GENERAL PRINCIPLES OF METALLURGY

Topic: 1

Principles and methods of extraction – concentration - reduction by chemical and electrolytic methods and refining

LONG ANSWER QUESTIONS

1. Write a note on ore dressing in metallurgy.

a. Concentration of the ore (ore dressing)

The removal of the undesired foreign impurities i.e., gangue, from the ore is called concentration (or beneficiation) of the ore. Either of the following methods is used for concentrating the ores:

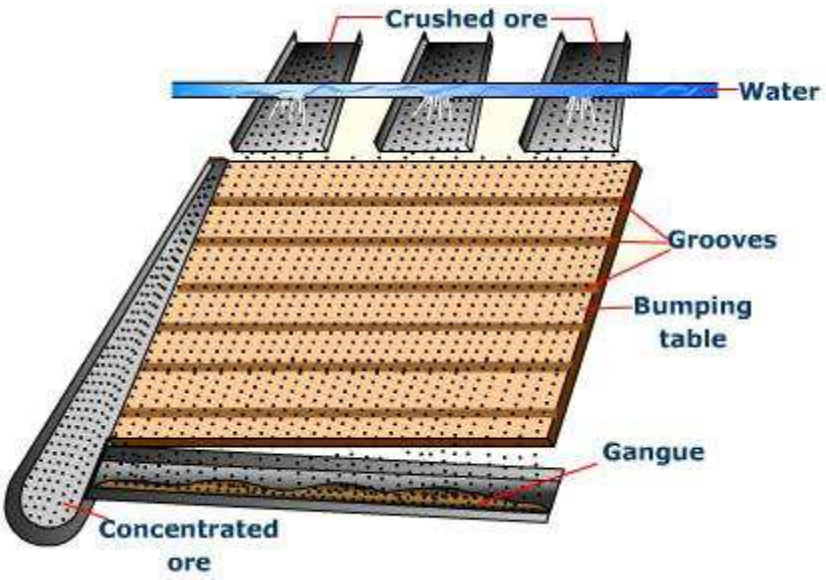
b. Hand picking

If the impurities present are quite distinct from the ore, and are of large size, these may be removed by hand picking. This method is slow and is generally adopted in the initial stages of concentration.

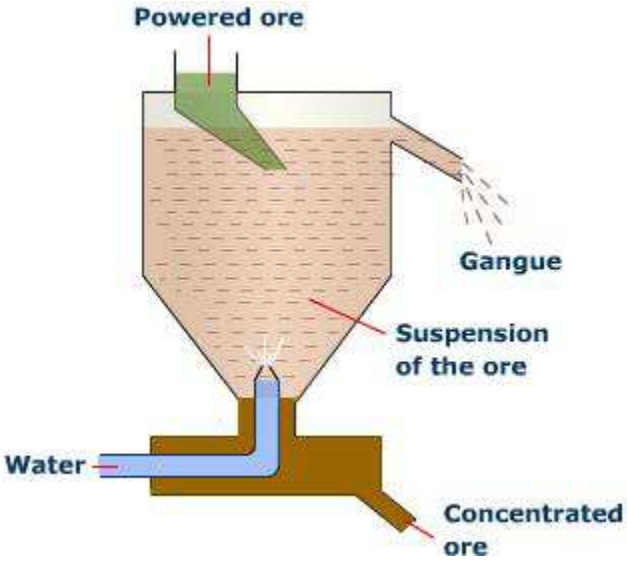
c. Gravity or levigation method

When the ore particles are heavier than the gangue particles, the ore is fed into a running stream of water and impurities are washed away. This separation is by way of gravity or levigation method and is commonly used for oxide ores such as hematite and native ore of Au, Ag, etc. In order to concentrate the ore in bulk, a slanting vibrating wooden table with wooden strips called riffles is introduced in the process. Such tables are termed Wilfley tables. The ore is continuously washed with a fine spray of water and the rocking motion sieves the heavier portions, while allowing the impurities to filter away.

Sometimes in the gravity method, a hydraulic classifier based on the gravity method is used. Ore is agitated by a powerful current of water pushing upwards through the bottom of a conical reservoir. The heavier ore particles settle down and are continuously removed from another opening near the bottom, while the lighter particles are washed away by water.



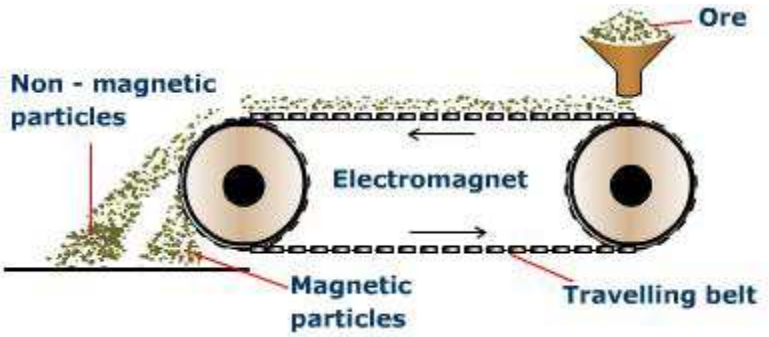
Wilfley table for washing of the ore



Hydraulic classifier

d. Magnetic separation

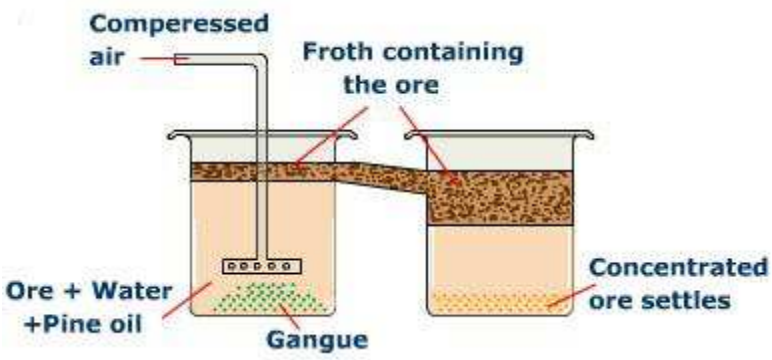
Magnetic separation is done especially in the case of haematite ore, whereby the powdered ore is dropped on to leather or brass conveyer belt, which moves over two rollers one of these rollers, is magnetic. When the ore passes over the magnetic roller, it sticks to the belt due to the force of attraction and falls nearer due to the force of attraction of the magnetized roller. The gangue falls over readily, further away. The ore and the magnetic impurity are collected as two separate heaps.



Magnetic separation

e. Froth flotation process

This process is used for concentrating sulphide ores; as such ores are preferentially wetted by oil while the gangue particles are wetted by water. Powdered ore is mixed with water and a little pine oil and the mixture is vigorously stirred by passing compressed air. The froth, which is produced rises to the surface and carries the ore particles along with it. The gangue is left behind



The froth flotation process

f. Leaching process

In this method, the ore is treated chemically with a suitable reagent that preferentially dissolves the active component of the ore. The concentrated ore form is then recovered from the solution by a suitable chemical method.

A typical example of ore concentration by leaching process is the purification of bauxite using NaOH solution as a leachant. The Bauxite is digested with concentrated solution of caustic soda at 150°C in an autoclave. The Aluminium oxide dissolves in NaOH leaving behind the insoluble impurities, which are removed by filtration.

$$Al_2O_3.2H_2O + 2NaOH \xrightarrow{150\,^{\circ}C} 2NaAlO_2 + 3H_2O$$

The solution of $NaAlO_2$ (sodium meta-alumiinate) is then treated with freshly prepared $Al(OH)_3$ when the entire aluminium in the solution gets precipitated as $Al(OH)_3$

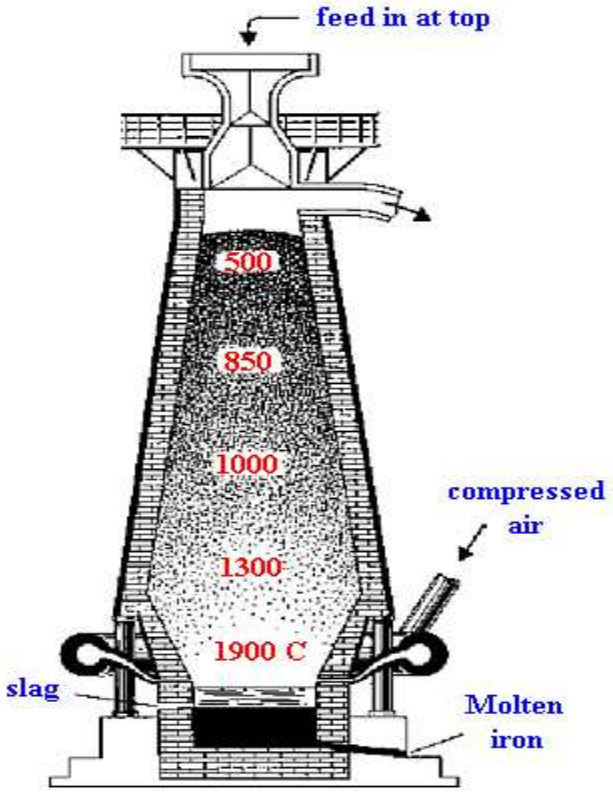
$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

The precipitate of $Al(OH)_3$ is removed, washed and dried to get Al_2O_3.

2. **Write an essay on furnaces used in metallurgy.**

a. Blast Furnace:

Blast furnace is a furnace which is used in Metallurgical process such as Smelting to reduce industrial metals from its respective ore, generally iron**.**



Blast furnace consists of a thick wall lined by silicon bricks which helps to retain the hot temperature. At the top of the furnace there is a cup & cone arrangement where the mixture of Ore, Calcium Carbonate & coke in the ratio 9: 3: 1n is placed and through the opening at the top, mixture of ore enters the furnace. Furnace contains two tuners to pass in the compressed air as shown above. The furnace contains one opening below the the cup and cone arrangement, which is the outlet for waste gases produced during the reduction. Other two openings at the bottom are the outlets for the cast iron and slag.

Blast furnace contains 4 zones where the different steps of reduction of the iron take place and they are differentiated with respect to the corresponding temperatures

Zones and Temperatures of Blast Furnace

1. **Zone of Reduction: -** It is the zone where the Iron ore gets reduced to iron oxide at the temperature of 850ºc

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

2 . **Zone of Slag formation**: - It is the zone where the slag is formed by the reduction of the Calcium Carbonate ($CaCO_3$) into Calcium Oxide (Cao) . Then it combines with silicon (SiO_2) to form Calcium Silicate ($CaSiO_3$) at 1000ºc

$CaCo_3 \rightarrow CaO + CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$

3. Zone of Fusion: It is the zone where carbon (C) reacts with ferric oxide (FeO) to give Iron (Fe) at 1300ºc

$FeO + 3C \rightarrow Fe + 3CO$

$CO_2 + C \rightarrow 2CO$

4. Zone of Combustion: - It is the zone where the compressed air is passed in which carbon (C) and oxygen (O_2) to form (CO_2) carbon Di Oxide

$C + O_2 \rightarrow CO_2$

Thus at the end of the process Iron (Fe) is got. This iron is also known as Cast Iron Or Pig Iron.

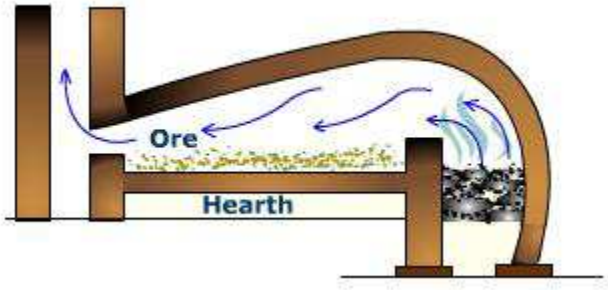
Reverberatory furnace:

A reverberatory furnace is a metallurgical or process furnace that isolates the material being processed from contact with the fuel, but not from contact with combustion gases. The term reverberation is used here in a generic sense of rebounding or reflecting, not in the acoustic sense of echoing.

. The heat passes over the hearth, in which the ore is placed, and then reverberates back. The roof is arched, with the highest point over the firebox. It slopes downward toward a bridge of flues that deflect the flame so that it reverberates. The hearth is made dense and

impervious so that the heavy matte, or molten impure metal, cannot penetrate into and through it, and the walls are made of a material that resists chemical attack by the slag. The process is continuous in the reverberatory furnace: ore concentrate is charged through openings in the roof; slag, which rises to the top, overflows continuously at one end; and the matte is tapped at intervals from the deepest part of the ore bath for transfer to a converter, where it is further refined.

Numerous technical innovations have improved the production capacity of this furnace, although its basic construction has remained the same. Roofs are made of refractory brick rather than the ordinary brick used earlier, and this has permitted higher temperatures and thus faster refining. Reverberatory smelting has recently been giving way to such newer processes as continuous smelting and the use of electric or flash furnaces.



A reverberatory furnace

Calcination is done on the hearth of a reverberatory furnace.

3. What are the common methods of extraction of metals?

From ore to metal

What are "ores"?

An ore is any naturally-occurring source of a metal that you can economically extract the metal from. Ores are commonly oxides - for example:

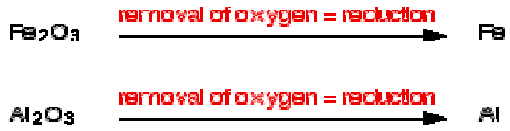
Bauxite	**Al_2O_3**
Haematite	**Fe_2O_3**
Rutile	**TiO_2**

. . . or sulphides - for example:

pyrite	**FeS_2**
chalcopyrite	**$CuFeS_2$**

Reducing the metal compound to the metal

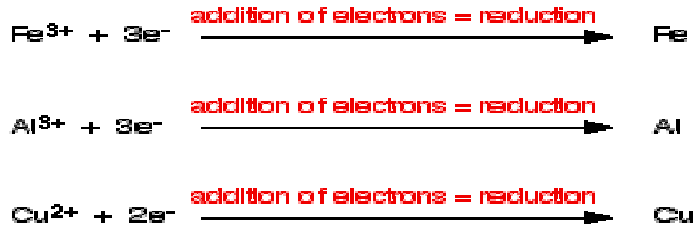
Why is this reduction? At its simplest, where you are starting from metal oxides, the ore is being reduced because oxygen is being removed.



However, if you are starting with a sulphide ore, for example, that's not a lot of help!

It is much more helpful to use the definition of reduction in terms of addition of electrons.

To a reasonable approximation, you can think of these ores as containing positive metal ions. To convert them to the metal, you need to add electrons - reduction.



Choosing a method of reduction:

There are various economic factors you need to think about in choosing a method of reduction for a particular ore. These are all covered in detail on other pages in this section under the extractions of particular metals. What follows is a quick summary.

You need to consider:

- the cost of the reducing agent;
- energy costs;
- the desired purity of the metal.

There may be various environmental considerations as well - some of which will have economic costs.

Carbon reduction

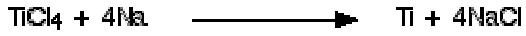
Carbon (as coke or charcoal) is cheap. It not only acts as a reducing agent, but it also acts as the fuel to provide heat for the process.

However, in some cases (for example with aluminium) the temperature needed for carbon reduction is too high to be economic - so a different method has to be used.

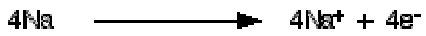
Carbon may also be left in the metal as an impurity. Sometimes this can be removed afterwards (for example, in the extraction of iron); sometimes it can't (for example in producing titanium), and a different method would have to be used in cases like this.

Reduction using a more reactive metal

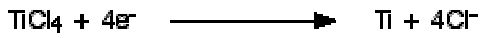
Titanium is produced by reducing titanium (IV) chloride using a more reactive metal such as sodium or magnesium. As you will see if you read the page about titanium extraction, this is the only way of producing high purity metal.



The more reactive metal sodium releases electrons easily as it forms its ions:



These electrons are used to reduce the titanium (IV) chloride:



The downside of this is expense. You have first to extract (or to buy) the sodium or magnesium. The more reactive the metal is, the more difficult and expensive the extraction becomes. That means that you have to use a very expensive reducing agent to extract the titanium. As you will see if you read the page about titanium extraction, there are other problems in its extraction which also add to the cost.

Reduction by electrolysis

This is a common extraction process for the more reactive metals - for example, for aluminium and metals above it in the electrochemical series. You may also come across it in other cases such as one method of extracting copper and in the purification of copper.

During electrolysis, electrons are being added directly to the metal ions at the cathode (the negative electrode).

The downside (particularly in the aluminium case) is the cost of the electricity. An advantage is that it can produce very pure metals.

Chemical Methods

a) **Calcination**: Calcination is a process in which the ore are usually carbonate or hydrated oxide is subjected to the action of heat in order of expel water from hydrated oxide and carbon dioxide from a carbonate. Calcination is generally done in a reverberatory furnace.

b) **Roasting:** Roasting is a process in which ores (usually sulphide ores) either alone or along with some other materials are subjected to the action of heat and air at temperatures below their melting points in order to bring about chemical changes in them. Calcination is also roasting but in this case we are concerned mainly with the changes due to the expulsion of some ingredients such as water, carbon dioxide and no other chemical change occurs. But during roasting chemical changes like oxidation, chlorination etc. takes places. Roasting is generally carried out in a reverberatory furnace or in a blast furnace.

c) **Leaching:** It involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical method.

SHORT ANSWER QUESTIONS

1. What is ore? On what basis a mineral is chosen as ore?

Ans: A mineral or an aggregate of minerals from which a valuable constituent, especially a metal, can be profitably mined or extracted.

A mineral is chosen as an ore or not depends on the following factor

- Percentage of metal in the ore
- Nature and magnitude of impurities present in the mineral
- The expenditure involved in the extraction process
- The industrial utility of the by-products in the extraction.

2. **How do metals occur in nature? Give examples to any two types of minerals.**

The compound of a metal found in nature is called a mineral. A mineral may be a single compound or a complex mixture. Those minerals from which metal can be economically extracted are called ores. Thus all ores are minerals but all minerals are not ores. Ores may be divided into four groups

i) Native Ores: These ores contain the metal in free state eg. Silver gold etc. These are usually formed in the company of rock or alluvial impurities like clay, sand etc.

ii) Oxidised Ores: These ores consist of oxides or oxysalts (eg. carbonates, phosphate) and silicate of metal. Important oxide ore includes, Fe_2O_3, $Al_2O_3.2H_2O$ etc. and important cabonate ores are limestone ($CaCO_3$), Calamine ($ZnCO_3$) etc.

iii) Sulphurised Ores: These ores consist of sulfides of metals like iron, lead, mercury etc. Examples are iron pyrites (FeS_2). Galena (PbS), Cinnabar (HgS)

iv) Halide ores: Metallic halides are very few in nature. Chlorides are most common examples include horn silver (AgCl) carnallite KCl. $MgCl_2.6H_2O$ and fluorspar (CaF_2) etc.

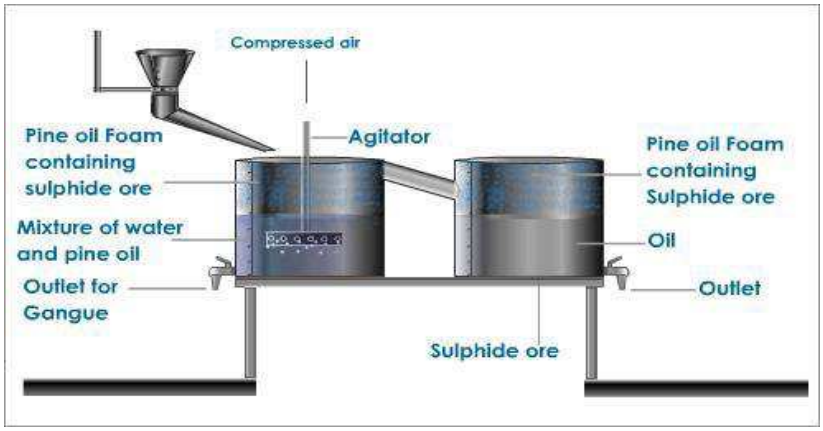
3. Write a short note on Froth floatation process.

<u>Froth Floatation</u>

i) Principle: Difference in the wetting properties of the ore and gangue particles. It is used for Sulphide ores only.

ii) Process:

- A mixture of water, pine oil, detergent and powdered ore is taken in a tank
- A blast of compressed air is blown through the pipe of a rotating agitator to produce froth
- Sulphide ore particles wetted and coated by pine oil rise up along with the froth (froth being lighter)
- Gangue particles wetted by water sink to the bottom of the tank (water being heavier)



Froth Floatation

- Froth containing the sulphide ore is transferred to another container, washed, and dried.

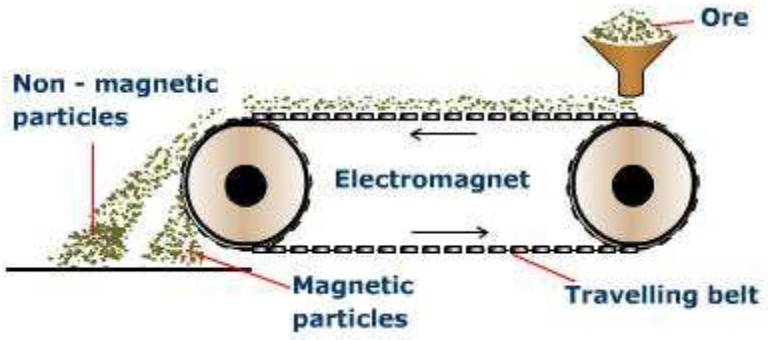
Note: Sulphide being more electronegative attracts the covalent oil molecules. The gangue being less electronegative is attracted by the water.

4. **Explain the method of magnetic separation.**

Magnetic Separation

i) **Principle:** Difference in the magnetic properties of the ore and gangue particles. It si used for Magnetic ores like pyrolusite (MnO_2) and chromite ($FeO.Cr_2O_3$)

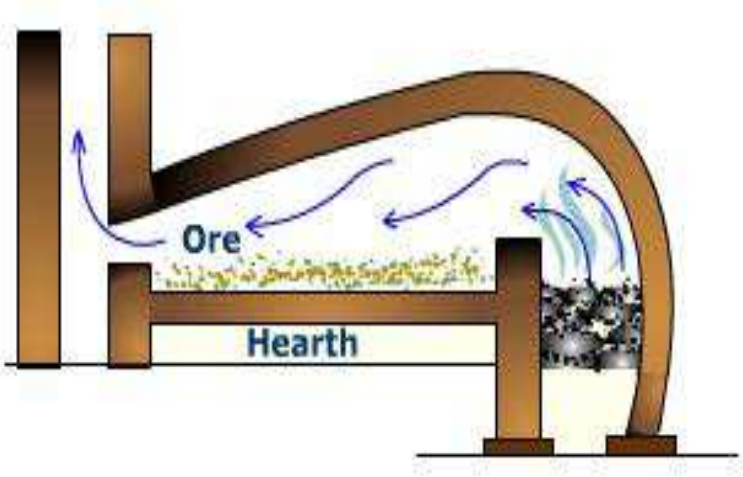
ii) Process:



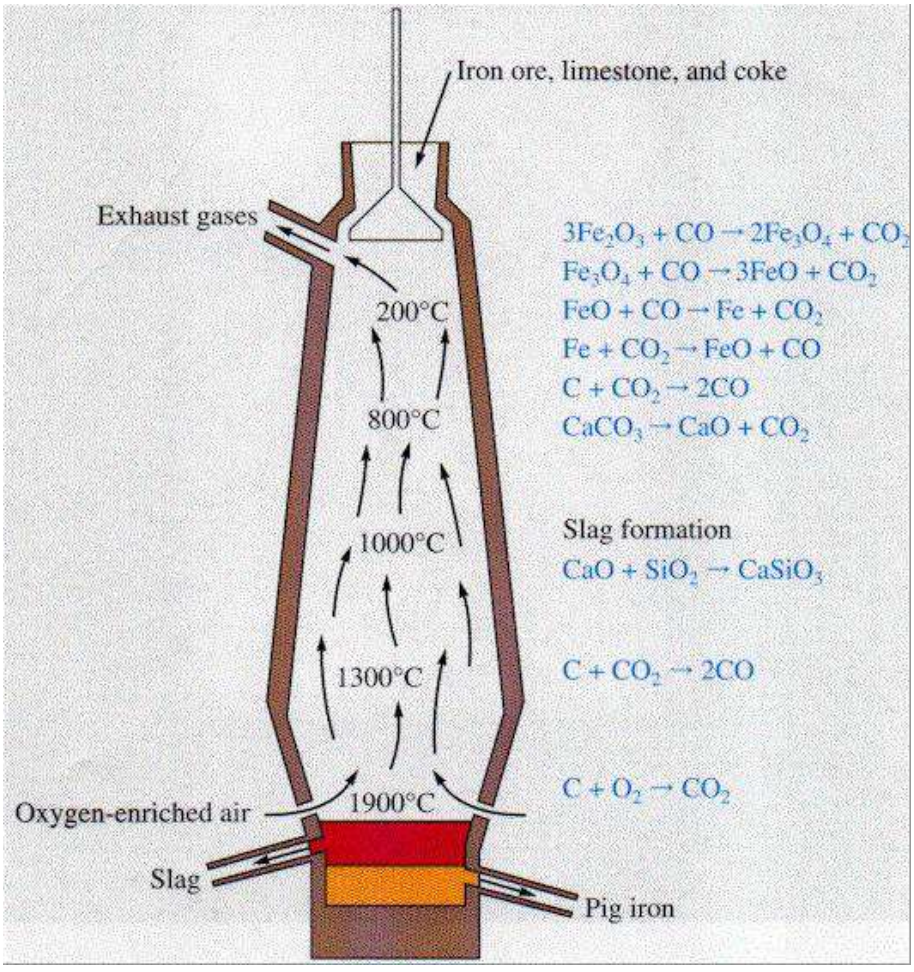
Magnetic Separation

- Powdered ore is dropped over a conveyor belt running over two rollers, one of which is magnetic.
- The magnetic ore particles get attracted to the magnetic roller and run along with the conveyor belt for a little longer than the non magnetic gangue.
- Gangue particles drop down first forming a heap.
- Then, the magnetic ore particles drop down forming a separate heap.
- Thus, two separate heaps of ore and gangue particles are formed.

5. **Draw a neat sketch of reverboratory furnace.**



6. **Draw a neat sketch of Blast furnace.**



7. Write notes on different Reduction Methods

Ans: **Chemical Reduction Methods**

In chemical reduction process, the choice of reducing agent depends upon the chemical reactivity of the metal.

Smelting (Carbon reduction method):

This method is used for the extraction of lead, zinc, iron, copper, manganese and tin. In this method, the roasted oxide ore is mixed with carbon (charcoal, coal or coke) and a flux, and is heated to a very high temperature in a suitable furnace. Carbon reduces the oxide to metal.

$$Fe_2O_3 + 3C \xrightarrow{heat} 2Fe + 3CO$$

$$SnO_2 + 2C \xrightarrow{heat} \underset{(molten)}{Sn} + 2CO$$

$$ZnO + C \xrightarrow{heat} Zn + CO$$

$$PbO + C \xrightarrow{heat} Pb + CO$$

$$Mn_2O_3 + 3C \xrightarrow{heat} 2Mn + 3CO$$

$$Mn_2O_3 + 3C \xrightarrow{heat} 2Mn + 3CO$$

Hydrogen reduction method: Hydrogen can reduce certain oxides to metals e.g.,

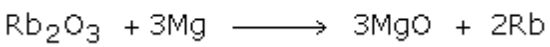
$$WO_3 + 3H_2 \xrightarrow{heat} \underset{Tungsten}{W} + 3H_2O$$

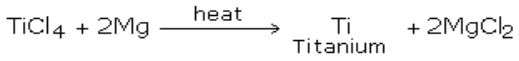
$$MoO_3 + 3H_2 \xrightarrow{heat} \underset{Molybdenum}{Mo} + 3H_2O$$

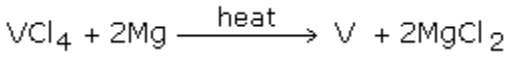
Carbon monoxide reduction method: In certain cases CO gas produced in the furnace itself can be used as a reducing agent. For example**,**

$$Fe_3O_4 + 4CO \xrightarrow{heat} 3Fe + 4CO_2$$

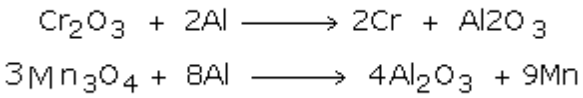
Magnesium reduction method: Oxides of certain metals are reduced by Mg e.g.,



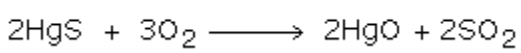




Aluminium reduction method (Alumino Thermic Process): Certain metal oxides cannot be reduced by carbon. Such metallic oxides can be reduced by aluminium powder. This process has been widely used to reduce TiO_2, Cr_2O_3 and Mn_3O_4 to get the corresponding metal.



Self-reduction method : When the sulphide ores of less electropositive metals like Hg, Cu, Pb, Sb etc., are heated in air, a part of the ore gets oxidized to oxide or sulphate, which then reacts with the remaining sulphide ore to give the metal and SO_2. This process is also known as self-reduction method.

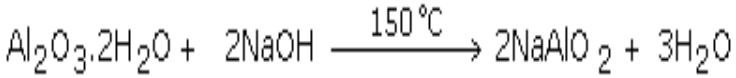


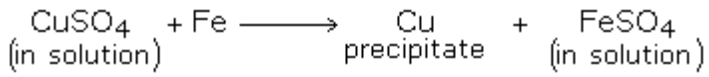


Reduction by more electropositive metals (precipitation or hydrometallurgy) :

This method is employed when leaching method had been used to concentrate the ore. The metals are obtained by reducing their ions in the solution as precipitates by a more electropositive metal. This method is also called as the hydrometallurgy method of reduction.

For example, when a heap of copper glance (Cu_2S) is exposed to air and water, it gets converted to copper sulphate. Copper is recovered from copper sulphate solution by adding some iron scrap to its solution.





Ag and Au are also recovered from the solutions of their complex cyanide salts by zinc scrap.

VERY SHORT ANSWER QUESTION

1. What is metallurgy?

Answer: The entire operation, involving all the physical and chemical processes in the extraction of metal from its ore, is called metallurgy.

2. How does the term "Ore" differ from "Mineral"? Give an example.

Answer: Minerals are naturally occurring chemical compounds of a metal, which may be associated with more impurities. But ore is a chosen mineral of a metal, from which metal is extracted profitably on a large scale, in pure form. For e.g., the ore of Fe is Haemetite, while the minerals having Fe may be magnetite, iron pyrites, spathic iron ore etc.

3. What are the three major steps involved in extraction of a metal after its ore is mined?

Answer: The three steps involved in extraction are:
1) Concentration of the ore to remove impurities.
2) Reduction of the ore to get the metal.
3) Purification of the ore.

4. Carbonates and sulphide ores are usually converted into oxide ores, why?

Answer: It is easier to reduce oxide as compared to carbonate and sulphide.

5. Name the types of reduction processes involved in metallurgy with an example for each.

Answer: The types of reduction processes involved in metallurgy are:
1) Electrolytic reduction of fused compound (chloride or oxide of very active metal). Example: K, Na, Ca Mg and Al
2) Chemical reduction of oxide by coke only, e.g., Zn is obtained from ZnO by reducing it with coke
3) Chemical reduction of oxide by CO gas, e.g., Fe is obtained from Fe_2O_3 gas by reducing it by CO gas

4) Self reduction for Cu extraction

$$Cu_2S + 2CU_2O \rightarrow 6Cu + SO_2$$

6. An ore gave SO_2on heating with oxygen. How will you concentrate this ore?

Answer: It is concentrated by Froth floatation process.

7. In metallurgy what do the terms gangue, flux, slag stand for? Give examples.

Answer: The term 'Gangue' is used for all the earthly impurities associated with the ore of the metal. These need to be removed before the extraction step. Example: In iron ore, sand SiO_2 is the main gangue. The term 'Flux' refers to the compound added during extraction, which reacts with a non fusible (high melting point) gangue and forms a fusible product called slag. This can then be removed by simple physical method. Example: In the blast furnace for extraction of iron, the flux added is limestone $CaCO_3$. This decomposes to give CaO (a basic oxide) which reacts with sand (gangue - an acidic oxide) and forms a fusible slag $CaSiO_3$. The term Slag refers to the easily fusible product formed between gangue and flux.

$$SiO_2 + CaO \rightarrow CaSiO_3$$

Gangue Flux Slag

8. In metallurgy, what does the term 'Roasting' stand for?.

Answer: Roasting is a chemical process where a sulphide ore is strongly heated in a current of O_2 to oxidize the ore. Therefore it is an oxidation process.
Examples:

$$2ZnS + 3O_2 \xrightarrow{\text{Roasting}} 2ZnO + 2SO_2 \uparrow$$

$$4FeS + 7O_2 \xrightarrow{\text{Roasting}} 2Fe_2O_3 + 4SO_2 \uparrow$$

9. Name the by-product formed during roasting and give one of its uses

Answer: SO_2 gas is the by-product formed and it is used for manufacture of sulphuric acid by the contact process.

10. How does roasting differ from calcination? Give equations.

Answer:

Sl. No	Roasting	Calcination
1.	Roasting is heating ore in the presence of air to oxidize it	Calcination is heating of the ore, in the absence of air to decompose it or drive volatile matter
2.	Roasting occurs at higher temperatures, higher than the melting point of the ore	Calcination occurs at temperatures lower than the melting point of the ore

11. Why are aluminium containers used to transport nitric acid?

Answer: Aluminium containers are used to transport nitric acid because concentrated HNO_3 renders aluminium passive by forming a thin strong protective oxide layer. This protective layer prevents further reaction with the acid.

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	Fe_2O_3
Magnetite	Tri iron tetroxide	Fe_3O_4
Iron Pyrites	Iron sulphide	FeS_2
Spathic iron ore	Ferrous Carbonate	$FeCO_3$

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 Fe_2O_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:

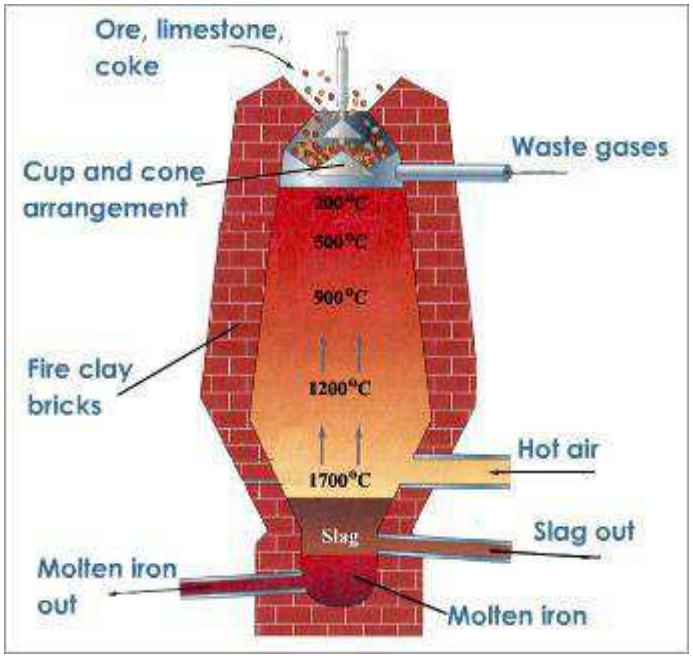


a) Dressing and Concentration of Ore: The iron ore is split into 2cm pieces and washed in water to remove sand, clay etc.

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: 2000^0C

$$C + O_2 \longrightarrow CO_2 + 97\,K \text{ cals}$$

Fusion Zone

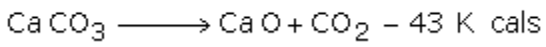
Reaction: Reduction of carbon dioxide to carbon monoxide

Temperature of the region: 1300º C

$$CO_2 + C \longrightarrow 2CO - 39 \text{ K cals}$$

Decomposition of Limestone

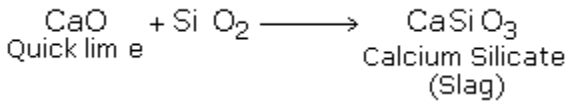
The lime stone ($CaCO_3$) decomposes to give carbon dioxide and quicklime (CaO)



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

Formation of Slag

The quicklime reacts with acidic impurities such as silica (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.

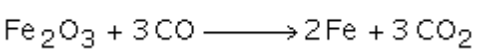


Reduction Zone

Reduction of haemetite to molten iron takes place here.

Temperature of the region: 500-700º C

In the upper region of the furnace, the CO reduces the haemetite to molten iron and oxidizes it self to 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 $CuFeS_2$
- Azurite blue $2CuCO_3\ Cu(OH)_2$
- Malachite $CuCO_3\ Cu(OH)_2$

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:-

$2CuFeS_2 + 3O_2$ --------- $Cu_2S + FeO + SO_2$

$S + O_2$---------- SO_2

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

$2Cu_2S + 3O_2$ ------- $2Cu_2O + 2SO_2$

$2FeS + 3O_2$ -------- $2FeO + SO_2$

- **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.

$FeO + SiO_2$ -------- $FeSiO_3$

$Cu_2O + FeS$----- $Cu_2S + FeO$

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.

$2Cu_2S + 3O_2$ ------- $2Cu_2O + 2SO_2$

$Cu_2O + Cu_2S$ ------- $6Cu + SO_2$

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.

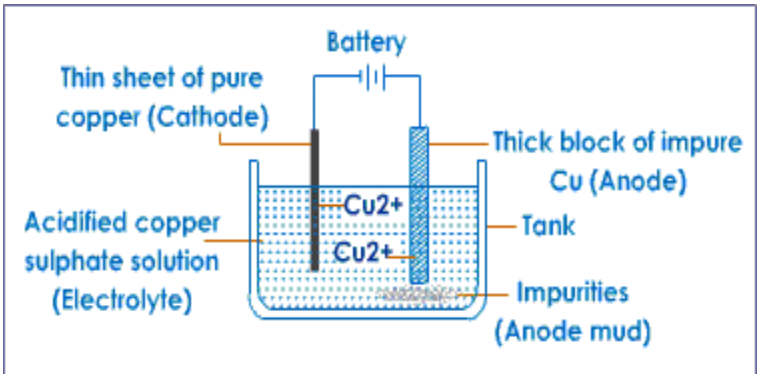
Refining

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 -

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^-$$



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

$CuSO_4$ ----------Cu^{2+} + SO_4^{2-}

H_2O -------- H^+ +OH^-

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

Cu^{2+} +$2e^-$ ------- Cu

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.

At the anode Cu - 2e------- Cu^{2+}

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

The impurities iron, zinc etc ionize and dissolves 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.e

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.

$S + O_2 \rightarrow SO_2\uparrow$

$4As + 3O_2 \rightarrow 2As_2O3$

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

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + S0_2$$

- **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, FeSiO3.

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

$$FeO + SiO_2 \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

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

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

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

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

- **Bessemerisation**:

The **matte** is transferred to bassemer 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

$$\mathbf{2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2}$$

$$\mathbf{2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2}$$

The iron oxides forms slag with silica.

$$\mathbf{FeO + SiO_2 \longrightarrow FeSiO_3}$$

The cuprous oxide reacts with more of Cu2S to form copper.

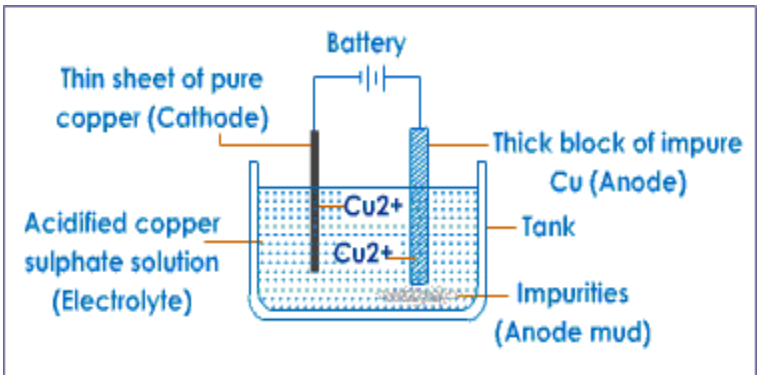
$$\mathbf{2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2}$$

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. 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.



Purification of Impure Copper

At anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

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, $ZnCO_3$

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.

$$2\,ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

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.

$$ZnO + C \text{ (at } 1673K) \rightarrow Zn + CO$$

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 $ZnSO_4$ solution containing a little of dil.H_2SO_4. 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 (Ag_2S), 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 (Ag_2S). 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.

$$Ag_2S + 4NaCN \rightleftharpoons \underset{\text{Sodium argento cyanide}}{2Na[Ag(CN)_2]} + Na_2S$$

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

$$Zn + 2Na[Ag(CN)_2] \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

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 numebr 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, Ag_2S, Horn silver or chlorargyrite, AgCl, Pyrargyrite or Ruby silver, $Ag_2S \cdot Sb_2S_3$.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. Sufide ores are concentrated by this method. Silver ore is prefrentially 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 remains in the solution as undissolvable partilcle. This makes the separtion of silver more effective since all other element and impurities are not soluble in water

$Ag_2S + 4NaCN \dashrightarrow 2Na[Ag(CN)_2] + Na_2S$

Sodium argento cyanide (soluble)

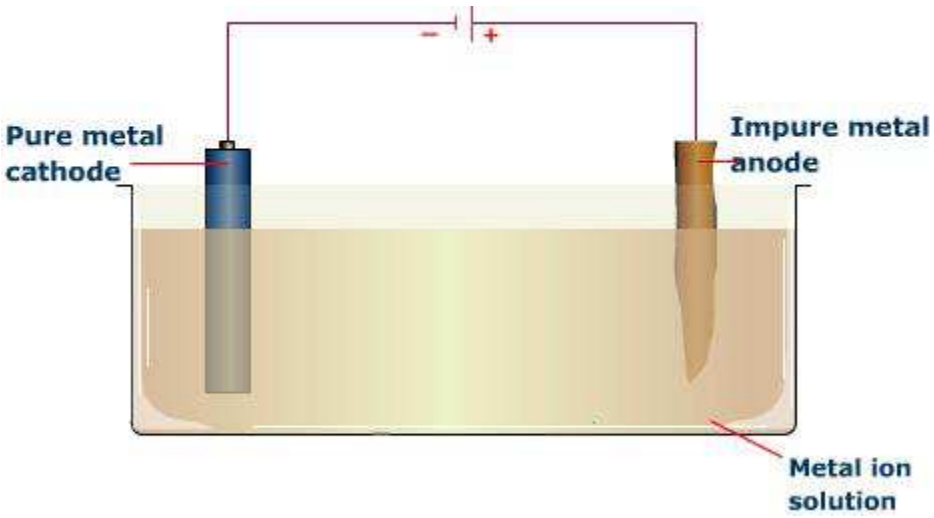
The solution containing sodium argento cyanide is filtered to remove insoluble impurities and filtrate is treated with zinc dust, silver gets precipitated. It is a displacement reaction where zinc being more reactive goes into the complex and Silver is thrown out

$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$

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:-

$2CuFeS_2 + 3O_2$ --------- $Cu_2S + FeO + SO_2$

$S + O_2$---------- SO_2

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

$2Cu_2S + 3O_2$ ------- $2Cu_2O + 2SO_2$

$2FeS + 3O_2$ -------- $2FeO + SO_2$

- **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.

$FeO + SiO_2$ -------- $FeSiO_3$

$Cu_2O + FeS$----- $Cu_2S + FeO$

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.

$2Cu_2S + 3O_2$ ------- $2Cu_2O + 2SO_2$

$Cu_2O + Cu_2S$ ------- $6Cu + SO_2$

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 CO_2, SO_2, organic matter, and moisture from the ore. For example,

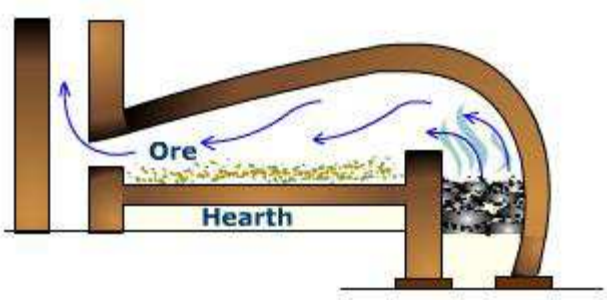
- It removes moisture from bauxite.

$$Al_2O_3.2H_2O \xrightarrow{heat} Al_2O_3 + 2H_2O_{(g)}$$

- It removes CO_2 from carbonate ores e.g.,

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \xrightarrow{heat} 2CuO + CO_{2(g)} + H_2O_{(g)}$$

$$\underset{\text{Dolomite}}{CaCO_3.MgCO_3} \xrightarrow{heat} CaO + MgO + 2CO_{2(g)}$$



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.

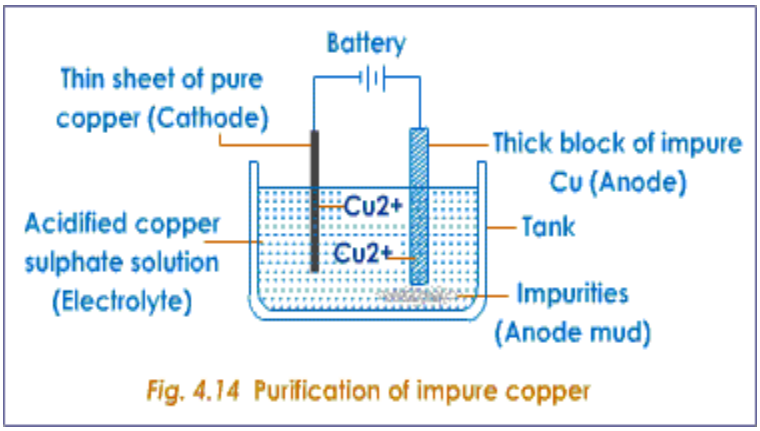


Fig. 4.14 Purification of impure copper

At anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

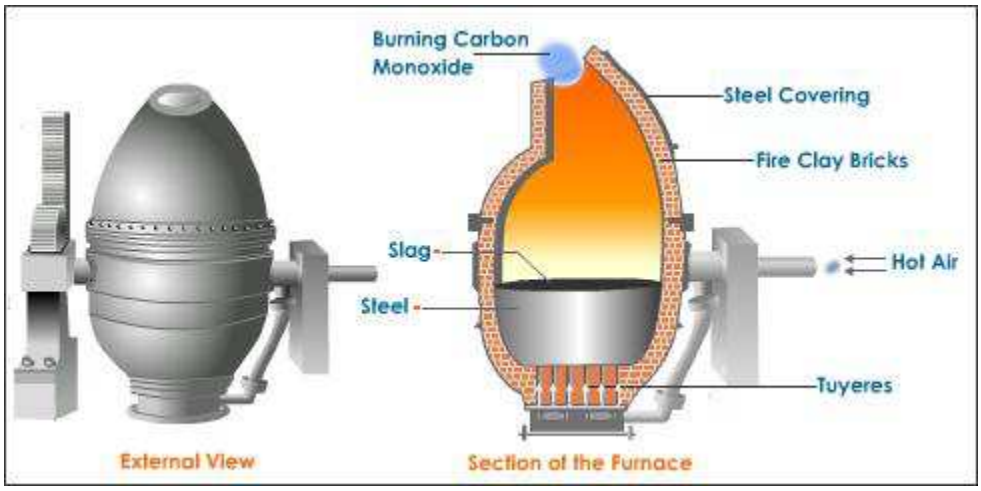
Impurities fall under anode and cathode mud.

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.

$$\underset{\text{manganese}}{2Mn} + O_2 \longrightarrow \underset{\text{manganese oxide}}{2MnO}$$

$$\underset{\text{silicon}}{Si} + O_2 \longrightarrow \underset{\text{silicon dioxide}}{SiO_2}$$

$$2C + O_2 \longrightarrow \underset{\text{carbon monoxide}}{2CO}$$
$$\text{carbon}$$

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.

$$MnO + SiO_2 \longrightarrow \underset{\text{manganous silicate slag}}{MnSiO_3}$$

$$4P + 5O_2 \xrightarrow[\text{oxidation}]{} 2P_2O_5 \text{ (phosphorus pentoxide)}$$

$$\underset{\text{lime}}{3CaO} + P_2O_5 \longrightarrow \underset{\text{calcium phosphate slag or Thomas slag (used as fertiliser)}}{Ca_3(PO_4)_2}$$

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 is purified by Baeyer's process?

<u>Bayer's Process</u>

Bayer's process involves concentration and dehydration of bauxite to alumina (Al_2O_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.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

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.

$$NaAlO_2 + H_2O + HCl \longrightarrow NaCl + Al(OH)_3 \downarrow$$

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:-

$$2CuFeS_2 + 3O_2 \text{ --------- } Cu_2S + FeO + SO_2$$

$$S + O_2 \text{ ---------- } SO_2$$

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

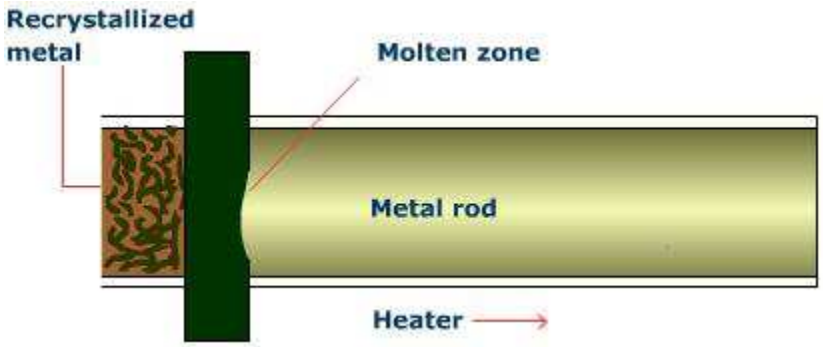
$$2Cu_2S + 3O_2 \text{ ------- } 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 \text{ -------- } 2FeO + SO_2$$

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 elecrolytically?

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 (Ag_2S). 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.

$$Ag_2S + 4NaCN \rightleftharpoons \underset{\text{Sodium argento cyanide}}{2Na[Ag(CN)_2]} + Na_2S$$

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

$$Zn + 2Na[Ag(CN)_2] \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

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

GENERAL PRINCIPLES OF METALLURGY

Topic: 3

Process of molten electrolysis of Al, Mg and Na

LONG ANSWER QUESTIONS

1. Explain the extraction of Aluminium from its ore.

Extraction of Aluminium from its Ore

Introduction to Extraction of Metals from Ores:

The process of extraction of metals from their ores is called metallurgy. Ores are generally associated with non metallic impurities of earthy and rocky material. Such materials are called gangue or matrix. The process of extraction depends upon the nature of impurities present in the ore. Common steps involved for extraction of metals are as follows:

(i) Crushing and grinding

(ii) Concentration of ore

(iii) Extracting metal from ore

(iv) Purification of metal

Extraction of Aluminium from its Ore:

Aluminium was an expensive and of little use for a long time. Its use increased in 1886, when Charles independently found a way to obtain the metal by electrolysis. Aluminium is most abundant metal on the earth's arust. The percentage of this metal in earth's crust is about 32% of total metals and 8.3% of total elements.

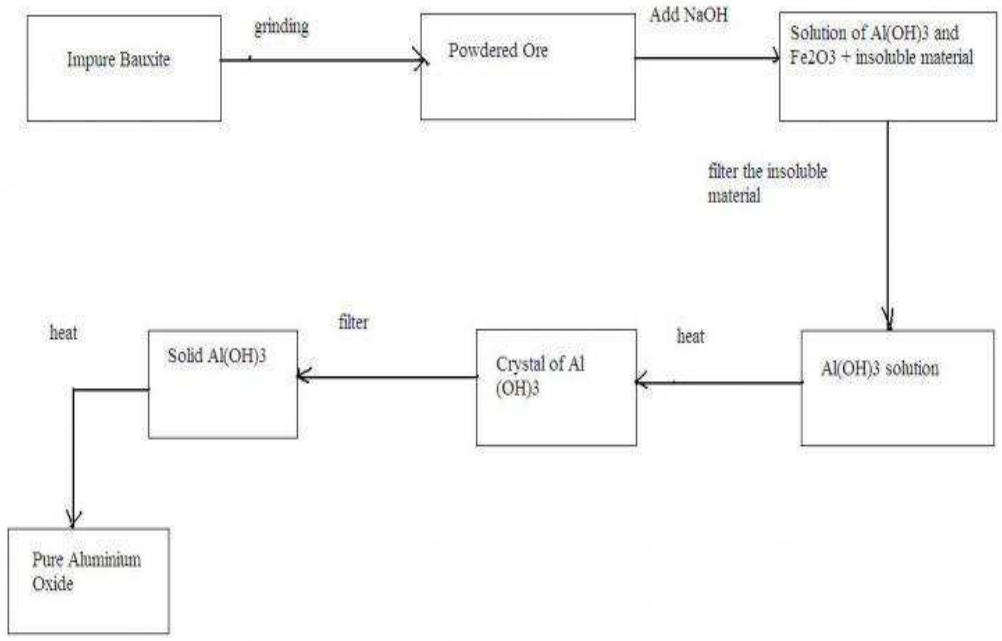
Extraction of Aluminium:

Major ore of aluminium is bauxite ($Al_2O_3.2H_2O$). It is an oxide of aluminium. Though, aluminium oxide can be reduced by chemical methods, but it is extracted from its ore by electrolysis, because it is highly reactive metal.

Steps of Extraction of Aluminium from its Ore:

The extraction of aluminium involves following steps:

(i) Purification: Bauxite ore contains lot of impurities which can be removed by treating it chemically. The sequence of its purification is shown in the flow chart given below:



Detailed Description of Flowchart:

1. Bauxite ore is crushed.
2. It is then treated with sodium hydroxide (NaOH). It results in the formation of $Al(OH)_3$, Fe_2O_3 and some insoluble material.

$$Al_2O_3 + 6NaOH \text{ ----------> } 2Al(OH)_3 + 3Na_2O$$

$$Na_2O + H_2O \text{ ----------> } 2NaOH$$

3. Iron oxide does not dissolve in NaOH and thus the products are filtered to get $Al(OH)_3$.
4. $Al(OH)_3$ is heated and it is decomposed into Al_2O_3 and H_2O.

$$Al(OH)_3 \text{ ----------> } Al_2O_3 + H_2O$$

5. Hence, pure aluminium oxide Al_2O_3 is obtained.

Electrolysis Method

In this process, pure Al_2O_3 is added in an iron tank. In this tank, cryolite (Na_2AlF_6) and some fluorspar (CaF_2) is also added to reduce the melting point of Al_2O_3. It also increases the conductivity and helps in breaking Al_2O_3 to form aluminium ions (Al^{+3}) and oxide ions (O^{-2}). Al^{+3} ions will move towards cathode and O^{-2} ions will move towards anode, where they are reduced and oxidised respectively into aluminium (Al) and oxygen (O_2).

The reaction taking place at cathode and anode are as follows:-

$$Al_2O_3 \text{ ----------> } 2Al^{+3} + 3O^{-2}$$

On Cathode: $2Al^{+3} + 6e^{-1}$ ----------> 2Al (metal)

On Anode: $6O^{-2}$ ----------> $3O_2 + 12e^{-1}$

Aluminium obtained from above process is 99% pure, which is further purified by using electrolytic method.

2. **Explain the methods of purification of metals.**

Ans: **Refining of Metals**

The metals so extracted are further refined by suitable methods. The electrolytic method is the most suitable method for refining the non-ferrous metals. The metals produced by any method given above are not very pure. These need further refining.This can be done by any of the following methods:

Liquation method:

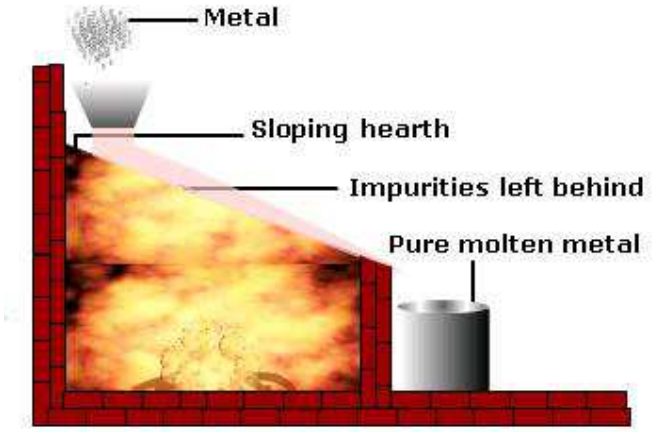
This method is used when the melting temperature of the metal is lower than that of the impurity and the impurities are not miscible with the metal. Metals like Bi, Sn, Pb, Hg etc., are purified by this method. The sloping floor of a reverberatory furnace is used to melt crude metal, when the pure metal flows down, the impurities are left behind.

Distillation

When metals have low boiling points e.g., mercury, zinc, cadmium etc., most of the impurities can be separated by distillation. Their vapours, on condensation in a suitable condenser give the pure metal.

Poling

Oxide impurity of impure metals can be purified by this method. Poles of green wood are used to stir the molten crude metal sample. The hydrocarbon organic matter in the poles acts as a reducing agent and reduces the oxide impurities. This method is used for refining copper.



The Liquation method

Oxidation or cupellation

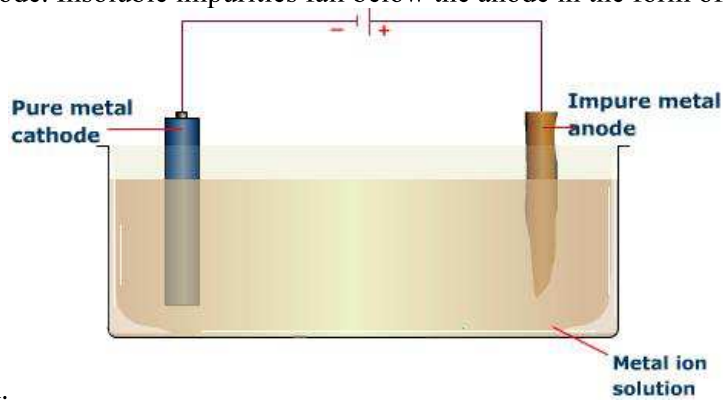
Impurities that can be oxidised to volatile products can be removed by oxidation. For example, the impurity of lead from silver is removed when lead is oxidized and led away by a current of air. Shining silver is left behind.

Molten pig iron is also purified by this technique in a Bessemer converter. The impurities in the form of volatile oxides, escape out.

Electrolytic method

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

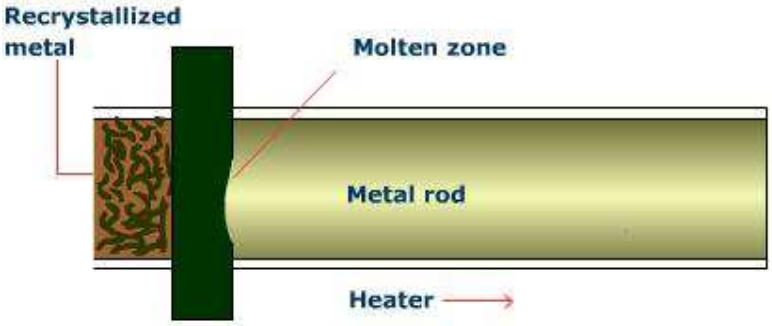


mud.

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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

Van Arkel method

In the Van Arkel method impure metal is first converted into one of its unstable compounds. Heating the unstable compound of the metal at higher temperatures, decomposes it to give pure metal. For example, pure titanium can be obtained from impure titanium by converting it into tetraiodide, and then decomposing this tetraiodide to pure Ti.

$$\underset{\text{Impure titanium metal}}{Ti} + 2I_2 \xrightarrow{250^{o}C} \underset{\text{Titanium tetraiodide}}{TiI_4} \xrightarrow[1400^{o}C]{250^{o}C} \underset{\text{Pure Titanium}}{Ti} + 2I_2$$

3. Mention any three minerals of Al. How is the ore purified?

Metallurgy of Aluminum

Common Name	Chemical Name	Formula
Bauxite	Hydrated aluminium oxide	$Al_2O_3.2H_2O$
Cryolite	Sodium aluminum fluoride	Na_3AlF_6
Corundum	Aluminium Oxide	Al_2O_3

Pure aluminium is a silvery-white metal with many desirable characteristics. It is light, nontoxic (as the metal), nonmagnetic and non sparking. Pure aluminium is soft and lacks strength, but alloys with small amounts of copper, magnesium, silicon, manganese, and other elements have very useful properties. ~Aluminium is the third most abundant element in the Earth's crust after oxygen and silicon

Extraction of Aluminium

Aluminum is extracted from its oxide ore "Bauxite". The extraction of aluminum involves the following steps.

- Purification of Bauxite
- Electrolysis of Alumina
- Refining

Purification of Bauxite to Alumina

Bauxite contains two main impurities Fe_2O_3 and SiO_2. These impurities must be removed in order to get good quality aluminum. These impurities make the aluminum brittle and liable to corrosion. Depending upon the nature of impurity present in bauxite, any one of the following methods can be used for the purification of bauxite.

Bayer's Process

Bayer's process involves concentration and dehydration of bauxite to alumina (Al_2O_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.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

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.

$$NaAlO_2 + H_2O + HCl \longrightarrow NaCl + Al(OH)_3 \downarrow$$

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

Action of Heat on $Al(OH)_3$

The precipitate of $Al(OH)_3$ is heated to a high temperature to obtain pure alumina.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Thus, pure alumina is obtained from bauxite.

Hall's Process

In this process, the pure alumina (Al_2O_3) obtained from Bayer's process is electrolytically reduced to aluminium.

$$\text{Pure Alumina} \xrightarrow{\text{electricity}} \text{Aluminium}$$

An electrolytic cell used is called the Hall's cell.

The Hall's cell is a steel tank lined inside with a layer of graphite which is made the cathode. The electrolyte consists of a mixture of fused (molten) alumina and cryolite. Cryolite is a flux and helps in lowering the melting point of alumina. A series of graphite rods dipped into the electrolyte serve as the anode.

When electricity is passed through the cell, the molten alumina dissociates forming Al^{3+} and O^{2-} ions,

$$Al_2O_3 \xrightarrow{\text{electricity}} Al^{3+} + 3O^{2-}$$

The Al^{3+} ions capture electrons of the cathode and get deposited at the bottom of the tank as molten aluminium.

The O^{2-} ions lose electrons to the anode and release oxygen gas. Some amount of carbon dioxide and carbon monoxide are also released, due to the reaction of oxygen atoms with the graphite anode.

Ionic Equations

At Cathode	At anode
Gain of electrons (reduction)	Loss of electrons (oxidation)
$Al^{3+} + 3e^- \longrightarrow Al$	$O^{2-} - 2e^- \longrightarrow O$
	$O + O \longrightarrow O_2 \uparrow$
	$C + O \longrightarrow CO_2$

Net reaction : $2Al_2O_3 \xrightarrow{\text{(electricity)}} 4Al + 3O_2 \uparrow$

The molten aluminium thus collected is removed from an outlet at the bottom of the cell.

4. Explain the metallurgy of Aluminium.

Extraction of Aluminium

Pure Aluminium metal is extracted from bauxite in a three-stage process.

a) Purification of Bauxite (Bayers Process) to obtain pure Alumina.

b) Electrolysis of pure Alumina in molten cryolite (Na_3AlF_6) (Halls process).

c) Refining of Aluminium (Hoopes process).

Purification of bauxite

Bauxite contains silicon dioxide (SiO_2), iron oxides and titanium(IV) oxide as impurities. The bauxite ore is digested with a concentrated solution of sodium hydroxide at 473-523 K and 35-36 bar pressure. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively leaving behind iron oxide and TiO_2, which are filtered off.

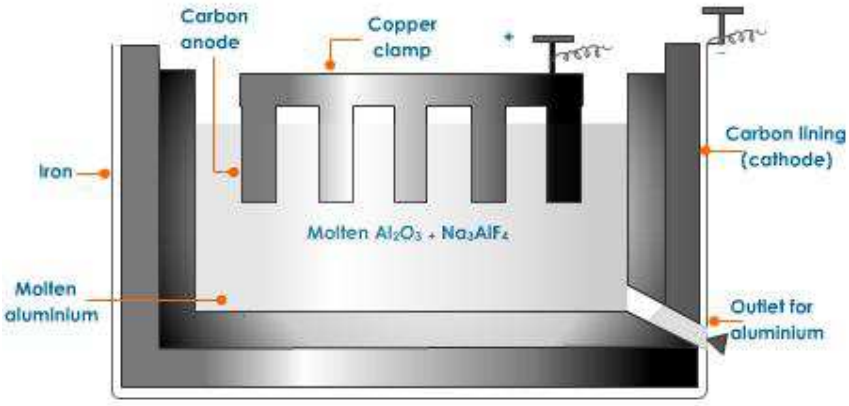
$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(l) \longrightarrow 2Na[Al(OH)_4]\,(aq)$$

The filtrate containing sodium aluminate and sodium silicate is diluted and seeded with freshly precipitated aluminium hydroxide, which induces the precipitation of aluminium hydroxide leaving behind sodium silicate in solution.

$$Na[Al(OH)_4]\,(aq) \xrightarrow{H_2O} Al(OH)_3\,(s) + NaOH\,(aq)$$

The aluminium hydroxide is filtered dried and calcined at 1473 K to yield pure alumina.

Electrolysis of pure alumina (Hall-Heroult process)



Hall's cell

Pure alumina is dissolved in molten cryolite (Na_3AlF_6) and is electrolyzed in an iron tank lined inside with carbon. Carbon lining serves as cathode while a number of carbon rods dipping in the fused electrolyte serve as anode. Cryolite improves the electrical conductivity of the cell, as alumina is a poor conductor. Moreover, cryolite lowers the melting point of the mixture to about 1250 K. Other impurities such as CaF_2, NaF and AlF_3 may also be added. The temperature of the electrolyte is maintained between 1200-1300 K.

On passing electric current, aluminium is liberated at the cathode and gets collected at the bottom of the tank from where it is removed. Oxygen liberated at the anode combines with the carbon of the anode to produce carbon monoxide, which either burns or escapes out. The reactions taking place during the electrolysis are:

$$\text{At cathode : } Al^{3+}\,(melt) + 3e^- \longrightarrow Al(I)$$

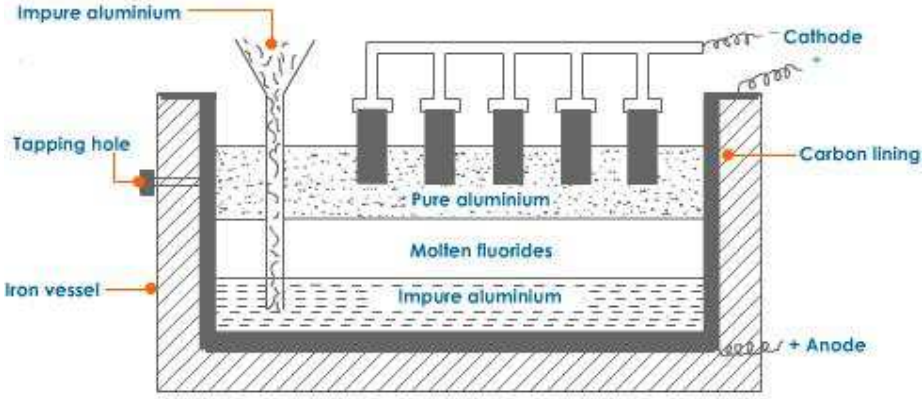
$$\text{At anode : } C(s) + O^{2-}\,(melt) \longrightarrow CO(g) + 2e^-$$

$$C(s) + 2O^{2-}\,(melt) \longrightarrow CO_2(g) + 4e^-$$

Since during electrolysis the carbon electrodes get consumed they have to be replaced periodically.

Refining of Aluminium (Hoop's process)

The metal obtained in the above step is about 99% pure and for most purposes it is taken as pure metal. However, further purification of aluminium can be carried out by Hoopes process. The cell consists of an iron tank lined with carbon at the bottom. A molten alloy of copper, crude aluminium and silicon is used as the anode. It forms the lower most layer in the cell. The middle layer consists of molten mixture of fluorides, of sodium aluminium and barium (cryolite + BaF_2). The upper most layer consists of molten aluminium. A set if graphite rods dipping in molten aluminium serve as cathode.



Purification of Aluminium by Hoop's cell

On passing current aluminium ions from the fused electrolyte are discharged at cathode and pure aluminium collects as the top layer. Meanwhile, an equivalent quantity of aluminium from crude alloy at the bottom goes into electrolyte in the middle layer. Crude aluminium is added from time to time and pure aluminium tapped off from the top.

5. Explain the extraction of Mg from its ores. Explain its properties and uses.

Ans: **Magnesium**

Magnesium belongs to group 2 of the periodic table along with other elements like Calcium (Ca), beryllium (Be), strontium (Sr), barium (Ba) and radium (Ra). These elements are called alkaline Earth metals. Due to their smaller size, the electrons are more tightly bound in them and so the first ionization energies are higher than those of the corresponding group 1 elements. The second ionization energies are almost twice the first ionization energies in these elements. Magnesium forms bipositive cations, but they are less electropositive than the alkali elements. In view of the smaller size of the atoms and ions, alkaline earth metals are denser and harder than the alkali metals and have higher melting points.

Occurrence

Magnesium being quite reactive does not occur in the free state in nature but in the combined state.

Minerals of magnesium

Extraction of magnesium

Magnesium metal is strong reducing agent and therefore, cannot be obtained by chemical reduction method. It is extracted by electrolysis of fused anhydrous salts.

A number of methods are available for the extraction of magnesium metal from its ores. The most widely used method is based on the electrolysis of magnesium chloride obtained from the seawater.

Dow's process

This process consists of the following steps:

- Magnesium ions present in the sea water are precipitated as magnesium hydroxide by the addition of slaked lime, $Ca(OH)_2$ to the sea water.

$$\underset{\text{in sea water}}{Mg^{2+}} + Ca(OH)_2 \longrightarrow Mg(OH)_{2(s)} + Ca^{2+}_{(aq)}$$

- Magnesium hydroxide is separated and converted to magnesium chloride by treatment with hydrochloric acid.

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

The magnesium chloride is crystallized as $MgCl_2.6H_2O$

- Fused magnesium chloride for electrolysis is obtained as follows:

Magnesium chloride hexahydrate is partially dehydrated by passing a current of dry hydrogen chloride gas. The magnesium chloride thus obtained is added to a molten mixture of sodium chloride and calcium chloride (35 : 50 : 15). Magnesium chloride melts under this condition with the loss of water at about 1000 K (700 - 725°C).

$$MgCl_2.6H_2O \longrightarrow MgO + 2HCl + 5H_2O$$

The molten mixture of $MgCl_2$, NaCl and $CaCl_2$ is electrolyzed in an iron cell through which an inert gas (or coal gas) flows to avoid any reaction between the liberated metal and oxygen / nitrogen of the air. The cell wall acts as the cathode, while the carbon rod dipping into the melt acts as anode. Magnesium is obtained at the cathode and chlorine is evolved at the anode. This chlorine is used in making hydrochloric acid, which is required for obtaining magnesium chloride.

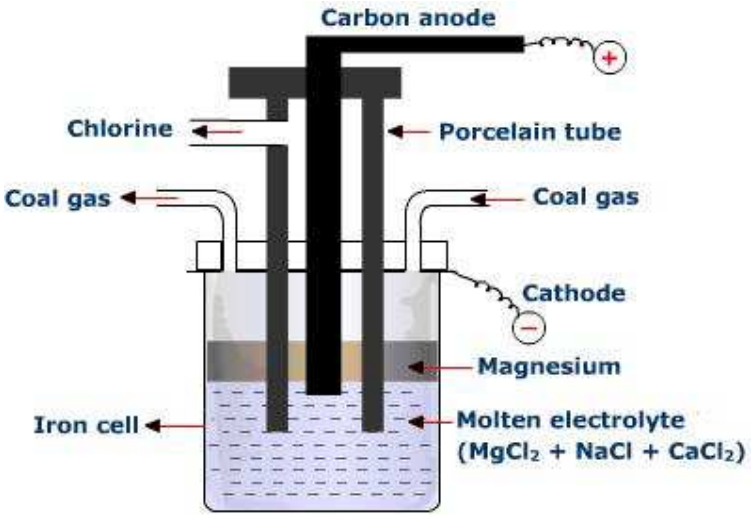
At cathode:

$$Mg^{2+} + 2e^- \longrightarrow Mg$$

At anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

The liberated metal being lighter than the electrolyte floats over the surface. Chlorine evolved at anode is obtained as a by-product. Metal of 99.9 per cent purity is obtained by this method.



Electrolysis of magnesium chloride

Physical Properties of Metals

- Magnesium is a silvery-white, soft and light metal (density = 1.75 g/mL).
- It melts at 651°C and boils at 1090°C. It sublimes in vacuum at 550°C.
- It is malleable and ductile.
- It is a good conductor of electricity and heat.

Chemical Properties of Magnesium

i) Action of air

Dry air has no effect on magnesium and calcium. In moist air, a thin layer of oxide gets formed on its surface. When heated in air, they burn with a dazzling light giving its oxide and nitride.

$$2Mg + O_2 \xrightarrow{\text{Heat}} 2MgO$$

$$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

ii) Action of water

Magnesium reacts very slowly with cold water, and slowly with boiling water to give hydrogen.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

When heated with steam, magnesium burns to give MgO and H_2.

$$Mg + \underset{\text{steam}}{H_2O} \longrightarrow MgO + H_{2(g)}$$

iii) Action of acids

Both magnesium and calcium react with all dilute mineral acids to produce hydrogen.

$$Mg + 2HCl \longrightarrow MgCl_2 + H_{2(g)}$$

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_{2(g)}$$

$$Ca + 2HCl \longrightarrow CaCl_2 + H_{2(g)}$$

$$Ca + H_2SO_4 \longrightarrow CaSO_4 + H_{2(g)}$$

- With dilute nitric acid, magnesium gives ammonium nitrate, and magnesium nitrate.

$$[Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + 2H\,] \times 4$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$

iv) Reducing action

Calcium and magnesium have very high affinity for oxygen. They reduce the oxides of metals and non-metals to the respective element.

$$K_2O + Mg \xrightarrow{\Delta} MgO + 2K$$

$$CO_2 + 2Mg \xrightarrow{\Delta} 2MgO + C$$

v) With non-metals

Magnesium combines with non-metals on heating.

$$Mg + S \xrightarrow{\Delta} MgS$$

$$Mg + Cl_2 \xrightarrow{\Delta} MgCl_2$$

vi) Displacement of less electropositive elements

Mg is highly electropositive; hence it displaces nearly all the metals from their salt solutions.

$$Mg + Pb(NO_3)_2 \longrightarrow Mg(NO_3)_2 + Pb$$

$$Mg + CuSO_4 \longrightarrow MgSO_4 + Cu$$

$$Mg + 2AgNO_3 \longrightarrow Mg(NO_3)_2 + 2Ag$$

Vii) Formation of alkyl magnesium halides

Magnesium reacts with haloalkanes in ether medium, to form alkyl magnesium halide, commonly called as the Grignard's reagent.

$$RX + Mg \xrightarrow{ether} \underset{\text{Grignard's reagent}}{R-Mg-X}$$

$$\underset{\text{iodoethane}}{C_2H_5I} + Mg \xrightarrow{ether} \underset{\text{ethylmagnesium iodide}}{C_2H_5-Mg-I}$$

Grignard's reagents are very useful synthetic reagents in organic chemistry.

Uses

- In flash light photography, fire works and signal fires.
- As a reducing agent for the preparation of silicon and boron.
- As a fuse in the alumino-thermic process.
- In the manufacture of light and high-tensile alloys such as magnesium aluminium alloy.
- As anodes for corrosion prevention.

6. Explain the extraction of Mg from Dolomite.

Extraction of Magnesium by Electrolysis

Magnesium is relatively active silvery white metal. At slightly below its melting point, it is malleable and ductile and can be
drawn into wire or rolled into ribbon in which form it is generally sold. It is a very light metal.

Introduction to extraction of magnesium by electrolysis

Magnesium does not tarnish in dry air but a layer of white oxide is formed on its surface in moist air. The atomic number of Magnesium is 12 and the atomic mass number is 24.305 and has electronic configuration of [Ne] $3s^2$

Extraction of Magnesium by Electrolysis

The magnesium comes from the name of the mineral magnesite, which in turn is believed to stem from the name Magnesia. The British chemist Humphry Davy discovered the pure element magnesium in 1808.

Magnesium does not occur in the native state. In the combined state it occurs very abundantly in the earth crust. Magnesite, MgCO3, Dolomite, MgCO3, CaCO3, Epsom salt, MgSO4, 7H2O Carnalite MgCl2 KCl.6H2O

Magnesium is prepared/ extracted on a large scale by the electrolysis of either fused magnesium chloride or magnesia.

The purified carnalite ore is the principal source for this process. A mixture of equal quantities of carnalite and NaCl is fused to a clear liquid at 973K. The alkali chloride prevents hydrolysis of magnesium chloride and increases the conductivity of the fused mass. The electrolysis of the fused mass is carried out in an atmosphere of coal gas in air tight iron cell which can hold 6-7 tonnes of the electrolyte. The temperature of the elctrolyte bath is maintained at 970K. The iron cell itself acts as a cathode unlike the anode consists of a carbon or graphite rod surrounded by a porcelain tube through which the liberated chlorine escapes. Molten magnesium being lighter than the electrolyte rises to the surface and is periodically removed with perforated ladle. The electrolysis is carried out in an atmosphere of coal gas so as to avoid the oxidation of molten magnesium. The metal thus obtained is 99.9% pure. It may be further purified by remelting with a flux of anhydrous magnesium chloride and sodium chloride

Reactions for Extraction of Magnesium by Electrolysis

The following are reactions for Extraction of Magnesium by electrolysis

At cathode the reaction is:-

$Mg^{2+} + 2e^-$ -------> 2Mg

At anode the reaction is:-

$2Cl^-$ ------> $Cl_2 + 2\ e^-$

7. Explain the extraction of sodium by Castner's process.

Extraction of Sodium:

The metal sodium, was prepared in 1807 by an English chemist,

Sir Humphery Davy by electrolysis of fused caustic soda. The method used for extracting sodium metals is,

- Castner's process: By the electrolysis of fused caustic soda.

Castner's process

Molten sodium hydroxide (caustic soda, NaOH) is electrolyzed using an iron cathode and nickel anode. A nickel wire gauze cylinder prevents the electrodes from touching each other. On passing electric current through the melt, sodium is liberated at the cathode and oxygen at the anode. The liberated sodium metal floats over the surface (lighter than fused caustic soda), and collects inside the receiving vessel where hydrogen prevents sodium from oxidation. Excess of the gas escapes from the outlet. Sodium is removed from time to time with the help of perforated spoons and kept under kerosene oil. The various reactions taking place during electrolysis are:

$$NaOH \xrightarrow{\text{melting}} Na^+ + OH^- \text{ (dissociation)}$$

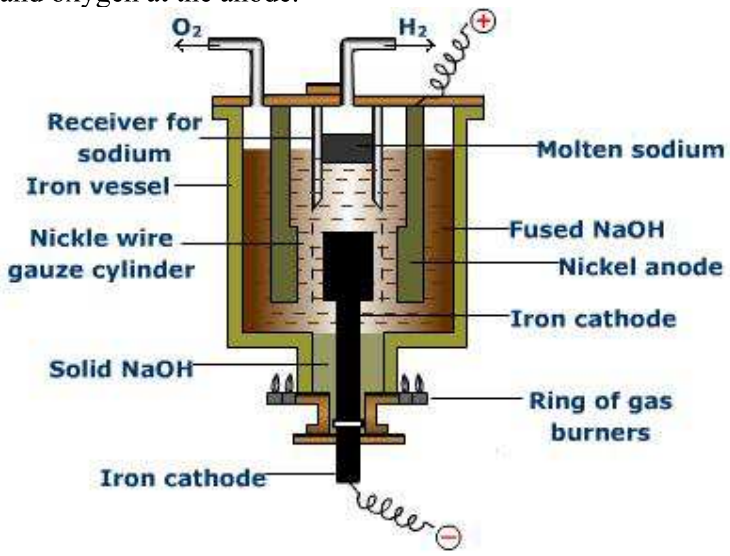
At cathode:

$$Na^+ + e^- \longrightarrow Na$$

At anode:

$$OH^- \longrightarrow \frac{1}{2} H_2O + \frac{1}{4} O_2 + 2e^-$$

Most of the water formed in the reaction gets evaporated, and the rest is electrolyzed into hydrogen and oxygen. Therefore, metallic sodium and hydrogen are liberated at the cathode and oxygen at the anode.



Castner's process

8. Explain the extraction of sodium by Down's process.

The metal sodium was prepared in 1807 by an English chemist, Sir Humphery Davy by electrolysis of fused caustic soda. The method used for extracting sodium metals is,

- Down's process: By the electrolysis of fused sodium chloride.

Down's process

In this process, molten sodium chloride (common salt) is electrolyzed using a graphite anode and a ring shaped iron cathode. The two electrodes are separated by a wire gauge partition to avoid the mixing of sodium and chlorine so formed. As Sodium chloride melts at a very high temperature of 1085 K, a mixture containing sodium chloride, potassium chloride and potassium fluoride (NaCl + KCl + KF) is employed. This mixture melts at about 850-875 K.

The reasons for lowering the temperature are:

- It is difficult to maintain a high temperature of 1085K.
- Sodium is volatile at this temperature and so a part of the metal formed may vaporize.
- At this high temperature chlorine produced as a by product corrodes the vessel.
- Metal at this temperature will be in a colloidal state and its separation will be difficult.

On passing electric current, chlorine is liberated at the carbon anode and escapes through the dome shaped steel hood outlet. Sodium rises from the cathode and remains in the wire gauze shell. The sodium produced is in molten state. Being lighter than the electrolyte it rises to the surface. As the level of molten sodium arises, it is forced into the receiver. The process is continuous and fresh salt is introduced to maintain the level of molten electrolyte high enough to allow sodium to rise into the iron pipe. Chemical reactions involved in this process are as follows:

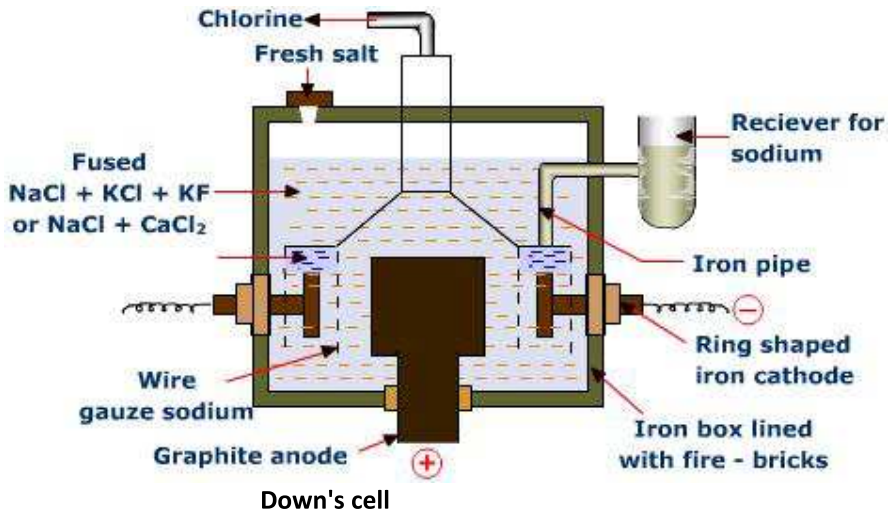
$$2NaCl \xrightarrow{\text{melting}} 2Na^+ + 2Cl^-$$

At cathode:

$$2Na^+ + 2e^- \longrightarrow 2Na$$

At anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$



Down's cell

Advantages of Down's process

- Sodium metal obtained has high degree of purity (99.5%).
- The starting material, sodium chloride is very cheap.
- Chlorine is obtained as a useful by-product.

SHORT ANSWER QUESTIONS

1. Explain the purification of bauxite.

Ans: Bauxite contains silicon dioxide (SiO_2), iron oxides and titanium(IV) oxide as impurities. The bauxite ore is digested with a concentrated solution of sodium hydroxide at 473-523 K and 35-36 bar pressure. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively leaving behind iron oxide and TiO_2, which are filtered off.

$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(l) \longrightarrow 2Na[Al(OH)_4]\,(aq)$$

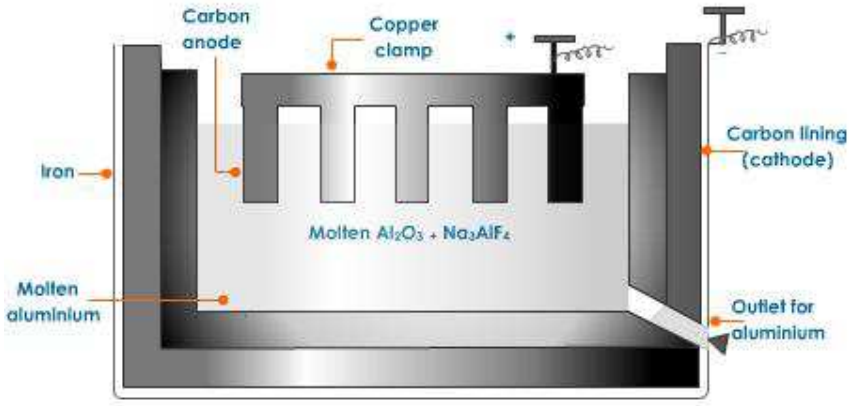
The filtrate containing sodium aluminate and sodium silicate is diluted and seeded with freshly precipitated aluminium hydroxide, which induces the precipitation of aluminium hydroxide leaving behind sodium silicate in solution.

$$Na[Al(OH)_4]\,(aq) \xrightarrow{H_2O} Al(OH)_3\,(s) + NaOH\,(aq)$$

The aluminium hydroxide is filtered dried and calcined at 1473 K to yield pure alumina.

2. Explain Hall-Heroult process of aluminium extraction.

Electrolysis of pure alumina (Hall-Heroult process)



Hall's cell

Pure alumina is dissolved in molten cryolite (Na_3AlF_6) and is electrolyzed in an iron tank lined inside with carbon. Carbon lining serves as cathode while a number of carbon rods dipping in the fused electrolyte serve as anode. Cryolite improves the electrical conductivity of the cell, as alumina is a poor conductor. Moreover, cryolite lowers the melting point of the mixture to about 1250 K. Other impurities such as CaF_2, NaF and AlF_3 may also be added. The temperature of the electrolyte is maintained between 1200-1300 K.

On passing electric current, aluminium is liberated at the cathode and gets collected at the bottom of the tank from where it is removed. Oxygen liberated at the anode combines with the carbon of the anode to produce carbon monoxide, which either burns or escapes out. The reactions taking place during the electrolysis are:

$$\text{At cathode : } Al^{3+}(\text{melt}) + 3e^- \longrightarrow Al(I)$$

$$\text{At anode : } C(s) + O^{2-}(\text{melt}) \longrightarrow CO(g) + 2e^-$$

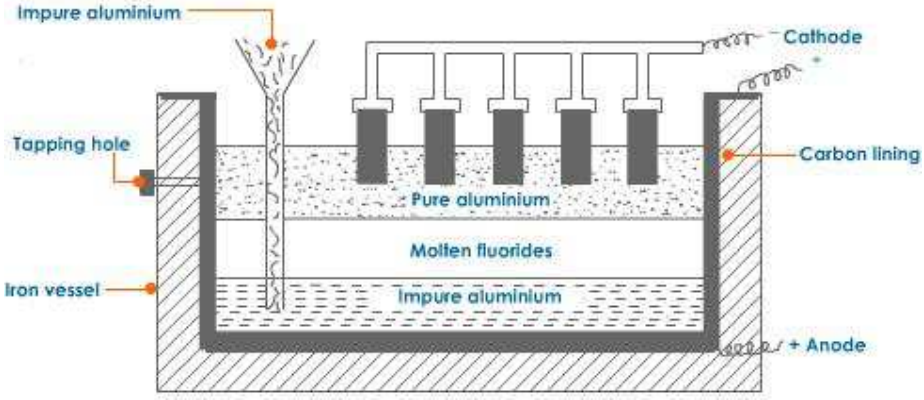
$$C(s) + 2O^{2-}(\text{melt}) \longrightarrow CO_2(g) + 4e^-$$

Since during electrolysis the carbon electrodes get consumed they have to be replaced periodically.

3. Explain Hoop's process of extraction of aluminium.

Ans: Refining of aluminium (Hoop's process)

The metal obtained in the above step is about 99% pure and for most purposes it is taken as pure metal. However, further purification of aluminium can be carried out by Hoopes process. The cell consists of an iron tank lined with carbon at the bottom. A molten alloy of copper, crude aluminium and silicon is used as the anode. It forms the lower most layer in the cell. The middle layer consists of molten mixture of fluorides, of sodium aluminium and barium (cryolite + BaF_2). The upper most layer consists of molten aluminium. A set if graphite rods dipping in molten aluminium serve as cathode.



Purification of aluminium by Hoop's cell

On passing current aluminium ions from the fused electrolyte are discharged at cathode and pure aluminium collects as the top layer. Meanwhile, an equivalent quantity of aluminium from crude alloy at the bottom goes into electrolyte in the middle layer. Crude aluminium is added from time to time and pure aluminium tapped off from the top.

4. **Give the names of important ores of Al and Mg.**

a) <u>Magnesium</u>

i) Magnesite $MgCO_3$

ii) Dolomite $MgCO_3.CaCO_3$

iii) Epsomite or Epsom salt $MgSO_4.7H_2O$

iv) Caranallite $MgCl_2.KCl.6H_2O$

v) Kieserite $MgSO_4.H_2O$

vi) Kainite $K_2SO_4.MgSO_4.MgCl_2.6H_2O$

b) <u>Aluminium</u>

i) Bauxite $Al_2O_3.2H_2O$

ii) Kaolin $Al_2O_3.2SiO_2.2H_2O$

iii) Cryolite Na_3AlF_6

iv) Felspar $K_2O.\ Al_2O_3.\ 6SiO_2$

5. **Write the important uses of aluminium**

Ans:

- Aluminium is used in packaging that includes drink cans, bottle tops, foil wrappings and foil containers. Food packed within this protects it from the changes caused due to exposure of the outer environment.
- The natural resistance to corrosion renders it useful in packaging. The aluminium oxide forms a protective layer as against the destructive layer formed by iron. Aluminium is impermeable and even in the shape of thin rolls; it traps the aroma and taste of the food. Since the metal is odourless and is non-toxic, thus making it perfect for packaging.
- Aluminium with its strength to weight ratio has a number of uses in transport industry. The alloys of aluminium use other elements to remove dislocations in its structure for the increase in its strength. Its lightweight property gives fuel efficiency when it is used in cars, trains and boats.
- The ductility of aluminium is higher than that of copper rendering them to be used in power lines and since aluminium is corrosion resistant, long distance distribution of electrical lines use aluminium wires.
- TV aerials, satellite dishes and the standard bulb bases are prepared of aluminium.
- Aluminium is extremely versatile and it is easily moulded, curved, tapered, bonded or cut to any desired shape. Buildings with insulated aluminium cladding are thermally efficient.
- Aluminium is used in the preparation of household products like kitchen appliances, utensils, indoor and outdoor furniture and in the making of tennis bats and golf clubs.

6. **Write a note on the extraction of sodium from sodium hydroxide**

Castner's process:

Molten sodium hydroxide (caustic soda, NaOH) is electrolyzed using an iron cathode and nickel anode. A nickel wire gauze cylinder prevents the electrodes from touching each other. On passing electric current through the melt, sodium is liberated at the cathode and oxygen at the anode. The liberated sodium metal floats over the surface (lighter than fused caustic soda), and collects inside the receiving vessel where hydrogen prevents sodium from oxidation. Excess of the gas escapes from the outlet. Sodium is removed from time to time with the help of perforated spoons and kept under kerosene oil. The various reactions taking place during electrolysis are:

$$NaOH \xrightarrow{\text{melting}} Na^+ + OH^- \text{ (dissociation)}$$

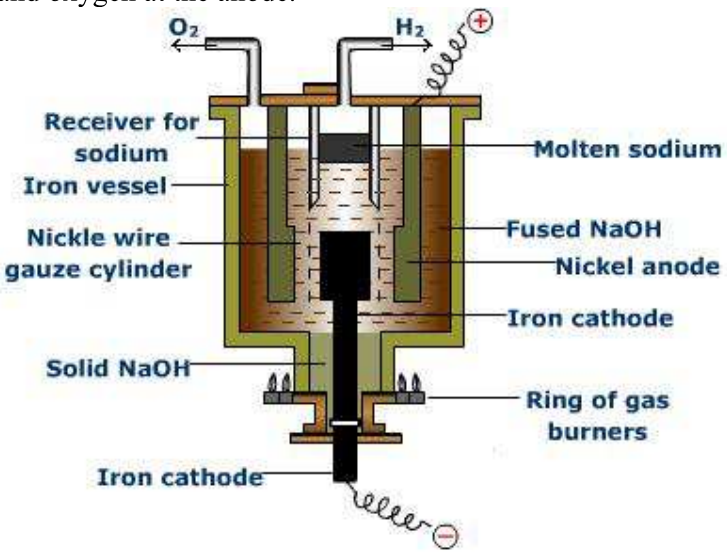
At cathode:

$$Na^+ + e^- \longrightarrow Na$$

At anode:

$$OH^- \longrightarrow \frac{1}{2} H_2O + \frac{1}{4} O_2 + 2e^-$$

Most of the water formed in the reaction gets evaporated, and the rest is electrolyzed into hydrogen and oxygen. Therefore, metallic sodium and hydrogen are liberated at the cathode and oxygen at the anode.



Castners process

7. **Write a note on the extraction of sodium using down's process.**

Down's process

In this process, molten sodium chloride (common salt) is electrolyzed using a graphite anode and a ring shaped iron cathode. The two electrodes are separated by a wire gauge partition to avoid the mixing of sodium and chlorine so formed. As Sodium chloride melts at a very high temperature of 1085 K, a mixture containing sodium chloride, potassium chloride and potassium fluoride (NaCl + KCl + KF) is employed. This mixture melts at about 850-875 K.

The reasons for lowering the temperature are:

- It is difficult to maintain a high temperature of 1085K.
- Sodium is volatile at this temperature and so a part of the metal formed may vaporize.
- At this high temperature chlorine produced as a by product corrodes the vessel.
- Metal at this temperature will be in a colloidal state and its separation will be difficult.

On passing electric current, chlorine is liberated at the carbon anode and escapes through the dome shaped steel hood outlet. Sodium rises from the cathode and remains in the wire gauze shell. The sodium produced is in molten state. Being lighter than the electrolyte it rises to the surface. As the level of molten sodium arises, it is forced into the receiver. The process is continuous and fresh salt is introduced to maintain the level of molten electrolyte high enough to allow sodium to rise into the iron pipe. Chemical reactions involved in this process are as follows:

$$2NaCl \xrightarrow{\text{melting}} 2Na^+ + 2Cl^-$$

At cathode:

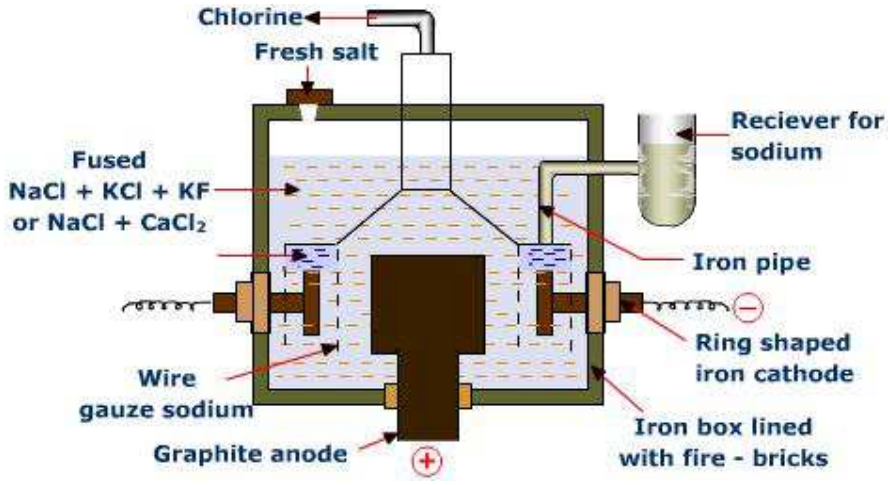
$$2Na^+ + 2e^- \longrightarrow 2Na$$

At anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

Advantages of Down's process

- Sodium metal obtained has high degree of purity (99.5%).
- The starting material, sodium chloride is very cheap.
- Chlorine is obtained as a useful by-product.



Down's cell

VERY SHORT ANSWER QUESTIONS

1. **What metal is purified by cupellation?**

Silver metal is purified by cupellation

2. **Explain polling**

Oxide impurity of impure metals can be purified by this method. Poles of green wood are used to stir the molten crude metal sample. The hydrocarbon organic matter in the poles acts as a reducing agent and reduces the oxide impurities. This method is used for refining copper.

3. **Define flux.**

An outside substance added oto lower the melting point is known as flux. The flux combines with gangue to fom slag.

4. Mention ay two furnaces that are generally used in metallugical processes.

Blast furnace and reverboratory furnace.

5. **What do reactions in a blast furnace take place?**

Reactions in a blast furnace take place in the body of the furnace

6. Can Zn exist in native state? Why or why not..

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

7. **Give the names and formulae of zn ores.**

Zinc Ores

The important ores of zinc are

i) Zinc blende, ZnS

ii) Calamine, $ZnCO_3$

iii) Zincite, ZnO

The chief ore of Zinc is Zinc blende

8. **Explain briefly the extaction of Zn.**

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.

$$2\,ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

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.

$$ZnO + C\ (\text{at } 1673K) \rightarrow Zn + CO$$

9. How Zn is purified?

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 ZnSO4 solution containing a little of dil.H2SO4. On passing electric current, pure zinc get deposited at the cathode.

10. Write the uses of Zn.

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

11. What is the purpose of adding KCl and NaCl to anhydrous $MgCl_2$?

Ans: A mixture of equal quantities of carnallite and NaCl is fused to a clear liquid at 973K. The alkali chloride prevents hydrolysis of magnesium chloride and increases the conductivity of the fused mass.

12. What are the reactions that take place in electrolysis of $MgCl_2$?

The following are reactions for Extraction of Magnesium by electrolysis

At cathode the reaction is:-

$Mg^{2+} + 2e^-$ -------> $2Mg$

At anode the reaction is:-

$2Cl^-$ ------> $Cl_2 + 2\ e^-$

13. What are the ores of sodium?

- Albite (soda feldspar) $NaAlSi_3O_8$
- Borax (as tincal) $Na_2B_2O_7.10H_2O$
- Glauber's salt $Na_2SO_4.10H_2O$
- Sodium chloride, (common salt) found as rock salt, in sea water and in lakes.
- Sodium nitrate ($NaNO_3$) as Chile saltpeter.

14. What are the advantages of Down's process of extraction of Sodium?

Advantages of Down's process:

- Sodium metal obtained has high degree of purity (99.5%).
- The starting material, sodium chloride is very cheap.
- Chlorine is obtained as a useful by-product