INORGANIC CHEMISTRY

CHAPTER- METALS AND METALLURGY

LECTURE NO. 1

DATE:- 19, JUNE, 2021

TIME: (9.00A.M.)

Elements

Metals

Non-metals

1) Noble metals occur in free state

2) Active metals occur in combined state

Metallurgy: - Metallurgy is the science and technology of extracting metals from their ores and alloys.

Mineral: - The naturally occurring substance which contains metal either in free state or combined state is called as mineral.

e.g. $Al_2O_32H_2O$ (Bauxite), Na_3AlF_6 (Cryolite), Fe_2O_3 (Haematite).

Ore: - It is a mineral from which metal can be extracted economically.

Types of Ores: - Active metals are occurs in nature in various types of ores.

1) Sulphide Ores: - Metals such as Fe, Cu, Hg, Zn, etc. occurs as their sulphides.

e. g. FeS (Iron pyrite), $CuFeS_2$ (Copper pyrite), HgS (Cinnabar) and ZnS (Zinc blende) etc.

2) Oxide ores: - Metals such as Fe, Zn, Cu, Al etc. occurs as their oxides.

e. g. Fe_2O_3 (Haematite), ZnO (Zincite), Cu_2O (Cuprite), $Al_2O_32H_2O$ (Bauxite).

3) Carbonate ores: - Metals like Fe, Cu, Zn, Ca etc. occurs in the form of carbonates.

e. g. $FeCO_3$ (Siderite), $CuCO_3$ (Malachite), $ZnCO_3$ (Calamine), $CaCO_3$ (limestone).

4) Sulphate ores: - The common sulphate ores are $BaSO_4$ (Barytes), $PbSO_4$ (Anglesite), $CaSO_4$ (Anhydrite) etc.

5) Halide ores: - The most common halide ores are the chlorides sand fluorides.

e. g. NaCl (Rock salt), CaF_2 (Fluorspar), AgCl (Horn silver), etc. Bromide and iodide of K and Mg are present in small amounts in sea water.

Various steps involved in metallurgical processes: -

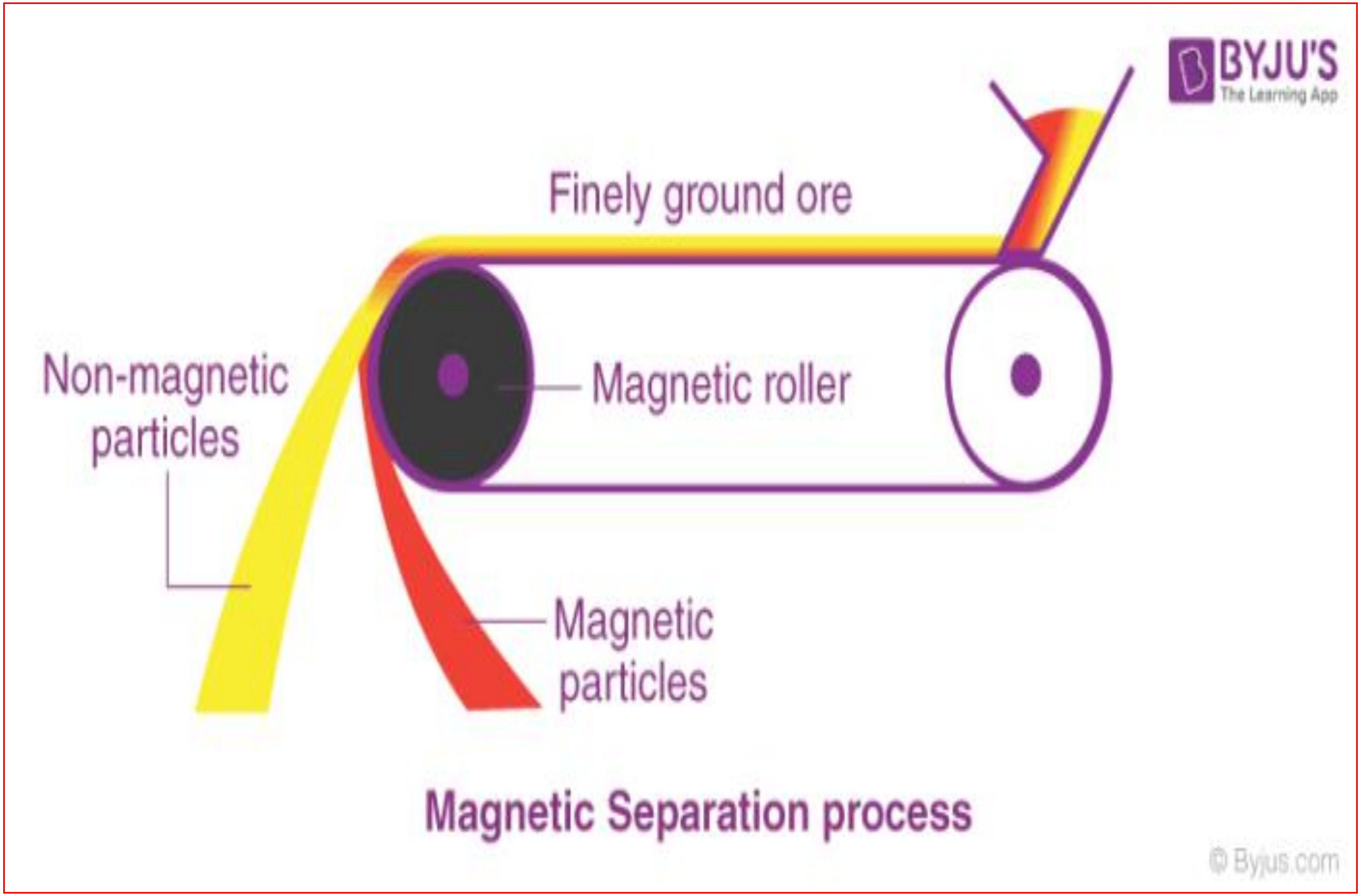
The various steps involved in the extraction of pure metal from their respective ores are concentration of the ore, calcination, roasting, reduction and refining.

Concentration of the ore: - It is the important operation in metallurgical process because the ores usually contains large quantities of unwanted impurities (Gangue) and are removed mechanically. Before the ore is subjected to metallurgical process, the ore material obtained from the earth crust is washed and crushed or grinded into powdered form. Then the further concentration of powdered ore is carried out in one or more of the following methods:

1) Hand picking: - Sometimes, the ore is separated from main stock in a sufficient degree of purity by simple picking it up by hand. Here the advantages of different colours and appearances of mineral bits or particles are taken. Then the adhering rocky material is eliminated by breaking the mineral particles with hammer.

2) Magnetic separation: - The principle of this method is that, to separate a magnetic ore particles from a non-magnetic particles those having practically same specific gravity.

In this process, a leather or rubber belt moving over two rollers, one of which is magnetic. The crushed ore is allowed to fall on a belt at one end and which passes over the magnetic roller. Then the magnetic particles of ore is attracted by the magnetic roller and falls nearer to the roller in a separate heap while the non-magnetic particles (impurities) fall further away in a another heap.


BYJU'S
The Learning App
Finely ground ore
Non-magnetic particles
Magnetic roller
Magnetic particles
Magnetic Separation process
© Byjus.com

3) Froth flotation method: - This method is based on the principle of preferential wetting of the solid surface by various liquid. Metallic sulphides (Ores) are wetted by certain oils like Pine oil and not by water.

In this process, the finely divided ore is added into water to which small quantity of oil (e. g. Pine oil) have been added. The water is agitated violently with air, when the froth is formed at the surface of water. Hence here the ore particles adhere to the foam bubbles forming froth while the impurity particles do not form such froth. Thus as a result of this, ore particles float on the surface while the impurity particles remain at the bottom of the tank.

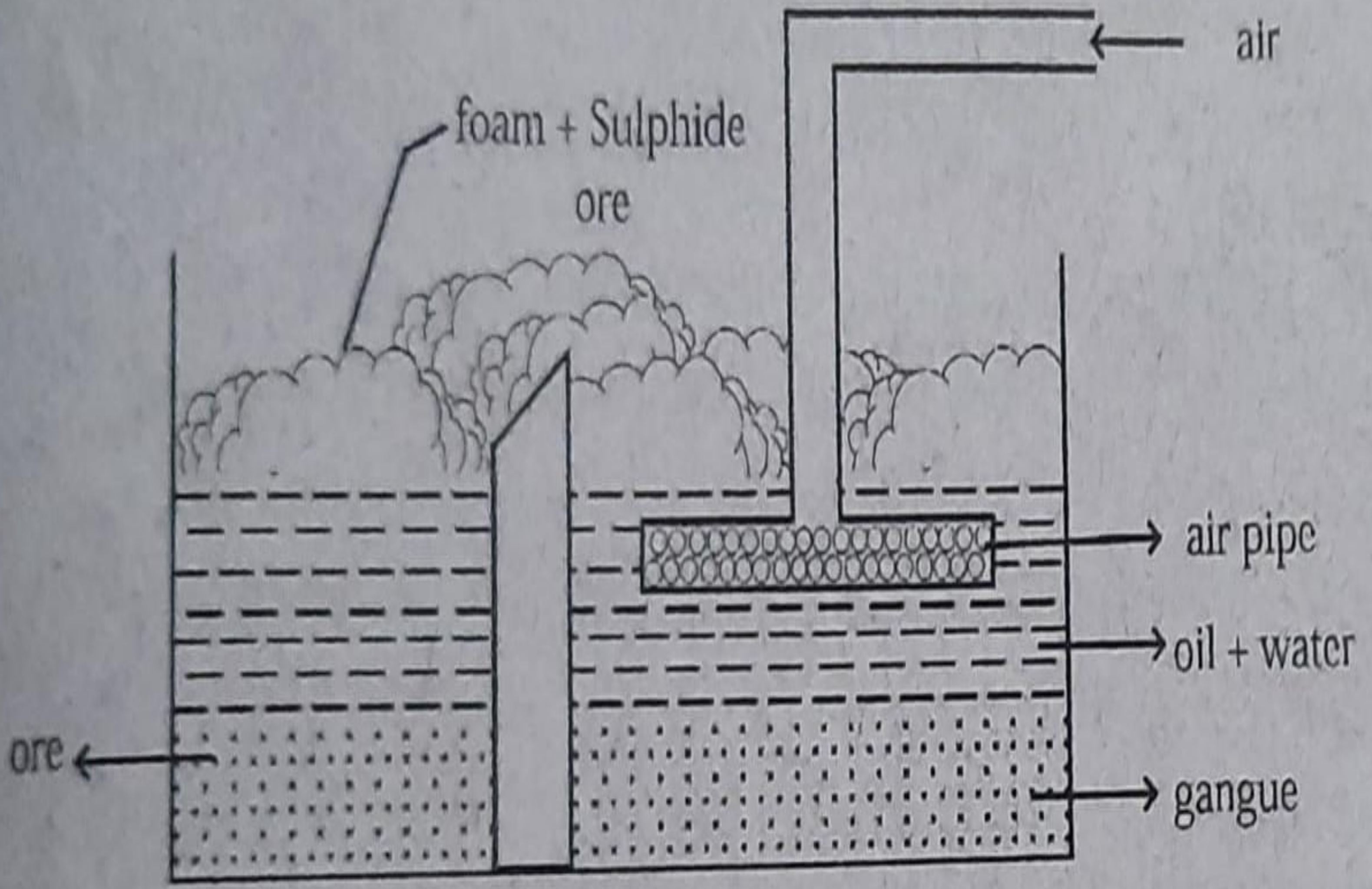
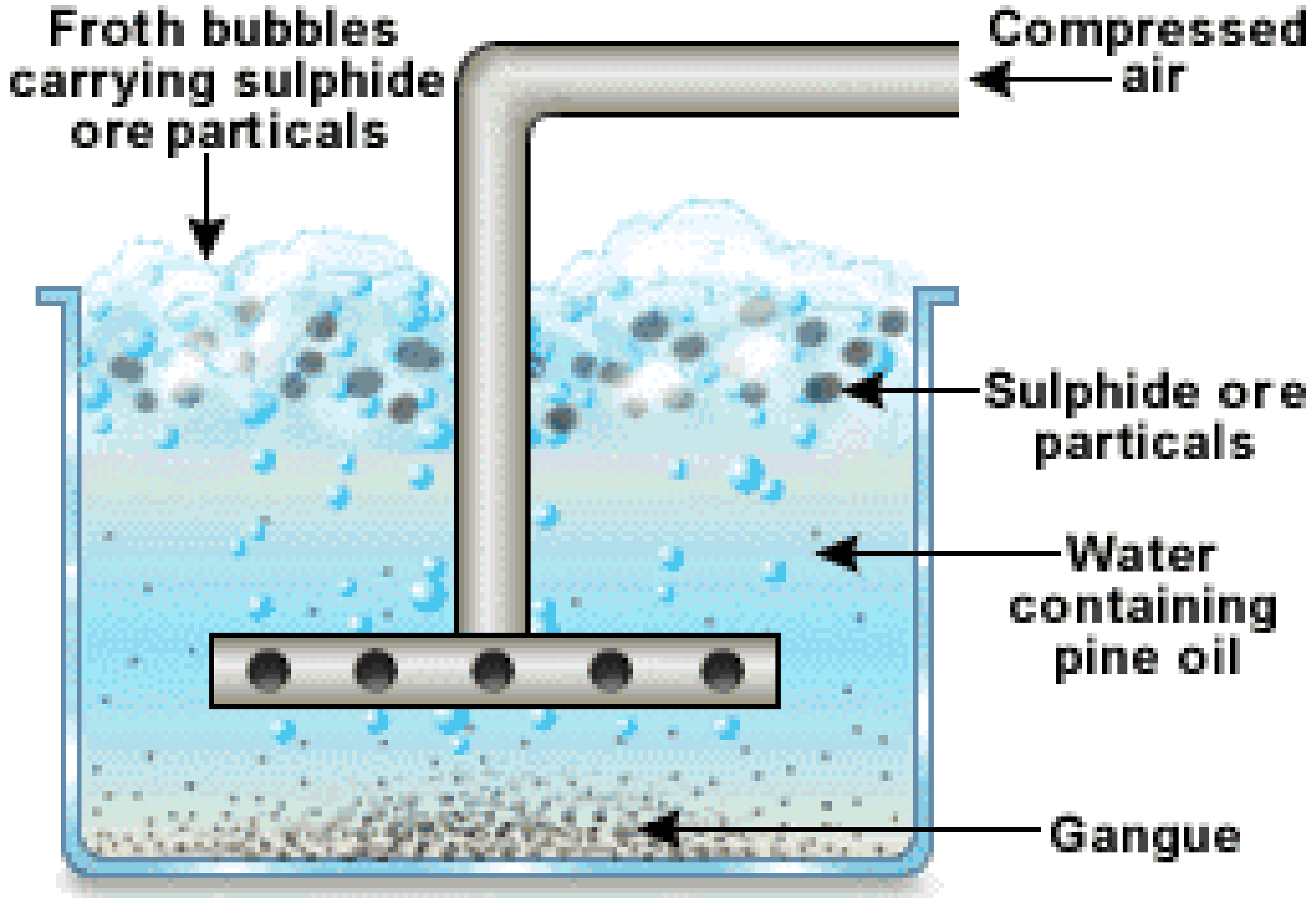
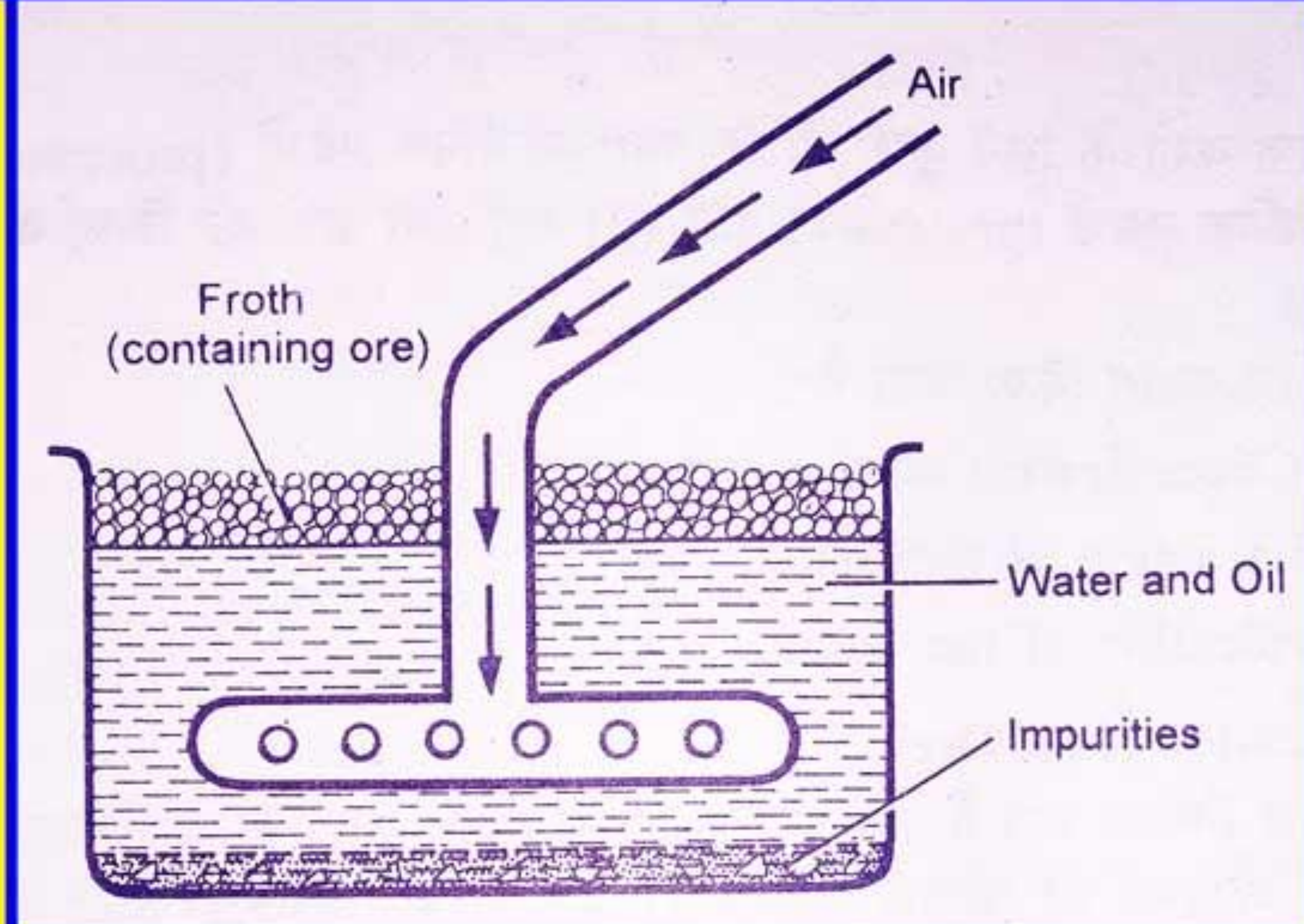


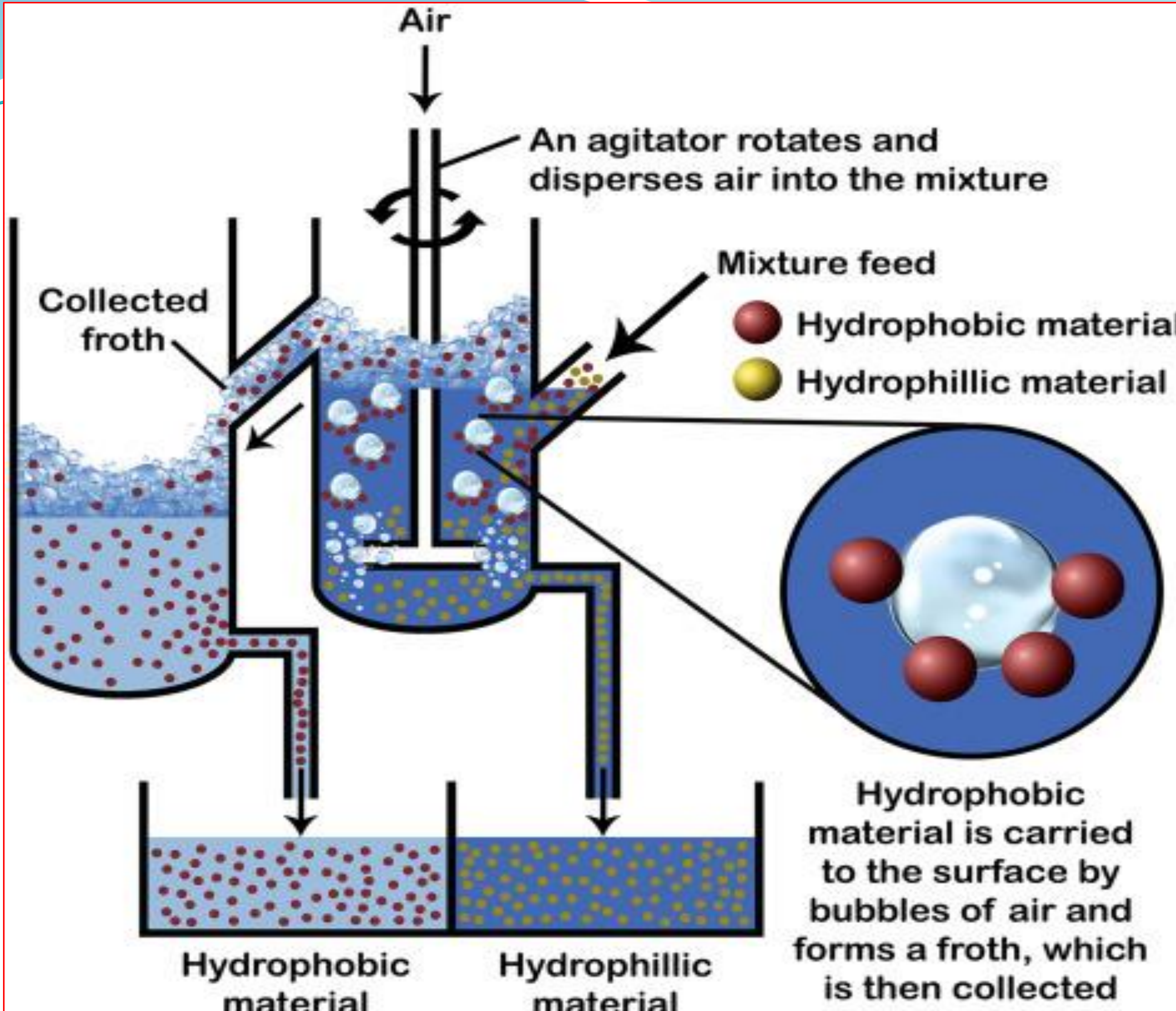
Fig. 4.2 Froth flotation process



Froth floatation process for the concentration of sulphide ores.

Froth Flotation Process




Air
An agitator rotates and disperses air into the mixture
Mixture feed
Hydrophobic material
Hydrophillic material
Collected froth
Hydrophobic material
Hydrophillic material
Hydrophobic material is carried to the surface by bubbles of air and forms a froth, which is then collected

In froth floatation process, the finely powdered sulphide ore particles are mixed with a small quantity of Pine oil and Na or K-xanthate. This mixture is then added into a water tank and water is agitated with air blast due to which the air bubbles adhere to the ore particles and floats them to form froth while impurity particles settle down at the bottom. The froth carries away along with it the sulphide ore particles in the side compartment. The foam separates and settles. Ore particles are collected at the bottom of the side tank. This process is known as the froth flotation process.

e. g. Indian Copper Corporation (at Bihar) daily treats about 2000 tones of Cu ore by this method.

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DATE:- 22, JUNE, 2021

TIME: (9.00A.M.)

4) Chemical separation or leaching: - In this method, the powdered ore is treated with some suitable reagent which may dissolve the ore but not the impurities. The impurities are then filtered off and the ore is removed from the solution by suitable chemical methods.

e. g. In the extraction of Al from bauxite ore (Al_2O_3, $2H_2O$) the finely divided ore is treated with hot NaOH solution. Alumina present in the ore dissolves forming soluble sodium meta-aluminate but the impurities are left behind as such and are filtered off. The filtrate is diluted which causes the precipitation of $Al(OH)_3$. This is then filtered off and the precipitate is calcined to get pure Alumina.

$$Al_2O_3, 2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$$

Sodium Meta-aluminate

(Soluble)

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

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

5) Gravity separation: - This method is based on the difference in the specific gravities of metallic ore and impurity particles. In this process, the powdered ore is agitated with water or washed with a stream of water. The lighter gangue particles were washed away and heavier ore particles are left behind and settle down.

For the above treatment either Wilfley table or hydraulic classifier is used. Wilfley table is a wooden table having a slanting floor on which long wooden strips called riffles are fixed. The powdered ore is suspended in a stream of water. The heavier ore particles collect behind the riffles and the gangue particles are carried away with the stream of water.

In hydraulic classifier, the powdered ore is dropped from the top of classifier and a strong stream of water is introduced from the bottom. The lighter impurity particles are carried by the water while the heavier ore particles settle down. Generally, oxide and carbonate ores are concentrated by this method.

Calcination: - It is a process of heating an ore strongly at a temperature insufficient to melt it. The purpose of calcination is to remove moisture and change the physical state of a ore. Calcination is generally done in a reverberatory furnace. It makes the ore porous.

e. g. 1) Iron ore containing oxides on calcination gives off moisture and becomes porous.

$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O\uparrow$.

3) Limestone on calcination looses carbon dioxide.

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$

2) when bauxite is calcined at high temperature, H_2O is removed and anhydrous Alumina is left.

$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O\uparrow$.

Roasting: - In this process, the ore is subjected to the action of heat in presence of air at a temperature below their melting points i. e. without fusion. The purpose of this method is to change the ore into the oxide or sulphate while, impurities are also oxidized and removed in the form of volatile substance. Then from these oxides the metal may be obtained by electrolysis or reduction respectively.

Roasting is generally carried out in the reverberatory furnace, in which the ore is heated by flames of a fuel. Usually sulphide ores are oxidized by this method.

e.g. $2ZnS + 3\,O_2 \rightarrow 2ZnO + 2SO_2\uparrow$

Sometimes sulphide is not converted into an oxide but to a soluble sulphate by partial roasting, Then, these soluble sulphate salts are leached out with water and used for further treatment.

$CuS + 2O_2 \rightarrow CuSO_4$

$ZnS + 2O_2 \rightarrow ZnSO_4$

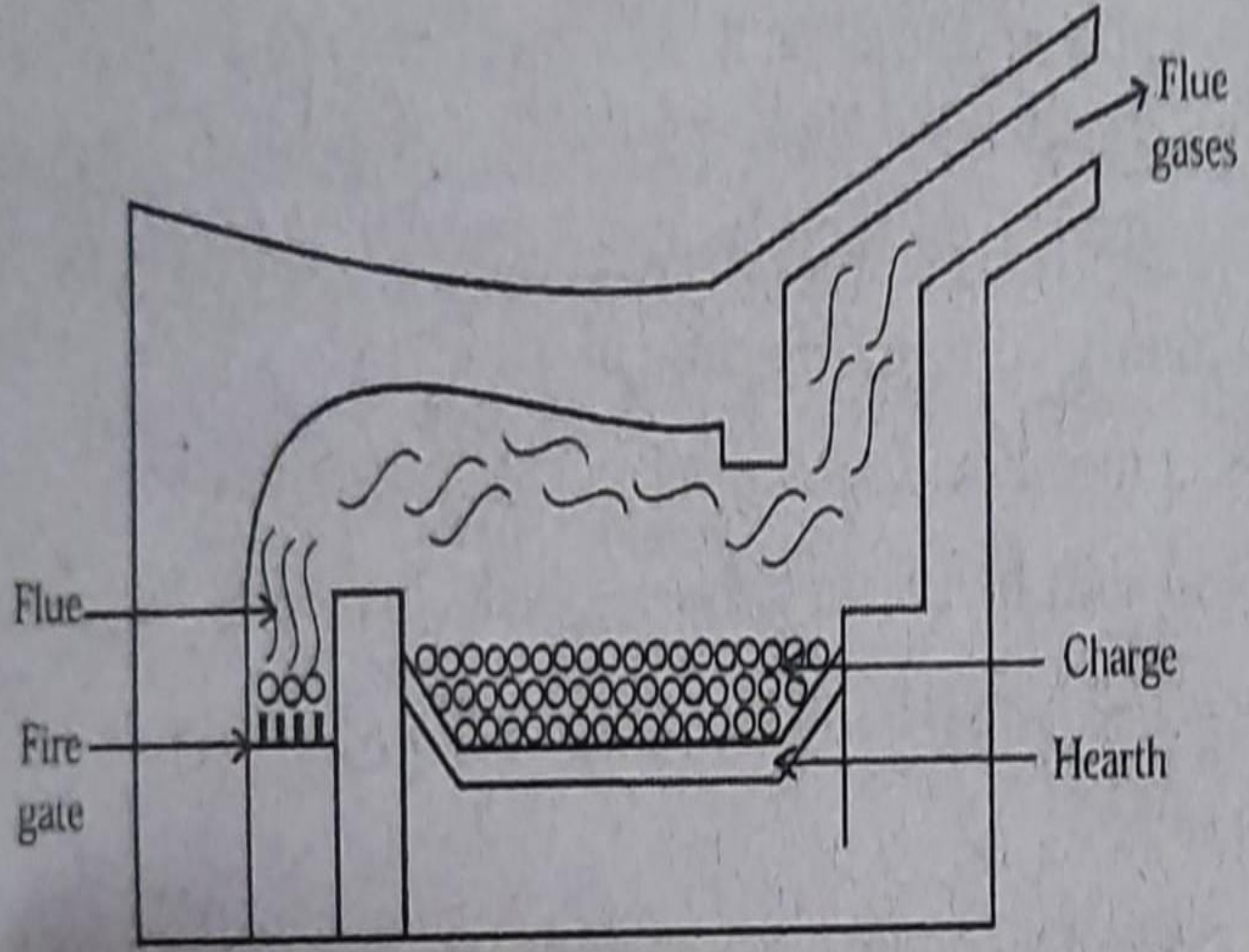

Fig. 4.3 Reverberatory Furnace

Reduction to free metals: - The roasted or calcined ore is then reduced to the metal (metallic state) and some of the important commonly used methods for the reduction are as follows:

a) Using powerful reducing agents

b) Using carbon reducing agent

c) Using air reduction (Autoreduction)

d) Using electrolytic reduction

e) Using wet process (Hydrometallurgy)

a) Using powerful reducing agent: -

For the extraction of less electropositive metal, the powerful reducing agents like H_2, CO, water gas ($CO + H_2$), Na, K, Al and Mg may be used.

Certain oxides of the metals like Cr and Mn etc. are very stable and are not reduced by powerful reducing agents. Then such oxides are reduced by Al powder. Because Al has a greater affinity for oxygen at high temperature. This process of reduction by Al is known as “Gold Schmidt’s Aluminothermic process”.

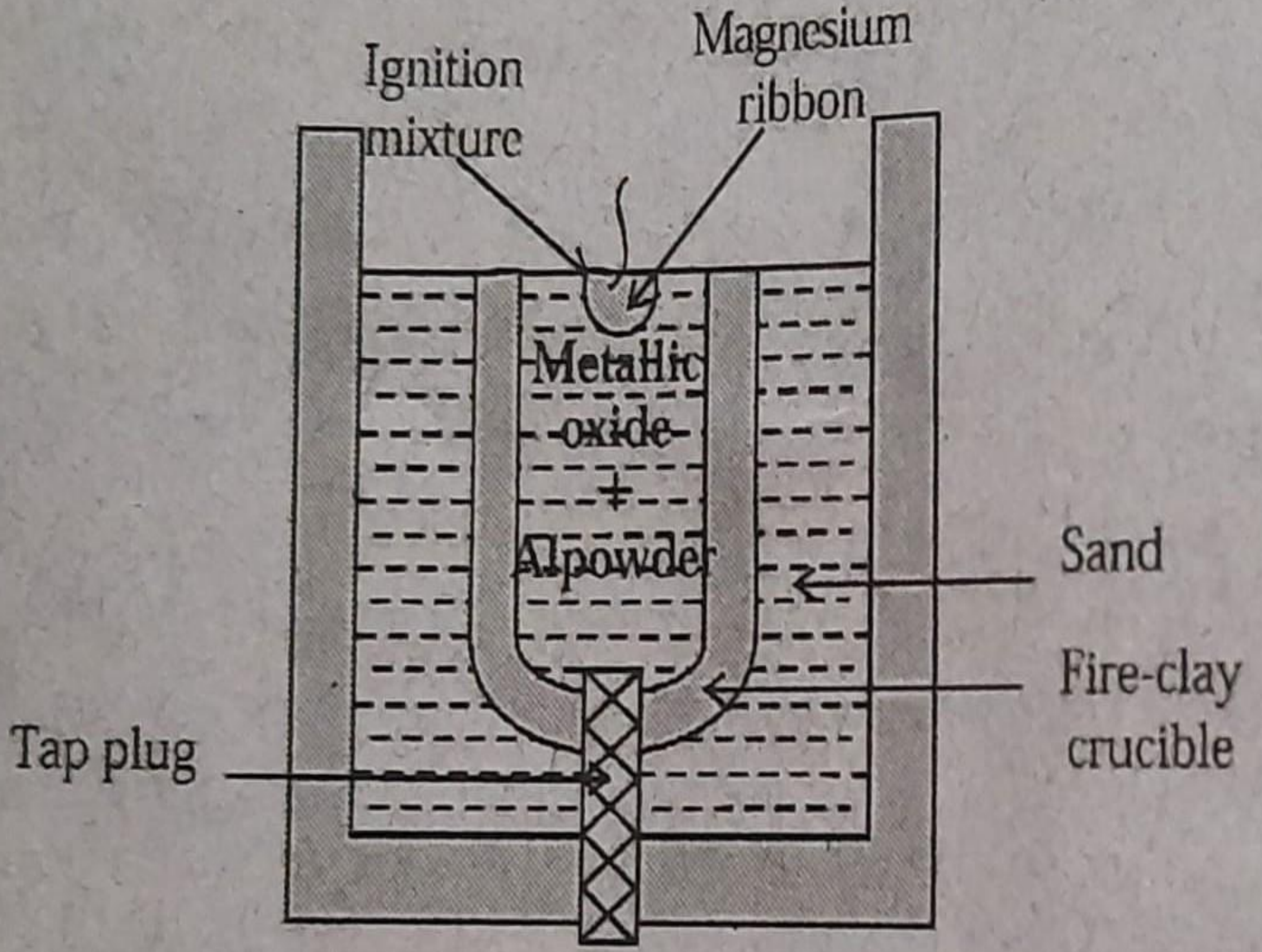

Fig. 4.4 Goldschmidt's Alumino thermic process

In this process, a metal oxide is mixed with Al powder in 3:1 ratio. This mixture is called as “thermite” and hence this process is also called as “thermite process”. In this method, the thermite (MO + Al powder) is ignited in a closed crucible by means of a lighted magnesium ribbon.

The reaction is highly exothermic; metal obtained in a molten state and settle down to the bottom and is removed by removing the tap plug. Al_2O_3 floats as slag and protect the metal from air oxidation.

b) Using carbon reduction process: -

This method is applicable for the oxides of metals like Pb, Zn, Fe, Cu etc. and are reduced by strongly heating them with carbon or Coke in a blast furnace. Because of this, carbon reduces the metal oxide into free metal. This process is called as "Smelting".

e. g. $MO + C \xrightarrow{\Delta} M\ (Molten) + CO$

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2\uparrow$

In this process carbon is also oxidized to CO_2 at temperature below 700°C and to CO at temperature above 700°C.

$C + O \rightarrow CO$ below 700°C

$C + O_2 \rightarrow CO_2$ above 700°C

The ore even after concentration contains some infusible impurities which have to be removed by converting it into some fusible mass called as ‘Slag’. For this conversion the ‘Flux’ is used. (Flux is a substance which is used to remove gangue) and the choice of flux depends upon the nature of the gangue.

e. g. If the gangue is acidic, then basic flux is used like CaO, MgOetc.

If the gangue is basic, then acidic flux is used like silica (SiO2), Borax, etc.

Gangue + Flux → Slag.

e. g. $SiO_2 + CaO \rightarrow CaSiO_3$

Acidic Basic Slag

The slag is not soluble in the molten metal, but it is lighter than molten metal. Hence, can be easily skimmed off from the surface of the fused metal.

c) Using air reduction (Autoreduction): -

By this method, the less active heavy metals like Hg, Pb, Sb, Cu etc. are separated from their oxides but these oxides are unstable towards heat. Hence, the use of any additional reducing agent is not necessary while only roasting in air is sufficient for the separation of metal.

e. g. Hg is separated from galena ore (HgS) by heating (roasting) it in air until a part is converted into oxide (HgO). On further heating in the absence of air, the oxide react with the unchanged sulphide to give Hg-vapour which are on condensation gives liquid Hg.

$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2\uparrow$

$2HgO + HgS \rightarrow 2Hg + SO_2\uparrow$

This process is known as "Air reduction process". Similarly, Cu and Pb are also extracted from their sulphide ore by this method.

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LECTURE NO. 3

DATE:- 25, JUNE, 2021

TIME: (3.00P.M.)

d) Using electric reduction (Electrometallurgy): -

Electrolytic reduction is mainly used in the extraction of alkali and alkaline earth metals. The extraction of highly electropositive metals by chemical reducing agents is extremely difficult. The oxides of these metals are very stable and have to be heated very strongly with carbon in order to reduce them to metal, But at high temperature, these metals combines with carbon to form carbides.

Hence, those highly electropositive metals are not extracted by any of the above extracting methods; these metals are extracted by the electrolysis of their oxides, hydroxides or chlorides in fused states.

In this process, some other salts are added to lower the melting point as well as vapour pressure of the metal under electrolysis and reduce the corrosion troubles. The metal is then liberated at the cathode by the electrolysis of their fused chlorides.

On fusion, $NaCl \rightarrow Na^+ + Cl^-$

On electrolysis, At cathode (-ve electrode), $Na^+ + e^- \rightarrow Na$

At anode (+ve electrode), $Cl^- \rightarrow Cl + e^-$

$$Cl + Cl \rightarrow Cl_2$$

The product of electrolysis react readily, hence a suitable arrangement has to be made to keep them separate.

e) Using Wet process (Hydrometallurgy): -

Hydrometallurgy is the treatment of obtaining the metal into solution by the action of suitable chemical reagent like NaCN solution or chlorine in presence of water and then the metal is extracted by electrolysis or by the use of proper precipitating agent.

The metals like gold (Au) and silver (Ag) can be precipitated from their salt solution by electropositive metals. i. e. Zn.

In Metallurgy of Ag, metallic silver is dissolved from its ore in dilute NaCN solution followed by air blowing, when silver goes into solution as the argento-cyanide complex. Then Ag is separated either by electrolysis or by precipitation adding electropositive metal Zn.

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

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

In Metallurgy of gold (Au), the ore is ground to a fine paste in NaCN solution and aerated by agitation for 2 days. Gold is precipitated by addition of zinc dust.

$4Au + 8 NaCN + O_2 + 2H_2O \rightarrow 4 Na[Au(CN)_2] + 4NaOH$

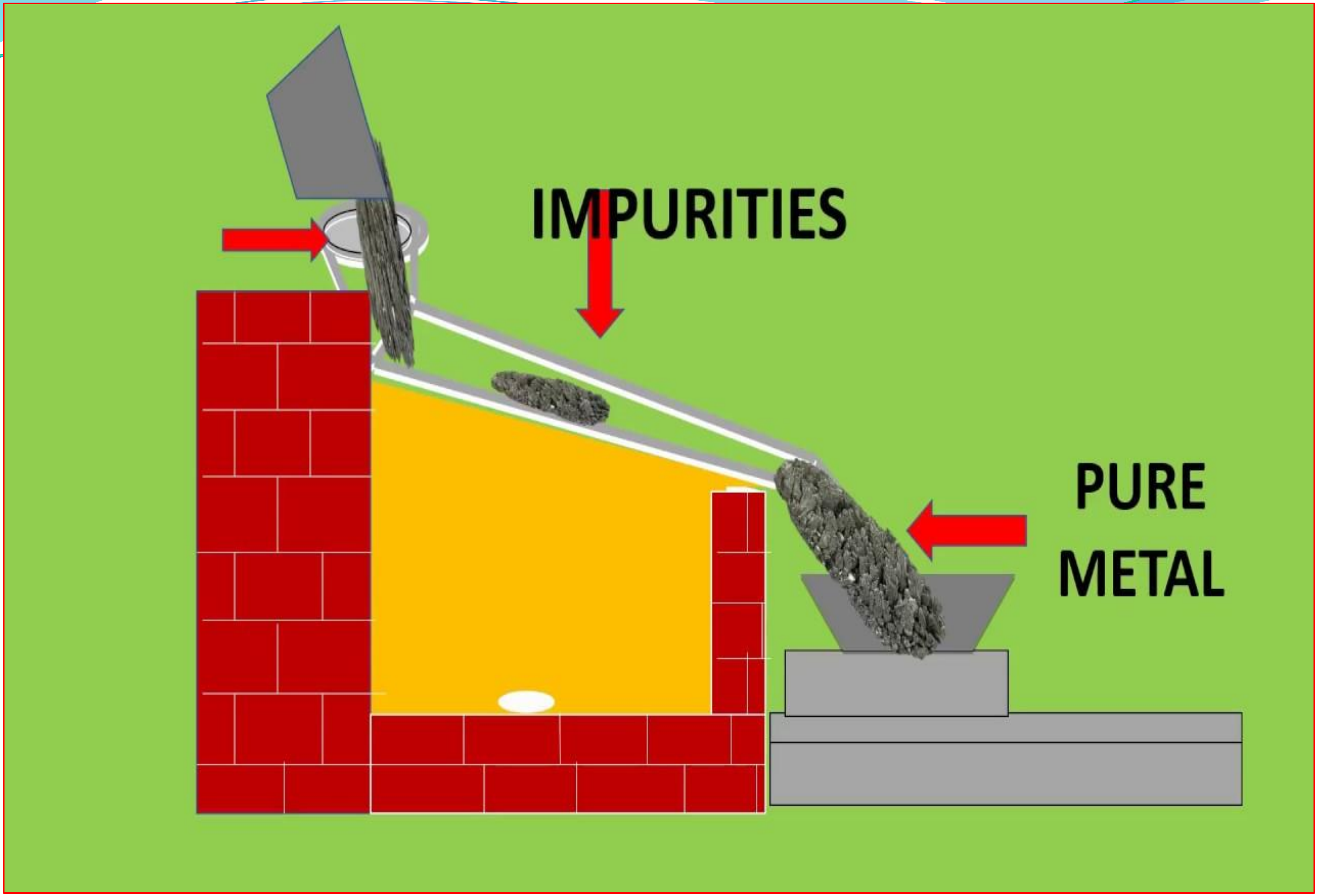
$2 Na[Au(CN)_2] + Zn \text{ (dust)} \rightarrow Na_2[Zn(CN)_4] + 2Au\downarrow$

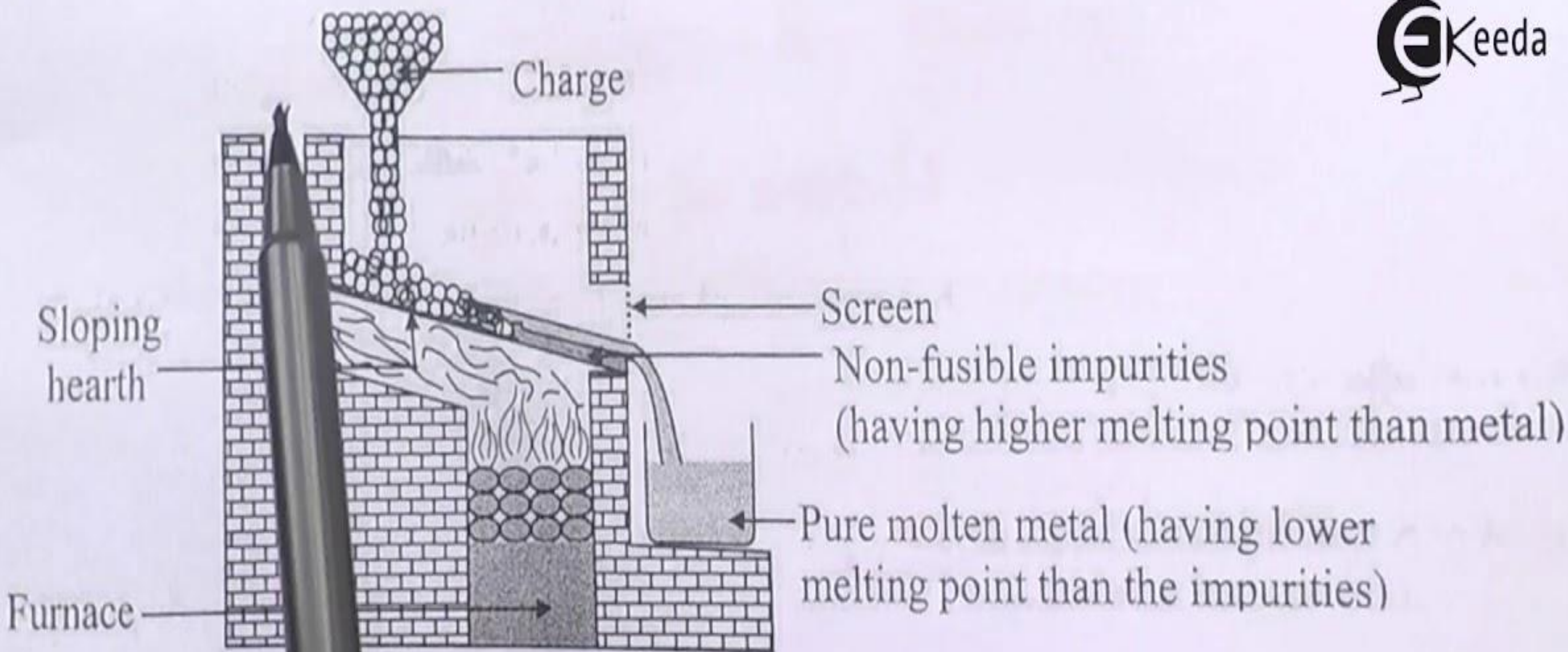
Refining of Metals or (Purification of metals): -

The metals obtained after the various metallurgical operations also contains small amount of impurities like oxides and sulphides of metals, other metals and nonmetals, flux or slag etc. Hence, it is necessary to purify the metal and this process of purification of metal is known as refining.

The impure metal is again subjected to number of purifying processes which depends on the nature of metal which is to be purified and the nature of impurities which are to be removed. Some of these processes are:

- **Liquation process: -** This process is used for refining of low melting or readily fusible metals like Pb, Sn, Bi while the impurities are less fusible and hence remains behind. Thus, in this process, an impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and allowed to flow away from the infusible impurities which leaving behind on the hearth.


IMPURITIES
PURE
METAL

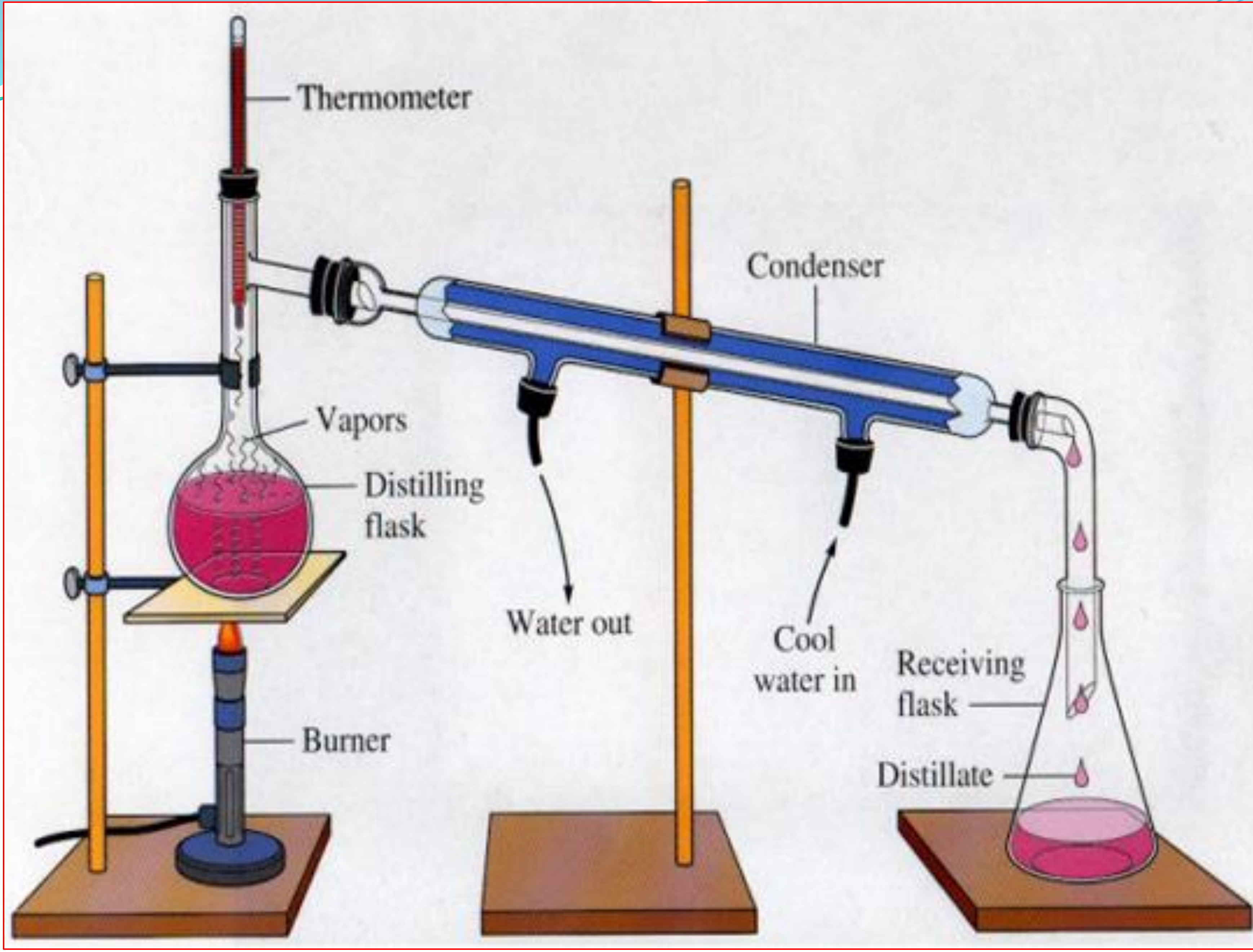

Charge
Screen
Non-fusible impurities
(having higher melting point than metal)
Sloping
hearth
Pure molten metal (having lower
melting point than the impurities)
Furnace

Liquation

•**Distillation process: -** This process is used for purification of volatile metals like Hg, Zn, and Cd. The impure metal is heated in a retort and its vapours are condensed in a receiver while the pure metal distills over, the non-volatile impurities are left behind in the retort.

•g. Zn is purified by distillation under reduced pressure. Then the first fraction (at low temperature) contains Cd, the middle fraction contains 99.99% pure Zn while the last fraction contains Pb, Fe, Cu etc.

•**Oxidation process: -** This process is used when the impurities present have a greater affinity for oxygen and are oxidized more readily than the metal in which they occurs. The impure metal is exposed in a molten state to the oxidizing and influence of the air in a suitable furnace. The oxides of the other metals which are formed are removed from the surface by skimming. Sometimes the oxides of the metal itself is added which provides the oxygen to impurities. e. g. Copper oxide to Copper.


Thermometer
Condenser
Vapors
Distilling flask
Water out
Cool water in
Receiving flask
Burner
Distillate

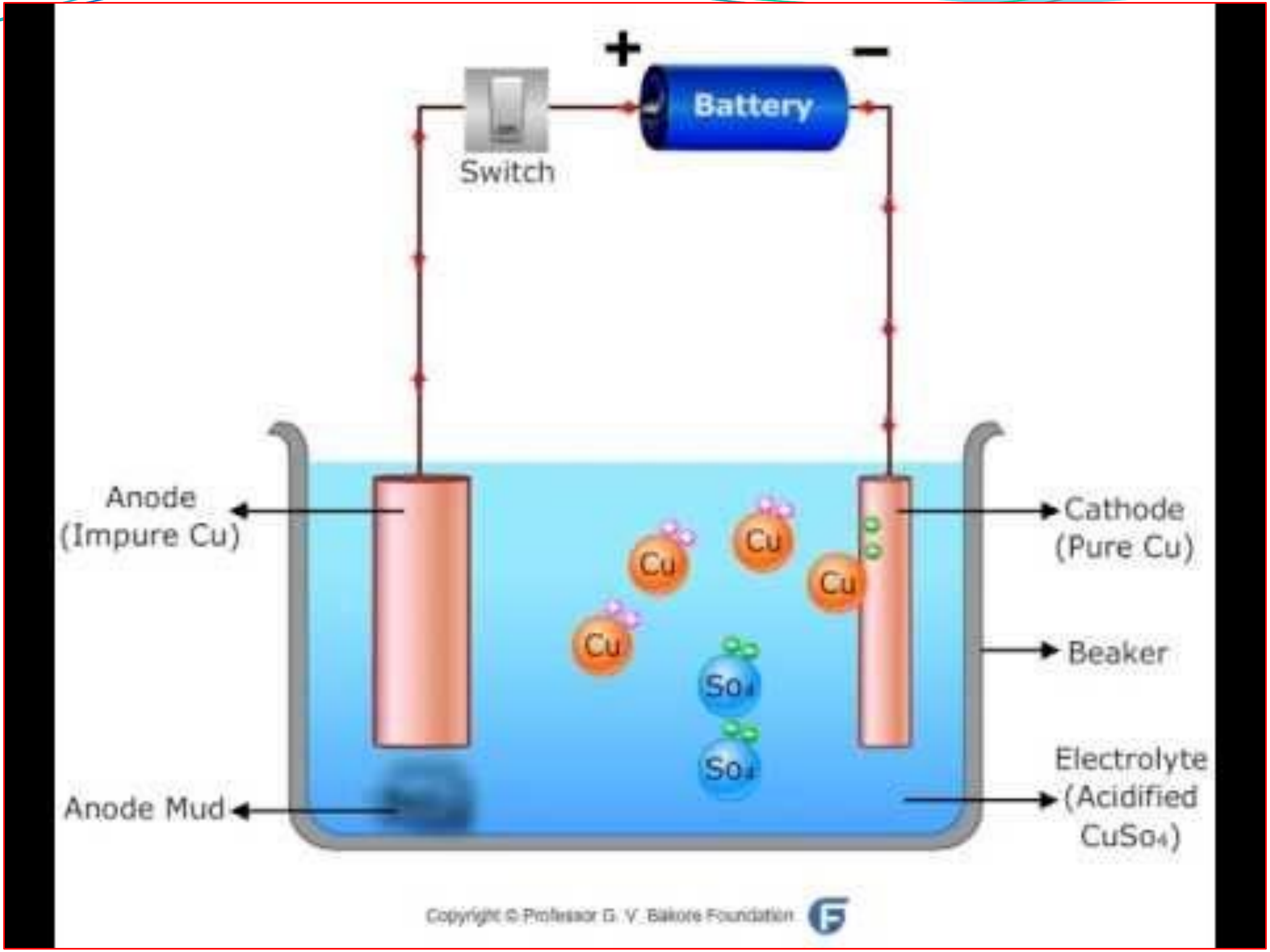
•Electrolytic refining: - A large number of metals like Cu, Cr, Zn, Ni, Al etc. are purified electrolytically. In this process, the impure metal is made as the anode of an electrolytic cell and a thin plate of the pure metal as cathode. While a solution of a simple salt of metal which to be refined is used as an electrolyte.

When an electric current of definite voltage is passed through the electrolytic bath, the pure metal gets dissolved and deposited on cathode. The electrode reactions are,

At anode, $M \rightarrow M^{+n} + ne^-$

At cathode, $M^{+n} + ne^- \rightarrow M$

Thus the net result is the transfer of metal from anode to cathode and the soluble impurities (more active metals) goes into solution while the insoluble impurities (less active metals) settle down at the bottom i.e.at the anode, hence are called as ‘anode mud’. Pure metal which is deposited on the cathode is then stripped off.


+
−
Battery
Switch
Anode
(Impure Cu)
Cathode
(Pure Cu)
Cu
Cu
Cu
Cu
Beaker
So4
So4
Electrolyte
(Acidified
CuSo4)
Anode Mud
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Thank You.

Stay Home, Stay Safe.