UNIT 10

Chemistry of metals

Metallurgy

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Differences between metals and non-metals:-

Metals	Non-metals
* Generally metals are hard except Lithium, Na and K.	* Generally non-metals are soft except graphite.
* Generally they are found in solid state except mercury.	* They are found in all three states.
* They are good conductor of heat and electricity.	* They are bad conductor of heat & electricity except graphite.
* They have metallic lusture.	* They don't have metallic lusture except graphite.
* They form electropositive ion by losing electron.	* They form electronegative ion by gaining electron.
* They are malleable & ductile.	* They are non-malleable & non-ductile.
* Mostly metallic oxides are basic in nature.	* Mostly non-metallic oxides are acidic in nature.
* They form unstable hydrides.	* They form stable hydrides.
* They form alloys.	* They do not form alloys except C, Si, P, S.
* They act as reducing agent	* They act as oxidising agent.

Metalloids:-

↳ The elements which properties of both metals and non-metals are called metalloids.

Characters of metalloids:-

i) They have properties of both metals & non-metals.

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ii) They are poor conductor of heat & electricity.
iii) They are neither malleable nor ductile.
iv) They form alloys.

Alloys:-
↳ Homogenous mixture of two or more metals or metal with non-metal is known as alloy.

Types of alloy:-

i) Ferrous alloys:-
↳ The alloy containing iron as one of the constituent element is known as ferrous alloys.
e.g:- Steel = Fe + C Stainless steel = Fe + C + Cr + Ni

ii) Non-ferrous alloys:-
↳ The alloy without involvement of iron as constituent element is known as non-ferrous alloy.
e.g:- Bronze = Cu + Sn Brass = Cu + Zn

iii) Amalgam:-
↳ The alloy of metal with mercury is known as amalgam.
e.g:- Na-Hg, Zn-Hg, Cu-Hg (Cuppor amalgam)
(Sodium amalgam) (zinc amalgam)

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Occurence of metals:-

↳ Metals are found in two states:-

i) Free state :- Less reactive element which do not react with oxygen, carbon dioxide and moisture of atmosphere are found in free state.
e.g:- noble gases, gold, platinum, etc.

ii) Combined state:- Reactive element which react with oxygen, carbon dioxide and moisture of atmosphere are found in combined state.
e.g:- haematite, magnitite, copperpyrite, etc. In combined state metals are found in the form of oxides hydroxides, carbonates, halides, sulphates, etc.

Occurence of metals in Nepal:-

↳ More than 85 types of minerals are found in Nepal. Some of them are tabulated below:-

	Metal	Mineral	places
1)	Calcium	Limestone/ Calcium carbonate	Chobhar (Ktm.)
2)	Magnesium	Magnesite	Udayapur
3)	Copper	Chalcopyrite	Udayapur/ Dolkha/ Makawanpur
4)	Iron	Haematite	Phulchowki (Lalitpur)

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Minerals:-

↳ Those naturally occuring substance which contains metals and non-metals are called minerals.

A mineral may not be suitable to extract metal due to following reasons:-

i) Mineral may contain desired metal in very low amount.
ii) Mineral may contain some impurities which are difficult to remove.
iii) Mineral may deposited in very less amount in nature.

Ores:-

↳ Those minerals from which metal can be extracted profitably (economically/&/conviently) are called Ores.

Extraction:-

↳ It is the process of obtaining pure metal from its ores.

Metallurgy:-

↳ It is the science that deals with the extraction of metals from its ores and production of metal products.

Metallurgy is of three types:-

i) Pyrometallurgy:- It is the method of extraction of metals from its ores by chemical reduction at high temp.

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ii) Electrometallurgy:-
↳ It is the method of extraction of metals from its ore by electrolytic reduction in ~~aqueous~~ aqueous solution or molten state of ore.

iii) Hydrometallurgy:-
↳ It is the method of extraction of metals from its ore by dissolving ore in aqueous solution or molten state of ore of suitable chemical reagent and subsequent by more active element.

Extraction of metal from its ore involves following three main steps:-

i) preliminary treatment
ii) Reduction
iii) purification or Refining

[1] preliminary treatment:-
↳ The purpose of preliminary treatment is to increase the concentration of desired component from the ore by removing impurities. It involves following process.

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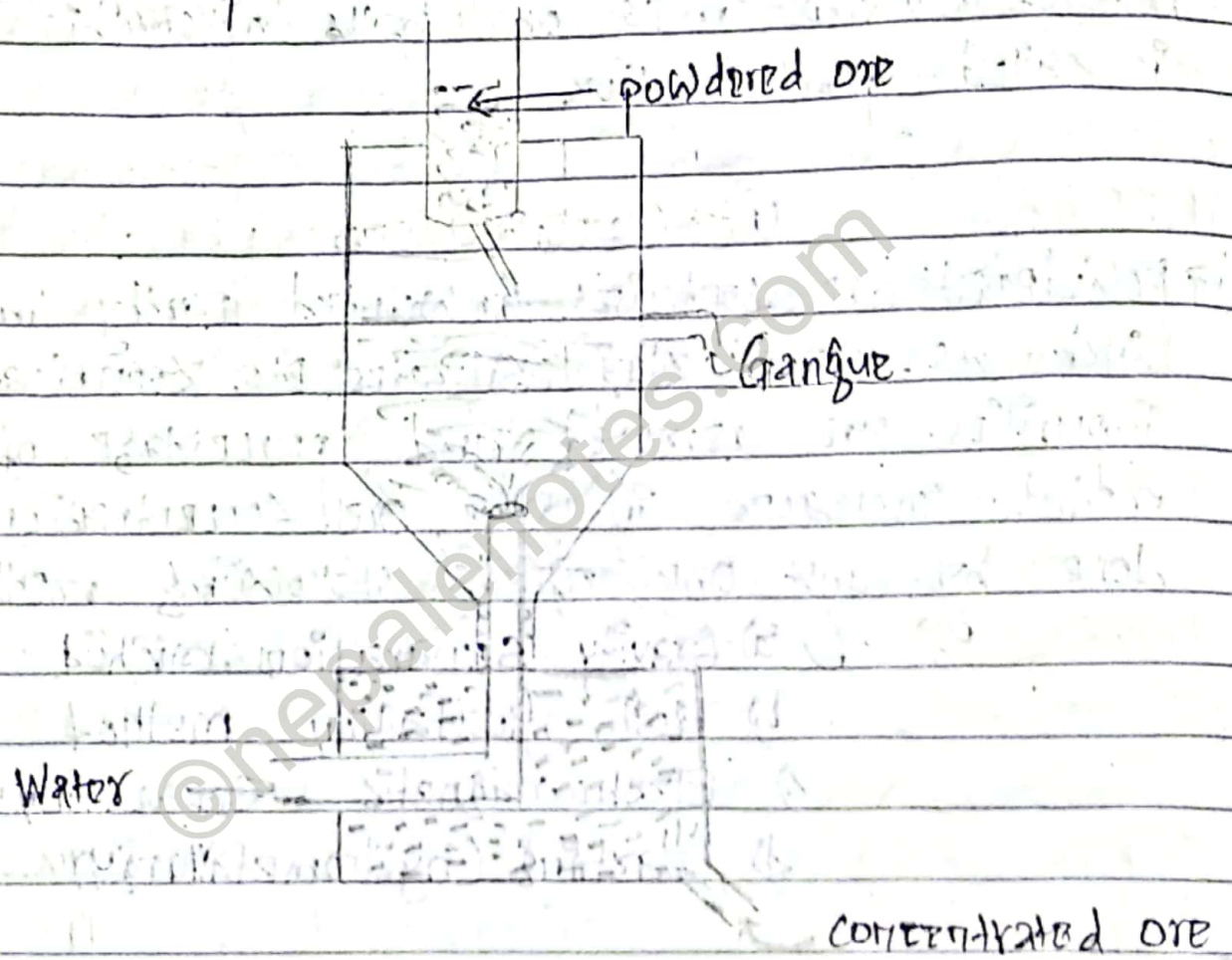
from the top and steam of water is introduced from the bottom of tank. The heavier ore particles collected at the bottom of the tank for further process. E.g:- bauxite, haematite.



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(b) Froth floation method:-

↳ This method is used for the concentration of sulphite ore such as zinc belende (ZnS), galena (PbS), cinnabar (HgS), chalcopyrite ($CuFeS_2$). This method is based on the principle that sulphite ores are wetted by pine oil while impurities are wetted by water. In this method powdered ore is mixed with pine oil & water in a big tank and agitated (stirred) by passing compre-

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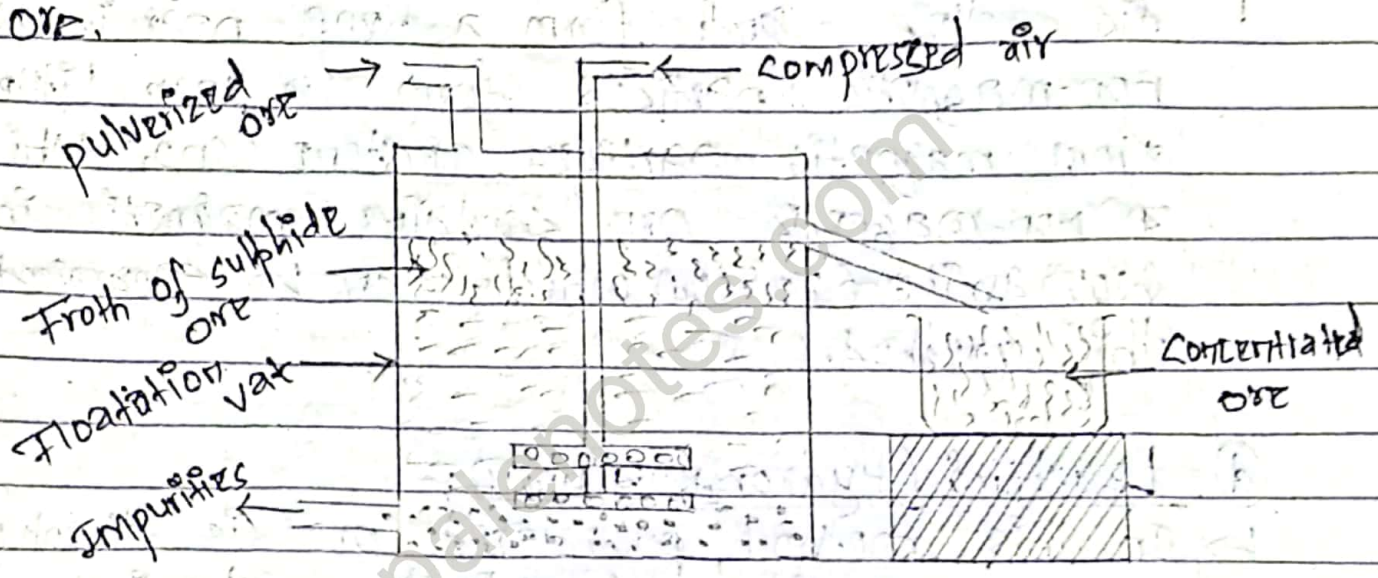
used air. Sulphide ores wetted by pine oil come at the surface of form froth while impurities are settled down at the bottom wetted by water. Froth from the surface is transferred into another tank and washed with water to recover ore.



(c) Electromagnetic Separation method:-

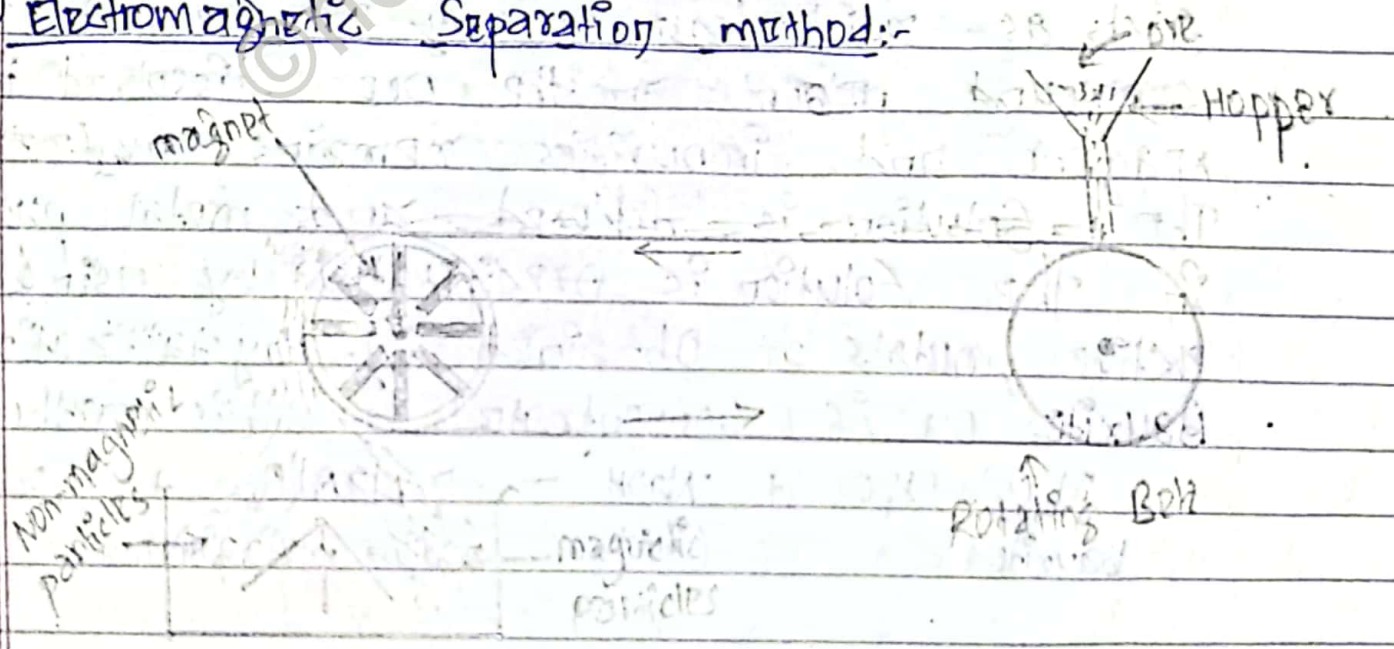


Fig: Electromagnetic separation method.

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This method is used for the separation of magnetic ores from non-magnetic impurities and vice-versa. In this method, powdered ore is dropped over a belt revolving around electromagnetic roller. Magnetic ore particles are attracted by electromagnetic roller and form a heap near it while non-magnetic particles form a heap little away from magnetic particles. Tinstone (SnO_2) which is a non-magnetic ore contains magnetic impurities Wolframite ($FeWO_4$) which can be separated by this method.

ⓓ **Leaching (Hydrometallurgy):-**

↳ In this method, powdered ore is dissolved in aqueous solution of suitable chemical reagent such as acid, base or any other reagent. The compound present in the ore dissolved in the reagent and impurities remains unaffected. The solution is filtered and metal present in the solution is precipitated out by using more active metals or obtained by crystallization. Bauxite ore is concentrated by this method.

$$\underset{\text{bauxite}}{Al_2O_3 \cdot 2H_2O} + \underset{\text{(hot)}}{NaOH} \longrightarrow \underset{\text{Sodium metaaluminate}}{NaAlO_2} + H_2O$$

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

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

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2. $Ag_2S + NaCN \longrightarrow AgCN + Na_2S$
Argentite (aq)

$AgCN + NaCN \longrightarrow Na[Ag(CN)_2]$
Excess Soluble complex

$Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + Ag \downarrow$
Zinc scrab Metallic Silver

(iii) Calcination:-

↳ The process of heating concentrated ore strongly in the limited supply of air or in the absense of air below the melting point of ore in order to convert into metallic oxide is called calcination. It is done for hydrated oxide, hydroxides and carbonates. During calcination following changes takes place:-

i) moisture is removed.
ii) Volatile impurities and organic matter are removed.
iii) Metal carbonate are changed into metal oxide.

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

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2 \uparrow$

iv) Hydroxides change into their metal oxide,

$CaCO_3 . Cu(OH)_2 \longrightarrow CuO + CO_2 + H_2O$
malachite

$Fe(OH)_3 \longrightarrow Fe_2O_3 + H_2O$

v) Water of crystallization is removed.

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

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(iv) Roasting:-

↳ The process of heating concentrated ore strongly in the presence of excess of air below its melting point is called roasting. It is done for sulphide ore and converts into metal oxide. During roasting following changes take place.

i) Moisture present in the ore is removed.
ii) Volatile impurities and organic matter present in the ore are formed.
iii) Sulphides ore are changed into metal oxide.

$$PbS + O_2 \longrightarrow PbO + SO_2$$
$$ZnS + O_2 \longrightarrow ZnO + SO_2$$
$$HgS + O_2 \longrightarrow HgO + SO_2$$

iv) Impurities like Sulphide (S), phosphorous (P), Arsenic (As) etc. are removed in the form of their oxide.

$$S + O_2 \longrightarrow SO_2 \uparrow$$
$$P + O_2 \longrightarrow P_2O_5 \uparrow$$
$$As + O_2 \longrightarrow As_2O_3 \uparrow$$

Both calcination and roasting are carried in reverberatory furnace.

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[2] Reduction:-

↳ Calcined or roasted ore is reduced into metallic from by reduction.

(i) Carbon reduction (smelting):-

↳ It is also known as smelting and defined as process of extracting metal from its oxide ore by fusion in the presence of carbon or coke. In this method calcined or roasted ore is mixed with calculated amount of carbon and heated above the melting point of ore in reverberatory furnace. During this process metal oxide is reduced into free metal as follows:-

$$PbO + C \longrightarrow Pb + CO$$

$$ZnO + C \longrightarrow Zn + CO$$

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

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Calcined or roasted ore may contain some infusible impurities which are difficult to remove. These infusible impurities are converted into fusible mass by adding a chemical substance called flux.

☆ Flux:-

↳ A chemical substance which is used to convert infusible impurities present in the ore into fusible mass is called flux. Flux is of two types:-

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i) Acidic Flux:-

↳ Acidic flux removes basic impurities.
For example:-, SiO_2 is acidic flux.

$$SiO_2 + CaO \rightarrow CaSiO_3 \text{ (slag)}$$

(acidic flux) (basic impurities) calcium silicate

$$SiO_2 + MgO \rightarrow MgSiO_3$$

(acidic flux) (basic impurities) magnessium silicate

ii) Basic Flux:-

↳ Basic flux removes acidic impurities.
For example CaO, MgO are basic flux.

$$SiO_2 + CaO \rightarrow CaSiO_3$$

(acidic impurities) (basic flux) slag

★ Slag:-

↳ The fusible mass formed by the combination of flux and infusible impurities is known as slag.
e.g:-

$$SiO_2 + MgO \rightarrow MgSiO_3$$
(slag)

(ii) Aluminothermite process:-

↳ certain metal oxides such as TiO_2, Cr_2O_3, Mn_3O_4 etc. cannot be reduced by carbon reduction method. This is because oxygen has more affinity for these metals than carbon. Such metal oxides are reduced by using aluminium powder as reducing agent because aluminium is more

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electropositive than these metals. In this method, metal oxide of these metal is mixed with aluminium powder and little amount of Barium peroxide (BaO_2). Barium peroxide is an oxidising agent and facilates ignition. The mixture of metal oxide, aluminium powder and barium peroxide is known as thermite. Hence, the process is known as aluminothermite. The mixture is placed in crusible and reaction is initiated by introducing a burning magnessium ribbon. Reaction takes place vigorously producing large amount of heat and metal peroxide in molten state.

$$3\ TiO_2 + 4\ Al \longrightarrow 2\ Al_2O_3 + 3\ Ti$$
$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr$$
$$3\ Mg_3O_4 + 8\ Al \longrightarrow 4\ Al_2O_3 + 9\ Mg$$

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(iii) Electrolytic reduction (Electrometallurgy):-

→ Active metals like alkali metals, alkaline earth metals and aluminium cannot be reduced by carbon reduction method. This is bacause these are better reducing agent than carbon. When these metal oxides are heated to high temperature during chemical reduction, metal produced react with carbon to form metal carbide. Therefore, such metals are extracted or reduced by the electrolysis of their oxide, hydroxides or halides in aqueous solution or molten state. During electro

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lysis metal deposited on cathode. For Example Sodium is extracted by the electrolysis of mixture of NaCl & $CaCl_2$ at 600°C.

$$NaCl \xrightarrow[\text{electrolysis}]{} Na^+ + Cl^-$$

at anode:

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

$$Cl + Cl \longrightarrow Cl_2$$

at cathode:

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

[3] Purification or Refining:-

↳ Metal obtained from high temperature reduction still contain impurities which are removed by purification. The method of removal of unwanted impurities from impure metal to get pure metal is known as purification or refining. Impure metal may contain following impurities:-

i) Other metals
ii) Non-metals like S, P, As, etc.
iii) Residual flux or slag
iv) Unreduced Oxides or Sulphides

Depending upon impurities and nature of metal following purification method can be used:-

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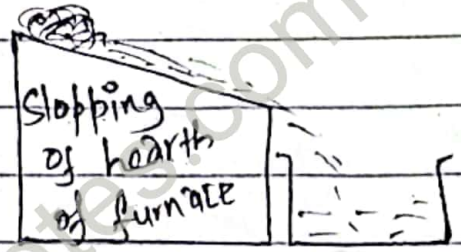
liquation:-

This method is used for the purification of those metals which have lower melting point than impurities such as Hg, Pb, Sn, Zn. In this method, impure metal is heated on the slopping hearth of furnace. Metal melts first & goes down leaving behind impurities.



Distillation:-

This method is used for the purification of metals having low boiling point than impurities. When impure metal is heated, pure metal distilled off leaving behind impurities. Vapour of pure metal condensed to get metal.

Electrorefining:-

This method is used for the purification of metal like Au, Cu, Ag. In this method, anode is made of impure metal & cathode is made of thin sheet of pure metal both anode & cathode are dipped in salt solution of that metal. On passing electricity anode dissolves and equivalent amount of pure metal get deposited on cathode. For example

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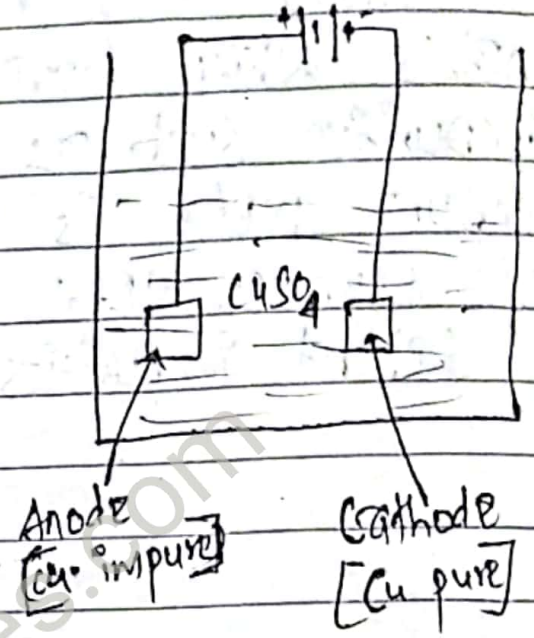
Purification of Copper involves following reaction:

1. At Anode,
$Cu \rightarrow Cu^{++} + 2e^-$
2. At Cathode
$Cu^{++} + 2e^- \rightarrow Cu$.



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extra
poling [Cu_2O + hydrocarbon $\xrightarrow{\Delta}$ Cu + CO_2 + H_2O]
zone refining (fractional crystallization)
Chromatographic Separation method for purification of Lanthanides
Mond's process (for Ni)
Van-Arkel method (for I_2)