

TYBSc CHEMISTRY C303

UNIT IV

THE PRINCIPLES OF METALLURGY AND CHEMISTRY OF Fe, Cu, Ni, U, Ag & Pb

Minerals: Metals occur in nature, sometimes free but mostly in combined state. Those found in free or in native state are Cu, Hg, Ag, Au and Pb.

The metals are found in the combined state with other elements and are obtained by mining from the earth are known as minerals i.e. Cu minerals are oxide ores – Cu_2O , $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, Sulphide minerals are Cu_2S , CuFeS_2 etc.

Ore: when a mineral contains sufficient quantity of a metal combined with other element from which it can be readily separated so as to render the extraction of metal of good quality probable. It is said to be an ore of metal.

All ores are minerals but all minerals are not ores.

i.e. Fe – $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ Haematite

Al – $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ Bauxite

U – U_3O_8 Pitchblende

Gangue or Matrix: The ores usually contains a large number of impurities like earth matters, rock stones, sand, lime stones, mica and other silicates. These impurities are known as gangue or matrix.

The ores are divided into four groups.

Native ores or Free State: The less reactive metals like Cu, Ag, Au, Pt, Hg and Pb occur in Free State. These metals are known as native ores.

Oxides ores: These ores are classified as:

Oxides and Hydroxides: The metals like Cu, Zn, Pb, Al, Sn, Cr, Mn, V, Fe, Ti, Mg, Be, Bi, etc occur as oxide and hydroxides.

i.e. $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ – Haematite

$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ – Malachite

Carbonate : The metals like Fe, Cu, Zn, Pb, Mn, Ca, Sr, Ba, Mg etc occur as Carbonate ore.

i.e. MgCO_3 – Dolomite

$\text{CaCO}_3 \cdot \text{MgCO}_3$ – Ca

Sulphate: The metals like Sr, Ca, Ba, etc occurs as sulphate ores.

i.e. Ca – Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Silicate : The metals like Cu, Zn, Ni, Al, Be etc occurs as silicate

i.e. Be – Beryl $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_3$.

Phosphate ores: The metals like Ca, Sr, are act as phosphate ores

i.e. Ca – Rock phosphate $\text{Ca}(\text{PO}_4)_2$.

Sulphide and Arsenide ores: The metals like Cu, Zn, Fe, Co, Ni, Pb, and Ag etc occur as sulphide and arsenide ores

i.e. Cu -- CuFeS_2 Copper pyrites
Ni – $(\text{Ni,Cu,Fe})\text{S}$ Pitchblende.

Halide ores: Including chlorides and oxychlorides metals like Na, K, Mg, Ag etc are obtained as Chlorides and Oxychlorides.

i.e. Na – Common salt NaCl
K – Carnalite, $\text{KCl.MgCl}_2.6\text{H}_2\text{O}$.

Nitrate ores: The metals like Na, K etc occurs in form of nitrate ores
i.e. Na – Chili salt peter, NaNO_3 .

Metallurgy: It is a branch of science dealing with the method of extraction of metals from their ores and preparation of alloys.

Generally few methods are used for isolation or extraction of metals.

Ore dressing or Concentration of ore:

The ores usually contains large quantities of impurities like earthy matter, rock, stones, mica, feldspar, etc. which is known as the gangue or matrix. Removal of these impurities from ore is called as ore dressing or concentration of ore.

During ore dressing the % of metal increases so it is known as concentration. The Purified ore is known as concentrate.

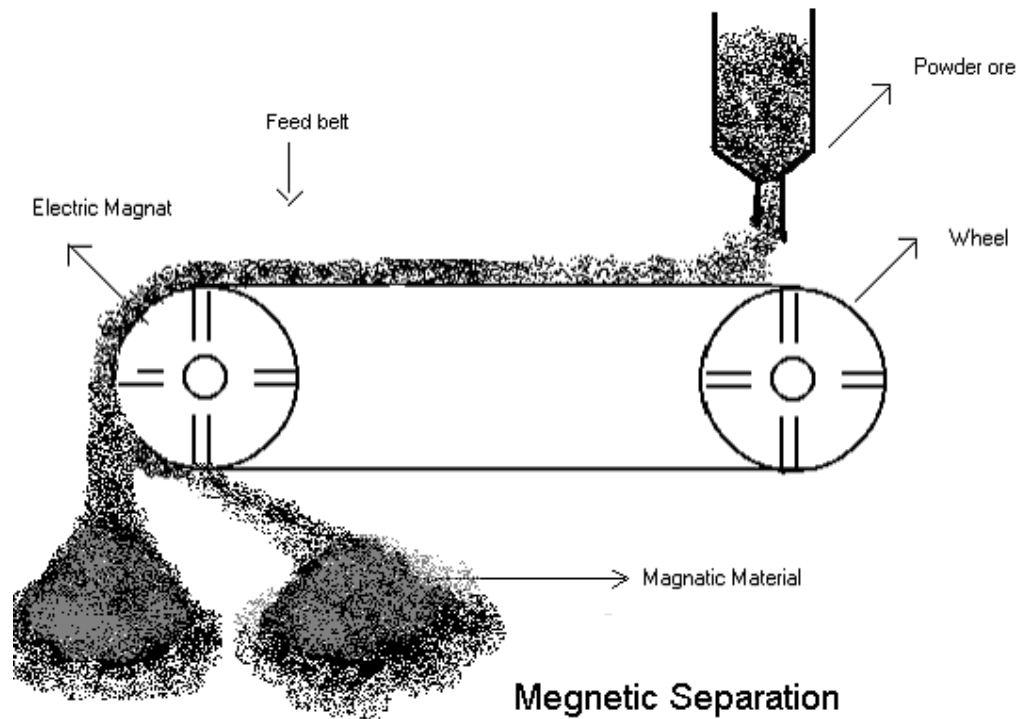
The operations carried out during ore dressing are as follows:

Hand picking: The ores can be separated by sufficient degree of purity by simply picking it by hand and breaking the rock stones with hammers.

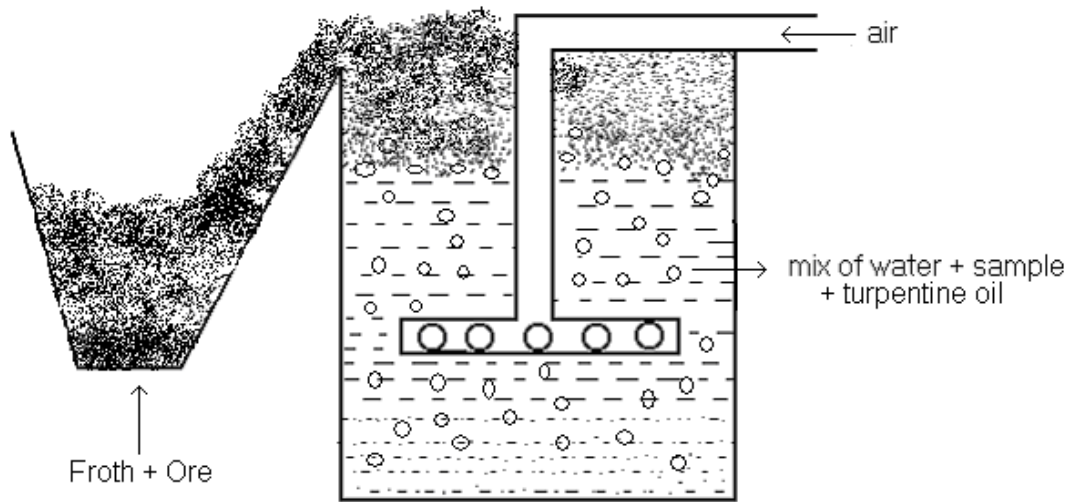
The specific gravity: The ores is crushed in jaw crushers and powdered in ball mills. If the ore and gangue have different specific gravity, and if the ore is lighter and gangue is heavier, then it is concentrated by gravity separation. In this method the powdered ore falls on jerky sloppy table and the stream of water is passed. So the ore is flown away with steam of water and impurities fall below table from where it is removed.

Magnetic separation: This method is used when ore and gangue having same specific gravity, but one is magnetic and the other is non-magnetic i.e. ore is magnetic and gangue is non-magnetic.

A thin layer of powdered ore is allowed to fall on a rubber belt, which moves horizontally and then passes over a pulley in a magnetic field. Gangue particles or the particles of a nonmagnetic mineral fall off as the belt becomes vertical. The magnetic particles are retained on the belt until they pass out of the influence of the magnet.



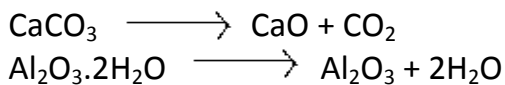
Froth floatation process: This process depends on the fact that certain minerals are wetted by oil, while gangue is wetted by water. Mainly this process is used for the concentration of sulphide ore of Cu, Pb, Zn, Hg, etc. The grounded powdered ore is taken into a big tank. To this a mixture of water and small quantities of terpentine oil or pine oil and suitable additive (Na_2CO_3) is added. Then compressed air is passed, so the whole mixture is agitated violently and froth is produced. The ore particles stick to the oil particles and come out on the surface as foam and it is collected. The impurities like earthy matters, rock stones, limestone, mica etc are wetted by water becomes heavier and settles down at the bottom of the tank. By using this process the sulphide ores of Cu, Zn and Pb are separated from impurities.



Froth formation process

Calcination and Roasting : For chemical reduction the concentrated ore is converted into oxide by calcination and roasting.

Calcination : It is the process of heating the ore at low temperature in the absence of any blast of air. The moisture, CO_2 , etc. are removed and the ore becomes porous i. e. when limestone is heated, CO_2 is given off and it is said to be calcinated. When bauxite is calcinated at high temperature, water is removed and anhydrous aluminum is left.



Roasting : It is a process of heating the ore strongly in excess of air . The roasting includes the following types.

Oxidizing roasting : The volatile impurities like S, LiS, Sb are removed as volatile. It is used for CuFeS_2 , ZnS , etc.

Blast roasting: The blast of hot air is passed through the ore for the expulsion of sulphur and metal is converted into oxide. This method is used for galena and copper pyrites.

Chloridising roasting: It means the conversion of a metal of ore into a chloride by heating with common salt in presence of air. Silver is converted to AgCl and then amalgamated for extraction of metal Ag.

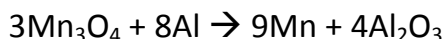
Sulphating roasting: It is partial oxidizing roasting, in which a sulfide is not converted to an oxide but soluble sulfate i.e. copper sulphide to copper sulphate. These soluble salts are taken out with water and used for further treatment.

Calcinations and roasting are carried out in reverberatory furnace, sometimes kilns are also used.

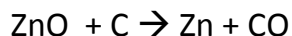
SMELTING: It is a general term used for various operations where by the metal is separated by fusion from ore.

Chemical reduction by using powerful reducing agent: For the extraction of rather less electropositive metal, powerful reducing agents such as H_2 , CO , water gas ($H_2 + CO$), Na , K , Be , Al , Ti , Mg may be used. Cr and Mn are obtained by reduction of their oxides by Al powder. This method is known as Gold

Schmidt Aluminothermic process: A mixture of metallic oxide and Al -powder is known as thermite and hence this process is also called Thermite process.



Carbon Reduction Process : The oxides of less electropositive metals like Pb , Zn , Cu , Sn , etc are reduced by heating them with coal or coke.

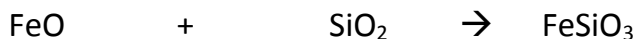


Flux and Slag : In order to remove infusible impurities a suitable substance known as Flux is added during reduction process to convert infusible impurities to fusible material, which is known as slag. The slag is lighter than molten metal hence it floats over metal and is removed from slag hole.

Ore + gangue + reducing agent + flux + heat \rightarrow metal + slag + Gases

The nature of the flux used depends on nature of impurity to be removed.

An acidic flux is used to remove basic impurity.



Basic impurity Acidic Flux Fusible slag

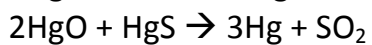
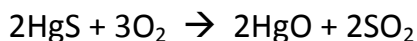
A Basic Flux is used to remove acidic impurity



Acidic impurity Basic flux Fusible slag

Some ores are self fluxing because they contain some gangue which is itself fusible and no foreign flux is required.

Air Reduction : This process is applicable to the extraction of less electropositive metals may be reduced without using any additional reducing agent, Higher temperature and anion present with metal bring this change i.e. cinnabar (HgS) is roasted in air (until a part is converted to oxide, HgO) on further heating in the absence of air the oxide reacts with unchanged HgS to give Hg .



this process is called Auto-reduction.

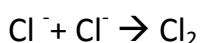
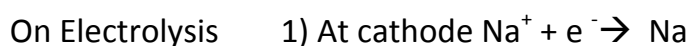
Electrolytic reduction : When the oxides of highly electropositive metal like alkali metals, alkaline earth metals, Al etc. are heated with carbon at high temperature, the metal combine with carbon and form carbide. These metals are extracted by electrolysis of their oxides, hydroxides and chlorides in fused state. Some other salt may be used to lower the melting point of the compound under electrolysis.

The addition of the salts helps in electrolysis in following ways:

To lower the vapor pressure of metal.

It reduces the corrosion troubles.

For example in manufacture of Na by electrolysis of fused mixture of NaCl and CaCl_2 , the reactions are as under.



Refining or purification of metals : The metals obtained after smelting contain greater or lesser amount of impurities. These impure metals are purified by various ways.

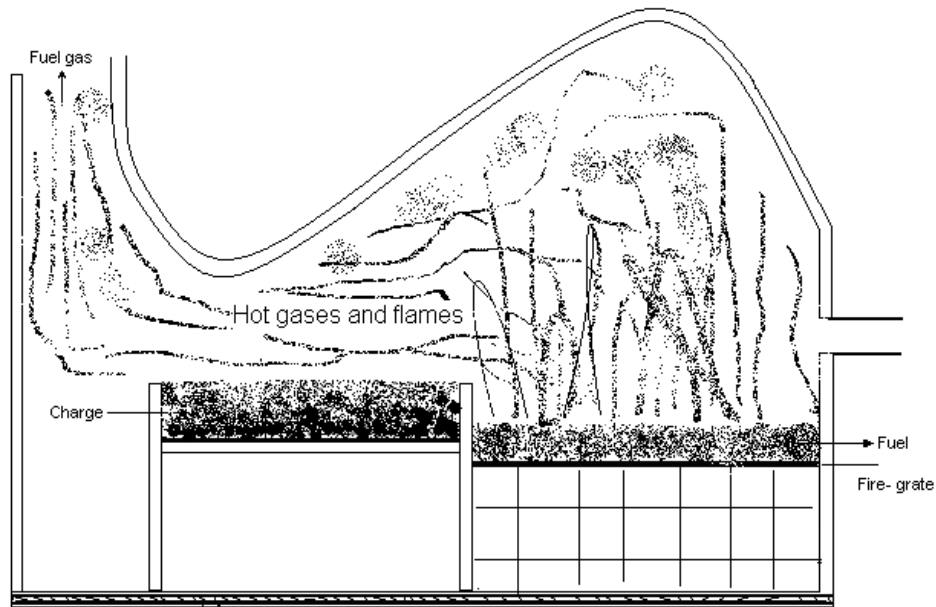
(1) Distillation (2) Liquidation (3) Sublimation (4) Electrolysis

Furnaces : The principal types of furnaces used in metallurgy are as follows :

Reverboratory furnace (2) Blast furnace (3) Open –hearth furnace

(4) Muffle furnace (5) Electrical furnace (6) Kilns.

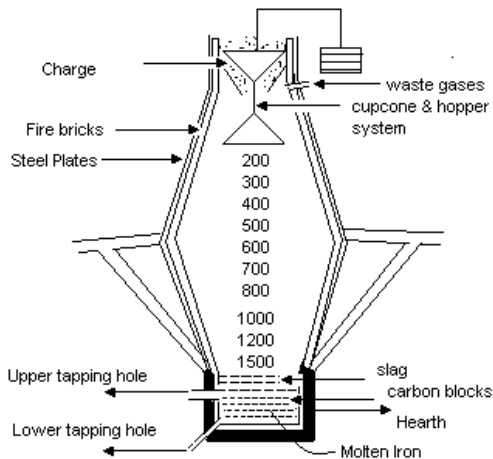
Reverboratory Furnace:



Reverberatory furnace

In this furnace the fuel is burnt in a separate part of the furnace, which is known as fireplace. The fireplace is closed at the bottom by iron bars on which the fuel is placed and burnt. The rest of the horizontal part is known as hearth or bed. The roof of the furnace is concave and takes bent towards the end away from the fireplace and communicates with the chimney. The charge is placed on the hearth and fuel is burnt on the fireplace so the hot gases and flames are deflected towards the hearth by the concave roof. Thus the charge is heated and it will not come in direct contact with fuel. Since the fuel does not come in direct contact with charge, the reverberatory furnace can be used for reduction as well oxidation process. For reduction the material is mixed with reducing agent like coke and carbon, while for oxidation it is heated in a current of air. The calcinations and roasting are carried out in this furnace.

Blast Furnace:

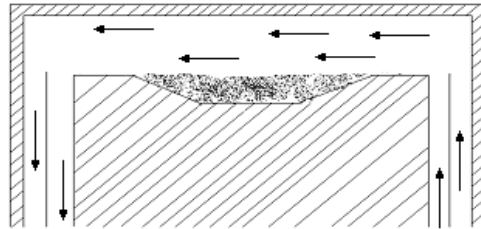


It has characteristic shape, it is about 30 meter in height and 6 to 9 meter in diameter. It is made up of steel plates. It is lined inside with fireclay bricks. The hearth maybe lined with carbon blocks for durability. On the top of this furnace is cup-cone and hopper system through which charge is introduced in the furnace. Air heated at 550-850°C by combination of waste gases is blown under pressure through tuyers or nozzles. The down coming charge meets the upward moving hot air blast. The temperature at tuyers is 1500°C and at top is 200-300°C .The product leaves from three places.

1. The molten iron is tapped from the base of the hearth every six hours or so.
2. The less dense molten fusible slag floating on the molten iron is tapped more frequently through separate outlet.
3. Waste gases escape through the exit near the top. These gases are purified before combustion.

Blast furnace is mainly used for manufacturing of cast iron.

Open Hearth furnace :



An open-hearth furnace.

This furnace is used for the manufacturing of steel and works on the regenerative principle of heat economy. This furnace is known as the Siemens-Martin Furnace. The furnace is heated by producer gas burning in the furnace over the hearth. The hot producer gas passes out from the other side of the furnace. In actual practice, the hot gases are made to pass through a brick chamber, and then the incoming cold gases are preheated by first passing through this chamber. In the regenerative system, the heat carried away by the fuel (hot) gases is not allowed to be wasted. The hot flue gases are passed through a brick chamber which gets heated, and the gases going out of this chamber are at a much lower temperature. After some time, the fuel gases are passed through this hot chamber, and the flue gases are made to heat another brick chamber. The fuel gases preheated in the chamber burn and supply more heat. After some time, the currents are again reversed.

Refractory Material : These are the substances, which can bear very high temperature without melting or becoming soft. A suitable refractory material bears the following properties:

These types of substance do not melt or soften to an appreciable extent upon exposure to intense heat.

They resist sudden and great extreme temperatures.

They support considerable pressure at high temperature without crumbling.

They resist corrosion of slag.

Refractory materials are used in the form of bricks for the internal lining of the material, flues, and hotter parts of the chimney. The commonly used refractory materials according to their acidic and basic nature are as follows:

1. Silica in form of gainster, quartz, sandstones etc. (Acidic)
2. Fire clays consisting of 50-65 % SiO₂ and 22-35 % Alumina (Semi neutral)
3. Graphite, chromite, bone ash (Neutral)
4. Lime dolomite manganese (Basic)

SiO₂ and kaolin resists temperature up to 1740°C bauxite bricks up to 1800°C alumina up to 2000°C and magnesia and chromite bricks up to 2200°C Graphite is one of the most valuable material for manufacturing of the furnace. Zirconia, ZrO₂ is one of the most refractory substances yet known and would up to 2600°C unchanged.

URANIUM EXTRACTION

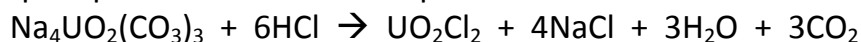
The chief ores of U are (1) Pitch blende OR Uraninite [U₃O₈] (2) Carnotite [K₂O. 2UO₃.V₂O₅.3H₂O] (3) Antunite {Ca[UO₂]₂(PO₄)₂.8H₂O} U is extracted by two processes: 1. Acid digestion process,

2. Alkali digestion process.

1. Acid Digestion Process: First of all pitch blende ore, U₃O₈ is concentrated by gravity separation process to remove sand, clay etc and then concentrated ore is roasted in excess of air, where S, As, Sb, are removed as their volatile oxides. If Ag is present in mineral, it is removed as insoluble AgCl by roasting the mineral with NaCl at 800°C. The roasted ore is digested with dil. H₂SO₄ in presence of MnO₂ for 24 hours where Ba, Pb, Ra etc are precipitated as insoluble sulphates and U goes in solution as UO₂SO₄ [Uranyl sulphate]. UO₂SO₄ present in solution is converted in sodium uranyl carbonate [Na₄UO₂(CO₃)₃] by addition of Na₂CO₃.



The solution containing Na₄UO₂(CO₃)₃ is now neutralized with HCl to form UO₂Cl [Uranyl Chloride] and then it is saturated with H₂S, so that Pb, Cu etc. can be precipitated as insoluble sulphides



UO₂Cl₂ is now treated with NH₄OH to obtain (NH₄)₂U₂O₇ [ammonium diuranate] and upon strong ignition it gives U₃O₈

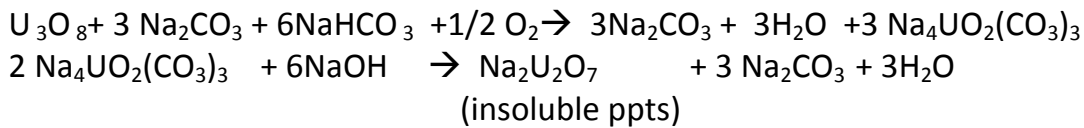
Upon reduction of U₃O₈ with C and heating in an electrical furnace gives U

98-99 % uranium is obtained by reducing with Al, Mg or Ca

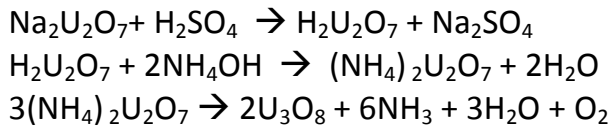
Berger reduced U₃O₈ by vapour of Ca in vacuum

2. Alkali Digestion Process: First of all pitchblende ore U₃O₈ is separated from sand, clay etc and then concentrated ore is roasted in excess of air where by S, As and Sb are removed as volatile oxides. If Ag is present, it is removed as insoluble AgCl by roasting the mineral with NaCl at 800 °C. Now the roasted ore is digested with Na₂CO₃-NaHCO₃ mixture solution where by U₃O₈ is

converted to $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ [sodium uranyl carbonate] . it is treated with NaOH to give $\text{Na}_2\text{U}_2\text{O}_7$ precipitates (sodium diuranate).



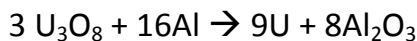
The precipitates of $\text{Na}_2\text{U}_2\text{O}_7$ is dissolved in dil. H_2SO_4 to give $\text{H}_2\text{U}_2\text{O}_7$ (Diuranic acid). Then it is treated with NH_4OH to give $(\text{NH}_4)_2\text{U}_2\text{O}_7$ which upon strong heating gives U_3O_8 .



The U_3O_8 is reduced by C to give U



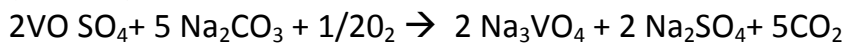
98-99 % pure U is obtained by reduction of U_3O_8 with Al.



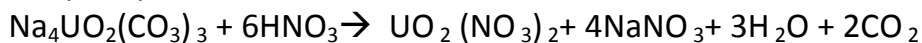
Extraction of U from Carnotite ore: In addition to U, carnotite also contains Ba, U, Fe, Al, Ra, etc. From this ore, U is obtained as byproduct. The heating is done by the steam. Most of the ore dissolves in HNO_3 , and the solution thus obtained is neutralized by NaOH and then treated with BaCl_2 and H_2SO_4 whereby Ba and Ra are precipitated as their insoluble sulphates, and U and V are converted in to UO_2SO_4 and VO_2SO_4 respectively. The filtrate also contains Fe and Al, is treated with excess of boiling solution of Na_2CO_3 which precipitates Fe and Al (reject) while UO_2SO_4 and VO_2SO_4 are converted into soluble $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ and Na_3VO_4 (sodium Vanadate) respectively.



(Soluble)



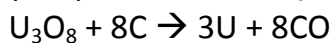
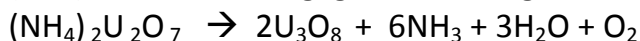
The solution containing $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ and Na_3VO_4 is neutralized with HNO_3 and treated with NaOH, which gives ppts of $\text{Na}_2\text{U}_2\text{O}_7$ of U while Na_3VO_4 do not precipitate.



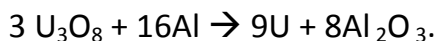
precipitates of $\text{Na}_2\text{U}_2\text{O}_7$ are converted into $(\text{NH}_4)_2\text{U}_2\text{O}_7$ as in alkali digestion process.



$(\text{NH}_4)_2\text{U}_2\text{O}_7$ on strong ignition in air gives U_3O_8



98-99 % pure uranium is obtained by reduction of U_3O_8 with Ca, Mg and Al.



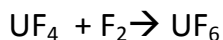
Properties of U:

The metal U resembles nickel in appearance. The pure U is white, malleable, takes polish, softer than steel, but becomes hard and brittle when alloyed with carbon and chilled. U melts at 1850°C. The powdered metal burns in air when heated at 190 °C in chlorine at 160 °C, and in fluorine at room temperature. It decomposes water slowly at room temperature and rapidly on boiling. It decomposes water slowly at room temp. and rapidly on boiling. It reacts with NH₃ at higher temperature to give N₂. It dissolves in dilute acids giving out hydrogen.

In ceramics, uranium compounds are sometimes used to give colored glasses like orange or yellow. Its salts have also been used as mordants for silk and wool. The metal and its carbide are one of the best catalysts in Haber's process for NH₃, Metal is used in nuclear reactions, uranium steels are also of technical importance.

UF₆[Uranium Hexafluoride] :

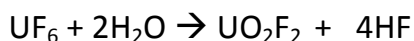
Preparation : It is obtained by direct combination of UF₄ and F₂



By reducing UF₄ with dry oxygen at about 800°C



Properties : It is a colorless volatile substance and melts at 64.1°C. It attacks many metals and a large number of organic compounds. It is readily hydrolyzed by H₂O to uranyl fluoride [UO₂F₂] and it is reduced to UF₄



Uses : It is used in separating the uranium isotopes and thus producing U²³⁵ nuclear fuel. It is a powerful fluorinating agent.

SILVER

The ores of silver are as follows.

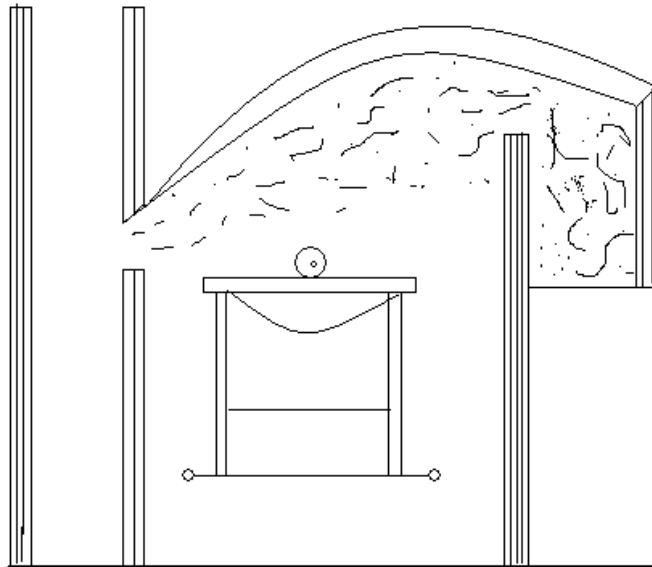
- Native state or free state. 2. Argentine [Ag₂S]
- 3. Ruby Silver [Ag₂SSb₂S₃] 4 Silver copper glance [(Ag₂Cu)₂S]
- 5. Horn Silver [AgCl]

Extraction of silver: Silver can be obtained by following processes.

Cupellation process : In this process silver ore is smelted with lead ores forming an alloy of lead and silver. Then the alloy is subjected to a process known as cupellation, where Pb forms lead oxide and silver is obtained in metallic form.

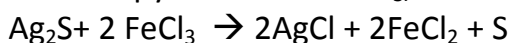
The process is known as cupellation process because the alloy is heated in a cupel or oval shaped wrought iron frame, which is filled with porous substance like boneash, barites or cement. There are two cupellation processes: (1) English Process (2) German Process.

i. **English Process :** In this process the cupel is movable and Pb is added in Pb-Ag alloy. The flames come up on the surface of the alloy mass and oxidized completely by air blast. It forms lead oxide from Pb, which is removed. The fresh Pb is added from time to time to replace the deficiency due to formation of lead oxide.



ii. **German Process :** The operation is completed in one step. The cupel is made up of limestone (65%), clay (30%), and Magnesium, Carbonate and iron oxide (5%). The alloy and required quantity of Pb is replaced in the cupel and heated in a furnace. The heat is regulated. When all Pb is converted to lead oxide and is removed, brilliant silver remains beneath and is collected.

[2] Amalgamation process or ratio process: Pyrites ore is mixed with salt and roasted. Then it is grounded and mixed thoroughly with Hg. The salt and roasted pyrites form FeCl_3 , which then reacts with Ag_2S .



The AgCl then reacts with Hg liberating silver.



The Silver dissolves in excess of mercury to form Amalgam. Mercury is recovered from amalgam by distillation while silver is left behind.

[3] Desilverisation of lead :

1. Parke's process: This process is based on the fact that

1. Molten Zn and molten Pb are immiscible
2. The Ag is ore soluble in molten Zn than in molten Pb.

Therefore when fused lead-silver alloy is treated with molten Zn, it dissolves most of Ag forming Zn-Ag alloy. This solidifies and floats on the surface and skimmed off by perforated ladders. The alloy when distilled gives the vapors of Zn leaving metallic silver behind.

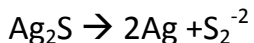
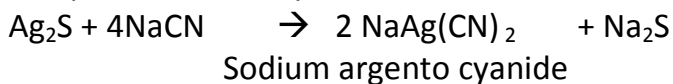
2. Pattinson's process : Desilverisation of lead containing very small amount of silver is carried out by Pattinson's process. This is based on the fact that on cooling a molten lead-silver alloy lead separates until concentration of silver rises to 2.4 % in the alloy and the entire mass solidified in block.

Argentiferous lead is melted and cooled. Crystal of lead is much poorer in silver hence separates and is removed with perforated ladles. The process of melting and cooling is repeated in above till the entire mass solidifies in block. Silver is recovered from the alloy by cupellation.

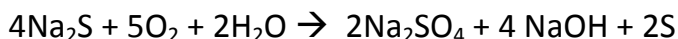
3. Bett's electrolytic Process : In this process argentiferous lead is used as anode, while pure lead sheet is used as cathode in electrolytic cell. An aqueous solution of leadfluorosilicate [PbSiF_6], Hydrofluosilicic [H_2SiF_6] and gelatin are used for electrolysis. Upon electrolysis, lead dissolves from the anode and gets deposited on the cathode. While silver along with gold and other impurities separates from the anode in form of slimy mass. This anode sludge is then subjected to cupellation to obtain refined Ag.

4. The cyanide process : This is the modern process for the extraction of silver and is carried out as under.

1. Concentration : The sulphide ore, Ag_2S concentrated by froth floatation process.
2. Treatment with cyanides : The concentrated ore is grounded to a very fine powder in ball mills. It is then treated with 0.4-0.6 % NaCN solution and the whole mass is agitated by air. Ag of ore forms a soluble complex ion with cyanide.

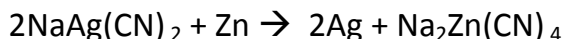


The above reaction is reversible. By blowing the air Na_2S is removed from the equilibrium mixture so the reaction can proceed in the desired direction.



The soluble sodium argento – cyanide is obtained by titration.

3. Recovery of Silver: Now Zn is added to the solution of sodium argentocyanide, Ag is precipitated as a dark amorphous mass.



The precipitated silver is obtained by titration is dried and fused when bright compact mass is obtained.

4. Purification: Ag obtained is refined by electrolysis from solution on AgNO_3 containing about 10 % HNO_3 solution. The impure Ag blocks acts as anode, while pure Ag Strips acts as cathode.

Separation of silver from gold: The separation of silver and gold is known as parting. It can be carried out by following methods.

1. Parting with H_2SO_4 : If Au is less than 20 % then this method is used. The alloy is treated with boiling H_2SO_4 . Ag goes into the solution as Ag_2SO_4 and Au remains unchanged as a spongy mass. By filtration, gold is obtained and from filtrate upon dilution with H_2O and by using Cu or Fe, Ag is obtained.

If gold is more than 20% some Ag is added from outside to reduce the % age of gold and then parting process is applied.

For this reason, the process is known as “quartution”.

2. Parting with Moebius method: In this electrolytic process, Ag-Au alloy blocks make the anode, while pure Ag acts as the cathode, the electrolysis is carried out in AgNO_3 solution, containing 1 % HNO_3 . During electrolysis, Ag dissolves from the anode gets deposited on the cathode, Au remains undissolved and is recovered.

AgNO_3 :

Preparation : It is obtained by dissolving Ag metal in warm dilute HNO_3 , and upon crystallization gives crystals or sticks. It is called “Lunar Caustic”.

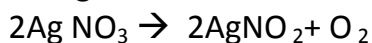


Properties :

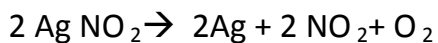
It is most important Ag salt.

In contact with organic substance it blackens and thus leaves black stains when comes in contact with hands or clothes.

It is highly soluble in water, M.P. 212°C , upon heating further, decomposes to AgNO_2 .



when heated to red heat, it further decomposes to metallic Ag.



with NH_3 it forms complex.



Uses : As laboratory reagent. In volumetric analysis for estimation of chlorides. Silver halides prepared from it are used in photography. It is used as marking ink in silvering mirrors, in surgery as Lunar caustic.

Photography : Photography is an art of producing pictures of illuminated object on chemically prepared surfaces, The photograph can be obtained from following stages.

Making a sensitive plate : Sensitive photographic plates are of two types (1) Plates (2) films. Dry Plates consists of sheets of clear glass, while films are made up of strips of celluloid and these are coated with emulsion. To make emulsion AgNO_3 , NH_4Br and gelatin are slowly heated together until reaction takes place between them.



The mixture is kept in a warm room, until the grains of AgBr begin to develop. This makes the metalloid more sensitive and the process is called repening. Now this jelly-like mass is shredded in machine. It is now soaked in distillation H_2O , melted and then dissolves out NH_4NO_3 from gelatin. The emulsion is now melted and the glass plates or the celluloid films are coated with it and sealed in light tight boxes.

Panchromatic plates: This emulsion has one great defect of being sensitive to only blue, violet and UV-rays, while the green yellow, orange and red rays are unaffected.

A number of photosensitizers were suggested by different workers to overcome this effect.

Vogel- Dyed plate with aniline (1873), with cyanin (Blue dye) (1834)

Tailfor and clayton-rosin-isochromatic plates

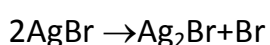
Eder- Erythrosin (red dye)

Kocnig - panchrome and arthrochrome- T finally pinacyanol (a greenish dye)

Babcock – Neocyanin

Exposer: To take a picture, the dry plate or film is put in camera and the exposed. In exposer,

Silver sub-bromide is produced, in which it reduces to silver

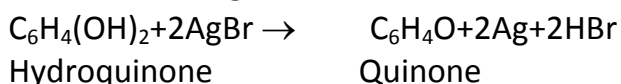


On the basis of photo electric effect the loss of electrons of halides makes more sensitive to reduction

Development: The plate or the film is now taken out from camera in dark and immersed in a developing bath, which consists of a very weak solution of some reducing agent, so only exposed parts are affected.

Recently, metal quinol or hydroquinone and amidol are used as modern developer, it is made as follows: Metal 1.0 gm, Na₂SO₃ (crystals) 85 gm, Hydroquinone 4.5 gm, Na₂CO₃ (Crystals) 1.6 gm, dissolved in warm water and make the solution one liter.

The portion of the plate most affected by light is easily reduced so becomes black, while those not affected by light remain white and correspond to black in the object. The value of the image is therefore negative to tone of the object and is called negative. The reaction is,



Hydroquinone Quinone

Factors affecting the development : Time and temperature are important factors which affects the development.

Temperature: All solution should be at same temperature below 13°C chemicals are unaffected above 24°C but there are changes in gelatin 20-25°C is the ideal temperature.

Time: Lower the temperature longer the time required, more time gives over development or under development.

Fixing: Plate cannot yet be exposed to light, because it contains sufficient amount of emulsion at the white point. It is immersed in a solution of Na₂S₂O₃(hypo) to dissolve out this balance of the emulsion.

A little, Na₂S₂O₃ is added to the fixing bath as preservative and some chrome alum for hardening the negative After mixing hypo should be removed by washings.

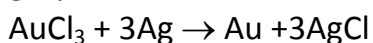
Printing: The process of printing is a repetition of making negative printing paper of two types.

P.O.P. papers coated with mix of AgCl, gelatin and silver citrate, The negative is placed against printing paper in a printing frame and exposed to sunlight. The process is slower, so it can be watched and controlled. After the image has come on the paper, it is fixed and toned.

Bromide paper requires very short time. Artificial or gaslight is sufficient to expose this.

Toning: Other metals to get different shades, may replace the silver in the print.

Generally Ag is replaced by Au or Pt, by immersing in solution of gold chloride or sodium auri chloride and potassium chloroplatinate. Gold solution gives golden tint ranging from brown to purple, white platinum produces shining gray.

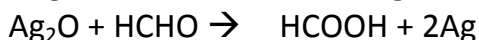


After treatment of negatives: An after treatment of a negative is necessary, when its image density is too low or too high. The method used for increasing

the image density is known as intensification, while that employed for lowering it is called reduction.

Silvering of Mirrors: Silvering of mirror is a process by means of which a thin and uniform layer of silver is deposited on a clean glass surface. It is employed for making looking glasses, concave mirrors and reflecting surfaces.

The process is based on the reduction of silver oxide by an organic substance like formaldehyde, tartrates, etc.



Two separate solution are prepared for these purpose, one is ammonical silver nitrate (20 gm AgNO_3 in 150 ml H_2O and then adding NH_4OH till the precipitates first formed and redissolved. It is made 320 ml.) [Tollen's reagent] The second solution consists of reducing agent.

The plate to be silvered is thoroughly cleaned with alcoholic KOH and then washed with water and dried. It is fixed in an enameled dish with paraffin wax so that only one of its side is exposed. The two solution are now poured over the surface in proper proportions and the mixture is given a slow motion by moving the dish to and fro.

After the silver has been deposited, the mirror is gently washed with water, dried and polished with soft cotton wool. The back is given a coat of a mixture of red lead and turpentine in order to get looking glass.

LEAD METALLURGY

Pb – Lead: The chief ore of lead is Galena, or lead sulphide (PbS), other ores are anglesite [PbSO_4], cerrusite [PbCO_3] The extraction of Pb is carried out by two methods

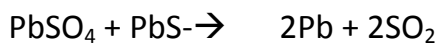
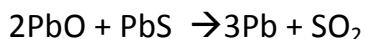
[1] Air reduction process: This process is used when ore are rich in lead. The steps are as follows:

Concentration: The ore, PbS [Galena] is crushed and sieved and concentrated by using froth floatation process.

Roasting: The concentrated ore is roasted on a reverboratory furnace. The ore is partially converted to PbO and PbSO_4 by controlling the air simply through the doors .



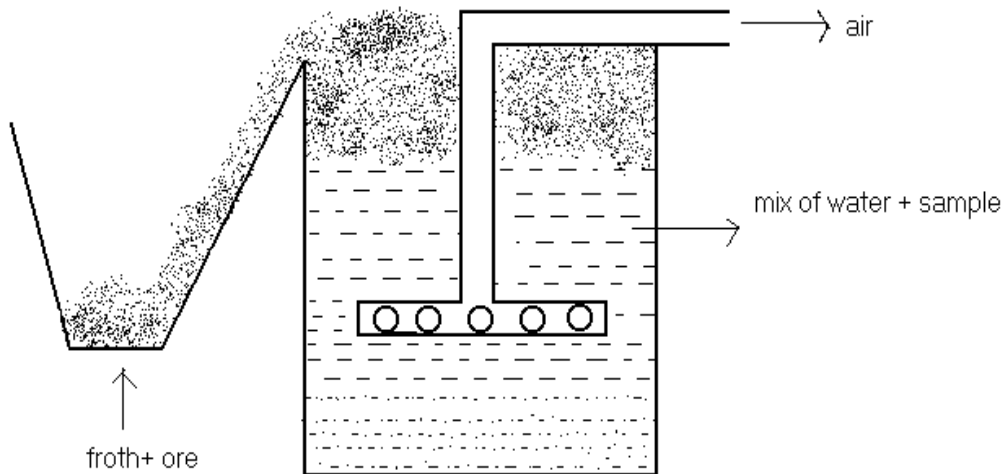
Now the air supply is reduced and the temperature raised up with more addition of PbS . The oxide and sulphate produced in 1st operation react with excess of PbS and reduced to metallic lead.



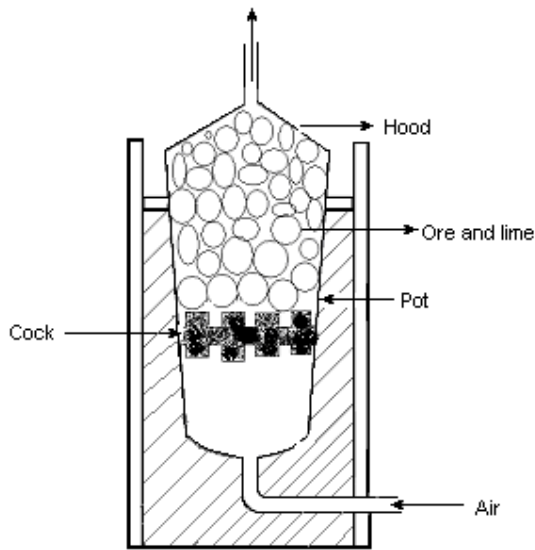
Thus in air reduction process roasting and smelting are done in the same reverberatory furnace at two different temperatures molten Pb is removed from the lower part of the furnace and purified.

[2] Carbon reduction process: This process is used for ores poor in lead content. It is carried out in the following steps.

Concentration: The ore is crushed and made fine powdered in ball mills and sieved. It is taken in big tank. To this, the mixture of water and small quantity of pine oil is added. Then the air is passed violently under pressure. The whole mixture is agitated, so it produces froth. The ore particles stick to oil particles and produces froth. The froth is lighter than water, and comes on upper surface from where it is collected in separate container. The impurities are wetted by water and settle down at the bottom and removed.



Forth formation procces



Sinterer for roasting of concentrated ore.

Roasting: The concentrated ore is roasted in a sinterer, which is mounted on trunnions for charging and discharging. There is a hood at the top and grating near the bottom. The slow blast of air is passed and is circulated through the charge by suction from the top of hood.

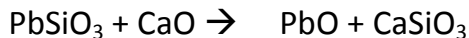
The charge made up of ore [PbS] and lime is placed on the coal fire at the grating PbS – changes to PbO.



The lime is used for two purpose:

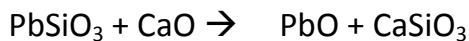
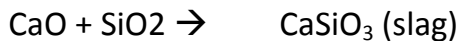
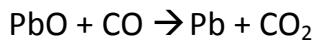
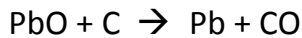
It is more basic than PbO, so prevents the formation of PbSO₄.

It prevents the formation of PbSiO₃, which would otherwise go into slag. If it is formed it decomposes.



Smelting: The sintered ore is broken into small pieces and placed in the blast furnace of the type as shown in figure 3.

As the charge moves down the following reactions occur.



(Lead Silicate)

The slag is lighter than molten Pb and thus floats over it and removed from the upper slag hole while the molten Pb is removed from the lower tapping hole:

Purification: The lead obtained by any of the methods contain large no of impurities like Bi, Cu, Sb, and Ag. The Bi, Cu, Sb, etc. are removed by softening process while Ag by various desilverization process.

Softening Process: The impure metal is melted in reverboratory furnace and air is passed, so impurities oxidized and the oxides are removed.

Desilverization Process: The lead is desilverised by following processes:

1.Parke's process : This process is based on the fact that (I) Molten Zn and molten Pb are immiscible. (II) The Ag is more soluble in molten Zn than molten Pb. Therefore when the silver containing Pb is mixed with molten Zn the Ag almost dissolves in molten Zn forming Zn-Ag alloy. This is solidified and floats on the surface is slimmed off by perforated ladles. The alloy when distilled gives the vapour of Zn. Leaving metallic silver behind and is collected. Lead is considerably reduced by repeating this process.

Uses or industrial applications:

It is used for making:

Water pipes and cable covering

Lead accumulators

Lead Shot

Lead Chambers for manufacturing of H_2SO_4

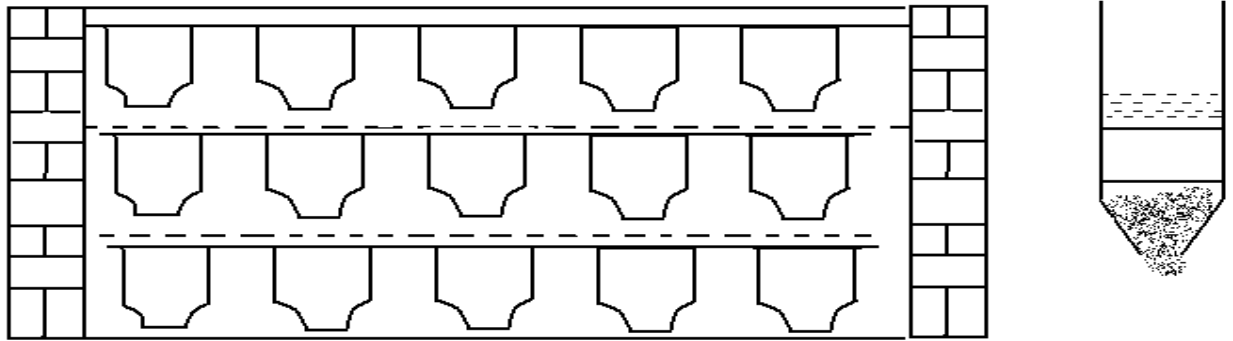
Lead pigments like Red lead, white lead, Chrome yellow, chrome red

Compounds of lead.

For manufacturing of alloys

White lead $2PbCO_3Pb(OH)_2$: At present white lead is the most important pigment. It is prepared by DUTCH PROCESS.

Dutch Process: This process is based on the action of CH_3COOH on metallic lead in presence of moist air and CO_2 . The process is essentially one of corrosion and takes place in the earthen pots glazed inside and provided with shoulders from which the pure lead strips are suspended. The pots are 8 inches high and 4 inches wide and contains a solution of 3% CH_3COOH at the bottom. So Pb does not come in direct contact with $CH_3.COOH$. Alternate layers of tan bark, pots and wooden planks are build up.



The heat developed by the fermentation of tan bark [something like leather] volatilizes the fluid, which in contact with atmospheric O₂ corrodes the Pb forming Basic acetate.

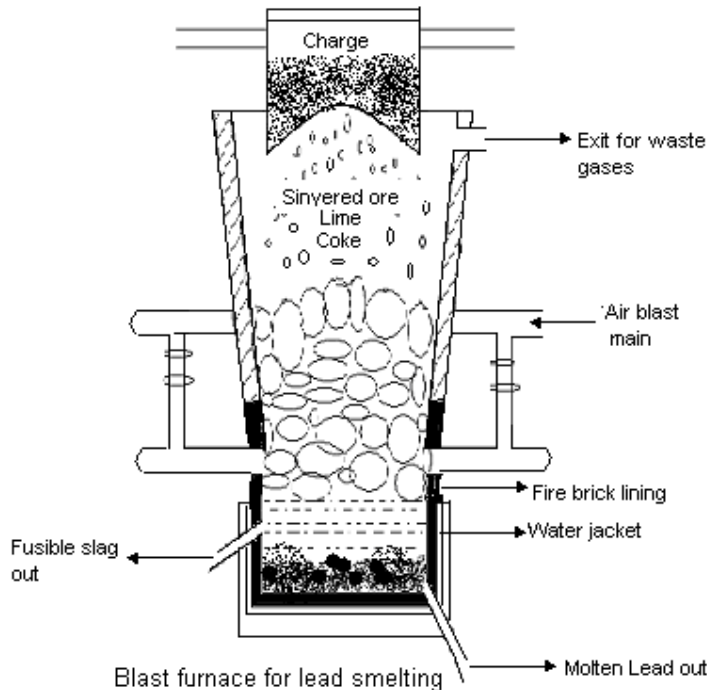


Basic lead acetate is finally decomposed by the CO₂ liberated in the fermentation process.



The CH₃OOH again react with more lead in presence of moisture and air corrosion produces more white lead via basic acetate. The cycle is continued. After reaction is subsiding the white lead is washed, grounded, collected and dried.

Uses: White lead is used as pigment in paints.



COPPER METALLURGY

Occurrence : Copper is widely distributed all over the world. The Ores are classified as follows.

Native ore or. Free state - Metallic copper – 5% of the total production.

Oxide ores - Cu_2O [Ruby copper), $\text{CuCO}_3\text{Cu}(\text{OH})_2$ [(green Malachite), $2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ (blue) Azurite)

Sulphide ores - CuFeS_2 [Copper pyrites], Cu_2S [Copper glance bornite)

The chief ore is CuFeS_2 (or $\text{Cu}_2\text{SFe}_2\text{S}_3$) copper pyrites.

Most of the world's copper supply is from sulfide ores.

Extraction of Cu : there are two methods for extraction of Cu .

Dry-process: This process is used when Cu content in the ore is large. It is known as pyrometallurgy.

Wet Process : It is used when Cu content in the ore is less. It is known as hydrometallurgy.

CuFeS_2 Contains FeS as impurity. So due to presence of FeS, Cu-metallurgy becomes more difficult. The reasons are as follows.

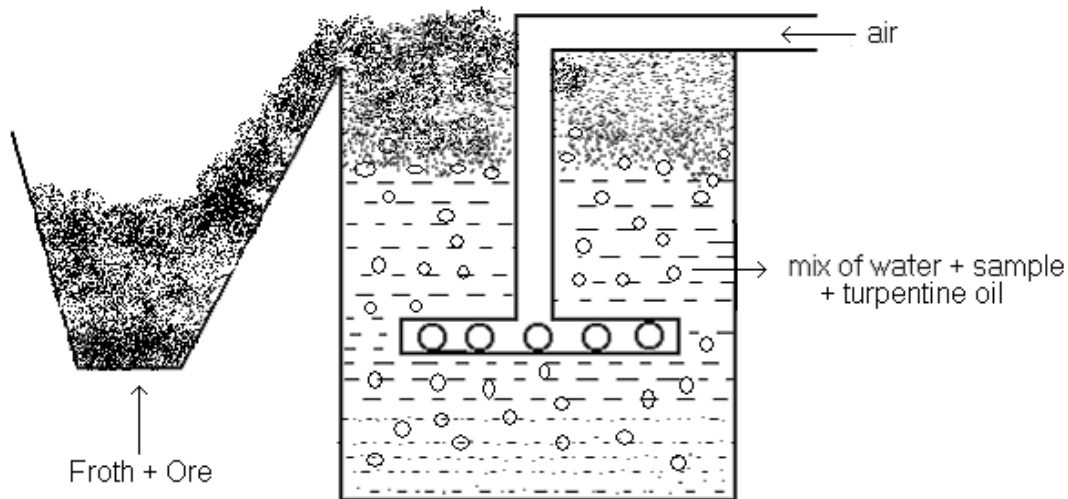
Cu has greater affinity for S than for oxygen. As temperature increases this affinity increases.

Fe has more affinity for Oxygen than for sulphur. This affinity increases as temperature increases.

S and O have affinity for each other than for Cu and Fe.

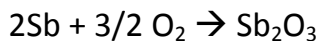
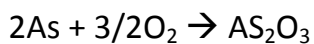
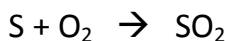
Dry Process: Dry process divided into following steps.

[1] Concentration : The ore containing sulfide is firstly concentrated by froth floatation process. The finely powered red ore is taken into big tank. To this mixture of mixture of water and a small quantity of pine oil turpentine oil and some active whole mixture is agitated. It produces froth. The ore particles stick to oil particles and froth is produced. The ore particles stick to oil particles and froth is produced. It is lighter than water. Coming on the upper surface from where it is collected in separate container. The impurities, earthy matter, sand, rocky stones, mica, etc are wetted by water, becomes heavier and settle down at the bottom of the tank. In this way ore is concentrated.

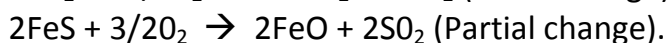
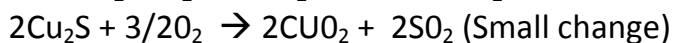
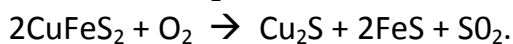


Froth formation process

[2] Calcination & roasting: The concentrated ore is roasted in a current of air at low temperature a reverboratory furnace. A large portion of free sulpher present as impurity is oxidized to SO_2 and removed as such. As and Sb are removed as volatile oxides, As_2O_3 and Sb_2O_3 respectively.

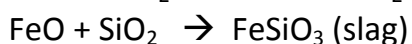
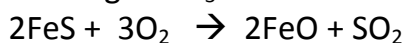


CuFeS_2 is converted as Cu_2S and FeS . These Cu_2S and FeS are further partially oxidized as Cu_2O and FeO .



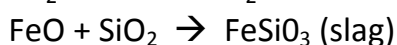
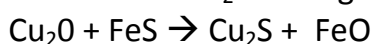
Thus SO_2 obtained as byproduct.

[3] Smelting : The roasted ore is mixed with coke and sand and smelted into blast furnace. During smelting gets oxidized to FeO. FeO then reacts with SiO₂ forming FeSiO₃ Ferrous silicate (Slag)



FeSiO₃ - slag is lighter than molten sulphides of Cu and Fe, hence it is removed.

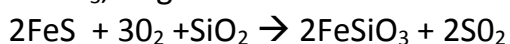
Cu₂O is also formed during roasting, reacts with FeS to give FeO. This FeO also reacts with SiO₂ forming Slag.



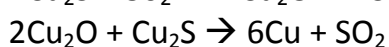
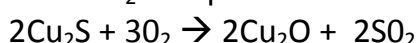
It is also removed

The molten mixture thus obtained during smelting contains mainly Cu₂S and FeS Molten Cu₂S with FeS (little) called matte and is removed through the slag hole matte is also removed through an outlet.

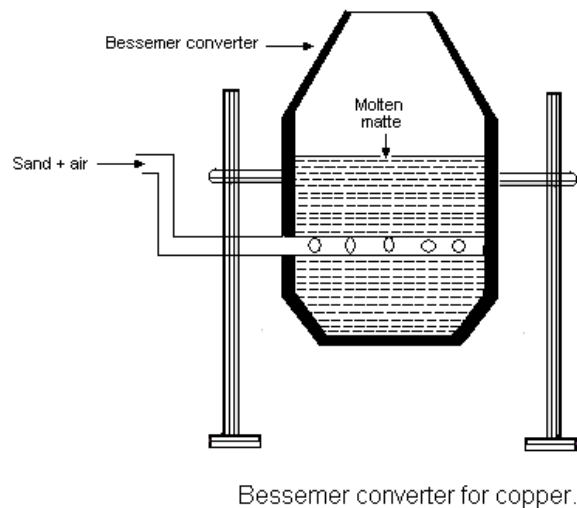
[4] Bessemerisation : Iron left in matte is removed by bessemerisation. It is carried out in Bessemer converter. Molten matte is poured in Bessemer converter and calculated quantity of sand is added. After adding sand Bessemer converter is kept upright and hot air is blown through it at high pressure. FeS oxidized to FeO. This FeO reacts with SiO₂ forming FeSiO₃, slag.



After, all FeS oxidized to FeO, Cu₂S start to convert Cu₂O : This Cu₂O reacts with Cu₂S to produce Cu in molten form.



This molten Cu is taken Out from Bessemer converter, when ore gets cooled. SO₂ gas comes out from it and produces blister on the Cu metal surface. The cu produced in this way is known as blister Cu. It is 95% pure containing Fe, Mn, Zn, Pb, Bi, Sn, Ni, Ag, Au, Pt and Cu₂O as impurities. It is used for utensils.



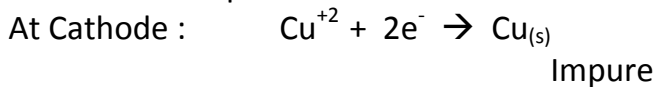
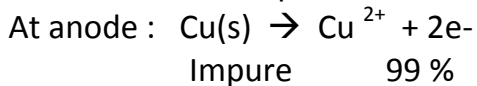
[5] Refining of Cu:

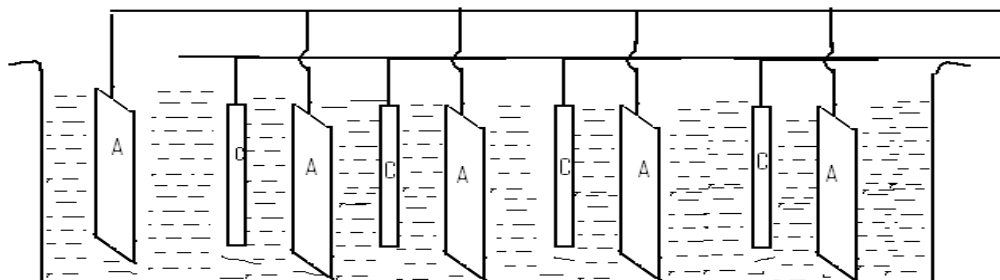
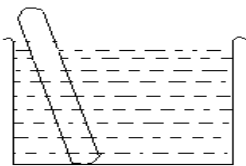
1. By polling Method : During bessemerization a small quantity of Cu₂O produced by air blasts remain unreduced. So it is removed by polling method.

Molten impure Cu is taken into reverboratory furnace. Upper surface is covered with coke layer and it is stirred with green wood pole. So hydrocarbon gases produced from wood pole reduces Cu₂O to Cu and if Cu₂O produced on upper surface also reduced by coke and in this way Cu₂O is removed. Cu obtained is 97 % pure.

2. Electrolytic Refining : The impure Cu is refined by electrolytic process. In this process impure Cu casts into large plates, which are used as anode and pure Cu acts as cathode. CuSO₄ and dil. H₂SO₄ solution are used as electrolyte.

During electrolysis impure Cu dissolves and forms Cu⁺² ion, which reduces at cathode and gets deposited on it. The impurities Ag, Au and Pt do not oxidize and fall to the bottom of electrolytic cell as anodic mud along with Cu₂O) and slag from where they recovered. Other impurities Zn, Pb, Fe, Sn, etc oxidized as their ions and remains in the solution, The Cu obtained is 99.9 % pure.





IRON METALLURGY

Iron readily occurs in free state, since it is highly reactive. Its important ores are (1) red hematite [Fe_2O_3] (2) Brown hematite or limonite [$\text{Fe}_2\text{O}_2\cdot 3\text{H}_2\text{O}$] (3) magnetite [Fe_3O_4] (4) Siderite [Fe CO_3]. Huge deposits of haematite are available in India in mayurbhanj (Orrisa), Singbhum (Bihar) and Mysore.

Iron ore is worked for three variety of iron, which differs from each other mainly in their carbon content.

Cast iron or pig iron : It is the most impure form of iron and contains the highest % of carbon (2-3%) and other impurities like Si, P, Mn & S (1.5%).

Wrought iron : It is the most purest form of iron and contains the lowest % of carbon (0.12-0.25%)

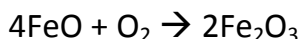
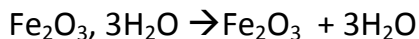
Steel : The % of C in this form is in between cast iron and wrought iron (0.25-2%)

Q. Describe the manufacture of cast iron

Cast iron is usually obtained from haematite ore. The steps are as follows :

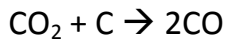
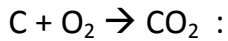
[1] Concentration : The impurities are removed as far as possible by hand picking and the ore is broken into pieces. It is now washed with water to remove the lighter impurities like sand, clay, etc. The washed ore is than concentrated by using magnetic separation process.

[2] Roasting : The concentrated ore is roasted with little coal in reverboratory furnace. During roasting, moisture, CO_2 , etc are removed as volatile oxides. The S content is lowered. FeO is converted into Fe_2O_3 . FeO also forms slag with SiO_2 , while Fe_2O_3 does not. The mass becomes porous.

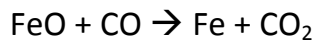
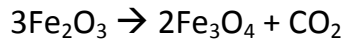


[3] Smelting : The roasted ore is mixed with limestone and desulphurised coke in the ratio of 8:1:4 and smelted in blast furnace. During smelting the following reactions take place in different zones of reactions.

Upper zone: This zone is near the mouth of furnace and is called the upper zone of the reduction. The temperature ranges from 400 to 700°C. In this zone coke burns in presence oxygen and hot air to form CO₂ which reduces to CO.



In this zone CO reduce Fe₂O₃ to spongy iron.

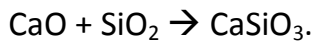


Spongy iron

At a temperature about 600°C a part of CaCO₃ gets decomposed to CaO.

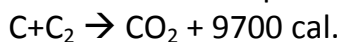


Central zone: The temperature ranges from 900 to 1200°C. It is called lower zone of reduction. The spongy iron, which comes down, meets CO, and decomposes to C partly [2C → CO₂+C]. The spongy iron absorbs C at about 1000°C, CaCO₃ almost completely decomposes to CaO and forms slag with SiO₂.



The slag is lighter than molten metal, floats over molten metal and is removed from the upper slag hole. The silicates phosphates, manganates reduce to Si, P and Mn. They are partly absorbed by slag and partly by iron.

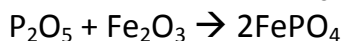
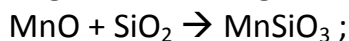
Lower zone : It is the hottest part of the furnace and called the zone of fusion. The temperature ranges from 1200-1500°C. In this zone coke burns by blast of hot air to produce CO₂ and heat.



The spongy iron melts at 1300°C and is collected at the bottom of hearth of the blast furnace. FeO reduces to Fe in this zone. If any silica or alumina is present it forms slag and as it is lighter than molten metal it floats on the surface and is removed from the slag hole. Slag prevents molten metal from oxidation. The molten metal is removed from lower tapping hole and is solidified. This is pig iron. This pig iron is remelted in a furnace heated by coke and cast or poured into moulds. This is known as cast iron.

Wrought Iron : Wrought iron is obtained from pig iron by removing the impurities by puddling process, in which the cast iron along with some scrap iron is placed on the hearth of the reverberatory furnace lined with haematite. Fe₂O₃ oxidizes C, S, Si, Mn and P to their respective oxides i.e. CO, SO₂, SiO₂,

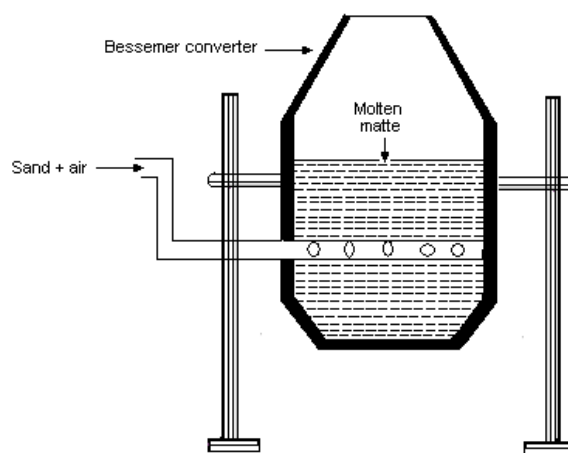
MnO and P_2O_5 , MnO and SiO_2 combine to give $MnSiO_3$ (slag): P_2O_5 with Fe_2O_3 to give $FePO_4$ (slag).



As the impurities are removed the melting point of the metal rises and iron becomes pasty mass, which is stirred and forms balls and blooms. They are spongy in nature due to large amount of slag present in them. The balls are taken out from the furnace and slag is removed by hammering. Finally iron is rolled into sheets and bars.

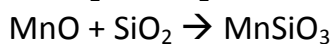
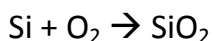
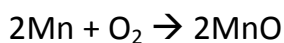
Uses: it is used to make anchors, wires, bolts, chains and agricultural equipments.

Steel:



Bessemer converter for copper.

Bessemer process : The molten pig iron is poured into a Bessemer converter which is made up of steel plates. It is lined with silica or mixture of lime and magnesia ($CaCO_3$, $MgCO_3$) when impurities of Mn, Si, etc. are present. When P is present dolomite is used. The Bessemer converter is kept upright and the hot air is passed Si and Mn are converted into SiO_2 and MnO and forms slag, which is removed.



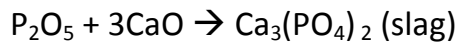
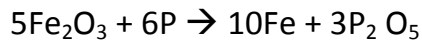
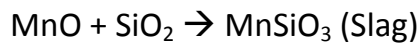
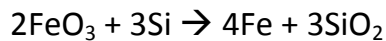
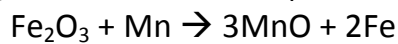
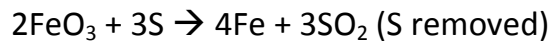
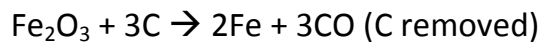
P is removed as phosphate.

As, Si, Mn and P are removed, then carbon is converted to CO. CO burns with blue flame at the mouth of the Bessemer converter.

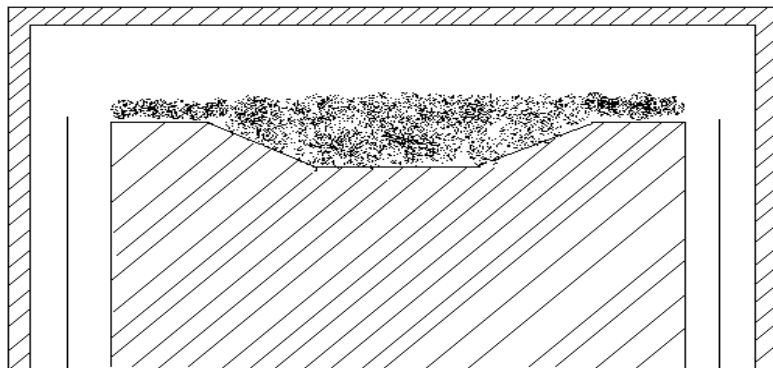
When flame is stopped than air blowing is stopped. Then required quality of carbon is added and it is distributed uniformly by passing air for some time. Some quantity of alumina and ferrosilicone are added to remove dissolve N₂ and O₂. Steel is obtained.

Open-hearth furnace : The charge which contains cast iron mixed with about 25-40 % of its weight of scrap iron low grade wrought iron & haematite (Fe₂O₃) and taken in furnace. The furnace is lined with silica or dolomite. The open hearth furnace is heated.

C and S are oxidized by haematite, Fe₂O₃ to CO and SO₂ while Mn, Si and P are removed as their slag.



Some quantity of charge is taken out from time to time and analyzed for carbon content. So carbon content is adjusted. Alumina and ferro silicone are added to remove dissolved N₂ and O₂. hence steel is manufactured.



Q. How open –hearth furnace process differs from Bessemer converter.

1. Impurities present in cast iron are oxidized by haematite and not by air as in Bessemer converter.

2. % of carbon and Si in charge is lowered by adding low grade wrought iron and scrap iron.

Q. Merits demerits of open –hearth furnace merits

1. The process is slower easy to work.
2. Temperature can be controlled as heating is done externally.

Samples can be examined from time to time. So composition and quality can be controlled.

In Bessemer process air is passed to oxidize some Fe as slag there is no loss of iron in open-hearth furnace.

Demerits :

The only disadvantage of open process is that the operation of this process completes in 5 to 10 hours in Bessemer process it takes only 20 minutes.

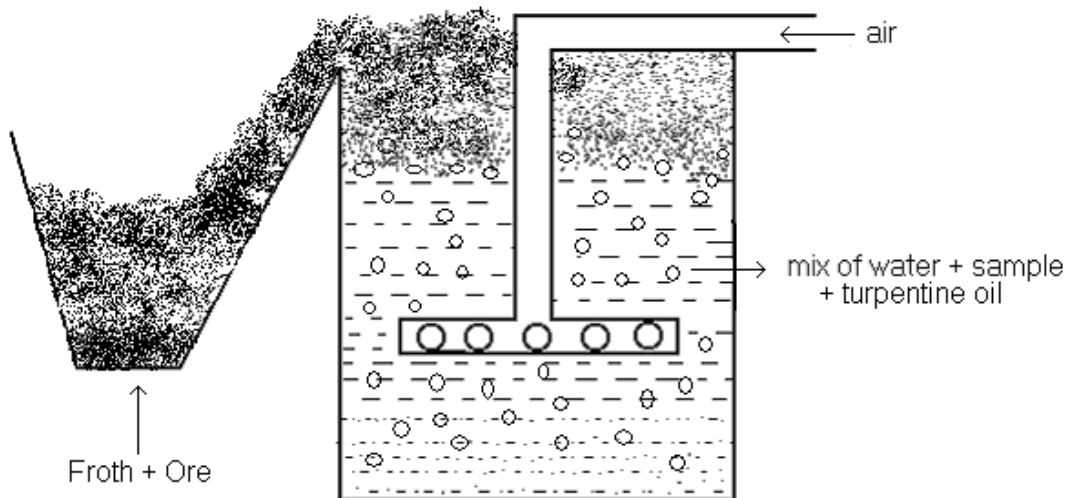
NICKEL METALLURGY

The chief ores of nickel are (1) smeltite [(Fe, Co Ni) As₂] (2) Kupfer nickel or nicolite, [NiAs] (3) pentlandite [(Ni, Cu, Fe)S].

nickel is mainly extracted from sulphide ores, i.e. pentlandite.

The process is carried out in the following steps.

[1] Crushing and Concentration : the pentlandite ore is crushed in big jaw crushers and then finely powdered in ball mills. The sulphide ore is then concentrated by using froth floatation process. The concentrated ore contains NiS, FeS and CuS as impurities.

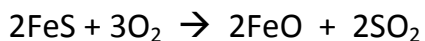
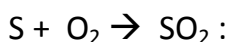


Froth formation process

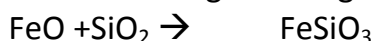
The ore containing sulphide is firstly concentrated by froth floatation process. The finely powered ore is taken into big tank. To this mixture of water and a small quantity of pine oil or turpentine oil and some additive salts are added. Then air is blown violently and whole mixture is agitated. It produces froth. The ore particles stick to oil particles. It is lighter than water coming on the upper surface from where it is collected in separate container. The impurities earthy sand rocky stone, mica etc are wetted by water, becomes heavier and settled down at the bottom of the tank. In this way ore is concentrated.

[2] Production of NiS: From concentrated ore FeS is removed by following steps.

1. Roasting : The ore is roasted in reverboratory furnace where by excess of S is oxidized as SO₂ and FeS is partly oxidized to FeO.



2. Smelting : The roasted mass is mixed with SiO₂, coke and some limestone and smelted in blast furnace. FeS is oxidized to FeO. FeO formed during roasting and smelting combines with silica and form slag.



At the same time, CaO combined with SiO₂ and form CaSiO₃ (slag)



Both FeSiO₃ and CaSiO₃ are slag and floats over the molten sulphides of Ni, Cu and Fe.

3. Bessemerization : The molten mass of sulphides of Ni, Cu, and Fe with a sufficient quantity of SiO is introduced into a Bessemer converter. A blast of hot air is passed under pressure. It oxidizes almost all S to SO₂ and FeS to FeO, which forms slag, FeSiO₃. The slag is removed and a sulphide of Ni, Cu and small quantity of Fe remains. The is known as matte.

[3] Recovery of Nickel : from matte nickel is obtained by following processes.

[I] Orford's Process : In this process, a separation of Cu and Ni is carried out by taking the advantage of

1. Difference in solubilities of Cu and Ni sulphides in Na₂S in which CuS is soluble in Na₂S.

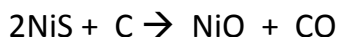
2. Difference in specific gravity between Cus and NiS containing dissolved CuS, the later is higher.

The matte is melted with NaHSO₄ and coke in a blast furnace. The coke reduces NaHSO₄ to Na₂S, which dissolves CuS in presence of NiS and Na

sulphides. The molten product is formed containing sulphides of Ni, Cu and Na. there are two layers of product.

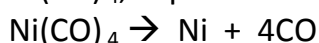
The upper layer is of Cu and Na sulphides and lower layer is of Ni, and Na sulphides. The upper layer of Cu – Na sulphide is lighter than Ni – Na sulphides, it is sent to cu-converter where cu is extracted and lower layer for Ni.

The lower layer is grounded and Na_2S is leached with hot water. The Cu is present in lower layer. So sulphide is calcinated with 15 % NaCl, it form CuCl_2 , which extracted with water. This NiS is converted to NiO.



[II] Mond's Process: The process makes the use of the formation and decomposition of $\text{Ni}(\text{CO})_4$, nickel tetrahedral carbonyl liquid (B.P.. 48.2°C) which decomposes at 180°C to Ni and CO.

NiS, CuS and FeS are roasted to NiO, CuO and FeO. The impure oxides are treated with water gas ($\text{H}_2 + \text{CO}$), at $250 - 350^\circ\text{C}$. At this temperature the hydrogen of water gas reduces, NiO and CuO to Ni and Cu, but FeO is not reduced. Now CO is passed over the product at 60°C , Ni forms volatile $\text{Ni}(\text{CO})_4$, Liquid.



The Ni – balls are remelted and cast into ingots Ni thus obtained is 99.9 % pure.

[4] Refining : Ni is further refined by electrolysis by a solution of nickel ammonium sulphate ($\text{NiSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$ saturated] at 25°C . A cast nickel black is used as anode and pure nickel as cathode. On passing electric current, impure nickel black dissolves and forms Ni^{+2} these ions moves towards cathode, reduces and deposited on cathode as Ni, Ag, Au and Pt are deposited below anode and anodic mud and obtained from this anodic mud.

INDUSTRIAL USES

Used in manufacturing of alloy.

Used in manufacturing of chemicals.

Used in Ni – Platimary

Used in manufacturing of Ni – steel.