

## GENERAL PRINCIPLES OF METALLURGY

### Topic: 2

### Occurrence and Principles of Copper, Zinc, Iron and Ag

### LONG ANSWER QUESTIONS

1. Explain the extraction of Iron from its ore.

**Metallurgy of Iron: The ore of iron are;**

Common Name	Chemical Name	Formula
Haematite	Ferric oxide	$\text{Fe}_2\text{O}_3$
Magnetite	Tri iron tetroxide	$\text{Fe}_3\text{O}_4$
Iron Pyrites	Iron sulphide	$\text{FeS}_2$
Spathic iron ore	Ferrous Carbonate	$\text{FeCO}_3$

**1. Occurrence of Iron:** Iron is quite reactive, so it is not found in Free State in nature. In the combined state, iron is found in the form of oxide, carbonate and sulphide. Iron occurs in the form of its sulphide in iron pyrites. It is not used commercially for the extraction because of its high sulphur content.

In India iron ores are found mainly in Bihar, West Bengal and Karnataka. The main iron and steel plants for the extraction of iron are located in Bhilai, Durgapur, Rourkela, Jamshedpur, Asansol and Bhadravathi.

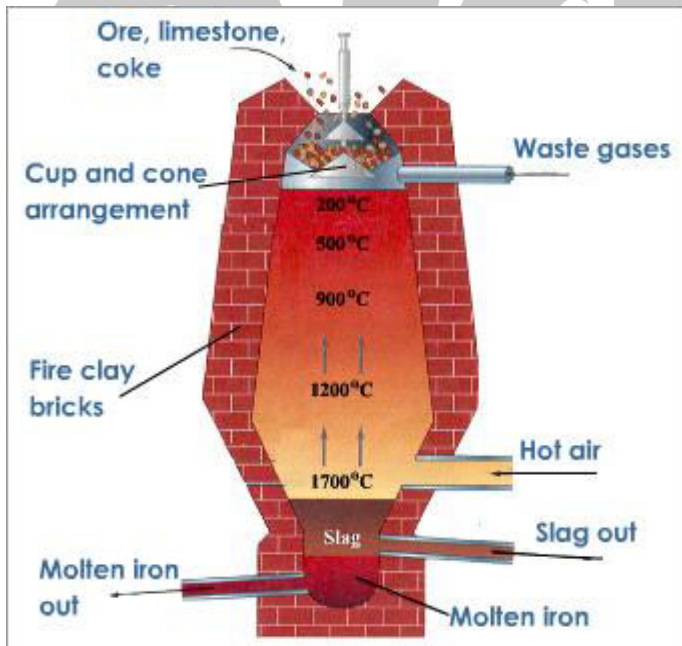
Most of the metal is produced from the iron (III) oxide ore called hematite  $\text{Fe}_2\text{O}_3$ . The ore contains silicon di oxide as impurity. Hence to obtain the metal from the ore,

- A reducing agent that can reduce hematite to metal is needed. The reducing agent used in blast furnace is carbon monoxide which is obtained by burning coke.
- A suitable flux to remove sand is also required. Sand is removed by using calcium oxide obtained by heating lime stone.

### Extraction of Molten Iron from Hematite:



- a) **Dressing and Concentration of Ore:** The iron ore is split into 2cm pieces and washed in water to remove sand, clay etc.
- b) **Calcination:** The washed ore is strongly heated in the absence of air to expel water sticking to it. The calcinations convert the carbonate ore into oxide.
- c) **Reduction:** The washed and dried hematite is mixed with measured quantities of coke and lime stone and fed into the blast furnace.
- d) **Reduction of Roasted Ore in the Blast Furnace (Smelting):** Blast furnace is a cylindrical furnace made by refractory bricks surrounded by a steel shell.



### Blast Furnace:

Height of the furnace: 60-100ft

Base of the furnace: 30-35 ft

Double cup and cone arrangement

- It allows the entry of charge into furnace but does not allow any gas to escape through it
- The gases escape through the outlets at the top of the furnace and are later burnt

### Tuyeres

- Circular pipes at the base of the furnace for the entry of hot compressed air
- The air is blown from the sides and the molten iron below into the hearth, is not oxidised by air.

### Outlets

- Outlet for slag
- Outlet for molten iron
- Roasted haemetite - 8 parts
- Coke - 4 parts

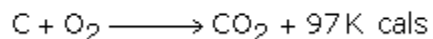
**Charge Added to the Blast Furnace with Calcium carbonate - 1 part**

### Reactions in Blast Furnace in Different Regions

#### Combustion Zone

**Reaction:** Combustion of coke will take place.

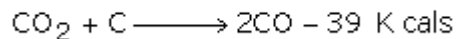
Temperature of the region: 2000°C



#### Fusion Zone

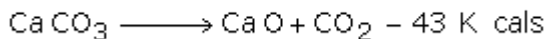
Reaction: Reduction of carbon dioxide to carbon monoxide

Temperature of the region: 1300° C



### Decomposition of Limestone

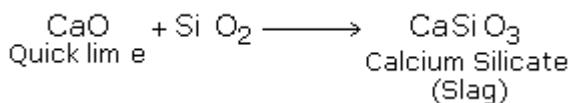
The lime stone ( $\text{CaCO}_3$ ) decomposes to give carbon dioxide and quicklime ( $\text{CaO}$ )



The above reaction is endothermic and the temperature in the region falls to about 800-1000°C.

### Formation of Slag

The quicklime reacts with acidic impurities such as silica ( $\text{SiO}_2$ ) and forms a slag which melts and collects above the iron at the bottom of the furnace. Slag is an easily fusible mass having a low melting point.



### Reduction Zone

Reduction of haemetite to molten iron takes place here.

Temperature of the region: 500-700° C

In the upper region of the furnace, the CO reduces the haemetite to molten iron and oxidizes it self to  $\text{CO}_2$ .



- The molten iron produced is collected, poured into moulds and solidified to give pig iron.
- Pig iron contains carbon, sulphur, phosphorus, silicon and manganese as impurities

## 2. Explain the extraction of copper.

### Extraction of Copper:

The ores of copper are

- Copper pyrite  $\text{CuFeS}_2$
- Azurite blue  $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
- Malachite  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

Copper is extracted from copper pyrites. The rocky impurities including silica and mud along with the ore is called gangue which has to be removed:

**Concentration of the ore:** Froath floatation process is applied to remove the gangue. The ore is mixed with pine oil and water which is put into a large tank. It is agitated with a current of compressed air. The ore is wetted by the oil and separates from the gangue in the form of froth. Gangue settles down.

### Roasting and Smelting

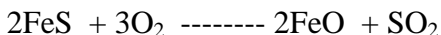
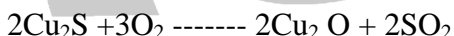
The extraction of copper includes Roasting, smelting and refining

- **Roasting** - Heating the ore in presence of air is roasting. The ore is roasted in excess of air in a furnace.

The following reaction occurs:-

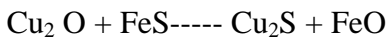
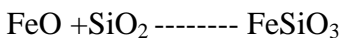


Sulphides of copper and iron will be oxidized to their respective oxides.



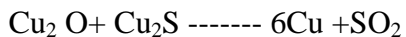
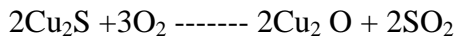
- **Smelting:**

The above process is done in blast furnace. The roasted ore will be mixed with coke and silica in the furnace. Hot air is passed over the above mixture. The ferrous oxide changes to its silicate.



The silicate of iron can be removed as it floats over the molten matte.

From the molten matte copper is removed by the process of Bessemerization. This is done in Bessemer converter. The above matte is put into it and air is blown thro it. The following reaction occurs and copper is obtained.



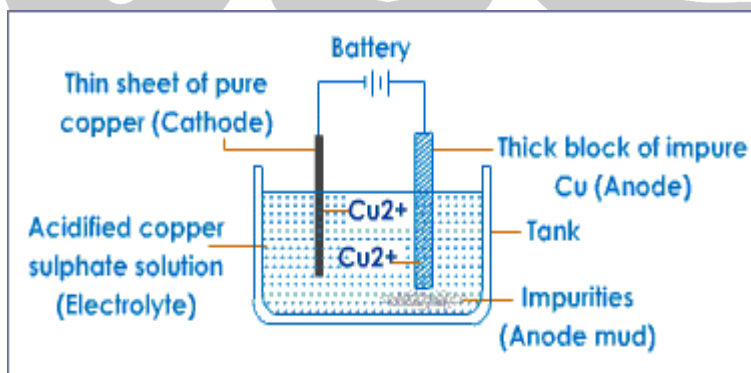
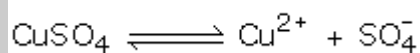
The copper obtained undergoes solidification. The copper obtained is called blister of copper. It contains some impurities like lead, arsenic, antimony etc. due to which the mechanical and electrical properties of copper are affected.

## Refining

Refining is the final step in extraction of copper. Refining is done by the process of electrolysis. Electrolyte: copper sulphate solution acidified.

### Electro refining of Copper

- Electrolyte - Aqueous copper sulphate solution (acidified)
- Cathode - Pure copper metal (thin rod)
- Anode - Impure copper metal (thick block)
- Dissociation of copper sulphate -



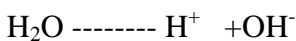
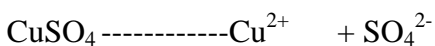
### Purification of Impure Copper

**Cathode** pure thin sheet of copper lined with graphite so that the deposited copper can be removed easily.

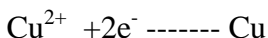
**Anode** blister copper (got above)

**Electrode reaction**

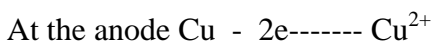
Copper sulphate dissociates



At the cathode the copper ion changes to copper atom by gaining two electrons which get deposited in the pure copper rod.



The sulphate ion and hydroxide ion move towards anode but none of them is discharged. The copper anode itself loses electrons and gives copper ion in the solution.



The impure block of copper thus will be used. The impurities settle at the bottom of the electrolytic cell. This is known as anode mud or slime.

The impurities iron, zinc etc ionize and dissolve in the copper sulphate solution. They are above copper in the activity series. So they can displace copper from copper sulphate solution.

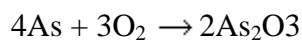
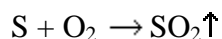
The weight of cathode will increase. The copper obtained is 100% pure.

**3. Write an essay on how copper matte is treated to get pure copper?**

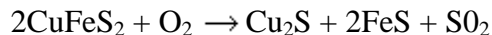
• **Roasting:**

The concentrated ore is heated in the presence of excess of air in a reverberatory furnace. During heating temperature is kept below its melting point. Following changes are observed.

- i. Moisture is expelled
- ii. Sulphur, arsenic and phosphorus impurities are expelled in form of their volatile oxides.



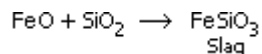
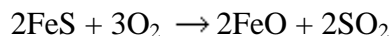
- iii. Copper pyrite ore is converted to ferrous sulphide and cuprous sulphide



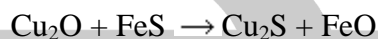
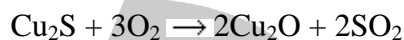
• **Smelting:**

Mixture of roasted ore, powdered coke and sand is heated in blast furnace. Following changes are observed:

- i. Oxidation of ferrous sulphide takes place and ferrous oxide thus formed reacts with silica to form fusible slag,  $\text{FeSiO}_3$ .



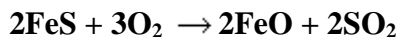
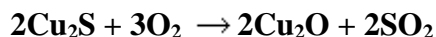
- ii. Cuprous oxide which is formed as a result of oxidation is partially converted back into cuprous sulphide.



From the base of the furnace molten mass called **matte** is removed.

• **Bessemerisation:**

The **matte** is transferred to bessemer converter, which is a pear-shaped furnace, lined from inside with magnesium oxide. Air blast in bessemer converter is added through Tuyers. The following reactions take place in the bessemer converter



The iron oxides forms slag with silica.



The cuprous oxide reacts with more of  $\text{Cu}_2\text{S}$  to form copper.

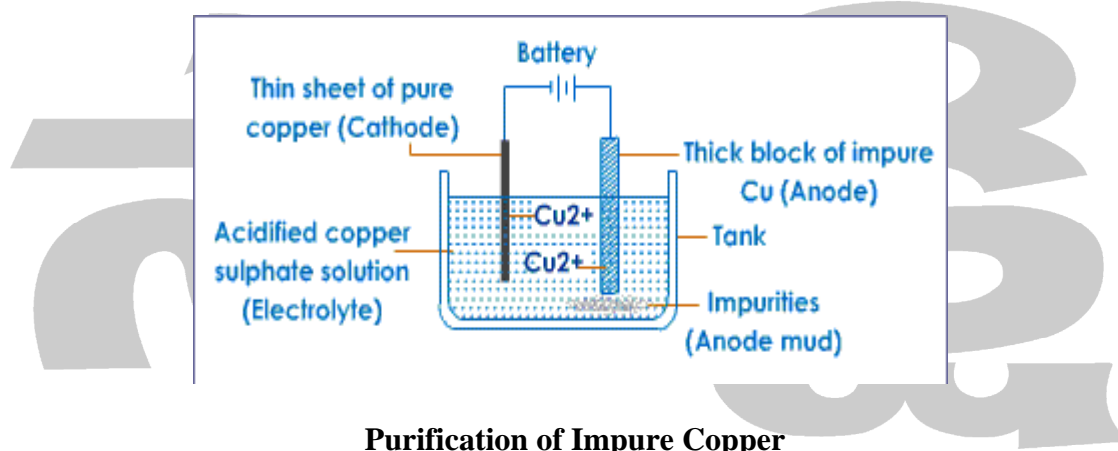




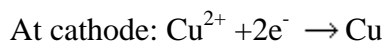
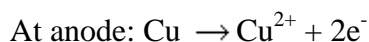
After the completion of reaction, the molten copper is poured off. As it cools, it gives up the sulphur dioxide dissolved in it which comes out in the form of bubbles thus giving the shape of blisters to the surface of copper, which is therefore, known as **Blister copper**.

• **Purification:**

- i. **Poling:** The blister copper is purified by melting it in a reverberatory furnace where it is exposed to an oxidising atmosphere. The impurities are expelled as volatile oxides. During this process the molten mass is stirred with long poles of green wood. The process is known as poling. The reducing gases evolved from the wood prevent the oxidation of copper.
- ii. **Electrolytic purification:** The crude copper obtained is then purified by electrolysis. Impure copper is made anode and a thin strip of pure copper is made cathode. An aqueous solution of copper sulphate, acidified with dil.  $\text{H}_2\text{SO}_4$  is used as electrolyte. During electrolysis anode starts dissolving due to oxidation whereas copper cathode becomes thicker due to decomposition of copper.



**Purification of Impure Copper**



Impurities fall under anode and cathode mud.

**4. Explain the extraction of Zinc from its ore.**

**Ans:**

Zinc is a bluish white metal and it is good conductor of heat and electricity. Because of the presence of metallic bonding. It is malleable and ductile.

Atomic number of Zinc is 30 and atomic mass number is 65.37. It is present in the Group 112 and period 4 in the periodic table.

## Introduction to zinc ore

Zinc does not occur in the native form since it is a reactive metal. However, in the combined state, zinc is widely distributed.

### Zinc Ores

The important ores of zinc are

- i) Zinc blende, ZnS
- ii) Calamine, ZnCO<sub>3</sub>
- iii) Zincite, ZnO

The chief ore of Zinc is Zinc blende

### Extraction of Zinc from its Ores.

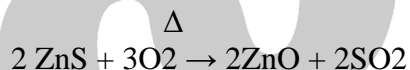
The extraction of Zinc from Zinc blende involves the following steps.

#### 1. Concentration

The ore is crushed and then concentrated by froth-floatation process.

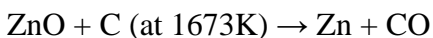
#### 2. Roasting

The concentrated ore is then roasted in the presence of excess of air at about 1200 K.



#### 3. Reduction

Zinc oxide is mixed with powdered coke and heated to 1673 K in a fire clay retort, in which ZnO is reduced to zinc metal.



### Purification

Zinc is purified by electrolytic refining. In this process, Impure Zinc is anode and cathode is of pure thin sheet of Zinc. The electrolyte is ZnSO<sub>4</sub> solution containing a little of dil.H<sub>2</sub>SO<sub>4</sub>. On passing electric current, pure zinc get deposited at the cathode.

### Uses of zinc

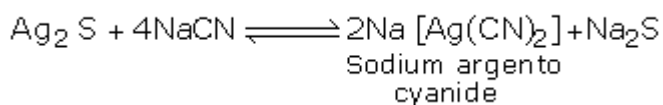
1. It is widely used for galvanizing iron sheets.
2. It is used in the extraction of gold and silver by the cyanide process.
3. Zinc plates and rods are used in batteries and dry cells.
4. Zinc dust and granulated zinc are used in laboratory as reducing agents.

## 5. Explain the extraction of Silver from its ores.

### Extraction of Silver

Silver also occurs both in combined state as well as in Free State. The important ores of silver are: Argentite ( $\text{Ag}_2\text{S}$ ), Copper silver glance, Horn silver, Ruby silver. The silver ores are found along with gold ores in some parts of India.

Silver is extracted from the ore-argentite ( $\text{Ag}_2\text{S}$ ). The process of extraction of silver is called as cyanide process as sodium cyanide solution is used. The ore is crushed, concentrated and then treated with sodium cyanide solution. This reaction forms sodium argento cyanide.



The solution of sodium argento cyanide combines with zinc dust and forms sodium tetra cyanozincate and precipitated silver. This precipitated silver is called spongy silver.



The spongy silver is fused with potassium nitrate to obtain pure silver. Then the silver obtained is purified by electrolytic process.

## 6. What for do we use Mac Arthur-Forrest cyanide process? Describe the metallurgy that uses this process.

### Silver Ore Extraction

Silver is the silver white metal with atomic number of 47 and atomic mass number of 108. It is highly malleable and ductile. It is a good conductor of electricity for this purpose it is used in electrical cabling. Silver salts are used in silvering of mirrors. Silver leaf is used in medicine, while silver amalgam is employed in dental filling.

### Introduction to silver ore extraction

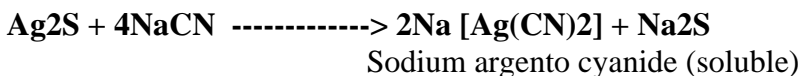
Silver is used in making inert electrodes which is used for preparing other metal. Silver occurs both in the native as well as in the combined state. The important ores of silver are Argentite or silver glance,  $\text{Ag}_2\text{S}$ , Horn silver or chlorargyrite,  $\text{AgCl}$ , Pyrargyrite or Ruby silver,  $\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ . The chief ore of silver is Argentite. The silver content in these ores is very small around 1%

## Mac-Arthur and Forrest's Cyanide Process for Silver Ore Extraction

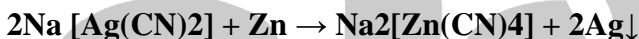
Silver is extracted from the argentite ore by the Mac-Arthur and Forrest's cyanide process. The various steps involved in silver ore extraction process are as follows.

The crushed ore is concentrated by froth-floatation process. Sulfide ores are concentrated by this method. Silver ore is preferentially wetted by froth and so they remain in the froth and the impurities are wetted by water.

The concentrated ore is treated with 0.4-0.6% solution of sodium cyanide for several hours. The mixture is continuously agitated by a current of air, so that Ag present in the ore is converted into soluble sodium argento complex. While the impurities remain in the solution as undissolvable particles. This makes the separation of silver more effective since all other elements and impurities are not soluble in water.



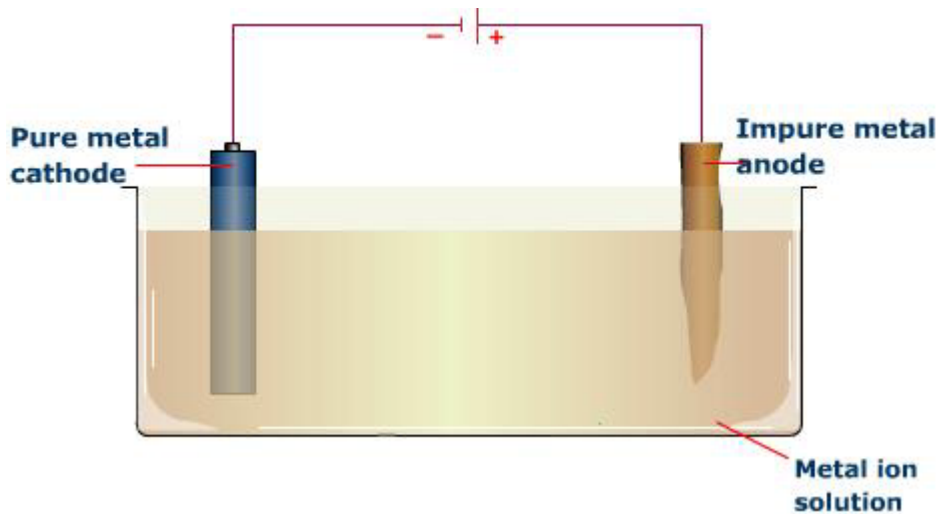
The solution containing sodium argento cyanide is filtered to remove insoluble impurities and filtrate is treated with zinc dust, silver gets precipitated. It is a displacement reaction where zinc being more reactive goes into the complex and silver is thrown out.



The impure silver is further purified by electrolytic refining. The impure silver is made the anode while a thin sheet of pure silver acts as the cathode. The electrolyte is silver nitrate acidified with 1% nitric acid. On passing electricity pure silver gets deposited at the cathode.

A large number of metals e.g., copper, silver, gold, nickel etc. are refined by this method. In an electrolytic cell the impure metal is made anode and a thin strip of pure metal is made cathode. A solution of a suitable salt of the concerned metal is used to fill the electrolytic cell. On passing electricity, the anode undergoes dissolution while the pure metal gets deposited at cathode. Insoluble impurities fall below the anode in the form of anode mud.

There are other methods as well but this is the preferred method for extraction of silver ore.



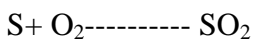
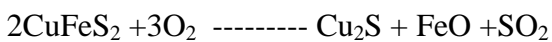
Electrolytic purification of a metal

### SHORT ANSWER QUESTIONS

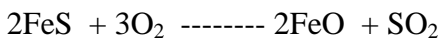
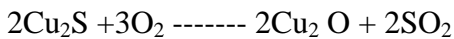
1. Write short notes on; a) roasting b) Calcination C) Smelting

- **Roasting** - Heating the ore in presence of air is roasting. The ore is roasted in excess of air in a furnace.

The following reaction occurs:-

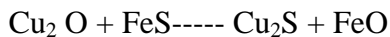
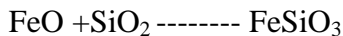


Sulphides of copper and iron will be oxidized to their respective oxides.



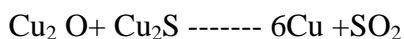
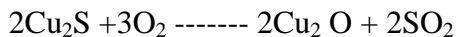
- **Smelting:**

The above process is done in blast furnace. The roasted ore will be mixed with coke and silica in the furnace. Hot air is passed over the above mixture. The ferrous oxide changes to its silicate.



The silicate of iron can be removed as it floats over the molten matte.

From the molten matte copper is removed by the process of Bessemerization. This is done in Bessemer converter. The above matte is put into it and air is blown thro it. The following reaction occurs and copper is obtained.

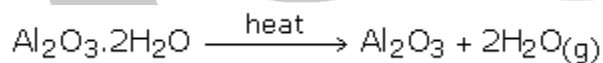


The copper obtained undergoes solidification. The copper obtained is called blister of copper. It contain some impurities like lead, arsenic antimony etc due to which the mechanical and electrical properties of. Copper is affected.

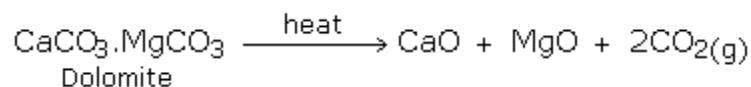
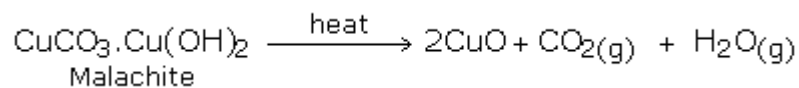
- **Calcination**

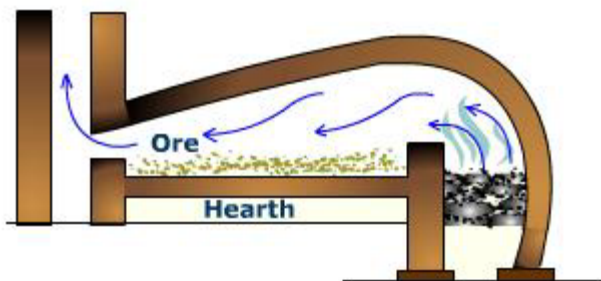
The concentrated ore is converted into oxide by calcination i.e., heating it strongly in the absence of air or roasting (heating it strongly in presence of air). This helps in removing volatile impurities like  $\text{CO}_2$ ,  $\text{SO}_2$ , organic matter, and moisture from the ore. For example,

- It removes moisture from bauxite.



- It removes  $\text{CO}_2$  from carbonate ores e.g.,



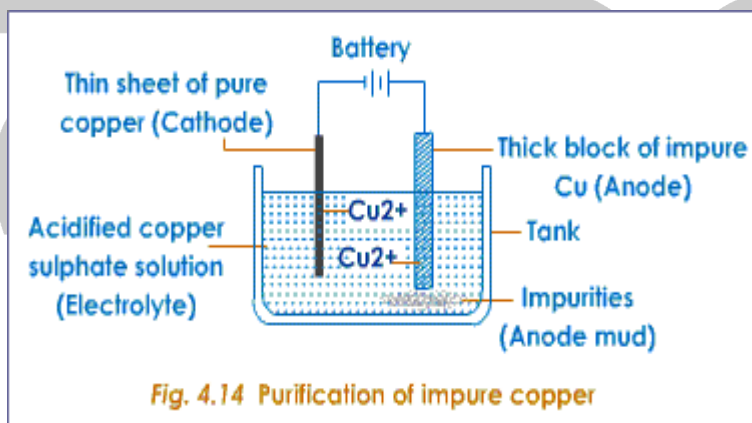


**A reverberatory furnace**

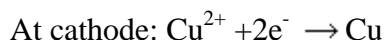
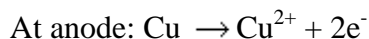
Calcination is done on the hearth of a reverberatory furnace.

**2. Write a note on the refining of crude copper metal.**

Ans: **Electrolytic purification:** The crude copper obtained is then purified by electrolysis. Impure copper is made anode and a thin strip of pure copper is made cathode. An aqueous solution of copper sulphate, acidified with dil.  $H_2SO_4$  is used as electrolyte. During electrolysis anode starts dissolving due to oxidation whereas copper cathode becomes thicker due to decomposition of copper.



**Fig. 4.14 Purification of impure copper**



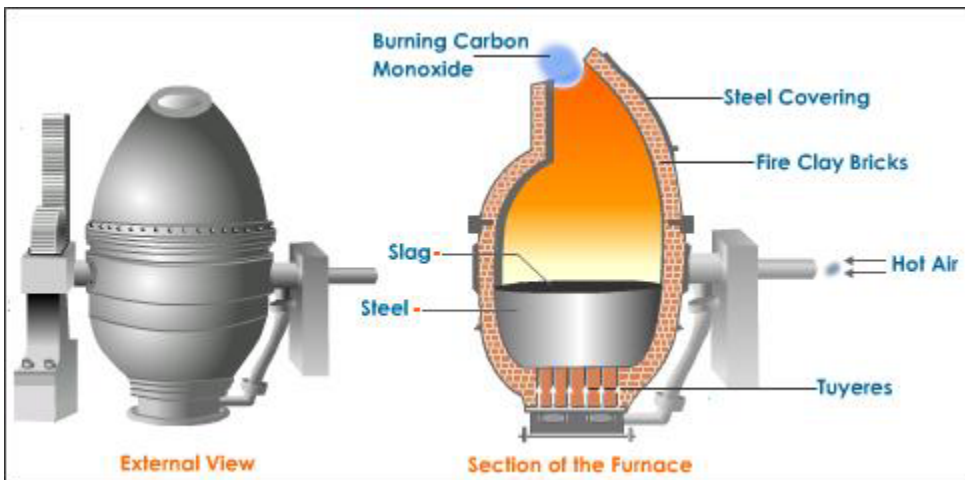
Impurities fall under anode and cathode mud.

**3. Describe any method to convert cast iron into steel of high quality.**

**The Bessemer process**

**Bessemer converter**

Bessemer converter is a pear-shaped furnace, 20 feet high and 10 feet in diameter. It is made of steel plates and is lined inside with brick to resist heat. There are number of holes at the base, called tuyeres, for air circulation. The converter can be rotated on a horizontal central axis.

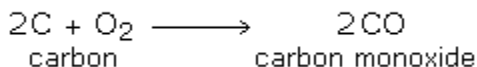
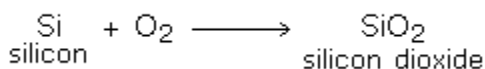
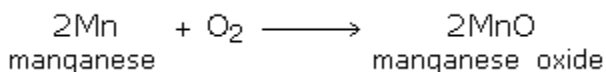


## The Bessemer converter

### Process

The Bessemer converter is turned into a horizontal position and molten pig iron is poured into it. A blast of hot air is sent through the tuyeres.

The converter is rotated so that it is vertical and hot air is blown continuously. In its upward travel through the converter, the air oxidises the impurities in pig iron.



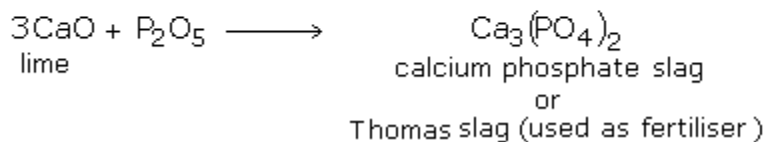
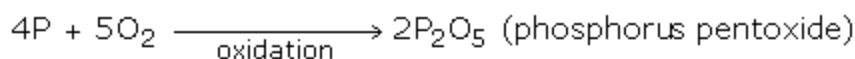
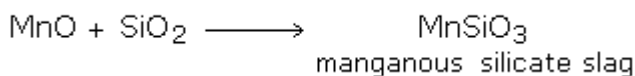
Manganese and silicon are oxidised to the respective oxides during the first 5 to 10 minutes. Carbon monoxide is liberated at a later stage and it burns with a blue flame at the mouth of the converter. When all the carbon is oxidised, the blue flame dies out. To convert pig iron to steel, the required amount of carbon is then added. This is in the form of an alloy of iron called spiegeleisen. It contains carbon and manganese besides iron. The resulting product is manganese steel, which is removed by tilting the converter.



**Note:** Adding a little aluminium or silicon-iron alloy to molten steel helps in removing dissolved carbon monoxide or nitrogen from the molten metals. Gas must not be left behind as an impurity. The presence of carbon monoxide or nitrogen can cause defects like blowholes in castings.

### Slag Formation

The impurities like manganese oxide and silicon dioxide formed during the initial stages of the Bessemer process are removed when they react with each to form a slag.



### Note:-

If the cast or pig iron contains phosphorus as an impurity, the converter should be lined with lime (CaO) and magnesia (MgO) instead of silica. Some lime is also added to the charge.

### 4. How Bauxite ore is purified by Baeyer's process?

#### Bayer's Process

Bayer's process involves concentration and dehydration of bauxite to alumina ( $\text{Al}_2\text{O}_3$ ).

#### Treatment with NaOH

Bauxite is treated with hot, concentrated NaOH solution.

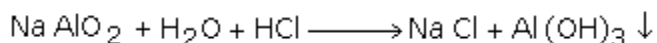
Aluminium oxide reacts with NaOH forming an aqueous solution of sodium aluminate. The impurities do not react.



On filtration, impurities are separated from the sodium aluminate solution.

#### Treatment with HCl

The filtrate containing sodium aluminate is acidified with hydrochloric acid to form a precipitate of aluminium hydroxide.



On filtration sodium chloride solution is obtained as a filtrate and is discarded. The pure aluminium hydroxide obtained as a gel is collected.

### VERY SHORT ANSWER QUESTIONS

1. What metal is purified by cupellation/

**Ans:** Ag is purified by cupellation.

2. Explain polling.

**Ans:** Removal of impurities from metal by using green wood pole is called polling.

3. Define flux.

**Ans** An outside substance added to the ore to lower the melting point is known as flux. Flux combines with gangue chemically and forms easily fusible slag.

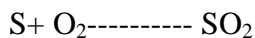
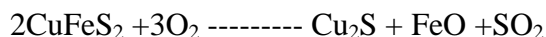
4. Where do reactions in a blast furnace take place?

**Ans:** The reactions in a blast furnace take place in the “**body of the furnace**”

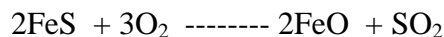
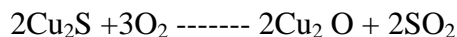
5. What are the changes take place during roasting?

**Ans: Roasting** - Heating the ore in presence of air is roasting. The ore is roasted in excess of air in a furnace.

The following reaction occurs:-



Sulphides of copper and iron will be oxidized to their respective oxides.

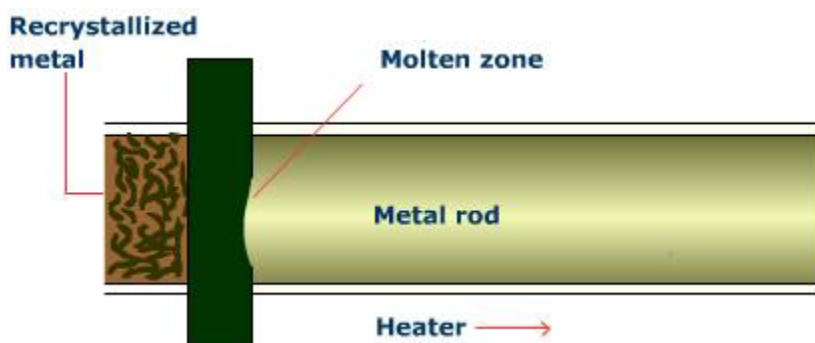


## 6. Write a note on zone refining.

### Zone refining method

When metals are required in an ultra pure state, the zone refining method is used. The principle employed states that the impurities, which lower the melting point of a metal remain preferentially dissolved in the liquid phase and purer metal will emerge in the solid phase.

In actual practice, a cylinder of impure metal is kept in a tubular furnace and the heater is made to move in one direction at a very slow speed. The solid material crystallizes as the heater moves along the tube, and the advancing zone contains liquid with higher impurity content. The process is repeated a number of times till the desired level of purity is obtained.



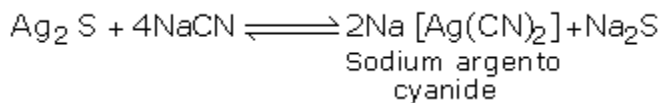
The Zone refining method

## 7. How crude silver is refined electrolytically?

**Ans:** The impure silver is further purified by electrolytic refining. The impure silver is made the anode while a thin sheet of pure silver acts as the cathode. The electrolyte is silver nitrate acidified with 1% nitric acid. On passing electricity pure silver gets deposited at the cathode.

## 8. Explain the extraction of silver from horn silver.

**Ans:** Silver is extracted from the ore-argentite ( $\text{Ag}_2\text{S}$ ). The process of extraction of silver is called as cyanide process as sodium cyanide solution is used. The ore is crushed, concentrated and then treated with sodium cyanide solution. This reaction forms sodium argento cyanide.



The solution of sodium argento cyanide combines with zinc dust and forms sodium tetra cyanozincate and precipitated silver. This precipitated silver is called spongy silver.



The spongy silver is fused with potassium nitrate to obtain pure silver. Then the silver obtained is purified by electrolytic process.

సాక్షి