LECTURER NOTES
ON
NON-FERROUS METALLURGY

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BY

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LECTURER METALLURGY

INTRODUCTION TO NON-FERROUS METAL EXTRACTION

In an extraction process, a specific amount of energy required to reduce or release a metal ion present in a compound (solid or liquid) in association with other elements and to collect the metal in its elemental form.

In nature, metals generally occur either in free form or in combined form. Generally, low reactive metals shows little affinity towards air, moisture, carbon dioxide or other non-metals present in nature. Such metals may remain in elemental or native (free) state in nature. Such metals are called *Noble Metals* as they show the least chemical reactivity. For example gold (Au), silver (Ag), mercury (Hg), and platinum (Pt) etc. Whereas, most of the metals are active to combine with air, moisture, carbon dioxide and non-metals like oxygen, sulphur, halogens etc. to form their compounds, like oxides, sulphides, carbonates, halides and silicates. i.e., in nature, they occur in a combined state.

A naturally occurring material in which a metal or its compound occurs is called a *mineral*. A mineral from which a metal can be extracted economically is called an *ore*. An ore is that mineral in which a metal is present in appreciable quantities and from which the metal can be extracted economically. The main active substances present in nature, expecially in the atmosphere are oxygen and carbon dioxide. In the earth's crust, sulphur (S) and silicon (Si) are found in large quantities. Most active metals are highly electropositive and therefore exist as ions. It is for this reason that most of the important *ores* of these metals occur as (i) oxides (ii) sulphides (iii) carbonates (iv) halides and (v) silicates. Some sulphide ores undergo oxidation by air to form sulphates. This explains the occurrence of sulphate ores. Ores are invariably found in nature in contact with rocky materials. These rocky or earthy impurities accompanying the ores are termed as *gangue* or *matrix.*

During metal extraction, the bulk of the metal is separated from the impurities present in the ore by using a system which invariably comprises more than one phase. The metal enters the metallic phase while the impurities enter the non metallic phase or phases. The driving force for the reactions involved in metal extraction depends on the differences in the chemical potentials of the chemical elements. During a chemical reaction, an element tends to move from a high to a low chemical potential state. In each extraction process, the basic aim is to create conditions conductive to such a transfer, which facilitates the extraction of a metal or its compound.

In metal extraction, a vast majority of metallurgical reactions are made to take place at elevated temperatures because then the ore compounds become relatively unstable, facilitating the release of the metal. This is the basis of pyrometallurgy, in electrometallurgy, the dissociation or decomposition of a compound in solution (i. e. reduction of an iron) is brought about to employing electric forces. In hydrometallurgy, the reduction process depends on the judicious manipulation of the chemical reaction taking place in an aqueous solution.

The process of extracting the metals from their ores and refining them is called *metallurgy*. The choice of the process depends upon the nature of the ore and the type of the metal. The metal content in the ore can vary depending upon the impurities present and chemical composition of the ore. Some common steps involved in the extraction of metals from their ores are:

i. Crushing and pulverization
ii. Concentration or dressing of the ore
iii. Calcination and roasting of the ore
iv. Reduction of metal oxides to free metal
v. Purification and refining of metal

MINERAL RESOURCES OF NON-FERROUS METALS IN INDIA:

Aluminium (Al): According to reliable sources, the East Coast of India has one of the world's largest deposits of bauxite. Since this deposit is rich in gibbsite and has low content in silica and titania, it is ideal for Bayer process for the extraction of alumina. Currently, India has an installed capacity of 320,000 tons for aluminium products, which is adequate to meet the present demand. Das Gupta (1979) has predicted that after 1990, the whole Europe, including the U.S.S.R., will have to rely largely of Africa and India for obtaining bauxite and alumina.

Antimony (Sb): Commercially exploitable deposits of antimony have been so far located in India, although small deposits of antimony ores have been found in Lahaul and Spiti (Himachal Pradesh). At present, the entire annual requirement, i.e. 500-700 tons, is being met by importing the metal, its ores, and concentrates.

Beryllium (Be): Berly, the chief ore of Be, occurs in pigmatites which is associated with grantes and is found in Rajasthan, Tamil Nadu, Jammu and Kasmir, and Bihar. At one time, almost the entire beryl output of India was being exported but the Atomic Energy Establishment (AEE) now handles its production and sale. Although beryllium is not produced on a commercial basis in India, substantial groundwork has been done at Bhabha Atomic Research Centre (BARC), Bombey, in beryllium production technology.

Chromium (Cr): The principal chromite deposits of India are located in Singhbhum district (Bihar), Karnataka, Krishna and Sawantwadi (Maharashtra), and Keonjhar district (Odisha). The chromite reserves of India, although estimated to be limited to about 17 million tons, should be able to meet the domestic requirement for a long period, and a production of 10,000 tons per annum can be sustained for years.

Nickel (Ni) and Cobalt (Co): The Cu ore belt passing through Singhbhum (Bihar) contains also a Ni ore body which may provide 1000 tons of nickel annually. In fact, India's nickel reserves are about 100 million tons, of which 6.5 million tons, averaging 0.85 % nickel, are located at Sukinada (Odisha). Ni has also been found associated, in very minute quantities, with the gold-quartz reefs at Kolar (Karnataka) and uranium ores at Jaduguda (Bihar). The traces of Co have been found along with Cu ores of Khetri and Mn ores of Kalahandi (Odisha).

Cadmium (Cd): Cadmium is recovered as a byproduct from the zinc smelters at Debari (Rajasthan), Vishakhapatnam (Andhra Pradesh), and Alwaye (Kerala). Indigenous sources meet most of the domestic cadmium requirements

Copper (Cu): About 90% of reserves are spread over Bihar, Rajasthan, and Madhya Pradesh, the most important deposits being located in the Singhbhum copper belt in Bihar. At present, Hindustan Copper Limited (HCL) is the sole producer of Cu in India is able to meet about 42% of country's requirements.

Gold (Au): India's gold reserves are estimated to be 3.15 million tons (1977); a majority of them located in Karnataka. The gold content of these reserves ranges from 5.65 to 19.98 gm/ton of ore. Minor deposits of gold have also been found in the Hutti gold field (Karnataka). The entire production of gold in India is by the govt. of India's Bharat Gold Mines Limited (BGML) & the Karnataka state-owned Hutti Gold Mines Company. In 1977, the Au production in India was 2854 kg compared with 3132 kg in 1976. This decrease can be attributed to the shrinkage reserves, because of which, the gold production is unlikely to go up in the future, unless, of course, new reserves are found.

Silver (Ag): India has no reserves of silver ores. However, small quantities of silver as a by-product during the indigenous refining of gold, copper, and lead; the major part coming from the lead smelters at Tundoo (Bihar) and the gold mines in Karnataka.

Lead (Pb) and Zinc (Zn): India has about 140 million tons of lead-zinc ores, of which nearly 118 million tons are located in two areas in Rajasthan, namely, the Zawar mines and the Rajapura-Dariba lead-zinc belt. The lead-zinc ores from Zawar mines are beneficiated at the site to produce both zinc and lead concentrate. These concentrates are then processed; the lead concentrate at Tundoo by the Hindustan Zinc Limited (HZL)'s smelter and the zinc concentrate by another HZL smelter at Dabari. In 1977, HZL produced 46,500 tons of zinc concentrate, which could meet about 36% of India's total demand for 1977-78. In 1978, the smelters at Tundoo and Visakhapatnam together produced 10,060 tons of lead.

Manganese (Mn): India is the 3rd largest producer of manganese in the world. The ore deposits presently worked in India are located in Singhbhum, Panchmahals (Gujarat), Balaghat (Madhya Pradesh), Bhandara and Nagpur (Maharashtra), Vishakhapatnam (Andhra Pradesh), Sandur and Shimoga (Karnataka), Bonai, Keonjhar, and Koraput (Odisha), and Banswara (Rajasthan). The total Mn reserves according to the Indian Bureau of Mines (1977), are estimated to be 108 million tons. In 1977, the total production of Mn ore in India was 1,774,000 tons

Magnesium (Mg): India has extensive deposits of Mg in the form of magnesite ($MgCO_3$), chiefly found in Chalk Hills of Salem district (Tamil Nadu). On the whole, India's in situ magnesite reserves are estimated to be 524 million tons, of which the existence of 33 million tons has been conclusively established. Apart from Salem district, the other important deposits are found in Idar (Maharashtra), Kurnool (Andhra Pradesh), Tiruchirapalli (Tamil Nadu), Coorg (Karnataka), Dungarpur (Rajasthan), and Singhbhum. It should be nooted that in some of these deposits, Mg is present as dolomite ($CaCO_3.MgCO_3$). Widespread reserves of dolomite and magnesium limestones are found in Tamil Nadu, Andhra Pradesh, Bihar, Madhya Pradesh, Rajasthan, and Odisha.

Molybdenum (Mo): Exploration surveys in Andhra Pradesh and Tamil Nadu have shown that primery molybdenite (MoS_2) occursin the quartz veins that traverse porphyritic granites and, at places, in the granite itself. Mo in a base metal sulphide that is association with Cu ores is found at Rekha and Bhatin in the Singhbhum district. Preliminary beneficiation of the Mo ores has indicated the recovery during concentration to be 95%.

Tin (Sn): Tin is not extracted commercial scale in India although tin deposits have been detected in Ranchi and Haziribagh (Bihar). The entire present requirement of almost 10,000 tons per year is being met by imports.

Titanium (Ti): Abundant quantities of ilimenite ($FeO.TiO_2$) are found in the beach sands along a 160 km stretch of the Kerala coast. In fact, a particular 23 km coastal strip contains 35 million tons of ilimenite and 3 million tons of rutile (TiO_2). The ilimenite from Kerela contains a high % (55 %) of titanium. Smaller deposits of ilimenite occur near Tuticorin (Tamil Nadu), Waltair (Andhra Pradesh), and Ganjam district (Odisha). The total reserves of ilimenite in the form of beach sands are estimated to be 133 million tons. Apart from the beach sand deposits, small quantities of massive and crystalline ilimenite are found in Bhagalpur district (Bihar) and Kisengarh and Jodhpur (Rajasthan). The beach sands of Kerala contain a mixture of minerals sands whose specific gravities vary from 2.3 (silica) to 4.9 (monazite).

Tungsten (W): The presence of tungsten minerals has been detected in certain parts of the country, namely, Chandapathan in Bankura district (West Bengal), Agargaon in Nagpur district (Maharashtra), and Degana (Rajasthan); the present production of tungsten comes from the first two sources. The volume of tungsten concentrate produced in 1977 was 43,046 kg, of which Rajasthan accounted for 90% and West Bengal for 10%.

Vanadium (V): India depends entirely on imports to meet its vanadium requirements although vanadium-bearing titaniferrous magnetite ($Feo.Fe_2O_3$) has been located near Dublabera in Singhbhum district and in Mayurbhanj district (Odisha). Also, a small deposit near Nausahi in Keonjhar district (Odisha) is also known to contain vanadiferrous iron ores. The total volume of vanadiferrous magnetite ores in India is estimated to be approximately 26 million tons.

Extraction Of Aluminium By Pyrometallurgical Process:

Common Minerals of Al:

Diaspore – $Al_2O_3.H_2O$ (Al % - 65.4)

Gibbsite - $Al_2O_3.3H_2O$ (Al % - 65.4)

Bauxite – Mixture of Diaspore and Gibbsite

Extraction of Al:

Extraction of Al by carbothermic reduction of Al_2O_3 in commercially not adopted because of

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

Extraction of Al salt in electrolysis not adopted because of decomposition of aqueous solution results evolution of H_2 gas at lower voltage. So, as Al^{+3} not occur. The H_2 over voltage insufficient to overcome 1.67 volt that the difference in potential between Al deposition and H_2 evolution.

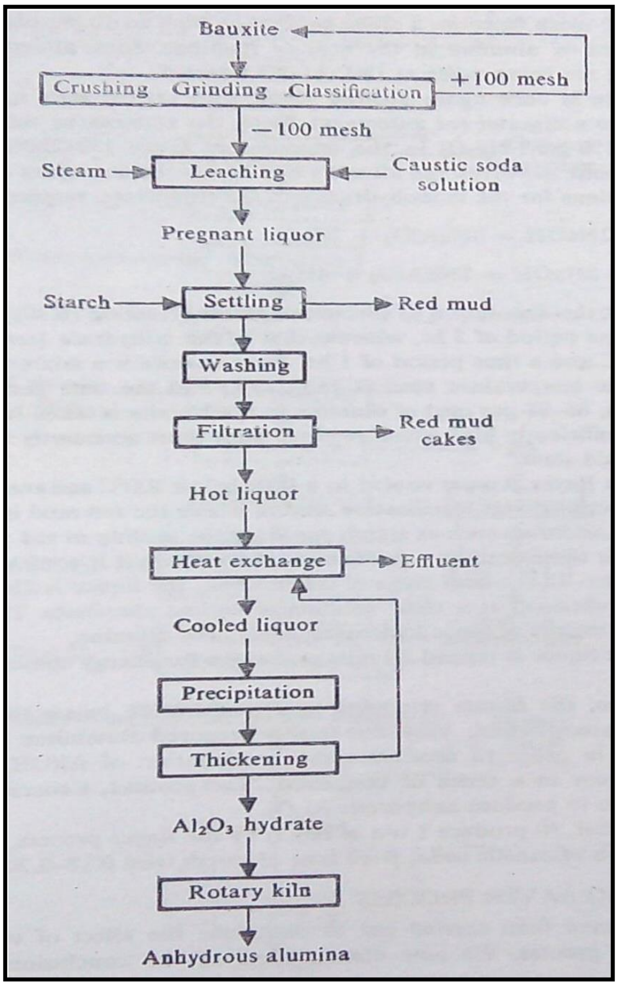
Extraction of Al in Hall – Heroult process: In this process, dissolved Alumina (Al_2O_3) in cryolite ($3NaF.AlF_3$) is electrolyzed, and Al_2O_3 obtain in pure form.

Extraction of Alumina in Bayer's process: In this process, $AlCl_3$ electrolyzed in a fused salt medium contains NaCl and LiCl to obtain alumina (Al_2O_3).

Bayer's Process for Alumina Production:

Bauxite initially leached by NaOH under high pressure (25 atm), and temperature (220^0 C) to form soluble $NaAlO_2$ (Sodium Aluminate) from which $Al(OH)_3$ is precipitate out. When $Al(OH)_3$ calcined, Al_2O_3 or alumina obtained.

Bauxite obtain in mines get crushed and ground to very fine size in jaw crusher and hammer mills, result in high SiO_2 content in finer fractions. Then SiO_2 remove/render by screening in 100 mesh sizes, SiO_2 content is about 10% after communution. Thus leads to enrichment of Al_2O_3 in coarser fraction.



Flow Sheet of Bayer's Process

Crushed bauxite once again ground with caustic soda (NaOH) in ball mill to yield slurry in which alumina dissolves in bauxite and dissolves in NaOH in a temperature (150-220)^0 C and a pressure of (5-25) atm. As a result, impurities leave a suspended solid. The reactions for monohydrate and trihydrate are given below

$$Al_2O_3.H_2O + NaOH \rightarrow NaAlO_2 + 2H_2O$$

$$Al_2O_3.3H_2O + NaOH \rightarrow NaAlO_2 + 4H_2O$$

Since bauxite is a mixture of mono and trihydrate contains (86-88) % alumina.

Then the liquor cooled little below 100^0 C and completely pressurized is to settling and clarification section red mud get deposited in presence of starch which speed of the settling. Any remaining red mud gets separated by a series of washers by encountering flow of hot water. After washing the solution the remaining residue consists of ferric hydroxide, silica and alumina.

Hot liquor tapped by heat exchanges to obtain cool liquor. Then cool liquor under precipitation carried out a temperature below critical point. Then $Al(OH)_3$ used for separation precipitate from liquor in a series of thickeners. The product, a coarse hydroxide is finally calcined in a rotary kiln to produce a anhydrous Al_2O_3.

Factors affecting Bayer Process:

- Finer bauxite gives better digestion of alumina in liquid liquor.
- Wet grinding is more efficient than dry grinding.
- Digestion accelerates at high temperature above 100^0 C.
- At low temperature below a limit cause lost of alumina. So, maintain the temperature at about boiling point of water.
- Sensible heat of recovered from hot liquor by heat exchangers.
- In precipitation stage, entire precipitates of alumina not allow because it may cause precipitation of silica along with alumina.
- For efficient calcinations of alumina in rotary kiln at 1400^0 C to give anhydrous alumina.

Hall – Heroult Process:

This process based on electrolytic decomposition of alumina dissolved in a liquid bath of cryolite. This process requires high purity alumina, cryolite and ash less C electrode. Since alumina is not an ionic. So, it is capable to dissolve in cryolite up to 15% at 1000^0 C. The synthesize of cryolite occur as reaction of HF with sodium aluminate where, HF form due to the reaction of CaF_2 in H_2SO_4 as

$$CaF_2 + (H_2SO_4)_{aq} \rightarrow 2(HF)_{aq} + CaSO_4$$

$$(Na_6Al_2O_9)_{aq} + 12(HF)_{aq} \rightarrow 2Na_3AlF_6 + (6H_2O)_{aq}$$

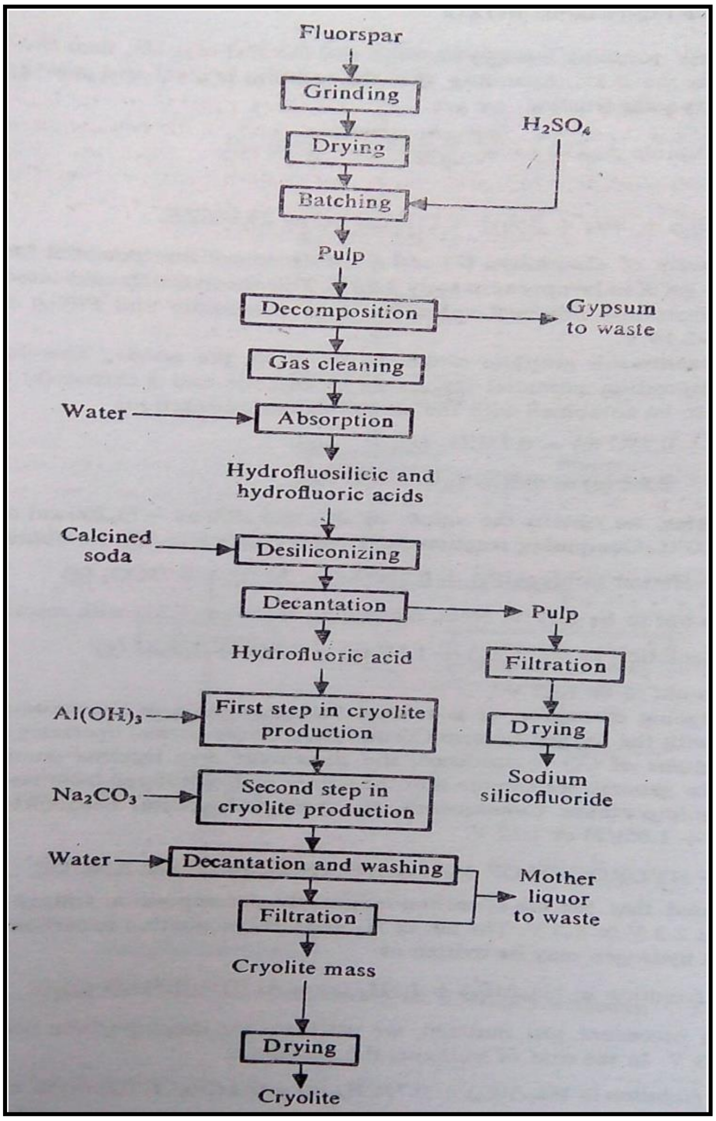
Cryolite bath get enhanced conductivity by addition of CaF_2 and NaF. At 1000^0 C density of molten cryolite is 2.1 gm/cm^3 and Al_2O_3 is 3.96 gm/cm^3. Al liberated heavier than bath and sinks at bottom. Higher the amount of Al_2O_3 in bath, the higher its density and consequently the sinking of Al is rendered more difficult.

Decomposition Potential of Al_2O_3 in dissolved in Cryolite:

- When anode is oxygen, decomposition potential of Al_2O_3 is about 2.1-2.15 v.
- Decomposition potential of graphite at anode is 1.12 v.
- Graphite aids the decomposition of Al_2O_3 because it reacts with O_2 to form CO and CO_2.

$$: \frac{1}{2} Al_2O_3 + \frac{3}{4} C \rightarrow Al + \frac{3}{4} CO_2$$

$$\frac{1}{2} Al_2O_3 + \frac{3}{2} C \rightarrow Al + \frac{3}{2} CO_2$$



Synthesis of Cryolite

Influence of H_2 or CH_4 injection at Anode:

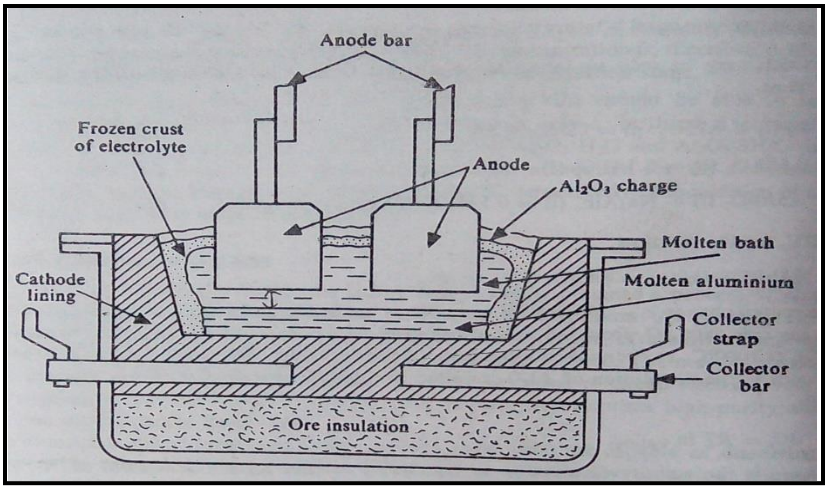
$$\frac{1}{2}Al_2O_3 + \frac{3}{2}H_2 \rightarrow Al + \frac{3}{2}H_2O$$

$$\frac{1}{2}Al_2O_3 + \frac{3}{4}CH_4 \rightarrow Al + \frac{3}{2}H_2 + \frac{3}{4}CO_2$$

Injection of H_2 or CH_4 would not be effective in appreciably reducing the decomposition potential of Al_2O_3. Injection may be effectively cut down graphite consumption and prove economical if H_2 or CH_4 available is cheaper. Actual decomposition potential is 5-7 volt, whereas

- Voltage need for electrolytic reduction: 1.7 volt
- Voltage drop across C lining: 0.6 volt
- Voltage drop due to anode resistance: 0.5 volt
- Voltage drop due to resistance of electrolyte: 0.8 volt
- Voltage drop due to contact resistance: 0.3 volt

Electrolytic Reduction Cell



Electrolytic Reduction Cell

The cell consists of rectangular refractory lining steel box with l=5 m, w=2 m, depth=1 m. Cathode lining consists of refractory bricks faced with C mixed tar binder. A consumable graphite electrode serves as anode. A Fe plate and Fe bar form the cathode are embedded in the C mixture. A tap hole is there, through which metal get collected at the bottom of the hole. C gets backed in steel mould to produce anode. Fe pins are inserted by electric contact. The baked C electrodes and cathode lining must be sufficiently strong and dense.

Cell Operation:

During operation, the cell bath is filled with cryolite and anode lowered into it. A current is passed through it until cryolite melts (M. Pt. – 990^0 C).

When bath attains a molten state addition of alumina commenced. The alumina decomposes to yield Al and O_2. The necessary heat being supplied by the resistance offered by both the electrodes and the electrolytes.

Anode Effect:

If alumina content of bath (normally 5-10%) falls below 2% then normal contact between the anode and bath is interrupted by the gas film in which abruptly increases positive resistance. As a consequence the normal operation ceases. This effect is called anode effect.

Under certain conditions, the electrolytes of fused salt is associated with the periodically occurring phenomena in which the terminal voltage increases to high value and current density decreases to a lower value from their normal value. This effect is known as anode effect.

If power consumption, electrolyte, and anode consumption increases during the process. Then, current density exceeds above critical current density.

Factors Affecting Anode Effect:

- Nature of electrolyte: Anode effect occurs most readily with fluoride and least with iodides, Bromides and Chlorides required large critical current density than iodide, fluoride both.
- Purity of electrolyte: Greater purity lower in current density and vice verse.
- Type of electrolytic Anode: The cryolite-Alumina melt anode effect at 4-5 amp/sq. cm. when C anode used and 7-8 amp/sq. cm. for graphite electrode.
- Temperature: Increase in temperature reduces the current density.

Cause of Anode Effect:

- Thermal Effect: Local overheating can lead formation of gaseous film which deposits anode from electrolyte.
- Electrostatic Causes: During electrolysis, gas bubbles form which is electrically charged. The charge may be originated from the anions discharged at the boundary of newly form gas bubbles at high current density. So, gas is partly ionized when gas bubbles acquires opposite charge to that electrode i. e. negative charge there will be formation of adherent gaseous film which could separate the molten electrolyte from anode.

Metallic Clouds or Fogs:

In the electrolysis, fused salt electrolyte, fine globules at the cathode metal get appear in electrolyte is known as metallic clouds.

Role of Cryolites in Electrolysis:

Al_2O_3 dissolve in cryolite and form Al^{+3}, O^{-2} (in solute) and Na^{+}, AlF^{3-}, F^{-} (in solvent).

Cathodic Reaction:

$$Al_2O_3 \rightarrow Al^{3+} + AlO_3^{2-}$$

$$Al^{3+} + 3\bar{e} \rightarrow Al$$

Anodic Reaction:

$$2AlO_2^{-} \rightarrow Al_2O_3 + 3[O] + 2e$$

$$6F^{-} + Al_2O_3 \rightarrow 2AlF_3 + 3[O] + 6\bar{e}$$

Simple molecular theories of electrolysis are based on the hypothetical dissociation reactions

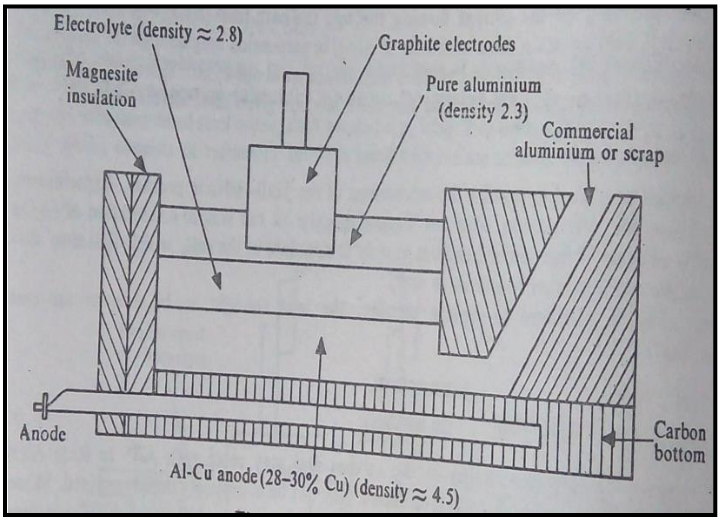
$$Na_3AlF_6 = NaAlF_4 + 2NaF$$
$$NaAlF_4 = NaF + AlF_6$$

Factors Affecting Electrolysis:

- Temperature: Increase in temperature, current efficiency increase. For every 4^0C rises 1% current efficiency increase. More number of side reaction and hence dissociation of metal in bath.
- Current Density: Current efficiency increase with increase in current density.
- Inter polar Distance: As the distance increases along the bath from bottom to top, current efficiency also increases.
- Addition of Al_2O_3: At Al_2O_3% is 4%, there no effect on current efficiency. But, decrease or increase in Al_2O_3 from 4% cause increase or decrease in current efficiency.
- Bath Density: With increase in bath density by AlF_3/NaF ratio. But, for large AlF_3% cause bath conductivity and fluidity decreases and volume increases i.e. current efficiency decreases.

Electro refining of Al:

Hoope's Process:



Three-Layer Process

To achieve high degree of purity three layer processes are employed as

- Bottom or Anode Layer: Specific gravity of this layer is maximum and consists of impure Al alloyed with Cu. This layer serves as anode.
- Middle or Electrolyte Layer: It consists of anhydrous fluorides and chlorides as AlF_3 36%, Barium Fluoride 18%, and CaF_2 16%.
- Top or Cathode Layer: Pure Al layer acts as cathode.

(at anode): $Al(liq) \rightarrow Al^{3+} + 3\bar{e}$

(at cathode): $Al^{3+} + 3\bar{e} \rightarrow Al(liq)$

Purity of metal is *99.99%*.

Uses of Al:

- Use as a good conductor
- Electrical application

Area of Extraction of Al:

- ALIND – Aluminium India
- HINDALCO – Hindustan Aluminium Corporation
- MALCO – Madras Aluminium Company

EXTRACTION OF TIN (SN):

COMMON MINERALS OF TIN:

Cassiterite: SnO_2

EXTRACTION OF TIN:

The concentration contains FeS are oxidize to oxide during smelting. Carbothermic reduction of SnO_2 is feasible at moderate temperature. At higher temperature $(1200\text{-}1300)^0$ C FeO is more stable. The difference in stability between FeO and SnO_2 used as the basis of selectivity of reducing SnO_2 to Sn. The difference in stability further reduce because slag has higher affinity for Tin oxide compare with iron oxide and tendency for attain separation ofTin from Fe becomes difficult. So smelting of Tin has done in 3 ways.

First stage, 99% obtain partially reduction of tin concentration almost all Fe in slag. The slag further reduced in 2 stages. First stage produce tin contain 5% and in the second stage tin contain 20% Fe. Third stage have very low % of tin. So, 2nd and 3rd stage subjected to liquation to eliminate Fe.

When Sn-Fe alloys heated to a temperature higher than melting point of Sn. The metal known as first run metal contain 99.9% Sn. Temperature progressively increase Fe content in Sn increase known as second run metal. Where, for taking smelting in rotary instead of reverberatory furnace of higher efficiency Sn recovery. First smelting slag is reduce and Sn volatile either in form of SnO or SnS. Clean slag discarded after reduction vapour pressure of SnS gteater than SnO. So, SO_2 presence is beneficial.

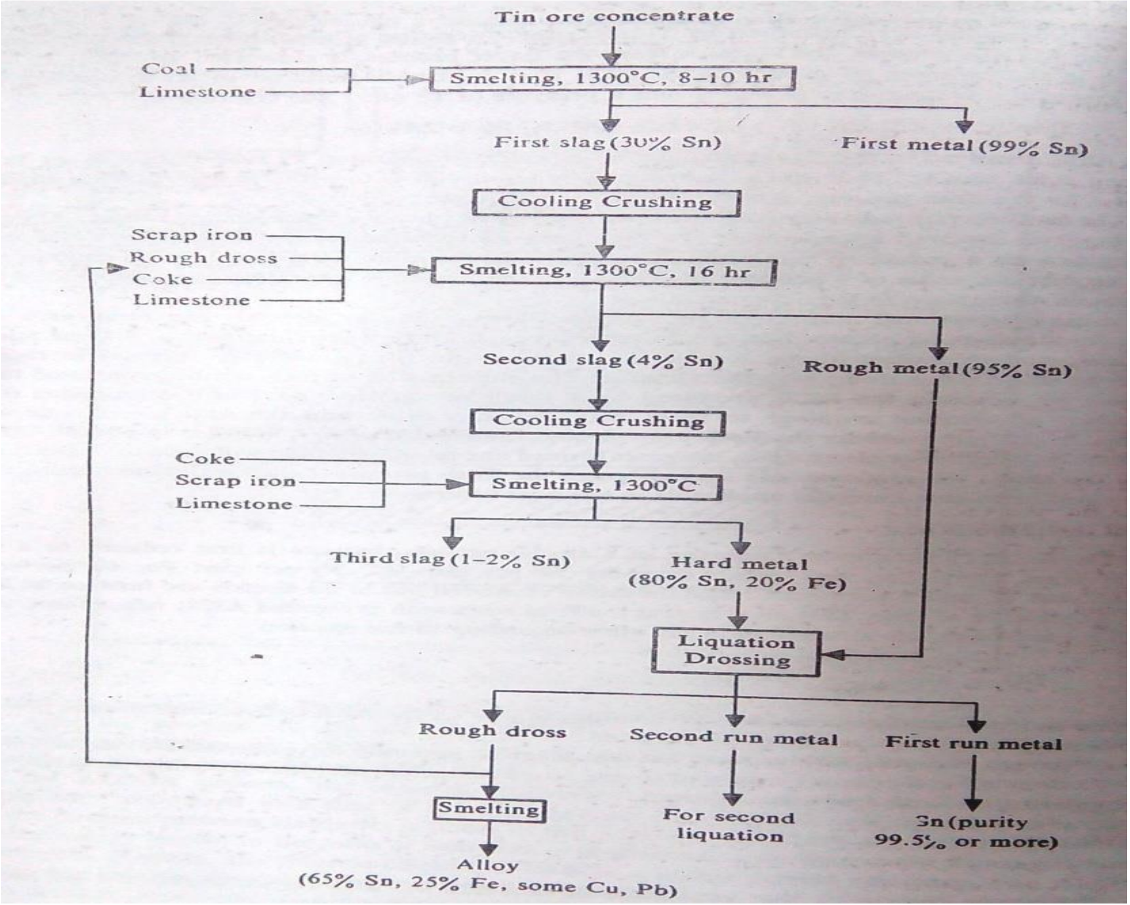
Refining of Tin:

There is mainly two methods of refining of Sn as Pyrometallurgical refining (or fire refining), and electro refining.

Pyrometallurgical Refining: Ultimate recovery of Tin is more than 85%. Principle is to several common impurities from intermetallic compounds with each other or with Sn. Thus, if impure liquid tin is cooled to a temperature just above the melting point of tin (232^0 C), these inter metallic compounds as Cu_2Sb, Cu_3Sn, Cu_3As, $FeSb_2$, $FeSn_2$, FeAl etc. have higher melting point than tin. So separate out and get floats. S adds to remove Cu in CuS form. AlAs and AlSb by addition of Al, As, and Sb eliminated.

$$2AlAs + 6H_2O = 2AsH_3 + 2Al(OH)_3$$

$$2AlSb + 6H_2O = 2SbH_3 + 2Al(OH)_3$$



Smelting of Tin Concentrate

Pulverize coal separate and precipitate out $AlCl_3$. Deleading of Sn by $SnCl_2$ based on

$$Pb + SnCl_2 = PbCl_2 + Sn$$

A Sn-Pb alloy removes from $PbCl_2$-$SnCl_2$ mixture by melting in contact with Zn.

$$SnCl_2 + PbCl_2 + 2Zn = 2ZnCl_2 + Pb - Sn$$

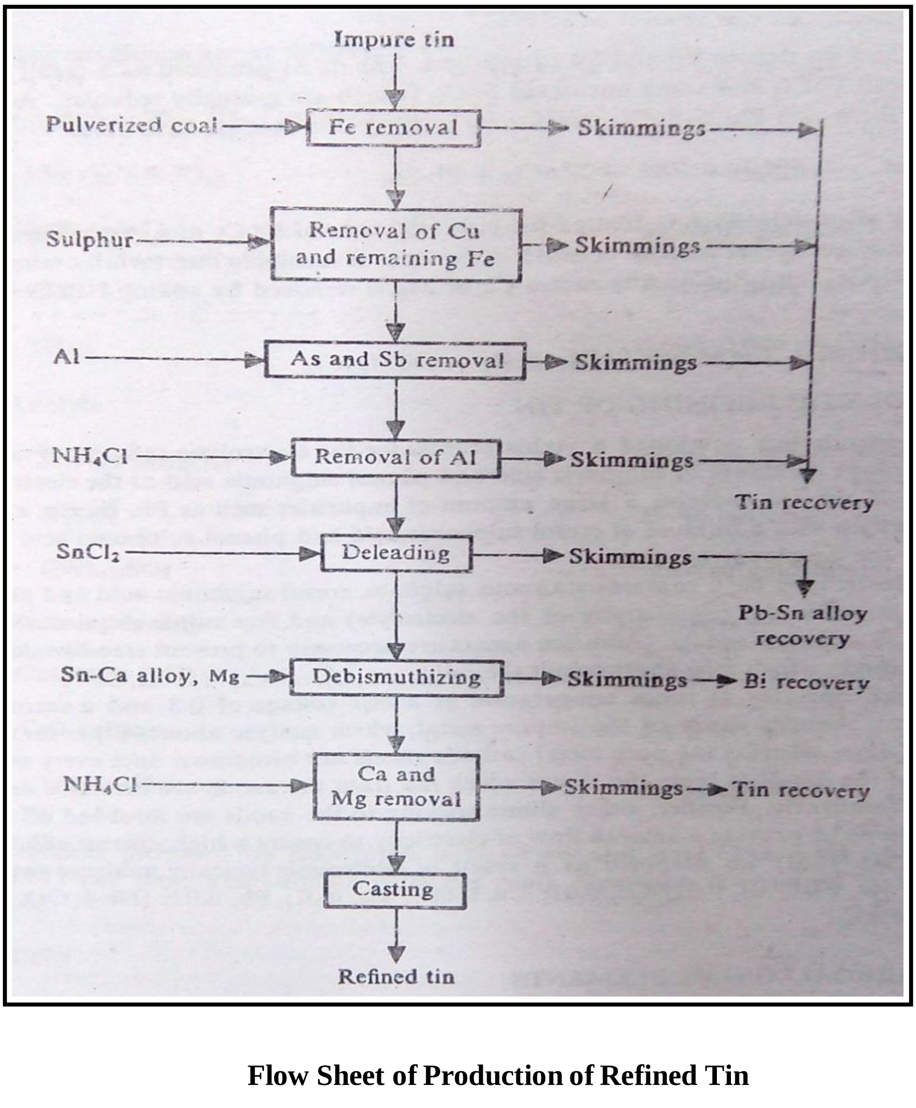
Any excess Ca or Mg is removed by adding NH_4Cl according to the reaction

$$2NH_4Cl + Ca(Mg) = 2NH_3 + H_2 + Ca(Mg)Cl_2$$

Electro Refining of Sn:

Using a mixture of H_2SO_4 and phenol sulphonic acid as electrolytes is feasible. If, Sn contains large amount of impurities such as Pb, Bi, Sb, As etc. Mixture of Cresol sulphonic acid and phenol sulphonic acid now used as electrolyte.

It is analyze 95% Sn dissolve in pure metal to obtain at cathode sheet of 99.95% Sn.



Flow Sheet of Production of Refined Tin

EXTRACTION OF CU IN PYROMETALLURGICAL PROCESS:

Common Minerals of Cu:

Cuprite :Cu_2O
Malachite: $CuCO_3.Cu(OH)_2$
Azurite: $2CuCO_3.Cu(OH)_2$
Chalcosite: Cu_2S
Chalcopyrite: $CuFeS_2$
Bornite: Cu_5FeS_4
Covellite: CuS

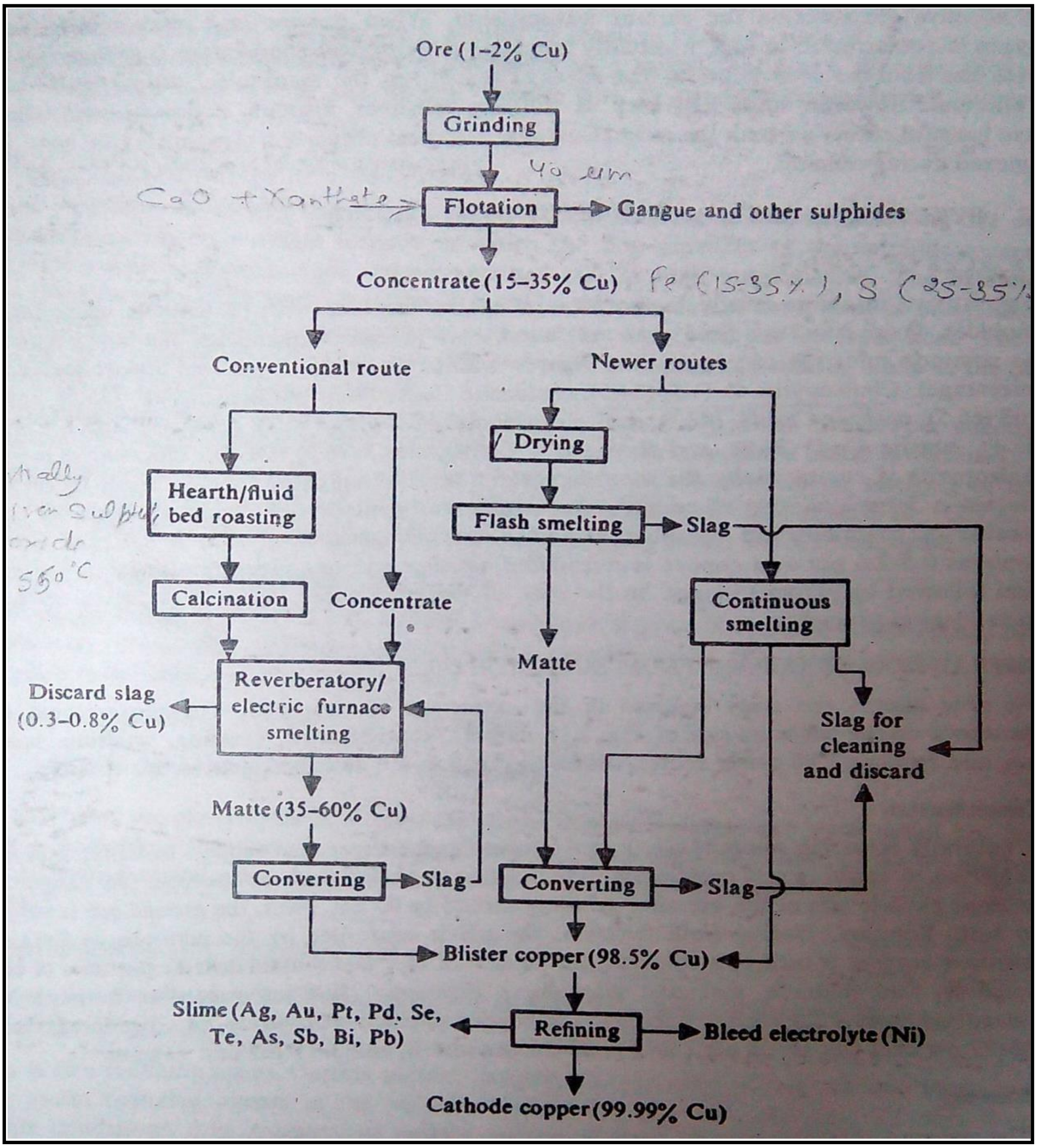
Extraction of Cu from Sulphide Ores:

The steps involved in extraction of Cu by conventional routes as concentration, roasting, smelting, converting and refining at the left side of the flow sheet drawn in fig 1.1 and newer route at the right side of the flow sheet.

(i) Conventional Route:-

Concentration: A naturally occurring Cu sulphide contains 0.5-2 % of Cu. To recover this, first we go for crushing and grinding to liberate sulphide grains from the gangue of average 40 µm sizes.

Then go for froth floatation, where addition of CaO as P^H controls and Xanthate as collecter, where we separate Cu sulphide from a mixture of Cu Sulphide, Lead Sulphide and Zinc Sulphide. The Cu Sulphide contains 15-35% Cu, 15-35% Fe, 25-35% S, 3-15% gangue.



Pyrometallurgical Extraction of Cu from Sulphide Ores

Roasting: The purpose of roasting to partially oxidized the iron sulphide present in Cu Sulphide which from slag in next i.e. smelting. Here the concentrate contains high iron sulphide and low Cu Sulphide content (<25%).

In conventional plant, roasting carried out in multiple hearth roaster with gradually downward movement of feed having gradual increase in temperature of each hearth by fuel firing as 550^0 C. Where as in newer route, roasting carried out in fluidized bed roaster at about 550^0C. The product is SO_2 gas which finally used for manufacturing for H_2SO_4.

The principal reactions takes place in roasted calcine contains Cu Sulphide and Fe oxides of Fe and mixed sulphates of Fe and Cu given as

$$2CuFeS_2 + 6.5O_2 \rightarrow 2CuO + Fe_2O_3 + 4SO_2$$

$$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4$$

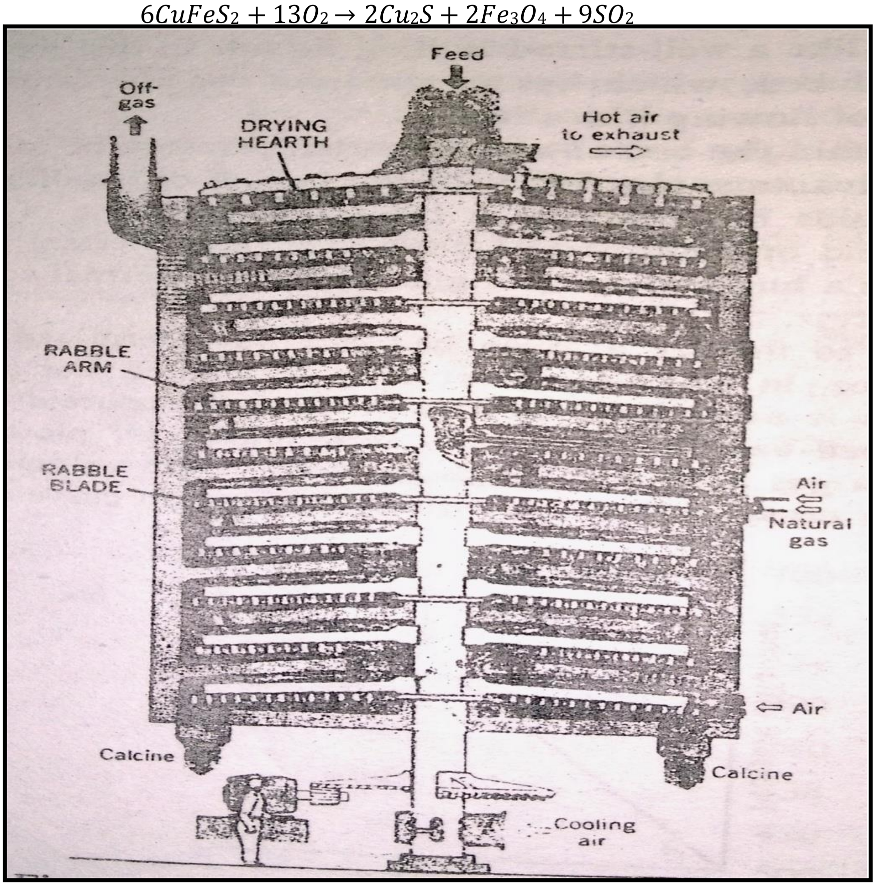
$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + 3SO_2$$

$$CuFeS_2 + 4.5O_2 \rightarrow 2Cu_2S + Fe_2O_3 + 3SO_2$$

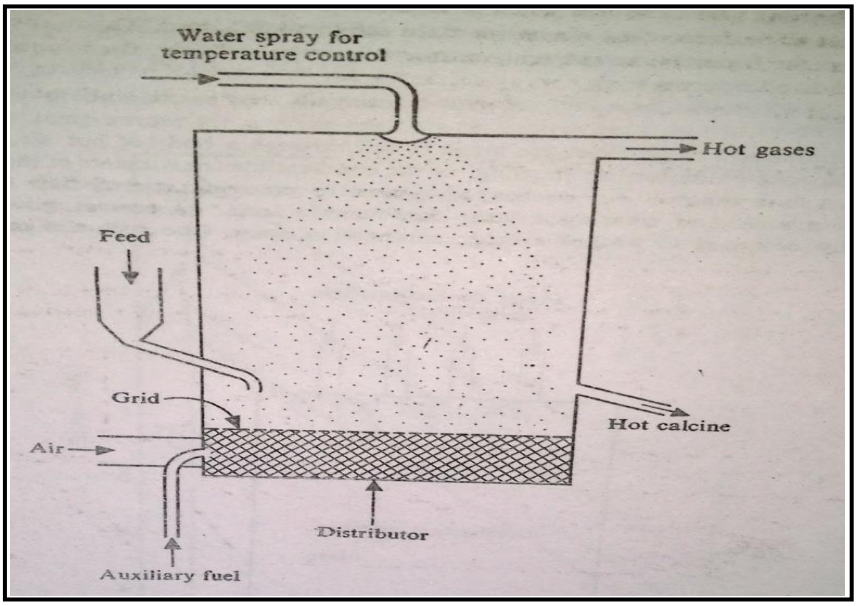
$$2CuFeS_2 + 7.5O_2 \rightarrow CuO.\,CuSO_4 + 2FeSO_4 + SO_2$$

$$3CuFeS_2 + 9.5O_2 \rightarrow 3CuO + Fe_3O_4 + 6SO_2$$

$$6CuFeS_2 + 13O_2 \rightarrow 2Cu_2S + 2Fe_3O_4 + 9SO_2$$



Multiple Hearth Roaster



Fluidized Bed Roaster

Smelting:

It seeks to separate the metal sulphides in an ore concentrate or calcine from the gangue by charging the furnace with suitable charge along with flux at about 1250^{0}C. During smelting two separate layers are formed, as slag and matte layer having specific gravity 2.8-gm/cm^3 and 5.0-5.5 gm/cm^3 respectively. If gangue and iron oxides present in the concentrate/calcine to be smelted combine during smelting to form iron silicate slag. If iron oxide insufficient the lime add as flux to form an iron calcium silicate slag. The melting point of slag approximately 1150^{0}C and for fluid slag with a low Cu content, the temperature at about 1250^{0}C.

Exchange reaction takes place between oxides and sulphides of Cu and FeS present in furnace charge.

$$2CuO + 4FeS \rightarrow 2Cu_2S + 4FeO + SO_2$$

$$2CuSO_4 + 2FeS \rightarrow Cu_2S + 2FeO + 3SO_2$$

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

These reactions occur because O_2 has a greater affinity for Fe than Cu in Ellingham diagram. The unoxidised iron sulphide reduces the higher oxides of iron to ferrous oxide as

$$10Fe_2O_3 + FeS \rightarrow 7Fe_3O_4 + SO_2$$

$$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$$

Smelting determine the extent of oxidation of FeS in charge to slag object is to produce a matte contains 35-45% Cu, 20-22% S, 25-35% Fe. Smelting not only minimize the loss of Cu to slag, but also provides a matte with a sufficient quantity of iron sulphide for use in the next stage as converting.

Smelting conventional route occur in reverberatory furnace and electric furnace, where in newer route flash smelting and continuous smelting takes place. The conventional route, electric furnace because a large volume of combustion gas generation avoided and facilities both recovery of so_2 and cleaning of furnace gases.

Converting: The purpose of converting is to remove Fe, S, and other impurities from matte. Generally side blown converter used.

The capacity of converter is 100-200 tons, 4m diameter and 9 m in length. Lined with a layer of Chrome-magnesite refractory about 40 cm thick. Oxidizing atmosphere inside the converter by supply of O_2 enriched air through the tuyere of 5 c.m. with 40 in number. The total volume of gas is 600 m^3/min. The product is blister Cu and slag. So, the Cu converting namely slaging stage and blister formation stage.

(i) Slaging Stage: The iron sulphide present in matte is oxidized and oxide is slaged out by addition of siliceous flux. The reactions are

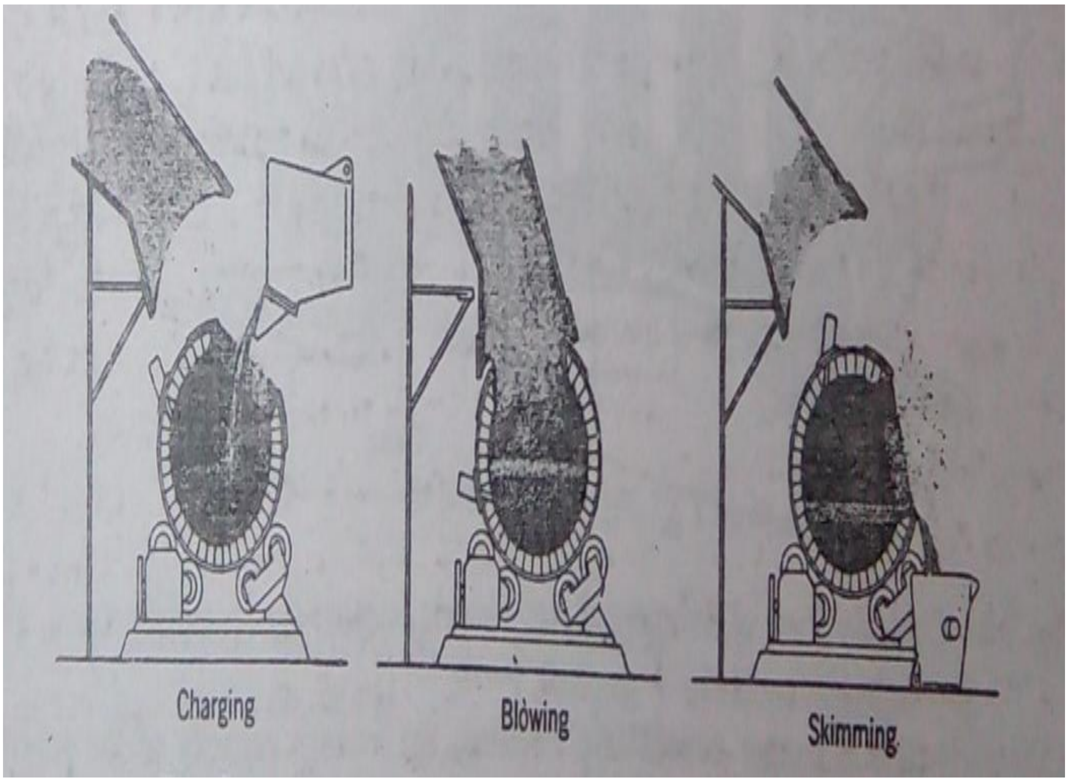
$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$2FeO + SiO_2 \rightarrow 2FeO.SiO_2$$

Mainly three process are done as

- Adding freshly obtain matte.
- Blowing of air.
- Slag gets skimmed off by tilting.

The slag contains 2-9% Cu, 40-50% Fe, 20-30% SiO_2, and 1-5% (CaO+MgO). Conventionally, Cu is recovered from the slag produce in converter by transferring the slag in molten state to a smelting furnace, where in case of newer process, metallic values of the slag recovered by employing either an electric furnace with provision for cleaning the slag or by slow cooling of slag followed by grinding and floatation.



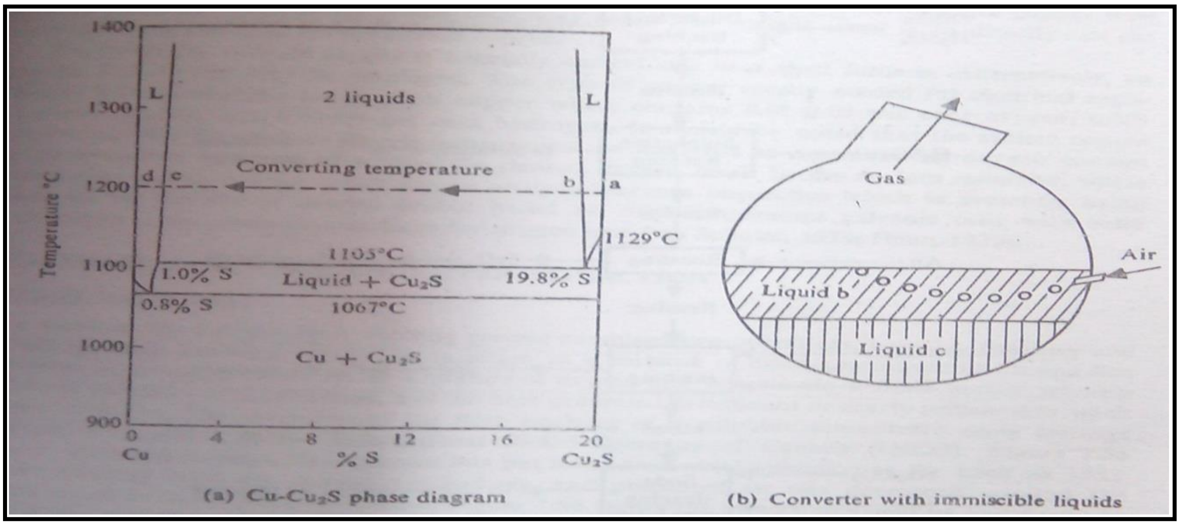
Converter Operation

(i) Blister Formation Stage: After slagging converter contains Cu_2S known as white metal because of its appearance. In blister Cu formation stage, Cu_2S is oxidized to form Cu by combination of reaction.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

$$3Cu_2S + 3O_2 \rightarrow 6Cu + 3SO_2$$



(a) Cu-Cu_2S phase diagram

(b) Converter with immiscible liquids

Operating Principles of Side blown Converter

When white metal (Cu_2S) is oxidized the S content in bath decrease about 19.5% andhence, the bath split into two layers as

- Top sulphide layer of less dense.
- Bottom Cu layer of more dense contain about 1.2% S.

As oxidation continues the sulphide layer (liquid b) decrease and Cu layer (liquid c)increase. The relative volume of two phases determined by Lever rule.

The blister Cu contents 0.02-0.05% S along with 0.2-0.5% dissolved O_2.

Refining:

The purpose of refining to get Cu extraction is twofold as

- First, to obtain metal in pure form.
- Second, to recover precious metals containing in blister Cu produced.

(i) *Fire Refining:* The purpose is to remove S from liquid blister Cu as SO_2 by oxidation with air and eliminates O_2 by introducing hydrocarbons. In this case, the refining is done in reverberatory furnace of 400 ton of capacity contains blister Cu get oxidized to recover Cu removing the impurities such as S, Fe, Se, Zn by converting its corresponding oxides and then skimmed off. But, some Cu also in the form of oxides.

To prevent Cu loss poling with green branches used to reduce Cu_2O using hydrocarbon or some other reducing gases. In this case, the purity of Cu obtained 99.97%.

Fire refining is also done in rotary type refining furnace, where blister Cu directly treated by blowing air.

(ii) *Electrolytic Refining:* The purpose is to further refined the fire-refined Cu by electrolysis. The electrolysis done in a electrolytic refining tank made of concrete or wood of 3-5 m deep and utilization minimum space with maximum cathode and anode area. The electrolyte is $CuSO_4$, H_2SO_4, some glue and alcohol at temperature $50\text{-}60^0$ C.

Cu transferred from crude anode to pure cathode. Impurities in blister Cu such as Fe, Co, Ni, Se, Te etc. go into the solution and precious metals get collected below anode known as anode slime.

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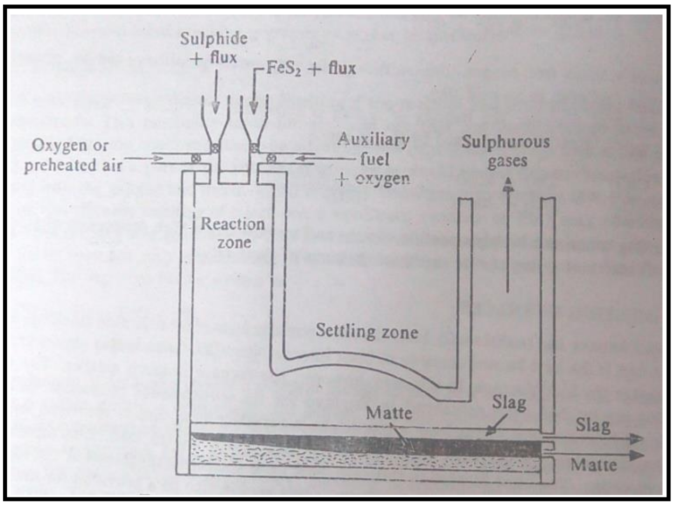
(ii) Newer Process:

Flash Smelting:



Flash Smelting

Process: Enriched preheated air or pure O_2 used to increase combustion rate and autogeneous smelting. The gases coming out rich of SO_2 due to high combustion rate and used for H_2SO_4 manufacturing.

Process is autogeneous provide exothermic heat. Air used as oxidant to preheated. The composition of concentrate used in flash smelting has Chalcopyrite ($CuFeS_2$) 66%, Pyrite (FeS_2) 24%, gangue (SiO_2) 10%. Whereas the Cu matte contains 70% Cu, 8% Fe, 22% S, slag contains Fe 40% at furnace temperature 1300^0 C.

Main reactions of flash smelting of Cu concentrate are mentioned below

$$CuFeS_2 + 0.5O_2 \rightarrow 0.5Cu_2S + FeS + 0.5SO_2$$

$$CuFeS_4 + 0.5O_2 \rightarrow 2.5Cu_2S + FeS + 0.5O_2$$

$$CuS + 0.5O_2 \rightarrow 0.5Cu_2S + 0.5SO_2$$

$$FeS_2 + O_2 \rightarrow FeS + SO_2$$

$$FeS + 1.5O_2 \rightarrow FeO + SO_2$$

$$FeO + 0.16O_2 \rightarrow 0.33Fe_3O_4$$

$$FeO + 0.5SiO_2 \rightarrow 0.5Fe_2SiO_4$$

$$Cu_2S + 1.5O_2 \rightarrow Cu_2O + SO_2$$

Continuous Smelting:

It encompass smelting and converting in a single vessel i.e. Cu concentrate charged at one end and Cu metal withdrawn continuously at the other end.

Mainly three are three processes, given below

(a) WORCRA. (b) Noranda. (c) Mitsubishi.

(a) WORCRA Process:

This name divided as the first 3 alphabets stands for the developers and last 3 alphabets for the place.

Features:

- Counter current movement of gas and concentrate. So, continuous production of blister Cu.
- Directly blister Cu i.e. metal instead of matte form.
- Combine smelting and converting.
- The heat required for reaction directly obtained as the reaction is exothermic.
- Counter movement cause continuous production of H_2SO_4 due to continuous extraction of gas.
- Cu% continuously obtains from slag by means of cleaning operation.

Process:

The process combines 3 different operations in a single furnace as

- Continuously smelting
- Continuously converting
- Continuously slag cleaning by conditioning and settling

Efficiency:

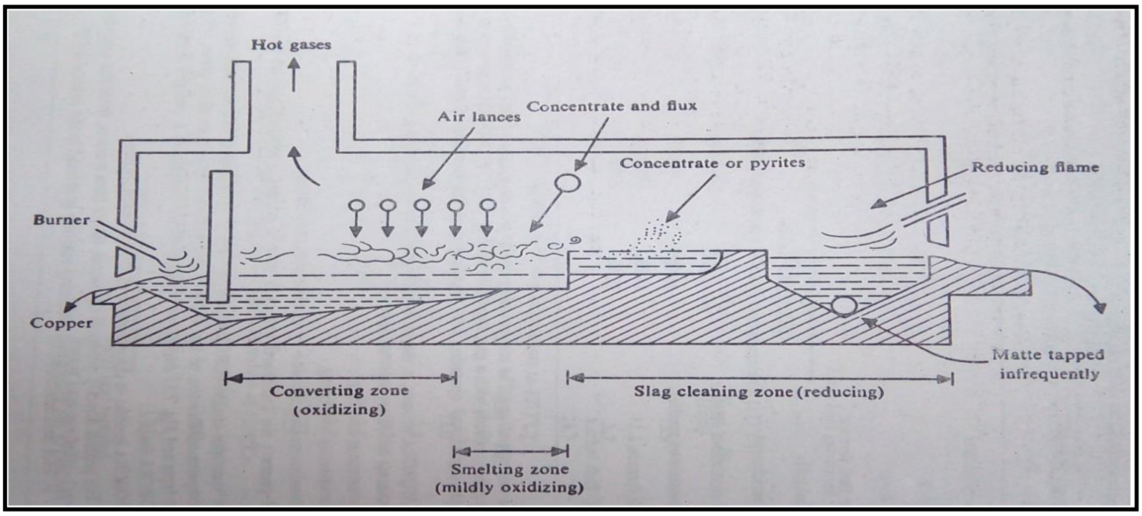
It increases by means of counter current movement increase the reaction surface area in the smelting and converting zone. Hence, effective removal of impurity occur i.e. mainly Fe due to counter movement of slag and matte. As a result, Cu gets reverted back to matte and obtain.

Advantage:

- Continuous process
- Capital cost low
- Concentrate passes large surface area. Hence accelerate the reaction.

Disadvantage:

- Not durable
- Operating cost is high



Vertical Sectional Diagram of Straight form of WORCRA reactor

(b) Noranda Process:

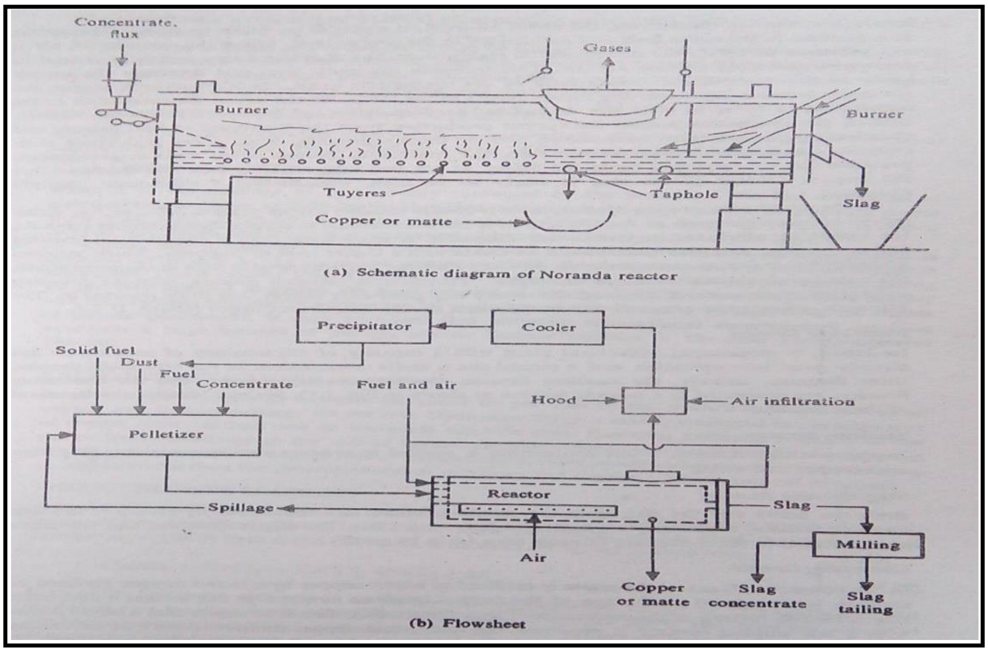
Principle: In this process, high grade Cu matte directly forms from the sulphide by means of air blown through the tuyeres to oxidize. The Cu or matte collected at the tap hole where the slag collected at the other tap hole at the slag end.

In this process, the slag contains high% Cu compare to WORCRA process. Mainly 3 layers present in the product as

- Cu – First layer.
- Matte – Second layer.
- Slag – Third layer.

Condition:

- If given air is more than the stoichiometric amount of air required for oxidation, then matte level decreases and Cu level increases.
- If insufficient air required for stoichiometric amount then unoxidised iron and S tends to combine with Cu to form matte. So matte level increases and Cu level decreases.
- If air supply is equal to the stoichiometric amount then both matte and Cu level get increases.



Schematic diagram of Noranda Process

(a) Mitsubishi Process:

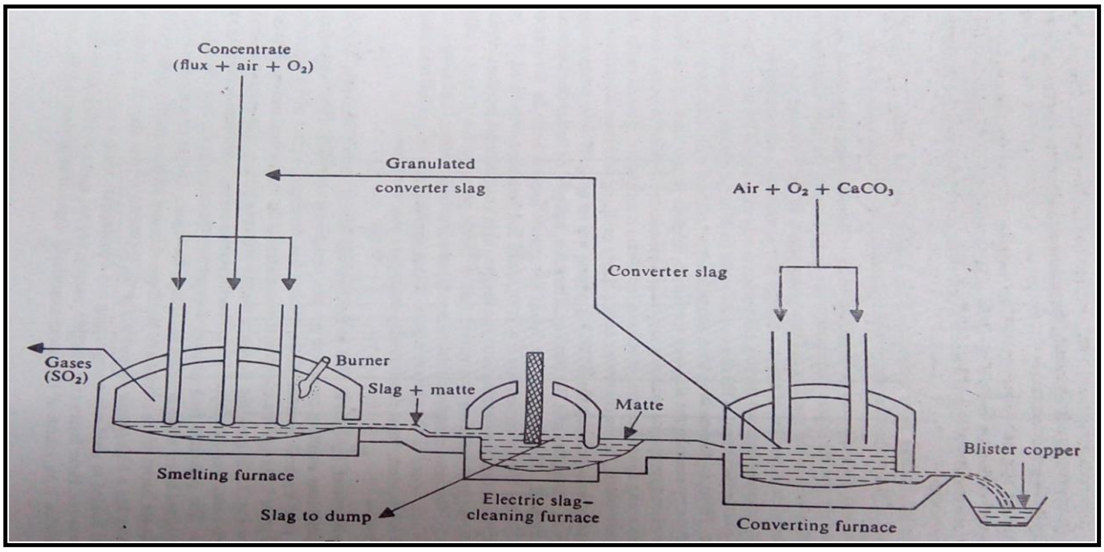
Principle: There are three furnaces such as smelting, slag cleaning and converting furnace are connected in a cascade manner. The product of one furnace goes to next furnace for next operation by means of gravity force.

Process:

First, in smelting furnace (wet concentrate + flux + air + O_2) is smelted to produced matte of 60-65% Cu and rest is slag.

Secondly, both matte and slag goes into slag cleaning furnace where slag get discarded and matte goes to next furnace operation.

Thirdly, in converting furnace matte oxidized to blister Cu by blow of O_2 enriched air and limestone add as slag. So slag discarded as lime ferrite. Blister Cu produced of low % S and hence, obstruct the transfer of Cu to lime ferrite slag.



Mitsubishi Continuous Smelting Process

Area of Extraction:

- HCL (Hindustan Copper Ltd.)
- Khetri mines
- Kholihana mines

Uses:

- Conducting element
- Alloying addition

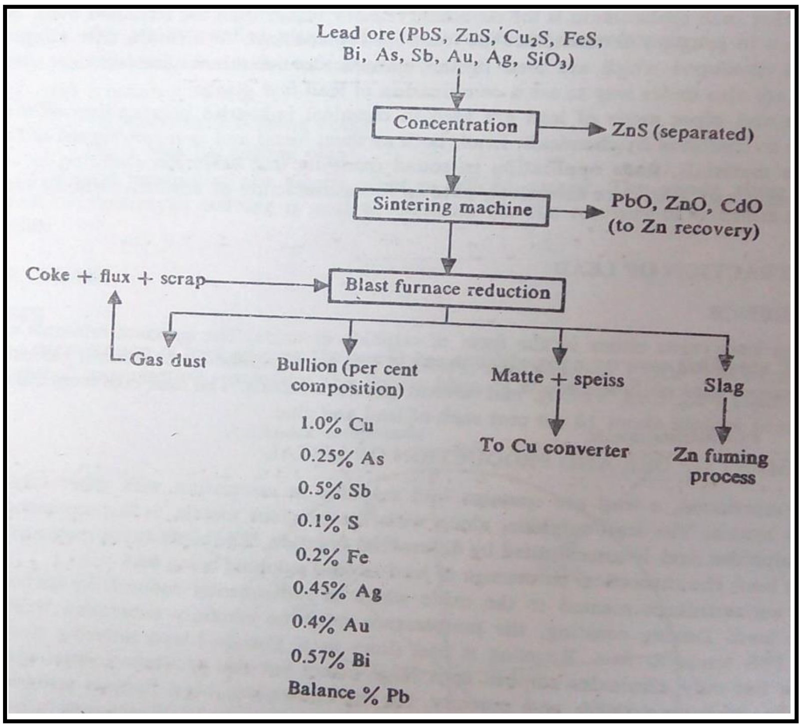
EXTRACTION OF Pb BY PYROMETALLURGICAL PROCESS:

Common Minerals of Pb:

Cerrusite: $PbCO_3$
Anglesite: $PbSO_4$
Galena: PbS

Extraction of Pb:

Production of Pb bullion:



Flow Sheet of Production of Lead Bullion

Complete Description of Flow Sheet (Extraction of Lead Bullion):

The concentrate roasted to oxides which get reduced by C at 800^0 C above to fuse PbS, which occur in Dwight-Lloyd sintering machine in which not only S eliminate but also produce sinter with liquidize properties. In this S% reduce from 16-18% to 1-2%.

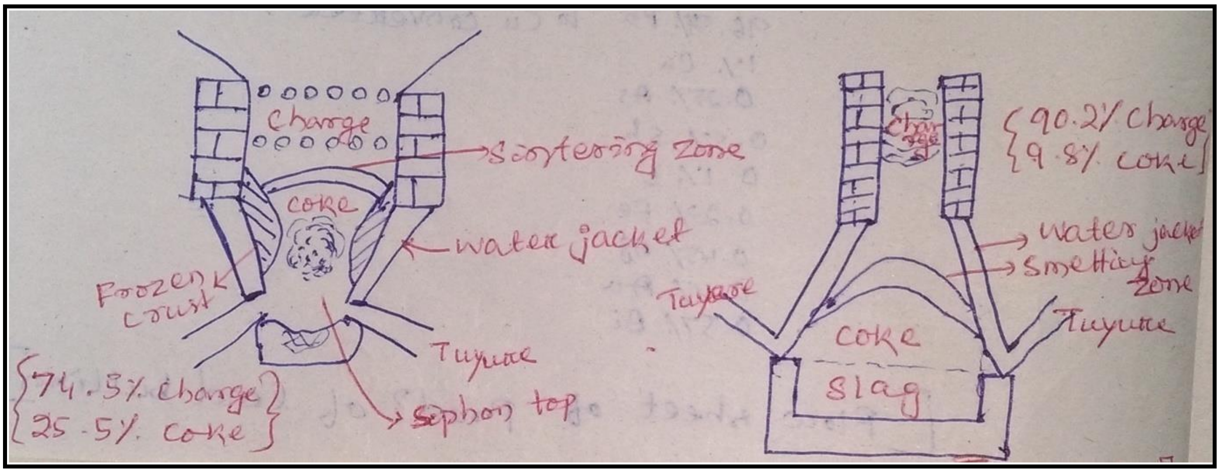
Now, up draught is more preferred compare to down draught because of

- Higher capacity
- Elimination of precipitate wind box Pb
- Production of high grade SO_2 gas

In, up draught air is admitted from perforated bottom gate. Heat liberated due to roasting of Galena ore out of temperature below fusion temperature.

Reaction 2.38: $2PbS + \frac{7}{2}O_2 \rightarrow PbO + PbSO_4 + SO_2$

Hence, free Pb gravitated to the wall of furnace, and was trapped out at working temperature 1000^0 C. Thick crust allow to accumulate slowly down even stopped reaction by the action of the air blast.



Molten Blast Furnace

Older Blast Furnace Reduction: Furnace decrease in area from throat downward a minimum being attend end at tuyere of area 4-5 m^2. Blast pressure increases resulting in volatization of lead. As increase volume of blast lead volatization decreases.

Siphon top: A device connects molten Pb in the crucible with a bowl shape which keeps the level of Pb in the crucible constant by withdrawn from the top.

Bosh: Purpose is to retard the descent of charge in front of tuyere as material melts away.

Newer Blast Furnace Reduction: Furnace area increases from the throat to downward at the end of tuyere in this case following advantages are occur

- Gases more evenly through charge
- Decreasing their velocity
- Decrease the amount of dust
- Here scrap used for reduction of unreduced PbO

PbO also helps in reducing PbS left unroasted in the sinter machine and hence, combine with Silica (SiO_2) in charge to form $2FeO.SiO_2$. Hence, lower the melting point of slag and increase the fluidity of metal layer.

$$PbSiO_3 + Fe \rightarrow FeSiO_3 + Pb$$

Finally helps to reducing the Pb as

:$PbO + Fe \rightarrow FeO + Pb$

Disadvantage of Newer Process:

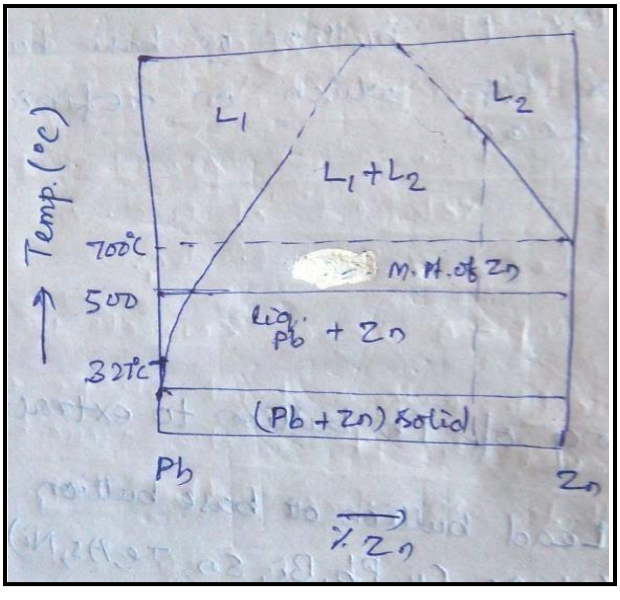
- A thick mushy layer form in between matte and slag which interfering into the separation
- A wide variation in temperature as 200^0 C at top to 1200^0 C at tuyere

In blast furnace reduction produce 4 distinct layers on the basis of their specific gravity as

- First layer – Slag Layer – Specific gravity 3.6
- Second layer – Matte Layer – Specific gravity 5.2
- Third layer – Speiss Layer – Specific gravity 6
- Forth layer – Lead Bullion/Base Bullion

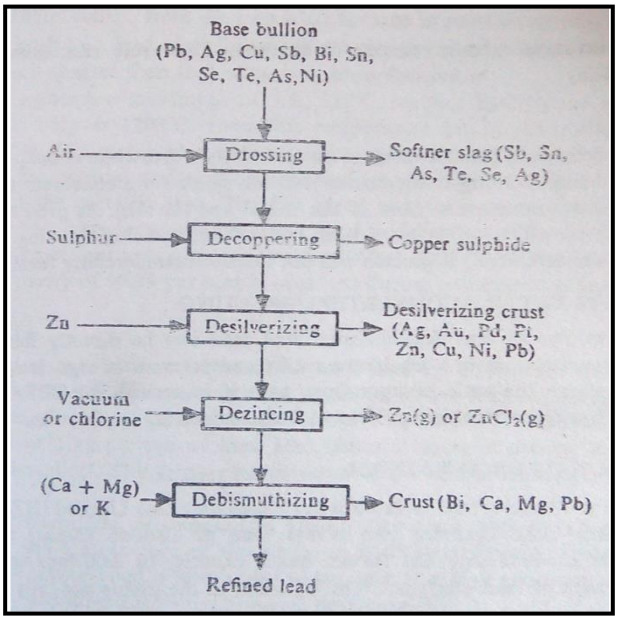
Refining of Pb Bullion to extract Pb:

Liquation: Refining technique for removing impurities from metal based on the factor such as difference in melting point of alloy components. So as a number of layers formed on the basis of their difference in density.



Lead Zinc Phase Diagram

The crude Zn containing of 5% Pb refined in a reverberatory furnace by slowly cooling of molten matte.



Refining of Lead Bullion

Drossing: It is the combine process of liquation and oxidation in reverbaratory furnace at around temperature 350^0 C at which many metals oxidized and skimmed off subsequently increase to $(500\text{-}550)^0$ C. At that temperature Cu get eliminates using S in the form of Cu_2S and at last softener slag (Sb, Sn, As, Te, Se) are removed.

Question 2.3: What do you mean by softening and why it is required?

Answer: Drossed bullion containing 1-1.5% of impurities as Sn, As and Sb treated in a softening furnace in oxidized condition. It required for refining of soft malleable Pb and hence, increases corrosion resistance. As presence of impurities Sn, As, Sb causes hardened of alloy. So softening required.

Desilverising of Pb (PARKE'S Process):

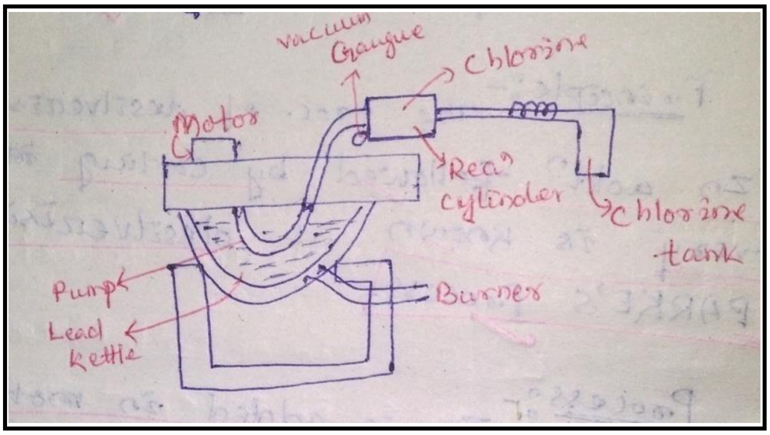
The process of desilverising of Pb by Zn addition followed by cooling for Ag recovery is known as desilverising of Pb or PARKE's process.

In this process, Zn is added in molten Pb because of high affinity of Zn for Ag and Au than Pb. Then two liquid layers such as

- Liquid Zn at the upper layer having Zn% of 0.6
- Liquid Pb at the bottom layer having Pb% of 1.5

As Zn layer (first layer) has higher melting point. So, solidify first.

Dezincing:



Dezincing Process

As Cl_2 reacting with Zn to give $ZnCl_2$ in an enclosed chamber cause left of Pb and falling on bath looks grayish scum surface (layer of bubble formation) which gets skimmed off.

At the end point, all Zn chlorinated and white crystal of $PbCl_2$ appeared on surface. Vacuum dezincing desilverised lead pump to kette i. e. bath enclosed by steel ball shaped with a stirrer and vacuum pump attached. As temperature rose to 540^0 C vacuum distillation carried out in reduction of Zn content from 0.6 to 0.002% in lead.

Debismuthizing:

The base bullion consist high Bi% which getseparated by addition of Ca and Mg to forms an insoluble intermetallic compound of Bi.

Refining of Lead bullion to get Pb using electrolytic reefing:

In the electrolytic cell, the pure Pb obtained by taking base or Pb bullion at anode where, electrolyte consists of a solution of $PbSiF_6$ (Lead Flouro Silicate) in H_2SiF_6 (Hydrogen Silicic acid). In this case, H_2SiF_6 get acted on white Pb. So, granulated Pb obtained to give $PbSiF_6$ in the next step.

Use of Pb:

- Manufacture of battery, cable, pigment, flexible sheet and pipe.
- Basic Pb carbonate such as $2PbCO_3.Pb(OH)_2$ used in Pb pigment form on basis of grade point. Also, litharge (PbO) used in reverberatory furnace for oxidation

- for pigmented varnish and glass production.
- Red Lead (Pb_3O_4): Higher oxide of Pb made by heating Litharge under control condition about 450^0 C and same use as Litharge.
- Lead Chromate: Normal yellow chromate made by the precipitate from the solution of Lead acitate and nitride to which Sodium Bicarbonate will be added.

Area of Extraction:

- HZL – Major production of Pb in Bihar (Tundoo)
- Visakhapatnam (Andhra Pradesh) – 15,000 tonne/year

EXTRACTION OF ZN BY PYROMETALLURGICAL PROCESS:

Common Minerals of Zn:

Sphalerite: ZnS
Zincite: ZnO
Franklinite: [$ZnO(Fe, Mn)_2O_3$]

Extraction of Zn from Sulphide Ores:

Mainly five important processes are there in extraction of Zn. Given as follows

1. Horizontal Retort
2. Vertical Retort
3. Electrothermic
4. Electrolytic
5. Imperial Smelting

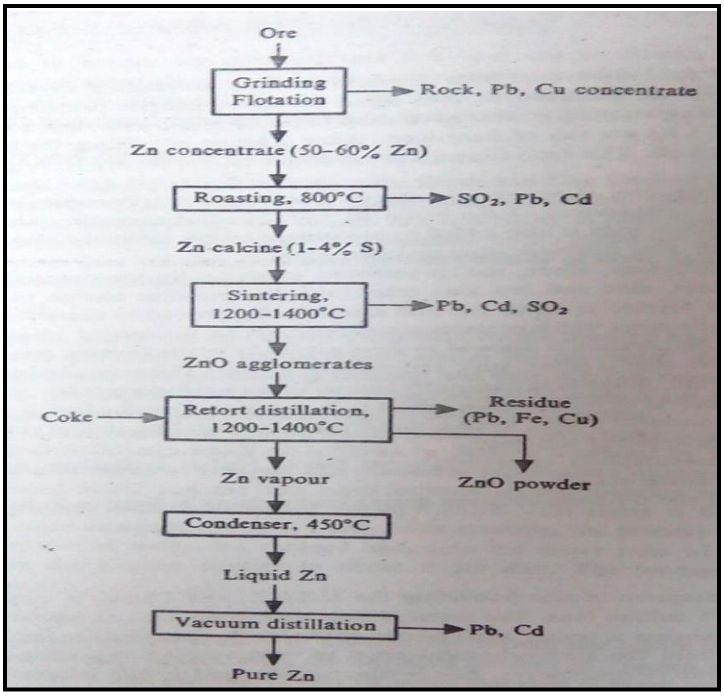
The first 3 processes are retort process. Horizontal retort made a major contribution to Zn production. Electrolytic process gives high degree purity at about 99.95%. In this case Si rectifiers incorporated in electrolytic cells to reduce power consumption and higher current density achieve.

Recently imperial smelting process (ISP) used, in which ZnO get reduces by use of molten lead to give Zn vapour which on condensation gives Zn.

$$ZnS + 1.5O_2 \rightarrow ZnO + SO_2$$
$$ZnO + CO \rightarrow Zn + CO_2$$

$$C + CO_2 \rightarrow 2CO$$

Extraction of Zinc by Reduction of ZnO by Carbon



Extraction of Zinc by Reduction of ZnO by Carbon

The technique of smelting and converting not applicable for Zn extraction because ZnS not melt even at 1500^0 C. Zn% 55 in concentrate treated under roasting, then it go for sintering where roasted oxide ground and agglomerates then go under C reduction to give Zn in vapour form. For volatisation hearth roaster used instead of other.

Initial stage roasting i.e. volatisation a hearth roaster employs. Then remaining PbS removed during sintering rather than high temperature. In order to prevent distillation of Pb present in Zn concentrate to obtain high grade Zn with low Pb in retort distillation.

In most cases, fluid bed roaster allotted instead of hearth roaster because of following advantages

- Autogeneous
- Good control over high through put of Zn calcine
- Generate SO_2 suitable for acid production

1. Horizontal Retort Reduction:

It is a 2m long, 0.25 m dia., 5-6 cm thick gas fired retort furnace made of clay used instead of metal retort because most metals gives alloy when heated with Zn. Here, first loose mixture of ZnO presence of coke breeze charged at 1400^0 C to volatize Zn which on condensation gives Zn.

2. Vertical Retort Reduction:

It is a 10 m height, 0.7 m dia., and 30 cm thick of capacity 7-10 tons Zn per clay made of SiC because has high conductivity approximately 5 times compare to horizontal retort.

3. Electrothermic Reduction:

It occurs in a vertical retort 15 m high, internal dia. of 24 m about 100 tons Zn per day. Electrodes of graphite introduce through SiC walls at two places near the bottom and at a zone of 9 m from the bottom. The gas liberate due to the reduction of charge contains 40-45% Zn, 45% CO, 5-8% H_2, 5-10% N_2. Avoid formation of blue oxide of Zinc (ZnO+Zn) quick condensation takes place. Residue contains 3-4% Zn. Zn recovery over 95%.

Zn product obtained in foregoing retort is known as Spelter.

Three distinct layers as

- Bottom layer is molten lead contains some Zn of 1.5%.
- Top layer is Zn contains some lead of 0.8%.
- Intermediate layer of Zn and Fe (15-20)% called hard metal.

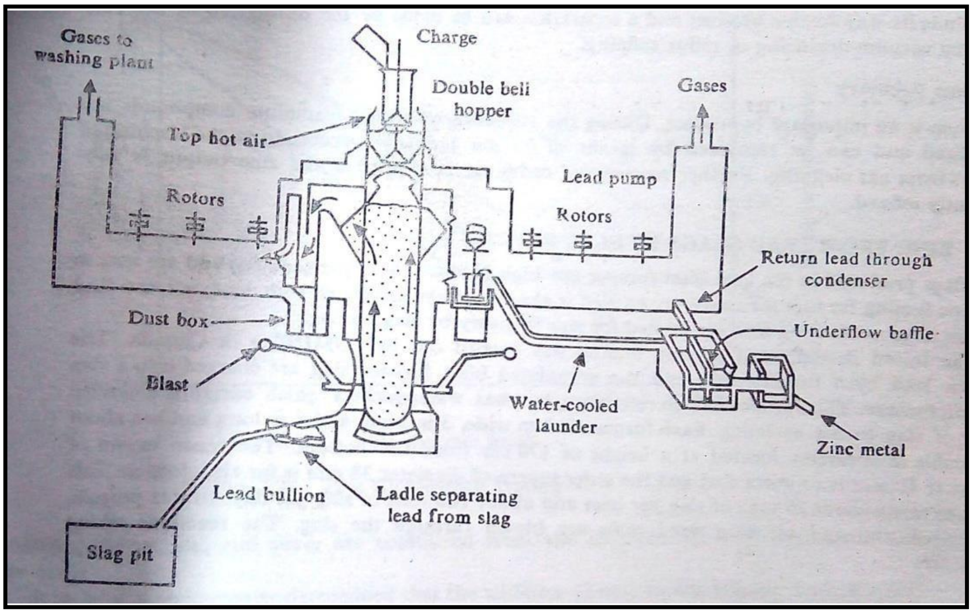
Zn layer further refined by fractional distillation because wide difference in boiling point of Zn (907^0 C), Cd (780^0 C), and Pb (1620^0 C) facilities the separation of one metal from the other.

4. Electrolytic Reduction:

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

5. Imperial Smelting Process (ISP):

The process inside the furnace based on reaction i. e. reduction of ZnO by C in the imperial blast furnace gives rise to Zn in vapour form which gets condensed by using molten lead.



Imperial Smelting Blast Furnace

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

- ISP furnace is of square cross section consists of water jacket brick lined shaft.
- Feed is given from the top of the furnace at positive pressure where we introduced preheated coke and sinter through a double bell charging system.
- ISP consists of two condensers.

Function of Condenser: These are used mainly for two purposes as

- Cooling of furnace gases resulting due to condensation of Zn
- Dissolving condensed Zn in molten Pb

The smelting reactions takes place in ISP are

$$C + \frac{1}{2}O_2 \rightarrow CO$$

$$C + O_2 \rightarrow CO_2$$

$$C + CO_2 \rightarrow 2CO$$

$$ZnO + CO \rightarrow Zn + CO_2$$

$$PbO + CO \rightarrow Pb + CO_2$$

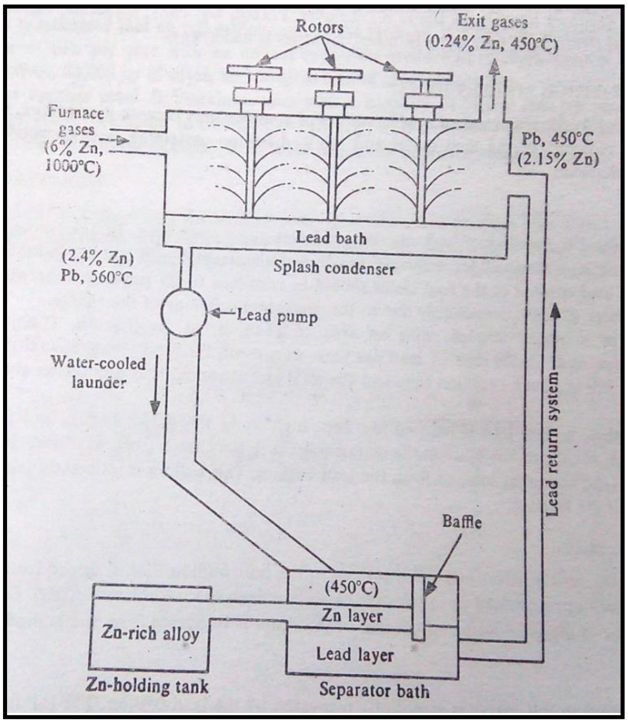
Carbon does not reduce ZnO until 1120^0 C, since at this temperature Zn gets vaporized. After reduction complete the molten slag and Pb are taken out from the furnace hearth at the melting point of the slag. Hence, Zn gets collected. So the reaction (2.31) may backward as due to the difference.

Lead Bullion (Rich 70-80% Pb):

It is the mixture of Pb and precious metal, where preheated coke 800^0 C and sinter 21% Pb are charged from the top of ISP furnace. So at bottom collect precious metals such as Au, Cu etc. and this liquid is known as Lead Bullion.

Advantages of ISP:

- Economical production of Zn.
- Efficiency overall high but Zn recovery expensive.
- Entire amount of Au, Sb etc. recover.
- Capacity large.
- Complete mixed charge of Zn and Pb simultaneously charged and recovered.
- Operational cost is low.
- No additional C required.



Zn from Lead Slag by Slag Fuming Process:

The process initiated by Consolidated Mining Smelting Corporation (COMINCO) of Trial, Canada.

Process:

The slag produce in lead bath or furnace are 15-18% Zn. Molten slag from lead blast furnace together with cold slag from dump get transformed by ladle and charged to the furnace. Then the treatment growing of molten slag by treated with mixture of pulverized fuel and air through tuyere. Hence, Zn get volatized and slag get solidified by means of water jacket in all sides of furnace except roof as roof is cover with fire bricks.

So, due to mixture of pulverized fuel and air through tuyere the reactions occur as

In bath,

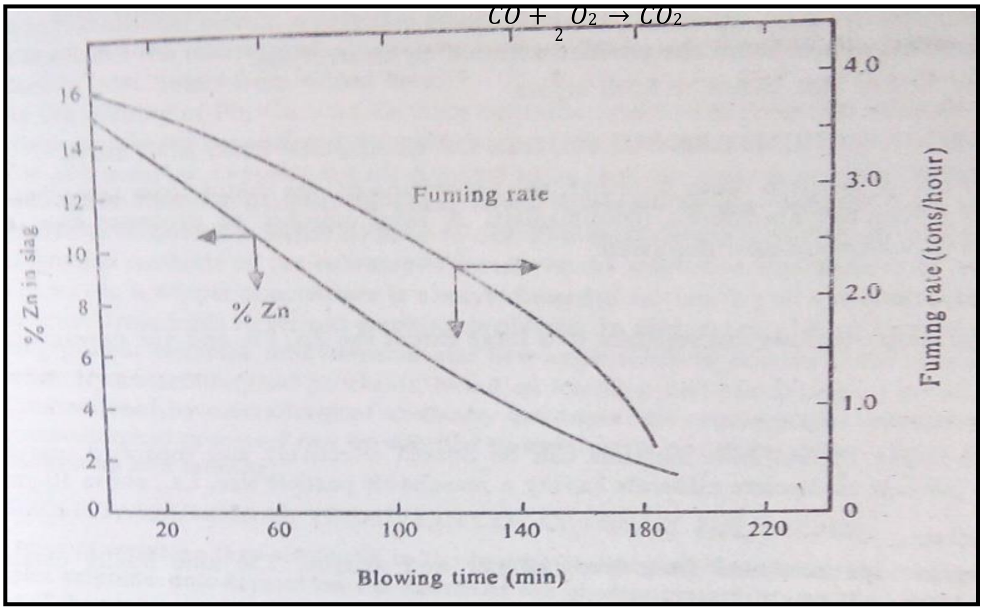
$$2C + {}_{2}O_2 \rightarrow CO + CO_2$$

$$CO + ZnO \rightarrow Zn + CO_2$$

Above bath,

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$



The excess heat gets collected by boiler located in gas collection system and the control of coal to air ratio determine the extent of heat released and maintained the bath temperature at about 1200^0 C.

First, the elimination of Zn is slow but reaching 1000^0 C get accelerate so Zn% 2.5%. Whereas Zn 1% in slag product contain 93-94% Zn. Fume leaves furnace at 1100^0 C by combustion which effected by water cooling tower at 200^0 C.

Then fume enters to big house where Zn collected and dispatched to Zn smelter on an electrolytic plant.

Uses or Applications:

- Zn extensively used as a protective coating for steel (Galvanization).
    - Restrict atmosphere corrosion by impervious basic $ZnCO_3$ layer.
    - Zn is more electropositive.
- Fabrication of Cu-Zn alloys i. e. brasses.
- Spraying – Zn used as for spraying in comparison to other metal on that metal which has low melting point.
- Rolled Zn: Usual method of cold working. Zn is rolled to sheet, plate, and strip. Where, sheet plates are rolled from 98.5% Zn.
- Pigment: Zn in the form of its oxides used in manufactured of paints.
- Alloys: Mainly Cu-Zn alloy produce of 30-37% Zn which is much less plastic when cold and worked about 500^0 C which mainly used as die casting alloy.

Area of Extraction:

- Zawar Mines (Rajstan).
- HZL (Hindustan Zinc Ltd.).
  COMINCO-BINANI at Kerela.

EXTRACTION OF Ni BY PYROMETALLURGICAL PROCESS:

Common Minerals of Ni:

Pentalandite – [$(NiFe)_9S_8$]

Violarate – [Ni_2FeS_4]

Extraction of Ni from Sulphide Ore:

Explanation of Flow Sheet:

Initial Treatment: The ore is a mixed Cu-Ni ore with nearly equal amount of Cu and Ni. The ore undergoes into grinding and froth floatation to produce a bulk concentrate which sent to copper cliff mill for separation of Cu concentrate, Ni concentrate and Pyrrohotite concentrate with iron sulphide with about 0.8% Ni.

Then the Cu concentrate subjected to O_2 flash smelting for Cu extraction. From Pyrrohotite after roasting iron oxide form and Ni separated by leaching. The Ni concentrate with about 10% Ni, 2% Cu, 40% Fe, and 30% S goes for extraction of Ni in next stage.

Roasting: In conventional process, the concentrate partially roasted to oxidize the iron sulphide either multiple hearth roaster or fluidized bed roaster. But fluidized bed roaster is more preferable because of

- High output and rich SO_2 gas stream generates
- Process is Autogeneous
- Temperature range $(550\text{-}600)^0$ C about 40% S oxidized

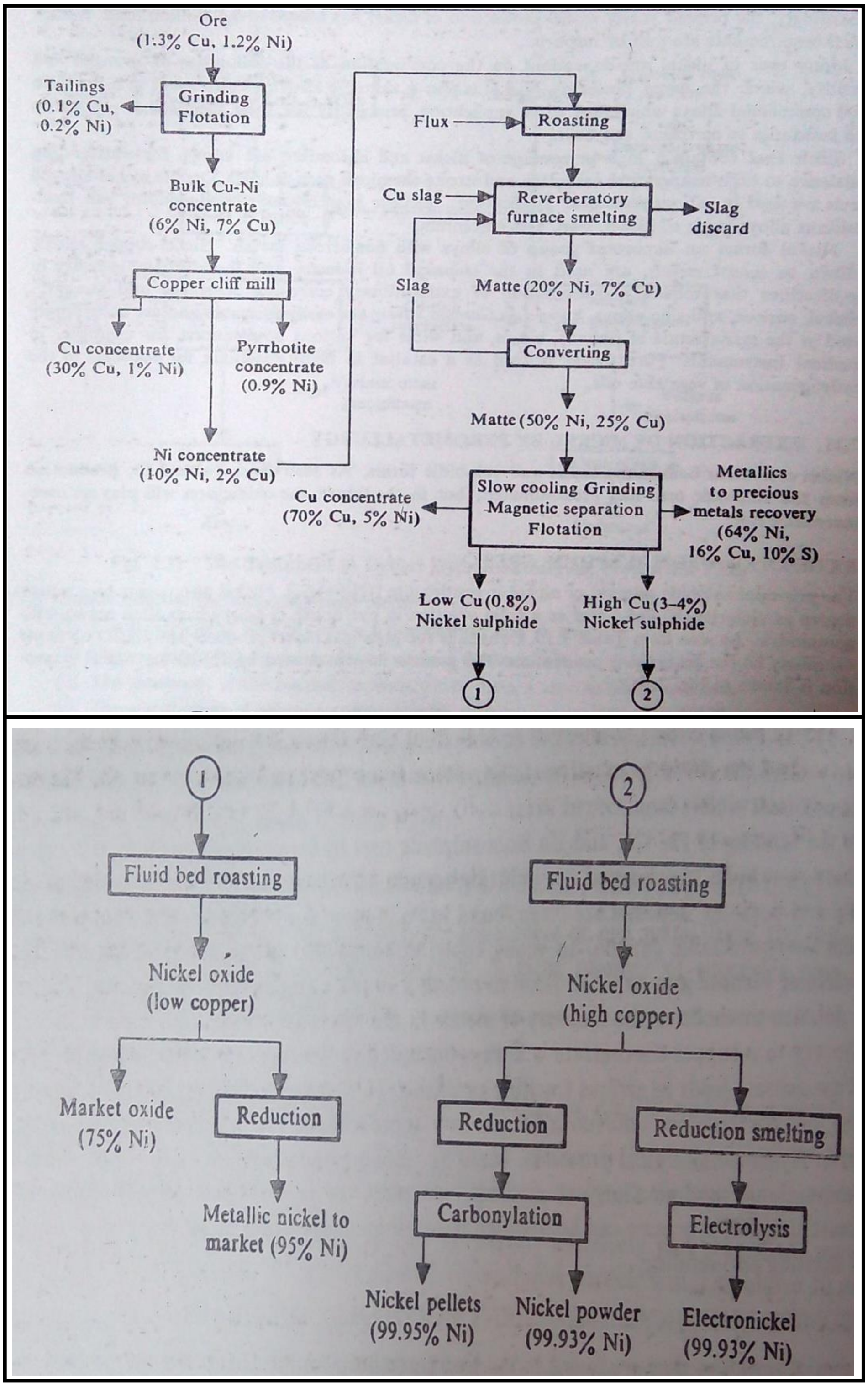
Smelting: The roasted calcine contains desired amount of siliceous flux is smelted in a reverberatory furnace to produce a matte containing Cu, Ni as 20%, 7% respectively where the slag discarded contains gangue and oxidized iron. There is also converter slag of both Ni and Cu converters are returned to the reverberatory furnace.

Converting: Furnace matte is converted to Ni enriched matte with 50% Ni, 25% Cu, 0.7% Fe, and 21.5% S at 1150^0 C in Pierce-Smith converter. The slag discarded contains 2% Ni, 1.5% Cu, 40% Fe, and 25% SiO_2 return to reverberatory furnace for recovery of Ni and Cu.

Slow Cooling: Converter matte subjected to slow cooling process from melting point to 400^0

C for 3 days to form three layers precipitate out as

- First layer, Cu_2S precipitate and grows
- Second layer, metallic Cu-Ni alloy at 700^0 C
- Third layer, solid Ni_3S_2 phase precipitate at 575^0 C



Magnetic Separation and Floating: Diphenyl guanidiene used as collector as well as frother rather than Xanthate. In floatation, Ni-Cu alloy contains 95% precious metals is undergo for magnetic separation for recovery of it. Cu_2S produced by floatation 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, and 22% S. High Cu-Ni sulphide with 72% Ni, (3-4) % Cu, 0.8% Fe, and 21% S at a temperature $(1100\text{-}1250)^0$ 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.

Refining Process:

1. Carbonyl Process for Refining Ni:

(i) Mond's Process:

In 1889, this refining process of Ni recovered by Carl Langer and Ludwig Mond. In this process, at temperature $(40\text{-}90)^0$ C metallic Ni combine with CO to give gaseous nickel carbonyl [$Ni(CO)_4$]. At higher temperature $(150\text{-}300)^0$ C $Ni(CO)_4$ decomposes to give Ni and CO gas. The reactions are

$$Ni + 4CO \xrightarrow{at\ 50^0C} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{at\ 230^0C} Ni + 4CO$$

Other forms of Carbonyls are volatile carbonyl [$Fe(CO)_5$], Co carbonyl in tetracarbonyl [$Co_2(CO)_8$] tricarbonyl [$Co_4(CO)_{12}$] form. Cu and other major elements are not form carbonyls.

(i) INCO Process:

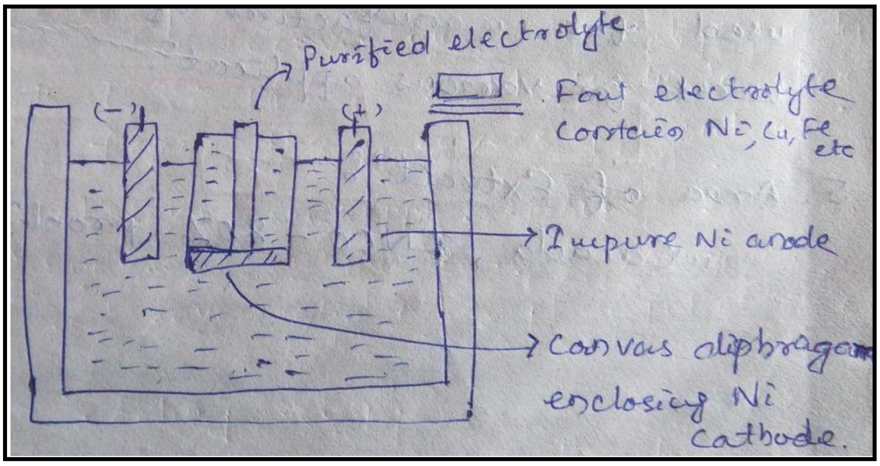
INCO Atmospheric Carbonylation Process:

The oxide first reduces to active Ni in the presence of H_2 at about 400^0 C. Then active Ni undergoes for carbonylation at 50^0 C to form $Ni(CO)_4$ then at 230^0 C goes for decomposed to Ni either in pellets about 1 cm dia or powder form about 3.5 µm size.

INCO Pressure Carbonylation Process:

The carbonylation reaction has 4 to 1 volume change permits at about 180^0 C and 70 atm pressure carbonyls of Ni, Fe, and Co formed. From which $Ni(CO)_4$ recovered by fractiona distillation and converted to metallic Ni in pellet decomposer or a powder decomposer.

2. Electrolytic Refining of Ni:



Electrolytic Refining of Ni

The Ni oxide reduce by coke in fuel fired furnace or electric furnace, and then cast into Ni metal anode. These anodes are electrolytically refined in a bath contains 60 gm/lit Ni^{+2}, 95 gm/lit SO_4^{2-}, 35 gm/lit Na^+, 55 gm/lit Cl^-, 16 gm/lit H_3BO_3. This electrolysis carried out at 60^0 C. Cu remove by cementation with active Ni powder, Fe and other impurities remove by aeration of electrolyte, Co remove by Cobaltic Hydroxide for further Chlorine oxidation. Electrolyzed Ni analyzes about 99.93% Ni.

Uses of Ni:

- Important alloying elements used in chemical processing, space research and nuclear reactor.
- Ni-Cu alloys known as Mnel metals are used in chemical oil industry and electric industry.
- Ni, Cu, and Zn alloys are known as German silver. It is used for manufacture of ribbons, bands, and wires for various applications.

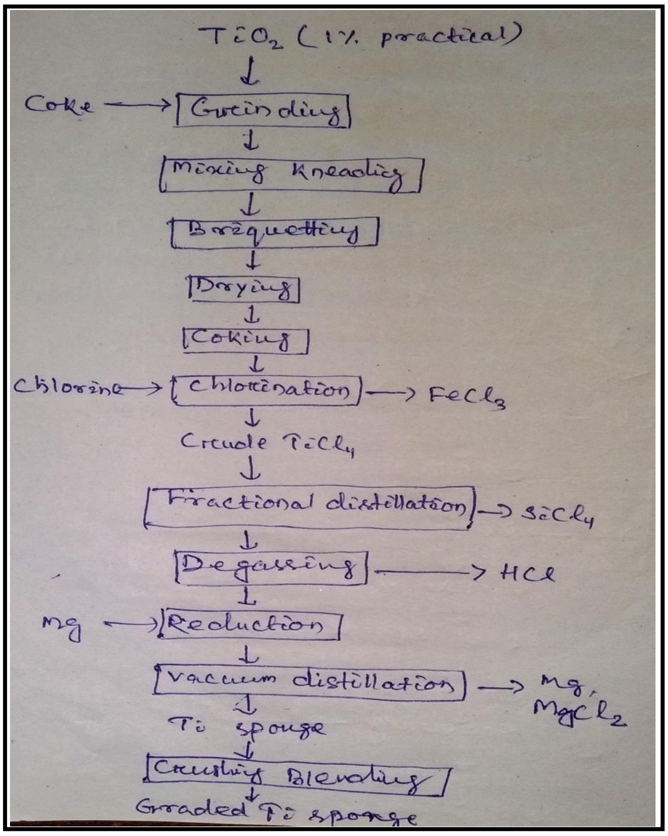
EXTRACTION OF TITANIUM:

Common Minerals of Ti:

Rutile: TiO_2

Ilimenite: FeO. TiO_2

Extraction of Ti:



Production of Graded Titanium Sponge

Kroll's Process:

The reduction reaction in Kroll's process can be written as

$$TiCl_4 + 2Mg \xrightarrow{800^0C} Ti + 2MgCl_2$$

The reaction is carried out in a stainless steel container for externally heating by gas or electricity. Exothermic reaction occurs. After reaction is over the Ti sponge is recover either by dissolving $MgCl_2$ and excess Mg by leaching with cold dilute hydrochloric acid or by distilling off $MgCl_2$ and excess Mg by vacuum heating. The residue is pure Ti sponge. The maximum yield is 96% because of

- Efficient Scavenger w.r.t impurity chlorides such as $FeCl_3$ and $AlCl_3$.
- Better conductivity of NaCl compares to $MgCl_2$ and hence, reaction is exothermic.
- NaCl-$MgCl_2$ leads a better separation of metal from slag.

Hunter Process:

The reduction of $TiCl_4$ by Na is to give Ti known as Hunter process and written as

$$TiCl_4 + 4Na = Ti + 4NaCl$$

The reaction is highly exothermic, there is a series of reactions occur as

$$TiCl_4 + Na = TiCl_3 + NaCl$$

$$TiCl_3 + Na = TiCl_2 + NaCl$$

$$2TiCl_2 = Ti + TiCl_4$$

$$2TiCl_3 = TiCl_2 + TiCl_4$$

$$TiCl_2 + 2Na = Ti + 2NaCl$$

$$3TiCl_2 = Ti + 2TiCl_3$$

$$TiCl_4 + 2Na \rightarrow TiCl_2 + 2NaCl$$

$$4TiCl_3 = Ti + 3TiCl_4$$

$$TiCl_3 + 3Na = Ti + 3NaCl$$

The reaction of sodium with titanium subchlorides in fused sodium chloride is an electro chemical nature and occurs same as like galvanic corrosion of iron.

At (anode): $2Na(sol) = 2Na^+(sol) + 2\bar{e}$

At (cathode): $Ti^+(sol) + 2\bar{e} = Ti(c)$

The anode reaction takes place at a metal surface where sodium metal, fused NaCl, Cl^- ions are available for salvation of Na^+ ions. The Cathodic reaction takes place at a metal site where soluble Ti in fused salt is available and Cl^- ions released completely in the anodic reaction.

Uses of Ti:

The sponge Ti produces in Kroll's process and ductile Ti produce in Hunter process. Main uses of Ti overally is

- Jet engine components
- Air frames
- Missiles and space craft

Area of Extraction:

- Tuticorin (Tamil Nadu)
- Kerala

Area of Extraction:

- Balivia
- Malaysia
- Indonesia