

Heavy Metals

Heavy metals are generally defined as metals with relatively high densities, atomic weights or atomic number for example:

- i) Copper (Cu) ii) Zinc (Zn) iii) Mercury (Hg) etc

1. Copper (Cu)

- Copper

Symbol : Cu

Atomic number : 29

Atomic mass : 63.57 (amu)

- Occurrence

Copper exists in nature in native as well as combined state. Major ores of copper are given below:-

- i. Copper pyrites or chalcopyrite's [CuFeS₂]
- ii. Copper glance [(Cu₂S)]
- iii. Malachite [CuCO₃.Cu(OH)₂] etc.

- Extraction of Copper

Copper is mainly extracted from its sulphide ore i.e. (Copper pyrites). The various steps involved in its extraction are from copper pyrites are as follows:

a. Crushing and Pulverization

Big lumps of ore are crushed using jaw crusher to get crushed ore which are pulverized using pulverizer or ball mills to get powdered ore.

b. Concentration

The ore is concentrated by froth floatation process. This method is a most suitable method for the concentration

of sulphide ore.

- Procedure

At first, powdered sulphide ore is taken in a container and wetted by pine oil and added water to make aqueous solution. Compressed air is passed through air pipe to the solution. Then the solution begins to rotate and all sulphide ores dissolved into pine oil and comes up as froth at the surface of the solution, which is skimmed off through side pipe as shown in the figure. The impurities (gangue) are preferentially wetted by water, become heavier and settle at the bottom of container. This process is repeated again and again to get more concentrated ore.

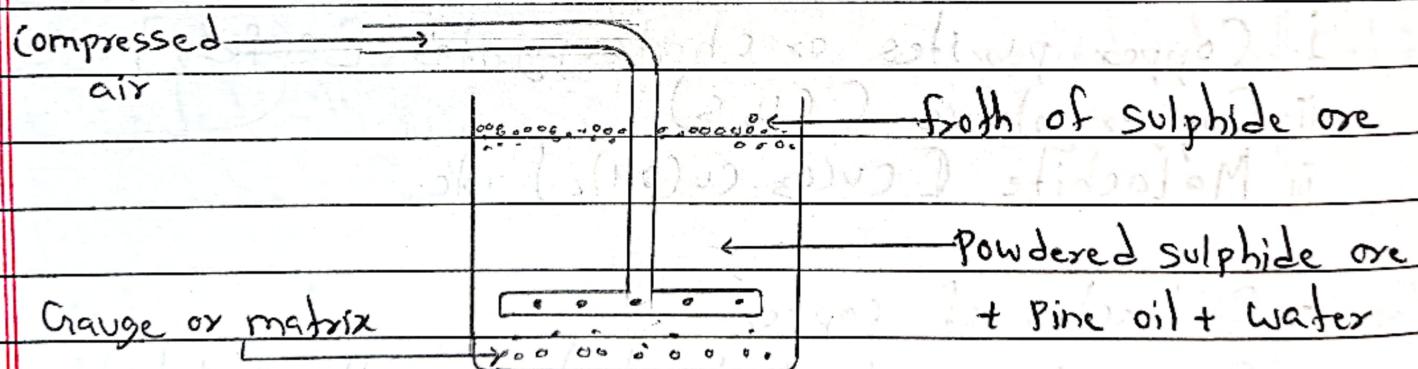


fig: froth floatation process

c. Roasting

The process of heating of ore strongly in the presence of excess air below its melting point is called roasting. It is generally used to convert sulphide ores into oxide ores.

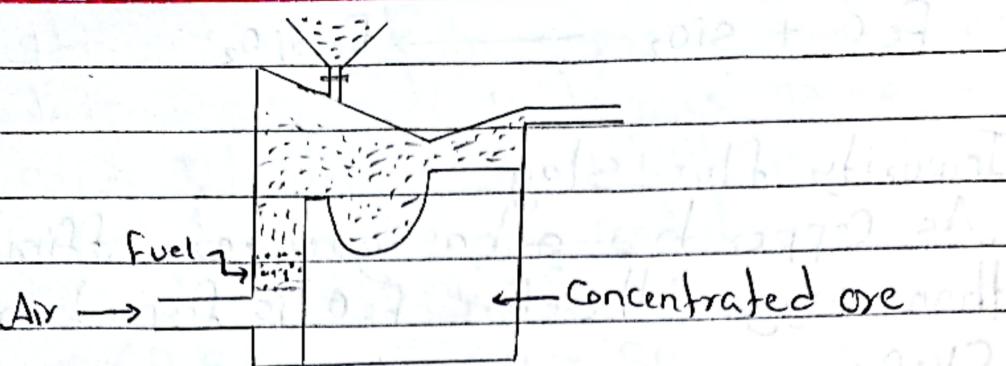
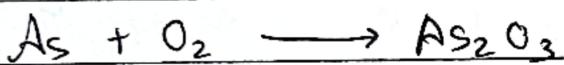
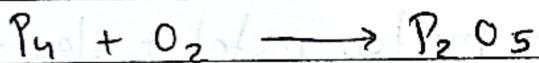
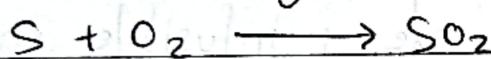


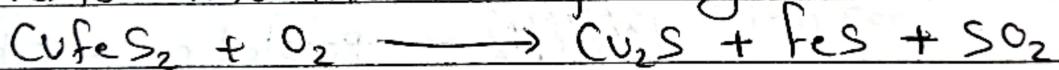
Fig: Reverberatory furnace

- Following changes takes place in roasting

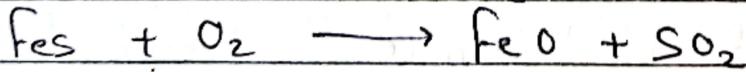
- a. If excess of supply of air is there, non-metallic impurities like S, P, As etc get oxidized. Most of such oxides gets evolved in gases.



- b. If the ore is sulphide, then concentrated ore is converted into the corresponding oxide.

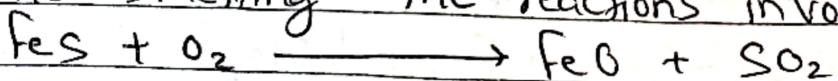


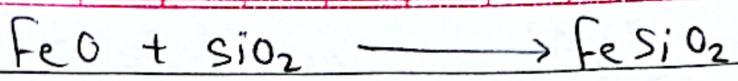
- c. These sulphides are further partially oxidized in cuprous and ferrous oxides.



- d. Reduction (Smelting)

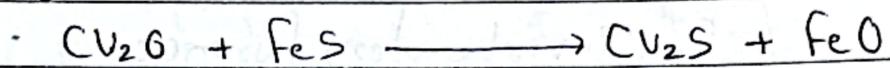
This is the method of reduction in pyrometallurgy. The process of heating calcined or roasted ore (oxide form) strongly in presence of suitable reduction reducing agent to get metal in molten state is called smelting. The reactions involved are;





Impurity flux Slag

As Copper has a greater affinity for sulphur than oxygen therefore FeO is formed in preference to Cu_2O .



The molten mass containing mostly cuprous sulphide and some traces of ferrous sulphide is called matte which contains about 50%. Copper. Slag forming the upper layer is removed.

The overall reaction in this process is:

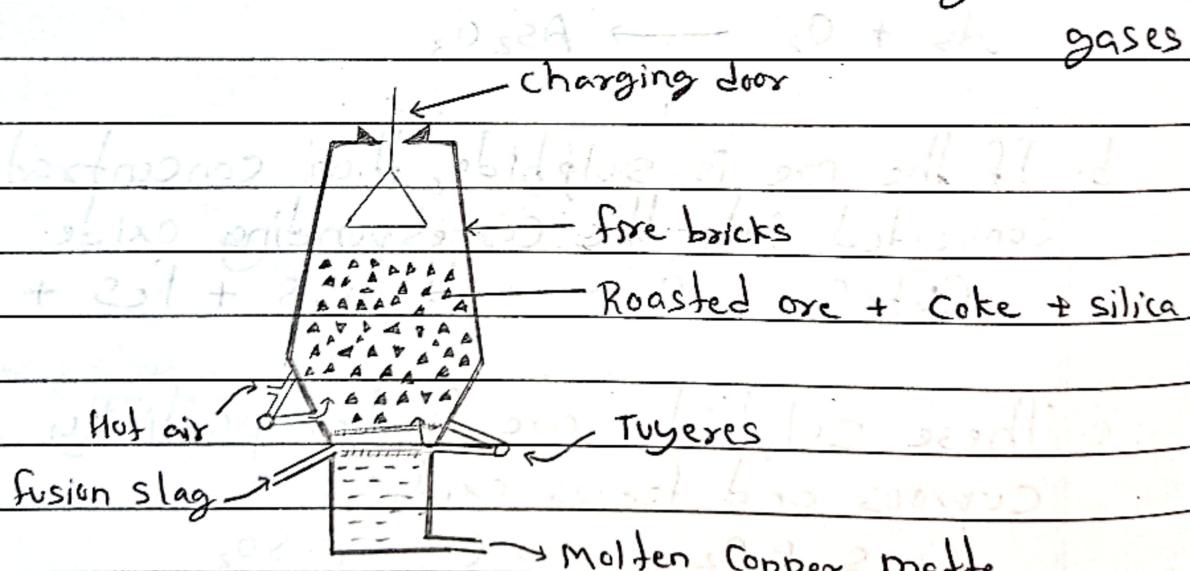
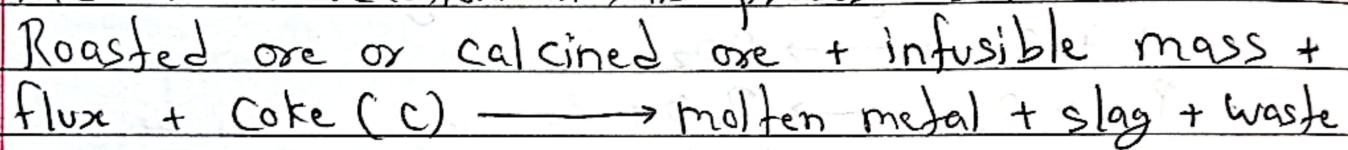
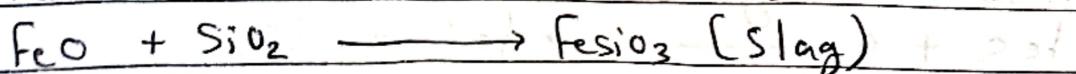
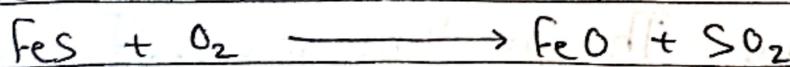


Fig: Blast furnace

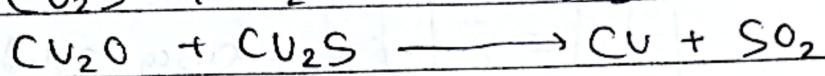
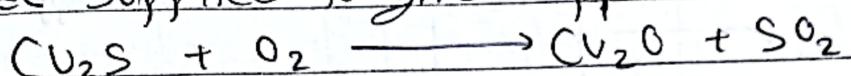
e. Bessemerization

The molten matte is mixed with a little silica and charged into a bessemer converter. A blast of air is blown through the side tuyeres.

The reactions involved are:



At this stage, some of the cuprous oxide which then reacts with more sulphide undergoes oxidation to form cuprous oxide which then react with more cuprous oxide supplied to give copper metal.



The air is then stopped and molten copper is poured into the moulds. During solidification, the dissolved gas (SO_2) continues going or escaping out giving a blister look to the surface. Due to this, copper so obtained is known as blister copper which is 98.1% pure.

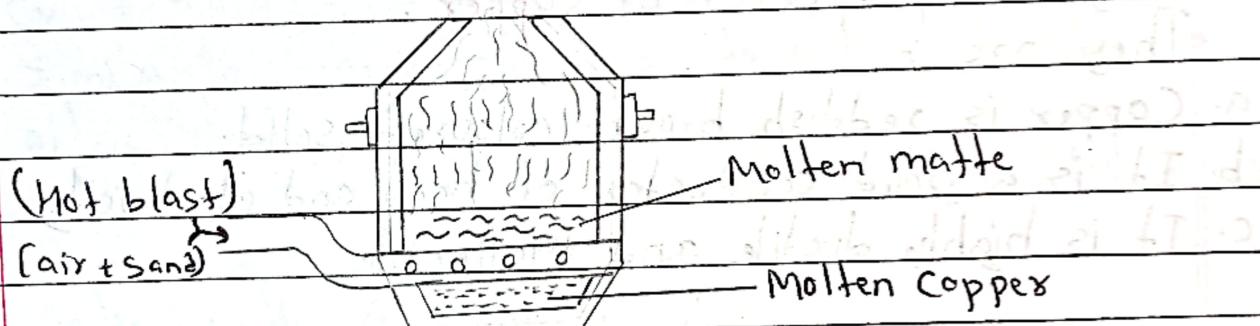


Fig: Bessemer Converter

f. Purification (Electrolytic Refining)

This is an important method of purification of metal. This method is applicable for purification of several metals like copper, silver, zinc etc.

For example:

Purification of Copper : Impure copper is made anode and thin sheet of pure copper is made cathode. Acidified CuSO_4 solution is taken as electrolyte. When D.C is passed through the electrolyte, copper gets dissolved from anode and gets deposited at cathode.

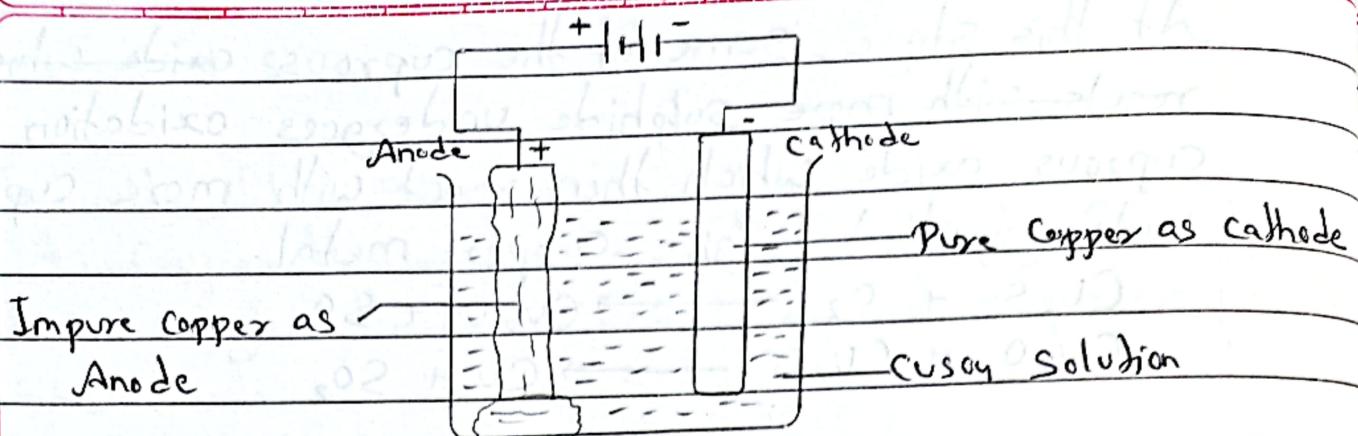
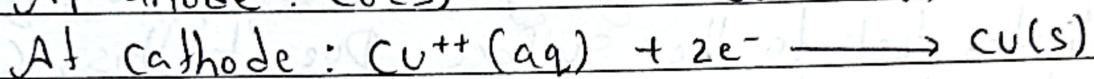
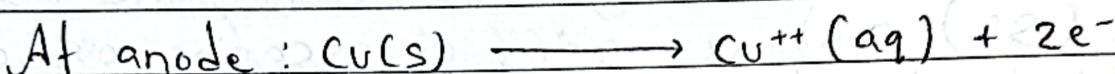


Fig: Electro Refining of Copper



Copper thus obtained is about 99.95% pure.

Physical properties of Copper:

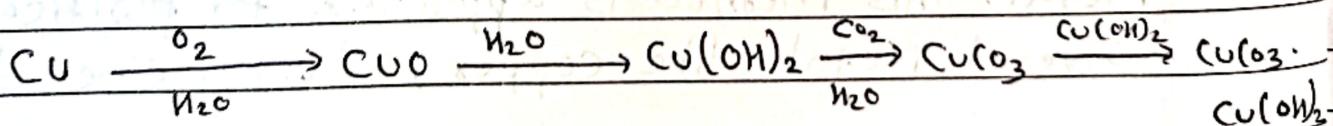
They are :-

- a. Copper is reddish brown coloured solid.
- b. It is a good conductor of heat and electricity
- c. It is highly ductile and Malleable

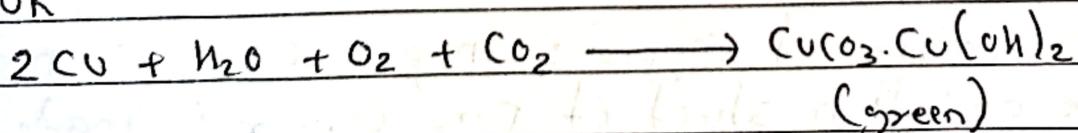
Chemical Properties of Copper

1. Action with air

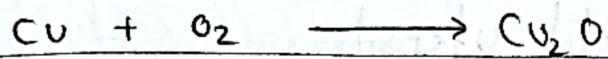
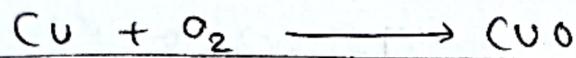
When copper is exposed to moist air, it forms thin green film of basic copper carbonate, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.



OR

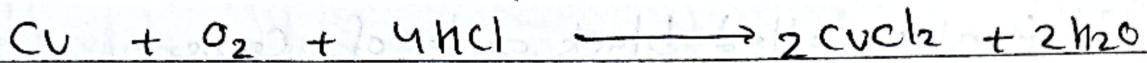
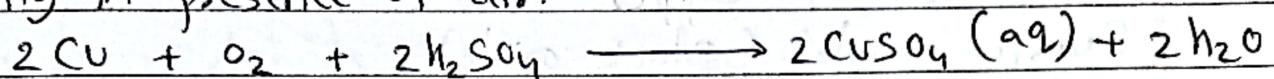


On heating copper with air, it forms cupric (black oxide) which changes to cuprous oxide (red oxide), if temperature exceeds 1100°C .

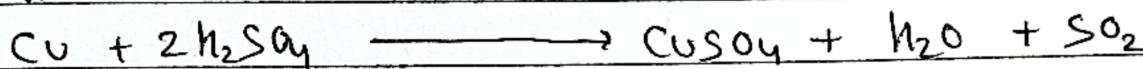


2. Action with Acids

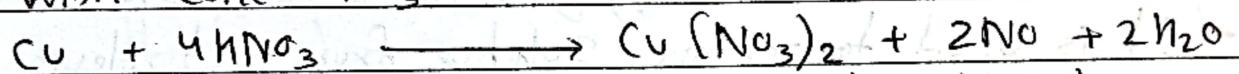
a. Non oxidizing warm and dilute acids displace Copper only in presence of air.



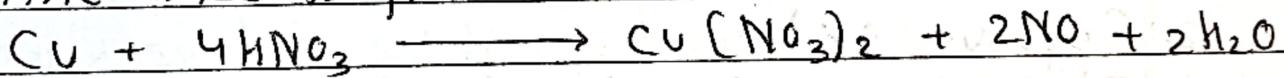
b. With Conc. H_2SO_4



c. With Conc. HNO_3

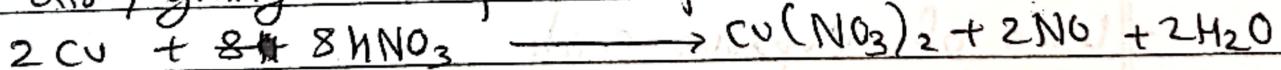


Similarly when copper reacts with dil. nitric acid, nitric oxide is produced.



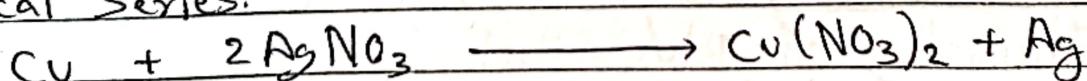
3. Action with Ammonia

Copper is dissolved in aqueous ammonia in presence of air, giving a complex compound.



4. Displacement Reaction

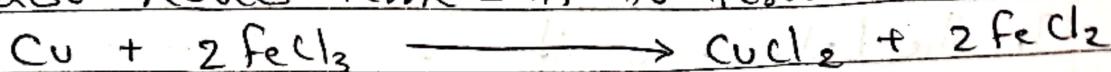
Copper can displace metals below it in electrochemical series.



5. Reducing Property of Copper

Copper is oxidized and behaves as reducing agent.

It also reduces ferric salt to ferrous salt.



USES of Copper

- a. It is used as household utensils.
- b. It is used in electroplating
- c. It is used to prepare coins, Ornaments etc.

Compounds of Copper

1. Cupric oxide (Black oxide)

- It is also called black oxide of copper.
- It is insoluble in water.
- Its molecular formula is CuO .
- Uses of Black Oxide
- It is used for colouring glass in blue or black colour.
- It is used to remove Sulphur from petroleum.
- Used as oxidizing agent.

2. Cuprous oxide

- It is also called red oxide of copper.
- It is also insoluble in water.
- Its molecular formula is Cu_2O .

- Uses of Cuprous Oxide

- It is used as enamel and pigment
- It is used as pesticide.

3. Blue vitrol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) {Blue vitrol}

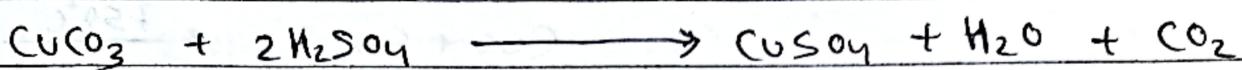
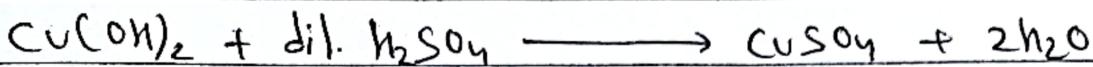
- Chemistry of Blue Vitrol

Copper sulphate pentahydrate is commonly called blue vitrol. In Nepali, it is called **nilo tutto**.

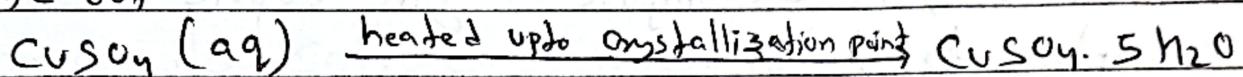
- Preparation

In the Laboratory, it is prepared by reaction of cupric

oxide or cupric hydroxide or cupric carbonate with dilute sulphuric acid.

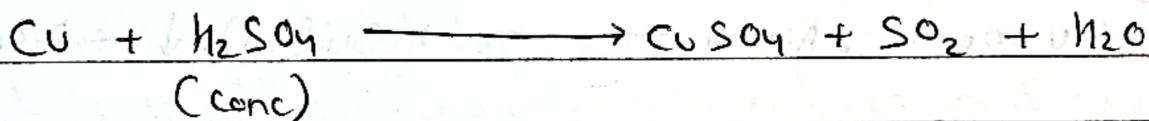


Copper sulphate solution is heated up to crystallization point and cooled where crystals of blue vitrol separate out.



- Copper reacts with hot and conc. sulphuric acid to form copper sulphate, sulphur dioxide and water

In the reaction:



Copper sulphate solution is heated upto crystallization point where and cooled, where crystals of blue vitrol separate out.

Properties

a. Colour

- Its hydrated salt is blue in colour.

b. Solubility and Nature

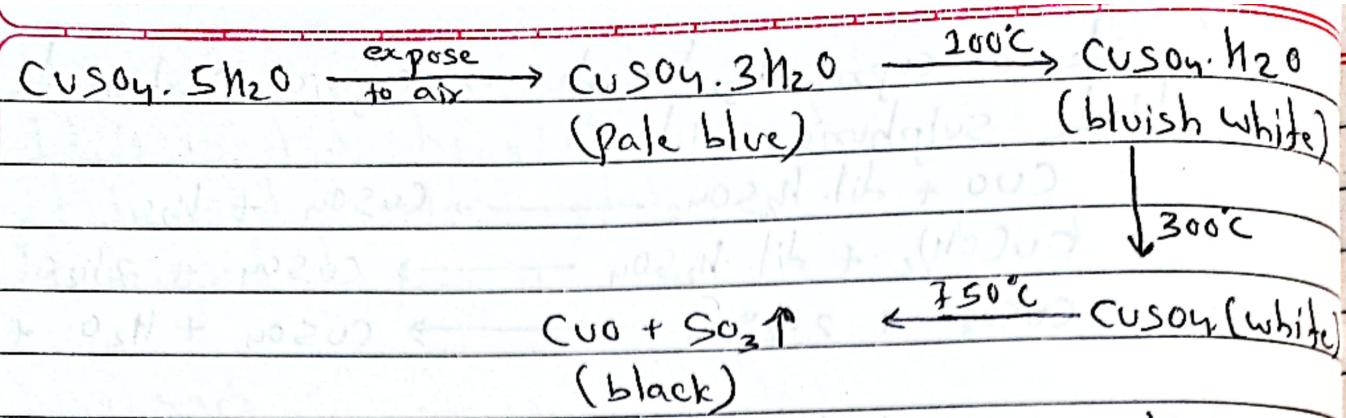
- It is highly soluble in water.

- It is acidic in nature due to cationic hydrolysis.



c. Action of Heat

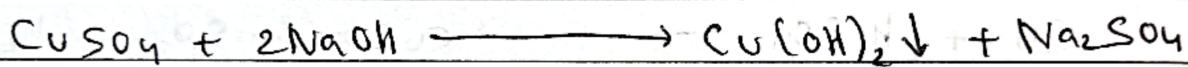
The following changes occurs when blue vitrol is heated:



While anhydrous salt turns blue as soon as it comes in contact with water. If anhydrous salt is heated at 750°C , it decomposes to give cupric oxide and sulphur trioxide.

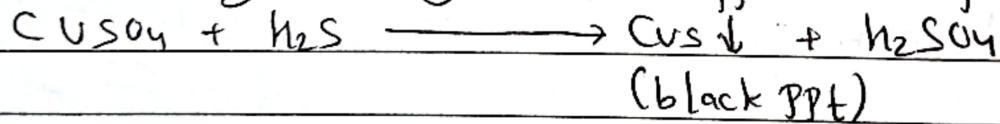
d. Action with alkalis

With NaOH solution, it gives bluish white ppt. of cupric hydroxide.



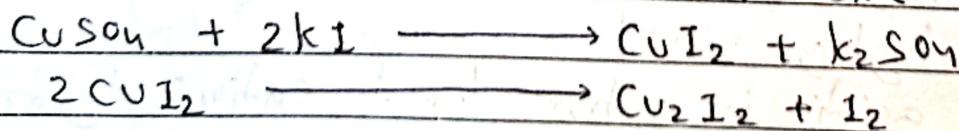
e. Action with Hydrogen Sulphide

With H_2S gas, it gives black ppt. of cupric sulphide.

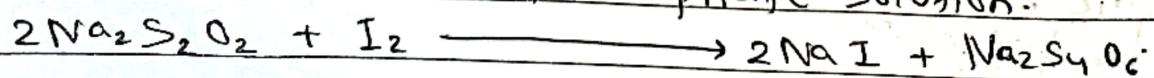


f. Action with Potassium Iodide

When solution of potassium Iodide is added to copper-Sulphate Solution, a dark brown precipitate is formed. This colour is due to liberation of iodine.

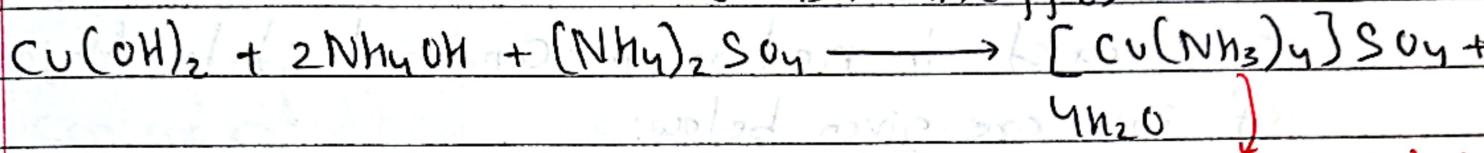
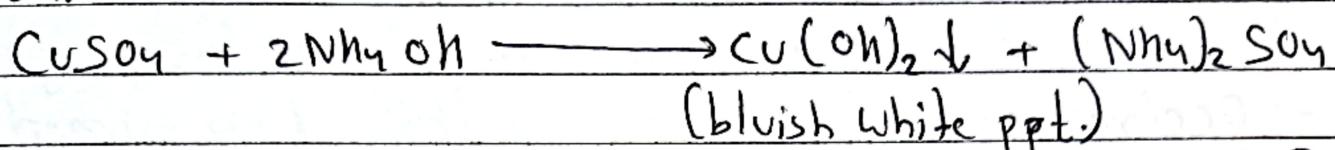


This reaction is used to estimate copper volumetrically by titrating iodine formed in the reaction against standard solution sodium thiosulphate solution.



g. Action with Ammonia

It gives deep blue solution of tetra-amine copper (II) Sulphate when treated with aqueous solution of ammonia.



Tetra amine Copper Sulphate

The complex salt $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ is known as schweitzer reagent and is used in the manufacture of artificial silk.

Uses of Blue Vitrol

- a. Used in electroplating and electrorefining
- b. It is used as fungicides, insecticides and germicides
- c. Used in medicine as antiseptic.
- d. Used as Lab reagent

2. Zinc (Zn)

Symbol : Zn

Atomic Number : 30

Atomic Mass : 65.37 (amu)

- Occurrence

Zinc exists in nature in combined state. Major ores of zinc are given below:

- a. Zinc blende : ZnS
- b. Calamine : $ZnCO_3$
- c. Red zinc : ZnO

- Extraction of Zinc

Zinc is mainly extracted from its sulphide ore (zinc blende). The various steps involved in the extraction of zinc from zinc blende are as follows:

1. Crushing and Pulverization

Big lumps of ore are crushed using jaw crusher to get crushed ore which are pulverized using pulverizer or ball mills to get powdered ore.

2. Concentration

The ore is concentrated by froth floatation process. This method is a most suitable method for the concentration of sulphide ores.

- Procedure

At first, powdered sulphide ore is taken in a container and wetted by pine oil and added water to make aqueous solution. Compressed air is passed through air pipe into the solution. Then the solution is

begins to rotate and all sulphur sulphide ore dissolved in to pine oil and come up as froth at the surface of the solution, which is skimmed off through side pipe as shown in the figure. The impurities (gangue) are preferentially wetted by water, become heavier and settle at the bottom of container. This process is repeated again and again to get more concentrated ore.

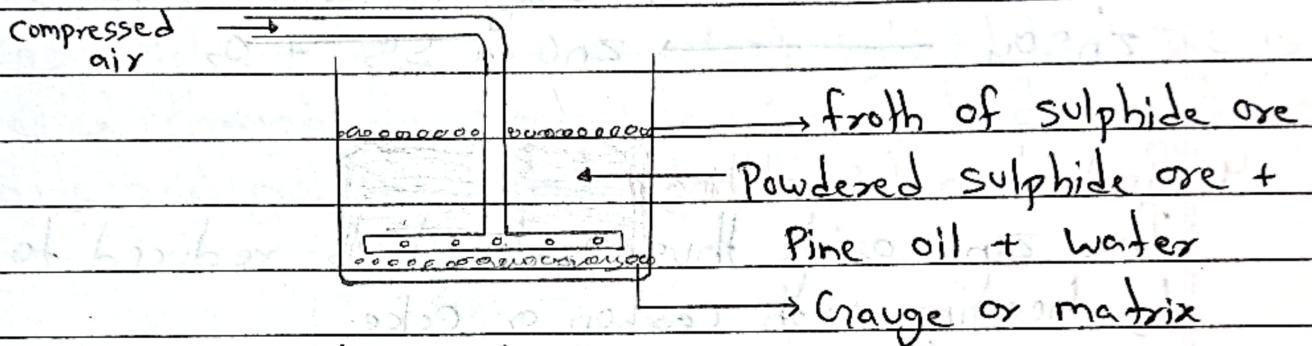


Fig: froth flotation Process

3. Roasting

The process of heating of ore strongly in the presence of excess of air below its melting point is called roasting. It is generally used to convert sulphide ores into oxide ores.

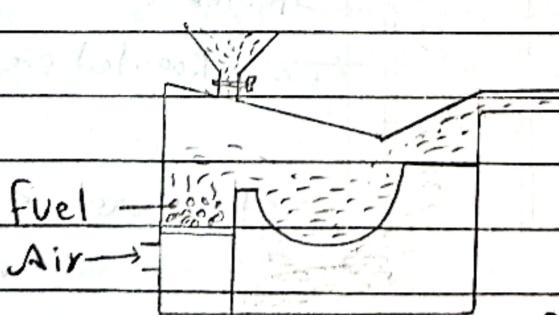
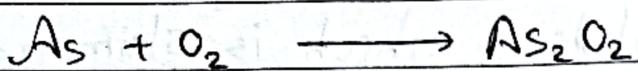
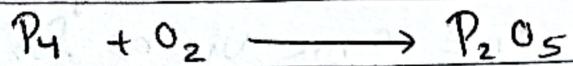
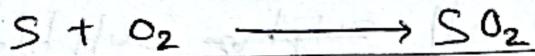


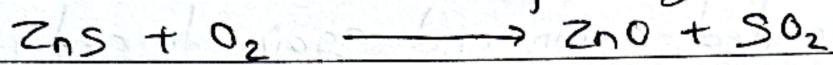
Fig: Reverberatory furnace

following changes takes place in roasting:

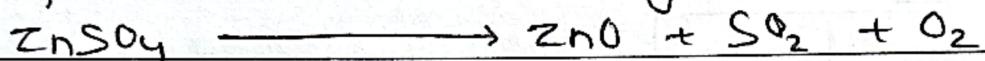
- If excess supply of air is there, no metallic impurities like S, P, As etc. get oxidised. Most of such oxides gets evolved as gases.



b. If the ore is sulphide, then concentrated ore is converted in to the corresponding oxide.



During roasting some of ore may converted into zinc sulphide avoid this roasting is done above 900°C.



4. Reduction (smelting)

The zinc oxide thus produced is reduced to metal by heating with carbon or coke.



To carry out reduction vertical retort process is modern and economic.

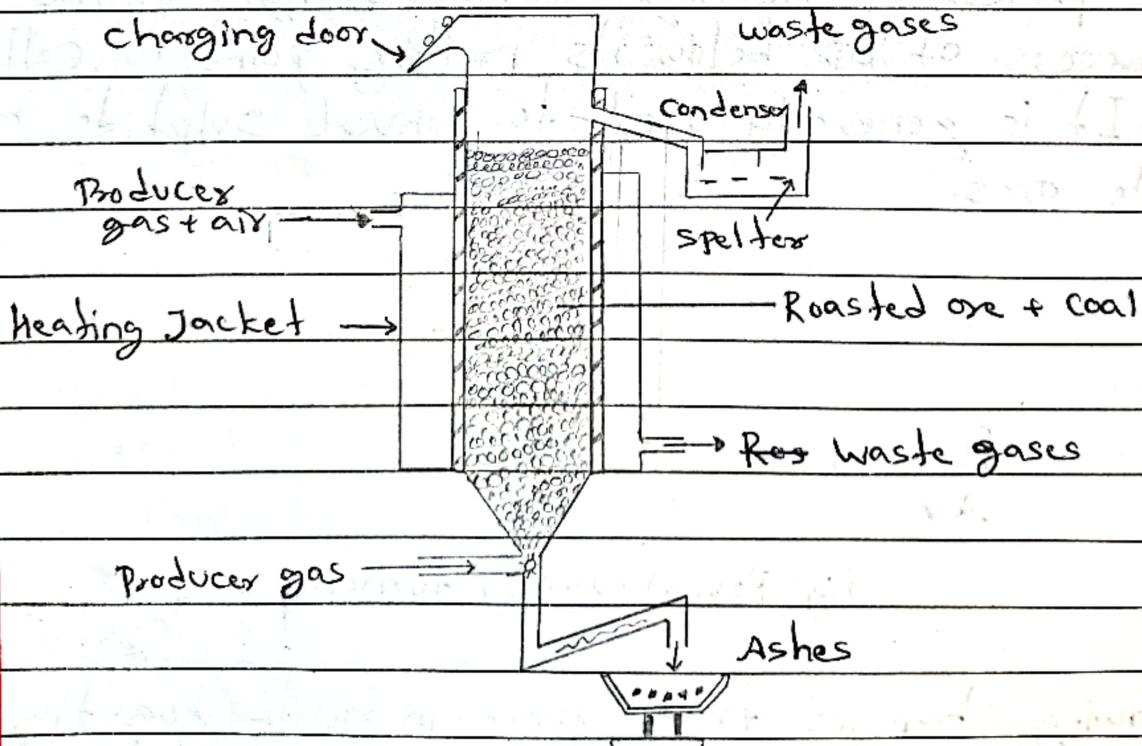


Fig: Vertical retort Process

5. Purification

(Electrolytic Refining)

This is an important method of purification of metal. This method is applicable for purification of several metals like copper, silver, zinc etc.

For Example:

Purification of zinc : Impure zinc is made anode and thin sheet of pure zinc is made cathode. Acidified $ZnSO_4$ solution is taken as electrolyte. When D.C is passed through the electrolyte, zinc gets dissolved from anode and gets deposited at cathode.

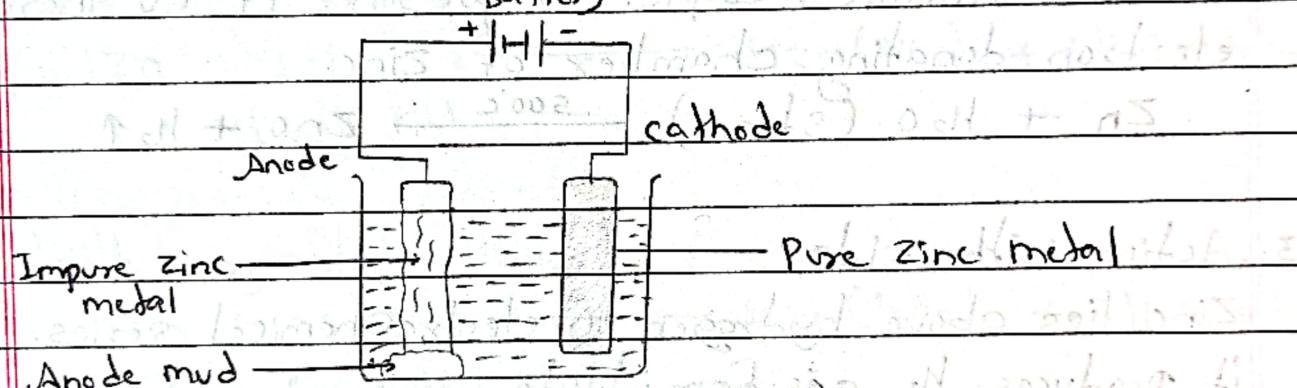
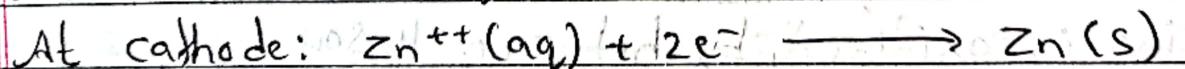
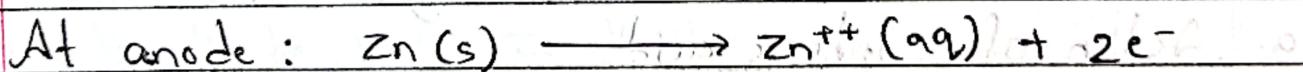


Fig: Electro refining of zinc



Physical Properties of Zinc

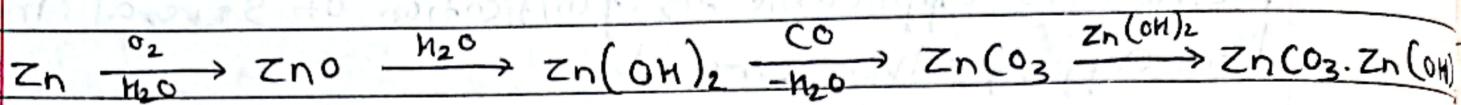
- a. Zinc is white and coloured solid.
- b. It is good conductor of heat and electricity.
- c. It is highly ductile and malleable.
- d. It is highly soluble in water.

Chemical Properties of Zinc

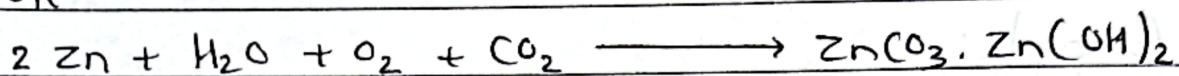
→ They are:

1. Action with air

When copper is exposed to moist air, it forms thin green film of basic copper carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

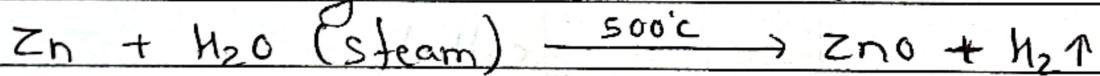


OR



2. Action with water

Pure zinc does not react with water. Impure zinc (commercial or granulated) decomposes steam to produce H_2 . Zinc in presence of Cu forms a Zn-Cu couple, which acts as electrochemical couple. So presence of Cu increases electron donating chamber of zinc.

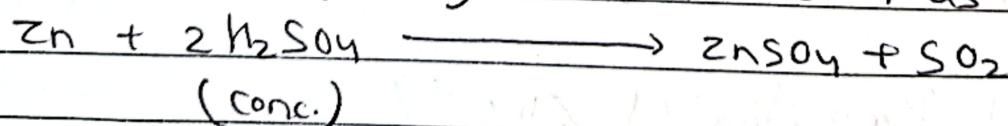


3. Action with acids

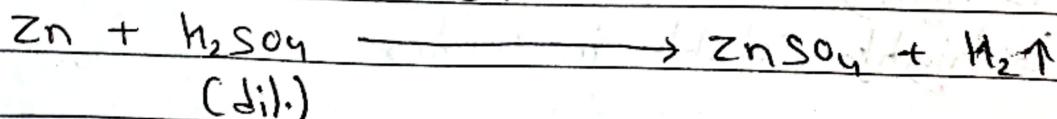
Zinc lies above hydrogen in electrochemical series. Therefore it produces H_2 gas from dilute, mineral and non-oxidizing acid. Zinc shows amphoteric nature. Hence, it reacts with acids as well as bases to give salts.

a. Action of sulphuric acid

Zinc is oxidized by hot conc. H_2SO_4 as



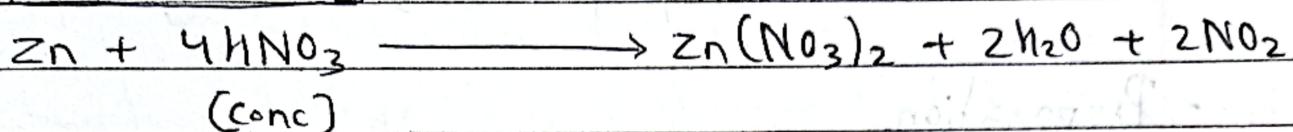
Zinc is oxidized by dil. H_2SO_4 to give ZnSO_4 . Zn displaces H_2 from dil. H_2SO_4 as:



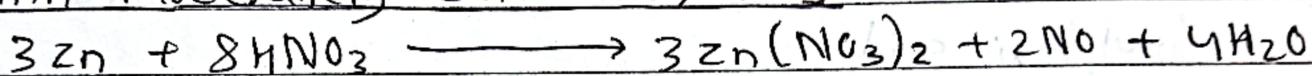
b. Action of nitric acid (HNO_3)

Zinc is oxidized by nitric acid to give $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. HNO_3 gets reduced to various products like NO_2 or NO or ~~N_2O~~ N_2O or NH_4NO_3 depending upon the concentration of nitric acid.

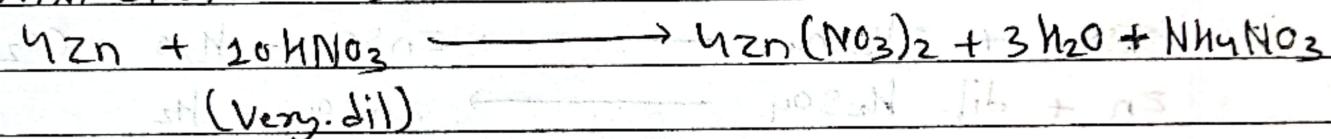
i. With conc. HNO_3



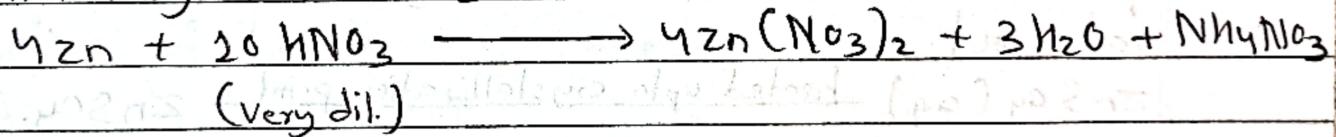
ii. With moderately conc. (1:1) HNO_3



iii. With dilute HNO_3

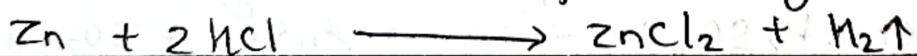


iv. With very dilute HNO_3



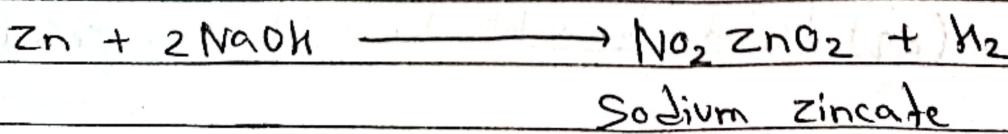
v. Action with HCl

With dilute HCl , Zn displaces H_2 gas



vi. Action with alkali

Zn reacts with alkalis (e.g. NaOH) to give sodium zincate.



5. Action with Non-metals

Zn reacts with non-metals such as S , Cl_2 etc. to give

Corresponding salts.

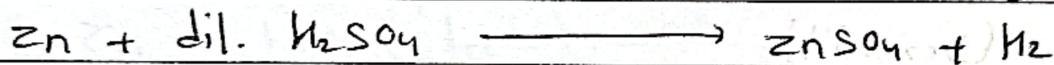
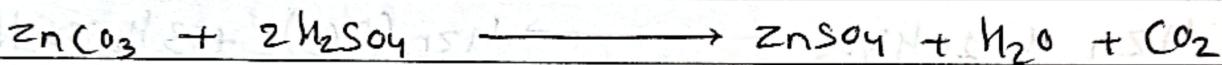
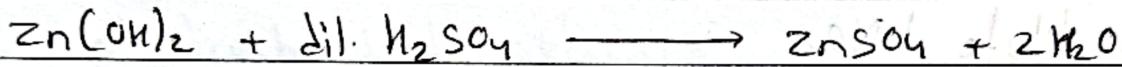
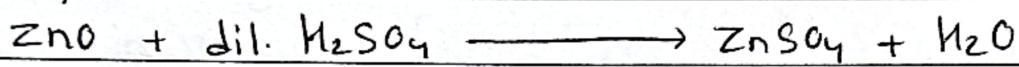
3. White Vitrol ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)

- Chemistry of White Vitrol

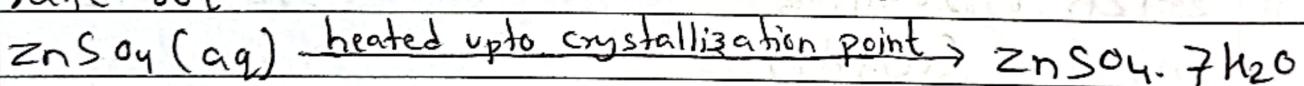
Zinc sulphate heptahydrate is commonly called white Vitrol. It can be prepared by following methods.

- Preparation

a. In the Laboratory, it is prepared by reaction of zinc oxide or zinc hydroxide or zinc carbonate with dilute sulphuric acid.



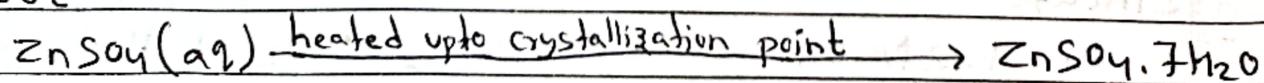
Copper sulphate solution is heated upto crystallization point and cooled, where crystals of blue vitrol separate out.



b. Zinc reacts with hot and concentrated sulphuric acid to form zinc sulphate, sulphur dioxide gas and water.



Zinc sulphate solution is heated upto crystallization point and cooled, white crystals of white vitrol separate out.



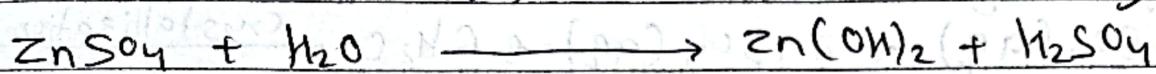
Properties

a. Colour

Its hydrated salt is white in colour or colourless.

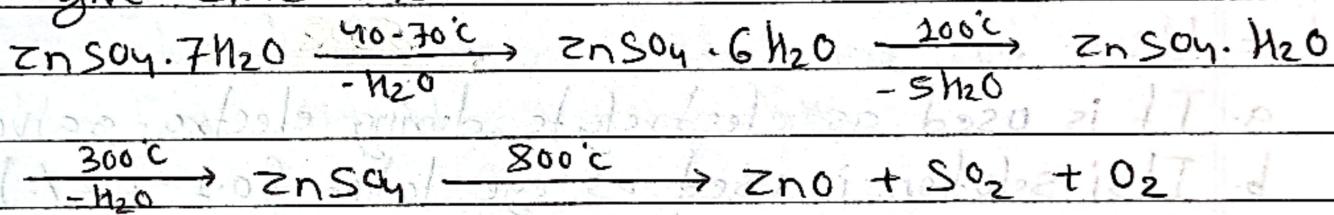
b. Solubility and Nature

- It is highly soluble in water.
- It is acidic in nature due to cationic hydrolysis.



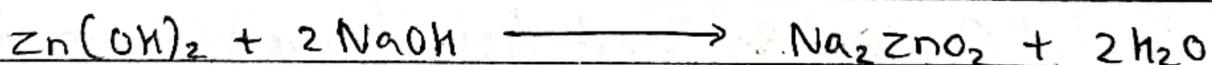
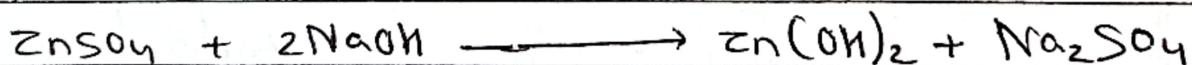
c. Action with heat

When white vitrol is heated to about 70°C . It loses one water molecule to give hexahydrated zinc sulphate. When temperature reaches to 100°C , it loses 5 more water molecule giving monohydrated ZnSO_4 . On heating the monohydrated ZnSO_4 , at 300°C gives anhydrous ZnSO_4 . Anhydrous ZnSO_4 , gets decomposed at 800°C to give zinc oxide.



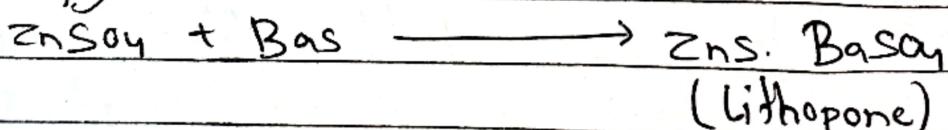
d. Action of Sodium Hydroxide

It reacts with NaOH to give white precipitate of Zn(OH)_2 which dissolves in excess NaOH to give sodium zincate.



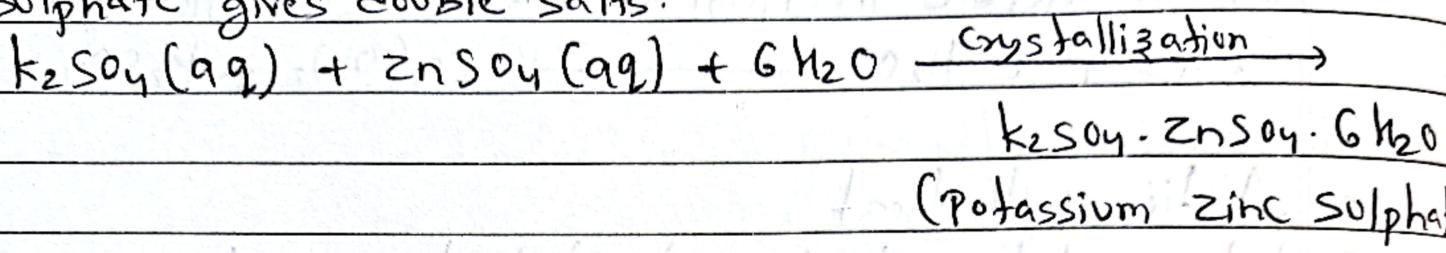
e. Reaction with barium sulphide

When zinc sulphate is treated with barium sulphide, double salt, lithopone is obtained, which is used as white pigment.



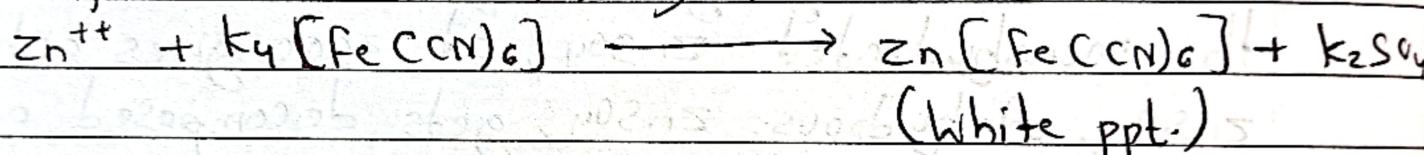
f. Formation of double salts

White Vitrol solution on crystallization with alkali metal sulphate gives double salts.



g. Action of Potassium ferrocyanide

Zn^{++} reacts with potassium ferrocyanide giving white precipitate of zinc ferrocyanide.



Uses

- It is used as electrolyte during electro-galvanization.
- Its solution is used as eye lotion (0.1 - 0.2%).
- It is used as mordant for dyeing.
- It is used for the preparation of lithopone which is a white pigment.

3. Mercury (Hg)

Symbol: Hg

Atomic No: 80

Atomic Mass: 200.59 (amu)

- Occurrence

The major ores of mercury are given below:

- Cinnabar (HgS)
- Tremannite (HgSe)
- Calomel (Hg₂Cl₂)

Extraction of Mercury

Mercury is mainly extracted from its sulphide ore (cinnabar). The various steps involved in its extraction from cinnabar are as follows:

a. Crushing and Pulverization

Big lumps of ore are crushed using jaw crusher to get crushed ore which are pulverized using pulverizer or ball mills to get powdered ore.

b. Concentration

The ore is concentrated by froth float flotiation process. This method is a most suitable method for the concentration of sulphide ores.

- Procedure

At first, powdered sulphide ore is taken in a carbon container and wetted by pine oil and added water to make aqueous solution. Compressed air is passed through ~~air~~ air pipe into the solution. Then the solution begins to rotate and all the sulphide ore dissolved

into pine oil and come up as froth at the surface of the solution, which is skimmed off through side pipe as shown in the figure. The impurities (gangue) ore preferentially wetted by water become heavier and settle at the bottom of container. This process is repeated again and again to get more concentrated ore.

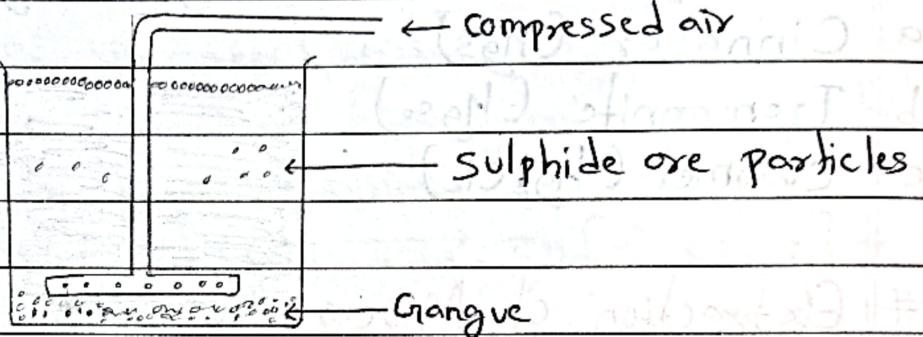


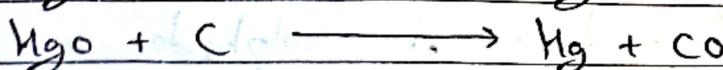
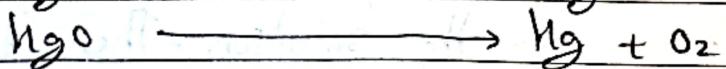
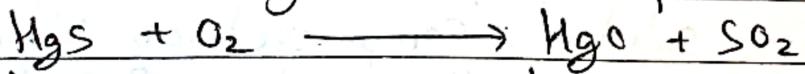
Fig: froth flotation Process

c. Roasting and Distillation

The process of heating of ore strongly in the presence of excess of air below its melting point is called roasting. It is generally used to convert sulphide ores into oxide ores.

The concentrated ore is mixed with coke and fed into in the shaft furnace. The furnace is heated by burning fuel, air is blown in, cinnabar is first oxidized to mercuric oxide then decomposed to mercury.

The mercury vapour along with waste gases come out from the furnace which is passed through water pipe of condensers as shown in the figure. Mercury vapour condenses and settle at the bottom of receiver while waste gases are escaped out.



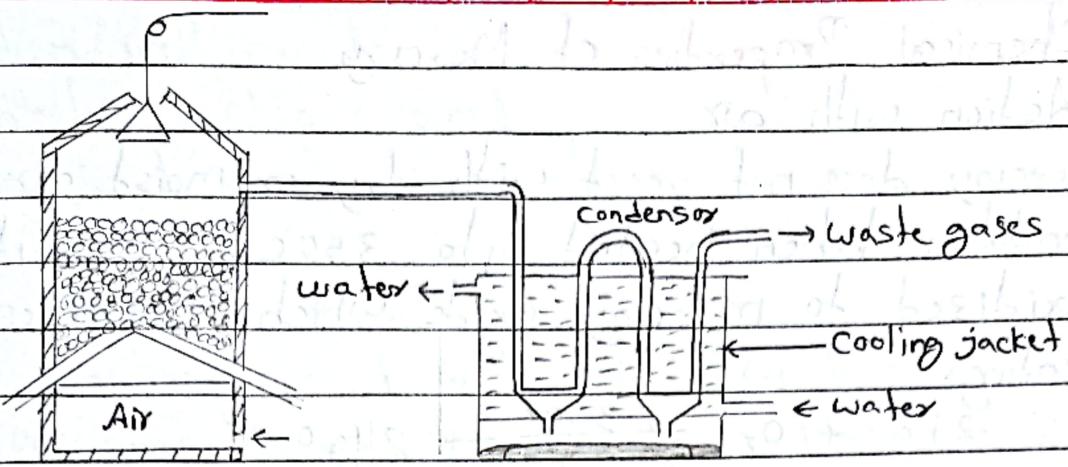


Fig: Distillation

d. Purification

Mercury thus obtained is not pure and contains Zn, Cu, Pb, Bi etc. as impurities.

It is purified by following steps:

a. filtration

Impure mercury is filtered through chamois leather to suspended impurities.

b. Treatment with 5% nitric acid.

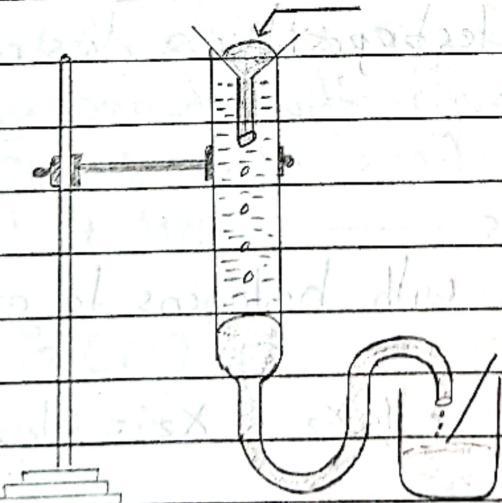


Fig: Purification of Mercury

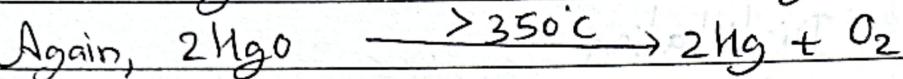
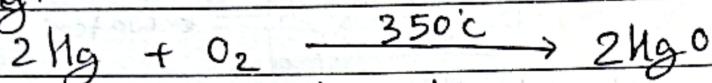
Physical Properties of Mercury

- It is a heavy, silvery-white liquid metal.
- It is a poor conductor of heat.
- It has a freezing point of -38.83°C and boiling point of 356.73°C .

Chemical Properties of Mercury

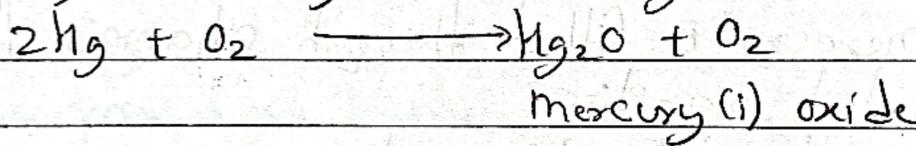
a. Action with air

Mercury does not react with dry or moist air at ordinary condition. When heated upto 350°C in air, it slowly gets oxidized to mercury oxide which decomposes on further heating.



b. Action with ozone

When mercury is brought in contact with ozone. It is oxidized to mercurous oxide (Hg_2O). So that mercury loses its meniscus and leaves a black mark on glass (tail). This special property of mercury called tailing of mercury.

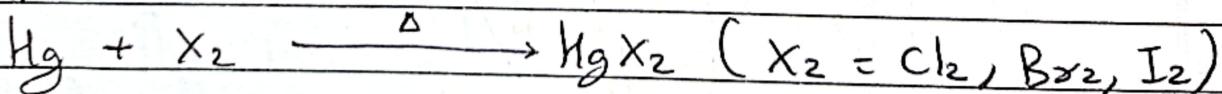


c. Action with water and alkali

Mercury being less electropositive, does not react with water and alkali.

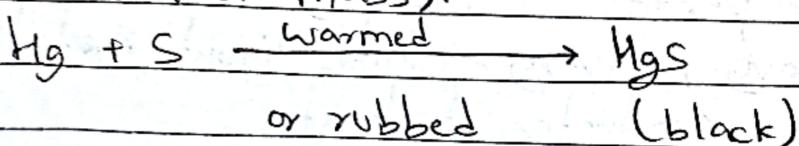
d. Action with halogens

Hot mercury combines with halogens to give respective halides.



e. Action with sulphur

Mercury warmed or rubbed with sulphur, gives mercuric sulphide (black mass).



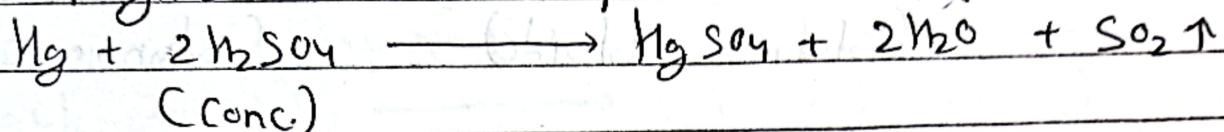
f. Action with acids

i. With hydrochloric acid

Mercury does not react with dilute and conc. HCl.

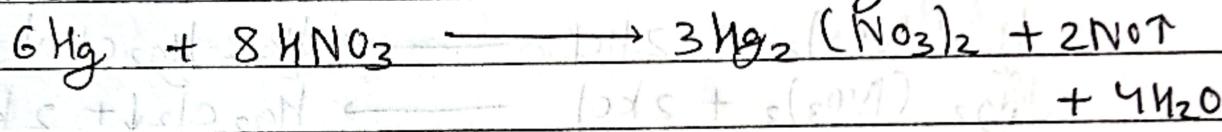
ii. With Sulphuric acid.

It does not react with dil. H₂SO₄ but hot and conc. H₂SO₄ gives mercuric sulphate and sulphur dioxide.



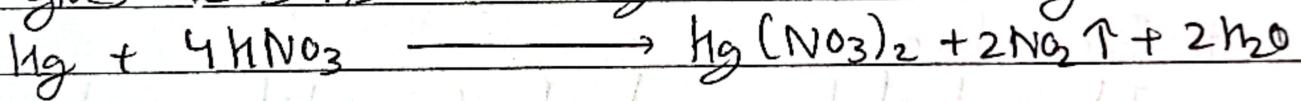
iii. With dil. nitric acid

It gives 'ous salt' and nitric oxide gas.



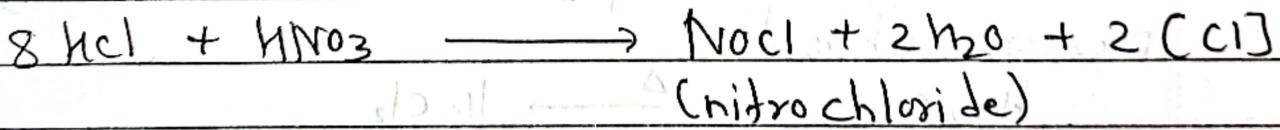
iv. With hot and Conc. nitric acid.

It gives 'ic salts' and nitrogen dioxide gas.



g. Action with aqueous regia

Mercury reacts with aqua-regia [conc. HCl and conc. HNO₃ in ratio 3:1] to form mercuric chloride.



Aqua regia is also called royal water or regal water.

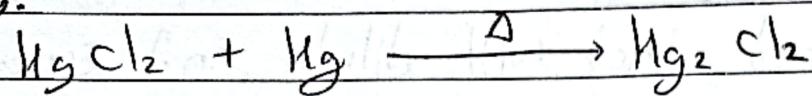
3. Mercurous Chloride or calomel (Hg₂Cl₂)

- Chemistry of calomel

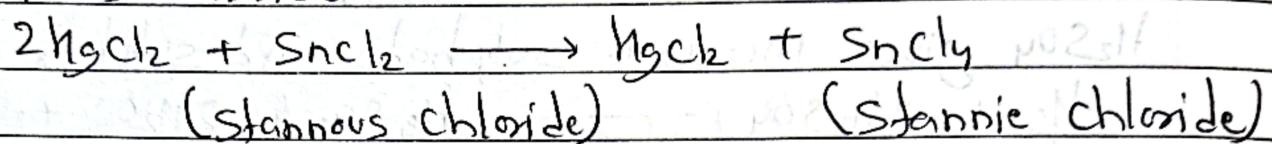
Mercurous chloride (Hg₂Cl₂) is commonly known as calomel. It can be prepared by following methods.

- Preparation

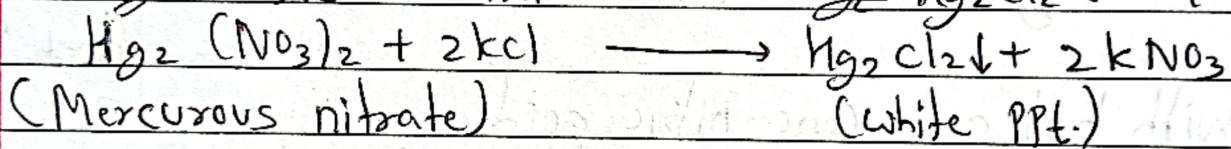
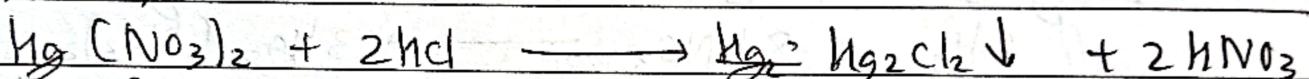
a. It is prepared by heating mercuric chloride with mercury.



b. It can be prepared by reducing mercuric chloride by stannous chloride.



c. It can also be prepared by treating a solution of mercurous nitrate with any soluble chloride such as HCl, KCl, NaCl etc.

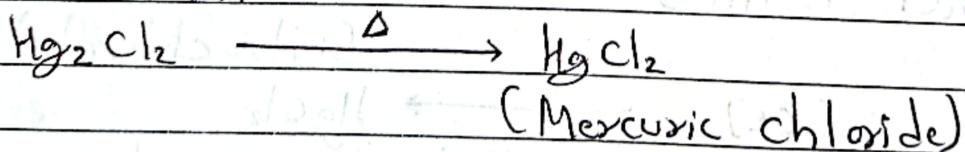


Properties

a. It is tasteless and odourless white powder.

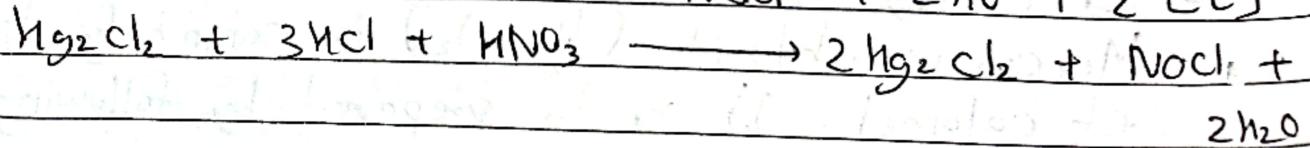
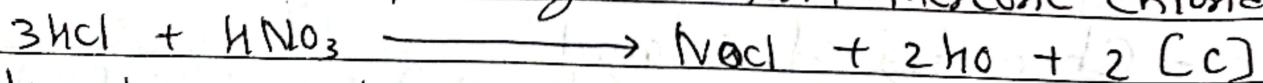
b It is sparingly soluble or almost insoluble in water.

c. On heating, it decomposes into metallic mercury and mercuric chloride.



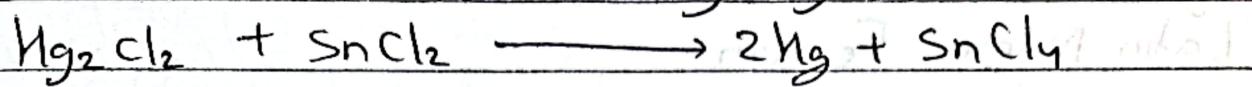
J. Action with Aqua-regia

It dissolves in aqua-regia to form mercuric chloride.



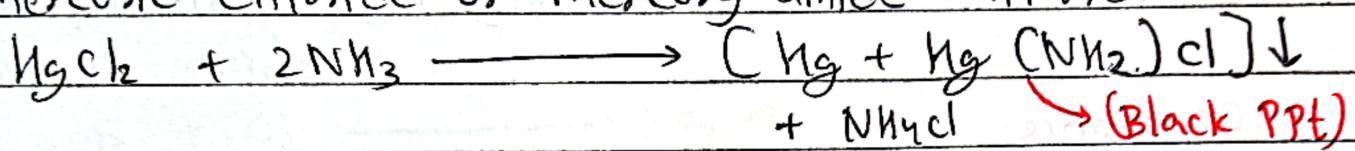
e. Action with stannous chloride

It is reduced to mercury by stannous chloride.



f. Action with ammonia.

On treatment with ammonia, it turns black due to the formation of metallic mercury and ammonia basic mercuric chloride or mercury amide chloride.



(Black Ppt)

Uses

- It is used as a purgative in medicine (to clean intestine)
- It is used for making calomel electrodes.
- It is used as fungicides etc.

4. Iron

Symbol: Fe

Latin Name: Ferrum

Atomic Number: 26

Atomic Mass: 55.85

Valency: 2 and 3

It is the second most abundant (next to aluminium) in earth crust. It is used in very large scale in industries.

Occurrence

It is not found in free state due to its reactive nature.

It occurs mostly as oxide, sulphide and carbonate ore.

Its important ores are:

i. Haematite (Fe_2O_3)

ii. Magnetite - Fe_3O_4

iii. Limonite - $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

iv. Iron pyrite - FeS_2

v. Siderite (Spathic ore) - FeCO_3

In Nepal iron is mostly found in Phulchoki, Ramechhap, Piuthan and Paurbat. It is mainly extracted from haematite and magnetite.

Extraction of Iron

Cast iron is generally extracted from haematite ore.

It involves the following steps:

a. Crushing and Concentration

The ore is first crushed in a crusher into small pieces and converted into powdered form in ball mills. It is then concentrated by gravity separation method to remove earthy impurities such as sand, clay etc. The washed ore is then concentrated by electromagnet.

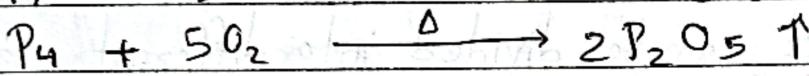
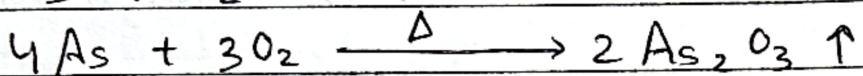
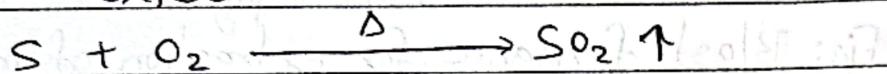
Separation process to remove magnetic impurities.

b. Roasting

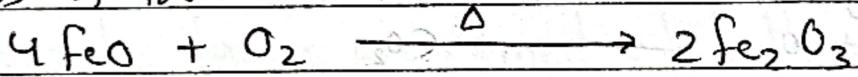
The concentrated ore is heated strongly in reverberatory furnace in the presence of excess of air. The following changes occurs.

i. Moisture is removed

ii. Sulphur, phosphorous and arsenic ore are removed as oxide.



iii. Ferrous oxide is oxidized to ferric oxide which prevent the formation of slag (ferrous silicate) and prevent the loss of iron.



c. Smelting

Smelting is carbon reduction process in which roasted ore is mixed with carbon and limestone and heated in blast furnace which is tall cylindrical made up of steel and lined inside with fire bricks to withstand high temperature. It is provided with double cup and cone arrangement to feed the charge from top and small piece pipes called tuyeres to admit blast of hot air and two outlet at the bottom to collect slag and molten metal.

The charge containing roasted ore, limestone and coke in the ratio of 8:24 is fed into the furnace and heated by blast of air at about 600°C.

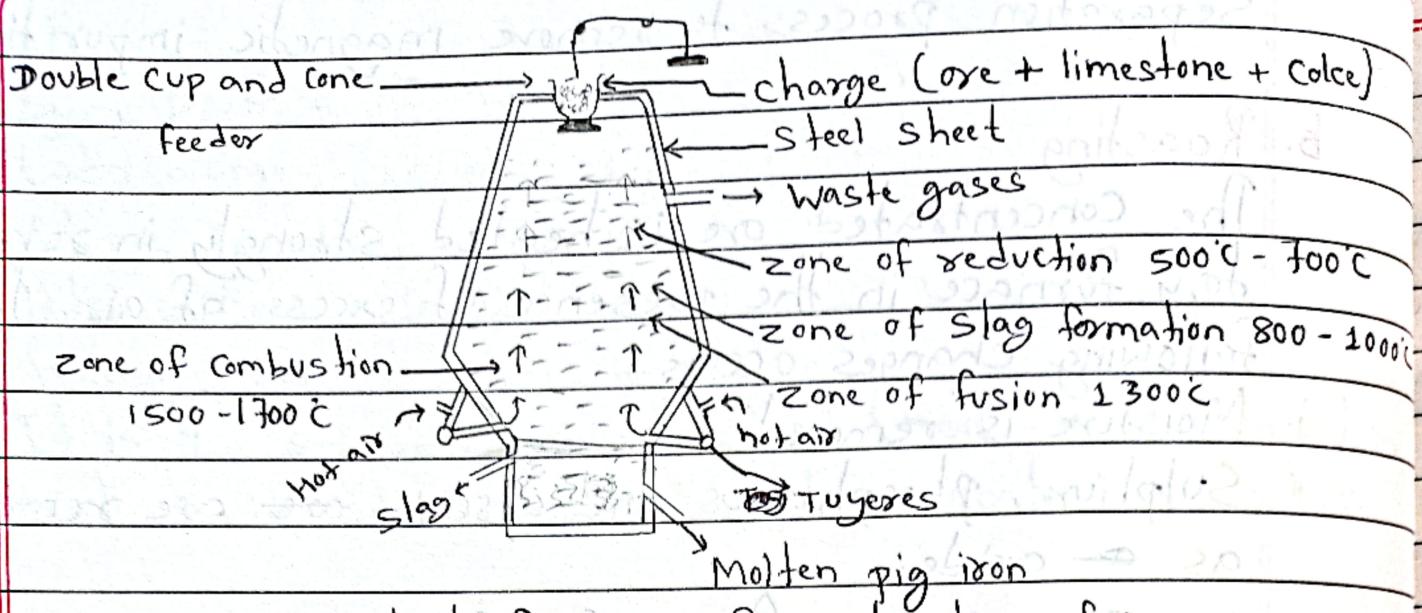
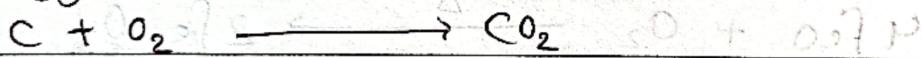


Fig: Blast furnace for extraction of Iron

Blast furnace can be divided into different parts on the basis of reaction involved.

a. Zone of Combustion

It is the lower portion of furnace. In this region, coke burns with oxygen to form carbon dioxide.



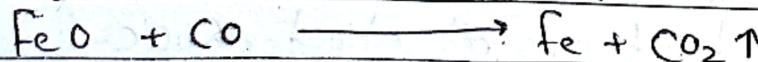
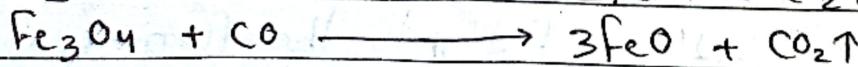
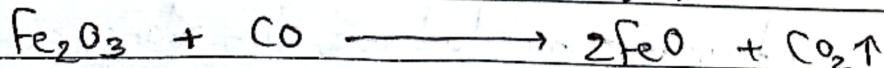
This is exothermic reaction. So, temperature increases upto 1500°C. In this region, upcoming carbon dioxide come in contact with coke and get converted into Carbon Monoxide



It is endothermic reaction. So temperature is lowered to 1200 - 1300°C. Carbon monoxide formed in this region acts as reducing agent.

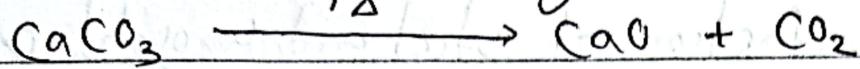
b. Zone of reduction

This is the upper portion of blast furnace and temperature ranges from 300°C - 700°C. In this region, carbon monoxide reduce oxide of iron into iron.

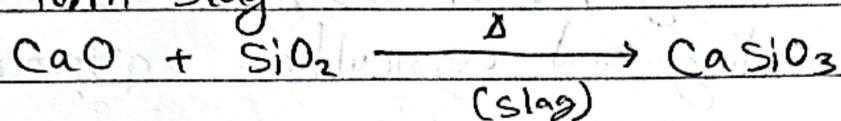


c) Zone of Slag formation

It is also the middle part of the furnace in which temperature ranges 900°C - 1000°C . In this region, calcium carbonate decompose to give CaO and CO_2 .



Lime acts as flux which combine with silica as impurities to form slag.



d) Zone of fusion

It is the lower portion of furnace having temperature around 1300°C . In this region, the spongy iron falling down starts to melt and dissolve small amount of carbon.

Two separate layers are formed at bottom of furnace.

Molten slag being lighter forms upper layer whereas molten metal forms lower layer. They are collected from two different outlets. Molten metal is solidified into blocks called pigs. So, iron obtained from this process is called pig iron or cast iron.

Varieties of Iron

There are three types of iron based on carbon content.

a) Cast iron or Pig iron

- It is the most impure form of iron and contain the highest percentage of carbon. It contains about 2-5% carbon along with little impurities such as silicon, manganese, phosphorus, sulphur etc.

(Fe_3C). The solidified pig iron when remelted can be cast into shape thus it is termed as cast iron. It is hard and brittle so it cannot be welded.

Uses:

- i. Used for manufacture of steel and wrought iron.
- ii. Finds extensive applications in casting various shaped articles such as toys, radiators, stools, sewage pipe, gas stoves, railing and agriculture equipment.

b. Wrought of Iron

It is the purest form of iron contents having lower percentage of carbon. It contains only 0.12 to 0.25% carbon along with some impurities like S, P, Mn, Si etc. Wrought iron is soft, ductile and malleable. It contains slag in the form of magnesia silicate which makes a tough and resistant towards corrosion.

Uses:

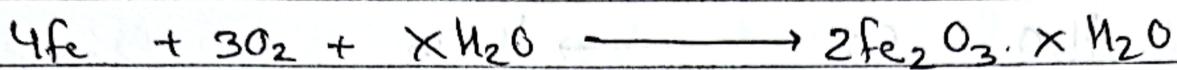
- i. Used in making chains, bolts, electric wires, shutters, rods, piano wires, anchors, fire bars etc.
- ii. Used to make magnets, in electric cranes and dynamo.
- iii. Used in construction of building, bridges etc.

c. Steel

Steel is an intermediate product containing carbon amount between cast iron and wrought iron. It contains carbon about 0.1% to 1.5% and little amount of S, P, Si and Mn. It also contains nickel, Manganese and chromium in small amount.

Rusting of Iron

Iron when exposed to moist air (air containing water vapour), an amorphous brown scale of hydrated ferric oxide of iron ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is formed on its surface which is known as Rust.



hydrated ferric oxide (rust)

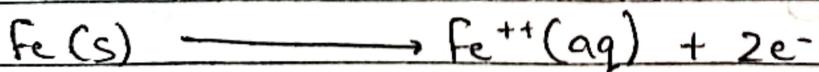
Theory of Rusting of Iron

A number of theories have been put forward to explain the phenomenon of rusting of which electrochemical theory best explain the mechanism of rusting.

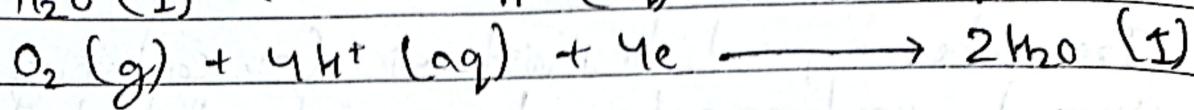
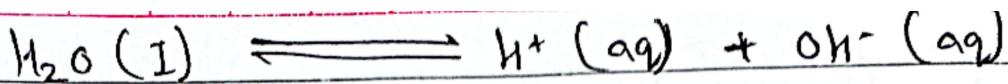
Electrochemical Theory

This is considered as the most reliable explanation about rusting. According to this theory, electrochemical cell is established on surface of iron. Different electrode potentials are developed at different portion of iron due to distribution of impurities or strains in the crystal. The portion having lower value of electrode potential develop as cathode and portion having high value of electrode potential develop as anode. Water containing oxygen and carbon dioxide act as a possit electrolyte.

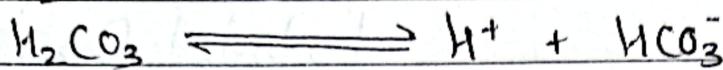
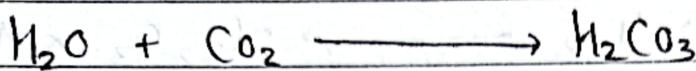
At anode: Iron get oxidized into ferrous (Fe^{++}) ion and liberated electron move toward cathode.



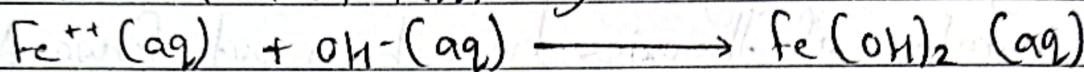
At cathode: Oxygen get reduced into water in presence of H^{+} ion. Hydrogen ion is liberated by ionization of H_2O .



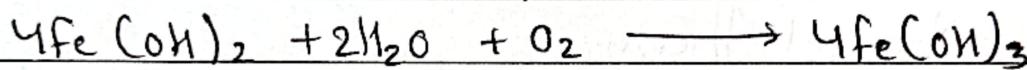
Hydrogen ion can also be formed by ionization of carbonic acid.



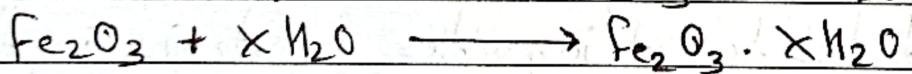
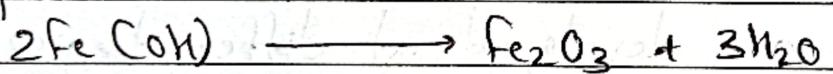
Fe^{++} ions move through water on the surface and combine with OH^- ion to form ferrous hydroxide.



Ferrous ion is further oxidised by atmospheric air in presence of water into ferric ions



Ferric hydroxide being unstable loses water molecule and decomposed into ferric oxide.



Prevention from Rusting

There are different methods developed to prevent iron from rusting.

- i. **Protective Coating:** Iron can be prevented from rusting by coating the surface of iron with any of the following coatings.
 - a. By coating the iron with non-corroding metals like Ni, Cr, Zn etc.
 - b. By coating with oil, grease, paints, varnishes, enamels etc. on the metal surface.
 - c. By the decomposition of a thin layer of oxide film or metallic film over the surface of iron. e.g. Fe_3O_4 etc.

ii) **Cathodic Protection**: In this process, iron is connected with more electropositive metals like Mg, Zn, Al etc. During this process, iron becomes cathode while more electropositive metals become anode and an electrochemical cell is thus established, the electropositive metals undergo corrosion in preference to iron. Thus iron is prevented from rusting. The process is known as cathodic protection.

iii) **Application of antirust solution (corrosion inhibitor)**: In this process, iron is treated with antirust solutions like potassium chromate, conc. HNO_3 , Phosphoric acid which prevents the iron from corrosion.

iv) **By Galvanizing iron**:

When iron is treated coated with a thin film of Zn, it is prevented from corrosion. This process is known as galvanization.

Compounds of Iron

A. **Ferric Chloride**: FeCl_3

It is an important chloride salt of iron with +3 O.S. It exists as dimer (Fe_2Cl_6) in vapour state and hydrated form such as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 12\text{H}_2\text{O}$ in crystalline state.

i. **Structure**

It is a covalent compound which in vapour form exists as a dimer.

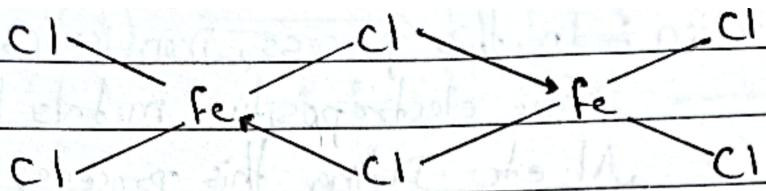
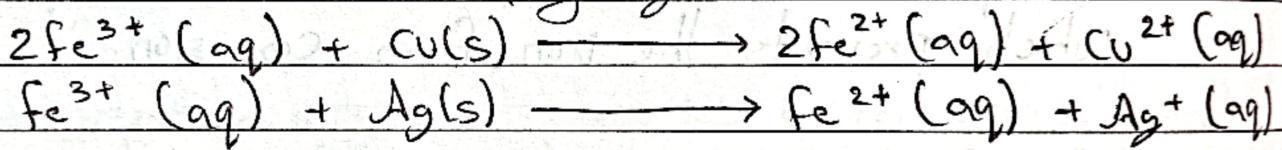


Fig: Structure of FeCl_3

In structure, each iron atom is tetrahedrally surrounded by four chlorine atoms, one by a co-ordinate covalent bond and 3 by covalent bond.

ii. Uses

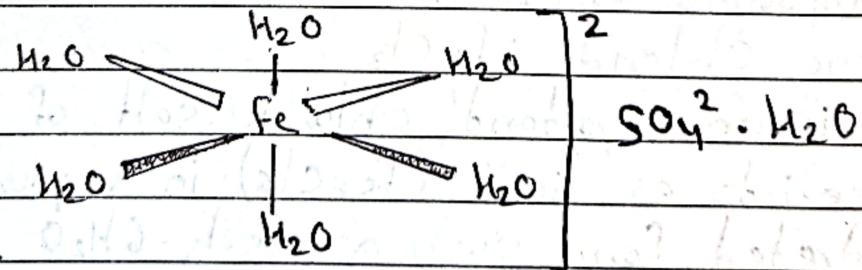
- It is used as antiseptic and coagulant (to stop bleed)
- It is used as mordant in dyeing industry.
- It is used as a laboratory reagent.
- It is used as an oxidizing agent.



B. Green Vitrol: ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

Green Vitrol is heptahydrated ferrous sulphate. It is a light green crystalline solid.

i. Structure



ii. Uses

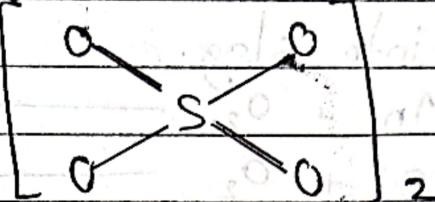
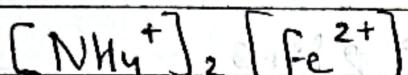
- It is used in the preparation of writing ink.
- It is used in volumetric analysis and titration.
- It is used as an insecticide.
- It is used in the preparation of Fe_2O_3 . Mohr's salt.

c. Mohr's Salt : $\text{[FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$

It is a double salt of ferrous sulphate and ammonium sulphate. It is also known as ferrous ammonium sulphate and is in the form of white powder.

i. Structure

The structure of anhydrous Mohr's salt is :



ii. Uses

- It is used as a reducing agent.
- It is used as primary standard solution in volumetric analysis in place of FeSO_4 to standardize KMnO_4 solution (since Mohr's salt is not oxidized so readily as FeSO_4).

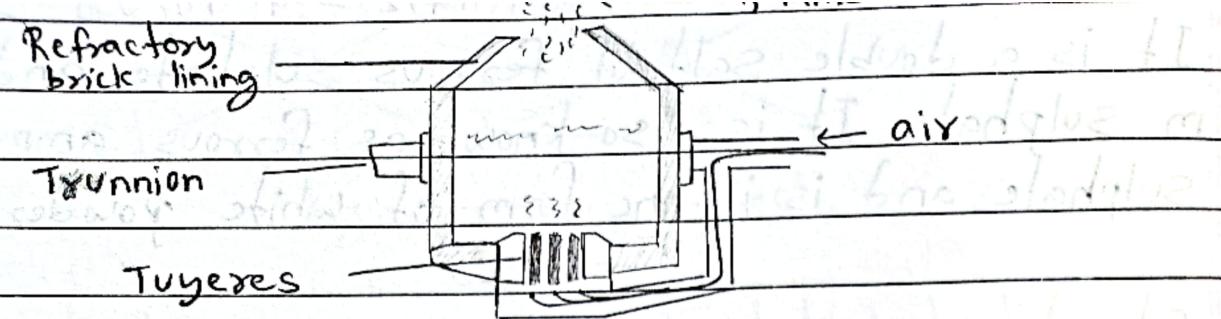
Manufacture of Steel

Steel is a form of iron containing 0.1 to 1.5% of carbon with little amount of mag. manganese. Steel can be manufactured from cast or pig iron by reducing carbon content and adding calculated amount of Mn, Cr and other elements.

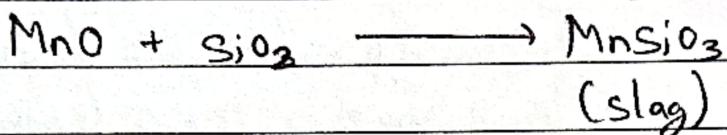
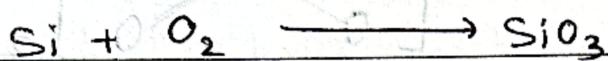
Steel can be manufactured by following methods.

a. Bessemer Process

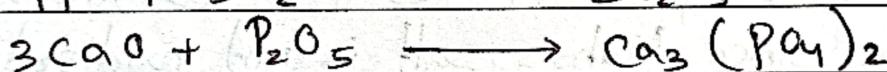
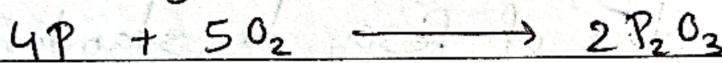
In this process molten cast iron from blast furnace is poured into the Bessemer converter which is an egg or pear shaped vessel made up of steel. It is supported on trunnion so that it can be tilted in desired position. Its base is perforated from which air is blown inside the converter as shown in the figure.



Impurities such as Mn, Si etc. are oxidized by air and converted into slag.



If impurities in cast are P and S, they are oxidized into acidic. They combine with lime magnesia to form slag



Calcium phosphate (Thomas Slag)

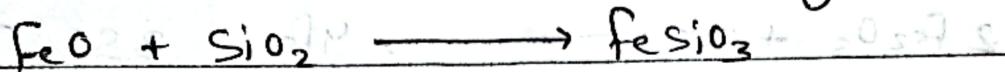
Thomas slag is used as chemical fertilizer to supply phosphorus.

The complete removal of impurities is indicated by formation of blue flame at the mouth of converter due to the formation of CO. When whole carbon is oxidized to CO, the blue flame dies off. Then a calculated amount of Spiegeleisen (alloy of Fe, Mn, C) is added and molten mass is agitated with blast of air to form steel.

Advantages of Bessemer Process

- It is the simplest and fast process.
- It requires very short time to complete the process.
- Limitations
- Low graded steel is obtained as process is fast and uncontrolled.

v. Some iron is lost in the form of slag.



b. Open Hearth Process [Siemen Martin's Process]

This process is used to manufacture high and fine quality steel in controlled way.

In this method cast iron is run directly from the blast furnace or to the hearth of the steel furnace where it is mixed with calculated amount of haematite (Fe_2O_3) and scrap iron with little lime. It is internally lined with SiO_2 or dolomite depending upon impurities present in cast iron.

Acid impurities - Lined with dolomite

Basic impurities - Lined with silica

The hearth is heated by producer gas at about 500°C to 1550°C . Impurities present in cast iron are oxidized by haematite ore. Some of the oxide oxides are removed as volatile gas whereas some are removed in the form of slag.

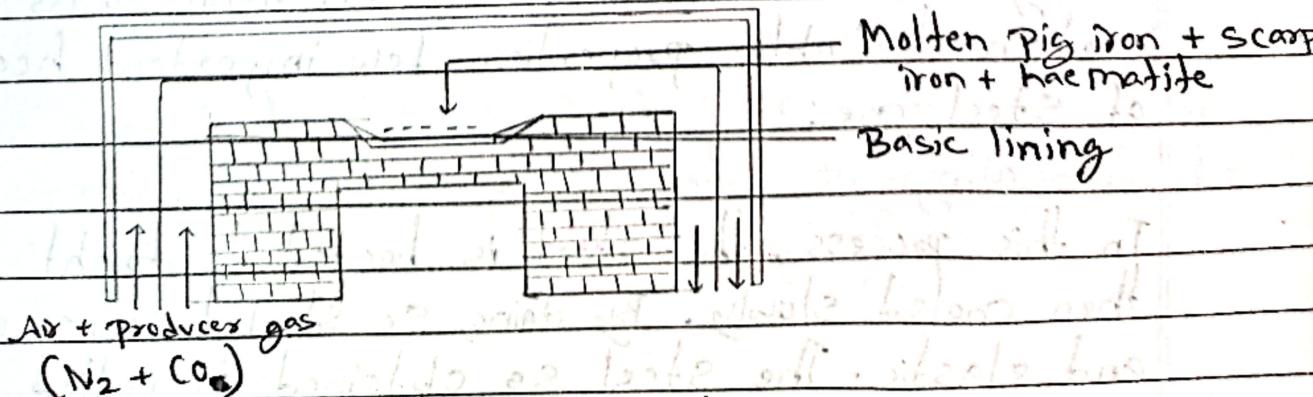
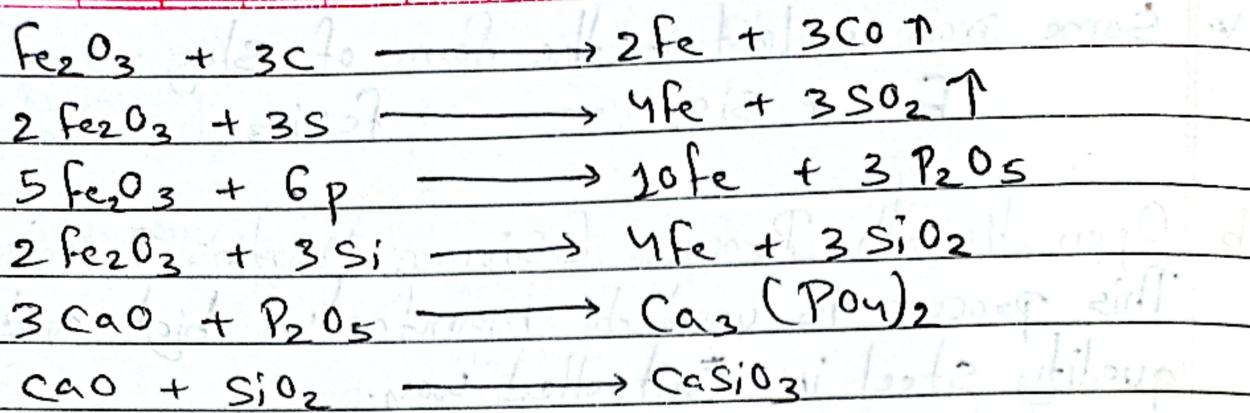


Fig: The Open Hearth



Slag being lighter floats on the surface which can be removed time to time. Small amount of molten mass is drawn out to check carbon content. Finally, calculated amount of Speigeleisen is added to obtain steel of desirable carbon content.

Advantages of Open Hearth Process

1. Steel of high quality can be obtained.
2. Scrap iron and haematite ore can also be used.
3. Composition of product can be checked time to time.
4. Iron is not lost in the form of slag.

Heat Treatment of Steel

Heat treatment of steel is the process of heating and cooling steel under controlled condition so as to obtain certain desirable properties. Few important heat treatments of steel are:

1. Annealing

In this process, the steel is heated to bright redness and then cooled slowly. By doing so steel becomes soft, ductile and elastic. The steel so obtained is called annealed-steel. Annealed steel is suitable in fabrication process.

2. Quenching or Hardening

When steel is heated to bright redness and is cooled suddenly

by plunging it into water or oil, hard, brittle and elastic steel is obtained. This process of heating steel is known as quenching or hardening and the steel so obtained is called hardened or quenched steel.

3. Tempering

In this process, the hardened or quenched steel is heated to a temperature much below redness (200°C - 350°C) and cooled slowly. The steel obtained is neither too hard nor too brittle. The steel is called tempered steel. Thus tempering of steel is the process of quenching followed by annealing. The tempered steel is used for making razor blades, knives, axes, watch spring etc.

4. Case Hardening

When the mild steel is heated with charcoal followed by quenching in oil, a thin coating of hardened steel is produced on its surface. This process is called case hardening. By case hardening steel becomes resistant to wear and tear and is used in the manufacture of armor plates and locomotive axles.

5. Nitriding of Steel

When steel is heated at about 700°C in an atmosphere of ammonia, iron nitride gets coated on the surface of steel. This process is called nitriding of steel.

Types of Steel

Stainless steel is an important example of special steel or alloy steel. It is an alloy of iron containing 74-80% of iron, 12-18% Cr, 1-8% of Ni and 0.2-0.3% of C. It resists corrosion, heat and action of organic acids.

It is used to make utensils, shaving blades, hospital equipments (surgical) etc.

Nature of steel based on carbon Content

i. Mild Steel: Mild steel contains 0.1 to 0.4% carbon.
Uses: For making wires and sheets.

ii. Medium Steel: It contains 0.2 to 0.5% carbon.
Uses: In construction.

iii. Hard Steel: It contains 0.5 to 1.5% carbon. It can be further hardened by heat treatment.

Uses: for making tools.

iv. Alloy Steel: Steel can be alloyed with many metals. Steel which in addition to carbon contains at least one metal like nickel, chromium, manganese, tungsten, molybdenum etc. having special properties is called alloy steel. For example, stainless steel, invar, chrome steel etc. These alloying metals impart certain special properties to steel.