

LECTURE NOTES
ON
NON FERROUS EXTRACTIVE METALLURGY



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LECTURE-01

INTRODUCTION TO NON-FERROUS METAL EXTRACTION

1.0- Non-ferrous ore reserves in India & non –ferrous industries in India

Extractive metallurgy- It deals with extraction of metals from its naturally existing ore/mineral & refining them.

Difference between Ferrous and Non-ferrous

FERROUS	NON FERROUS
1. Contain iron as a compound	1. Do not contain iron
2. Show magnetic properties	2. Do not have magnetic properties
3. Do not much expensive due to higher supply	3. Expensive due to lower supply
4. Most are heavy in weight metal	4. Most are low weight metals
Ex-Steel, Carbon steel, alloy steel, iron	Ex-Al, Cu, Sn, Brass, Bronze, Ni

Distinction between Mineral and Ore

<u>MINERAL</u>	<u>ORE</u>
● Minerals are naturally occurring inorganic solid compound with crystalline structure and a definite range of chemical. ● All Minerals are not ore. ● Clay is a mineral of aluminum.	● Ore is the rock form which the metal is extracted in a convenient and economical way. ● All ores are mineral. ● Bauxite is the main ore of aluminum.

Types of ores-

- i) Oxide ore- Fe_2O_3 , Fe_3O_4
- ii) Sulphide ore-

iii) Halide ore- Magnesium chloride in seawater

Distribution of non-ferrous ore in India-

1. Copper- The Balaghat mines in M.P, Khetri mines in Rajasthan Singhbhum Dist of Jharkhand
2. Bauxite- Orissa, Andhra Pradesh, Chhattisgarh, Gujarat, Maharashtra and Jharkhand, Amakantak, Plateau region of Bilaspur katri
3. Gold- Kolar Gold field, Hati Gold field in Raichur
4. Magnesium- Chalk Hills(Tamil Nadu), Almora(Uttarakhand)

2.0-Extraction of metals from an oxide ores

2.1- Extraction of Aluminium-

Details about Al:-

Atomic No:- 13

Atomic Weight-27amu

Density-2.702 gm/cm³

M.P-660.37°C

B.P-2467°C

Common minerals of Aluminium- Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)

Extraction of Al:- Extraction of aluminium by carbothermic reduction of Al_2O_3 is commercially not adopted because of

- Required high temperature
- Undesirable Al carbide form
- Refractories required for this process are expensive and also not readily available

Properties of Al:-

- High ductility
- Corrosion resistance

- High electrical conductivity
- Strong affinity for oxygen
- Nontoxic
- Brilliant surface finish

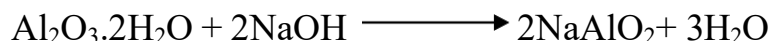
Aluminium extraction done in two process-

- i) Bayer's process ii) Hall Heroult's process

2.1.1- Describe the Bayer's process of Alumina production:

Bauxite concentration of ore or purification of pure i.e conversion of bauxite to alumina. In this process aluminium produced from pure alumina. Hence to purify bauxite and to remove the impurity we use Bayer's process. Bauxite is grinded finely and heated to remove volatile impurities.

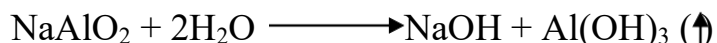
Step:1-Bauxite is heated under pressure with concentrated caustic soda solution per 2-8 hours at 140-150° C.



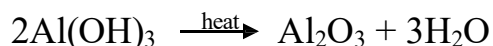
(Alumina) (Conc. Caustic Soda) (Sodium meta aluminate)

Insoluble impurities are left behind which are called **RedMud**, which consist of ferric oxide, sand etc. Which are remove by filtration.

Step:2- Diluting sodium meta aluminate by water and cooling to 50°C.



Step:3- The precipitated is filtered washed dried & ignited at 1000°C



Hence we don't get pure alumina in this process. To get pure alumina we used Hall Heroult process.

In this process, AlCl_3 electrolyzed in a fused salt medium contains NaCl & LiCl to obtain Al_2O_3 (Alumina). In this process we can't use bauxite in directly electrolysis

process because it contains a lot of impurities in bauxite. Bauxite contains 50-60% alumina and 10% TiO_2 , 20% Fe_2O_3 , and 5% SiO_2 . Aluminium is produced from pure alumina (Al_2O_3). Hence to purify bauxite and to remove the impurities, a process called bayer's process is used.

Bayer process: various steps involved are

1. Leaching
2. Precipitation
3. Calcination.

Leaching: Bauxite is initially leached with NaOH. Leaching conditions are High pressure (22atm) and High temperature (220°C). Al_2O_3 is converted to soluble sodium aluminate (NaAlO_2). Next, $\text{Al}(\text{OH})_3$ precipitated is calcined at 1200°C and dried Al_2O_3 is obtained.

Various chemical reactions in Bayer's process:

Bauxite is a mixture of monohydrate and trihydrate. The reactions for the monohydrate and trihydrate are $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (monohydrate) + $2\text{NaOH} = 2\text{NaAlO}_2 + 2\text{H}_2\text{O}$ $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (trihydrate) + $2\text{NaOH} = 2\text{NaAlO}_2 + 4\text{H}_2\text{O}$ Monohydrate requires a temperature of 230°C and 3 hr Trihydrate requires a temperature of 180°C and 1 hr Since bauxite is a mixture of above both it requires 180 to 220°C and a time of 2.5 hr.

Precipitation: Precipitation of $\text{Al}(\text{OH})_3$ is done by cooling. During precipitation, very fine freshly prepared pure aluminium hydroxide is added to accelerate the precipitation reaction. $\text{NaAlO}_2 + 3 \text{H}_2\text{O} = \text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ (monohydrate)(Gibbsite) + NaOH.

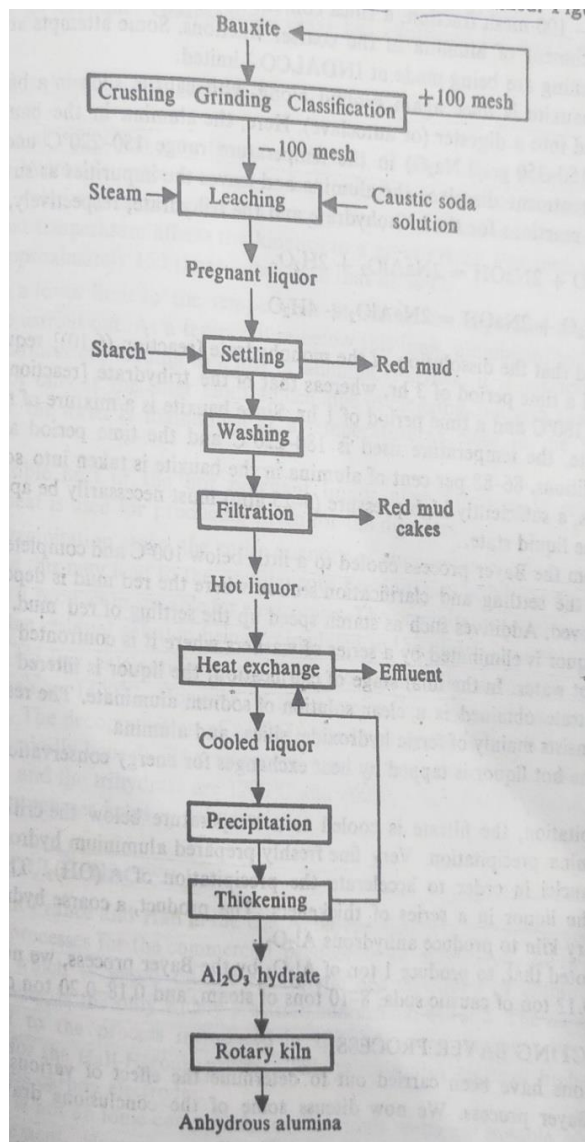
Calcination: Here aluminium hydroxide is calcined at 1200°C to obtain anhydrous alumina.

Factors Affecting Bayers Process Size of the Bauxite:-

- Finer bauxite gives better the digestion of alumina in the liquid liquor.

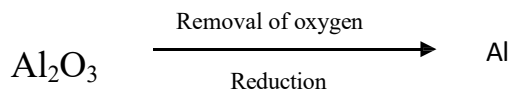
- Wet grinding is more efficient than dry grinding.
- At low temperature below a limit cause lost of alumina. So, maintain the temperature at about boiling point of water (100°C).
- In precipitation stage, entire precipitates of alumina not allow because it may cause precipitation of silica along with alumina.

Flow sheet of Bayer's process-



2.1.2- Explain the fused salt electrolysis of alumina by Hall-Heroult's process:

In this process dissolved alumina (Al_2O_3) in cryolite ($3\text{NaF} \cdot \text{AlF}_3$) is electrolyzed, & Al_2O_3 obtain in pure form.



Properties of alumina-

- ✓ It is a stable oxide.
- ✓ It is a reactive metal.
- ✓ It forms strong bond with oxygen.

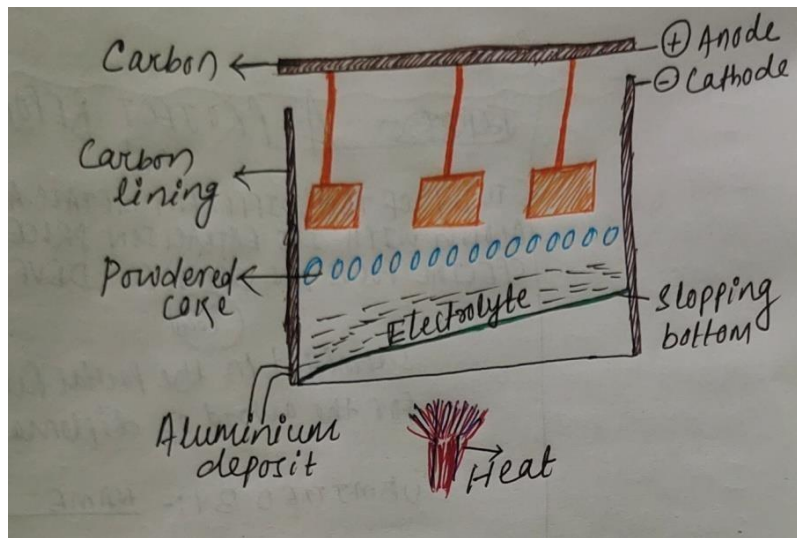
Process: In this process we want reduction of alumina (Al_2O_3) removal of oxygen to get pure aluminium. So we do electrolytic reduction i.e. passing electric current into molten state of a substance. Here we convert alumina into molten state with one anodic plate and cathodic plate i.e. positive & negative respectively. By the aluminium goes towards positive plate and O_2 goes towards negative plate. By this the bond of Al_2O_3 breaks.

Problem: As we need alumina (Al_2O_3) in molten state. It required high temperature i.e 2050°C . By that aluminium melts and vapourised. Al_2O_3 is a very bad conductor of non-electrolytic but we need electrolyte for electrolytic reduction. So that Hall Heroult added two new substances i.e. cryolite (Na_3AlF_6) & Flurospar (CaF_2).

Cryolite (Na_3AlF_6): Its lower the melting point and it is a very good electrolyte which increases the productivity.

Flurospar(CaF_2): It increases conductivity and also used as a solvent.

Electrolyte: $\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6 + \text{CaF}_6$ in ratio (1:3:1)



Properties of powdered coke:

- It prevents heat loss by radiation.
- It prevent burning of anode.

Ions present: $\text{Al}_2\text{O}_3 \longrightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$

$\text{Na}_3\text{AlF}_6 \longrightarrow 3\text{Na}^+ + \text{Al}^{3+} + 6\text{F}^-$

$\text{CaF}_2 \longrightarrow \text{Ca}^{2+} + 2\text{F}^-$

At Anode: $\text{O}_2 \longrightarrow 2\text{e}^- + \text{O}$ (Unstable)

$\text{O} + \text{O} \longrightarrow \text{O}_2$ (Stable)

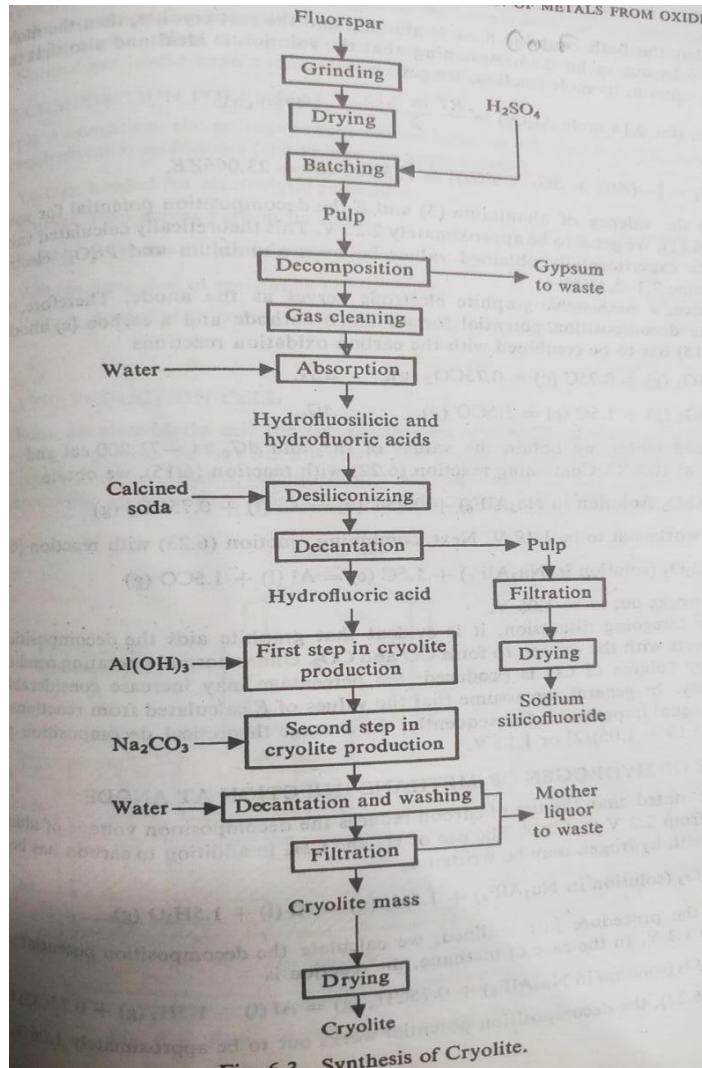
At Cathode: $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$

2.1.3- Discuss anode effect-

It is a polarization phenomenon at the anode in fused salt electrolysis. If alumina content of bath (normally 5-10%) falls below 2% then normal contact between the anode and the bath is interrupted/ broken by the gas film mainly it produces (CH_4 & CF_4) film at the anode & insulate the anode.

Factors affecting anode effect:

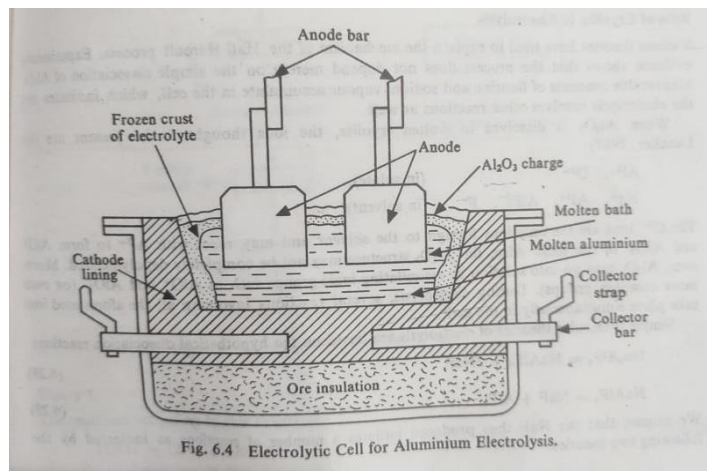
- Nature of electrolyte-Anode effect occurs mainly with fluoride.
- Purity of electrolyte- Greater purity lower is current density & viceversa.
- Current density (J) $= I/A$
- Temperature- When temperature increases current density decreases.



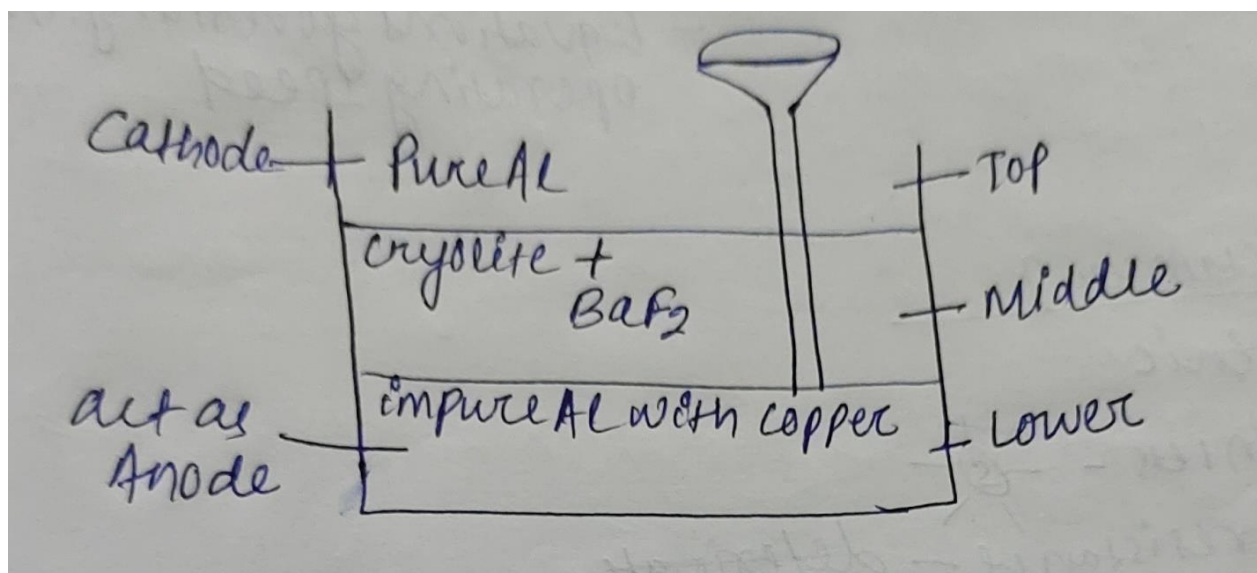
2.1.4- Explain the method of refining of aluminium

ELECTROLYTIC REFINING OF Al (BY HOOPE'S PROCESS):

The purity of metal produced by Hall Heroult process is not sufficient for most electrical application. So to achieve higher degree of purity are electrolytic method known as “**Three layer process**” or Hoope’s method is applied to get 99.99% Aluminium.



CONSTRUCTION OF CELL- This is an electrolytic process. Electrolytic cell is made up iron, which is lined with carbon at the bottom. The cell contains three layers of fused mass. The lower layer consists of impure Al with copper which acts as anode. The middle layer consists of a solution of cryolite & Barium fluoride(BaF_2). The upper layer consists of pure aluminium which act as cathode.



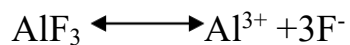
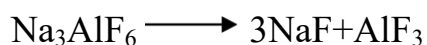
This three layers are separated from each other due to difference in specific gravity.

WORKING OF CELL-

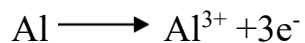
At high temperature (Na_3AlF_6) cryolite decomposes into NaF & AlF_3 , AlF_3 produces Al^{3+} ions in middle layer on passing electric current, Al^{3+} from middle layer migrate to the upper layer i.e. cathode reduced to aluminium by gaining $3e^-$. Equal no. of Al^{3+} are produced by the loss of $3e^-$ in the lower layer i.e. anode and migrate to the middle layer. Refined Al is tapped off periodically to which is about 99.99% pure.

Chemical Reaction during the process-

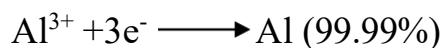
Decomposition of cryolite:



At Anode (Bottom layer)



At Cathode (Top layer)



Overall Reaction- $\text{Al}^{3+} + \text{Al} \longrightarrow \text{Al} + \text{Al}^{3+}$

Factors affecting Hall Heroult process-

- Increase in temperature (bath) decreases the current efficiency.
- For every 4°C rise in bath temperature the current efficiency falls by 1%.
- Higher the temperature more number of side reaction form.

2.1.5- State the uses of aluminium

- It is widely used in our daily life because it is cheaper.
- Al is a good conductor of electricity & used in electrical transmission wire.
- Al is used as container metal in electrical conductor, in aluminium sheet, decorative paints, aeroplane parts.

What is Froth flotation process?

In this method powdered ore is taken with water & pine oil. The slurry in tank is vigorously (continuously) stirred by passing compressed air to produce froth. Lighter sulphide ore is wetted by pine oil and comes to the surface with froth while impurities settle down at the bottom. The froth with ore is skimmed off & dried to get concentrated ore.

2.2- EXTRACTION OF TIN

Details of Tin-

Atomic Number-50

Atomic weight-118.71amu

Density-7.31 gm/cm³

Melting point-231.9°C

Boiling point-2270°C

Common minerals of Tin- Cassiterite (SnO₂)

Properties of Tin-

- Tin is soft.
- Tin is non-toxic
- Tin is highly corrosion-resistant & fatigue resistant.
- Tin has a low melting point. So used for soldering purposes.
- Tin is highly malleable(able to be shaped).
- Tin is easy to recycle.

Area of Extraction-

Balivia, Malaysia, Indonesia. In India little deposit of tin in Madhya Pradesh

2.2.1- Explain the process of Tin ore concentration-

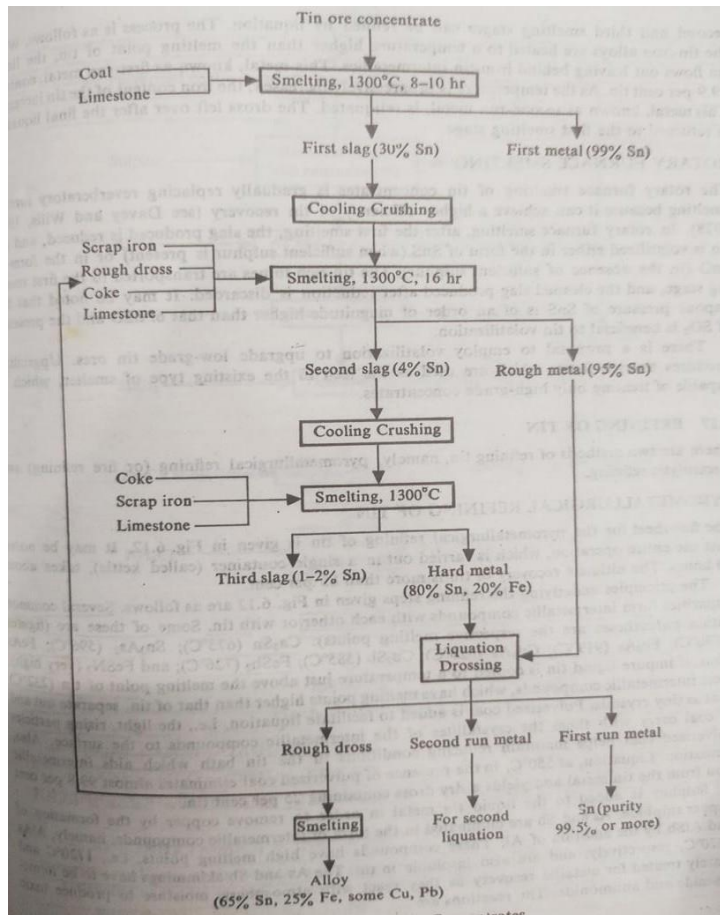
SnO_2 is the most important mineral of Tin. SnO_2 mainly contains FeS_2 hence need gravity separation method and also associated with impurities & metallic sulphide such as Galena, chalcopyrite, iron pyrite.

2.2.2- Explain the process of concentrate smelting for tin extraction-

Firstly, the tin ore is crushed and grinded then forth flotation process is carried out then we get tin ore concentrate then we go for smelting. For this smelting purpose the tin ore found by the below process is converted to oxide which are in sulphide state then the tin ore is smelted in a furnace at 1300°C then the slag phase which is in FeO stage is separated.

For high grade purity of tin ore the tin obtained from the primary stage for smelting is smelted further to get pure tin. For smelting purpose ore, limestone is used to melt & remove the impurities in slag from the tin ore their smelting process is carried out 2-3 times to get 99.99% pure tin.

Flowsheet of Tin-



2.2.3- Describe the process of refining of Tin-

The refining of tin ore is done in two processes-

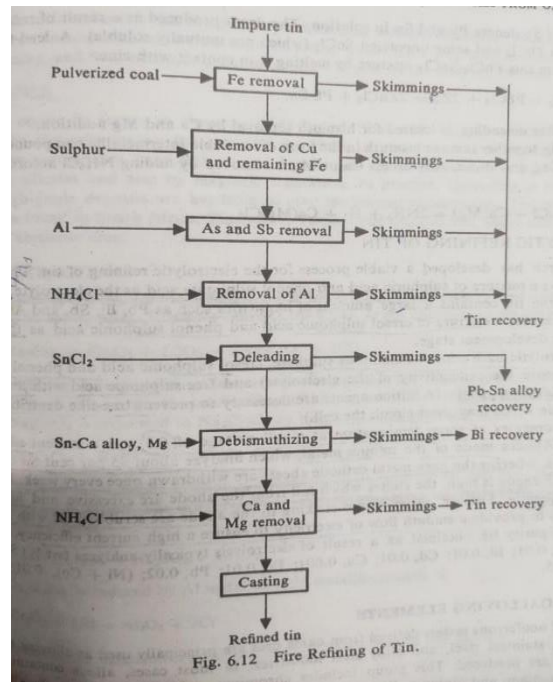
- i) Fire refining
- ii) Electrolytic refining

Fire refining-

- The impure tin is taken in a container known as kettle & this process takes up to 40-50 hr for recovery of pure tin i.e. more than 85%.
- Some common impurities like Ca_3Sn (675°C), Sn_3As_2 (596°C), FeAs (1030°C), Fe_2As (919°C), Cu_3As (825°C), Cu_2Sb (585°C), FeSb_2 (726°C), FeSn_2 (1100°C) have very high melting points.

- From intermetallic compound with each other or with tin.
- As the pure tin melting point is 232°C . To get pure tin, the liquid tin at 1300°C is cooled up to the melting point of tin. But the intermetallic compound which are form by the impurities have higher melting point than tin.
- So when the impure liquid tin is cooled the different temperature get solidified & give tiny particles.
- This tiny particle are flowed on the liquid tin and are separated then pure tin is available.
- The second phase known as liquation is carried out in the tin metal which heated upto 550°C . In this, some amount of pulverised coal is added to maintained the temperature.
- Some flux are added to remove 99.8% Fe form the liquid tin & pure tin is obtained.
- So to remove copper from the liquid tin a third process is carried out in which some amount of sulphur is added to remove copper forming copper sulphide. In this process some amount of aluminium is added to remove Arsenic & Stabium by giving intermetallic compound AlAs & AlSb .
- This intermetallic compounds have high melting point i.e. 1720°C & 1070°C & also insoluble in tin. These As & Sb have to be skimmed (remove) immediately & treated for metallic recovery. As they react with atmospheric moisture to produce toxic arsenide(As^{3-}) & antimonide (Sb^{3+}).

Flowsheet of Fire refining of Tin-



ii) Electrolytic refining-

In electrolytic refining impurities like Pb, Bi, Sb & As are removed from the impure tin which act as anode in the same.

Pure tin is taken as cathode & a mixture of cresol sulphuric acid & phenol sulphonc acid is taken as electrolyte. The electrolytic bath content stannous sulphate, cresol sulphonc acid & phenol sulphonc acid (to improve the conductivity of electrolyte) and free sulphonc acid with β -naphthol & glue as addition agents.

(Addition agents are necessary to prevent tree like dendritic structure deposits on cathode which may short-circuit the cell). The cell operates at a room temperature at a cell voltage 0.3V and a current efficiency of 85% anode.

2.2.4-State the uses of tin-

- Tin is used in soldering of steel as it posses high magnetic strength & low m.p.

- Tin is used as coating, plating & polishing purpose as it has high resistance to corrosion.
- It is widely used in the manufacture of food containers made of steel.
- In shipping industry, it is used as an anti-fouling agent for boats & ships to prevent them from algae, or marine organism.

3.0-Extraction of metals from sulphide ores

Copper is mainly extracted from its sulphide ore because when ore is subjected to roasting some of it is oxidised to Cu_2O which reacts with the remaining Cu_2S to give copper metal. In this Cu_2S behaves as reducing agent.

3.1- Pyrometallurgical Extraction of copper-

Details of copper

Atomic number-29

Atomic weight- 63.54amu

Melting point- 1083°C

Boiling point- 2595°C

Density- 8.94gm/cm^3

Common minerals of Cu-

COPPER OXIDES	CHEMICAL FORMULA	COPPER SULPHIDES	CHEMICAL FORMULA
Cuprite	Cu_2O	Chalcocite	Cu_2S
Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$	Chalcopyrite	CuFeS_2
Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Bornite	Cu_5FeS_4
Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Covellite	CuS

Copper deposits in India-

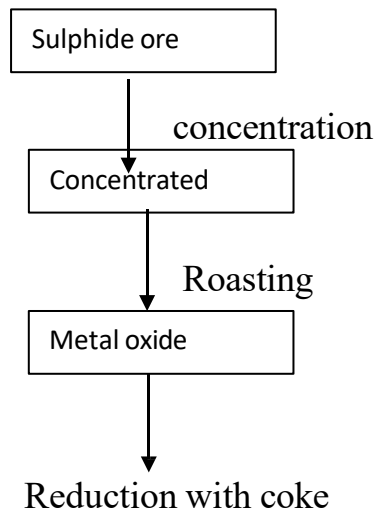
Singbhum district (Jharkhand), Khetri belt(Rajasthan), Sikkim, UP, AP

Area of extraction-

HCL(Hindusthan Copper Limited)

Khetri mines, Kholihana mines

What are the process adopted after concentration of sulphide ore for extraction of metal?



3.1.1- Describe the process of roasting of copper ore-

Copper is mainly extracted from its sulphide ore.

Steps in extraction-

Concentration → Roasting → Smelting → Refining

(Froth flotation)

We use fluidized bed roaster or multiple hearth roaster for roasting can't reverberatory furnace or copper blast furnace for smelting. We need to have ore of metal here ore is chalcopryrite (CuFeS_2). It contains CuS & FeS and there are soe major process of copper.

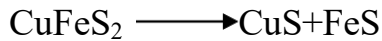
- i) Concentration
- ii) Flotation
- iii) Roasting
- iv) Matte smelting

- v) Converting
- vi) Refining

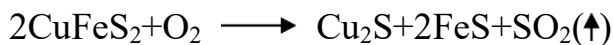
Step-1: Ore should be crushed & grind to become powdered form. Then concentration of ore taking place (aim is to remove impurity).

Step-2: In flotation process copper should be in chamber which contains water. In water we add pine oil & we agitate and formation of bubbles takes place and this bubble stick to copper ore and takes the surface.

Step-3: They we take that cleaned ore for roasting we fluidized bed roaster at 550°C (roasting means it is a particular ore in presence of oxygen below melting point). In this process the ore CuFeS_2 that contains FeS oxidized partially

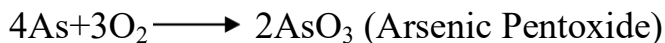
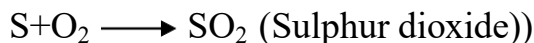


Then CuS oxidied to form Cu_2O

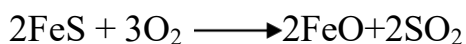
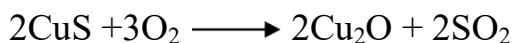


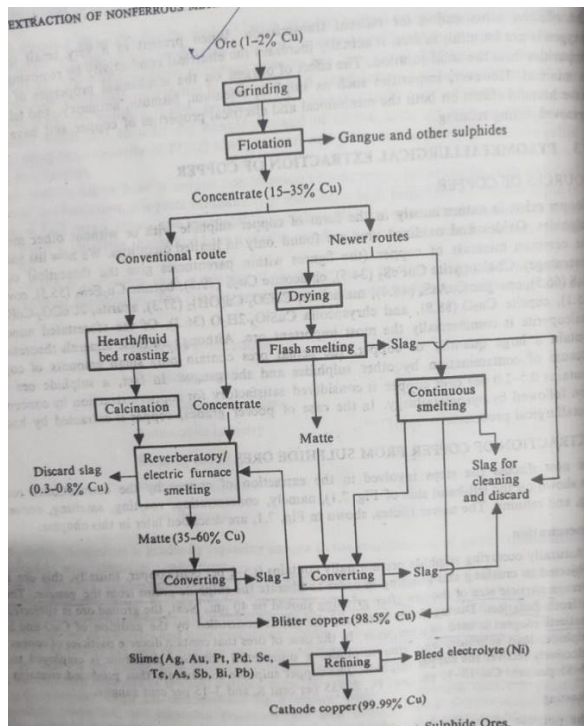
(Copper (Oxygen) (Copper sulphide) (Iron sulphide)
pyrite)

During roasting moisture, volatile impurities are removed (Sulphur, phosphorous, Arsenic & antimony) which are present as impurities are removed as volatile oxide)



Then cuprous & ferrous sulphide or further oxidise to there oxides.

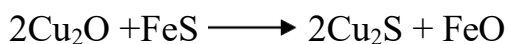
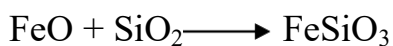




3.1.2-Describe the process of matte smelting of copper ore- (reduction takes place)

Step-4: Smelting process is carried out to separate the metal sulphide from the copper ore. The roasted ore is mixed with powdered coke and sand & heated in a blast furnace or reverberatory furnace. It is made up of steel plates lined inside with fireclay bricks. Hot air 1250°C is introduced from tuyeres near the base of the furnace. Hot air converted FeO into FeSiO₃ (Ferrosilicate).

As a result following changes occur-



As a result of smelting to separate molten layer formed at the bottom of the furnace the upper layer consist of slag & is removed as base. And the layer is called **MATTE**. (It is a mixture of Cu₂S & FeS). The product of smelting is **COPPER MATTE**.

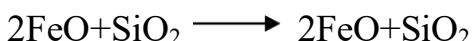
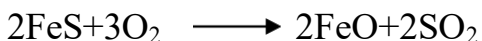
3.1.3-Describe the process of converting of copper matte:-

Step 5: Converting stage- The purpose of converting is to removed FeS& other impurity from the matte. For this the molten matte produced in smelting process is charged into a side blown converter which is a cylindrical vessel with

a capacity of 100-200 ton or matte. In converter the atmosphere is highly oxidise because oxygen is blown into the molten matte through tuyeres.

Then this converting stage is composition of two stage named as Slagging stage & Blister formation stage.

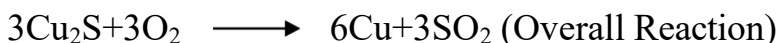
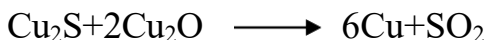
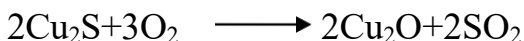
SLAGGING STAGE- In the slagging stage the FeS present in the matte is oxidised and the oxide is slagged out by the addition of silicious flux.



During converting the oxidation of iron sulphide generate sufficient heat to over count the heat losted of the surrounding & to maintain the matte and slag in the molten state. The slag obtained form this process has 2-9%Cu, 40-50%Fe, 20-30%SiO₂, 1-5% CaO+MgO.

Copper is recovery from the slag produced in a converter transfer to a smelting furnace. Here matte particle present in the slag in settle down at the bottom & the slag can be discard.

BLISTER FORMATION STAGE- After slagging stage has been completed the converter contains Cu₂S called white metal., because of it appearance. In blister Cu formation stage Cu₂S is oxidised to form Cu by combination of reaction.

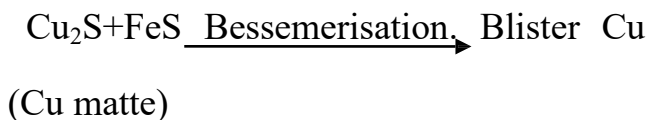


Why this Cu is called blister copper?

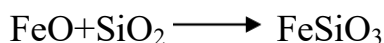
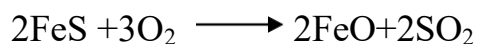
The Cu so obtained is called blister Cu because SO₂ hidden in it escapes out producing blister on the surface. In this process during this reaction the amount of sulphur is decreased & the amount of Cu is increased. The Cu found in this is called blister Cu due to its blistery appearance.

Bessemerisation of Cu extraction-

Converting of Cu matte to blister Cu is called Bessemerisation.



Matte contains Cu_2S & some unreacted FeS along with Silica. It is converted into Cu in a special furnace “Bessemer Converter”. When air is blown through the matte several reaction takes place:



Impurities in Blister Copper-

- Blister Cu is 98% pure.
- It contains impurities mainly As, Zn, Pb, Ag, Fe.
- These impurities mainly affect the electrical as well as mechanical properties of copper.
- Blister Cu is refined by electrolysis process.

3.1.4- Explain the refining of copper-

Step-6: There are two types of refining

- i) Fire Refining
- ii) Electrolysis Refining

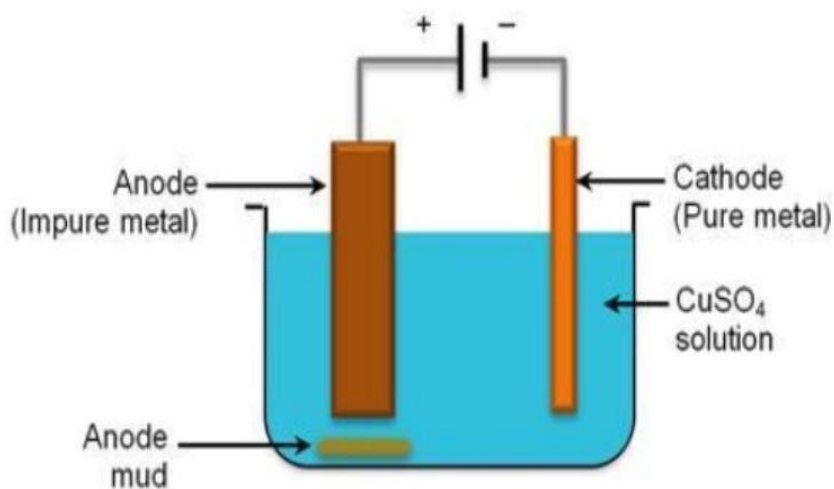
FIRE REFINING- The main purpose of fire refining is to remove sulphur from blister Cu as SO_2 by oxidation with air and then oxygen is removed by using hydrocarbon. The fire refining is conducted in a reverberatory furnace with a capacity of 400tons. The fuel is used for temperature natural gas, oil or pulverised coal. The process continued 12-16 hr in refining furnace. The surface of blister Cu

is oxidised & the blister Cu_2S is converted to Cu_2O . Then after this oxygen is removed by hydrocarbon are used to pure Cu. The purity of fire refining Cu is around 99.7%.

ELECTROLYTIC REFINING- In this step blister Cu is converted to pure Cu through electrolytic refining.



The electrolysis done in a electrolytic refining tank made up off concentrate or wood of 3-5m long, shell 1m wide & 1m deep and utilization minimum space with maximum cathode & anode area. The electrolyte is CuSO_4 mixed with some amount of H_2SO_4 to increased conductivity at temp 50-60° C blocks of blister Cu are used as anode and this sheets of Cu used as cathode. The cathode plates are coated with graphite to remove depositing copper. When the electrolysis process starts Cu is transferred from the crude anode to pure cathode.



ELECTROLYTIC REFINING OF COPPER

Impurities in blister copper such as Fe, Co, Ni go into solution and the precious metal collect below the anode known as **Anode slime**. Hence in the area of cathode the concentration of Cu^{2+} ion decreases & the water in the electrolyte is electrolyzed releasing hydrogen which lowers the current efficiency, but in the area of anode the concentration of Cu^{2+} ion increases.

3.1.5- Uses of Copper-

- Copper is mainly used for making electric wires, sheets, utensils, coins, electroplating, making alloys.
- Copper also used in medicines.
- Copper+Zinc =Brass
- Copper+nickel=Monel metal
- Copper+tin =Bronze
- Copper+ Iron + steel=Stainless steel
- Copper+ aluminium=duraluminium

3.2- Pyrometallurgical extraction of Lead-

Details about Pb-

Atomic Number-82

Atomic weight-207.21amu

Density-11.34 gm/cm³

Melting point-327.40° C

Boiling point-1737° C

Common minerals of Pb-

Pb oxides	Chemical formula	Pb sulphides	Chemical formula
Anglesite	PbSO ₄	Galena	PbS
Cerussite	PbCO ₃		

Properties of lead-

- Lead has low melting point, heaviest metal, most malleable, easy to shaping and working.
- It has resistance to atmospheric underground and salt water corrosion.
- It is soft and has extreme workability.
- Lead has excellent anti-friction property.
- Resistance to sulphuric acid.
- Low cost and ductility.

Extraction plants in India-

Tundoo (Bihar)

Vishakapatnam (Andhra pradesh)

3.2.1-Explain roasting and sintering of lead ore-

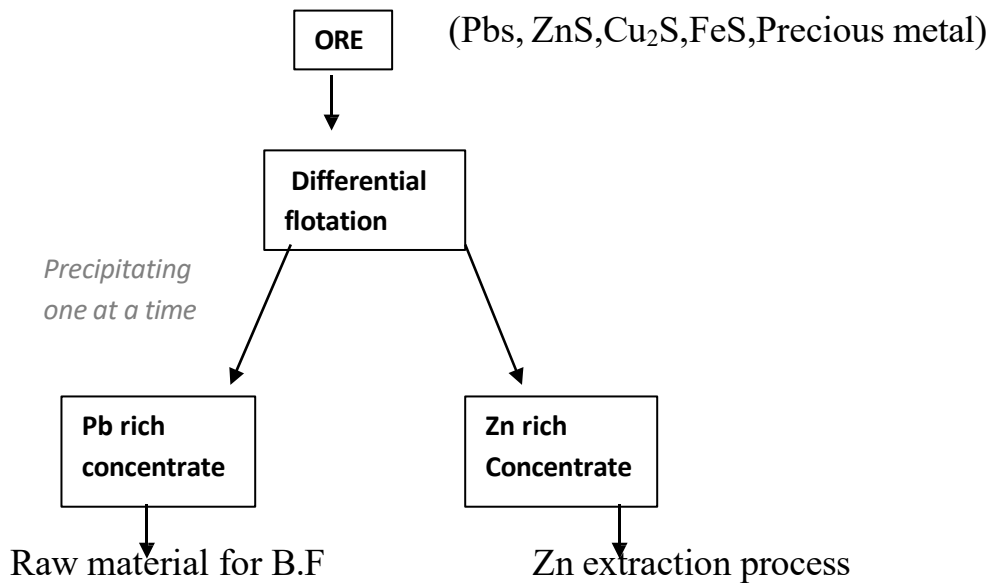
Extraction of Pb done in 3 phases-

1-Concentration of ore

2-Roasting & Sintering

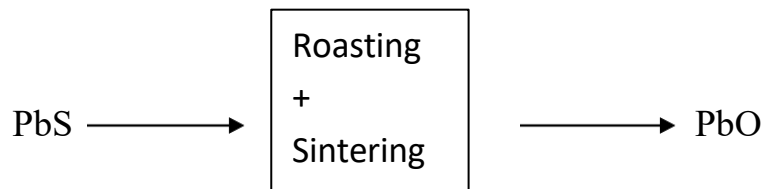
3-Reduction in blast furnace

1. Concentration of Ore-



The ore Galena (PbS) is grind into fine powdered so as to increase surface area for extraction of lead. The main aim of concentration is to remove impurities. The lead ore contains lead sulphide with other sulphide & precious metal. The lead sulphide along with precious metal is fast separated from other sulphide and is concentrated by differential flotation process. The concentrate may contain 60-80% Pb.

2. *Roasting & Sintering-*

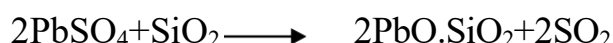
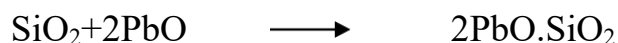
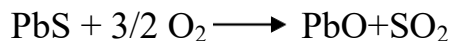


During roasting, the concentrated ore roasted to oxides which is subsequently reduced by carbon & temperature must be control because above 800°C PbS tends to fuse.

Roasting is done in Dwight llyod sintering machine. This machine is not only eliminates sulphur to a large extend but also produces sinter of good

strength & porosity. During sintering process, the sulphur content of the concentrate is reduced from 16-18% to 1-2%. This machine operates at around 800° C and produces 200-1600 tons of sinter per day.

The reaction takes place during roasting are:



The process of extraction of lead by blast furnace smelter-

The furnace used for smelting of lead is rather small when compared with the blast furnace used for pig iron production. Its total weight is around 8m, top diameter 3m, crucible depth 3/4m & stack height 5m operating temperature always kept less than 1200°C. The bosh temperature is just above the temperature 200° C because lead has very low melting point 327°C. So there is a chance of losing lead as fumes thus at the top of the furnace we use electrostatic precipitators. So as to recover the lead fumes from the outgoing gaseous.

Blast furnace raw material:

- Sinter(PbO)
- Flux(Limestone & Quartz)
- Coke-reducing agent
- Scrap iron

Limestone & Quartz are added to the charge in order to form a slag containing gangue material.

Purposes of Scrap iron-

Scrap iron helps in reducing residual PbS left unroasted in the sintering machine. It combines with silica present in the charge to form $2\text{FeO} \cdot \text{SiO}_2$ which lowers melting point of slag thus rendering it more fluid at operating temperature.

It reduces the lead loss- $\text{PbSiO}_3 + \text{Fe} \longrightarrow \text{FeSiO}_3 + \text{Pb}$

Finally it helps in reducing PbO i.e $\text{PbO} + \text{Fe} \longrightarrow \text{FeO} + \text{Pb}$

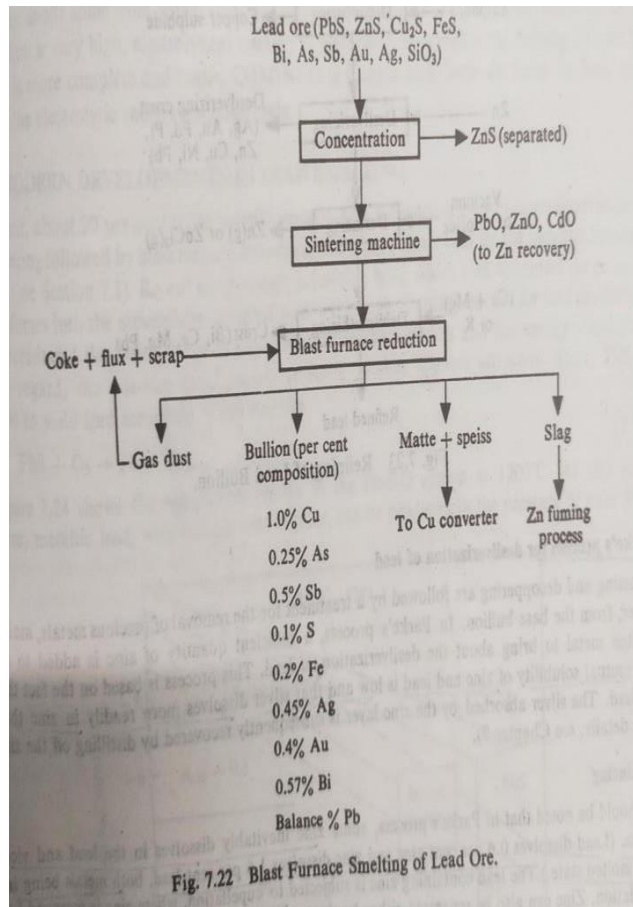
The smelting process produces 4 distinct layer of products

1st layer-Slag

2nd layer-Matte containing copper

3rd layer- Speiss (FeAs₄+impurities)

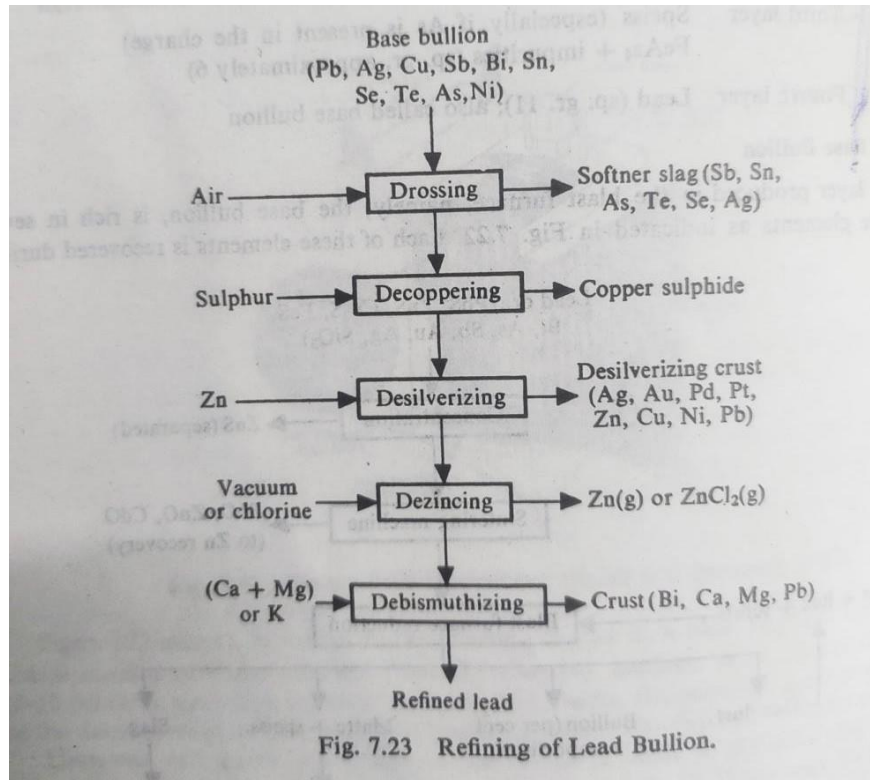
4th layer- Lead (called as Base Bullion)



Blast furnace smelting of lead ore

PROCESS OF REFINING OF LEAD BASE BULLION:

The lead rich layer produce in the blast furnace namely, the base bullion is rich in several other valuable elements. Each of this elements is recovered in the following step:



DROSSING- Drossing is a combination of liquation & oxidation usually carried out in a reverberatory furnace. Base bullion is first subjected to drossing at around 350°C. At 350°C metals like Sb, Sn, As, Te, etc get oxidised and are skimmed off.

DECOPPERING- Decoppering is the removal of dissolved copper from lead bullion. After drossing the temperature is raised to 500-550°C. Sulphur is added to eliminate copper in the form of copper sulphide.

DESILVERIZING- Desilverizing is the removal of silver from base bullion. After drossing & decoppering precious metal are removed from base bullion. In PARKE'S process sufficient quantity of zinc is added because the mutual solubility of zinc & lead is low & silver dissolves more readily in the zinc than lead. The silver absorbed by the zinc layer is subsequently recovered by distilling off the zinc.

DEZINCING- Zinc & lead are mutually soluble lead dissolve 0.6% of zinc; zinc dissolves 1.6% of lead & both metals being in molten state. The lead containing zinc is subjected to cupellation, where zinc is removed by oxidation. Zinc can also be separated by application of vacuum or with chlorine.

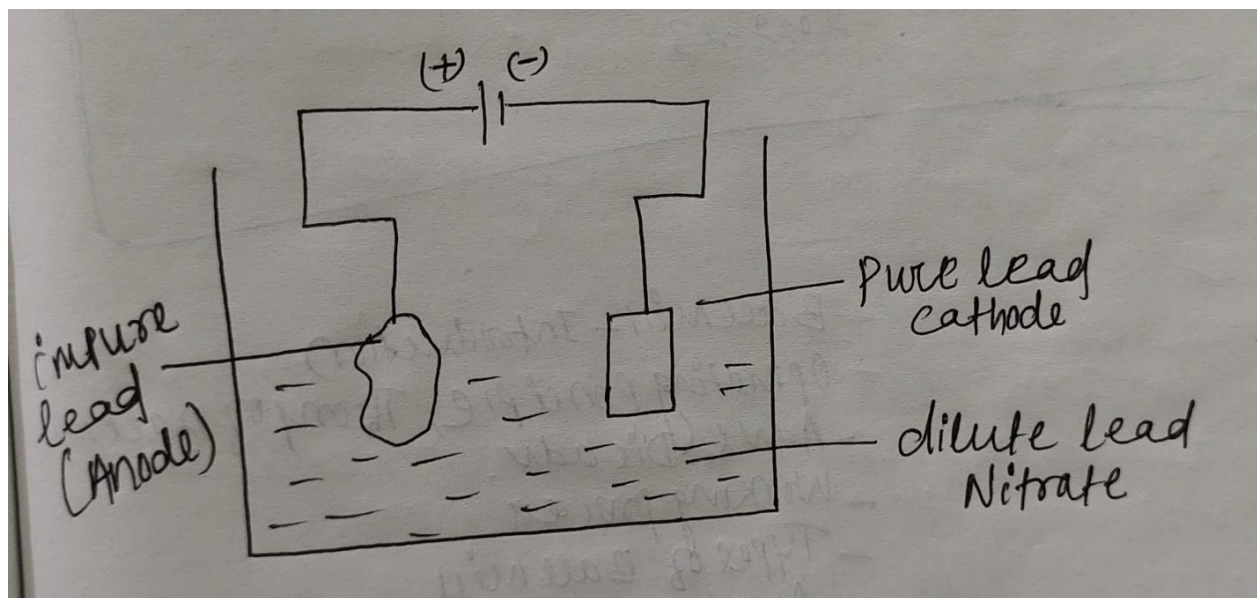
What is Cupellation?

The process of recovering Au & Ag from lead rich bullion is called cupellation.

DEBISMUTHIZING- In base bullion bismuth is present in large quantity. Bismuth can be separated by addition of calcium & magnesium to form an insoluble intermetallic compound.

ELECTROLYTIC REFINING-

To refine lead base bullion by electrolytic process have proved unsuccessful by most attempt. For electrolytic refining of lead the electrolyte consists of a solution of PbSiF_6 (lead fluorosilicate) in H_2SiF_6 (Hydrogen silicic acid). Here anode is made up of impure lead & the cathode is made up of pure lead & the electrolyte consists lead ions.



At Anode: $\text{Pb} \longrightarrow \text{Pb}^{2+} + 2\text{e}^-$

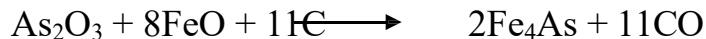
At Cathode: $\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb(S)}$

During electrolysis, impurities such as Bismuth, Arsenic, Antimony & the precious metals collect at the cell in the form of an anode slime from which they can be readily recovered. If the impurity content of the base bullion is very high, electrolytical refining is preferable to conventional refining because the recovery is more complete & easier.

What is speiss?

When un volatilized As reacts with Fe & C to form speiss.

OR A molten phase consists primarily Fe, As which is commonly encountered in lead smelting operation. Mainly speiss closely relate in presence of As & Fe in blast furnace.



Speiss have high content of Cu which get recovered by treated it in converter to get Cu in blister form. Finally, the Pb bullion get from the blast furnace which on refining produced pure lead.

EXTRACTION OF ZINC

3.3-Pyrometallurgical and Hydrometallurgical method of extraction of zinc-

Details about zinc-

Atomic Number-30

Atomic Weight-65.38 amu

Density- 7.13 gm/cm³

Melting point- 419.5° C

Boiling point-910° C

Zinc ore & their chemical formula-

Zinc oxides	Chemical formula	Zinc Sulphides	Chemical formula
Smith Sonite	ZnCO ₃	Zinc blend/Sphalerite	ZnS
Zincite	ZnO		

Franklinite	$[\text{ZnO}(\text{Fe},\text{Mn})_2\text{O}_3]$	
Willemite	Zn_2SiO_4	

Properties of Zinc-

1. Zinc is bluish white metal with low melting point and boiling point.
2. In electrochemical series zinc position is high.
3. Zinc protects steel from corrosion (Galvanisation)
4. Zinc is a coarse grained metal.

Area of extraction-

- Zawar mines (Rajasthan)
- HZL (Hindustan Zinc Ltd)
- COMINCO- BINANI at Kerala
- Zinc production countries are Canada, Belgium, Australia, Mexico, USA, etc.

List the extraction method & technique-

- Pyrometallurgical extraction
- Hydrometallurgical extraction

Pyrometallurgical Extraction-

- In their sulphide ore is heated to 800°C to convert S to SO_2 , SO_3 , Sulphate.
- After elimination of S, ZnS is converted to ZnO , which can be reduced in carbon atmosphere to metallic zinc.
- Extraction of zinc from sulphide ore contains mainly 5 important processes.
 - 1- Horizontal Retort
 - 2- Vertical Retort
 - 3- Electrothermic process
 - 4- Electrolytic process
 - 5- Imperial smelting

3.3.1- Describe the roasting of zinc ore concentrate-

Roasting of Zinc ore Concentrate-

- Main purpose of roasting is to convert ZnS to ZnO.
- Roasting is necessary because ZnS cannot be reduced to metallic zinc during distillation.
- Zinc ore concentrate by drying flotation technique lead (Pb), copper concentrate eliminate by such process.
- The ZnS concentrate which content 55% of zinc is roasted at a temperature about 800°C.

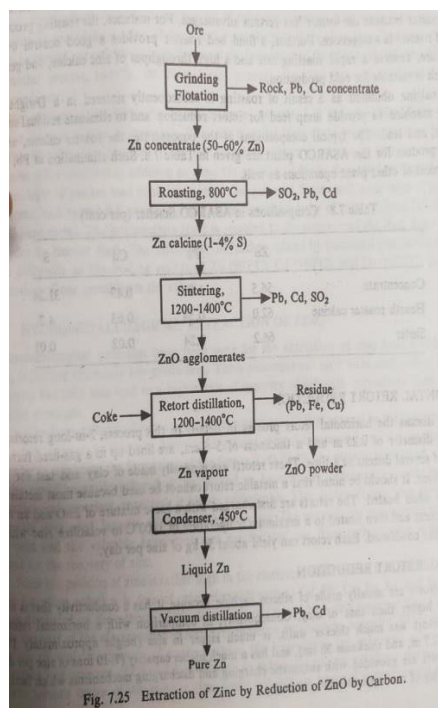
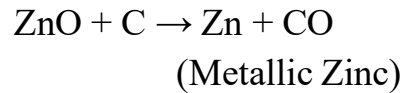


Fig. 7.25 Extraction of Zinc by Reduction of ZnO by Carbon.

- The resultant roasted oxide is first ground and agglomerated and then sintered at 1200°C so as to provide a feed in the form of lump for retort reduction.
$$\text{ZnS} + 1.5 \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2 (\uparrow)$$
- The Zinc Sulphide concentrate always content lead sulphide in order to eliminate lead sulphide to a large extent during roasting i.e. by volatilization process.
- In most cases roasting is carried out in a fluidised bed roaster rather than hearth roaster because roasting process is autogeneous in fluidised bed roaster and also it provides a good control over temperature.

Extraction of Zinc by Carbon reduction-

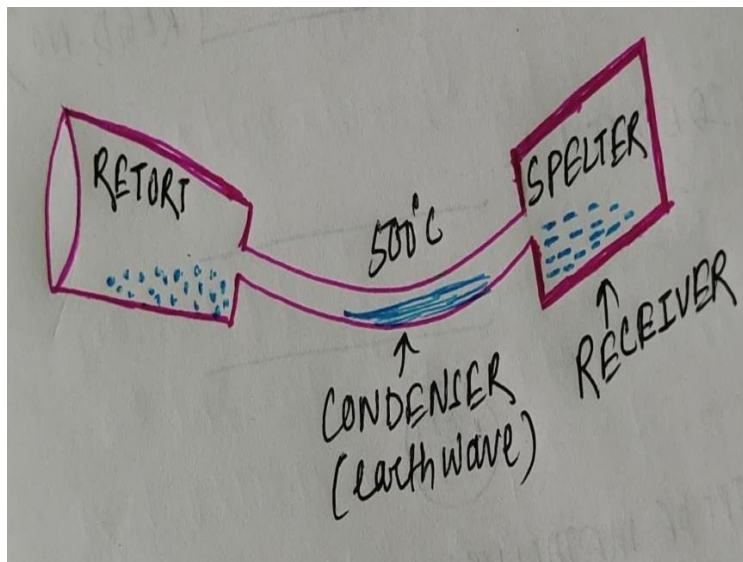
- The Zinc oxide obtained in roasting is reduced by carbon in the temperature range 1200°-1400°C, this process is called distillation.



- Reductant used is carbon.
- The zinc which distils off is collected in condenser.
- The zinc that we get is in impure form to make pure zinc we go for refining process.

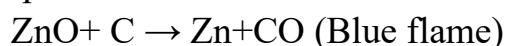
3.3.2-Explain how zinc is extracted by vertical retort process

1.Horizontal Retort-



- In horizontal retort process, retorts are placed in horizontal position in this process 2m long, retort each having a diameter of 0.25m and thickness of 5-6cm are lined of a in a gas fired furnace made up of clay used instead of metal retort because most metal gives alloy when heated with zinc.
- Retort are filled with charge which consist of ZnO & reducing agent (powdered coke or Anthracite coal).

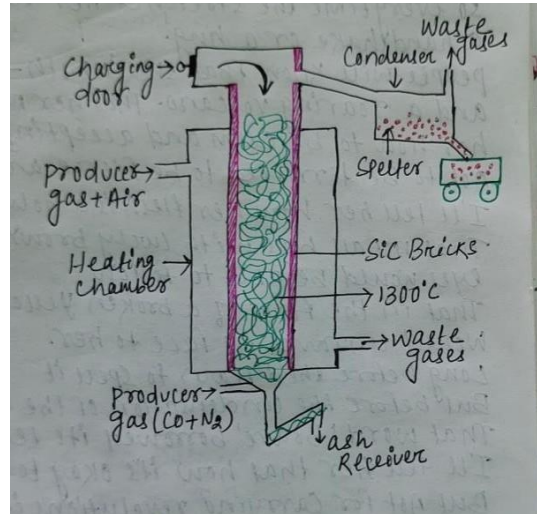
- Reducing agent should contain low ash and sulphur content.
- ZnO is reduced by reducing agent in the temperature range 1200-1400°C. This process is called distillation process.
- Whole process of reduction & distillation takes nearly 12hrs.
- Fire is now put in the temperature of the retort is generally raised as the temperature is raised the CO (Carbon monoxide) gas is expelled.
- Finally expelled CO gas burns with blue flame.
- Blue flame indicates that CO is getting rapidly reduced and the distillation of Zn (production of Zn) has started.
- The Zn vapour obtained is cooled to obtain zinc liquid.



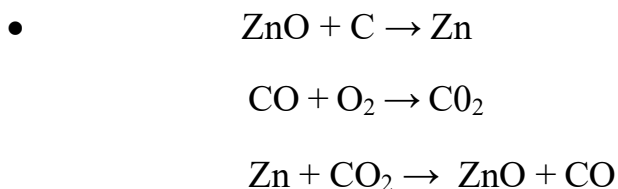
Difference between Horizontal retort & Vertical retort

Horizontal Retort	Vertical Retort
1. Retort is horizontal	1. Retort is vertical
2. Zinc vapour is cooled by air condenser	2. Zinc vapour is cooled by zinc liquid.
3. Capacity can be varied.	3. Capacity is fixed
4. It is a continuous process.	4. It is a fixed process
5. Separate feeding arrangement is required.	5. No separate feeding arrangement is required.

2. VERTICAL RETORT-



- A vertical retort is shaped rectangular in cross section.
- It is a 10m height, 0.7m diameter & 30cm thickness of capacity, 7-10 tons of zinc per day made up of SiC bricks because it has high conductivity approximately 5 times compare to horizontal retort.
- Most retorts are provided with automatic charging and discharging mechanism.
- A vertical retort can be also used for electrothermic reduction as the charge descends zinc oxide in the concentrate is reduced by reducing agent (powdered coke) in the temp of 1300°C.



- Zn vapour is obtained are cooled to produce Zinc liquid.

3. ELECTROTHERMIC PROCESS FOR ZINC

It occurs in a vertical retort 15m high, internal dia of 24m about 100 tons Zinc per day. Electrodes of Graphite are introduce through SiC walls at two places near the bottom. The gas liberated due to the reduction of charge contains 40-45% Zn, 45%CO, 5-8%H₂, 5-10%N₂. The Zinc condensation has to be carried out quickly to avoid the formation of the blue oxide of zinc (ZnO+Zn). Residue contains 3-4% Zn.

4. ELECTROLYTIC REDUCTION-

In this case when Zn immersed in their salt solution rapidly establish a reversible potential. Since the activation over potential is low, the displacement behaviour exhibits a good correlation with the electrochemical series of standard potential.

3.3.3-Explain the refining of zinc

REFINING OF ZINC SPELTER

Zn recovery from this process is over 95%. Zn product obtained in previous retort process is known as Spelter. Spelter on melting produces three distinct layers as-

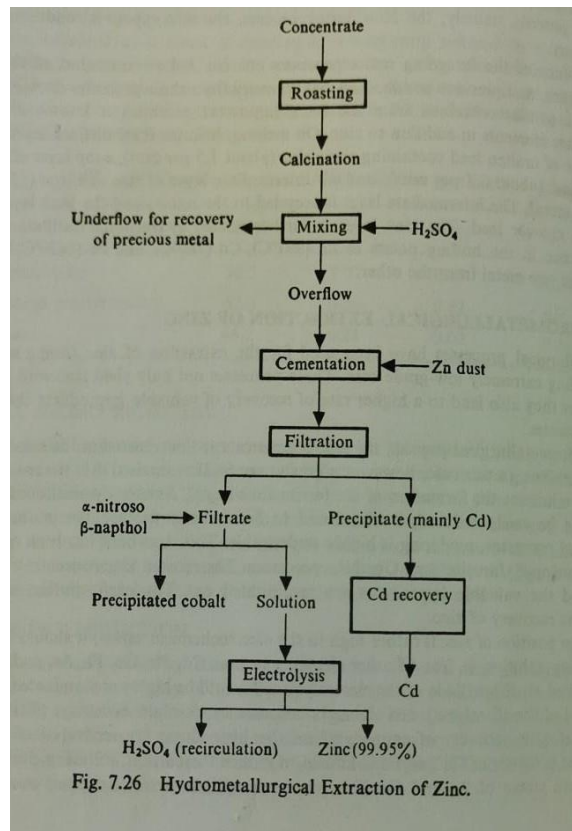
- i) Bottom layer- Molten lead contains some zinc of 1.5%
- ii) Top layer- Zn contains some lead of 0.8%
- iii) Intermediate layer-Zn & Fe(15-20%) called hard metal.

TOP LAYER	←	Zn+Pb(0.8%)
INTERMEDIATE LAYER	←	Zn+Fe(15-20%)
BOTTOM LAYER	←	Molten Pb+Zn(1.5%)

3.3.4- Explain the process of leaching & preparation of zinc base solution

HYDROMETALLURGICAL EXTRACTION OF ZINC-

In hydrometallurgical process, the zinc concentrated is first roasted in the same manner as in the retort process. The roasted zinc concentrate is dissolve in an acid and the valuable by product are precipitated out. The leach solution is finally electrolyzed for the recovery of zinc.



Steps involved in hydrometallurgical process-

- i) Preparation & roasting of ore for leaching
- ii) Leaching of calcine (roasted product)
- iii) Purification of leach solution
- iv) Electrolysis of pure solution

The flowsheet for the hydrometallurgical extraction process for zinc is based on the following scheme-

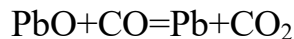
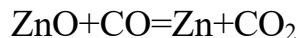
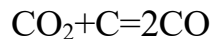
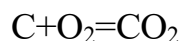
1. Dissolution of the zinc calcine in sulphuric acid
2. Precipitation of cadmium by adding zinc dust to the leach solution i.e. Cementation.
3. Precipitation of cobalt from leach solution by adding α -nitroso- β -naphthol.
4. Adjustment of the PH of the leach solution to about 5.3
5. Electrolysis of the purified leach solution using a cell with a Pb-Ag anode & an Al cathode.

5. IMPERIAL SMELTING PROCESS- In the ISP, ZnO is reduced by carbon to produce zinc. The reduction is carried out in an Imperial smelting blast furnace, in which, the zinc that is evolved in the form of a vapour which gets condensed by using molten lead.

Principle- The process is carried out by using counter current principle, where the blast and preheated air given to the furnace through the tuyere & the preheated air given to the furnace through the tuyere & the preheated coke get charged from the top.

- ISP furnace is of square cross section which is operated at 1000°C.
- It consists of a water jacketed brick lined shaft.
- Feed is given from the top of the furnace at positive pressure where preheated coke & sinter are introduced through double bell charge system and it is reacted to form zinc vapour.
- Blast furnace gases generated during reduction, pass upward through the charge and are evenly divided between two condensers. Each condenser consists of bath of molten lead.
- **Function of condenser:** These condensers serve 2 purposes:
 1. Cooling of furnace gases resulting due to condensation of Zinc.
 2. Dissolving the condensed zinc in molten lead.

The smelting reactions takes place in ISP are-



Retorts in condensers capable of generating an intense spray of lead droplets. This helps faster cooling of cooled to a temperature of about 440° C.

Zinc Separation-

The Pb-Zn (4.5%Zn) at a temperature of 550° C is send to separate through water cooled launders. It is cooled to a temperature of about 440° C. During cooling Pb is saturated with Zn. Excess zinc emerges from the Pb-Zn alloy. The excess zinc floats on the surface of lead because of less density, where it is separated & the lead (4.1% Zn) is continuously returned to the condenser. The Zinc is collected in a holding tank & treated with metallic sodium to remove arsenic.

Products of zinc blast furnace-

Zinc vapours (collected at top and condensed)

Slag (tapped from bottom)

Lead bullion (tapped from bottom)

Advantages of ISP-

- Economical production of Zinc.
- Efficiency overall high but zinc recovery expensive.
- Operational cost is low.
- Entire amount of Au, Sb, etc recover.
- Capacity large.
- No additional carbon required.

ISP furnace operates in the U.K, France, Germany, Japan, Zambia & Canada.

3.3.6- State the uses of zinc-

1. Zinc is used in Die casting production.
2. Zinc is used as battery (as electrode).
3. Zinc is used in brass & bronze alloy.
4. Zinc sulphide along with phosphorous used in fluorescent lightining fixtures and television.
5. Zinc sulphide is used in manufacture of pigment lithopone.
6. Zinc used in galavanising. This is the measure use of zinc.

3.4-Pyrometallurgical method of nickel extraction-

EXTRACTION OF NICKEL

Details about Nickel-

Atomic Number-28

Atomic Weight-58.69 amu

Density- 8.98 gm/cm³

Melting point- 1452°C

Boiling point-2900°C

COMMON MINERALS OF NICKEL-

Pentlandite-[(NiFe)₉S₈]

Violarite-[Ni₂FeS₄]

PROPERTIES OF NICKEL-

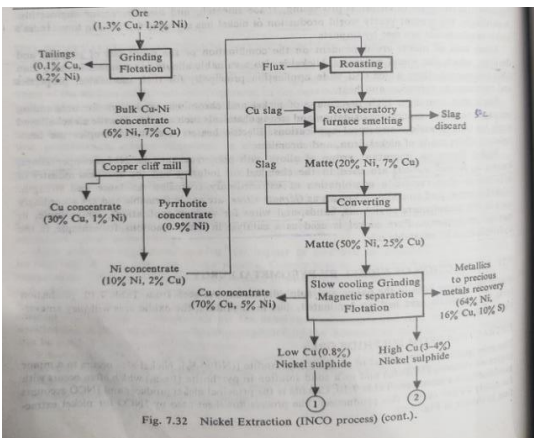
- High strength & ductility
- Resistance to corrosion & heat
- Resistance to high temperature oxidation & strong chemicals

AREA OF EXTRACTION-

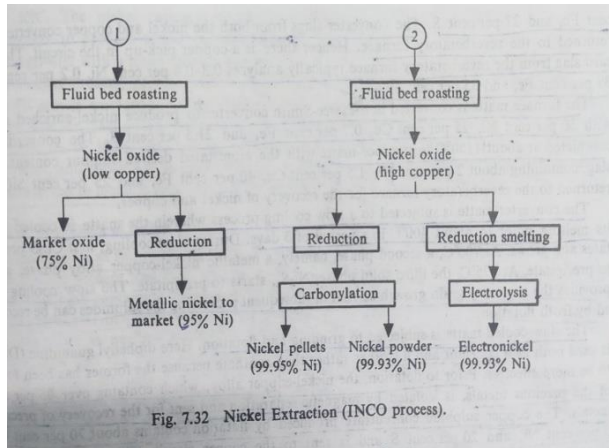
Canada, INCO-80% production

EXTRACTION OF NICKEL FROM SULPHIDE ORE-

Initial treatment- The ore is a mixed Cu-Ni ore with nearly equal amount of Cu-Ni (1.3%Cu & 1.2%Ni). To produce concentrate of nickel, the nickel ore subjected to



grinding, froth flotation method. These ore produced a bulk concentrate which sent to copper cliff mill for separation of Cu concentrate, Ni concentrate & pyrrhotite concentrate with iron sulphide with about 0.9%Ni.



3.4.1-Explain the roasting of nickel ore-

Roasting- Roasting means heating of ore in the presence of air which converts sulphide ore into oxide form. Roasting is done at a temperature of 550-600°C. During roasting some amount of flux is also added. The roasted calcine is melted in a reverberatory furnace to produce a matte containing the Cu & Ni values (20%Ni & 7%Cu) & a slag containing the gangue & oxidised iron. The Ni concentrate containing about 10% Ni, 2% Cu, 40% Cu, 30% S is sent to a smelter for Ni extraction. Here NiS and CuS remains unaffected.

3.4.2- Explain the method of smelting of nickel concentrate-

Smelting- In the smelting stage, the concentrate is first partially roasted to selectively oxidize the iron sulphide. This is done either in a multiple hearth roaster or in a fluidized bed roaster. But fluidized bed roaster is more preferable because of-

- High output & rich SO₂ gas stream generates
- Process is Autogeneous
- Temperature range (550-600)°C about 40% 'S' is oxidized.

There is also converter slag of both Ni & Cu converts are returned to the reverberatory furnace.

Converting- The furnace matte is converted to Ni enriched matte with 50% Ni, 25% Cu, 0.7%Fe & 21.5% S at 1150°C in pierce-smith converter. The slag discard contains 2%Ni, 1.5%Cu, 40%Fe & 25%SiO₂ return to reverberatory furnace for recovery of Ni & Cu.

Slow cooling- Converter matte is subjected to slow cooling process wherein the matte is cooled from its m.p to about 400°C in a period of 3 days to form three layers precipitate out as-

- First layer, CuS₂ precipitate & grows
- Second layer, metallic Cu-Ni alloys at 700°C start to precipitate
- Third layer, Solid NiS₂ phase precipitate at 575°C

Magnetic separation & Floating- In flotation, Ni-Cu alloy contains 95% precious metals is undergo for magnetic separation for recovery of it. Cu₂S produced by flotation contains 70%Cu, 5% Ni, 20%S. Ni sulphide recovered as a low Cu-Ni sulphide with 74%Ni, 0.8%Fe, 0.8% Cu & 22%S. High Cu-Ni sulphide with 72%Ni, (3-4%)Cu, 0.8%Fe & 21%S at a temperature (1100-1200)° C roasting produce granular nickel oxide.

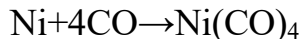
Final Treatment- Low Cu-Ni oxide is marketed directly as Nickel oxide or reduced to metal. High Cu-Ni oxide sends for refining by carbonyl process and other half by electrolytic refining.

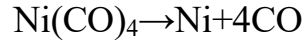
3.4.3- Explain the method of refining of nickel-

REFINING PROCESS-

1. Carbonyl process for refining Ni-

Mond's process- In 1889, this refining process of Ni discovered by Carl Langer & Ludwig mond. In this process, at the temperature (40-90° C) CO combine with metallic nickel to form a gaseous nickel carbonyl [Ni(CO)₄]. At higher temperature (150-300)° C. Ni(CO)₄ decomposes to give pure Ni & CO gas. The reactions are-





For refining Ni, impure Ni related with CO gas, impure Ni related with CO gas above 50° C. This causes volatile Ni carbide to be formed. The Ni carbonyl produced is decomposed at about 230° C in either pellet decomposers to produce nickel pellets at about 1cm dia or in powder decomposers to produce powder with a mean particle size of about 3.5µm.

The nickel carbonyl gas pass through another which is kept at 230° C, which contain metallic nickel shots. Here the metallic nickel dissociate & solid nickel is precipitate, the nickel shots and the gas is recycled in 1st reactor. This process is carried out at atmosphere by increasing the pressure. So, in mond's process nickel carbonyl recovered by selective fraction distillation. Later converted to in a powder decomposer or solid decomposer.

2. Electrolytic refining-

- The nickel oxide is oxide is first reduced to melt by smelting with coke in fuel fired furnace or in an electric furnace & then cast into nickel metal anodes.
- These anodes are electrolytically refined in a bath containing 60gm/lit Ni²⁺, 95gm/lit SO₄²⁻, 35gm/lit Na⁺, 55gm/lit Cl, & 16gm/lit H₃BO₃.
- Electrolyte is a solution of nickel sulphate, sodium chloride and H₃BO₃.
- Electrolysis is carried out at 60°C at a current density of 170A/m²
- On the passage of current, nickel dissolve from anode with Cu & Fe and the nickel plating out on the cathode sheet.
- The electrolyte is purified by following step. Cu is removed by cementation with active nickel powder.
- Iron & other impurities are removed the reaction of electrolyte & the addition small amount of chlorine to ensure oxide to form iron hydroxide precipitate.
- Cobalt is removed as cobalt hydroxide by further chlorine oxidation. At this stage, impurities like As, Pb are removed.
- The purified electrolyte is pumped back to cathode compartment. The electrolysed nickel content about 99.9% Ni, 0.05% Co, 0.005% Cu, 0.002%Fe, 0.001% S, 0.0002% As & 0.001% Pb.

- The insoluble sludge at the bottom of the tanks contain precious metal. Hence, it is treated to recover the valuable metal like platinum, gold, silver, etc.

3.4.4-State the uses of nickel-

- In the field of space research, nuclear reactor & chemical processing.
- Ductile nickel alloy steels are usually used in various structural applications.
- Electric heater and thermocouples use heat resistance alloy made up of Ni, Fe, Cr.
- Cu & Ni alloy are known as **MONEL METALS** & are used in the chemical oil industry and electric industry where corrosion resistance & strength is required.
- Ni, Cu & Zn alloys are known as **GERMAN SILVER**. It is used for manufacture of ribbons, bands, wires & musical instruments for various applications.
- Pure Ni is used as a catalyst in Mond's reaction.

4.0- Extraction of metals from Halides-

4.1- Describe extraction of titanium-

Details about Ti:

Atomic Number- 22

Atomic weight- 47.90

Density- 4.54 gm/cm³

Melting point- 1668°C

Boiling point- 3260°C

Common minerals of Ti-

Rutile- TiO₂

Ilmenite- FeO.TiO₂

Senaite- {(Fe.Mn.Pb)O.TiO₂}

Properties of Ti-

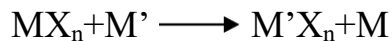
- The strength-to-weight ratio of Ti is very high.
- Corrosion resistance is better than stainless steel (18-8).
- Titanium alloys retained their strength even at higher temperature & so less creep.

Area of Extraction- Kerela, Tuticorin (Tamilnaidu)

METALLOTHERMIC REDUCTION OF HALIDES-

Halides are chlorides, fluorides, and hydrides of metals. A number of rare and reactive metals are produced by reduction of halide by another metal. In metallothemic reduction we use a target metal which forms strong halides. The metal which forms more stable halides are considered as reducing agent in this process.

The basic reaction is:

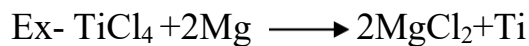


Where,

M' & M are two different metals

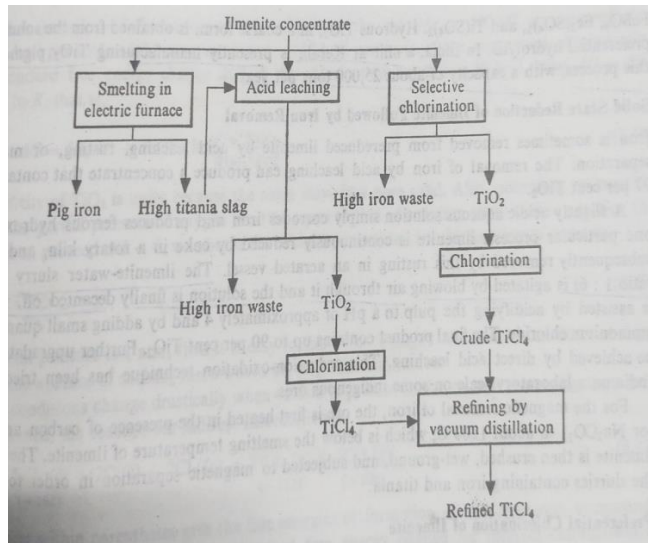
X is a halogen

N is number of atoms



4.1.2-Explain the type of treatment given to titanium ore-

To obtain Titanium from Ilmenite, the ore must be upgraded to a titania-rich product containing over 90% TiO_2 . Sometimes this upgraded ilmenite is known as Synthetic Rutile. Ilmenite contains titania & ironoxide in bound form & therefore cannot be upgraded by physical method. First iron oxide is removed by preferential chemical reaction with suitable reagent.

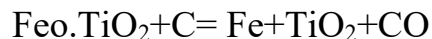


The methods used are as follows:

- The reduction smelting of ilmenite with carbon & a suitable flux resulting in a titania rich slag & pig iron.
- The direct leaching of ilmenite with acids under atmospheric pressure or high pressure resulting in the preferential dissolution of iron.
- The selective halogenations of iron oxide to produce volatile iron halides.

Electric smelting of Ilmenite-

- TiO_2 is a stable oxide & cannot be easily reduced.
- Carbon smelting is an electric furnace therefore produces pig iron and a high titania slag.
- High titania slag containing 90% TiO_2 , 5-10% Fe, & other gangue.



- The titania ferrous slag may be subsequently subjected to acid treatment for titania extraction.

Acid leaching of Ilmenite-

It is possible to selectively leach iron oxide present in Ilmenite by hot concentrated acids. These oxides can be leach faster, using this liquid particle size, higher temperature & high pressure. Since ferrous oxide is more leachable, ilmenite is first subjected to partial pre-reduction. Then the partially reduced Ilmenite containing ferrous oxide & titania is then leached to remove iron.

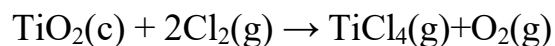
Halogenation of Ilmenite-

- The halogenation of Ilmenite aims at forming a volatile iron halides using reagent such as Cl, Br, HCl, NH₄Cl or heating a particular ore in presence of halogens.
- Chlorination reaction are most important for selective chlorination of Ilmenite (for chlorination, the minerals taken in a powdery form is briquetted with charcoal & a binder like tar, starch & ferric chloride).
- The removal of volatile iron halides leaves a TiO₂-rich residue. This residue itself may be chlorinated at 800-850° C in the presence of carbon to produce TiCl₄.
- This process is conducted either in a static bed chlorination using hard porous briquettes or in a fluid bed chlorinator employing granulated charge.
- TiCl₄ vapours contain some ferric chloride. The efficient separation of ferric chloride and a high collection efficiency of products are achieved by using a series of condenser & cyclone separator, maintained at different temperature.

4.1.3-Explain the process of chlorination & magnesium reduction for titanium extraction-

Chlorination of Ilmenite-

- The TiO₂ has to be chlorinated to produced TiCl₄ i.e. suitable for metal metal production. Chlorination is carried out in presence of carbon if there is no carbon in the system. It is very difficult to remove oxygen as TiO₂ is a stable oxide, if we add carbon it remove oxygen in the form of carbon monoxide.
- The reaction is-

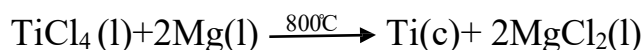


- Iron oxide in Ilmenite ore easily chlorinated by presence of carbon by variety of chlorinating agent.

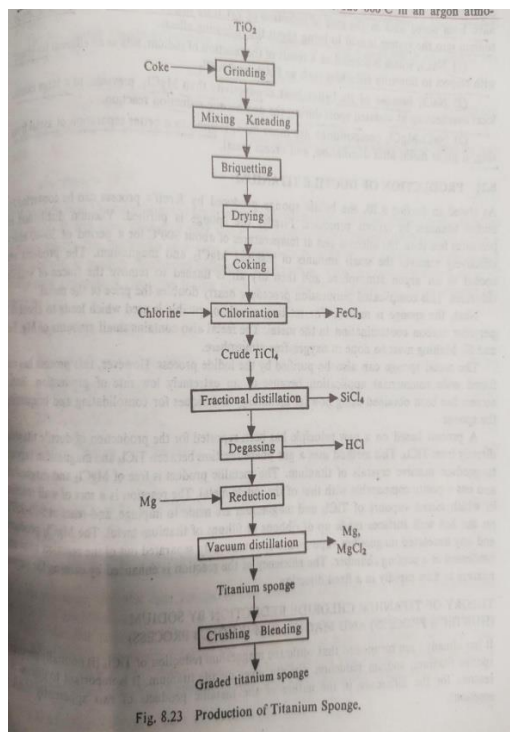
- For chlorination, the minerals taken in a powdery form is briquetted with charcoal & a binder (asphalt, starch, molasses then ferric chloride). The rate of chlorination of iron oxide is depends on several factor.
- The best result have been obtained by using ferric chloride as a binder, a fine particle size, smaller carbon content in the briquette & higher temperature.
- The chlorinating agent that have been used as chlorine, hydrogen chloride & various gas mixture such as carbon monoxide. The chlorination of Ilmenite at 500-600°C in the presence of carbon & ferric chloride (FeCl₃) binder yields product that contains about 90%TiO₂.
- The reaction may be accelerated using by catalyst such as CuO, PbO. MnO₂, CaO etc.
- By increasing the temperature 900-1000° C, we can obtained residue reacher in TiO₂ i.e 95-98%.
- In titanium extraction, magnesium is used as reducing agent.

KROLL'S PROCESS-

The successful commercial production of titanium was done by magnesium reduction (Kroll's process). It produces a spongy, brittle to produce ductile metal from this sponge. The reduction reaction in krolls process is TiCl₄.



This reaction is carried out in a stainless steel container which has a provision for external heating by gas or electricity. As the reaction is exothermic, it helps in maintaining the temperature. After the reaction is over, the titanium sponge is recovered either by dissolving MgCl₂ and the excess magnesium by leaching with cold dilute HCl or by distilling off MgCl₂ and excess magnesium by vaccum heating.



The residue is a pure titanium sponge. Several precaution have to be taken during reduction. The reduction chamber has to be first heated to a high temperature of about 900°C and flushed with hydrogen to eliminated all oxygen in order to avoid the oxidation of magnesium. All possible MgO coating is thus removed and temperature is lowered to 800-850° C.

4.1.4-Explain the process of refining of titanium by distillation-

The brittle sponge produced by distillation process can be converted into ductile by various process.

Firstly, the sponge is purified. Vaccum distillation at pressure less than 100 micron at temperature about 900°C for a period of 30-40 hrs. This distillation effectively removes the small amount of residual, MgCl₂ & Mg. The production are cooled in an argon atmosphere and then dry air is fluished to remove the traces of volatile chlorides. This is a very costly process. Next the sponge is melted in a carbon crucible. Melting must be done in an oxygen free atmosphere.

4.1.5- State the uses of titanium-

- It is used in jet engine components, spacecraft, airframes etc.
- Chemical Industries, aerospace industries.
- Pure titanium is used in the form tubes, rods, bars, & forging.

- It is used as deoxidiser for ferro alloy.

5.0-Extraction of precious metals-

GOLD EXTRACTION

Deatils about Gold-

M.P-1064°C

B.P.-2700°C

Atomic number- 79

Specific gravity- 19

Ore of Gold- Sylvanite-[(Au.Ag)₂. Te₂]

Calaverite-[(Au.Ag)₃.Te₂]

PROPERTIES OF GOLD-

- High formability & ductility
- High resistance to oxidation & chemicals
- It is too soft in pure state
- It is a very heavy metal
- It is not attacked by common acids & is soluble in aqueous region.

5.1-Explain extraction of gold process-

Gold is extracted by following process-

- a) Amalgamation Process
- b) Cyanidation Process
- c) Chlorination Process

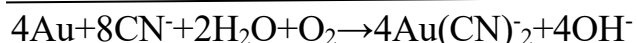
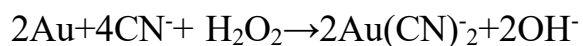
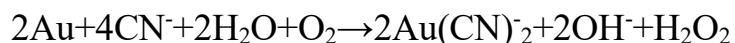
Amalgamation Process- In this process, a slurry made up off wet ground gold ore is allowed to flow down a sloping surface lined with copper. The surface is contionously washed with an amalgam of silver and mercury. The amalgam takes up the gold from the slurry and the metal is subsequently recovered from the

amalgam by distilling off mercury. The amalgamation process yields a low recovery of gold .i.e. 40-60%.

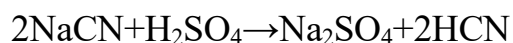
Chlorination Process- The chlorination process aims to chlorinating an ore of gold at high temperatures to produce soluble gold chloride(AuCl_3). Gold may be subsequently precipitated as a sulphide by passing H_2S through the solution. Finally, the sulphide is smelted to yield the metal.

5.2- Explain the process of cyanidation for gold extraction-

Cyanidation Process- The cyanidation process aims at dissolved in gold present in the ore in an NaCN solution. The kinetic aspect of cyanidation process is cyanide leaching takes place more readily when O_2 is bubbled through the NaCN solution so as to cause intense aeration and when an additional oxidizing agent such as H_2O_2 is present. A higher rate of leaching is obtained by passing oxygen under pressure. The reactions may be written as-



NOTE- NaCN is a highly poisonous chemical. An even more poisonous chemical, namely HCN gas, is produced if any acid such as H_2SO_4 is present in the system. The reaction is-



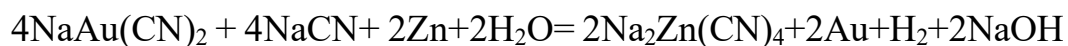
This reaction implies that loss of leaching agent goes towards chemicals to guard against such a loss an alkali is added during the reaction.

RECOVERY OF GOLD-

Gold is recovered from cyanide solution by following methods-

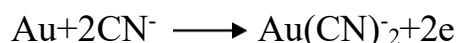
- 1) The cementation process
- 2) The electrolytic process
- 3) The selective absorption process

CEMENTATION PROCESS- In cementation process, gold is precipitated from the cyanide solution by adding zinc dust or aluminium powder. Zinc can be easily separated from gold. The cemented gold is purified by heating, which zinc volatilizes. Despite this advantage, a certain amount of zinc (20-40%) is trapped in the gold during cementation. Some zinc is also dissolved by the cyanide and is lost. Cementation reaction may be written as-

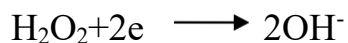
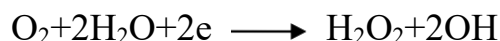
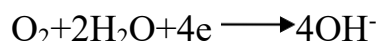


ELECTROLYTIC PROCESS- In electrolytic process, the leached gold cyanide solution is placed in a simple electrolytic cell. The reaction at cathode is a reduction step & at anode is a oxidation reaction.

At Anode-



At Cathode-



Electrolytic refining is carried out at voltage of 2.5-2.0 volt and ampere 600-1500 amp/m³.

SELECTIVE ABSORPTION PROCESS-

In this process, the complex gold cyanide ion is absorbed, at the room temperatures on a special prepared carbon powdered surface. When the carbon powder is heated in the presence of H₂O, the complex is released into the aqueous phase.

The metal is thus preferentially separated from various other impurities. Subsequently the metal can be recovered in the elemental form either by cementation or electrolysis process.

5.3-State the uses of Gold-

1. It is used for making jewellery, dental alloy gold/ coated base metal & part of scientific instruments.

2. It is used for decorative purpose because of high ductility.
3. Manufacture of containers and pipes.
4. Preparation of certain ayurvedic medicines park.

6.0- PRODUCTION OF SECONDARY METALS-

Explain the process of production of Copper-

Process of production of copper-

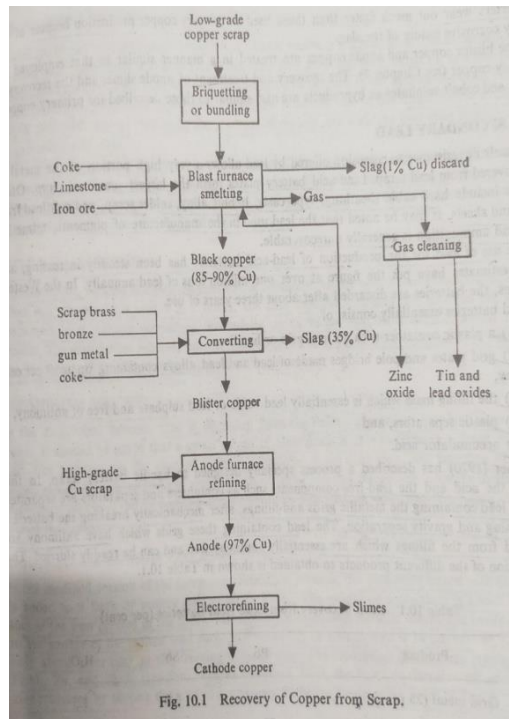


Fig. 10.1 Recovery of Copper from Scrap.

The copper scrap originates from foundries fabrication and user industries. The breakdown is as follows: dross, spillages and skimmings from foundries; punching, turnings and brings from fabrications; scrap, cable, wires radiators from cars, buses, bronze, brass from user industries. The scrap dealers sort out the scrap accordingly to the grade & composition.

Normally a rotary type furnace that is 5-7m in length & 3m in diameter is used to melt and cast the copper for re-rolling to wire rods. The contaminated scrap containing iron, machine parts carrying brass and bronze is subjected to electromagnetic separation in order to separate iron.

This leaves behind a composite scrap which has to be smelted and refined to recover copper and associated metals. For extraction of copper from low grade copper scrap, the compacted scrap is smelted in a B.F. along with a return converter slag, a flux and a reductant so as to produce molten black copper and a discarded steel.

The furnace gases which contain zinc, tin are sent to bag houses to recover valuable oxides fumes molten black copper is sent to a converter with high grade brass or bronze or metal scrap is added to it. Coke is fed into the converter as feed. The converter slag is sent into the blast furnace.

The converter which contains oxides of Zn, Sn, Pb ore sent gas cleaning equipment. Then, blister copper is subjected to fire refining to remove sulphur from liquid blister copper. It is carried in a reverberatory furnace. Fire-refined copper is further refined electro fine refined. Copper is cast in the form of anode & a pure of copper is used as cathode.