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:

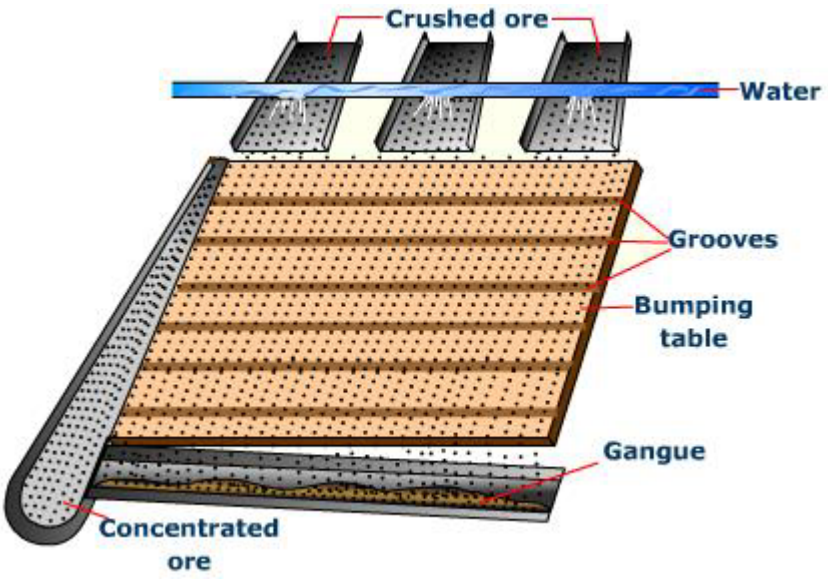
b. Hand picking

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.

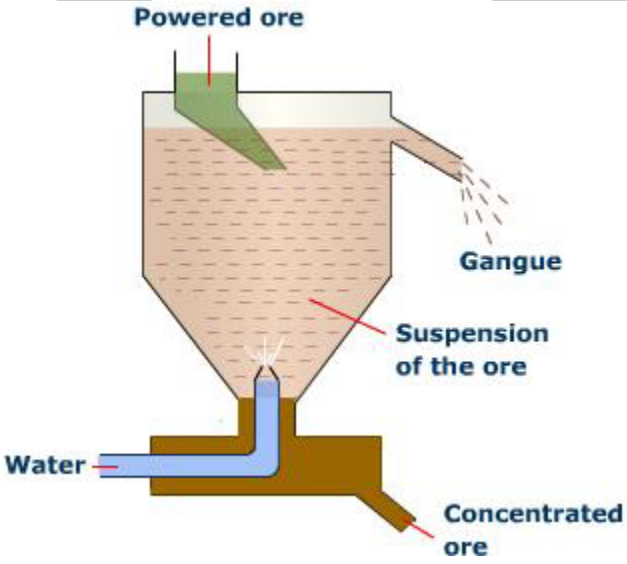
c. Gravity or levigation method

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.



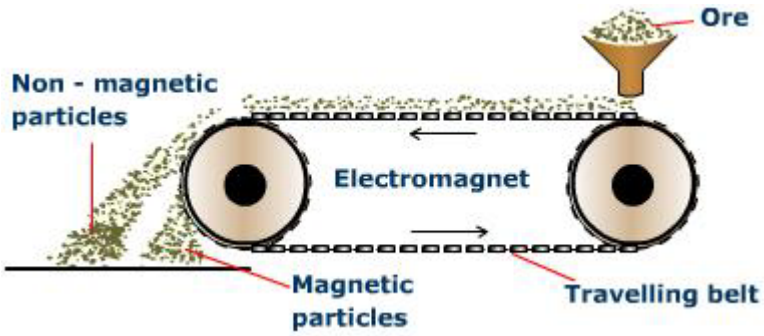
Wilfley table for washing of the ore



Hydraulic classifier

d. Magnetic separation

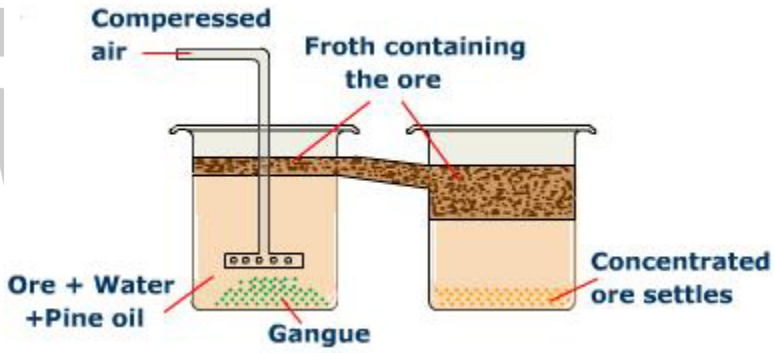
Magnetic separation is done especially in the case of haematite ore, whereby the powdered ore is dropped on to leather or brass conveyer belt, which moves over two rollers one of these rollers, is magnetic. When the ore passes over the magnetic roller, it sticks to the belt due to the force of attraction 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 $Al(OH)_3$

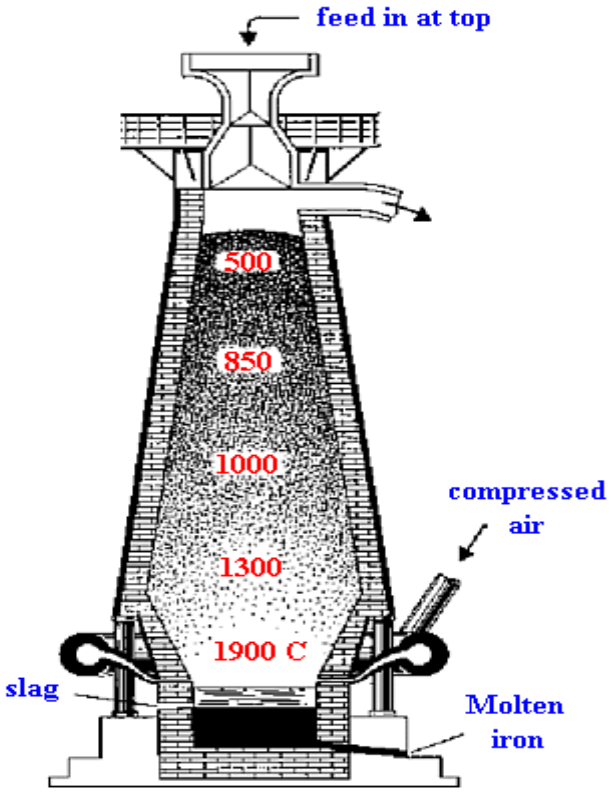
$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

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.

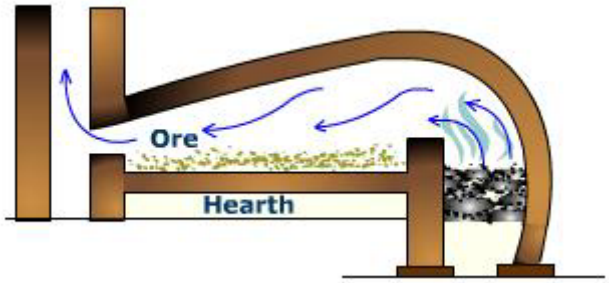
Reverberatory furnace:

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:

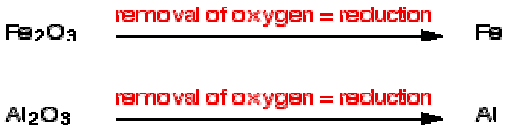
Bauxite	**Al_2O_3**
Haematite	**Fe_2O_3**
Rutile	**TiO_2**

. . . or sulphides - for example:

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

Reducing the metal compound to the metal

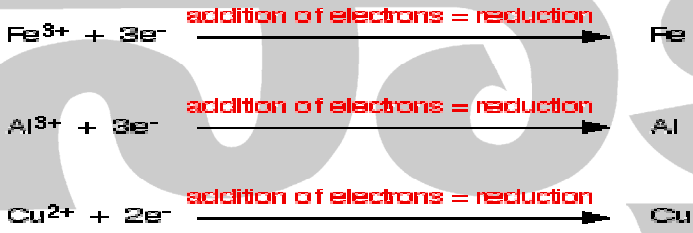
Why is this reduction? At its simplest, where you are starting from metal oxides, the ore is being reduced because oxygen is being removed.



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.

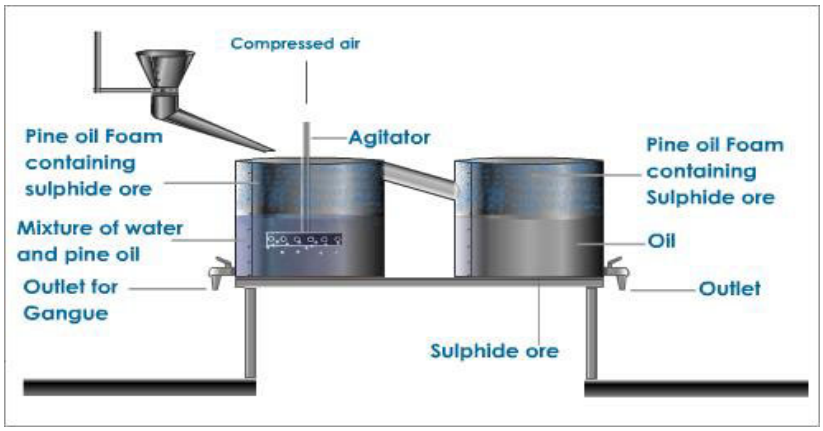
3. Write a short note on Froth floatation process.

Froth Floatation

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.

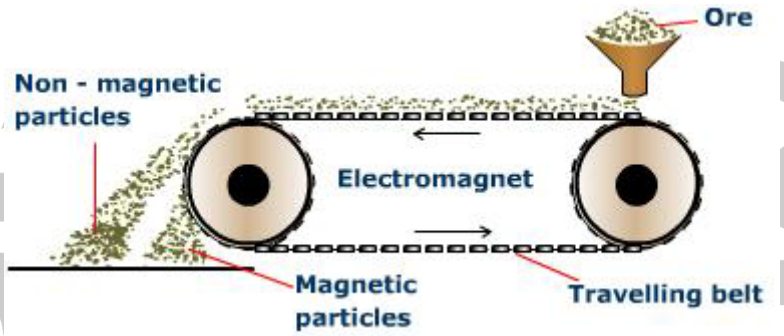
Note: Sulphide being more electronegative attracts the covalent oil molecules. The gangue being less electronegative is attracted by the water.

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 ($FeO.Cr_2O_3$)

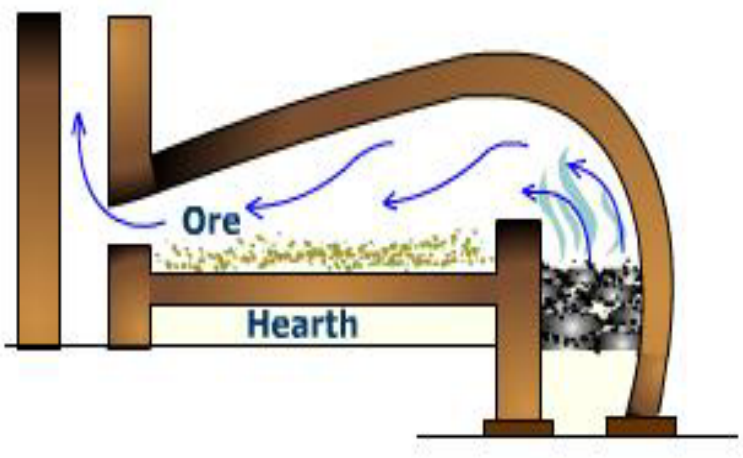
ii) Process:



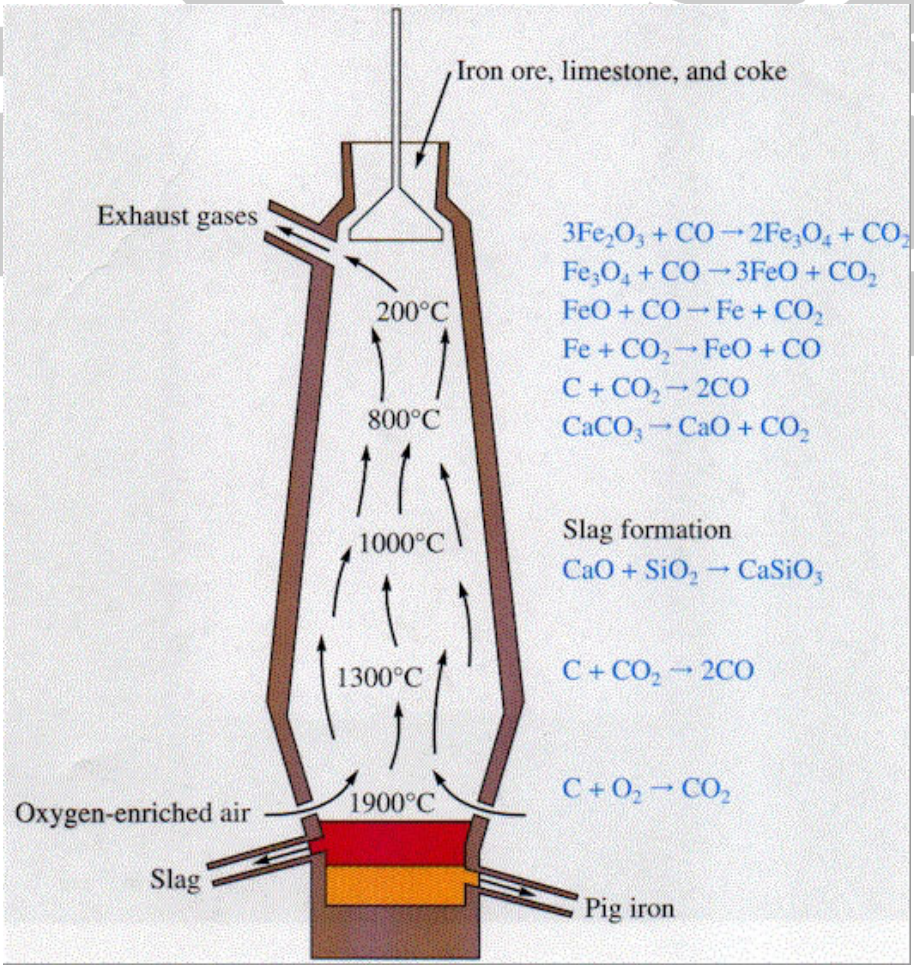
Magnetic Separation

- 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.,

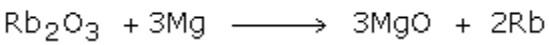
$$WO_3 + 3H_2 \xrightarrow{heat} \underset{Tungsten}{W} + 3H_2O$$

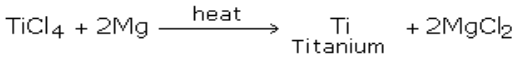
$$MoO_3 + 3H_2 \xrightarrow{heat} \underset{Molybdenum}{Mo} + 3H_2O$$

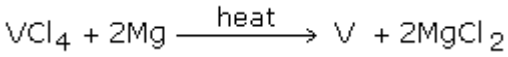
Carbon monoxide reduction method: In certain cases CO gas produced in the furnace itself can be used as a reducing agent. For example**,**

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

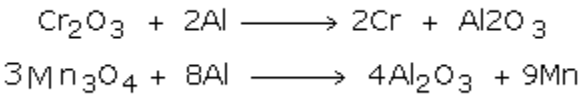
Magnesium reduction method: Oxides of certain metals are reduced by Mg e.g.,



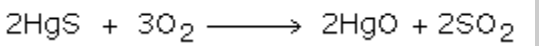




Aluminium reduction method (Alumino Thermic Process): Certain metal oxides cannot be reduced by carbon. Such metallic oxides can be reduced by aluminium powder. This process has been widely used to reduce TiO_2, Cr_2O_3 and Mn_3O_4 to get the corresponding metal.



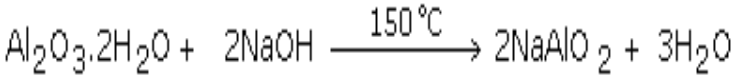
Self-reduction method : When the sulphide ores of less electropositive metals like Hg, Cu, Pb, Sb etc., are heated in air, a part of the ore gets oxidized to oxide or sulphate, which then reacts with the remaining sulphide ore to give the metal and SO_2. This process is also known as self-reduction method.



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.



$$\underset{\text{(in solution)}}{CuSO_4} + Fe \longrightarrow \underset{\text{precipitate}}{Cu} + \underset{\text{(in solution)}}{FeSO_4}$$

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_2 on 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.

$$\underset{\text{Gangue}}{SiO_2} + \underset{\text{Flux}}{CaO} \rightarrow \underset{\text{Slag}}{CaSiO_3}$$

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.