Chapter-10

Chemistry of Metals

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Metallurgy

The process of extraction of metals from its ore is called metallurgy

Types of Metallurgy

1. ~~From~~ Pyrometallurgy
   It is the method of extraction of metal from its ore by chemical reduction at high temperature.

2. Electrometallurgy
   It is the method of extraction of metal from its ore by electrolytic reduction in the molten or aqueous state.

3. Hydrometallurgy
   It is the method of extraction of metal from its ore by dissolving the ore in a suitable chemical reagent and precipitating it with other more active metals.

Process of Metallurgy

1. Crushing and Pulverization
   Big lumps of ores are crushed using jaw crushers to get crushed ~~ore to~~ ore which is pulverized using a pulverizer or stamp mill to get powdered ~~or~~ ore.

2. Concentration
   Powered ore ~~may~~ may contain unwanted earthy impurities which are known as gangue ~~or~~ or matrix.

The process of removal of these ~~eart~~ earthy impurities from the powdered ~~ore~~ ore is called concentration ~~for~~ (ore dressing). On the basis of the nature of ore, it is done by one or more of the following process.

i. Hand Picking

ii. Froth floatation Process

In this process, ~~Powered~~ Powdered ore is taken in a tank containing water and a small amount of pine oil. The mixture is heated by passing a blast of air. Impurities are wetted by water and get collected at the bottom of the tank. Ore particles are wetted by oil and come to the ~~sur~~ surface as ~~fr~~ froth. The froth is skimmed off ~~the~~ to collect concentrated ore.

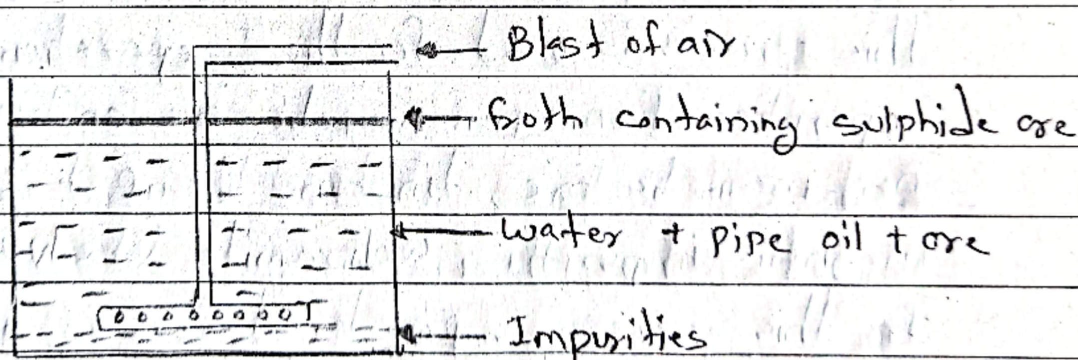
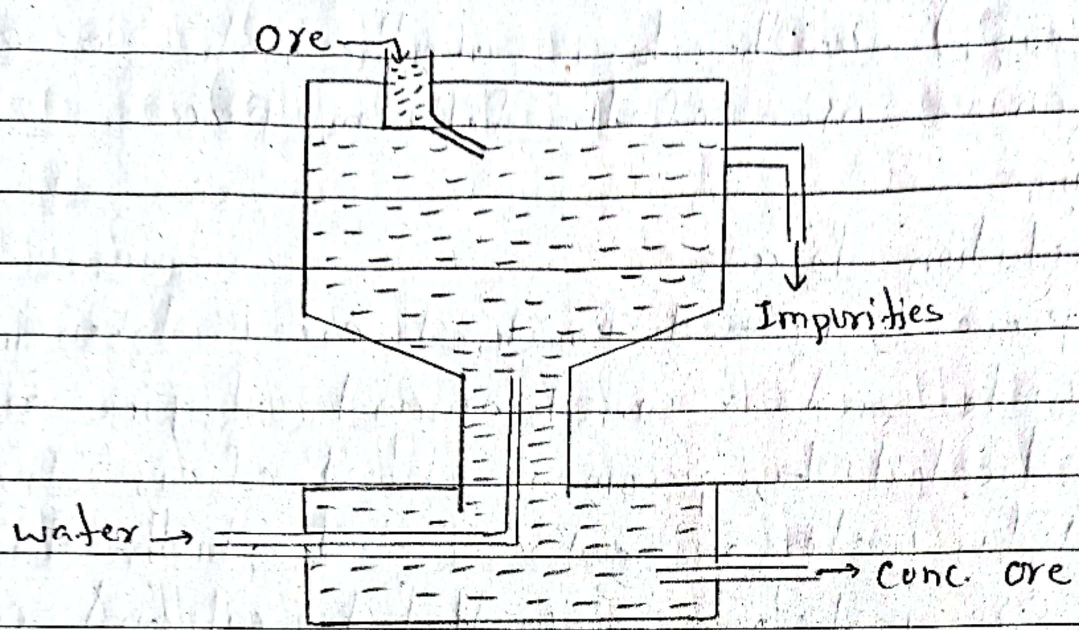


Fig: Froth floatation Process

iii. ~~Gravitati~~ Gravity Separation Process

This process is based on the difference in density of ore and ~~mixture~~ matrix. It is used for the concentration of oxide ores like haematite (Fe_2O_3)

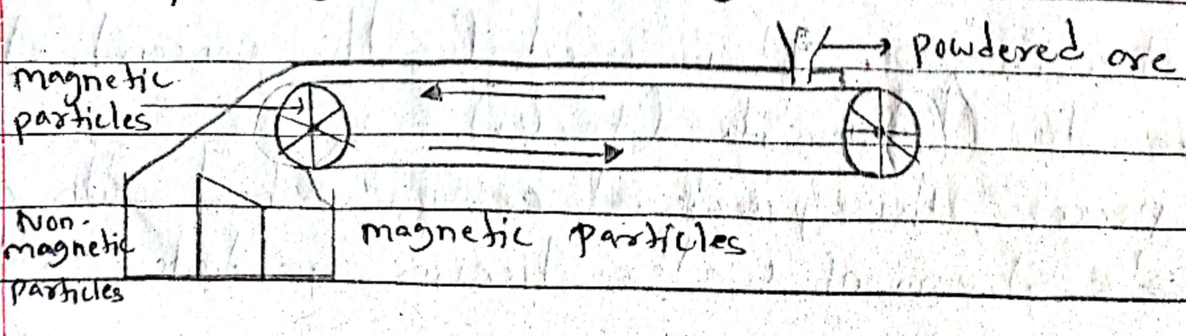
In this process, the powdered ore is washed with an upward ~~ste~~ stream of water. Heavier particles settle down washing the lighter impurities.



iv. Magnetic Separation Process

This process is used for the separation of magnetic impurities from non-magnetic ore and vice-versa. For eg. non-magnetic ore, tinstone (SnO_2) is separated from magnetic impurity, wolframite ($FeWO_4$).

In this process, powdered ore is dropped over a belt revolving around the electromagnetic roller. Magnetic particles are attracted by a magnetic roller and form a heap near the belt while non-magnetic particles form a heap away from the magnetic particles.



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v. Leaching (a chemical Separation Process)

In this method, the ~~or~~ ore is treated with a suitable chemical reagent. The compounds of the ores dissolves whereas the impurities remain unaffected.

Example:

Bauxite is purified by reacting it with hot ~~NaOH~~ NaOH to get sodium metal ~~alumine~~ aluminate which on heating with water followed by ignition gives alumina.

$$Al_2O_3 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$
(Bauxite)

$$NaAlO_2 + 2H_2O \xrightarrow{\Delta} NaOH + Al(OH)_3$$

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

3. Calcination and Roasting

A. Calcination

The process of ~~hea~~ heating concentrated ore in the absence or limited supply of air below the melting point to convert into oxide is called calcination. Following changes takes place during calcination.

i. Volatile impurities and ~~moistured~~ moisture ~~are~~ are removed.

ii. Impurities like S, P, As get oxidized

$$S + O_2 \longrightarrow SO_2$$

$$P_4 + 5O_2 \longrightarrow 2P_2O_5$$

$$4As + 5O_2 \longrightarrow 2As_2O_5$$

iii. Carbonate or hydroxide ores are decomposed into oxidies ores.

$ZnCO_3$ (calamine) $\longrightarrow$ $ZnO + CO_2$

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

B. Roasting

The process of heating concentrated ore in presence of an excess supply of air below the melting point to convert into oxide is called roasting. Following changes takes plac

i. Volatile impurities, organic matter and water of ~~crystall~~ crystallization are removed.

ii. Sulphide ores are oxidized into oxide ~~ore~~ ores.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

Both calcination and roasting are carried out in a reverberatory furnace.

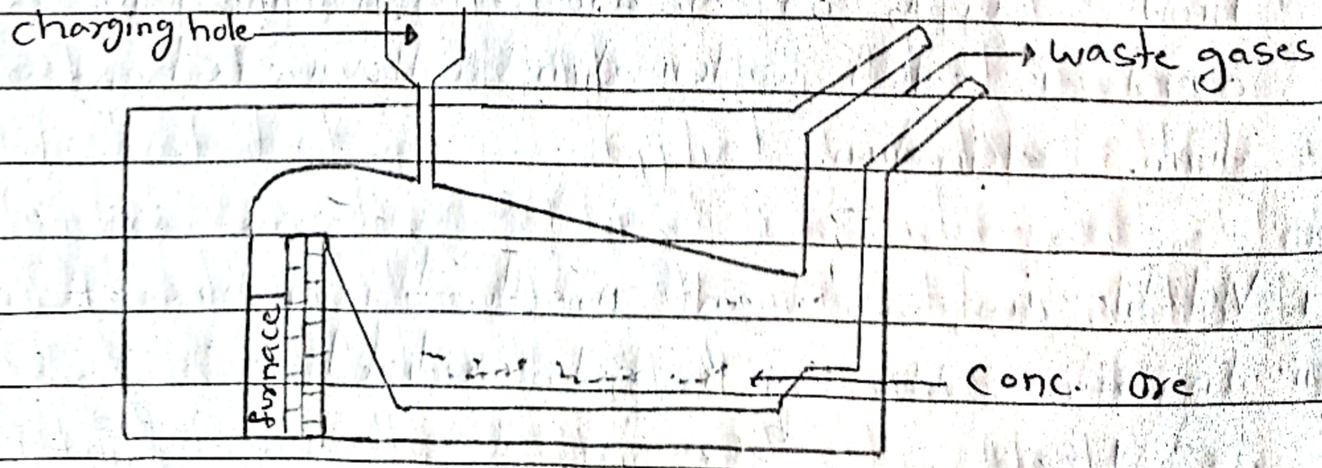

Fig: Reverberatory Furnace

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4. Reduction

It is used for converting metallic oxide into metal. The common reducing agent used in metallurgy are coke (C), CO, H_2, Al, Mg, Zn etc. The reduction is done by the following processes:

i. Reduction by Carbon (smelting)

It is the process of heating calcined or roasted ore strongly in presence of coke to get metal in the molten state. Ores after calcination or roasting contain some refractory materials as impurities. The materials which do not melt and don't get volatilized at high temperature are called refractory impurities. The substance used in smelting to convert refractory infusible material into light fusible mass is called flux.

$$\text{Refractory material (infusible material)} + \text{flux} \rightarrow \underset{\text{(fusible mass)}}{\text{slag}}$$

Flux may be acidic or basic

i. Acidic flux

They are used to remove basic impurities like FeO, MnO, CaO etc. as their slag. Eg. silica (SiO_2), borax ($Na_2B_4O_7 \cdot 10H_2O$) etc.

$$CaO\ (\text{impurities}) + SiO_2\ (\text{flux}) \longrightarrow CaSiO_3\ (\text{slag})$$

ii. Basic flux

They are used to remove acidic impurities like SiO_2, P_2O_5 etc. as their slag. Eg. CaO, MnO etc.

SiO_2 (impurities) + MgO (flux) ⟶ $MgSiO_3$ (Slag)

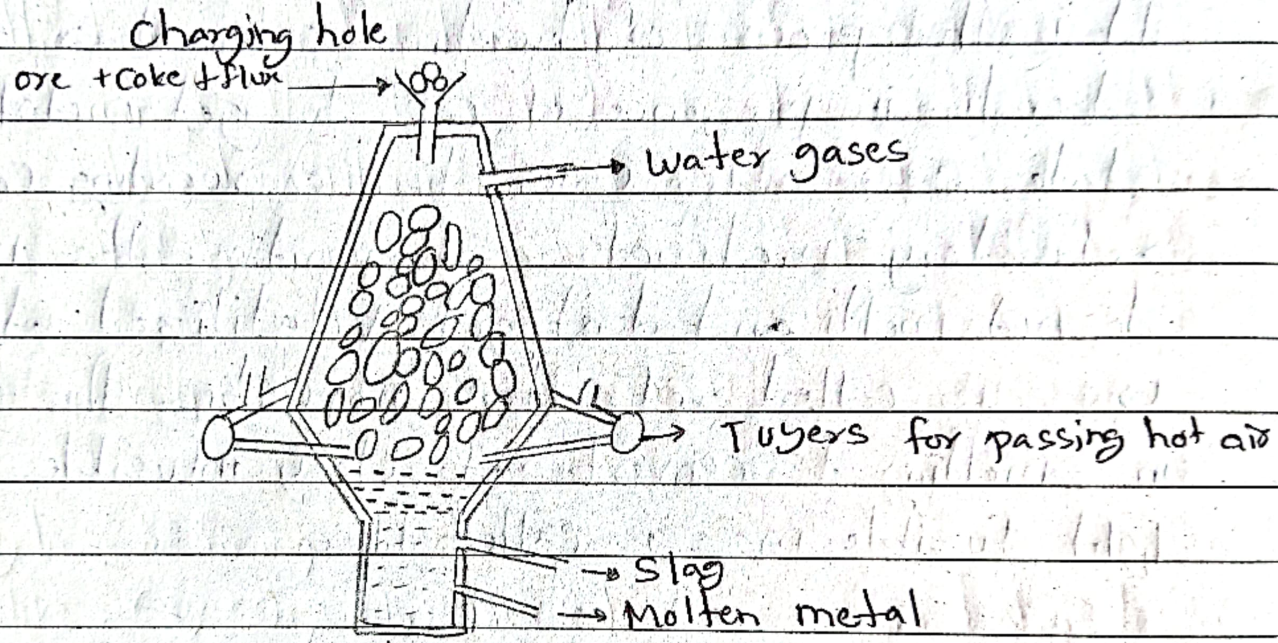


Fig: Blast furnace

During smelting, roasted or calcined ore is mixed with coke and suitable flux in a blast furnace. The blast of hot air is supplied from the bottom of the furnace. In doing so, metallic oxide gets reduced to metal and flux reacts with infusible impurities to give slag. In the hearth of the furnace, molten metal is obtained at the bottom and slag floats over the molten ~~met~~ metal.

ii. Reduction by Aluminium (Alumino thermite reduction)
In the alumino-thermite process, the mixture of roasted or calcined ore and aluminium (the mixture is called thermite) is mixed with barium peroxide and suitable flux in a large crucible. Burning 'mg' is introduced in the crucible to ~~sta~~ start ignition. A large amount of energy is released as the reaction is ~~exo~~ exothermic. The The metallic oxide is reduced to metals in the molten form which is collected at the bottom.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + Heat$$
$$3MnO_2 + 4Al \longrightarrow 3Mn + 2Al_2O_3 + Heat$$

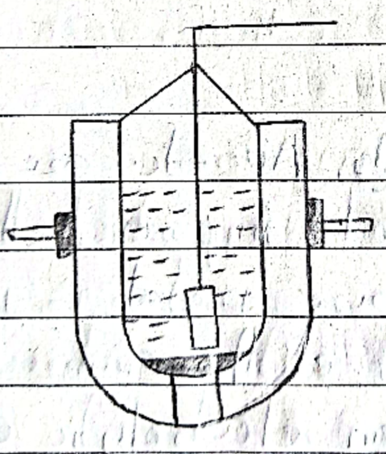


fig: Alumino thermite Process

iii. Electrolytic Reduction
In this method, the fused state of the ore is ~~sub;~~ Subjected to electrolysis. In doing so, metal is obtained at the cathode. Eg: In metallurgy of sodium by Down's Process.

5. Purification of Metals (Refining)

Metals obtained after reduction are associated with many impurities. The methods to purify metals mainly depends upon the ~~nato~~ nature of metal and impurities. Some methods of purification are given below:

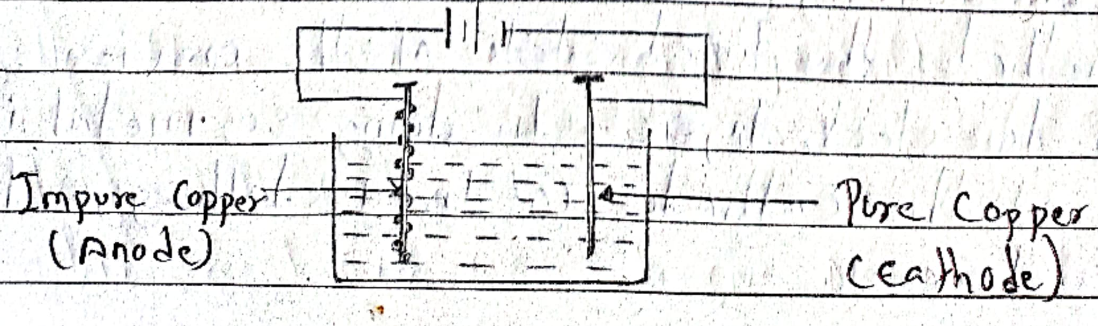
i. Poling

This method is used when the metal oxides are present as impurities (Cu, Pb). In this method, molten metal is stirred with poles of greenwood. The hydrocarbon present in the greenwood reduces metal oxide into free metal. Eg:

$$Cu_2O + CH_4 \rightarrow Cu + CO + H_2O$$

ii. Electrolytic Refining

Metals like Cu, Zn, Ag, Au etc. are refined by this method. In this method, impure metal is made anode, and a thin sheet of pure metal is made cathode and a suitable metal salt of the same metal is taken as an electrolyte in an electrolytic cell. When the electric current is passed through the cell, metal from the anode dissolve and deposits as a pure metal in the cathode.



Alkali Metals: Sodium And Its Compounds

Down's Process

Theory:

Melting point of NaCl is lowered by adding ~~Nac~~ $CaCl_2$.

$$NaCl \xrightarrow{CaCl_2,\ 600^\circ C} Na^+ + Cl^-$$

When electricity is passed through the molten NaCl, the following reactions takes place.

At Anode:

$$Cl^- \longrightarrow Cl + e^-] \times 2$$

$$Cl + Cl \longrightarrow Cl_2$$

At cathode

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

Cell Reaction: $2Na^+ + 2Cl \longrightarrow 2Na + Cl_2$

Process:

The electrolytic cell used in ~~the~~ this process is Down's cell which is a cylindrical steel vessel lined with refractory fire bricks. Anode is graphite at the centre of the cell arising from the bottom and cathode is cylindrical iron with a hood. Two electrodes are separated by iron wire gauze which keeps the products of electrolysis apart. On passing electricity through molten electrolyte, sodium ~~is~~ is discharged at the cathode which being lighter than molten sodium chloride, rises up and collected and packed in steel drums in ~~kex~~ kerosene oil. At the anode, chlorine gas is liberated and escapes through hood.

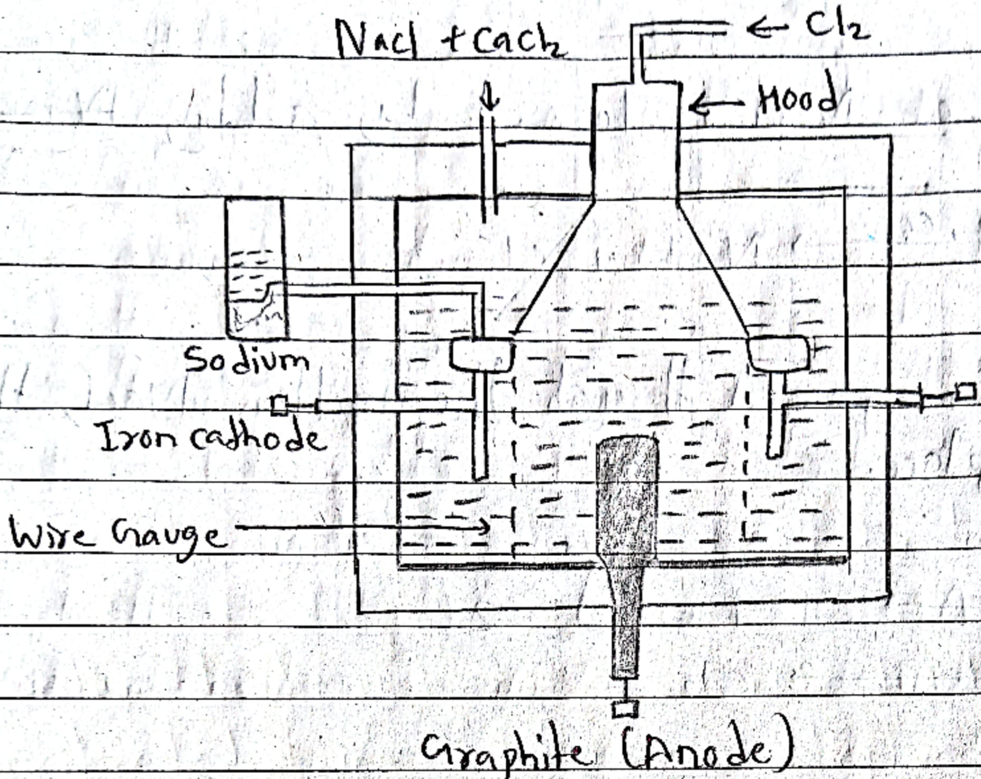


Fig: Down's Cell for extraction of Na

Advantages:

i. Sodium is obtained in pure form.

ii. Chlorine obtained as a by product has many industrial uses.

iii. Rock salt and impure salt can directly be used.

Chemical Properties

1. Action with Air

When sodium is heated with oxygen it burns with golden yellow flame giving oxide and peroxide.

2. Action with water

Sodium react with water to give Naoh and hydrogen.

3. Action with Acid

$2Na + 2HCl \longrightarrow 2NaCl + H_2$

4. Action with non metals

$2Na + Cl_2 \longrightarrow 2NaCl$

$2Na + S \longrightarrow Na_2S$ (Sodium sulphide)

$12Na + P_4 \longrightarrow 4Na_3P$ (Sodium Phosphide)

Uses of Sodium

i. It is used in sodium vapor lamps to illuminate streets.
ii. It is used in electricity.
iii. It is used as a catalyst.
iv. It is used as a reducing agent.
v. It is used to prepare many organic compound

Sodium Hydroxide (NaOH)

Manufacture of NaOH by Diaphragm Cell

A ~~diag~~ diaphragm cell is an electrolytic cell that consists of a steel tank with two compartments separated by a diaphragm of asbestos or metal oxide with a polymer. Graphite or titanium rod acts as an anode. Steel mesh acts as as a cathode.

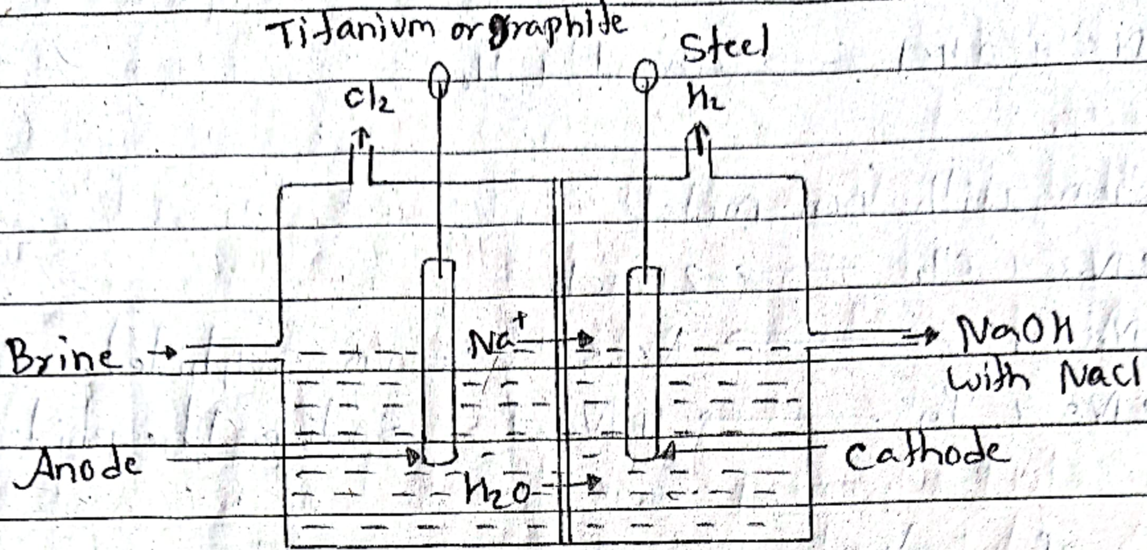


Fig: Manufacture of NaOH by diaphragm cell

Sodium hydroxide can be manufactured by electrolysis of saturated brine solution using diaphragm cell.

$NaCl\ (aq) \rightleftharpoons Na^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

$Na^+ + OH^- \longrightarrow NaOH$

Chemical Properties of NaOH

1. Action with carbon monoxide

$NaOH + CO \longrightarrow HCOONa$ (Sodium formate) c/w

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2. Precipitations Reactions

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$FeCl_3 + 3NaOH \longrightarrow Fe(OH)_3 + 3NaCl$$

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$

Manufacture of Washing Soda by Solvay or Ammonia soda Process

Principle :

Brine solution saturated with ammonia gas reacts with CO_2 to form sodium bicarbonate.

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate is sparingly soluble in water due to unreacted NaCl. The filtered product of heating gives Na_2CO_3

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

Sodium carbonate solution is crystallized to get washing soda.

$$Na_2CO_3 \xrightarrow{crystallization} Na_2CO_3 \cdot 10H_2O$$

Washing soda

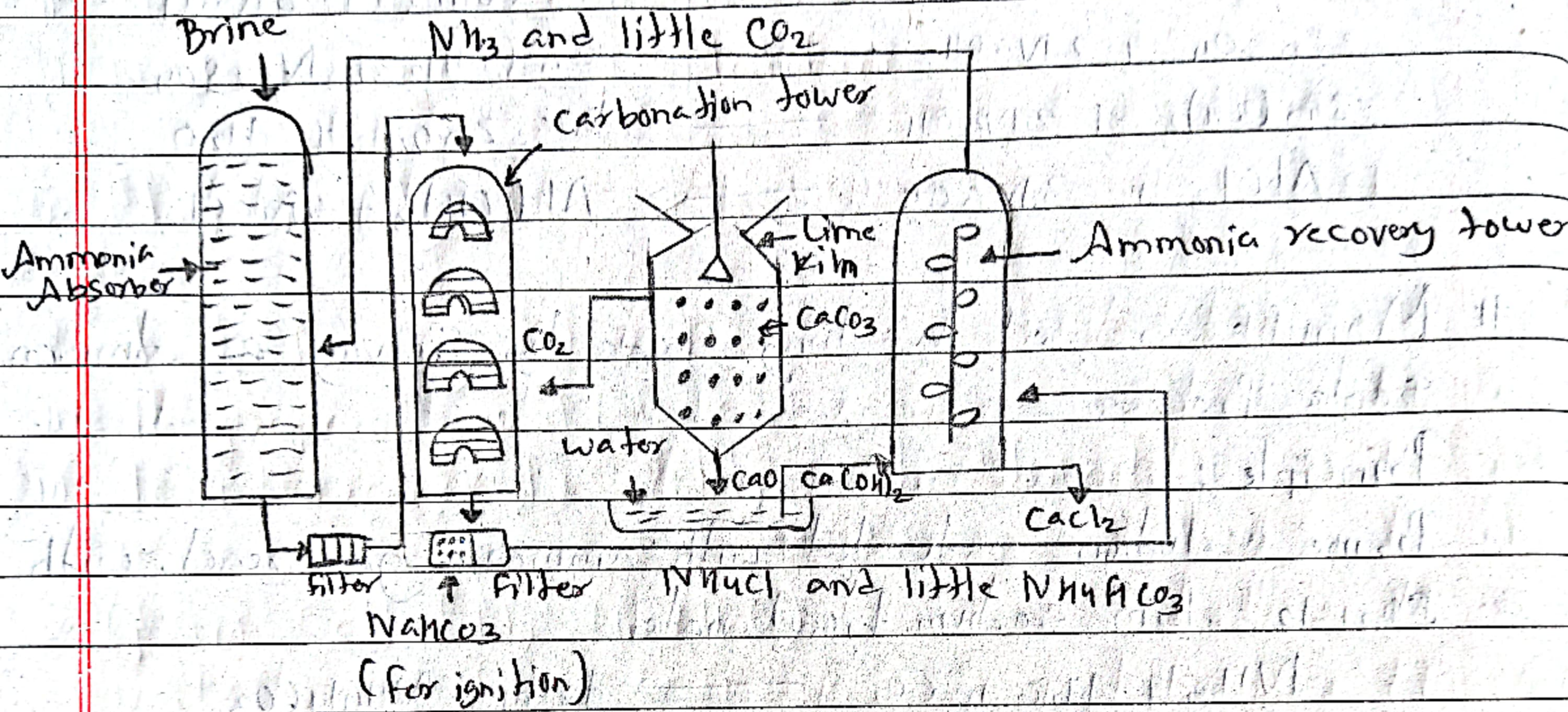

Fig: Solvay Process for manufacture of washing Sod

Chemical Properties

1. Action with water

$$Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + H_2CO_3$$

2. Action with carbon dioxide

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

3. Action with salts

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$$

$$Na_2CO_3 + MgCl_2 \longrightarrow MgCO_3 + 2NaCl$$

$$Na_2CO_3 + ZnCl_2 \longrightarrow ZnCO_3 + 2NaCl$$

Uses

i. Manufacture of glass
ii. Making wood, paper, detergents etc.
iii. Softening of hard water

Alkaline ~~Earth~~ Earth Metals

The elements of group 2 or IIA in the modern periodic table i.e. beryllium (Be), Magnesium (Mg), calcium (Ca), strontium (Sr),

1. Quick lime (CaO)

Uses

i. Preparation of soda-lime.
ii. Drying Agent
iii. Manufacture of glass, bleaching powder etc.
iv. Flux in metallurgy
v. Production of the ~~lim~~ limelight

2. Plaster of Paris ($CaSO_4 \cdot \frac{1}{2} H_2O$ or $2CaSO_4 \cdot H_2O$)

Uses

i. In surgery for setting broken or fractured bones.
ii. In making casts for toys, statues etc.
iii. In making blackboard chalks.
iv. In making artificial marble.

3. Bleaching Powder ($CaOCl_2$)
Uses
i. As bleaching agent
ii. As germicides and disinfectants
iii. In the manufacture of chloroform

4. Magnesia (MgO)
Uses
i. As refractory Material
ii. To prepare crucible
iii. To neutralize the acidity of the stomach.

5. Epsum Salt ($MgSO_4.7H_2O$)
Uses
i. Purgative in medicine
ii. To correct magnesium and sulphur deficiency in the soil.
iii. As desiccant.

Solubility of hydroxides, carbonates and sulphate of alkaline

The solubility of alkaline earth metal (OH) decreases with decreasing size of alkaline earth metals. Calcium and Magnesium hydroxide are slightly (sparingly) soluble and other metal hydroxide are slightly soluble.

→ For any compound to be soluble in water, its lattice energy must be less than hydration energy.

The energy released when one mole of a compound is formed from its constituent ions under standard conditions is called lattice energy.

$$\text{Solubility} \propto \frac{1}{\text{Lattice energy}}$$

→ The energy released when one mole of an ionic compound is completely hydrated by water at standard conditions is called hydration energy.

$$\text{Solubility} \propto \text{Hydration energy}$$

More is the difference in the size of cation and anion, more will be the solubility.

Solubility of hydroxides

As we move down the group, the size of cation increases and the difference between the size of ions decreases which decreases Lattice energy and hence solubility increases.

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

Increasing order of solubility.

Solubility of sulphates and carbonates

The size of sulphate and carbonate is large. ~~As~~ As we move down the group, the difference between the size of ions increases which increases lattice energy and hence solubility decreases.

$$BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$$

$$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

Decreasing order of solubility

Stability of carbonates and nitrates of alkaline earth metals

As we move down the group, lattice energy of carbonates and nitrates of alkaline earth metals increases due to which their ~~solubit~~ stability increases down the group.

$$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$$

$$Be(NO_3)_2 < Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2 < Ba(NO_3)_2$$

Increasing order of stability.

~~Incre~~