

Unit: 7 Study of Heavy Metals

7.1 Copper

Occurrence of copper

Copper occurs in native as well as combined states. Native copper is found in the USA, Mexico, Russia and China. The common ores of copper are.

1. Chalcocite or copper glance (Cu_2S).
2. Cuprite or Ruby copper (Cu_2O).
3. Chalcopyrite or copper pyrites (CuFeS_2).
4. Malachite green [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$].
5. Azurite(blue)[$\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$]

In Nepal, copper occurs in free and as chalcopyrites in Chitwan, Mekanpur, Udaypur, Chisapani Gadhi.

Extraction of copper from copper pyrites (CuFeS_2).

Copper is mainly extracted from copper pyrite ore. The various steps involved in the extraction of copper from the copper pyrites ore are described below.

1. **Crushing and pulverization:** The collected big lump of ore is crushed in jaw crushers and then pulverized in ball mills. The powdered ore is then taken for concentration.
2. **Concentration:** The powdered ore is concentrated by the froth floatation method. The powdered ore is agitated with a mixture of pine oil and water in a floatation tank by blowing compressed air. The pure ore particles come to the surface with froths which are the skimmed off and impurities gangue particles settle down at the bottom. In this process, copeer content concentration is increased to 25-30 %.

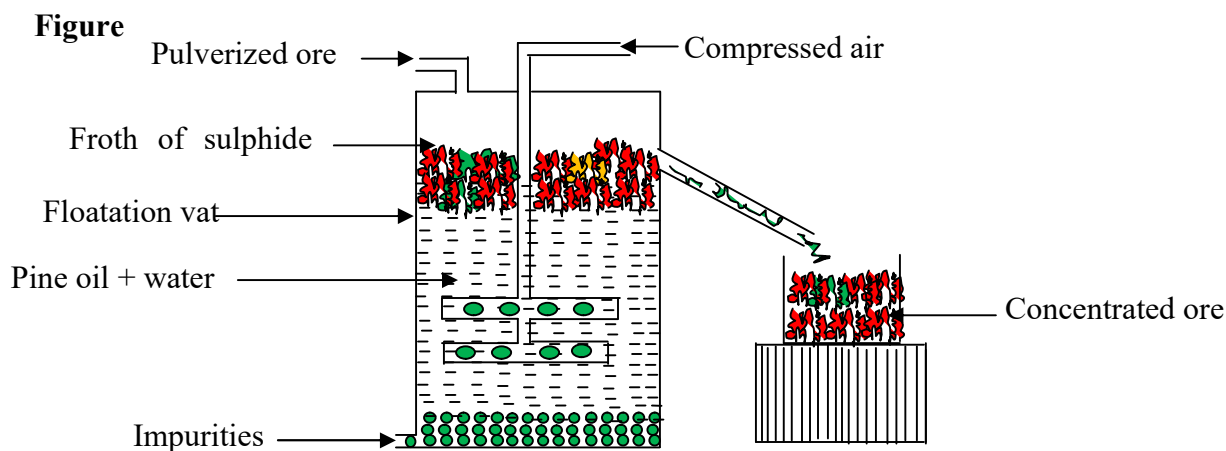
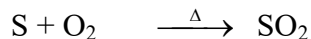
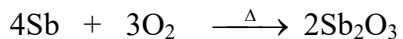
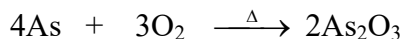
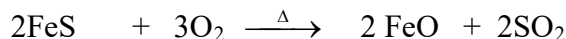
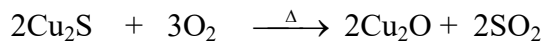
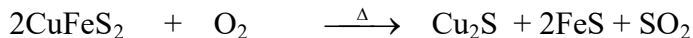


Fig: Froth floatation process

3. **Roasting:** The concentrated ore is heated strongly in the presence of air on the hearth of reverberatory furnace. In this process impurities like arsenic, antimony, sulphur etc are removed as their volatile oxides. Moisture and organic matters are removed.



The copper pyrite ore is partially converted into sulphides of iron and copper. Further sulphides are partially oxidized into cuprous oxide and ferrous oxides.



Therefore, roasted ore mainly contains a mixture of Cu_2O , Cu_2S , FeS and FeO .

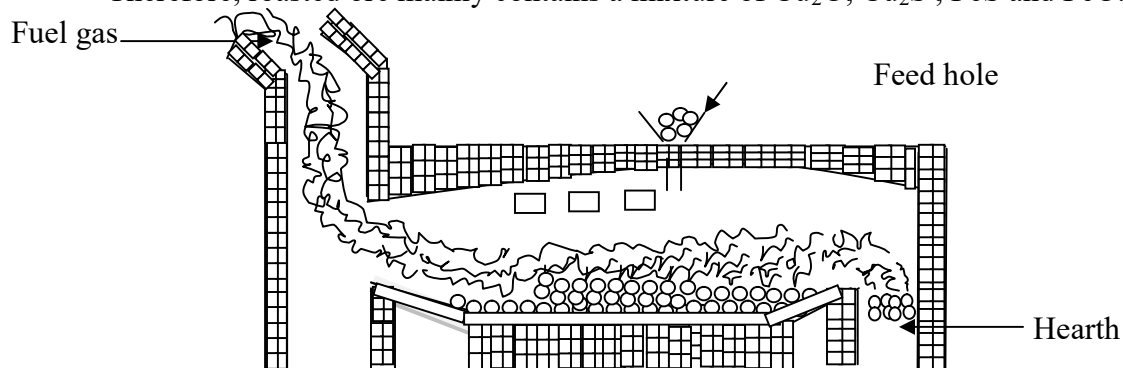
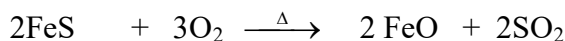


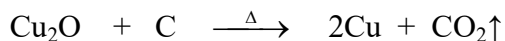
Fig. Reverberatory furnace

4. **Smelting:** The roasted ore is then mixed with powdered coke and sand and heated strongly in the blast furnace about 4.5 -6 meter high and 2 meter in diameter. It is made of steel lined inside with fire clay brick. Hot air at about 800°C is introduced from **tuyeres** near the base of the furnace. The coke burns and about 100°C is produced. Here, following changes occur.

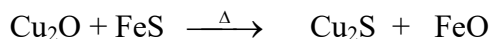
Ferrous sulphide and Cu_2S is oxidized into ferrous oxide



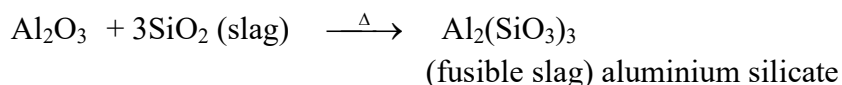
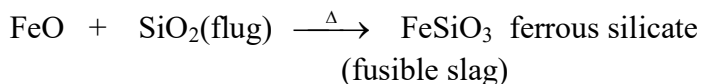
Some of cuprous oxides get reduced by coke



Some cuprous oxide again reacts with FeS to give back Cu_2S .



Alumina and iron oxide combine with silica to form fusible slag.



The slag being lighter floats on the surface forming a layer which is removed through the slag hole from time to time. The molten mass containing about 40-45% of metal, Cu_2S and some trace of FeS is called matte or coarse metal which forms lower layer in the blast furnace and is taken out from the tapping hole at the bottom.

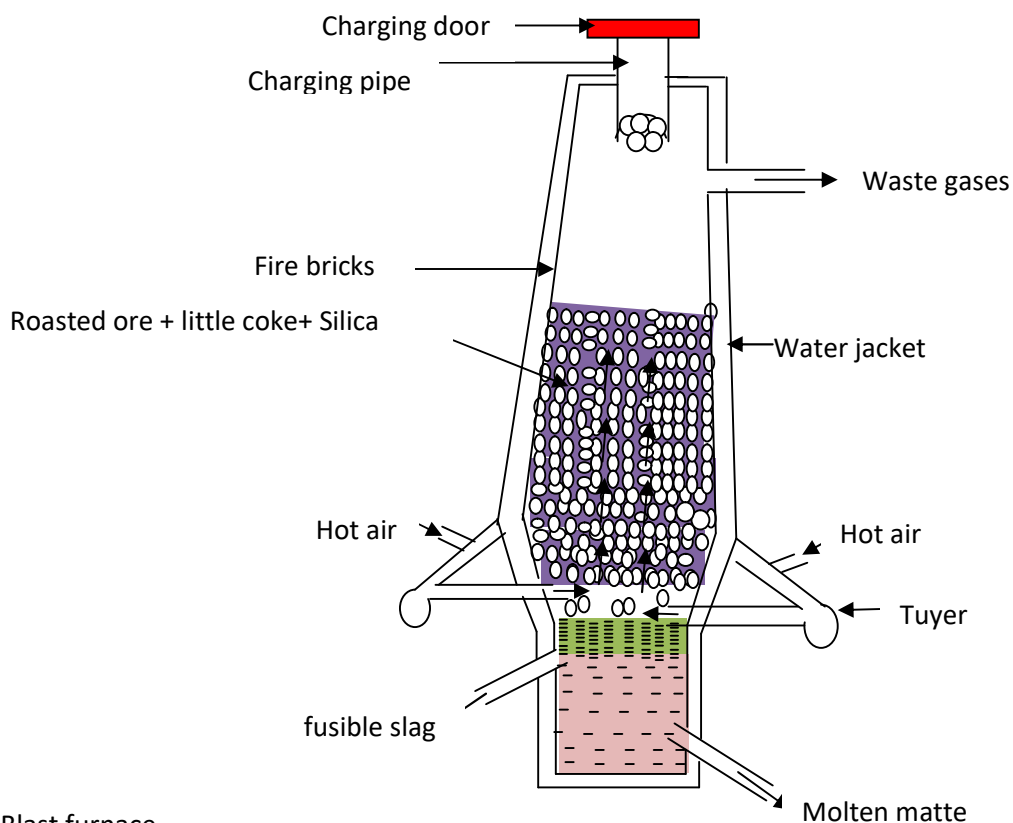
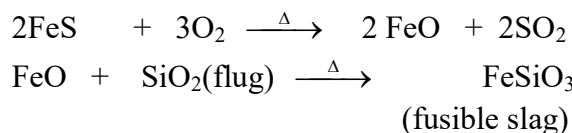
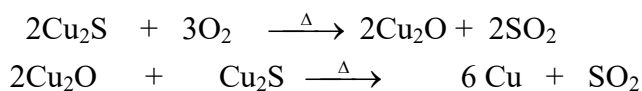


Fig. Blast furnace

5. Bessemerization: The matte is mixed with little silica and charged into a Bessemer converter. It is pear shaped steel furnace lined with refractory materials like silica, lime etc and is mounted on pivots so that it can be tilted. A blast of hot air is admitted through tuyeres from the base of the converter. FeS present in matte is oxidized to FeO which combine with silica to form slag.



Slag thus formed floats on the surface of the molten mass and removed. The copper sulphide undergoes oxidation to form cuprous oxide which reacts with copper sulphide to give metallic copper.



After completion of reaction, the converter is tilted and the molten metal is poured into moulds and cooled to escape dissolved gases. However, some of the gas bubbles are

entrapped during solidification giving blister appearance. Therefore, metal thus obtained is called blister of copper and it is 98% pure copper.

Figure.

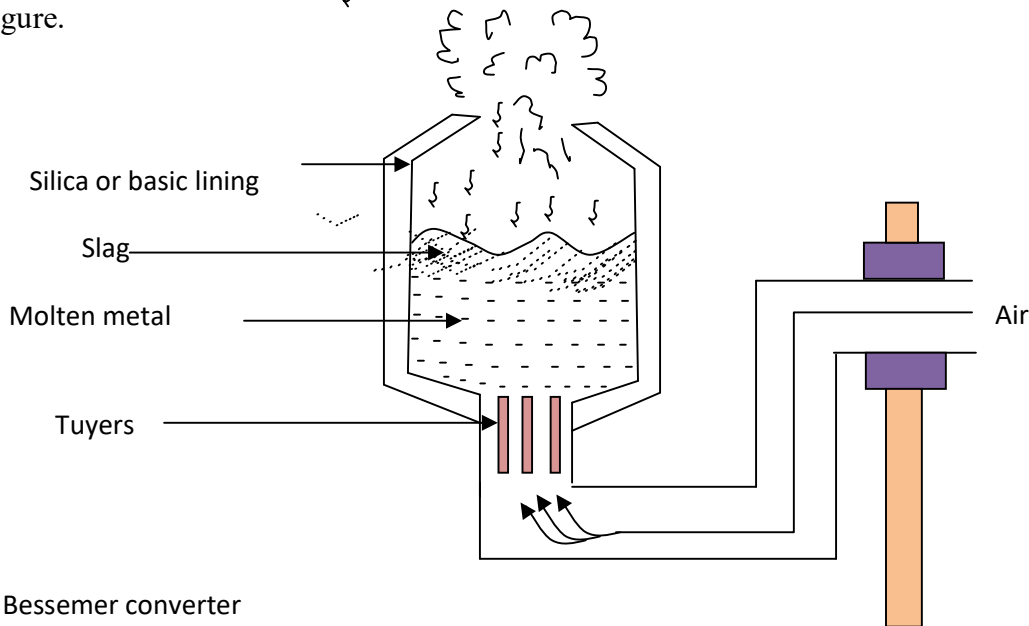


Fig. Bessemer converter

6. **Refining:** The metal crude metal is refined in following steps.

a).Bessemerisation: The molten metal is retaken in a Bessemer converter. The impurities are converted into slag and thus formed slag is removed

b).Poling: Remaining cuprous oxide is reduced back to copper by stirring the molten metal green poles of wood. The hydrocarbons present in these poles reduce the cuprous oxide to metallic copper. Copper thus obtained is 99.5 %.

c).electrolytic refining: In this method, a thin sheet of pure metal is made cathode and the block of crude metal is made anode. When an electric current is passed , impure copper from the anode goes in to solution and pure copper from solution gets deposited at cathode. The impurities like zinc, nickel, iron etc get collected below the anode as anode mud.

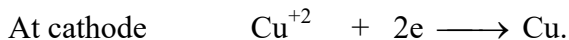
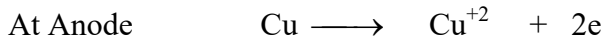
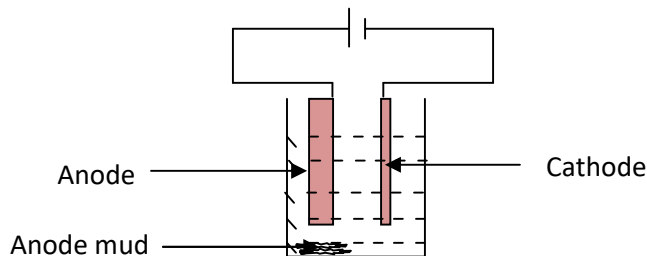
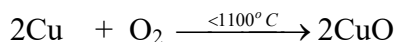
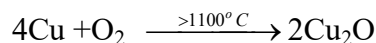


Figure.

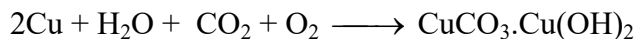


Chemical properties

1. **Action with air:** On heating in dry air, it forms cuprous and cupric oxide .



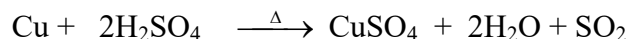
But in moist air and in presence of air, green basic carbonate is formed.



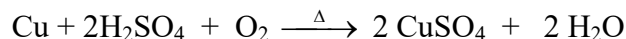
Basic copper carbonate.

2. **Action with acids:**

a). **Hot and conc H_2SO_4 :** On heating it with H_2SO_4 , copper sulphate, water and SO_2 is formed.

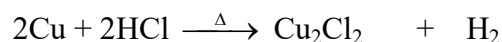


In dilute, it reacts in presence of air

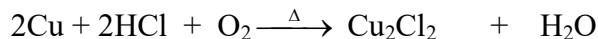


b). **Action with HCl:**

When HCl gas is passed over heated copper, Cu_2Cl_2 with hydrogen is formed.



In presence of oxygen



c). **Action with HNO_3 .**

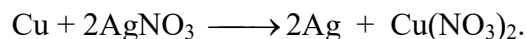
➤ **With hot & conc. HNO_3**



➤ **With dilute HNO_3**

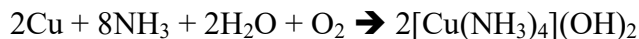


3. **Action with metal ions:** Copper can reduce some metal ions in their aqueous solution. It can displace metal lying below it in electrochemical series.



4. **Action with ammonia:**

Copper dissolves in aqueous ammonia in presence of air and gives deep blue complex compound.



(tetra amine copper (II) dihydroxide)

Uses of copper

1. It is used in electrical cable. Electrical appliances.
2. It is used in making utensils and containers.
3. It is used in electroplating.
4. Its compound nilo tutho is used as insecticide.

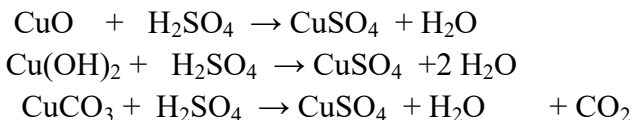
Compounds of copper

Copper Sulphate $CuSO_4 \cdot 5H_2O$

Pentahydrated copper sulphate $CuSO_4 \cdot 5H_2O$ is known as Blue vitriol and nilo tutho in Nepali.

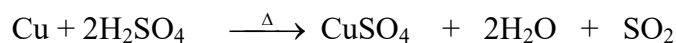
Preparation

- Lab preparation:** It can be prepared by reacting its oxide, hydroxide or carbonate with dil. sulphuric acid in the lab.



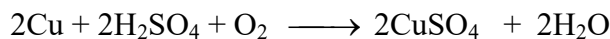
Thus formed copper sulphate solution is evaporated to form crystal of copper sulphate.

- It can be also prepared by the action copper with hot and conc. H_2SO_4 .

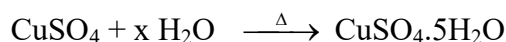


Manufacture

Copper sulphate is manufactured on large scale by heating scraps copper with dil. H_2SO_4 in presence of air.



From the solution of $CuSO_4$, crystals are obtained by concentrating and cooling.

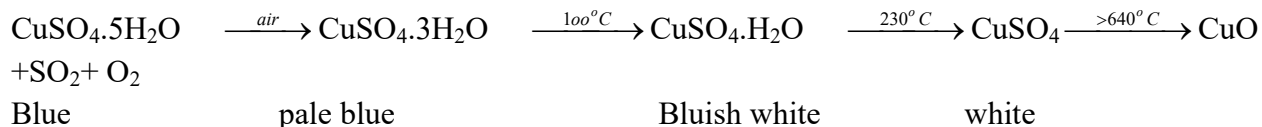


Properties

Physical properties

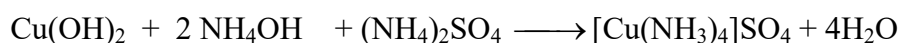
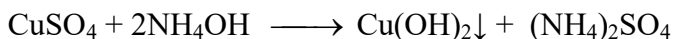
- It is blue crystalline solid.
- It is readily soluble in water.
- Its aqueous solution is slightly acidic in nature.
- Action with heat.

On heating, it loses water of crystallization in stages



Chemical properties

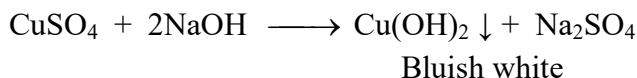
- Action with ammonia:** When ammonia is passed to $CuSO_4$ solution, bluish white ppt. of $Cu(OH)_2$ is seen and adding excess of ammonia, a deep blue coloration of soluble tetra amine copper (II) sulphate is observed.



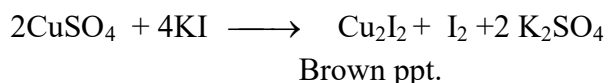
2. **Formation of double salt : copper sulphate forms double salts like** $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$



3. **Action with alkali:** Copper sulphate reacts with NaOH or KOH to give a bluish white ppt of cupric hydroxide.



4. **Action with KI:** $CuSO_4$ reacts with KI to form dark brown ppt. of Cu_2I_2 is formed.



Uses

1. In medicine as an antiseptic.
2. It is used in agriculture as fungicide and germicide.
3. It is used in electroplating.
4. It is used for manufacture of dyestuff or mordant in dyeing.

Black oxide of copper (CuO, cupric oxide)

Cupric oxide is commonly known as “black oxide of copper”

Chemical formula: CuO

Uses

1. It is used as oxidizing agent
2. It is used to prepare colored glass.
3. It is used to estimate carbon and hydrogen present in organic compounds.

Red oxide of copper (Cu₂O)

Chemical formula: Cu_2O

Uses.

1. It is used in glass industry to make red glass.
2. It is used as protective paint to avoid rusting.
3. It is used to prepare cuprous chloride.

18.2 Zinc

Occurrence

Zinc does not exist in free state and always is obtained in the combined state. Chief Ores of zinc are,

- | | |
|--------------------------|---|
| 1. Zinc blende | ZnS |
| 2. Calamine or zinc spar | ZnCO ₃ |
| 3. Zincite or red zinc | ZnO |
| 4. Willimite | 2ZnO.SiO ₂ or Zn ₂ SiO ₃ |
| 5. Franklinite | ZnO.Fe ₂ O ₃ |

In Nepal, Zinc is mainly found in Lari, Mailung Khola, Ganesh Himal, Todke, Phulchoki and Sisa dohan.

Extraction of zinc from zinc blende

The extraction of zinc from zinc blende is carried out by **carbon reduction process**. This process involves following steps.

- Crushing and pulverization:** The big lumps of ore are first crushed by jaw crusher into small pieces and then pulverized in ball mills. This process removes rocky materials from the ore.
- Concentration:** Concentration of powdered sulphide ore is done by froth floatation process. The ore is placed in a tank containing water and little pine oil where it is agitated by blowing blast of the air. The sulphide ores are preferentially wetted by oil and come along the surface as froth which are skimmed off. The impurities are preferentially wetted by water and will remain at the bottom of the tank.

Figure

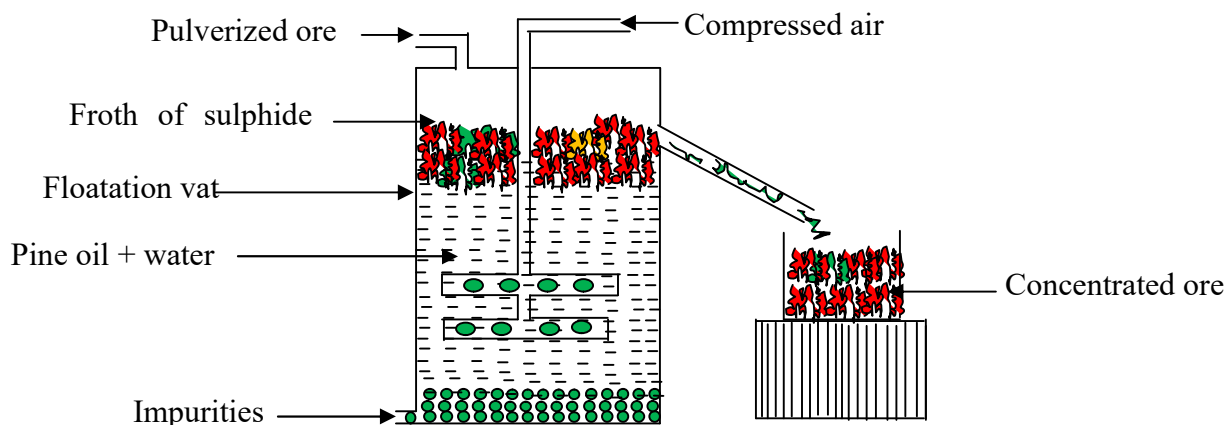
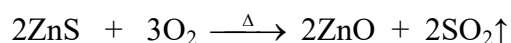
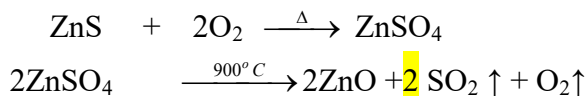


Fig: Froth floatation process

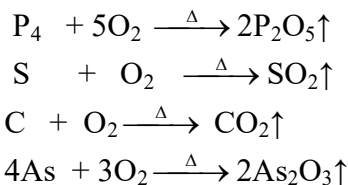
- Roasting:** The concentrated ore is then roasted in a reverberatory furnace at about 900°C in presence of excess of air where sulphide ore gets converted into the oxide.



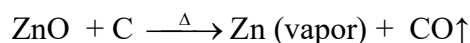
During this process, some of the ore may get converted into zinc sulphate which later decomposes at 900°C to zinc oxide.



In this process, impurities like S, P, As, Sb etc are removed as their volatile oxide.



4.Reduction (Smelting): The roasted ore and coke are mixed in 2:1 ratio and are made into small briquets which are then fed in to retort **furnace** through the charging door. The retort is heated externally to about 1400°C by burning producer gas in the heating jacket and the Zinc oxide is reduced to zinc which gets converted in to vapor form.



The vapor zinc and CO is carried out in the condenser by mild current of producer gas passed to the retort from the bottom. The zinc obtained from condenser after release of volatile impurities is called spelter zinc. The residual waste materials are taken out from the bottom by roll-discharge mechanism

Figure

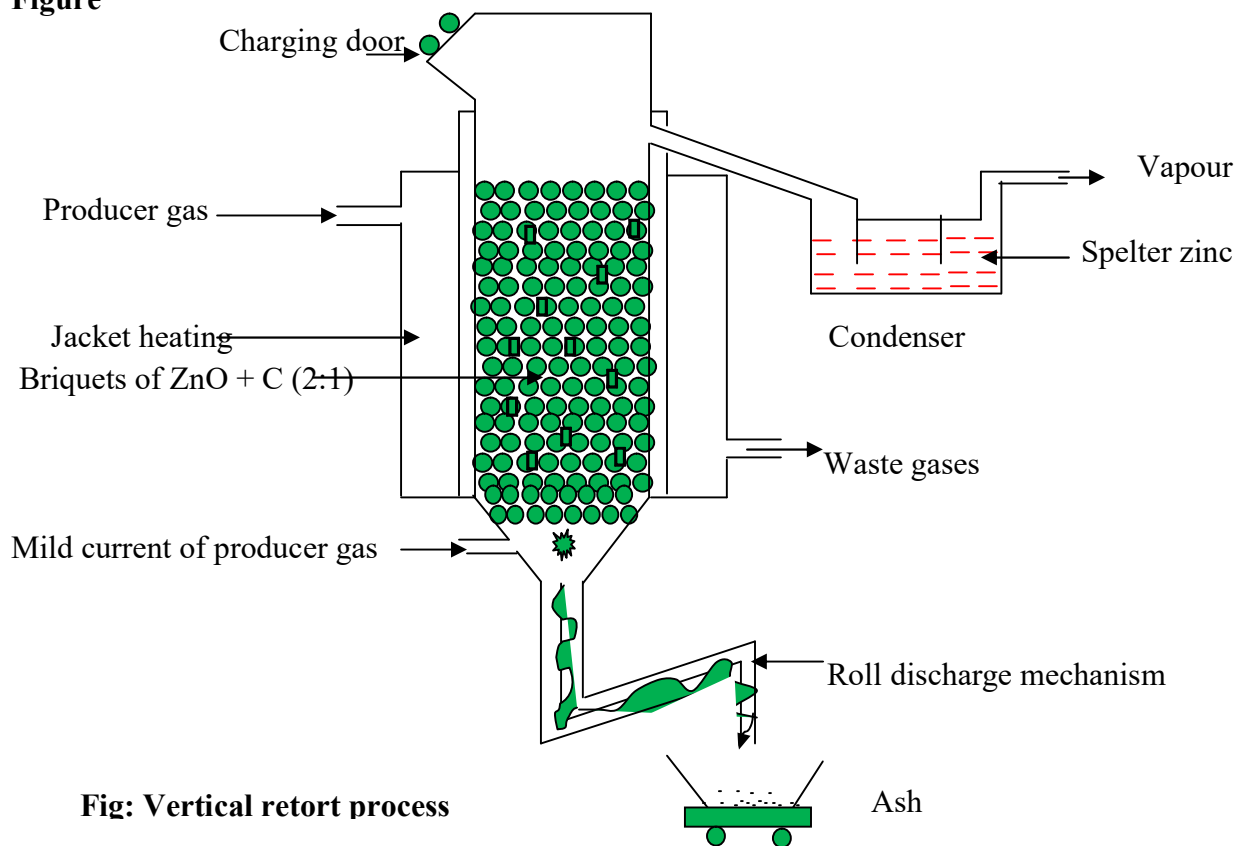


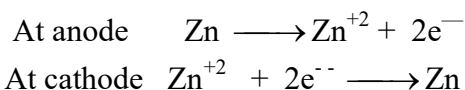
Fig: Vertical retort process

5. Refining (purification): The zinc thus obtained contains impurities like Pb, Fe, Cd, As, Sb etc. These impurities are removed from the crude zinc by following methods.

a). **Liquafication:** In this method, Impure zinc metal is melted on the slopping hearth of a reverberatory furnace. the molten zinc flows down while non-fusible impurities are left behind.

b). **Fractional distillation:** the impurities like lead and iron have higher b. p. (1620°C & 3000°C respectively) than that of zinc (907°C) while cadmium has lower b.p. (767°C) than Zinc. When crude zinc is distilled at 1000°C , zinc and cadmium distilled off first and further redistillation of distillate at about 800°C , only cadmium is distilled off leaving behind zinc.

c). **Electrolytic refining:** In this method, thin pure zinc metal is made cathode and the sheet of impure metal is made anode. When electricity is passed, the pure metal gets deposited at cathode and other impurities remain at the bottom of anode as anode mud. After this process, 99.5% pure zinc is obtained.



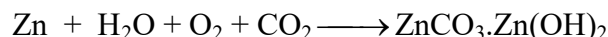
Properties

Physical properties

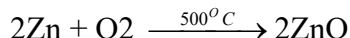
1. It is bluish white metal.
2. Its m.p. is 420°C and b. p. is 907°C .
3. It is good conductor of heat and electricity.
4. It is somewhat brittle at ordinary temp. but malleable and ductile at 100°C - 150°C .

Chemical properties

1. **Action with air:** Dry air can't affect zinc but it gets tarnished in the moist air due to formation of film of basic zinc carbonate.



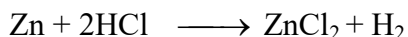
On heating up to 500°C , it catches fire and forms ZnO



2. **Action with acids**

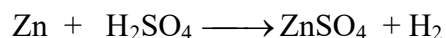
With HCl:

Zn reacts with HCl to give Hydrogen gas.

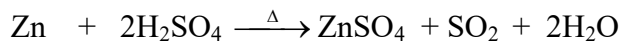


With H₂SO₄:

In case dil. H₂SO₄: Hydrogen gas is produced

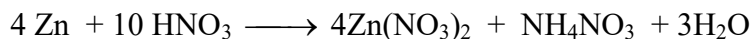
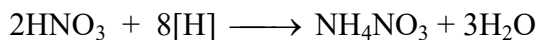
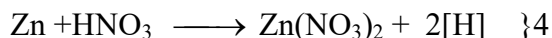


On heating with conc. H₂SO₄: It evolves sulphur dioxide gas

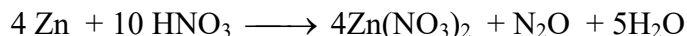


With HNO₃

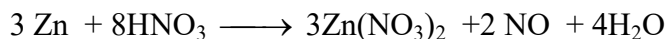
With very dil. HNO₃:



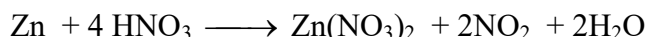
With dilute HNO₃



With moderately conc. HNO₃



With hot and conc. HNO₃

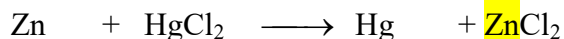
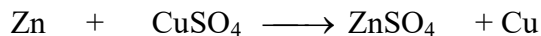


3. Action with alkali: On heating with caustic alkali, hydrogen gas is evolved.



4. Displacement reaction:

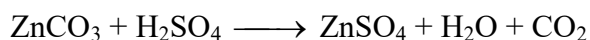
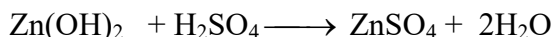
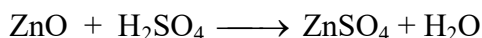
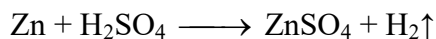
Zn can displace copper and mercury from their salt solution.

**Uses of Zinc**

1. It is used for galvanization.
2. It is used as electrode.
3. It is used in lab for preparation of H₂ gas.
4. It is used in preparation of alloy like brass (Zn +Cu).

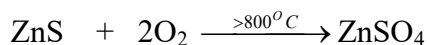
Compounds of Zinc**White Vitriol ZnSO₄·7H₂O****Preparation**

1. It can be prepared by the action of dil. H₂SO₄ on zinc, zinc oxide, zinc hydroxide and zinc carbonate.



On crystallization, crystals of zinc sulphate can be obtained as ZnSO₄·7H₂O

- It can be prepared by heating zinc blende with excess air at moderate temperature.



Thus obtained zinc sulphate is dissolved in water to get its saturated solution, evaporated upto crystallization point and crystals are collected as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

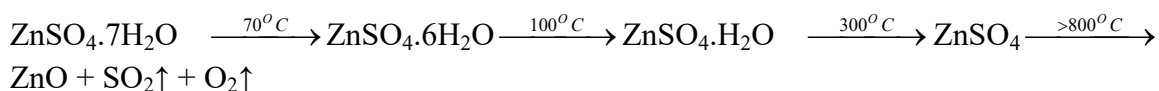
Properties

Physical

- It is colorless crystalline solid.
- It is soluble in water.

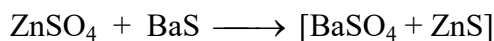
Chemical properties:

- Action with heat: white vitriol losses successive number of water molecules on heating and finally gets decomposed

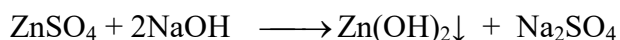


- Action of BaS:**

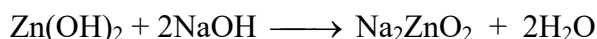
When ZnSO_4 is treated with BaS, double salt called Lithophone



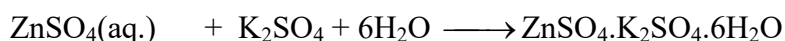
- Action with NaOH: White ppt. of zinc hydroxide is formed.



Excess of NaOH forms sodium zincate



- Action with K_2SO_4 : When it mixes with equimolar mixture of K_2SO_4 .



Uses of white vitriol

- It is used in medicine as an eye lotion.
- It is used in the manufacture of lithopone.
- It is used in preserving hides.
- It is used in preparation of other compounds of zinc.

7.3 Mercury

Latin name: Hydragyrum (Hg)

Occurrence:

- i). It occurs in small quantity in free or native state.
- ii). It occurs mainly as sulphide ore called cinnabar(HgS).

Extraction:

Mercury can be extracted from its sulphide ore i.e. from cinnabar and involves following steps

1.Crushing and Pulverization: The ore is first crushed in the jaw crusher and then powdered in ball mills.

2.Concentration: The powdered ore is concentrated by the froth floatation process. In this process, the ore is mixed with water containing a little pine oil in a big tank and agitated by blowing blast of air. The ore particles come to surface along with froth and is skimmed off.

Figur

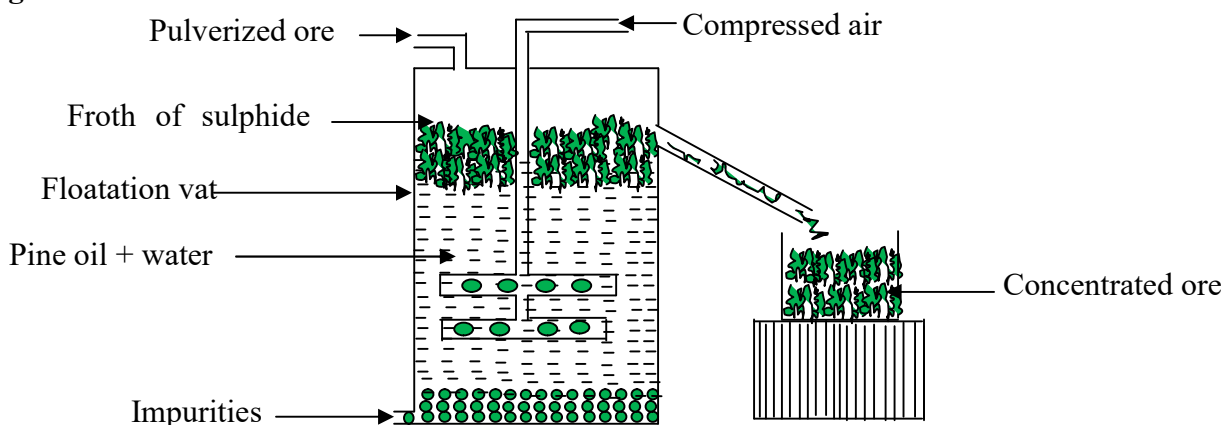
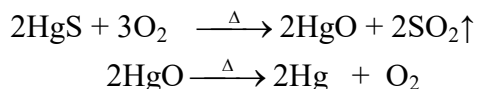


Fig: Froth floatation process

3.Roasting and distillation: The concentrated cinnabar is then subjected to a combined process of roasting and distillation. Roasting is done in modern plant called “Shaft furnace” where charcoal and lime are mixed with the concentrated ore and then heated by the current of air at about 500°C-600°C. Here, mercuric oxide is formed and further decomposed to mercury and oxygen.



The mercury vapor along with gas comes out from the furnace and is cooled in water pipes where mercury vapour gets condensed and settle down at the bottom of the reservoir.

Figure

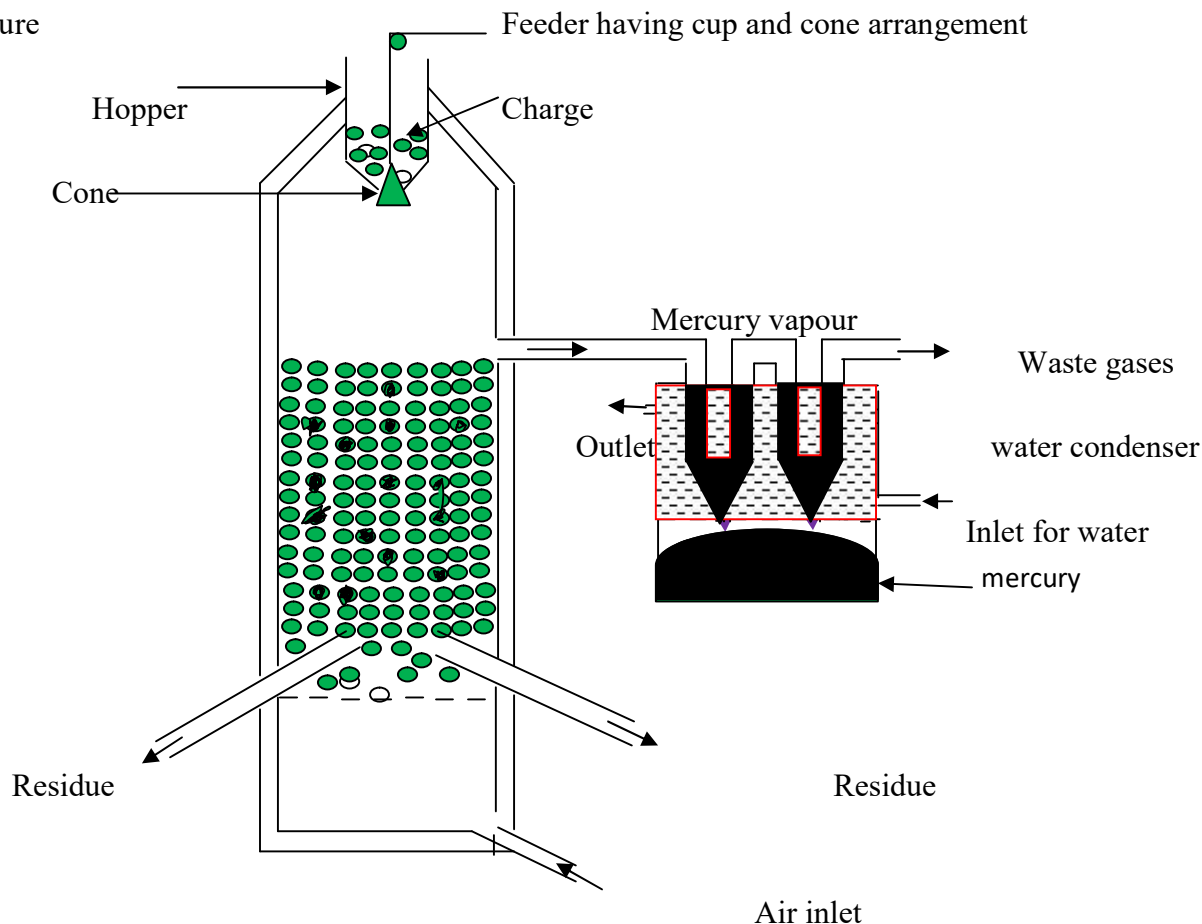


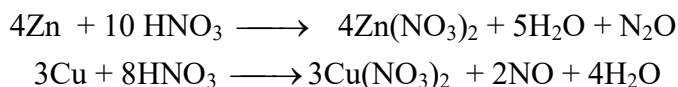
Fig: Shaft furnace

Advantages of modern process

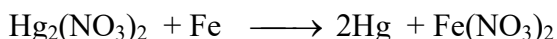
- i). It is continuous.
- ii). Loss of mercury vapor is very small.
- iii). Cinnabar of all grades can be employed.

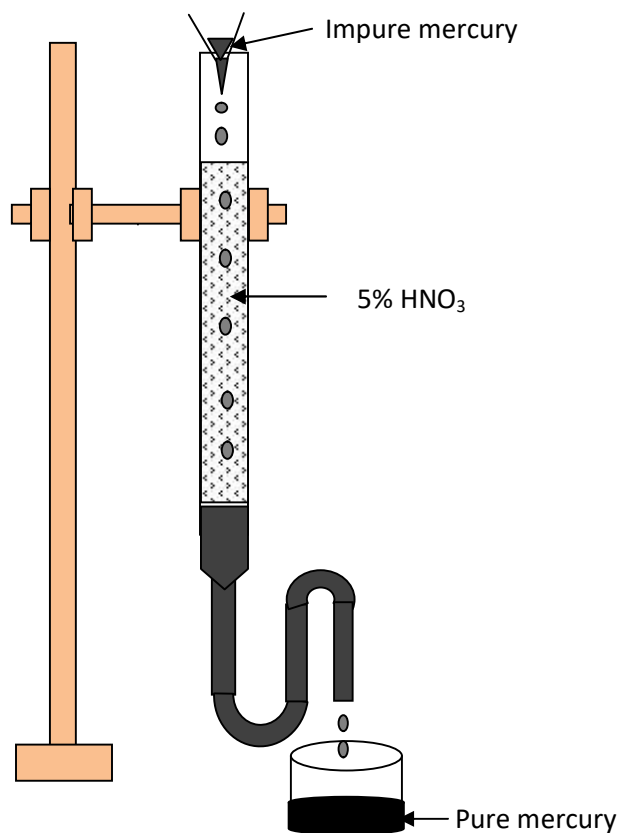
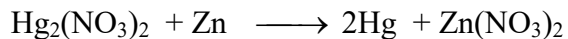
4. Purification: Mercury thus obtained is not pure and contains copper, zinc, bismuth and lead as impurities. Purification is carried out in following steps.

- a). Filtration: Certain metals present in crude mercury are partially oxidized in the air and form very thin layer of oxide on the surface which is removed by filtration through chamois leather.
- b). Treating with dil. HNO₃: Mercury containing impurities like Cu, Fe, Zn etc is allowed to drop through a tube containing 5% nitric acid solution where impurities metals form their nitrate leaving pure mercury.



If any mercurous nitrate is formed reacts with metal impurities to give back mercury.





c) Distillation: The mercury thus obtained even may contain Au, Ag , Pt etc. as impurities. These are removed by distillation under reduced pressure.

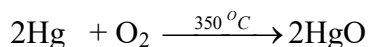
Properties

Physical properties

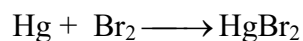
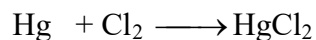
1. It is silvery white liquid.
2. Its melting point is -38.4°C and b.p. is 357°C .
3. It is a very heavy metal with specific gravity.
4. It is very good conductor of heat and electricity.

Chemical properties

1. **Action with air:** At ordinary temperature, mercury doesnot react with air but on heating , it gives mercuric oxide.

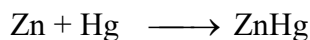
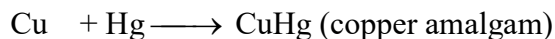


2. **Action with halogens:** Mercury readily combines with halogens to form halide.



3. **Action with metals (amalgam formation):**

Except Fe and Pt, all metals form alloys with mercury known as amalgams.



4. Action with acids

With H_2SO_4

Dilute H_2SO_4 does not affect mercury but conc. H_2SO_4 gives mercuric sulphate.

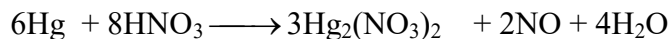


With HCl

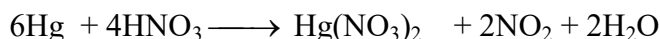
Mercury is not affected by dilute and conc. HCl

With HNO_3

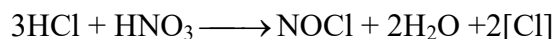
with dil. HNO_3



With conc. HNO_3



5. Action with aqua regia:



Uses of mercury

1. It is used in thermometer and in barometer.
2. It is used in preparation of amalgam.
3. It is used in ayurvedic medicine as “Para Vasma”
4. It is used to prepare alloy.

Poisoning of mercury

Mercury vapor is poisonous and if inhaled can cause giddiness, tremors, lungs damage and brain damage. Inorganic mercurous salt and organic mercury compounds are extremely poisonous. Ary or alkyl mercury compounds are so poisonous that they can cause brain damage, deafness and even death.

Pollution

Mercury passes into environment by burning of fossil fuels like coal. Large number of mercury disperses from alkali industry and agriculture industries. Mercury thus dispersed from industries into water and atmosphere undergoes translation in plants and animals and finally goes to human body through food and water.

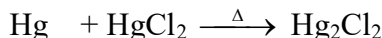
Compounds of Mercury

Calomel (Hg₂Cl₂)

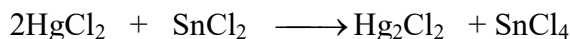
Mercurous chloride is commonly known as 'Calomel'

Preparation

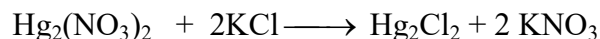
1. By heating HgCl₂ with Hg



2. It is prepared by heating HgCl₂ and SnCl₂.



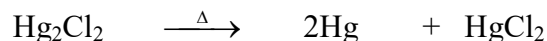
3. By treating soluble chloride with mercurous nitrate solution.



Properties

Physical properties

1. It is colorless amorphous substance.
2. It is insoluble in water and sublimes off on heating.
3. It is decompose on heating

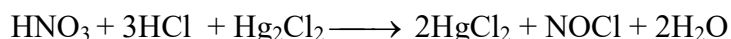


Chemical properties

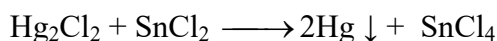
1. Action with ammonia: It reacts with ammonia solution to form black ppt of metallic mercury plus mercuric amino chloride.



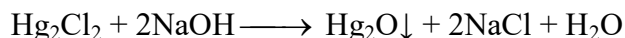
2. Action with aqua regia: It dissolves in aqua regia to form soluble mercuric chloride(HgCl₂)



3. Action with SnCl₂: It reacts with aqueous solution of SnCl₂ to form grey ppt.



4. Action with NaOH: Mercurous chloride reacts with NaOH or KOH to form mercurous oxide.



Uses of Hg₂Cl₂

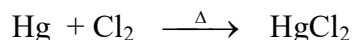
1. It is used in purgative medicine.
2. It is used as calomel electrode.

CORROSIVE SUBLIMATE (HgCl₂)

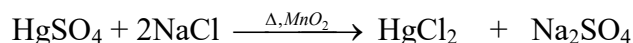
Mercuric chloride is commonly known as corrosive sublimate

Preparation:

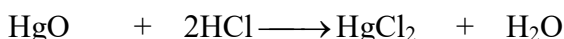
1. It is prepared by heating mercury with excess chlorine.



2. It is prepared by heating mercuric sulphate with sodium chloride.



3. It is also prepared by treating HgO with dilute HCl.

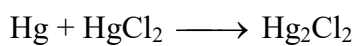


Properties

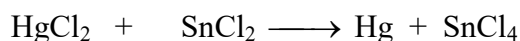
1. It is white crystalline solid.
2. It is sparingly soluble in cold water but soluble in hot water.
3. It is poisonous compound.

Chemical properties:

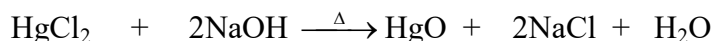
1. Action with mercury: When it reacts with mercury, it forms mercurous chloride.



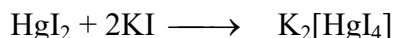
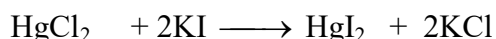
2. Action with SnCl₂: HgCl₂ gets reduced when treated with SnCl₂



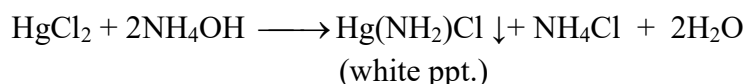
3. Action with alkalis: on heating HgCl₂ solution with caustic alkali, a yellow ppt of mercuric oxide appears.



4. Action with KI solution: when HgCl₂ solution is treated with KI solution, a scarlet ppt of HgI₂ is formed which dissolves in excess KI solution to give Nessler's reagent.



5. Action with ammonia: it reacts with ammonia to give white ppt. of mercuric amino chloride.



Uses

1. It is used to prepare Nessler's reagent.
2. As a preservative of timber, hides and fur.
3. As an antiseptic to sterilize surgical instrument.
4. As a fungicide in agriculture.

7.4 Iron

Occurrence

Iron is the fourth most abundant element in the earth crust. It rarely occurs in Free State due to its high reactivity nature. The most important ores of iron are,

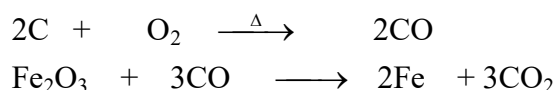
- i). Haematite, Fe_2O_3
- ii). Magnetite , Fe_3O_4
- iii). Iron pyrite , FeS_2
- iv). Limonite, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
- v). Siderite or Spathic ore, FeCO_3 .

Extraction of Iron from haematite ore

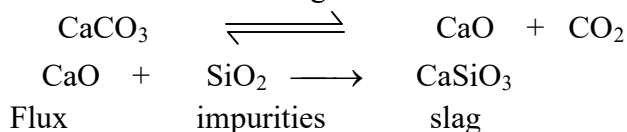
Cast iron is manufactured from haematite ore

Principle

The oxide ore is heated with coke and limestone where haematite ore gets reduced to iron



Silica and other impurities present in the ore react with calcium oxide (flux) obtained from limestone and removes as slag in the form of molten calcium silicate.

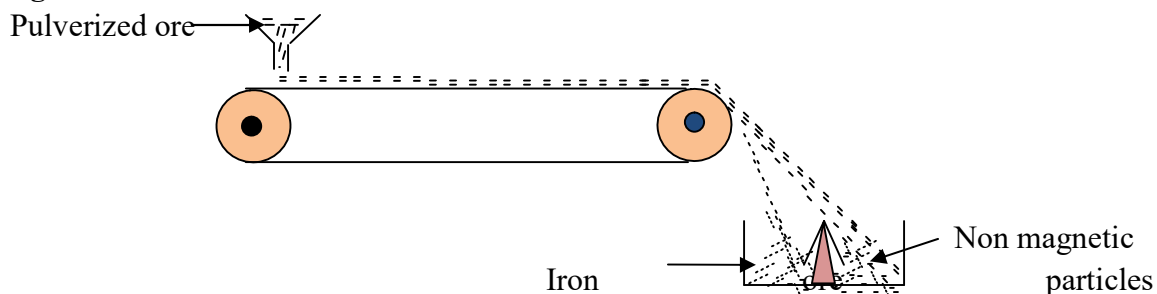


Metallurgical process

Various steps involved in the extraction of iron from haematite ore are

1. **Crushing and pulverization:** The collected big lump of ore are crushed in jaw crushers and then pulverized in ball mills. The powdered ore is then taken for concentration.
2. **Concentration:** The crushed ore is washed with steam or cold water. Lighter impurities are removed and heavy ore settles at the bottom. The washed ore is then concentrated by electromagnetic separation where impure magnetic ore and non magnetic impurities like sand are separated.

Figure

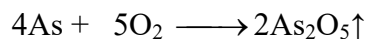
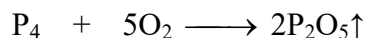
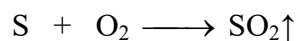
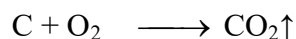
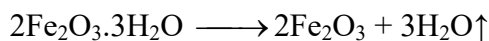


impurities

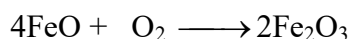
Fig: magnetic separation

3. Roasting or calcinations: The concentrated ore is then heated with a little of carbon in a reverberatory furnace in excess of air (roasting). The main changes in the roasting are,

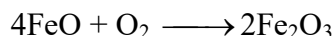
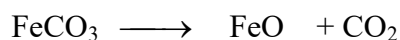
i) Moisture, carbon, sulphur, phosphorous and arsenic are removed as their oxides



ii). Ferrous oxide is changed into ferric oxide.



iii). Iron carbonate if present also decomposes to FeO which is further converted to Fe₂O₃.



In addition to chemical changes, this process makes the ore porous, thus making the ore more suitable for reduction to metallic iron.

4. Smelting: The calcined or roasted ore is mixed with coke and limestone and is then taken for smelting where iron oxide gets reduced to metallic iron. Smelting is carried out in a **blast furnace**.

Blast Furnace

The blast furnace is a tall cylindrical vessel made of steel with inner lining of fire proof bricks and is 80 to 120 feet in diameter. The top part of furnace has a cup and cone arrangement through which the charge is automatically introduced. A blast of hot air which is pre-heated to around 700 °C is forcefully introduced from the lower part of the furnace through tuyers. Base of the furnace contains two holes-one for drawing out of slag and another for the molten metal while upper part is provided an out let for the exit of waste gases.

Figure:

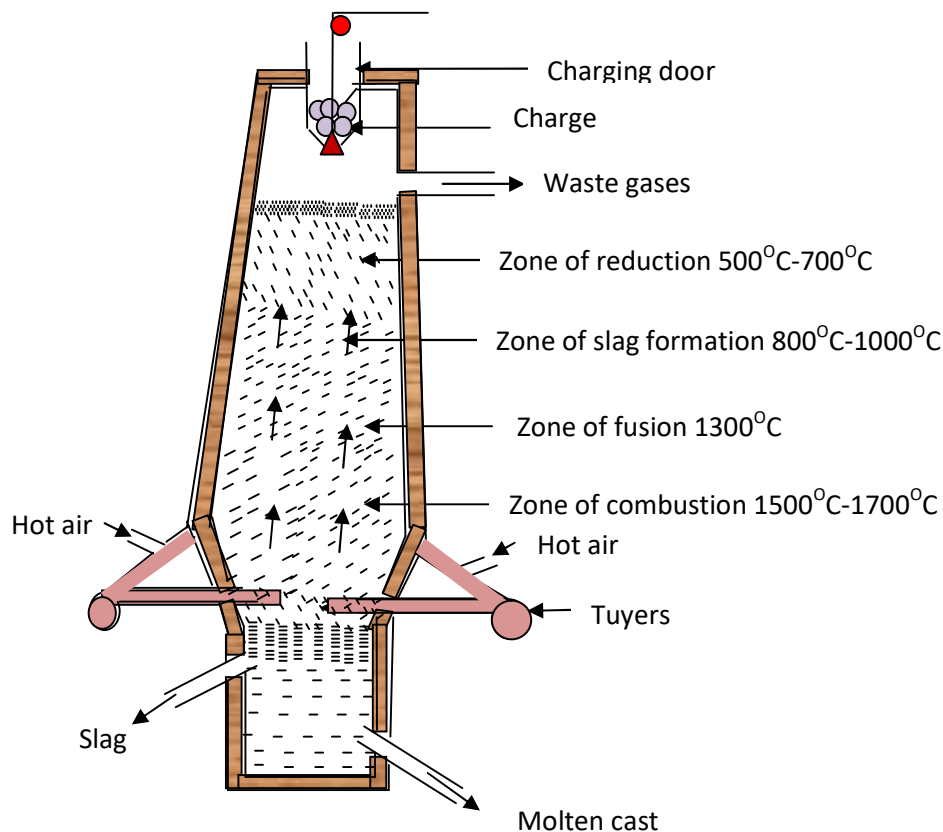


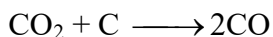
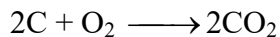
Fig. Blast furnace

Reactions inside the blast furnace

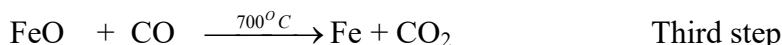
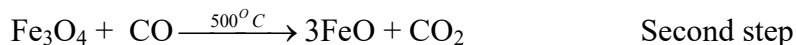
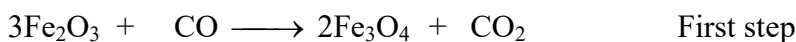
As the charge moves down, It passes through different temperature zones where various chemical changes takes place. The different zones are,

a).Zone of Preheating: This is the upper most part of the furnace where temperature ranges from 300°C-400°C. In this zone, moisture and other waste gases are removed.

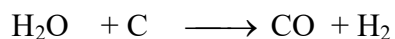
b). Zone of reduction: In this zone, temperature range is 500°C-700°C. Iron oxide obtained from roasting is reduced to spongy iron by CO as formed by burning of coke.



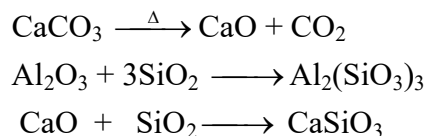
Reduction of iron oxide occurs in following steps



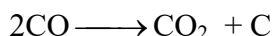
Any moisture and nitrogen present give CO and cyanogens



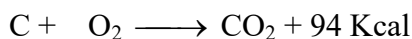
c). Zone of slag formation: In this zone, temperature ranges from 800°C-1000°C where limestone is completely decomposed to give CaO and CO₂. CaO acts as a flux and combines with silica and alumina present as impurities in the ore and form fusible slag.



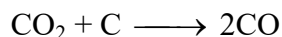
d).Zone of Fusion:The spongy iron formed in the reduction zone fuses into molten iron in this zone.The molten iron absorbs carbon, phosphorous , silicon and sulphur. The spongy iron meets upcoming CO and decomposes part of CO to CO₂ and C.



e).Zone of combustion: It is the hottest region of furnace in which pre-heated air comes in contact with falling coke along with oxide ore. Carbon burns to produce CO₂.



As the reaction is exothermic, temperature reaches up to 1500°C-1700°C. Thus formed CO₂ moves up, combines with the layers of hot coke and get reduced to CO.



At the end of smelting, molten slag settles down and floats over the molten iron on the base of the furnace. The molten slag and molten iron are taken out from the separate outlets. Thus obtained molten iron is called pig iron and is re-melted in the vertical furnace and cast into mould. Therefore it is also called cast iron.

Varieties of commercial Iron

i).Cast or Pig iron: It contains 2.5%-4.5% of carbon and small quantities of sulphur, phosphorous, manganese and silicon. It is granular and very brittle. Its melting point is 1227°C and solidifies with expansion. It is used to prepare stove, pipes, toys. Radiator etc.

ii).Wrought iron: It is the purest form of commercial iron containing 0.12% to 0.25% carbon and less than 0.25% of the other impurities like S,P,Si, Mn etc. It is soft, grey and tough. It is fibrous in structure, malleable and ductile. It is prepared by heating cast iron in a reverberatory furnace lined with iron oxide.Its melting point is 1500°C.

iii).Steel:It is the intermediate form of iron between cast and wrought iron and contains 0.25%-2.0% of carbon along with traces of S, P, Si, Mn etc as impurities.It may be malleable or brittle and its hardness varies with carbon content. Its melting point is 1300°C-1400°C.

Properties of iron

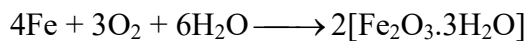
Physical properties

1. Pure iron is soft white solid but ordinary iron is grayish crystalline solid.
2. It is malleable and ductile.

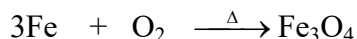
- Its m.p. is 1525°C and b.p. is 2450°C .
- It is good conductor of heat and electricity.

Chemical properties

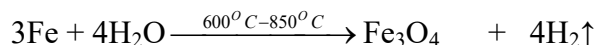
1.Action with air: it is not affected by dry air at normal temperature but gets rusted in moist air.



On heating strongly with air, it forms ferro-ferric oxide.



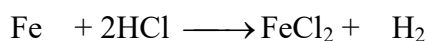
2.Action with water: It is not attacked by water at normal condition. On heating at $600\text{-}850^{\circ}\text{C}$, it reacts with water vapour releasing H_2 gas.



3. Action with acids

i).With dil. And conc. HCl

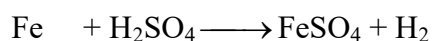
It gives H_2 gas with dil. And conc. HCl



ii). With H_2SO_4

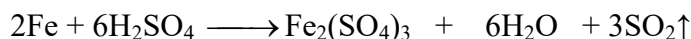
with dilute H_2SO_4

Iron reacts with dil. H_2SO_4 to give H_2 gas.



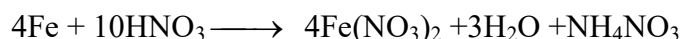
With conc. H_2SO_4

It gives ferric salt with SO_2 gas

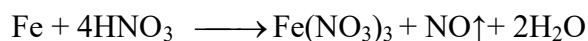


iii). With HNO_3

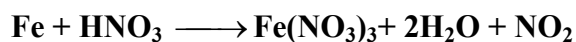
With dil. HNO_3



With Moderately conc.



With conc. HNO_3

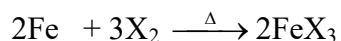


5. Action with alkalis

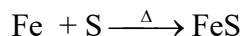
It does not reacts with alkalis

6. Action with halogens

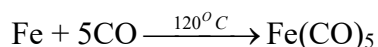
On heating, Fe combines with halogens to give halides



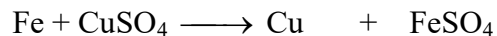
7. Action with sulphur: When iron is heated with sulphur, ferrous sulphide is obtained.



8. Action with CO: On heating Fe with CO at about 120°C , it forms iron carbonyl.



9. Action with CuSO_4 solution: Iron can displace copper from CuSO_4 solution.



Uses of iron

1. It is used for construction
2. It is used in household utensil.
3. It is used in alloy.
4. It is used in medicine.

Manufacture of Steel

Steel is intermediate form of pig iron and wrought iron. Therefore, it is manufactured either by adding carbon to wrought iron or by removing some carbon present in pig iron. Steel can be manufactured by any of the following process.

- a). Bessemer process
- b). Open hearth process.

A). Bessemer process

Figure

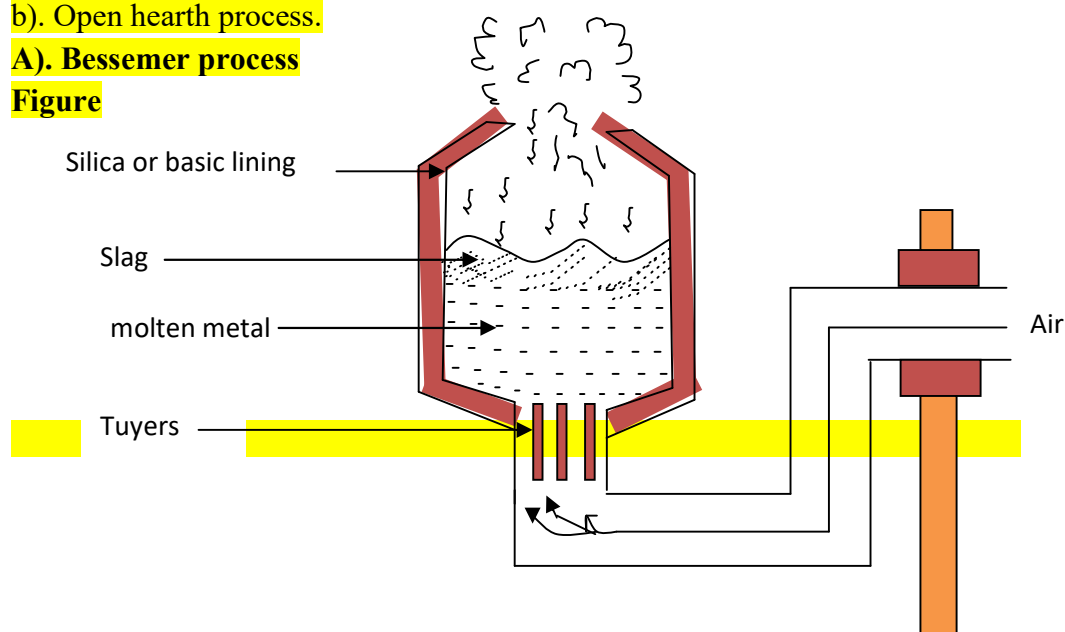
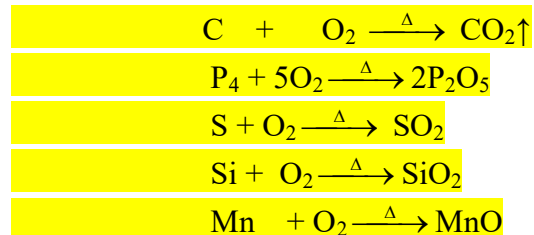
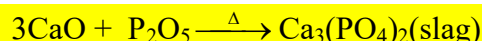
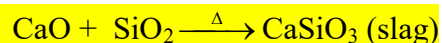
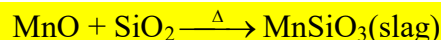


Fig: Bessemer converter

Steel is manufactured in a pear shaped furnace called Bessemer converter made of steel with the internal lining of basic substance (MgO or CaO) or acidic substance (SiO₂) depending upon the nature of impurities present.

In this process molten cast iron is poured into the furnace and a blast of hot air is passed into the furnace from its bottom so as to maintain temperature 1600^oC where impurities are oxidized.





After removing all impurities as volatile oxides and slag, pure iron is obtained which then is converted in to steel by pouring required amount of carbon in the form of spiegeleisen (an alloy of Fe, Mn and C) and after few minutes, steel is poured out by tilting the converter.

Merit:

It is a very rapid process.

Demerit: It is difficult to control and fine quality of steel can't be produced.

a. Basic Oxygen method:

b). Open hearth process

In this process, a mixture of molten cast iron, scrap iron(wrought or other) and hematite ore is taken in an open hearth furnace with the internal lining of basic(MgO or CaO) or acidic (SiO₂) substance depending upon the nature of impurities present and then hot gas is passed into the furnace where reaction occurs as

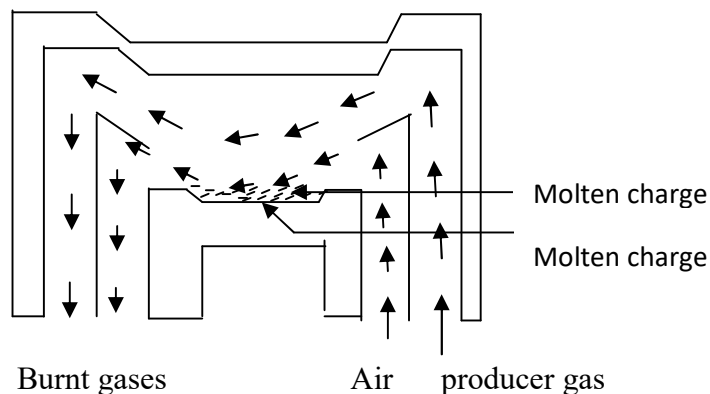
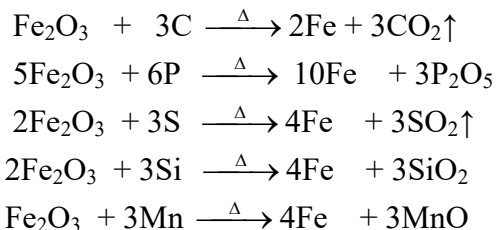


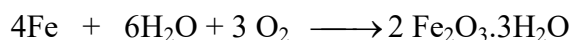
Fig: open hearth furnace

Rusting (Corrosion) of iron and its prevention

Rusting (Corrosion)

The phenomenon of the formation of amorphous brown scale of hydrated oxide of iron on its surface in the presence of air and moisture is called rusting of iron.

When iron comes in contact with moist air, the surface of the iron slowly gets converted to rust, a mixture of ferric hydroxide and ferric oxide $\text{Fe}(\text{OH})_3 \cdot \text{Fe}_2\text{O}_3$ or $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.



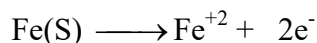
Theory of rusting

Various theories have been developed to explain the mechanism of rusting but electrochemical theory is quite important among them

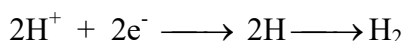
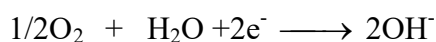
Electrochemical theory

When impure iron comes in contact with water containing dissolved CO_2 , SO_2 and oxygen, an internal voltaic cell is set up. The iron and other metals as impurities construct electrodes while water containing dissolved gases acts as electrolytes. The formation of rust on the surface of iron takes place through following steps,

At Anode: iron in contact with water acts as anode and gets oxidized to Fe^{2+} ion by losing electrons



At cathode: The electrons thus liberated at anode move through iron metal to electrolyte where oxygen and H^+ ions get reduced into OH^- and hydrogen.



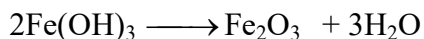
Ferrous ion and hydroxide ion combine to give ferrous hydroxide



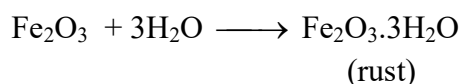
The Fe^{+2} ions in aqueous solution get oxidized in the presence of air to Fe^{+3} which combines with hydroxide ions to form ferric hydroxide.



Ferric hydroxide decompose to give ferric oxide



Ferric oxide absorbs moisture from air to form brown powdery mass of hydrated ferric oxide called rust.



Prevention of rusting

In order to avoid corrosion or rusting, following prevention methods may be applied.

1. **Sacrificial protection:** In this method, iron is coated with more electropositive metals like zinc, magnesium, aluminium etc. These metals get oxidized and become rusted prior than iron. Since coated metal itself get rusted before rusting of iron, this process is called sacrificial protection.
2. **Barrier protection:** A coating is applied on the surface of metal (iron) so that it acts as a barrier between metal and moist air. The barrier protection is done by any one of the following process,
 - i). By a thin coating of paints, varnishes, enamels, lacquers etc.
 - ii). By coating of oil, grease, coal tar, paints etc.
 - iii). By coating iron surface with metallic film of corrosion resistant metal like Zinc, Nickel, Chromium, Tin etc. for e.g. galvanization, chrome-plating, nickel-plating etc.
 - iv). **Barf's protection:** When iron is heated to redness in the presence of steam, an uniform adherent film of ferrous ferric oxide (Fe_3O_4) gets deposited on the surface of iron which protects iron from rusting.
3. **Application of antirust:** When iron is treated with certain antirust solution, a passive layer is developed on the surface. For e.g. conc. Nitric acid, phosphoric acid or alkaline sodium phosphate acts as anti-rust solution. When iron is treated with phosphoric acid solution, an insoluble iron phosphate is formed on the surface of iron.

7.5 Silver

Symbol: Ag

Latin name: Argentum

Atomic number: 47

Atomic mass : 107.9 amu

OCCURRENCE: Silver is found in free as well as combined state in nature.

Important ores of silver are

1. Argentite or silver glance, Ag_2S
2. Ruby silver , $3\text{Ag}_2\text{SbS}_3$
3. Silver copper glance, $\text{Cu}_2\text{S}.\text{Ag}_2\text{S}$
4. Horn Silver, AgCl

Extraction of silver by cyanide process

Silver metal is extracted from argentite ore (Ag_2S) by cyanide process. The various steps involved are,

- 1. Crushing and Pulverization:** The ore is crushed in jaw crusher and then is powdered in ball mill.
- 2. Concentration:** The powdered ore is concentrated by froth floatation process. In this process, the ore is mixed with water containing a little pine oil in a big tank and agitated by blowing blast of air. The ore particles come to surface along with froth and are skimmed off.

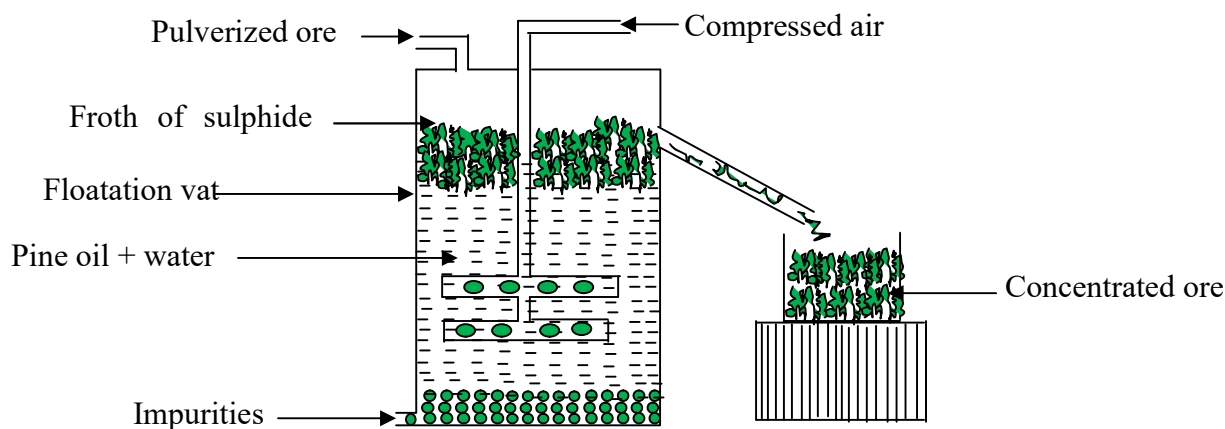


Fig: Froth floatation process

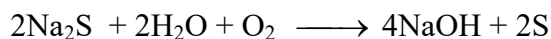
Fig . Froth floatation method

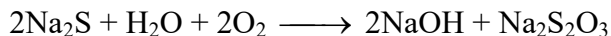
3. Preparation of sodium Argentocyanide:

The concentrated ore is treated with dilute solution of (0.5%) sodium cyanide and the mixture is continuously agitated by current of air. The metallic silver or silver sulphide goes into solution due to formation of soluble complex of sodium argentocyanide.



The reaction is reversible, air helps the reversible reaction to proceed for completion by oxidizing sodium sulphide to sodium thiosulphate and sulphur

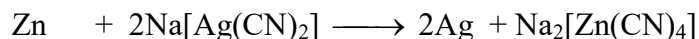




If ore is horn silver, then complex sodium argentocyanide and NaCl



4. **Precipitation:** The above solution containing sodium argentocyanide is filtered to remove impurities and then treated with scrap zinc which displaces silver from the solution.



The precipitated silver is separated out by filtration, dried and fused with potassium nitrate to get bright compact mass of silver.

5. Purification: Thus obtained silver is purified since it contains impurities like Zn, Cu, Au, Pb etc. The purification is carried out by following methods.

a). Electrolytic method: In this method, thick strip of impure silver metal is made anode and a thin strip of pure silver is made cathode. AgNO_3 solution with 1% HNO_3 is used as electrolyte. When current is passed, pure silver gets deposited on the cathode. Zinc, Cu, remains in the solution and Au if present settles below anode as anode mud.

b) Cupellation: Small amount of lead if present as impurities can be removed by cupellation process.

Uses of silver

1. It is used in medicines as tonic.
2. Its alloy with copper is used for making jewellery.
3. Silver bromide is used in photography.
4. Its salt is used in silvering of mirror.

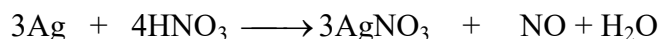
Compounds of silver

Silver nitrate(AgNO_3)

Silver nitrate is also known as Lunar Caustic.

Preparation

It is prepared by heating silver with dilute nitric acid. The solution is then concentrated and cooled to separate silver nitrate crystals out.



Uses

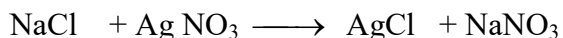
1. It is used as laboratory reagent.
2. It is used in medicines, photography.
3. It is used in manufacture of hair dyes, indelible ink (permanent).

Silver chloride (AgCl)

It is also commonly called as horn silver.

Preparation

It is prepared by adding hydrochloric acid or any soluble chloride to silver nitrate solution.



Uses

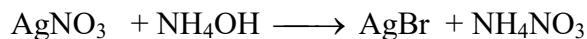
1. It is used in photography.

Basic chemistry behind photography (Excluded in syllabus)

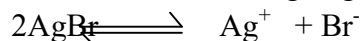
Photography is based on the effect of light on silver bromide. It involves following steps.

1. Making sensitive film

A emulsion is made by mixing silver nitrate and suspension of gelatin in a solution of ammonium bromide with continuous stirring in a dark. The AgBr thus formed is applied on celluloid and dried which gives photosensitive film.

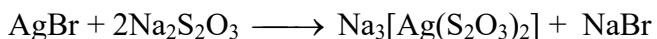


2. **Exposure:** The photosensitive film is loaded in a camera and exposed to the image of an object focused to it where AgBr gets decomposed.



3. **Developing:** The exposed plate is dipped in a developer bath containing mild reducing agent like pyragallol, hydraquinone etc for sometime in which silver bromide is further reduced and the image becomes visible.

4. **Fixing:** The developed film is dipped into dil. Solution of hypo or sodium thiosulphate. Hypo acts as a fixer and removes unaffected AgBr.



The plate is then carefully washed and dried in air. The picture is now called negative

5. **Printing:**

The negative is placed on a printing out paper (POP) coated with AgBr and both are exposed to light. The exposed POP is subjected to developing and fixing as before. The paper is dried on hot plate which the final photograph of object.

“Thanks”

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