Grade - XI

Content Area: Inorganic Chemistry

Unit-10 CHEMISTRY OF METALS

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10.1 Metals and Metallurgical Principles- 5TH

- Definition of metallurgy and its types - Hydrometallurgy, Pyrometallurgy, Electrometallurgy
- Introduction of ores
- Gangue or matrix, flux and slag, alloy and amalgam
- General principles of extraction of metals (different processes involved in metallurgy) concentration, calcination and roasting, smelting, carbon reduction, thermite and electrochemical reduction
- Refining of metals (poling and electro-refinement)

Introduction

Metals are usually solid, hard, opaque (except Hg- which is liquid at room temperature), shiny, lustrous when freshly cut. They are good conductor of heat and electricity. They are **malleable** (can be hammered into **thin sheets**) & **ductile** (can be drawn into **wires**). Their ionization potential and electronegativity are low hence they can easily lose their valence electrons & gets oxidized so acts as very **good reducing agent**. They usually form basic oxides with some exceptions. Examples Na, K, Mg Ca, Al, Ga, Zn, Cu, Fe, Au etc.

Metals can be extracted from oxide, sulphide, carbonate, hydroxide ores etc.

Ores

The minerals which contain significant amount of metal & from which metal can be extracted profitably and economically are called ores. All the ores are minerals. Example:
i) **Bauxite** ($Al_2O_3.2H_2O$) is **ore of Al metal**
ii) **Copper pyrite** ($CuFeS_2$) is **ore of Cu**

Minerals

The naturally occurring substances from which metal cannot be extracted profitably and economically are called minerals. All minerals are not ores. Example:
i) **Clay** ($Al_2O_3.\ 2SiO_2.\ 2H_2O$) is **mineral of Al**
ii) **Copper pyrite** ($CuFeS_2$) is **minerals of Fe**

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Metallurgy

The process by which metal can be extracted (obtained) in pure and free state from their respective ores is called **metallurgy**. There are following types of metallurgy

Pyrometallurgy is the technique of extraction of metals by using fire or heating ore at high temperature in presence of suitable reducing agents. **Extraction of Fe, Zn, Cu, Hg**

Hydrometallurgy is the technique of extraction of metal from their respective ores by dissolving metal ores in suitable solvent and then followed by precipitation of metal by suitable chemicals. **Extraction of Ag, Au**

Electrometallurgy is the technique of Extraction of metal is from their respective ores by electrolysis in molten or aqueous state. **Extraction of Na, K, etc.**

Gangue or Matrix

The unwanted earthy impurities like sand (silica), mud, etc. present in ore is called gangue or matrix.

Flux

The **flux** is chemical substance which is added in calculated amount to remove gangue present in ore in the form of **slag**.

$$\text{Flux} + \text{Ganuge} \xrightarrow{\Delta} \text{Slag}$$

Flux is chosen on the basis of nature of the gangue present in ore. If gangue is acidic, then basic flux is used & if gangue is basic then acidic flux is used.

If the impurities are acidic (P_2O_5, SiO_2) then ***basic flux*** ($CaCO_3$, CaO, MnO) is used.

$$\underset{\substack{\text{Calcium oxide}\\\text{(basic flux)}}}{CaO} + \underset{\substack{\text{Phosphorous pentoxide}\\\text{(acidc impurity)}}}{P_2O_5} \xrightarrow{\Delta} \underset{\substack{\text{Calcium phosphate}\\\text{(slag)}}}{Ca_3(PO_4)_2}$$

If the impurities are basic (CaO, MgO, MnO, FeO) then ***acidic flux*** (SiO_2) is used

$$\underset{\substack{\text{Magnesium oxide}\\\text{(basic gangue)}}}{MgO} + \underset{\substack{\text{Silicon di oxide}\\\text{(acidc flux)}}}{SiO_2} \xrightarrow{\Delta} \underset{\substack{\text{Magnesium silicate}\\\text{(slag)}}}{MgSiO_3}$$

Neutral flux: CaF_2 (Florspar) used to increase the fluidity of molten metals.

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Slag

It is the product formed by the reaction of flux and impurity (or gangue) during extraction of metal from its ore.

i.e. Slag = flux + gangue.

It is generally neutral. Lighter than molten metal & can be used as fertilizer.

Example: $Ca_3(PO_4)_2$ (Calcium phosphate)

$$\underset{\substack{\text{Calcium oxide}\\\text{(basic flux)}}}{CaO} + \underset{\substack{\text{Phosphorous pentoxide}\\\text{(acidc impurity)}}}{P_2O_5} \xrightarrow{\Delta} \underset{\substack{\text{Calcium phosphate}\\\text{(slag)}}}{Ca_3(PO_4)_2}$$

Alloy

Alloy is homogenous mixture of metal with other metal or nonmetal.

Examples: Brass ($Cu + Zn$), Bronze ($Cu + Sn$), Steel ($Fe + C$), stainless steel ($Fe + C + Cr + Ni$) etc. depending on the iron as constituent element that is present.

It may be classified into two different categories.

a. **Ferrous alloy**
   An alloy in which one of the constituent elements is iron then such type of alloy is called ferrous alloy. Example: steel, stainless steel.
b. **Non-ferrous alloy**
   An alloy which does not contain iron as one of the constituents, then such type of alloy is called non-ferrous alloy. Example: brass, bronze etc.

Alloy is prepared for following purpose;

- To increase the hardness and strength of metal.
- To improve the color of metal.
- To lower melting point of metal.
- To make metal less corrosive.

Amalgam

- Amalgam is an alloy of mercury with other metal.
  Example: Sodium amalgam (Na-Hg), Zinc amalgam (Zn-Hg).

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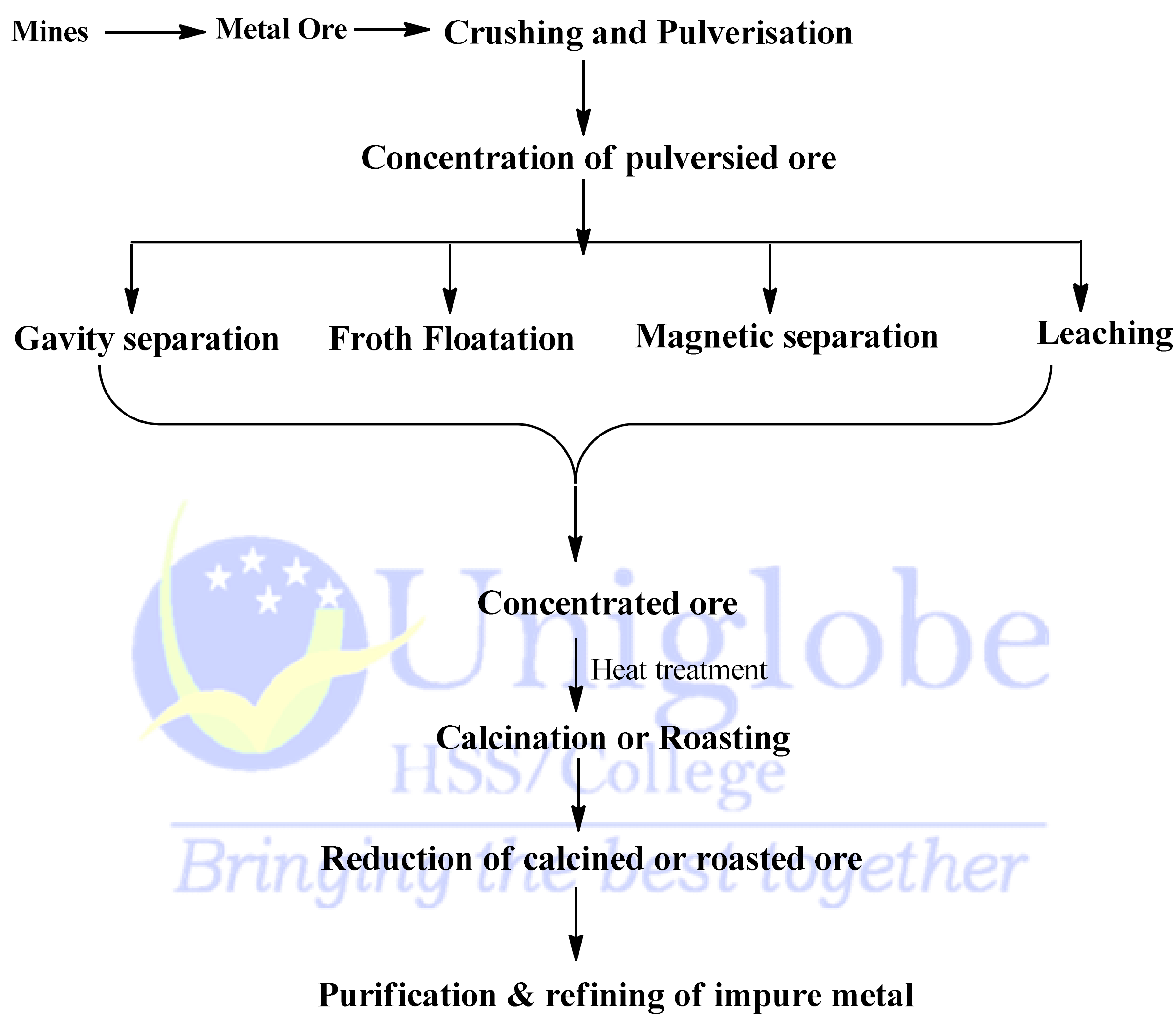
<u>Different Steps involved extraction of metal from their ores (Metallurgical process)</u>



Fi.g. *Outlines of the method of extraction of metal from their ores (pyrometallury)*

1. **Crushing & Pulverization**

Big lumps of ores are crushed by using jaw crusher and pulverized into powder form by using ball mills.

2. **Concentration or Dressing**

The process of removing ***gangue particles (or unwanted earthy impurities-like mud, sand etc.)*** from pulverized ore is called concentration of ore. Based on nature of ore, the concentration is of following types:

a) **Gravity separation**

The **oxide ores** like tin **stone (SnO_2), hematite (Fe_2O_3)** etc. are concentrated by this process.

Working principle: Based on the difference in specific gravity or densities of the ore and the impurities (gangue).

Process: The powdered or pulverized ore is washed with running water by which the lighter impurities washed away and heavier ore particles are settled down at the bottom.

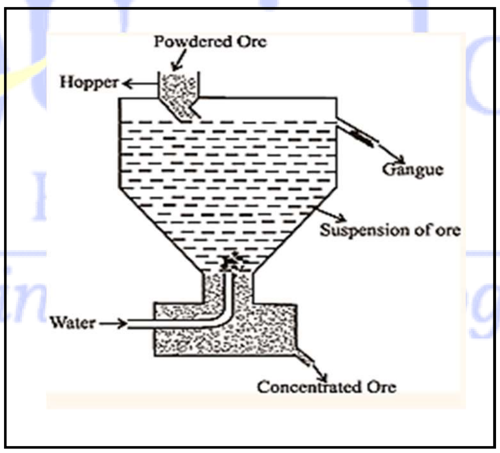


Fig. Gravity separation

b) **Froth Floatation process**

The **sulphide ores** like **Zinc blend (ZnS), Galena (PbS), Copper pyrites ($CuFeS_2$), Silver glance (Ag_2S), Cinnabar (HgS)** etc. are concentrated by this process.

Working principle: Based on the differences in the wetting property or affinity of the ore towards oil and impurity or gangue towards water

Process: The powdered ore is mixed with pine oil or eucalyptus and water in the floatation tank. The mixture is then agitated by blowing air. The sulphide ore which is wetted by oil comes to surface with froth while the impurities settled at the bottom of tank with water.

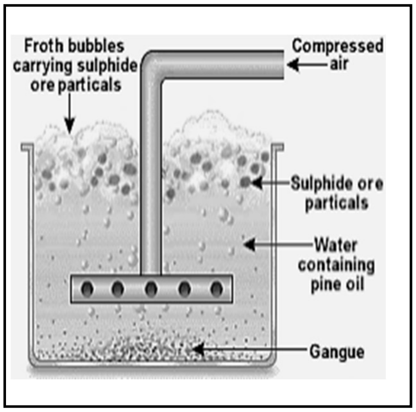


Fig. Froth Floatation

c) <u>Electro Magnetic separation</u>

The **non-magnetic ore like** tin stone (SnO_2) containing wolframite ($FeMnWO_4$) as **magnetic impurities or magnetic ore** like magnetite (Fe_3O_4) or Iron Chromite [Fe $(CrO_2)_2$] & **nonmagnetic impurity** like silicon oxide (SiO_2) etc. are concentrated by this process.

Working Principle: Based on the difference in magnetic properties of ore particles& gangue particles.

Process: The powdered ore is dropped over a conveyer belt moving around two electromagnetic rollers. The magnetic particles (ore or gangue) is attracted towards magnetic rollers and collected nearer to magnets and the non-magnetic particles (ore or gangue) drops away from the roller.

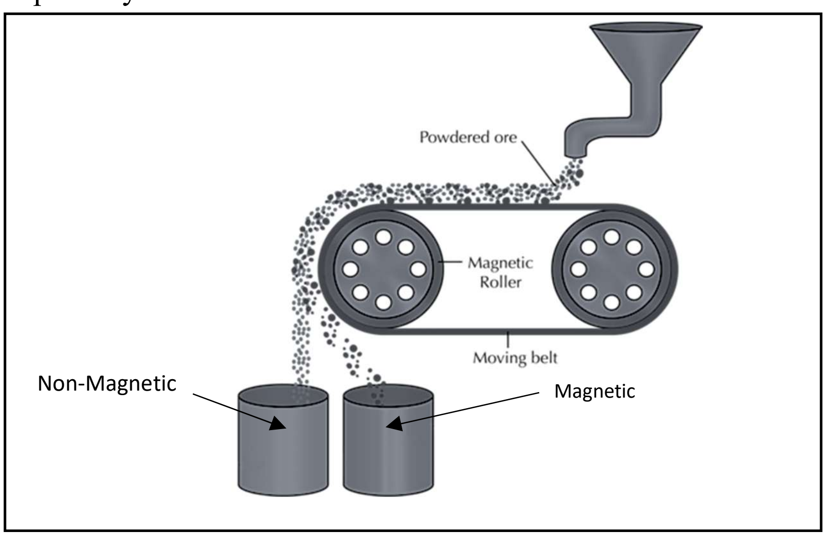


Fig. Electromagnetic Separation

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d) Leaching

It is used when ores are soluble in such solvent in which impurity (gangue) are not dissolved. Eg Bauxite ore: ($Al_2O_3.2H_2O$) can be concentrated by this process.

Working principle: Based on difference in the solubility of ore and impurity (gangue) in suitable solvent.

Process: The powdered ore such as bauxite containing impurities such as Fe_2O_3, Fe $(OH)_3$ etc. is dissolved in hot concentrated NaOH solution. In this process the impurities will undissolved which is removed by filtration process. The filtrate contains sodium meta-aluminate gets hydrolyzed to give precipitate of Al $(OH)_3$ which is then dried and heated to convert it into Al_2O_3. This is an example of ***alkaline leaching* process** because alkali (NaOH) is used as solvent.

$$Al_2O_3.\,2H_2O + 2NaOH \xrightarrow{\Delta} \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + 3\,H_2O$$

$$NaAlO_2 + 2\,H_2O \xrightarrow{\Delta} \underset{\text{Aluminium hydroxide ppt}}{Al(OH)_3} + NaOH$$

$$2Al(OH)_3 \xrightarrow[\Delta]{} \underset{\text{Aluminium oxide}}{Al_2O_3} + 3H_2O$$

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3. Preliminary Heat treatment of concentered ore

The main purpose of preliminary heating of concentrated ore is to convert the ore into respective oxide which is later reduced into metal. Other benefits of heat treatment are

i) Removal of excess moisture from concentrated ore.

ii) Removal of volatile impurities like S, As, P etc. in the form of their respective oxides i.e., SO_2, As_2O_3, P_2O_5, etc.

Heat treatment can be done is followings ways: i) Calcination or ii) Roasting.

The **calcination** is usually carried out in **reverberatory furnace** and **roasting** is usually carried out in **rotary hearth furnace or in multiple hearth furnace**.

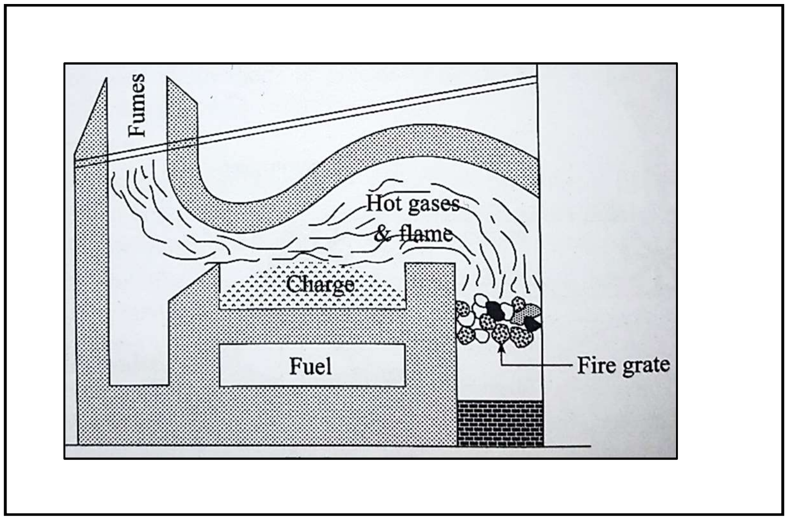

Fig. Furnace for calcination or roasting

Calcination

The process in which concentrated ore of metal is converted into its oxide by **heating the ore below its melting point in absence of air (or limited supply of air)** is called calcination.

- The ore obtained in calcination process is called ***calcined ore.***
- It is usually carried out for oxides & carbonates ores (i.e. oxygen rich ores).

During the calcination,

i) Moisture & water of crystallization is removed,
ii) Carbonates and hydroxide ores are converted into their respective oxides.
iii) Ore becomes porous and easy to handle.

Reactions involved during calcination,

$Fe_2O_3.2H_2O \longrightarrow Fe_2O_3 + 2H_2O$

(Hematite)

$Al_2O_3.3H_2O \longrightarrow Al_2O_3 + 3H_2O$

(Bauxite)

$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$

(Dolomite)

$ZnCO_3 \longrightarrow ZnO + CO_2$

(Calamine)

$CuCO_3.\ Cu(OH)_2 \longrightarrow 2CuO + H_2O + CO_2$

(Malachite)

Roasting

The process in which concentrated ore of metal is converted into its oxide by **heating the ore below its melting point in excess supply of air** is called roasting.

- The ore obtained in roasting process is called ***roasted ore.***
- It is usually carried out for sulphide ores (i.e. oxygen deficient ores).

During roasting process,

i) Moisture is removed,
ii) Volatile impurities like S, As, P are removed in the form of their oxides SO_2, As_2O_3 and P_2O_5 respectively.
iii) Sulphide ores are converted into their respective oxides.

$$S + O_2 \xrightarrow{\Delta} SO_2$$

$$P_4 + 5O_2 \xrightarrow{\Delta} 2P_2O_5$$

$$4As + 3O_2 \xrightarrow{\Delta} 2As_2O_3$$

iv) Sulphide ores are converted into their respective oxides.

$$\underset{\text{(Zinc Blend)}}{ZnS + O_2} \xrightarrow{\Delta} ZnO + SO_2$$

$$\underset{\text{(Galena)}}{PbS + O_2} \xrightarrow{\Delta} PbO + SO_2$$

$$\underset{\text{(Cinnabar)}}{HgS + O_2} \xrightarrow{\Delta} HgO + SO_2$$

Note: *To avoid sulphate formation, the roasting is done at high temperature (900^{O}C) in regular supply of air. At very high temperature, the sulphate if formed is decomposed into respective oxide.*

$$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$$

$$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + SO_2 + O_2$$

4. Reduction (Extraction)

The process in which the calcined or roasted ore is reduced by using suitable reducing agent in order to get metal in free state is called reduction.

The reduction is carried out by any of following process:

a) **Smelting** (Reduction by using Carbon)
b) **Gold-Schmidt's Alumino- Thermic (or thermite) process** (Reduction by using Aluminium)
c) **Electrolytic reduction** (Reduction by using Electron)

a) Smelting

The process in which the calcined or roasted ore is reduced by using carbon (in the form of coke or charcoal) as reducing agent is called smelting.

Smelting is usually carried out in ***blast furnace.***

Process

In this process the oxides of metal obtained after calcination or roasting are mixed with carbon along with suitable ***flux*** to remove impurities (gangue) in the form of ***slag*** and heated at high temperature to reduce metal oxide into metal.

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

$$CuO + C \xrightarrow{\Delta} Cu + CO$$

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

Sometime CO produced in the reaction may also acts as reducing agent.

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$$

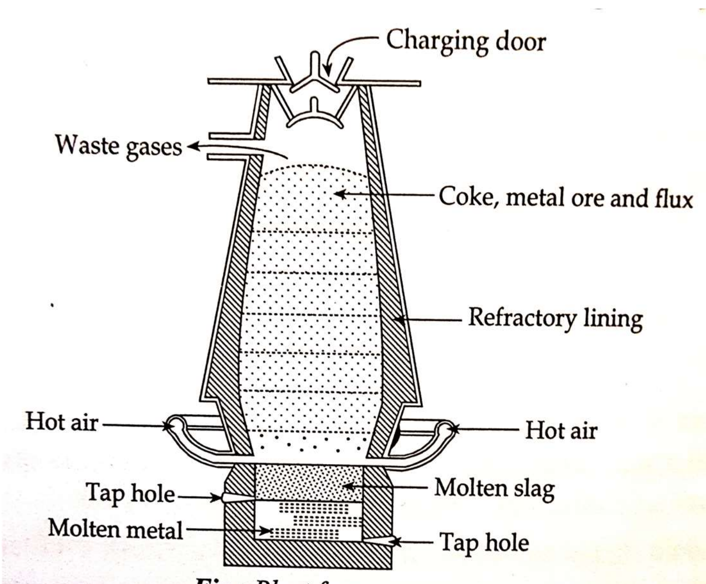

***Fig.:** Blast furnace*

b) <u>Alumino-Thermic (or thermite) process</u> (Reduction by using Aluminum)
The process in which the calcined or roasted ore is reduced by using Al powder as reducing agent is called Gold Schmidt's Alumino Thermic process.

Procedure
The oxide of metal is mixed with Al powder and little barium peroxide (BaO_2). The mixture is then transferred into crucible as shown in fig below. The charge is then ignited with the help of magnesium ribbon, a vigorous reaction takes place and oxide of metal is reduced into metal. The melted metal is collected at the bottom of the crucible under alumina.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr + heat$$

$$3MnO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Mn + heat$$

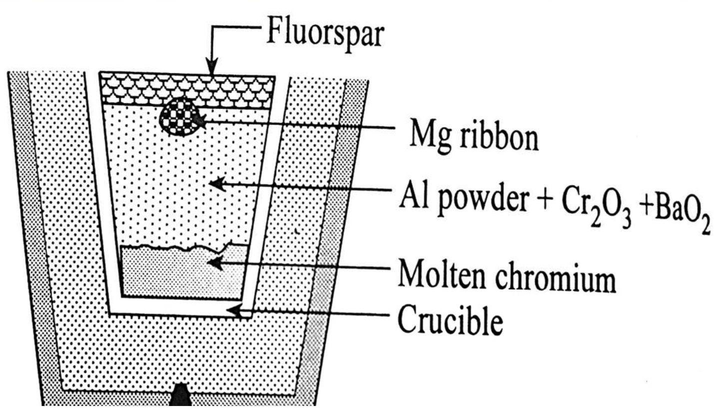

Fig. Alumino thermic process

***Fig:** Aluminothermic process for chromium*

c) **<u>Electrolytic reduction</u>-** (Reduction by electrons) **(Electrometallurgy)**

The process in which the metal is obtained in free state by electrolysis of their molten or fused salt is called electrolytic reduction. The pure metal is reduced at cathode.

For example: Na metal is obtained from **electrolysis of fused or molten NaCl** by **Down's Process**.

$$NaCl \longrightarrow Na^{+} + Cl^{-}$$

At Cathode (at –ve electrode) – Reduction reaction takes place

$$Na^{+} + e \longrightarrow Na$$

At Anode (at +ve electrode) –Oxidation reaction take place

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

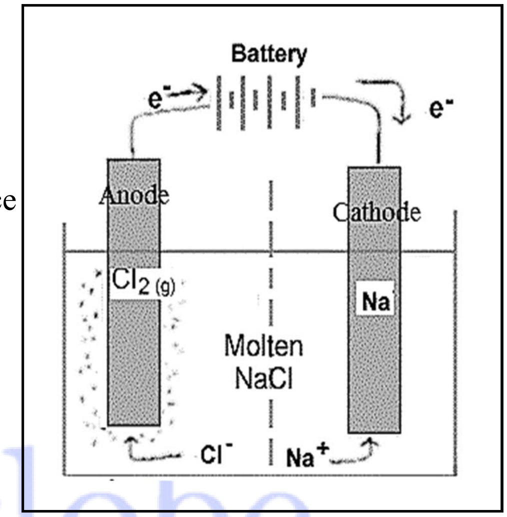

Fig. Extraction of metal by electrolytic method

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Important Note:

- Highly electropositive or active metals like Na, Mg, Ca etc. can be obtained by this process.
- Aqueous solution cannot be used because active metal produced reacts with water to give H_2

$$2Na + H_2O \longrightarrow 2NaOH + H_2$$

- Carbon cannot be used for the reduction of such ore because at high temperature such active metal forms carbides. For example,

$$Ca + 2C \xrightarrow{\Delta} CaC_2$$

5. Purification or refining of crude metal

The metals obtained from any of the above process (except electrolytic method) contain many types of impurities (trace of other metal, Si, P, unreacted oxides & sulphide etc.) which can be removed by the following process:

a) Poling
b) Electrolytic refining

a) Poling

This method is employed for those metals which contains their own oxide as impurities. Pb, Cu metals can be purified by this method.

In this method, impure molten metal in tank is stirred constantly with green pole of wood. During the poling, the hydrocarbons (for e.g. CH_4) of green pole are oxidized into their oxide and metallic oxide which is present as impurities are reduced into metal.

$$3Cu_2O + \underset{\text{(from green poles)}}{CH_4} \longrightarrow 6Cu + CO + H_2O$$

b) Electrolytic refining

In this method, an electrolytic cell is taken in which impure metal is made anode, pure metal is made cathode and soluble salt of metal is used as electrolyte. When the current is passed, then crude metal dissolves from anode and pure metal is deposited at cathode while impurities are settled at the bottom of the tank near anode (which is called **anode mud**).

- Cu, Sn, Pb, Al, Ag, Zn etc. are purified by this method.

At Anode (Impure Cu)

$$\mathbf{Cu \longrightarrow Cu^{++} + 2e^-}$$

At Cathode (Pure Cu)

$$\mathbf{Cu^{++} + 2e^- \longrightarrow Cu}$$

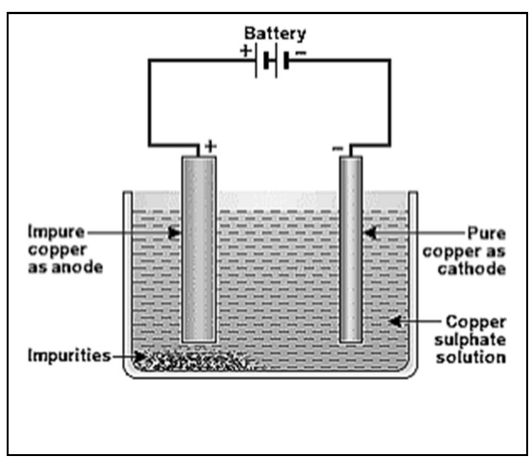

Fig. Electrolytic refining

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