voltage (V) and current (kA); and b) average voltage per hour per cell of row 1 at the normal current density (411 A/m^2). Reference voltage 3,290 mV [TAM 93]*

Pumps continuously supply each tank with an electrolyte flow rate of 500–580 l/min. The composition of the electrolytic solution is of 53 g/l zinc and 148 g/l H_2SO_4. The composition of the bleed (overflow) electrolyte is 48 g/l zinc and 153 g/l H_2SO_4. The bleed electrolyte is mixed with a purified solution that contains 146 g/l zinc and is re-injected into the cells. Each cathode is extracted after 24 hours. The deposition rate is equal to 164 kg/hour per cell.

2.6.2. *Ammonium chloride zinc electrolysis*

Electric arc furnace dusts contain too many chlorides and fluorides for zinc oxide to be dissolved and electrolyzed in a sulfuric medium.

The Ezinex process [OLP 00] is based on the electrolysis of zinc ammonium chloride solutions, see Chapter 1, section 1.5.2.3. The anodic reaction produces nitrogen, which depolarizes the anode and decreases the cell voltage by about 1 V compared to the electrolysis in sulfuric medium.

The overall reaction can be written:

$$Zn(NH_3)_2Cl_2 + 2/3\ NH_3 \rightarrow Zn(s) + 2\ NH_4\ Cl + 1/3\ N_2$$

– at the cathode:

$$Zn(NH_3)_2^{2+} + 2\ e \rightarrow Zn(s) + 2\ NH_3$$

– at the anode:

$$2\ Cl^- \rightarrow Cl_2 + 2\ e$$

$$Cl_2 + 2/3\ NH_3 \rightarrow 2\ HCl + 1/3\ N_2$$

The cathodes are made of titanium sheets 3 mm thick; the anodes are made of graphite plate 40 mm thick.

For an aqueous solution of NH_4Cl (250 g/l) and ClNa (50 g/l) at 53°C and pH 5.8–6.2, the cathodic potential -1.1 V (SCE)[2] varies slightly with current density between 100 and 1,000 A/m^2 for contents in Zn > 10 g/l. The anodic potential varies with current density from 1.15 V (SCE) at 100 A/m^2 to 1.35 V (SCE) at 1,000 A/m^2. For current densities of 310 A/m^2, the applied voltage is 2.9 V. The consumption of energy is equal to 2,560 kWh/kg.

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[2] SCE: standard calomel electrode. See also SHE: standard hydrogen electrode

2.6.3. *Sodium zincate electrolysis*

The Zimaval process [FER 00] has been developed to recover zinc from saline and alkaline batteries. The dissolution of zinc is performed by a caustic attack and the solution is subjected to electrolysis in a strong alkaline medium:

– at the cathode:

$Zn(OH)_4^{2-} + 2\ e \rightarrow Zn + 4\ OH^-$

$E° = 0.36$ V in an alkaline medium (7.5 N);

– at the anode (see reaction [2.3.2]):

$2\ OH^- \rightarrow O_2 + H_2O + 2\ e$

$E° = 1.31$ V

The electrolysis of a solution containing 50 g/l Zn is performed under a strong current density (1,000 A/m^2) and 4 V in order to obtain a fine zinc powder in the form of a cake deposited at the cathode.

2.7. Electrorefining of lead

The problem associated with lead electrowinning comes from the various valences $Pb/Pb^{2+}/Pb^{4+}$. In the electrolysis of lead chloride, Pb^{2+} ions present in the electrolyte are reduced at the cathode into Pb°, but they are simultaneously oxidized at the anode into Pb^{4+} ions with the formation of PbO_2 around the anode. Many studies have been carried out to avoid the problem. Although a large number of processes have been developed, there is no industrial operation [OLP 93, PRE 95].

Pure lead can be produced from bullion containing Sb, Bi, Ag and Cu impurities by electrorefining, see Chapter 7, section 7.5 (Betts process) [O'K 00]. Lead is dissolved at the anode in the form of Pb^{2+}, and reduced at the cathode to give Pb° ($E°_{Pb/Pb^{2+}}$= -0.126 V). There is no hydrogen production, as the over-voltage for the release of hydrogen is very high on lead. The electrolyte is H_2SiF_6 (140 g/l) + $PbSiF_6$ (60–100 g Pb). Zn is dissolved in the electrolyte but is not reduced at the cathode. As Sb, As and Bi impurities are nobler than lead, they are not dissolved in the electrolyte. The precious metals are gathered in the slimes. The characteristics of the electrolysis are: current density of 230 A/m^2, applied voltage ranges from 0.3–0.5 V, consumption of energy equal to 168 kWh/ton of Pb. The Faraday efficiency is 90–95%.

2.8. Electrorefining of tin

The electrorefining of tin presents several advantages compared to thermal refining (see Chapter 7, section 7.6): it eliminates most of the impurities in a single operation and allows the precious metals − Au, Ag, Cu − to be recovered in the anodic slimes. The less noble impurities, Ni, Fe and Zn, are dissolved but not deposited at the cathode. However, the electrochemical potential of lead is close to the electropotential of tin.

The electrolyte contains sulfuric acid, the current density is equal to 100 A/m^2 and the applied voltage is 0.3 V. Tin is kept in the electrolytic bath in the form of Sn (II) by the addition of a sulfonic acid. During the electrolysis, passivation of the anode occurs due to the formation of a $PbSO_4$ layer that has to be progressively removed [CUY 05].

2.9. Cobalt electrowinning

Electrowinning is a predominant operation for the recovery of cobalt [PEE 09, WAN 06]. Industrial electrowinning of cobalt is performed in either chloride or sulfate media using insoluble anodes: titanium coated with noble metal oxides for chlorine evolution and lead (alloyed with antimony) anodes in sulfate media. Lead anodes show high over-potentials for oxygen production. The anodes are bagged to collect the chlorine gas produced. The cathodic deposition of cobalt is accompanied by some hydrogen generation ($E°_{Co2+/Co} = -0.28V$). The energy consumption is in the order of 5.3−6.5 kWh/kg for sulfate solution electrolysis with a current efficiency of 60−80% and 3.1−3.7 kWh/kg for chloride solution electrolysis with a current efficiency of 90%.

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Chapter 3

Halide Extraction Processes

3.1. Overview of the halide extraction processes

The use of halides in extractive processes has made the large scale production of some of the rarest reactive metals (titanium, zirconium, etc.) possible. Other applications are feasible but halogens are costly reagents and they are seldom regenerated cheaply in the process. Halide metallurgy is not used for common metals.

The main industrial productions of metals relying on the transformation of ores into chlorides involve chlorination in the presence of carbon (carbochlorination) with Ti and Zr ores, as well as magnesia MgO.

The carbochlorination of alumina ores into chlorides allowing their separation by a physical method has been largely studied. So has the carbochlorination of Bayer alumina for the production of aluminum by chloride electrolysis (see [VIG 11c], Chapter 9, section 9.2.4). The industrial use of these processing routes are not contemplated, however, mainly for economical reasons (the cost of anhydrous $AlCl_3$).

Reduction of the oxides of these very reactive metals (Ti, Zr, Mg, Al) due to their high affinity for oxygen cannot produce high purity metals. Carbothermic reduction yields carbides (see Chapter 4, section 4.3.3.1). Carbon will reduce TiO_2 to titanium with carbon and oxygen dissolved in it. At 2,400 K, the maximum titanium content obtainable is 89%, with 6% carbon and 5% oxygen. Metallothermic reduction with magnesium or calcium cannot be complete due to the high solubility of oxygen in these metals (Zr can dissolved in up to 29% of oxygen atoms, even at low temperature, see [VIG 11a], Figure 2.2.5, Chapter 4, section 4.7.3 and

Chapter 9, section 9.4.1 in [VIG 11c]). So a very specific metallurgical processing route has been developed. It is based on the conversion of ores into intermediate gaseous chlorides, which allow separation of the components of the ores by physical operations (see [VIG 11c], Chapter 1, section 1.2.5.1) and subsequent reduction of the chlorides by metallothermic processes, avoiding the presence of oxygen.

The chlorination of copper oxide by the gaseous mixture chlorine + air is used in the processing of nickel mattes (see Chapter 3, section 3.4.1.7 and Figure 3.4.3) and allows the separation of copper as a gaseous chloride and of nickel as solid chloride.

The selective chlorination of zinc and copper oxides allow separation of the non-ferrous metals (Zn, Cu) from ferrous metals in steel scraps by passing a gaseous mixture (chlorine + air) over steel scrap [TEE 99], see section 3.2.3.5.

Chlorination in the presence of CO and carbochlorination (in the presence of C(s)) of Co, Ni, Mo, V, Ta and Nb oxides have been studied in order to recover them from spent catalysts (Co, Ni, Mo and V) for the hydrodesulfurization of petroleum fractions [GAB 94] or from tin slags resulting from the pyrometallurgical extraction of tin from cassiterite concentrates (SnO) containing 2% Nb and Ta oxides [GAB 97].

Electronic silicon is obtained by hydrogen reduction of the silicon chlorides $HSiCl_3$ and $SiCl_4$, whose distillation leads to very pure compounds (see [VIG 11c], Chapter 10, section 10.16).

The deposits of Mo and W in thin layers on the silicon transistors are obtained by thermal decomposition (chemical vapor deposition or CVD) of the corresponding chlorides and fluorides, $MoCl_6$ and WF_6.

This chapter presents the conversion processes of the oxides into chlorides and their metallothermic reduction.

3.2. Chlorination processes

Conversion of oxides into chlorides can be achieved by three reactions: chlorination in gaseous mixtures $Cl_2 + N_2$ (see reaction [3.2.1]); chlorination in gaseous mixtures of $Cl_2 + CO$ (see reaction [3.2.5]); and carbochlorination in the presence of carbon C(s) (reaction [3.2.6]).

3.2.3. *Carbochlorination of ores*

Carbochlorination of ores converts all of the oxides present into chlorides, which allows their separation by condensation (separation of $FeCl_2$-$FeCl_3$(s) and $TiCl_4$(g)), or by distillation (separation of Zr and Hf), see [VIG 11c] Chapter 1, section 1.2.5 and 1.2.6 and Figure 1.2.6.

3.2.3.1. *Carbochlorination of ilmenite*

The flowsheet of the carbochlorination processing route of the titanium ore, ilmenite, is shown in Figure 3.2.10. The conversion of ilmenite into chlorides in the presence of carbon is performed at around 800°C under vacuum or an inert gas atmosphere in order to avoid the presence of traces of oxygen:

$$FeTiO_3(s) + 3\ Cl_2(g) + 3/2\ C(s) \rightarrow FeCl_2(g) + TiCl_4(g) + 3/2\ CO_2 \qquad [3.2.16]$$

Selective chlorination of iron oxide in ilmenite can be achieved by operating at low temperatures between 600 and 700°C [RHE 90]. For a slag (TiO_2 71%, FeO 11%, SiO_2 5.2%, and Al_2O_3 5.5%) successive chlorination of the oxides occurs between 400 and 900°C. $FeCl_2$(s) is formed between 400 and 550°C, $TiCl_4$ between 550 and 600°C, silicon and aluminum chlorides between 650–850°C and $MgCl_2$ above 900°C [GUE 80].

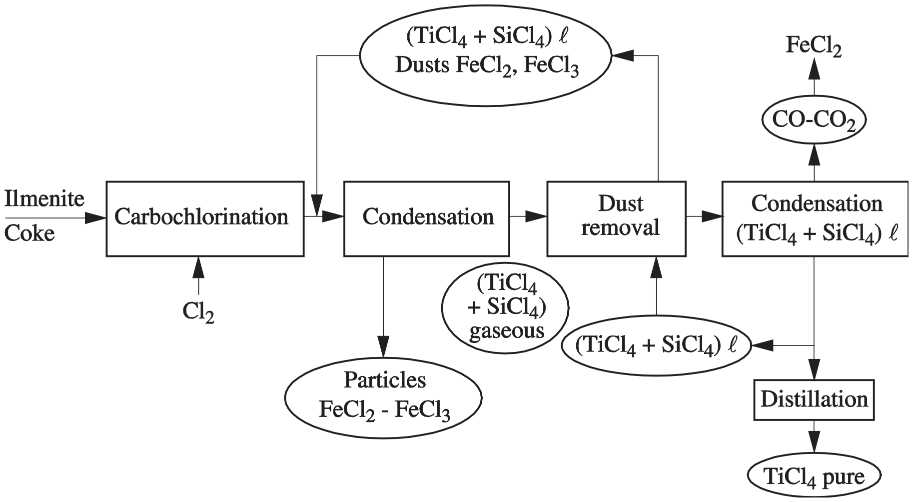


Figure 3.2.10. *Flowsheet of the carbochlorination of ilmenite ($FeTiO_3$)*

Industrially, the carbochlorination of ilmenite and rutile is performed in a fluidized bed, either at high temperature (950–1,100°C) with petroleum coke, or at 700°C starting from mixed pellets of slag and bituminous coking coal particles plus a binder. Pellets are subjected to coking at 500°C and annealing at 900-1,000°C, to obtain good contact between the particles of the pellets.

3.2.3.2. *Carbochlorination of zircon*

The processing route of the zirconium ore, zircon, is shown in [VIG 11c], Figure 10.9.1. The carbochlorination is carried out at 1,200°C (see reaction [3.2.8]):

$$ZrSiO_4 + 4\ Cl_2(g) + 4\ C(s) \rightarrow ZrCl_4(g) + SiCl_4(g) + 4\ CO(g) \qquad [3.2.17]$$

This reaction is highly endothermic and its standard affinity increases with temperature:

$$A° = -\Delta G° = 130 \text{ kcal/mol (at 1,000°C)}$$

The kinetics of this reaction have not been much studied, and there is no satisfying mechanism to suggest what really happens. Unlike the carbochlorination of titanium and zirconium oxides, whose rates are of the first order with respect to chlorine, in the case of zircon the reaction rate is of zero order with respect to chlorine concentration. This suggests that chlorine is strongly adsorbed on the solid particles so the concentration of chlorine in the gas phase has no effect on the reaction rate [MAN 74]. Zircon is chlorinated in an electrothermally-heated fluidized bed reactor using calcined petroleum coke. Temperatures of 1200°c or above appear to be required to obtain acceptable chlorine efficiency and reaction rates (see [VIG 11c], Chapter 3, section 3.4.2 and Figure 3.4.4).

Although this transformation has been industrially performed for a long time, just a few results are available.

3.2.3.3. *Carbochlorination of aluminum ore*

The carbochlorination of aluminum (non-bauxite) ore, also known as kaolin clays, has been studied as a step in a processing route for the production of pure alumina (see Figure 3.2.11), or for the production of aluminum by $AlCl_3$ electrolysis (see [VIG 11c], Chapter 9, section 9.2.4). It requires a preliminary calcination step to drive off the water as steam reacts with $Cl_2(g)$ to give extremely corrosive HCl. If the calcination is complete (zero water content) the aluminum constituents of the ore no longer react with chlorine.

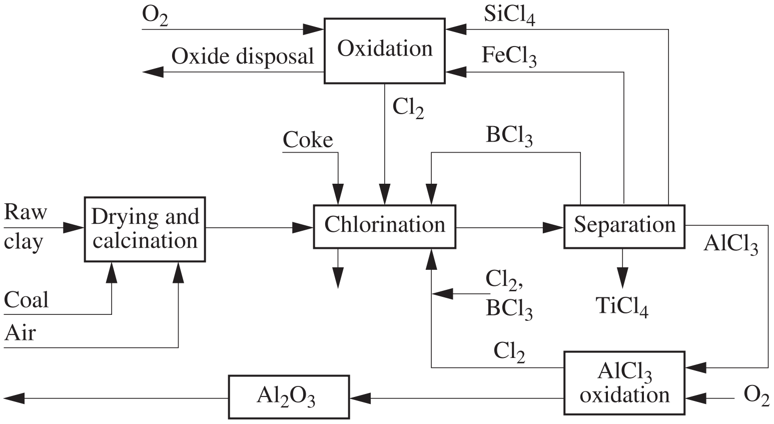


Figure 3.2.11. *Carbochlorination of aluminum ores (clay). Processing steps [DEU 79]*

3.2.3.4. *Carbochlorination of magnesia*

The carbochlorination of magnesia is carried out in order to obtain anhydrous magnesium chloride for subsequent electrolysis (see [VIG 11c], Chapter 9, section 9.2.1):

$$2\ MgO(s) + C(s) + 2\ Cl_2(g) \rightarrow 2\ MgCl_2(l) + CO_2 \qquad [3.2.18]$$

It is occurs in a vertical oven around 800°C and gives anhydrous liquid $MgCl_2$. The transfer of liquid chloride to the electrolysis cells is a problem.

3.2.3.5. *Oxychlorination*

This is chlorination in an air plus chlorine medium. By blowing a gaseous mixture (chlorine + air) over steel scrap at 800°C it is possible to separate the non-ferrous metals (Zn,Cu) from ferrous metals. Zinc and copper oxides are converted into chlorides. The oxygen potential is such that iron oxide is prevented from being converted into chloride, see Figure 2.4.4 [TEE 99].

3.3. Reduction of halides

3.3.1. *Hydrogen reduction*

The only gaseous reducing agent of chlorine is hydrogen, due to the reaction leading to the formation of hydrochloric acid:

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl \qquad [3.3.1]$$

$A° = 21{,}770 - T \log T + 5.22\ T$ (in cal/mol of HCl)

$A° = 42$ kcal/mol of Cl at 0°C

Hydrogen can reduce W, Mo, Nb and Ta chlorides with the formation of hydrochloric acid (see [VIG 11a], Figure 2.4.3):

$$2/5\ NbCl_5 + H_2 \rightarrow 2\ HCl + Nb(s) \qquad [3.3.2]$$

Silicon chlorides ($SiCl_4$) can be reduced under a strong flow rate of hydrogen to keep the HCl partial pressure as low as possible and thus make the affinity of the reaction positive:

$$A = A° + RT \log p_{H2} / (p_{HCl})^2$$

The reduction of titanium and zirconium chlorides with hydrogen is not possible:

$$TiCl_4(g) + 2\ H_2(g) \rightarrow 4\ HCl(g) + Ti(s) \qquad [3.3.3]$$

$$A° = 4\ A_f°(HCl) - A_f°(TiCl) = -93{,}620 - 5.8\ T \log T + 55.53\ T \text{ (cal/mol)}$$

as the standard affinity of the reaction is negative up to very high values.

Silicon and silicon or tungsten deposits in the electronics industry are performed by reduction of chlorides by the CVD process (see section 5.6):

$$WF_6(g) + 3\ H_2(g) \rightarrow W(s) + 6\ HF(g)$$

$$SiCl_4 \text{ (or Si } HCl_3) + 2\ H_2(g) \rightarrow Si(s) + 4(3)\ HCl(g)$$

3.3.2. *Metallothermic reduction*

Production of Ti, Zr and U metals is performed industrially by chloride (fluoride) metallothermic reduction with Mg, Na and Ca [GER 01].

3.3.2.1. *Reduction of titanium and zirconium chlorides*

Two metallothermic reduction processes of titanium and zirconium chlorides have been developed. The first one is based on the use of magnesium, the Kroll process; the other one uses sodium, the Hunter process, which is no longer used [KRO 40].

Metallothermic reduction of chloride can be represented by the following overall reaction:

$$Ti(Zr)Cl_4(g) + 2\ Mg(Na)(l) \rightarrow 2\ MgCl_2(l) + Ti(Zr)(s) \qquad [3.3.4]$$

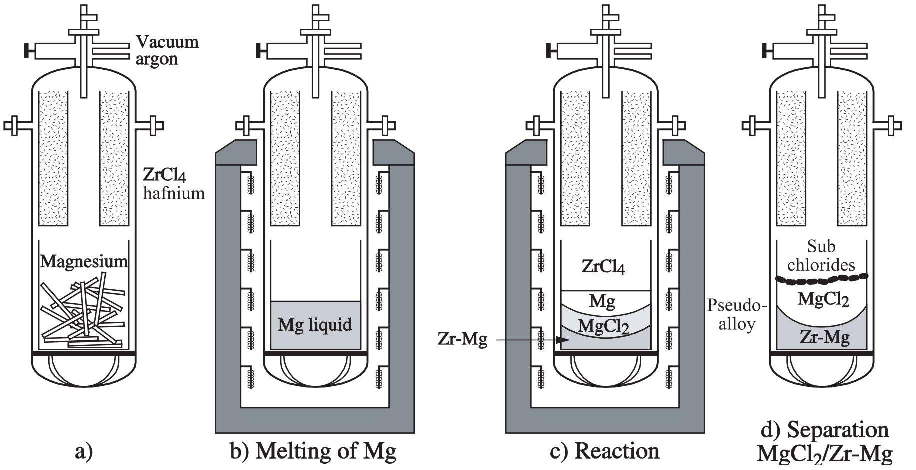
Metallothermic reduction of titanium and zirconium chlorides is thermodynamically possible, as shown in the Ellingham diagram in [VIG 11a], Figure 2.4.3, the standard affinity of magnesium chloride formation being much higher than that of titanium and zirconium chlorides:

$$\Delta H° = -420.4\ \text{kJ/mol};\ \Delta G° = -306.5\ \text{kJ/mol of Ti at } 900°C$$

The Kroll reactor and the different steps of the batch operation are represented in Figure 3.3.1. The retort is a closed vessel made of refractory steel within which the solid reactants are put. Zirconium chloride is put in an annular basket, and magnesium at the bottom of the reactor (see Figure 3.3.1a) with a slight argon overpressure. The reactor is put in a furnace with two heating zones (see Figure 3.3.1b): a lower zone where magnesium is melted (T = 648°C); and an upper zone allowing the progressive sublimation of zirconium chloride $ZrCl_4$ (Ts = 331°C). The zirconium chloride vapors are heavier than argon. They fall and come into contact with the liquid magnesium free surface, which is at 800°C. Gaseous $ZrCl_4$ reacts with liquid Mg. The mechanism of this reaction is not known. Owing to its strong exothermicity and high magnesium vapor pressure (278 mm Hg at 1,000°C) a reaction occurring at the surface of the liquid bath between the gaseous chloride and the magnesium vapor is possible. Whatever the mechanism of this reaction, formation of globules (with a diameter of about 10 µm) of zirconium occurs. As zirconium is not miscible with magnesium, the zirconium globules fall to the bottom of the reactor, dragging liquid magnesium with them (see Figure 3.3.1c). At the end of the operation, when the entire zirconium chloride has been converted into zirconium, we have (from bottom to top) a "pseudo-alloy Zr-30% Mg" layer, a layer of magnesium chloride and a few residual sub-chlorides (see Figure 3.3.1d). The reactor is opened and the different phases are separated mechanically.

The reduction is strongly exothermic. To avoid it running away due to the increase in temperature, thermal control of the operation is essential. This is ensured by control of the sublimation rate of zirconium chloride. This significant heat release means the reactor must be of moderate size in order to allow evacuation of the calories. Production with such a reactor is in the order of 100 kg/hour of Zr.

The reduction of titanium chloride is carried out in the same way. As titanium chloride is gaseous at 136°C, it is continuously fed into the retort, its feed rate being the operating parameter. The reaction occurs at 900°C in an argon atmosphere [NAG 04].



a) b) Melting of Mg c) Reaction d) Separation $MgCl_2$/Zr-Mg

Figure 3.3.1. *Reduction of $ZrCl_4$: Kroll Process: reactor and operation stages [TRI 90]*

The separation of zirconium (or titanium) from magnesium is performed by vacuum distillation of the pseudo-alloy in a batch annealing furnace at about 1,000°C (see [VIG 11c], section 1.2.2). Magnesium is vaporized and recovered in a condenser and is then recycled leaving behind a zirconium (titanium) sponge.

Numerous continuous processes have been designed and tested at the pilot level. One of the aims is to obtain titanium in the form of uncontaminated powder.

A continuous vapor-phase reduction process [HAN 98] has been developed. Mg and $TiCl_4$ vapors are injected into a pipe heated to 1,000°C. They react with the formation of very fine submicronic particles of Ti (by homogeneous nucleation, see [VIG 11a], Chapter 5, section 5.3). $MgCl_2$ forms a liquid bath in which the titanium particles fall. The problem is then the subsequent separation of the submicronic titanium particles.

A continuous process has been proposed, shown in Figure 3.3.2. $TiCl_4$ gas is injected in a liquid layer of $MgCl_2(l)$ and the reaction occurs at the interface between the magnesium chloride and magnesium layers (the solubility of magnesium in $MgCl_2$ ranges from 0.25–0.40% between 800 and 1,200°C). The titanium particles that are formed at this interface fall through the magnesium chloride layer and gather at the bottom of the reactor.

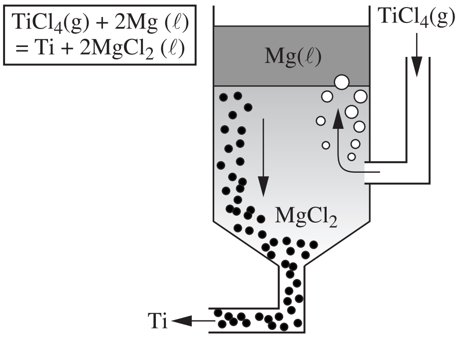


Figure 3.3.2. *$TiCl_4$ metallothermic reduction: a conceptual process for continuous titanium production by $TiCl_4$ gas injection into magnesium through molten salts [DEU 98]*

In the Armstrong continuous process (see Figure 3.3.3), $TiCl_4$ vapor is injected into a stream of molten sodium. The sodium feed rate is in excess of the stoichiometric requirement for sodium reduction of $TiCl_4$. The excess sodium cools the reaction products and carries them to separation stages, where the excess sodium and salt are removed. The reaction product is a continuous stream of powder. The titanium particles are recovered by filtration.

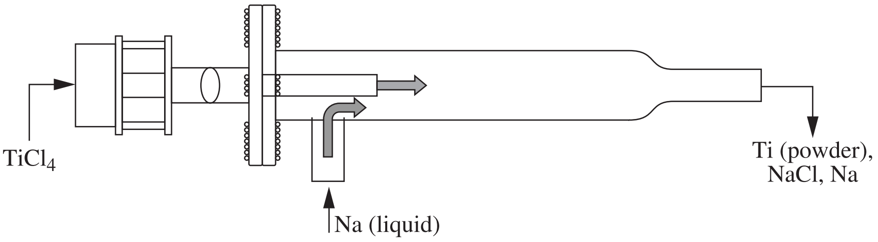


Figure 3.3.3. *$TiCl_4$ metallothermic reduction – the Armstrong process: injection of $TiCl_4$ vapor into a pumped liquid sodium [CRO 03]*

NOTE.– Electrolytic processes with molten salts coming from the reduction of $TiCl_4$ have been developed (see [VIG 11c], section 9.2.5).

3.3.2.2. *Production of uranium (metal)*

$UF_4(s) + 2\ Ca(s) \rightarrow U + 2\ CaF_2\ \Delta G° = -135$ kcal/mol [3.3.5]

$UF_4(s) + 2\ Mg(s) \rightarrow U + 2\ MgF_2\ \Delta G° = -79$ kcal/mol

The production of uranium is a batch operation in a retort filled up with an intimate mixture of tetrafluoride and magnesium, closed and then heated in a batch annealing furnace. The exothermic reaction starts when the temperature reaches 600°C. The boiling point of UF_4 is equal to 1,480°C under $p = 1$ atm. The uranium falls to the bottom of the retort ($T_M = 1\ 132°C$) and is covered by a slag of magnesium fluoride ($T_F = 1{,}261°C$) [EDW 00].

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