UNIT - 1

Water Technology

BOILER FEED WATER

- The water fed into the boiler for the production of steam is called boiler feed water.
- Boiler feed water should be free from turbidity, oil, dissolved gases, alkali and hardness causing substances.
- If hard water obtained from natural sources is fed directly into the boilers, the following troubles may arise.

REQUIREMENTS OF BOILER FEED WATER

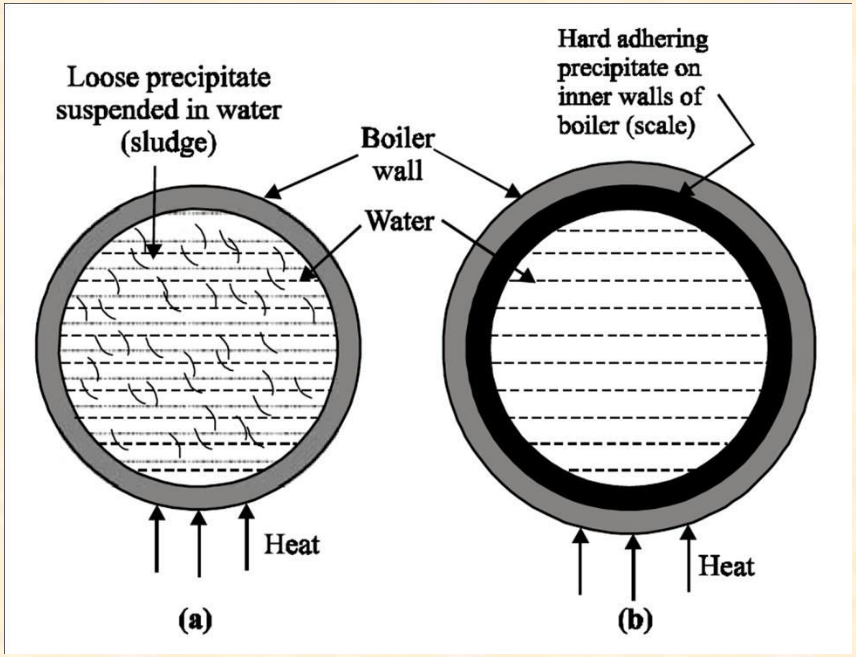
	Specifications	Disadvantages
1.	Boiler feed water should have zero hardness.	Scales and sludges will be produced, which prevents efficient heat transfer.
2.	It must be free from dissolved gases like O_2, CO_2.	It leads to boiler corrosion.
3.	It should be free from suspended impurities.	Produces wet steam.
4.	It should be free from dissolved salts and alkalinity.	Produces caustic embrittlement, which causes brittlement of boiler parts.

Boiler troubles (or) Disadvantages of using hardwater in boilers

1. Scale and sludge formation,
2. Priming and foaming (carry over),
3. Caustic embrittlement,
4. Boiler corrosion.

Scale and Sludge Formation in boilers

- When water is continuously converted into steam in boilers, the concentration of dissolved salts in water increases progressively.
- When the concentration of the salts reaches their saturation point, they are thrown out in the form of precipitates on the inner walls of the boilers. The least soluble one gets precipitated first.



a) Sludge in boiler b) Scale in boiler

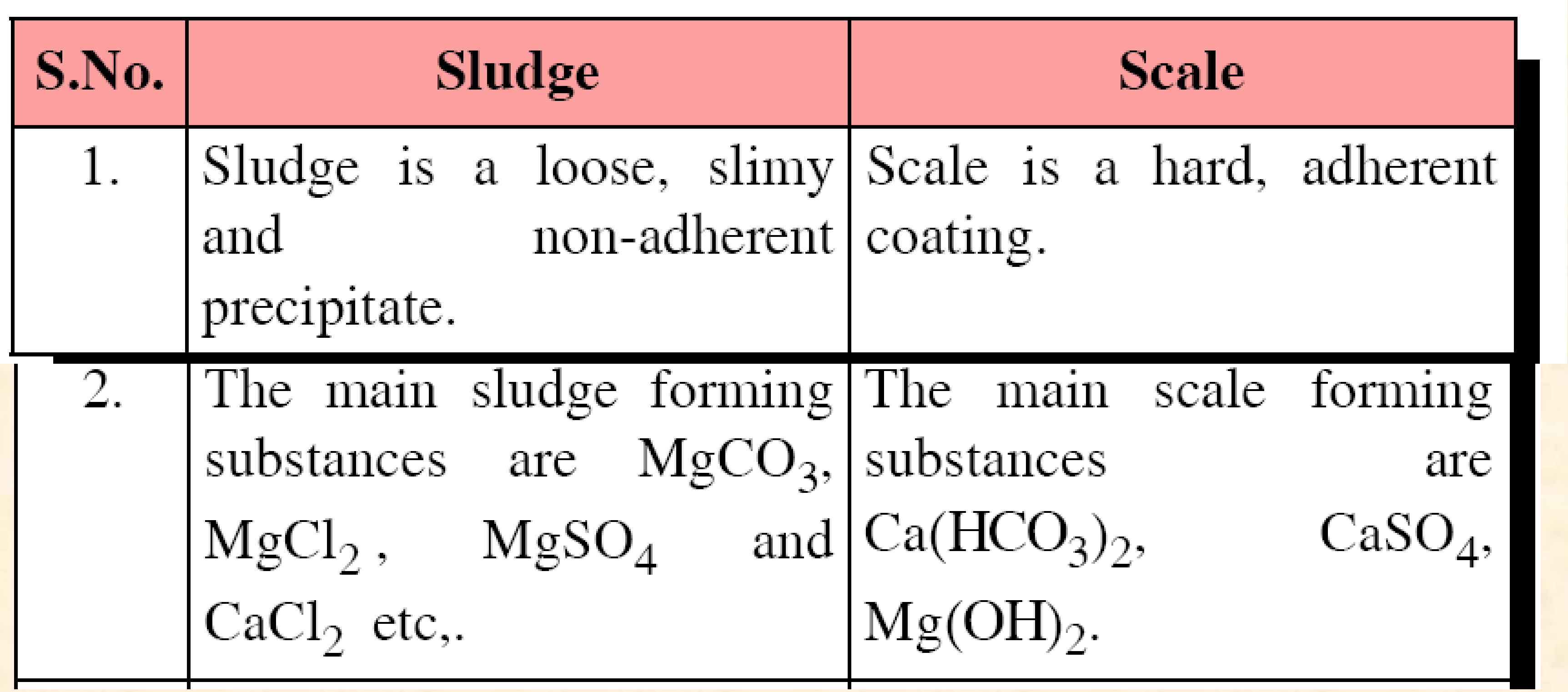
Sludge

If the precipitate is loose and slimy it is called sludge. Sludges are formed by substances like $MgCl_2$, $MgCO_3$, $MgSO_4$ and $CaCl_2$. They have greater solubilities in hot water than cold water.

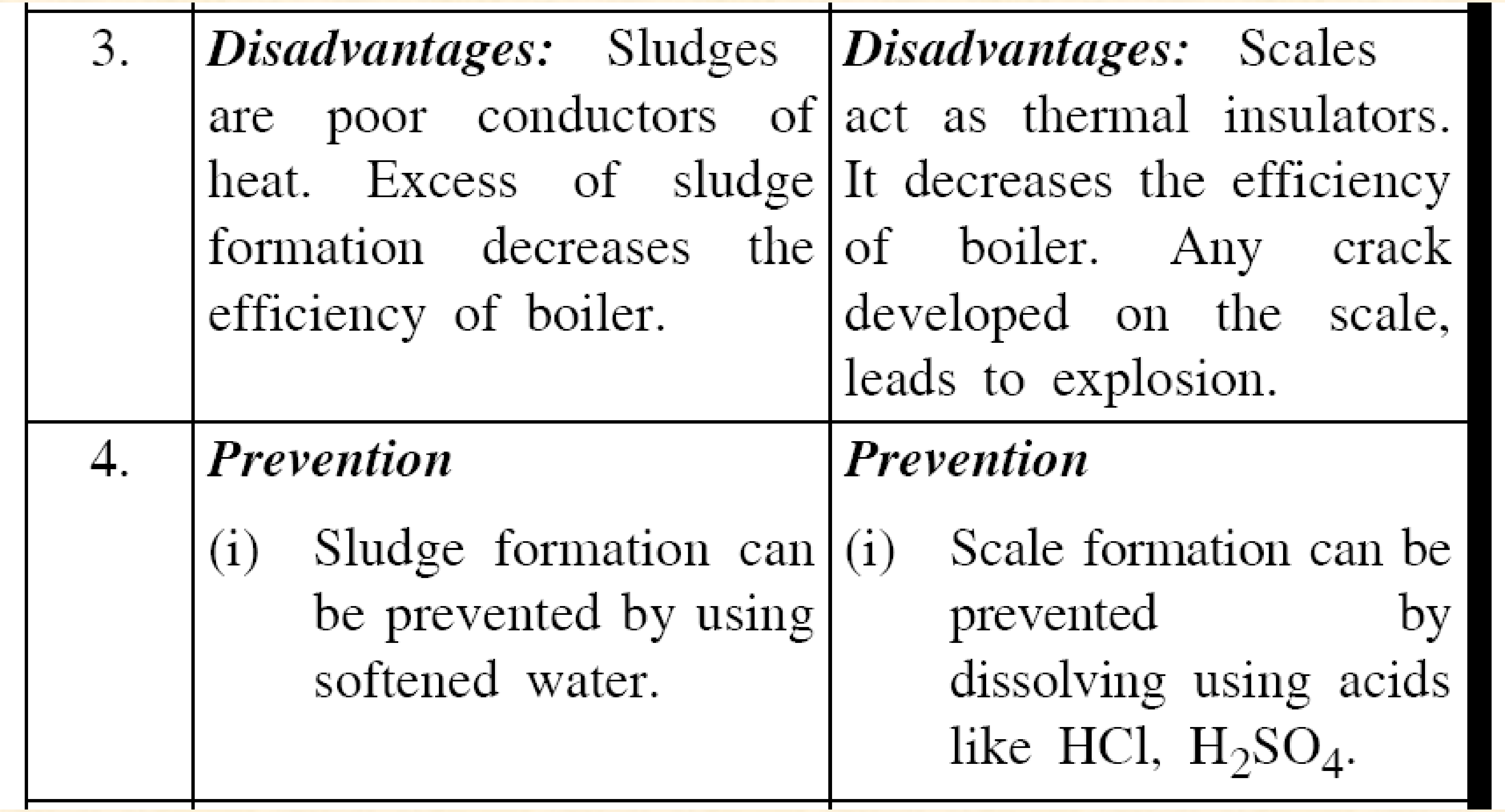
Scale

On the other hand, if the precipitate forms hard and adherent coating on the inner walls of the boiler, it is called scale. Scales are formed by substances like $Ca(HCO_3)_2$, $CaSO_4$ and $Mg(OH)_2$.

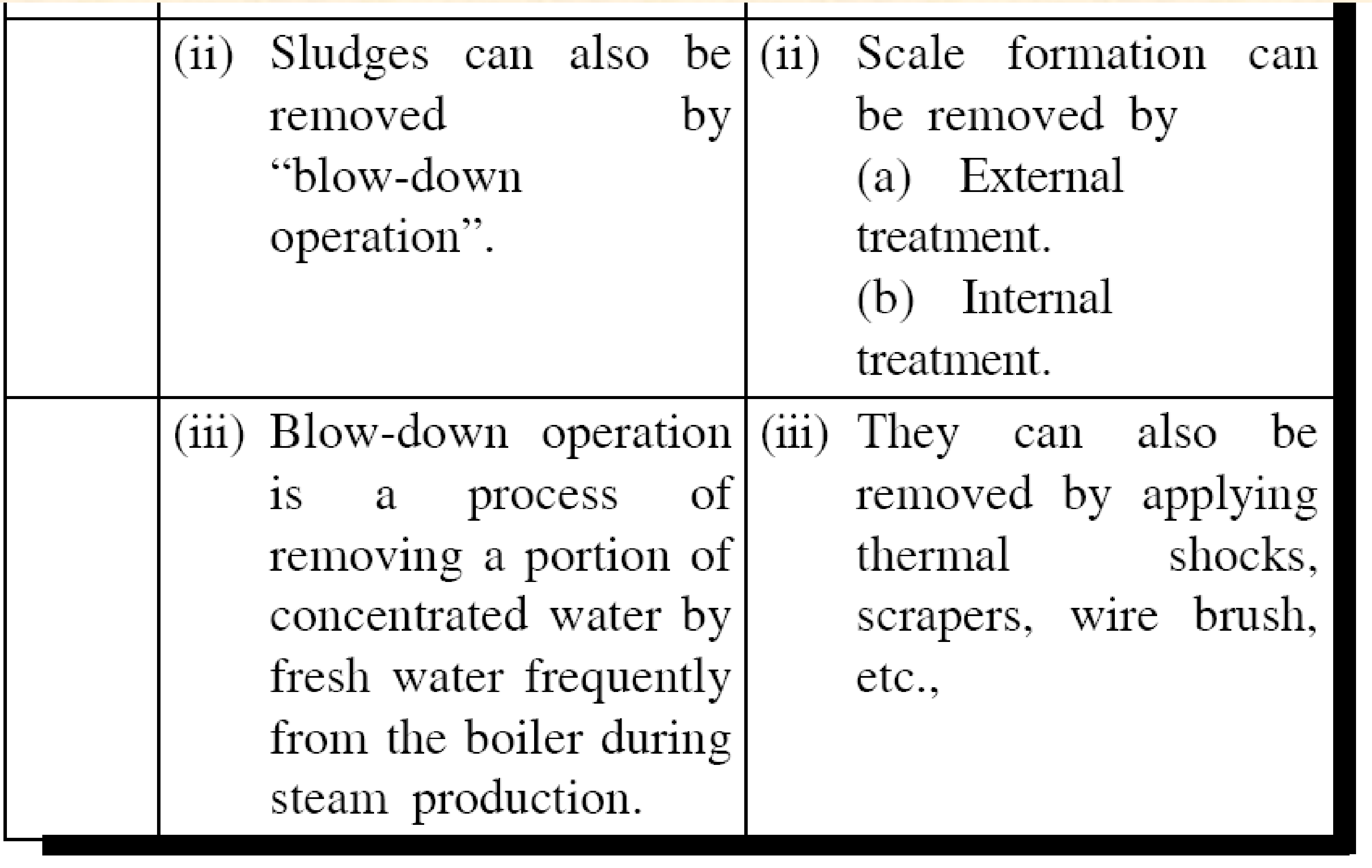
Table 1.2 Comparison of Scales and Sludges



S.No.	Sludge	Scale
1.	Sludge is a loose, slimy and non-adherent precipitate.	Scale is a hard, adherent coating.
2.	The main sludge forming substances are $MgCO_3$, $MgCl_2$, $MgSO_4$ and $CaCl_2$ etc,.	The main scale forming substances are $Ca(HCO_3)_2$, $CaSO_4$, $Mg(OH)_2$.



3.	***Disadvantages:*** Sludges are poor conductors of heat. Excess of sludge formation decreases the efficiency of boiler.	***Disadvantages:*** Scales act as thermal insulators. It decreases the efficiency of boiler. Any crack developed on the scale, leads to explosion.
4.	***Prevention*** (i) Sludge formation can be prevented by using softened water.	***Prevention*** (i) Scale formation can be prevented by dissolving using acids like HCl, H_2SO_4.



	(ii) Sludges can also be removed by "blow-down operation".	(ii) Scale formation can be removed by (a) External treatment. (b) Internal treatment.
	(iii) Blow-down operation is a process of removing a portion of concentrated water by fresh water frequently from the boiler during steam production.	(iii) They can also be removed by applying thermal shocks, scrapers, wire brush, etc.,

Priming and Foaming (Carry Over)

- **During the production of steam in the boiler, due to rapid boiling, some droplets of liquid water are carried along with steam. Steam containing droplets of liquid water is called wet steam.**
- **These droplets of liquid water carry with them some dissolved salts and suspended impurities.**
- **This phenomenon is called carry over. It occurs due to priming and foaming.**

Priming

Priming is the process of production of wet steam.

Priming is caused by

(i) High steam velocity,

(ii) Very high water level in the boiler,

(iii) Sudden boiling of water,

(iv) Very poor boiler design.

Prevention

Priming can be controlled by

(i) Controlling the velocity of steam,

(ii) Keeping the water level lower,

(iii) Good boiler design,

(iv) Using treated water.

Foaming

- The formation of stable bubbles above the surface of water is called foaming.
- These bubbles are carried over by steam leading to excessive priming.

Foaming is caused by the

(i) presence of oil, and grease,

(ii) presence of finely divided particles.

Prevention

Foaming can be prevented by

(i) adding coagulants like sodium aluminate, aluminium hydroxide,

(ii) adding anti-foaming agents like synthetic poly amides.

Caustic Embrittlement (Intercrystalline Cracking)

- *Caustic embrittlement means intercrystalline cracking of boiler metal.*
- *Boiler water usually contains a small proportion of Na_2CO_3. In high pressure boilers this Na_2CO_3 undergoes*
- *decomposition to give NaOH.*

$$\boxed{Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2}$$

This NaOH flows into the minute hair cracks and crevices, usually present on the boiler material, by capillary action and dissolves the surrounding area of iron as sodium ferroate.

$$Fe + 2NaOH \text{ ----> } Na_2FeO_2 + H_2\uparrow$$

This causes brittlement of boiler parts, particularly stressed parts like bends, joints, rivets, etc., causing even failure of the boiler.

Prevention

Caustic embrittlement can be prevented by

(i) using sodium phosphate as softening agent instead of sodium carbonate.

(ii) by adding tannin, lignin to the boiler water, which blocks the hair cracks.

Boiler Corrosion

Corrosion in boilers is due to the presence of

1. Dissolved Oxygen.
2. Dissolved Carbon Dioxide.
3. Dissolved Salts.

1. Dissolved Oxygen

Dissolved oxygen in water is mainly responsible for the corrosion of boiler. The dissolved oxygen in water attacks the boiler material at higher temperature.

$$4Fe + 6H_2O + 3O_2 \longrightarrow 4Fe(OH)_3 \downarrow$$

Removal of Dissolved Oxygen

Dissolved oxygen can be removed by chemical or mechanical methods.

(a) Chemical Method

Sodium sulphite, hydrazine are some of the chemicals used for removing oxygen.

$$2Na_2SO_3 + O_2 ---> 2Na_2SO_4$$

$$N_2H4 + O_2 ---> N_2 + 2H_2O$$

Hydrazine is found to be an ideal compound for removing dissolved oxygen in the water, since the products are water and inert N_2 gas.

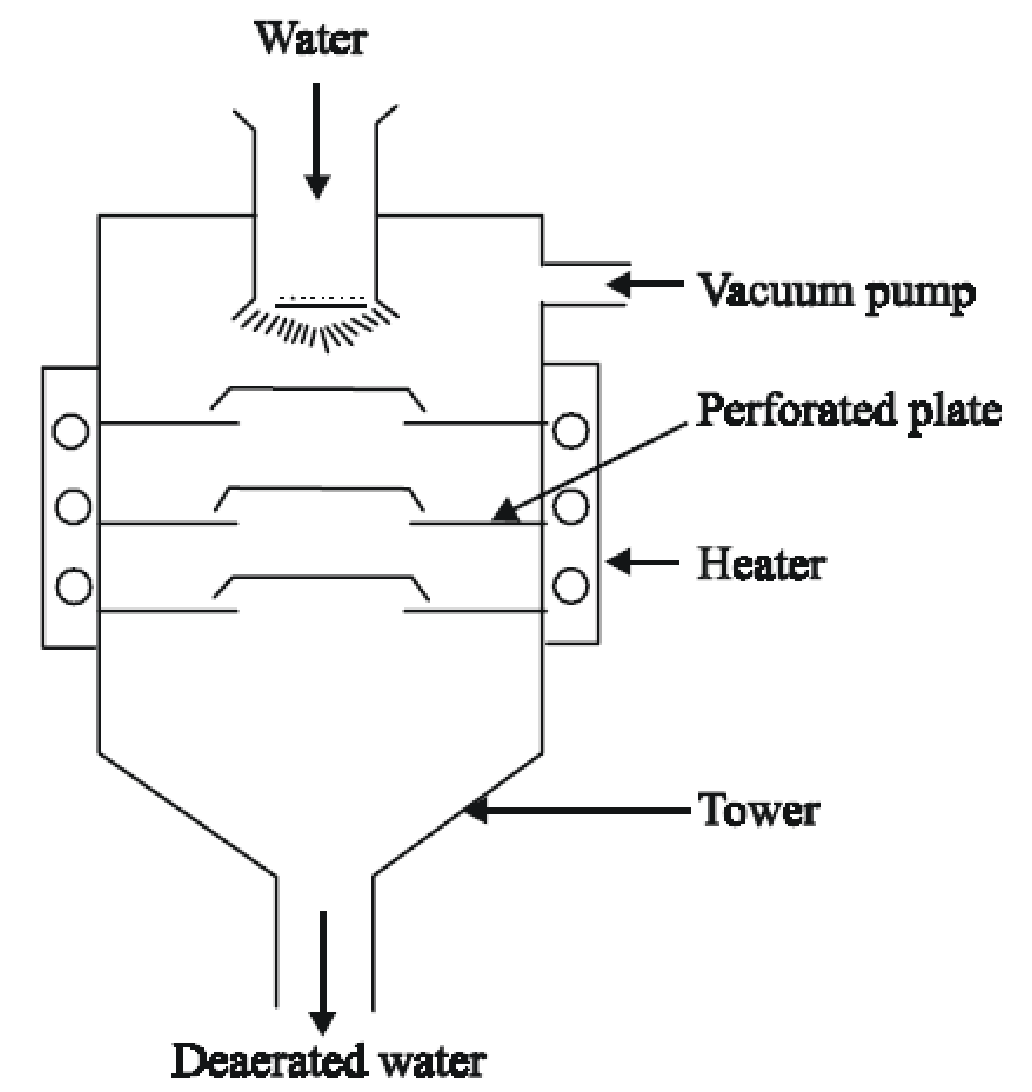
(b) Mechanical De – aeration

Dissolved oxygen can also be removed from water by mechanical deaeration (Fig.)

In this process, water is allowed to fall slowly on the perforated plates fitted inside the tower.

The sides of the tower are heated, and a vacuum pump is also attached to it.

The high temperature and low pressure produced inside the tower reduce the dissolved oxygen content of the water.



Mechanical Deaeration of Water

2. Dissolved Carbon Dioxide

Dissolved carbon dioxide in water produces carbonic acid, which is acidic and corrosive in nature

$$CO_2 + H_2O \text{ ––––> } H_2CO_3$$

Carbon dioxide gas is also produced from the decomposition of bicarbonate salts present in water.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

Removal of Dissolved Carbon Dioxide

(a) Carbon dioxide can be removed from water by adding a calculated amount of NH_4OH into water.

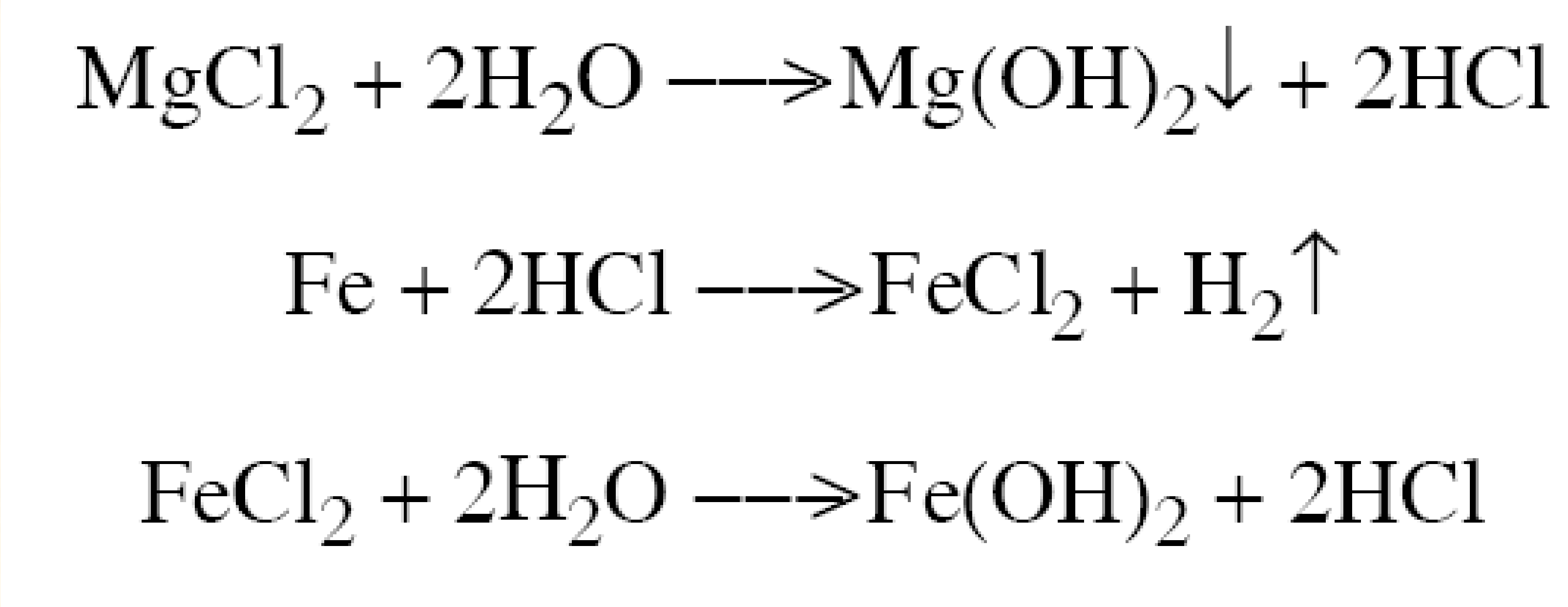
$$2NH_4OH + CO_2 \text{ ---> } (NH_4)_2CO_3 + H_2O$$

(b) Carbon dioxide along with oxygen can also be removed mechanically by de-aeration method.

3. Dissolved $MgCl_2$

Acids, produced from salts dissolved in water, are also mainly responsible for the corrosion of boilers.

Salts like $MgCl_2$, $CaCl_2$, etc, undergo hydrolysis at higher temperature to give HCl, which corrodes the boiler.



$$MgCl_2 + 2H_2O ---> Mg(OH)_2\downarrow + 2HCl$$

$$Fe + 2HCl ---> FeCl_2 + H_2\uparrow$$

$$FeCl_2 + 2H_2O ---> Fe(OH)_2 + 2HCl$$

Removal of Acids

Corrosion by acids can be avoided by the addition of alkali to the boiler water.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

REQUIREMENTS OF BOILER FEED WATER

	Specifications	Disadvantages
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3.	It should be free from suspended impurities.	Produces wet steam.
4.	It should be free from dissolved salts and alkalinity.	Produces caustic embrittlement, which causes brittlement of boiler parts.

SOFTENING or CONDITIONING METHODS

Water used for industrial purposes should be free from hardness producing substances, suspended impurities and dissolved gases etc. The process of removing hardness producing salts from water is known as softening (or) conditioning of water.

Softening of water can be done in two methods

1. **External conditioning.**
2. **Internal conditioning.**

EXTERNAL CONDITIONING

- It involves the removal of hardness producing salts from the water before feeding into the boiler.
- The external treatment can be done by the Demineralisation or Ion-exchange process.

Ion Exchange (or) Demineralisation process

- **This process removes almost all the ions (both anions and cations) present in the hard water.**
- **The soft water, produced by lime-soda and zeolite processes, does not contain hardness producing Ca^{2+} and Mg^{2+} ions, but it will contain other ions like Na^{+}, K^{+}, SO_4^{2-}, Cl^{-} etc., On the other hand D.M.**
- **(Demineralised) water does not contain both anions and cations.**

- Thus a soft water is not demineralised water whereas a demineralised water is soft water.
- This process is carried out by using ion exchange resins, which are long chain, cross linked, insoluble organic polymers

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- This process is carried out by using ion exchange resins, which are long chain, cross linked, insoluble organic polymers

1. Cation Exchanger

Resins containing acidic functional groups ($-COOH$, $-SO_3H$) are capable of exchanging their H+ ions with other cations of hard water. Cation exchange resin is represented as RH_2.

Examples

(i) Sulphonated coals.

(ii) Sulphonated polystyrene.

$R - SO_3H$; $R - COOH \equiv RH_2$

2. Anion Exchanger

Resins containing basic functional groups ($-NH_2$, $-OH$) are capable of exchanging their anions with other anions of hard water.

Anion exchange resin is represented as $R(OH)_2$.

Examples

(i) Cross-linked quaternary ammonium salts.
(ii) Urea-formaldehyde resin.

$R-NR_3OH$; $R-OH$; $R-NH_2 \equiv R(OH)_2$

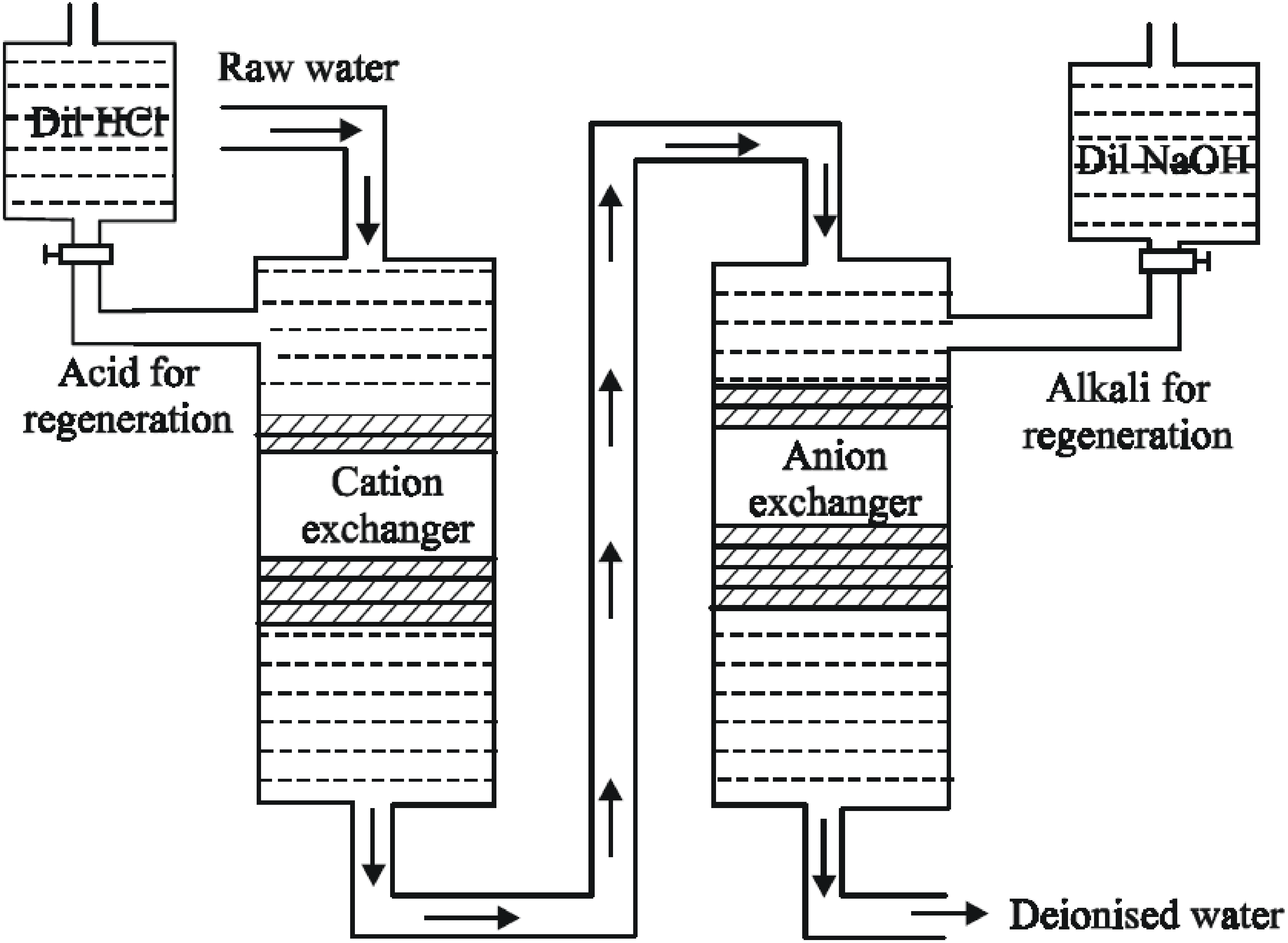
Process

The hard water first passed through a cation exchange column, (Fig.) which absorbs all the cations like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, etc., present in the hard water.

$$RH_2 + CaCl_2 --> RCa + 2HCl$$

$$RH_2 + MgSO_4 --> RMg + H_2SO_4$$

$$RH + NaCl --> RNa + HCl$$



Demineralization Process

The cation free water is then passed through a anion exchange column, which absorbs all the anions like Cl^-, SO^{2-}, HCO^{3-}, etc., present in the water.

$R'(OH)_2 + 2HCl$ ---> $R' Cl_2 + 2H_2O$

$R'(OH)_2 + H_2SO_4$ ---> $R'SO_4 + 2H_2O$

The water coming out of the anion exchanger is completely free from cations and anions.

This water is known as demineralised water or deionised water.

Regeneration

When the cation exchange resin is exhausted, it can be regenerated by passing a solution of dil HCl or dil H_2SO_4.

$RCa + 2HCl \longrightarrow RH_2 + CaCl_2$

$RNa + HCl \longrightarrow RH + NaCl$

Similarly, when the anion exchange resin is exhausted, it can be regenerated by passing a solution of dil NaOH.

$$R'Cl_2 + 2NaOH ---> R'(OH)_2 + 2NaCl.$$

Advantages of ion-exchange process

(i) Highly acidic or alkaline water can be treated by this process.

(ii) The water obtained by this process will have very low hardness (nearly 2 ppm).

Disadvantages of ion – exchange process

(i) Water containing turbidity, Fe and Mn cannot be treated, because turbidity reduces the output and Fe, Mn form stable compound with the resin.

(ii) The equipment is costly and more expensive chemicals are needed.

INTERNAL CONDITIONING OR INTERNAL TREATMENT OR BOILER COMPOUNDS

It involves the removal of scale forming substance, which were not completely removed in the external treatment, by adding chemicals directly into the boiler. This chemicals are also called **boiler compounds.**

Carbonate Conditioning

Scale formation can be avoided by adding Na_2CO_3 to the boiler water. It is used only in low pressure boilers. The scale forming salt like $CaSO_4$ is converted into $CaCO_3$, which can be removed easily.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4.$$

Phosphate Conditioning

- Scale formation can be avoided by adding sodium phosphate. It is used in high pressure boilers.
- The phosphate reacts with Ca^{2+} and Mg^{2+} salts to give soft sludges of calcium and magnesium phosphates.

$$\boxed{3\,CaSO_4 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4) + 3Na_2SO_4.}$$

Calgon Conditioning

- Calgon is sodium hexa meta phosphate $Na_2\,[Na_4(PO_3)_6]$.
- This substance interacts with calcium ions.
- Forming a highly soluble complex and thus prevents the precipitation of scale forming salt.

$$\boxed{2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4.}$$

DESALINATION OF BRACKISH WATER

- The process of removing common salt (sodium chloride) from the water is known as **desalination.**
- The water containing dissolved salts with a peculiar salty or brackish taste is called **brackish water.**

(i) Fresh Water –

Contains < 1000 ppm of dissolved solids.

(ii) Brackish water –

Contains > 1000 but < 35,000 ppm of dissolved solids.

(iii) Sea water –

Contains > 35,000 ppm of dissolved solids.

Reverse Osmosis (RO)

- When two solutions of different concentrations are separated by a semi-permeable membrane, solvent (water) flows from a region of lower concentration to higher concentration. This process is called **osmosis.**
- The driving force in this phenomenon is called **osmotic pressure.**

- If a hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration side, the solvent flow is reversed i.e solvent flows from higher concentration to lower concentration.
- This process is called **reverse osmosis** (Fig.1.6). Thus, in the process of reverse osmosis pure water is separated from salt water.
- This process is also known as super-filtration.
- The membranes used are cellulose acetate, cellulose butyrate.

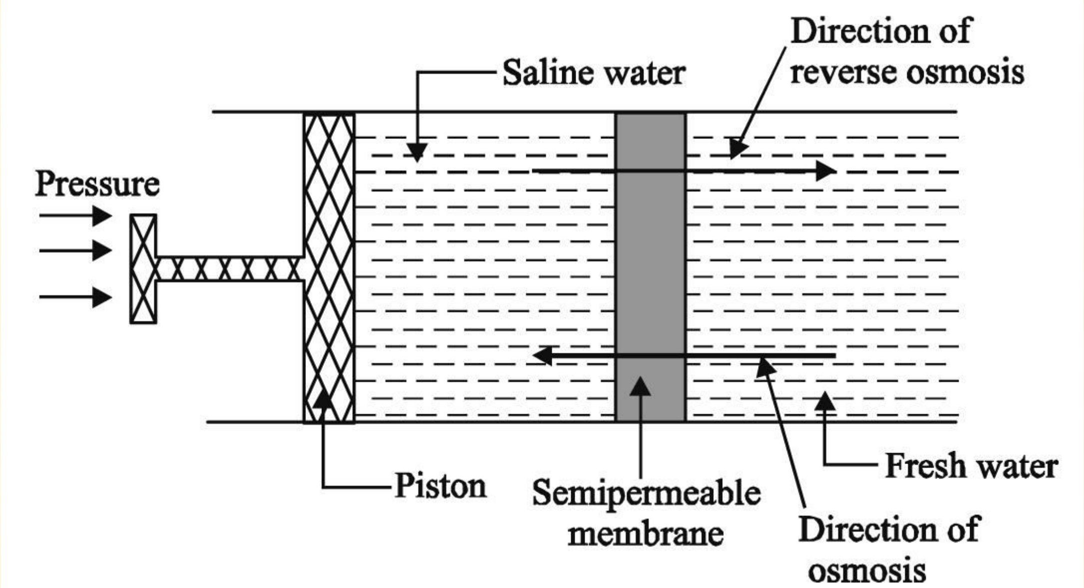


Fig. 1.6 Reverse osmosis

Advantages

- The life time of the membrane is high, and it can be replaced within few minutes.
- It removes ionic as well as non-ionic, colloidal impurities.
- Due to low capital cost, simplicity, low operating, this process is used for converting sea water into drinking water.

THE END

Corrosion

and its control

1. Native State

- The metals occur in native (or) free (or) uncombined state are non-reactive with the environment.
- They are noble metals exist as such in the earth crust. They have very good corrosion resistance.

Example → **Au, Pt, Ag**

2. Combined State

Except noble metals, all other metals are reactive and react with environment and form stable compounds, as their oxides, sulphides, chlorides and carbonates. They exist in their form of stable compounds called ores and minerals.

Example → Fe_2O_3, ZnO, PbS, $CaCO_3$ etc.,

2.2.1 How and Why Corrosion Occurs

- The metals are extracted from these compounds (ores).
- During the extraction, these ores are reduced to their metallic states.
- In the pure metallic state, the metals are unstable as they are considered in excited state ie., higher energy state.
- Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form metal compounds, which are thermodynamically stable, ie., lower energy state.

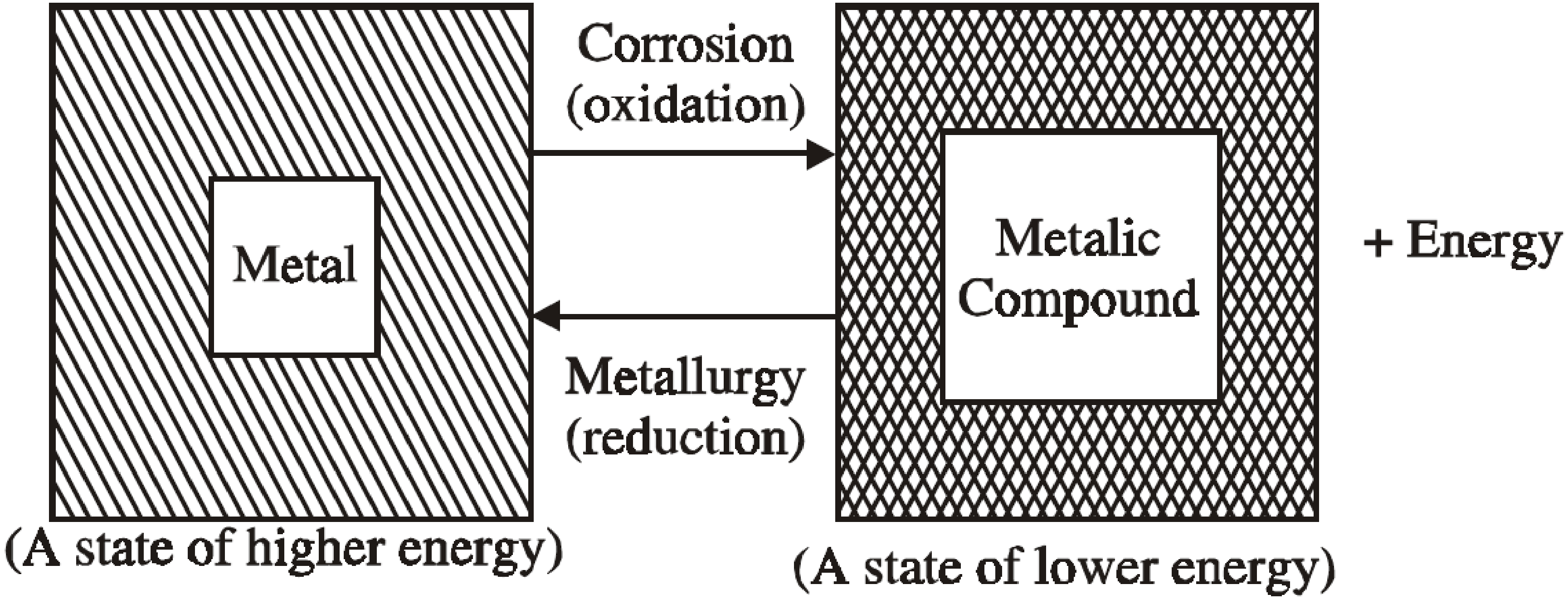


Fig. 2.1 Corrosion and oxidation process

Hence, when metals are used in various forms, they are exposed to environment, (such as dry gases, moisture, etc.,) the exposed metal surface begins to decay ie., conversion into more stable compound. This is the basic reason for metallic corrosion.

Due to corrosion, some useful properties of metals such as electrical conductivity, ductility and malleability etc., are lost.

2.3 CONSEQUENCES OF CORROSION

1. **Due to formation of corrosion product over the machinery, the efficiency of the machine gets lost.**
2. **The products gets contaminated due to corrosion.**
3. **The corroded equipment must be replaced frequently.**

Continued ......

4. Plant gets failure due to corrosion.
5. It is necessary for over design to compensate for the corrosion.
6. Corrosion releases toxic products, health hazard, etc.

2.4 CLASSIFICATION THEORIES OF CORROSION

Based on the environment, corrosion is classified into

(i) Dry or Chemical corrosion, and

(ii) Wet or Electrochemical corrosion

Mechanism of Dry Corrosion

(i) **Oxidation occurs first at the surface of the metal resulting in the formation of metal ions (M^{2+}), which occurs at the metal / oxide interface.**

$$M \text{------>} M^{2+} + 2e^-$$

(ii) Oxygen changes to ionic form (O^{2-}) due to the transfer of electron from metal, which occurs at the oxides film / environment interface

$$\frac{1}{2} O_2 + 2e^- \text{------>} O^{2-}$$

(iii) Oxide ions reacts with the metal ion to form the metal-oxide film.

$$M + \frac{1}{2} O_2 \text{------}> M^{2+} + O^{2-} \equiv MO$$

(Metal-oxide film)

Once the metal surface is converted to a monolayer of metal-oxide, for further corrosion (oxidation) to occur, the metal ion diffuses outward through the metal-oxide barrier.

Thus the growth of oxide film commences perpendicular to the metal surface (Fig. 2.2).

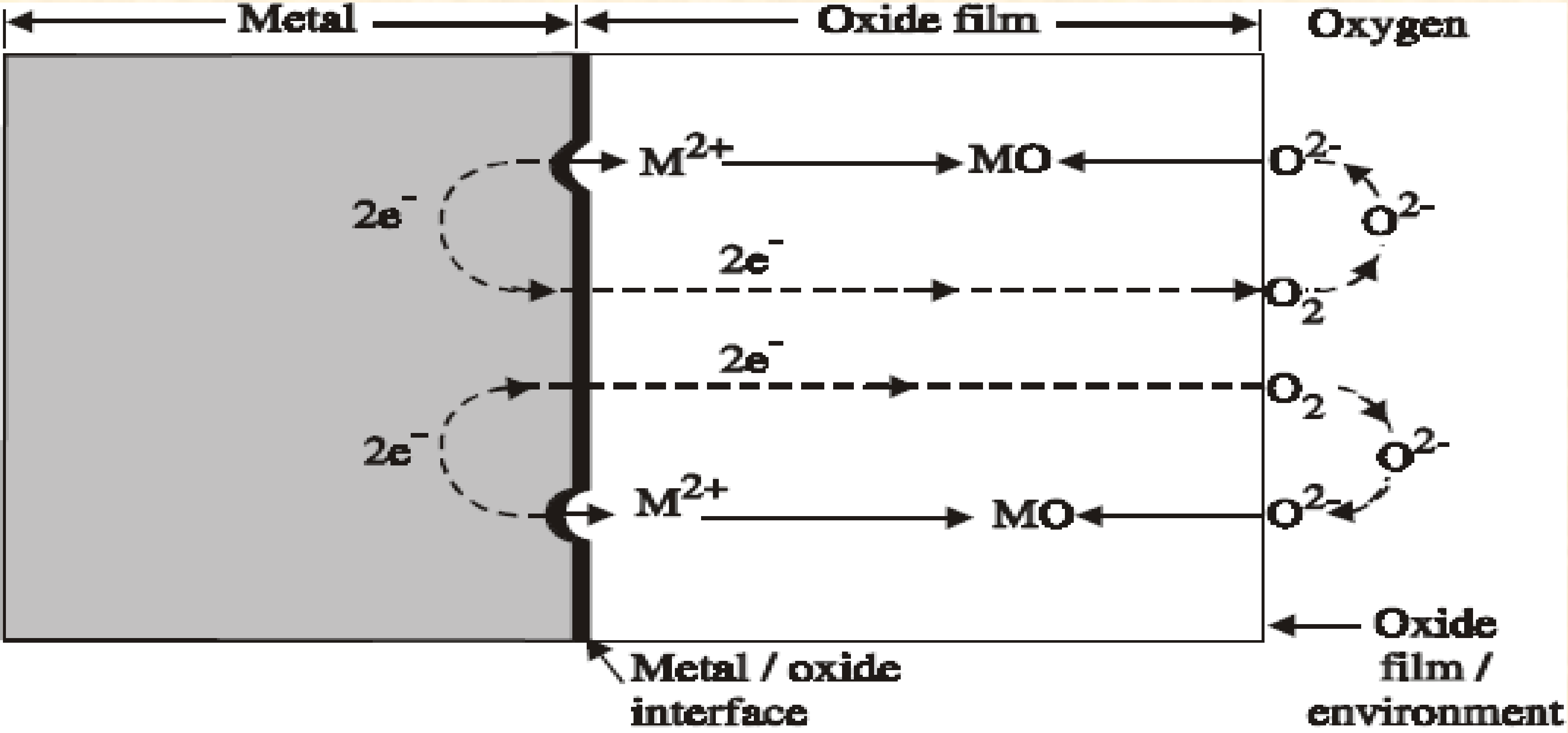


Fig 2.2 Mechanism of Oxidation corrosion

Nature Of Oxide Film

The nature of oxide film formed on the metal surface plays an important role in oxidation corrosion.

(i) Stable Oxide Layer

A stable oxide layer is a fine-grained in structure, and gets adsorbed tightly to the metal surface. Such a layer is impervious in nature and stops further oxygen attack through diffusion. Such a film behaves as a protective coating and no further corrosion can develop.

Example

Oxides of Al, Sn, Pb, Cu, etc., are stable oxide layers.

(ii) Unstable Oxide Layer

Unstable oxide layer is mainly produced on the surface of noble metals, which decomposes back into the metal and oxygen.

$$\text{Metal Oxide} \rightleftharpoons \text{Metal} + \text{Oxygen}$$

Example

Oxides of Pt, Ag, etc., are unstable oxide layers.

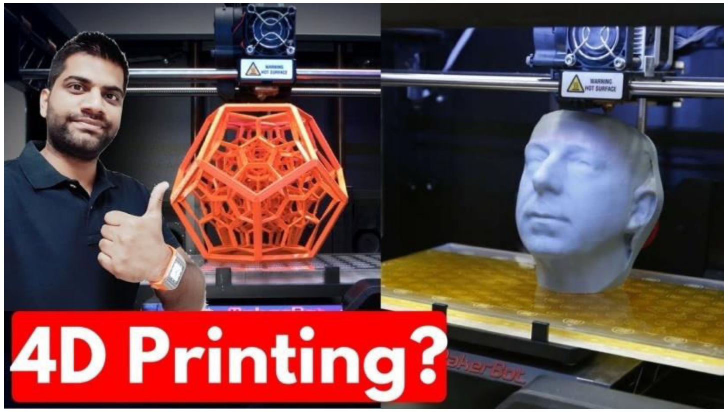
(iii) Volatile Oxide Layer

The oxide layer volatilizes as soon as it is formed, leaving the metal surface for further corrosion.

Example

Molybdenum oxide (MoO_3) is volatile.

UNIT –III



POLYMERS

INTRODUCTION

- ✓ Polymers were discovered long before anyone understood what they were. It wasn’t until 1920 that German chemist Hermann Staudinger (1881–1965) made his macromolecular hypothesis, suggesting that polymers are actually giant molecules formed by the permanent attachment of countless smaller molecules. Through careful experiments, he proved his hypothesis to be correct and was rewarded with the 1953 Nobel Prize in Chemistry.
- ✓ The word is derived from the Greek, *Poly-* means "many" and *-mer* means "part" or "segment". *Mono* means "one". So, monomers are those itty bitty molecules that can join together to make a long polymer chain.

Polymers

Definition

Polymers are macromolecules with high molecular weight formed by repeated linking of monomers, by covalent chemical bonds.

Example:

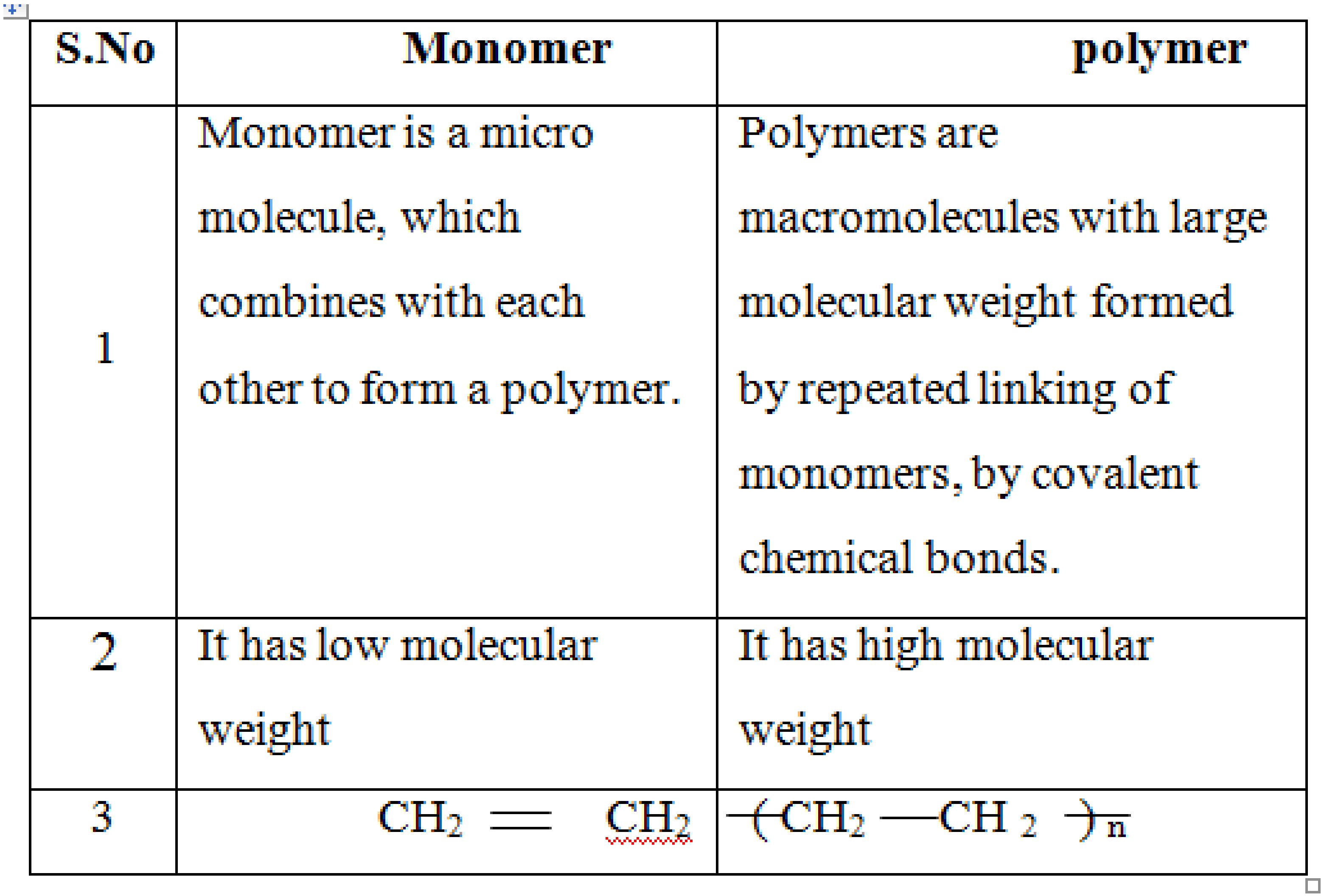
Polyethylene is a polymer formed by repeated linking of large number of ethylene monomers.

Although the chemical properties of polymers are similar to those of analogous small molecules, their physical properties are quite different. Every polymer has its own characteristics, but most polymers have the following general properties.

Characteristics of Polymers

- ✓Low Density
- ✓Low coefficient of friction
- ✓Good corrosion resistance
- ✓Good mouldability
- ✓Excellent surface finish can be obtained
- ✓Poor tensile strength
- ✓Low mechanical properties
- ✓Poor temperature resistance
- ✓Can be produced transparent or in different colors

Difference between Monomer and polymer



S.No	Monomer	polymer
1	Monomer is a micro molecule, which combines with each other to form a polymer.	Polymers are macromolecules with large molecular weight formed by repeated linking of monomers, by covalent chemical bonds.
2	It has low molecular weight	It has high molecular weight
3	$CH_2 = CH_2$	$-(CH_2 - CH_2)-_n$

Classification and Nomenclature of polymers

There are many types of polymers including synthetic and natural polymers.

Natural polymers

Natural polymers are the polymers exist as natural resources, such as cellulose, which is the main constituent of wood and paper.

Synthetic polymers

Polymers made by artificially using chemicals are called as synthetic polymers. **Ex** Bakelite, Neoprene, Nylon, PVC (Polyvinyl chloride), Polystyrene, etc.

Further it can be nomenclature into

i) Homopolymer
  a) Linear homopolymer
  b) Branched homopolymer
  c) Cross - linked homopolymer
ii) Heteropolymer (or) Copolymer
  a) Random polymer
  b) Block polymer
  c) Graft polymer
iii) Homo chain polymer
iv) Hetero chain polymer and stereo specific polymer

Nomenclature of Polymer

i) Homopolymer

A polymer containing same type of monomer units (M) is known as homopolymer. **Ex:** Polyethene, Polypropylene

Types of homopolymer

The homopolymer are subdivided into the following three types based on the manner in which monomers are arranged.

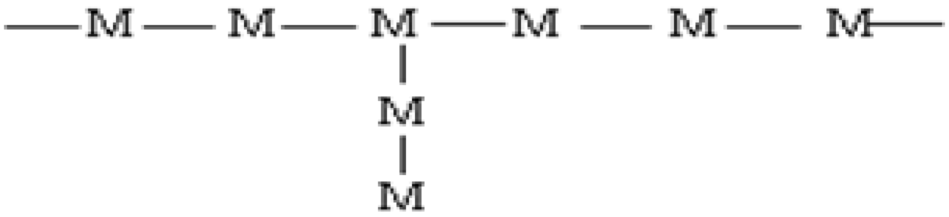
a) Linear homopolymer:

If same monomers are arranged linearly, then it is known as linear homopolymer.

— M — M — M — M — M — M —

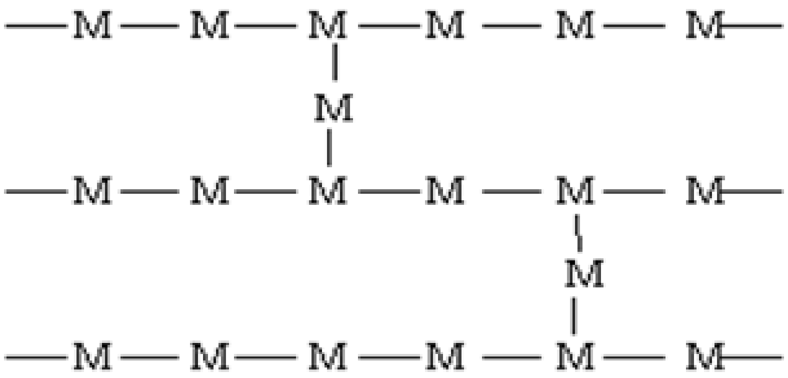
b) Branched homopolymer:

If same monomers are arranged branch wise, then it is known as linear Branched homopolymer.



c) Cross-linked homopolymer:

If same monomers are arranged in cross linked manner, then it is known as Cross-linked homopolymer.



ii) Heteropolymer or copolymer

A polymer containing more than one type of monomers (M1, M_2, & M_3) is known as copolymer or Heteropolymer.

Ex: Polyamide (Nylon), Polyester (Terylene)

Types of copolymer

The copolymers are subdivided into three types as,

a) Random copolymer:

If different polymers are arranged randomly then it is known as Random copolymer

$$-M_1-M_2-M_3-M_2-\ M_1-M_3-M_1$$

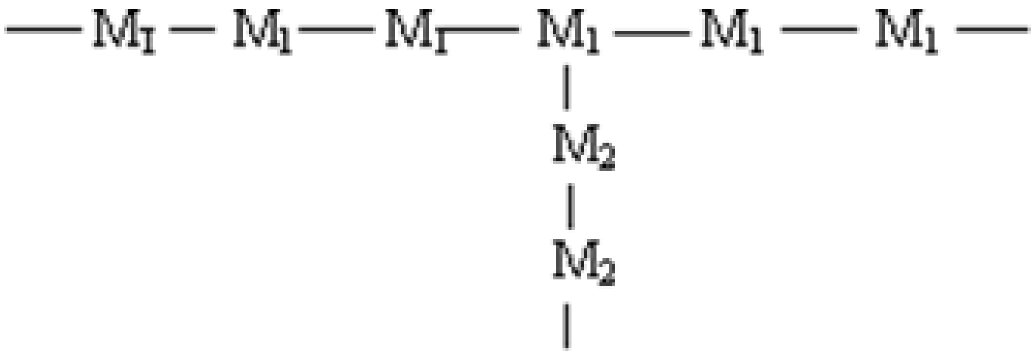
b) Block copolymer:

If different monomers are arranged block wise then it is known as Block copolymer

$$-M_1-M_1-M_2-M_2-M_3-M_3-$$

c) Graft copolymer:

If one of the different monomers act as back bone and other monomers are arranged branch wise then it is known as Graft copolymer



$$-M_1-M_1-M_1-\underset{\begin{array}{c}|\\M_2\\|\\M_2\\|\end{array}}{M_1}-M_1-M_1-$$

iii) Homochain polymer:

If the main chain of a polymer is made up of same species of atoms, it is called as homochain polymer.

Ex: Polythene, Polypropylene

$$-C-C-C-C-C-$$

iv) Heterochain polymer:

If the main chain of a polymer is made up of different atoms, it is called as heterochain polymer.

Ex: Polyamide (Nylon), polyester (Terylene)

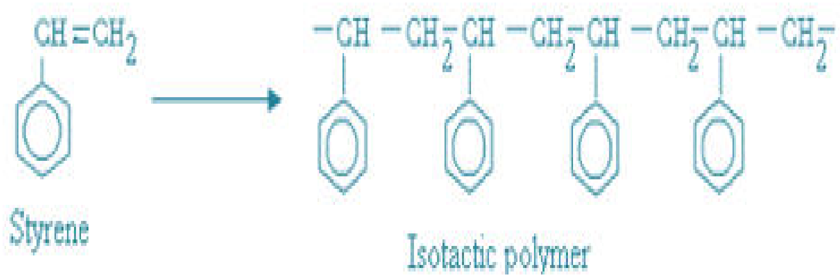
$$-C-C-O-C-C-N-$$

v) Stereo specific polymer:

“The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain is called as ***Tacticity”***. This varying degree of randomness will affect the strength and melting point of the polymer. The less random, the stronger the polymer and the higher the melting point. Hence tacticity affect the physical properties of the polymer. This orientation results in three types of stereo-regular polymers.

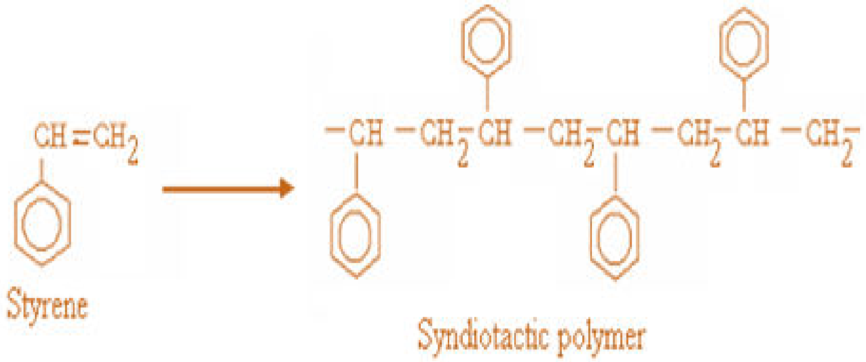
a) Isotactic polymer:

This is a very regular type of polymer chain. If the functional groups (benzene rings) are on same sides of the main chain is called as isotactic polymer.



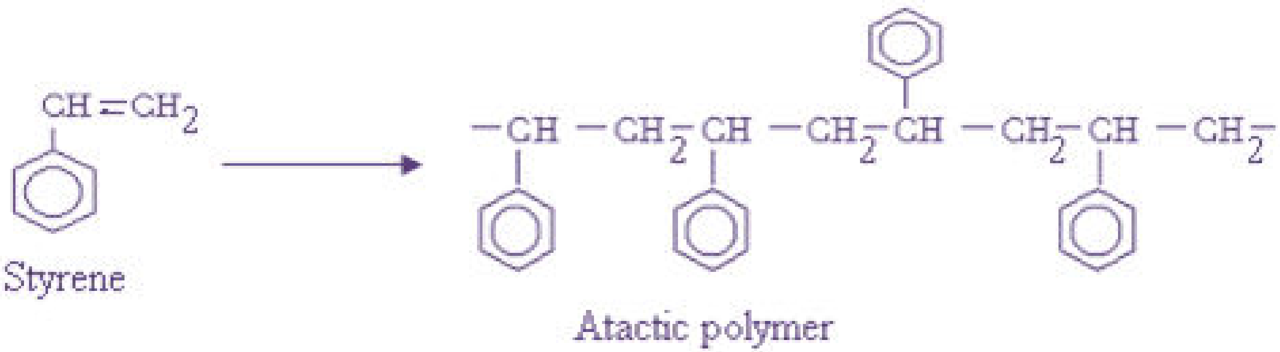
b) Syndiotactic polymer:

If the functional groups are arranged on alternate sides of the main chain is called as syndiotactic polymer. This allows the chains to pack into crystals. It is crystalline, rigid, and high melting, and not penetrated readily by solvents.



c) Atactic polymer:

If the functional groups are arranged randomly in the main chain is called as Atactic polymer. The irregularity prevents the chains from packing closely to each other. It is amorphous. It is comparatively soft, low melting, and becomes swollen in solvents.



Polymerization:

Polymerization is a process in which large number of small molecules combines to give a big molecule called polymer with or without elimination of small molecules like water, HCl.

Degree of polymerization

The number of repeating units (n) in a polymer chain is known as the degree of polymerization. It is represented by the following relationship.

$$\text{Degree of polymerization} = \frac{\text{Molecular weight ofpolymer}}{\text{Molecular weight of monomer in polymer}}$$

$$4CH_2=CH_2 \longrightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

In this example four units of ethylene molecule present in the polymer chain. So the degree of polymerization is 4.

Polymers with low degree of polymerisation are known as **Oligo Polymers**, their molecular weight ranges from 500 – 5000.

Polymers with high degree of polymerisation are known as **High polymers**, and their molecular weight ranges from 10,000 – 2, 00,000.

TYPES OF POLYMERISATION

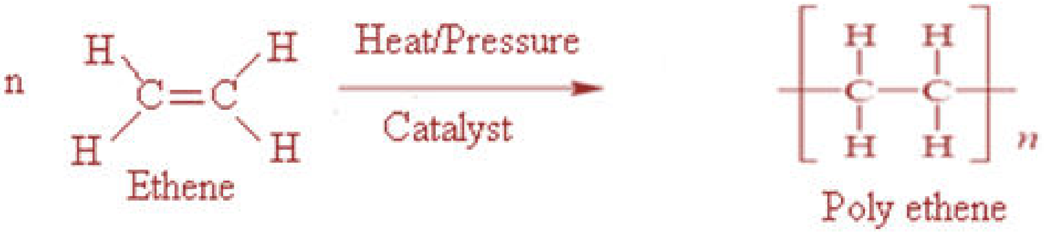
Polymerization can be classified into following three types.

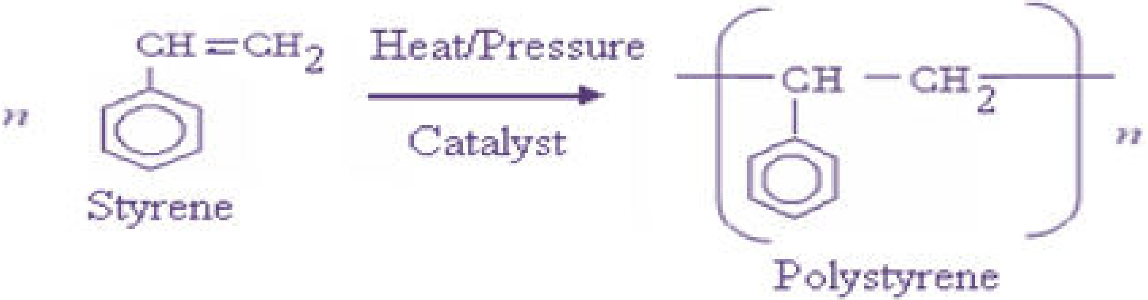
1. Addition polymerization
2. Condensation polymerization (or) Stepwise polymerization
3. Co-polymerisation

ADDITION POLYMERIZATION

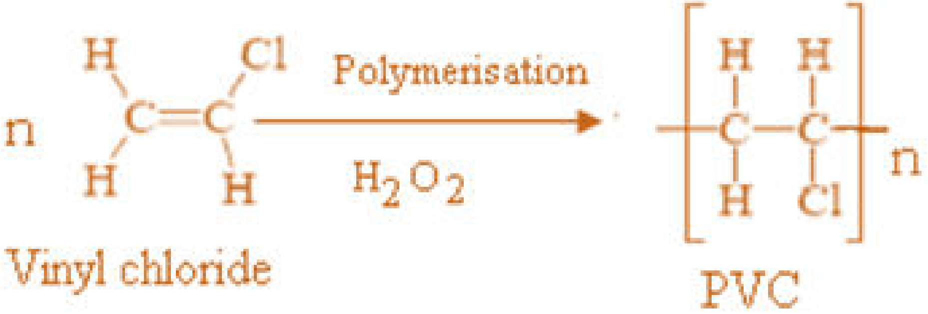
Addition polymerisation is a reaction that yields a polymer, which is an exact multiple of the original monomeric molecule. Such a monomeric molecule usually contains one or more double bonds. During the addition polymerisation reaction the double bonds breaks and becomes a single bond unit with functional sites on either side of the monomer unit. Many such units attach to form a polymer molecule. In this addition polymerisation, there is no elimination of any molecule.

Some of the examples of addition polymerisation are the formation of poly ethene, poly styrene, PVC etc...



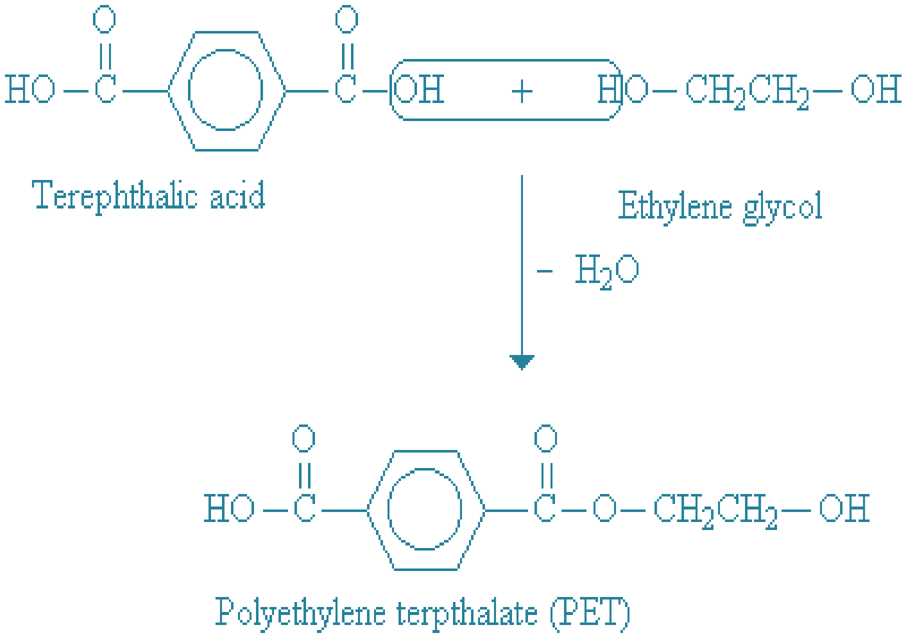


Polyvinyl chloride is obtained by heating water emulsion of vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide under pressure

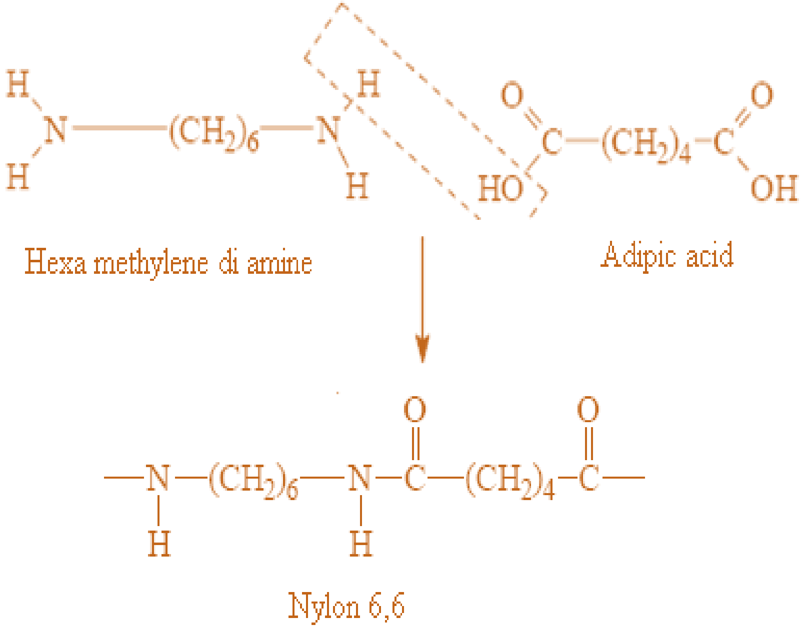


Condensation polymerisation (or) Stepwise polymerisation:

Condensation polymerisation is a reaction between the simple polar groups containing monomers, which yield a polymer with the elimination of a small molecule like H_2O, HCl etc. Ex: Poly ester, Nylon, Nylon6/6, Novolac



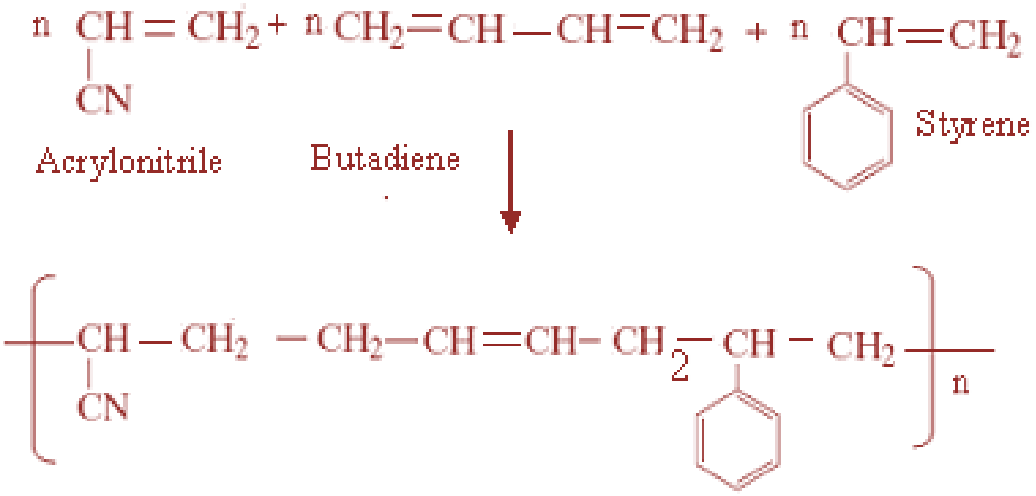
It is prepared by the condensation of terephthalic acid and ethylene glycol



Hexamethylene Diamine and adipicacid condense to form a polymer nylon6,6

Copolymerisation

It is the joint polymerisation in which two or more different monomers combine to give a polymer. High molecular weight polymers obtained by copolymerization. Copolymerisation is mainly carried out to vary the properties of polymers such as hardness, strength, rigidity etc...



Poly Acrylonytrile co Butadiene styrene

Comparison between Addition Polymerization and Condensation Polymerization

S. No	Addition polymerisation	Condensation polymerisation
1	The monomers must have at least one multiple bond	The monomers must have at least two identical (or) different functional groups.
2	Monomers add to give polymer and no other by product is formed	Monomers condense to give polymer with the elimination of molecules like HCl.H_2O etc.
3	The molecular weight of the polymer is a multiple of the molecular weight of monomer	The molecular weight of the polymer is not a multiple of the molecular weight of monomer
4	Thermoplastics are produced	Thermosetting plastics are produced
5	Homochain polymer is formed	Heterochain polymer is formed
6	Longer reaction times give higher yield	Longer reaction times are required to get high molecular weight polymer.
7	High molecular weight polymer is formed	Molecular weight of the polymer rises steadily through out of the reaction.

Free Radical Polymerisation Mechanism

Addition polymerisation can be explained by any one of the following mechanism.

- ✓ Free radical polymerisation
- ✓ Ionic polymeraisation
- ✓ Co-ordination polymerisation

Free radical mechanisms occur in the following three steps.

i) Initiation

ii) Propagation and

iii) Termination

i) Initiation

Step-I

Initiators are chemicals that produce the chain initiating species (free radicals). The chain initiators undergo homolytic cleavage when excited.

The above steps can be represented as

$$I \longrightarrow 2I^{\bullet} \text{ (or) } 2R^{\bullet} \text{ (Free radicals)}$$

Some of the commonly used initiators are given below,

$$CH_3COO-OOCCH_3 \xrightarrow{70-90^{\circ}C} 2(CH_3COO)^{\bullet}$$

Acetyl peroxide

$$H_3C-\underset{CH_3}{\overset{CN}{C}}-N=N-\underset{CH_3}{\overset{CN}{C}}-CH_3 \xrightarrow{80-90^{\circ}C} 2(H_3C)_2\overset{CN}{C}^{\bullet} + N_2\uparrow$$

2,2 Azobis Isobutyronitrile

(AIBN)

Step-II

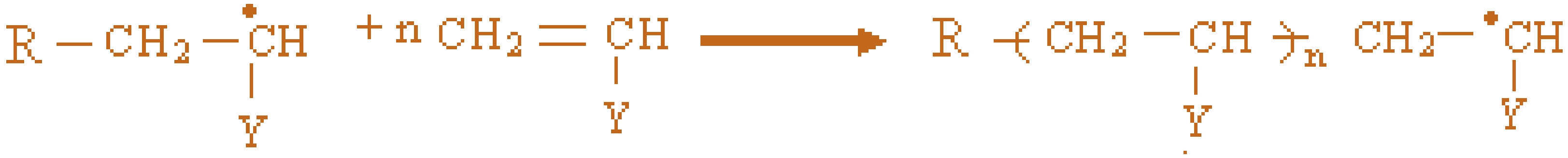
When the free radicals obtained from step I is added to first monomer to produce chain initiating species.

$$R^{\bullet} + CH_2{=}\underset{\displaystyle Y}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{\displaystyle Y}{\underset{|}{\dot{C}H}}$$

Free radical Monomer Chain initiating species

ii) Propagation

The chain initiating species involving successive addition with another monomer to give long chain polymer. This process goes on continuing producing a high molecular weight polymer. Thus the process of growth of long chain with the help of chain initiating species is known as propagation.



$$R-CH_2-\underset{\displaystyle Y}{\underset{|}{\dot{C}H}} + n\,CH_2{=}\underset{\displaystyle Y}{\underset{|}{CH}} \longrightarrow R\left(CH_2-\underset{\displaystyle Y}{\underset{|}{CH}}\right)_n CH_2-\underset{\displaystyle Y}{\underset{|}{\dot{C}H}}$$

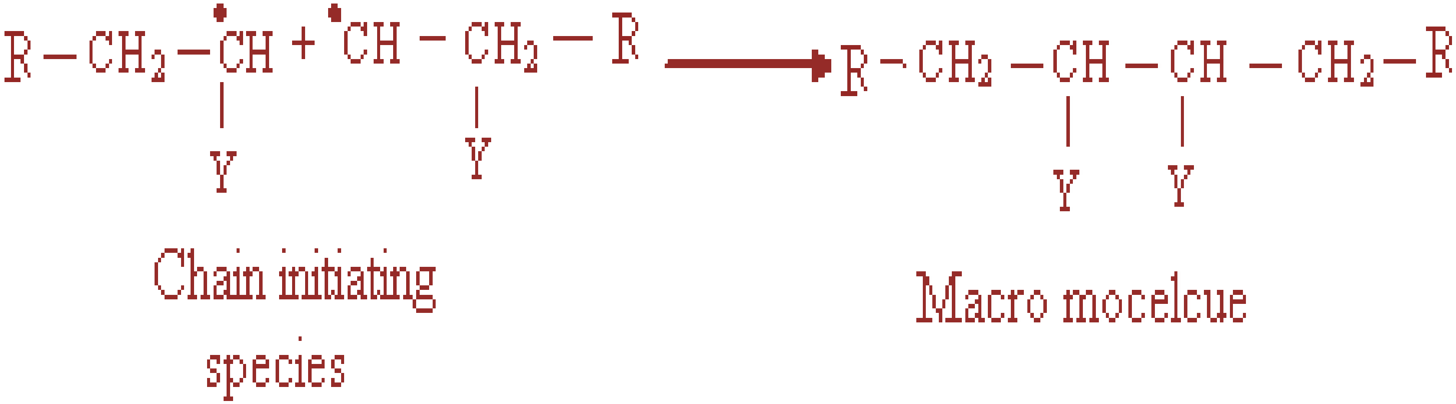
Chain initiating species

iii) Termination

Termination of the propagation of polymer chain may occur either by coupling reaction or disproportionation.

a) Coupling reaction

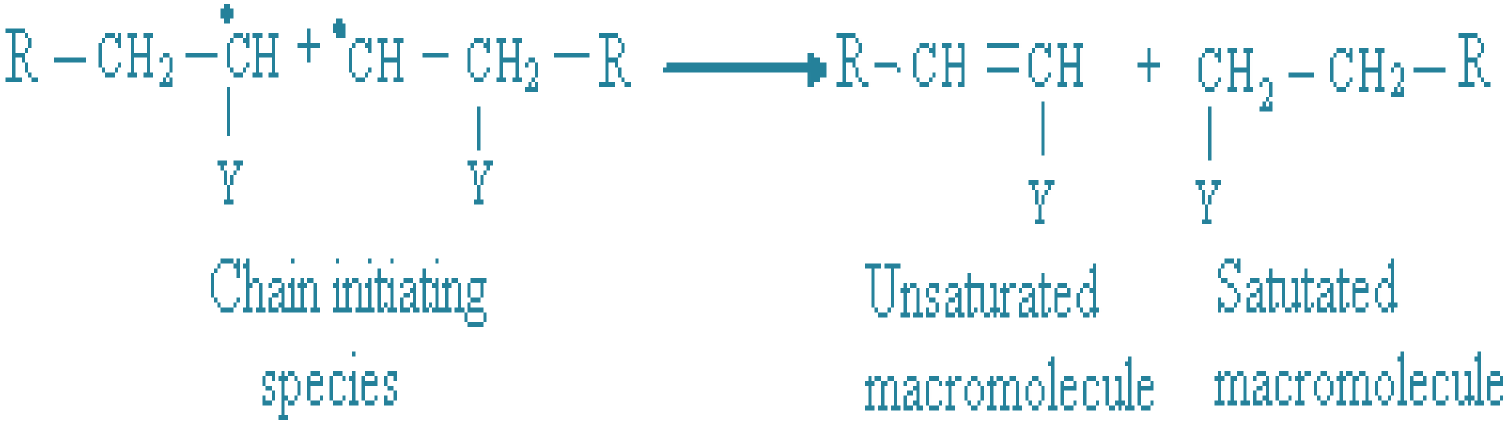
In this reaction free radical of one chain end combine with free radical of another chain to form a covalent compound.



$$R-CH_2-\underset{\underset{Y}{|}}{\overset{\bullet}{C}H}+\overset{\bullet}{C}\underset{\underset{Y}{|}}{H}-CH_2-R \longrightarrow R-CH_2-\underset{\underset{Y}{|}}{CH}-\underset{\underset{Y}{|}}{CH}-CH_2-R$$

b) Disproportionation

This type of chain termination reaction is brought about by the transfer of a hydrogen atom from one reactive chain end to other forming saturated and unsaturated compounds



$$R-CH_2-\underset{\displaystyle Y}{\overset{\bullet}{C}H} + {}^{\bullet}\underset{\displaystyle Y}{CH}-CH_2-R \longrightarrow R-CH=\underset{\displaystyle Y}{CH} + \underset{\displaystyle Y}{CH_2}-CH_2-R$$

Plastics

Plastics are high molecular weight organic materials which can be moulded into any desired shape by the application of heat and pressure in the presence of a catalyst. The plastics are compounded with resins, fillers, plasticizers, pigments, lubricants and Catalyst.

Classification of plastics

The plastic is usually classified depending on the type of resin used for its manufacture. Based on their thermal behavior, resins are classified into two types

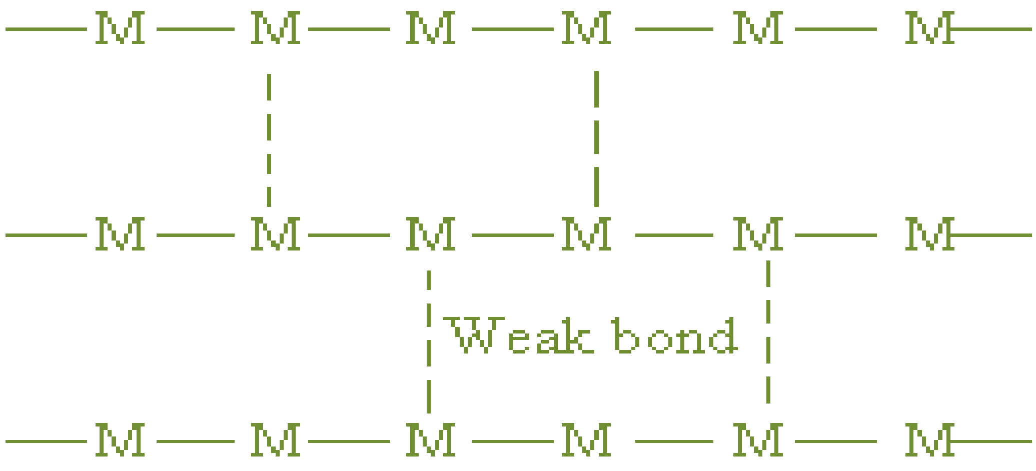
- ✓ Thermoplastic resins and
- ✓ Thermosetting resins

Thermoplastic resins

These are resins which soften on heating and become hard and rigid on cooling. By a reheating to a suitable temperature, they can be softened, reshaped and reused.

They are soft, weak and less brittle. They are soluble in some organic solvents because of their weak intermolecular forces.

Example: poly ethylene, polyvinyl chloride.

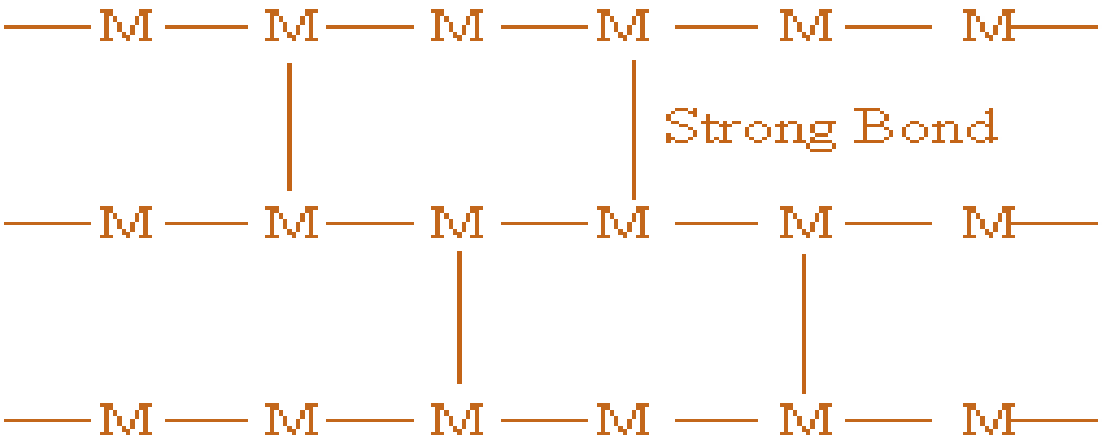


Thermoplastic resin

Thermosetting resins

These are resins which harden or gain strength on heating and once set, they cannot be softened again.

Ex: Bakelite, Poly ester.



Thermosetting resin

They are hard, strong and more brittle. They are insoluble in almost all organic solvents because of their strong bonds and cross linking

Difference between Thermoplastic resins and Thermosetting resins

S. No	Thermoplastic resins	Thermosetting resins
1	They are formed by addition polymerisation	They are formed by condensation polymerisation
2	They consist of linear – long chain polymers	They consist of three dimensional net work structures.
3	They are soften on heating	They do not soften on heating
4	They are soft, weak and less brittle	They are hard, strong and more brittle
5	They are soluble in some organic solvents because of their weak intermolecular forces.	They are insoluble in almost all organic solvents because of their strong bonds and cross linking.
6	Example: poly ethylene, polyvinyl chloride.	Example: Bakelite, Poly ester

INDIVIDUAL POLYMERS

Preparation, properties and uses of various industrial polymers like PVC, Teflon, Poly carbonate, Polyurethane, Nylon-6.6 and Poly ethylene terephthalate (PET) are discussed in detail below.

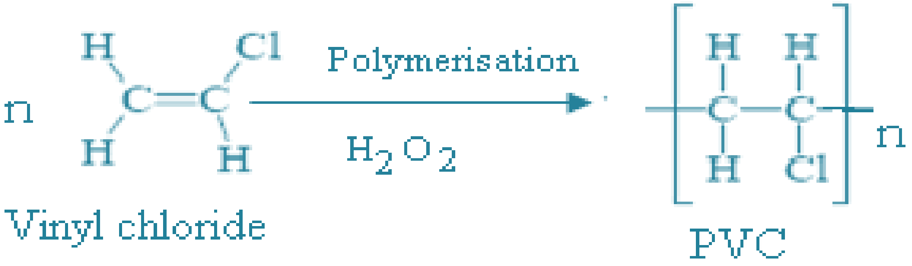
Polyvinyl Chloride (PVC)

Preparation: Preparation of PVC involves the following two steps.

Step-I: Vinyl chloride is prepared by treating acetylene with hydrogen chloride at 60 – 80^{0}C in the presence of metal chloride as catalyst.

$$CH \equiv CH + HCl \longrightarrow CH_2 = CHCl$$

Step-II: Polyvinyl chloride is obtained by heating water emulsion of vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide under pressure.



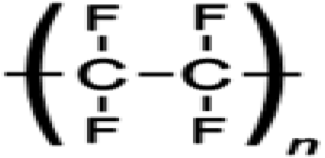
Properties:

1. PVC is colourless, odourless and chemically inert powder.
2. It undergoes degradation in presence of heat (or) light.
3. It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons such as ethyl chloride.
4. It tends to be rather hard and rigid due to chlorine present in polymers.

Uses:

It is used to make a wide range of things including pipes, plastic windows, electrical cable insulations, sheet materials for flooring and other uses, footwear, clothing, table cover and rain coat.

.**Teflon** (Poly tetrafluoroethene) (Fluon)

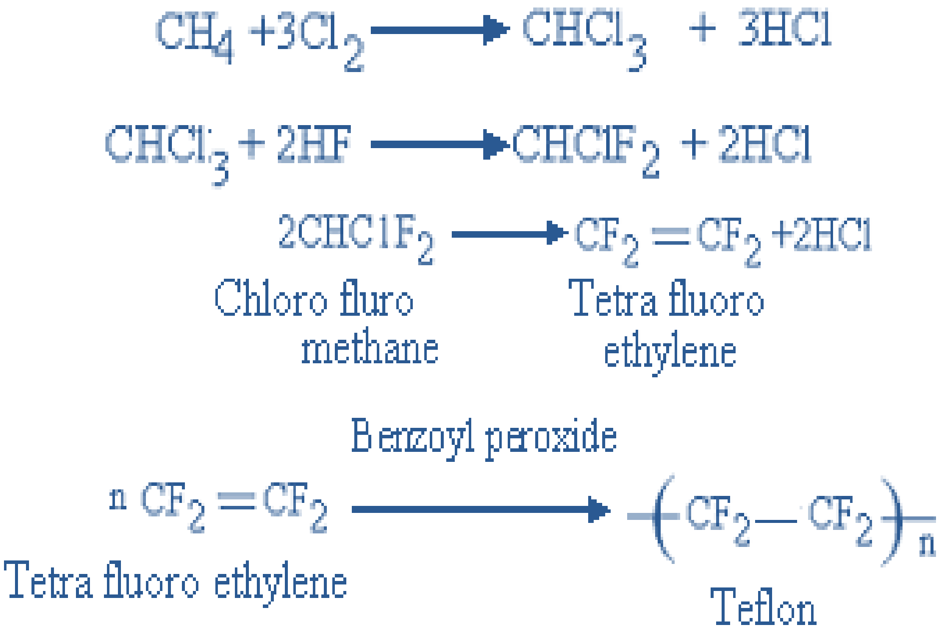


$$\left(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right)_n$$

Teflon was first discovered by Roy J. Plunkett in 1938 and introduced as a commercial product in 1946.

Preparation:

It is prepared by the polymerisation of tetrafluoroethylene in the presence of benzoyl peroxide under pressure.



$$CH_4 + 3Cl_2 \longrightarrow CHCl_3 + 3HCl$$

$$CHCl_3 + 2HF \longrightarrow CHClF_2 + 2HCl$$

$$2CHClF_2 \longrightarrow CF_2{=}CF_2 + 2HCl$$

$$n\,CF_2{=}CF_2 \xrightarrow{\text{Benzoyl peroxide}} \left(CF_2-CF_2 \right)_n$$

Properties:

1. It has high density (2200 kg m^{-3}) but low dielectric constant and co efficient of friction.

2. Teflon is extremely tough, flexible material possessing high softening point (about 350^0 C) due to the presence of fluorine atoms.

3. It possesses extremely good electrical and mechanical properties

4. It is chemically resistant towards all chemicals (except hot alkali metal & F)

5. It is very good corrosion resistant cooling materials.

Uses:

1. It is used for making gaskets, packing, pumps parts, tanks linings, etc.

2. It is used as a very good electrical insulating material in motors, cables, transformers, electrical fittings

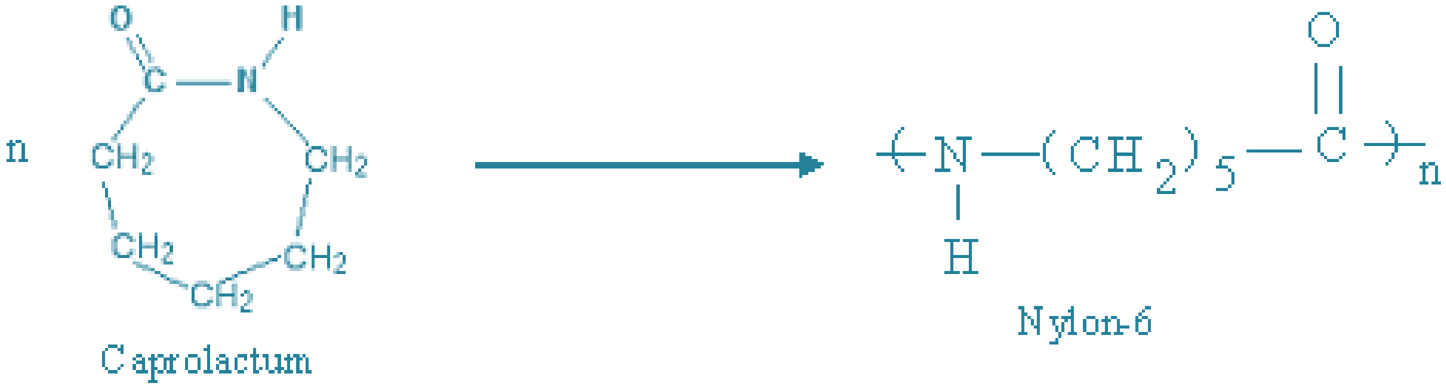
3. It is also used for making non-lubricating bearings, chemical carrying pipes, etc.

4. It is used in making non-sticking stop cocks for burettes and kitchen materials.

Polyamides:

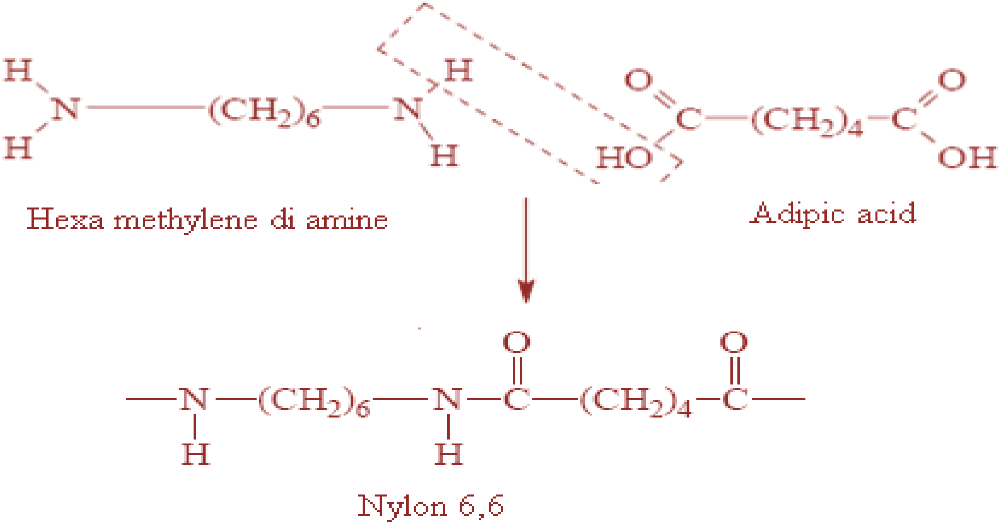
Nylon-6

Nylon-6 is prepared by self polymerisation of Caprolactum.



Nylon 6, 6

It is prepared by condensation of Hexamethylene Diamine and adipic acid



Nylon -11

It is prepared by self –condensation of ω-amino undecanoic acid.

$$n\ H_2N-(CH_2)_{10}-COOH \xrightarrow{\text{Self-condensation}} -\!\left(\overset{H}{\overset{|}{N}} -(CH_2)_{10}- \overset{O}{\overset{\|}{C}} \right)_n\!-$$

Properties

✓ Nylons are insoluble in common organic solvents but soluble in phenol and formic acid.

✓ They possess high thermal stability and good abrasion resistance.

✓ They are translucent, whitest, horny and high melting polymers.

✓ They possess low coefficient of friction.

Uses:

✓ Nylons are used for making filaments for ropes, bristles for tooth-brushes and films, etc.

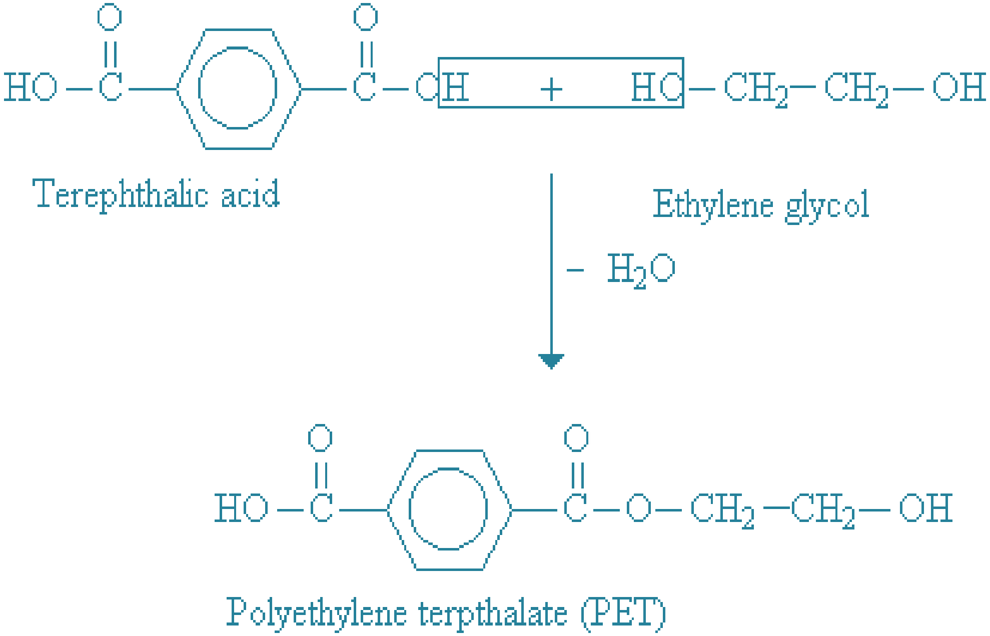
✓ Nylon-6 and Nylon -11 are mainly used for moulding purpose for gears, bearings, etc.

✓ Nylon 6.6 is used for fibers, which is used making socks, dresses, carpets, etc.

POLYESTER RESINS

Polyethylene terephthalate (PET)

The commonly known polyester resin is called as polyethylene terephthalate (PET), which is commercially known as Terylene or Dacron. It is produced by the condensation of ethylene glycol and terephthalic acid.



Properties:

1. It is highly resistant to acids, but less resistant to alkalies because of the presence of – OH groups
2. The fiber has high stretch and wrinkle resistance

Uses:

1. It is a good fiber forming resin material used in textiles.
2. It is also used in aircrafts, helmets, and battery boxes.

Rubber

Rubbers (or) elastomers are non-crystalline high polymers, which have elastic properties and other –like properties.

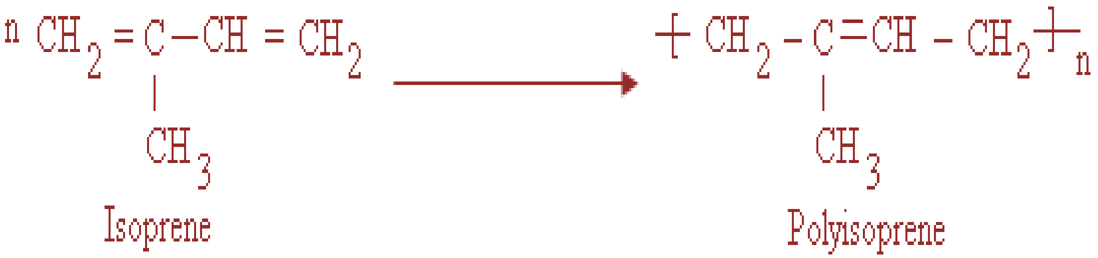
Types of rubbers

Rubbers can be obtained from two sources, which may be natural or artificial.

1. Natural rubber
2. Synthetic rubber)

Natural rubbers

Natural rubber is obtained from the milk (latex) of trees as “Hevea brasiliensis” which is a dispersion of isoprene. During the treatment of latex, these isoprene molecules undergo polymerisation to form long coiled chain of poly isoprene.



$$n\ CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2 \longrightarrow \left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2\right]_n$$

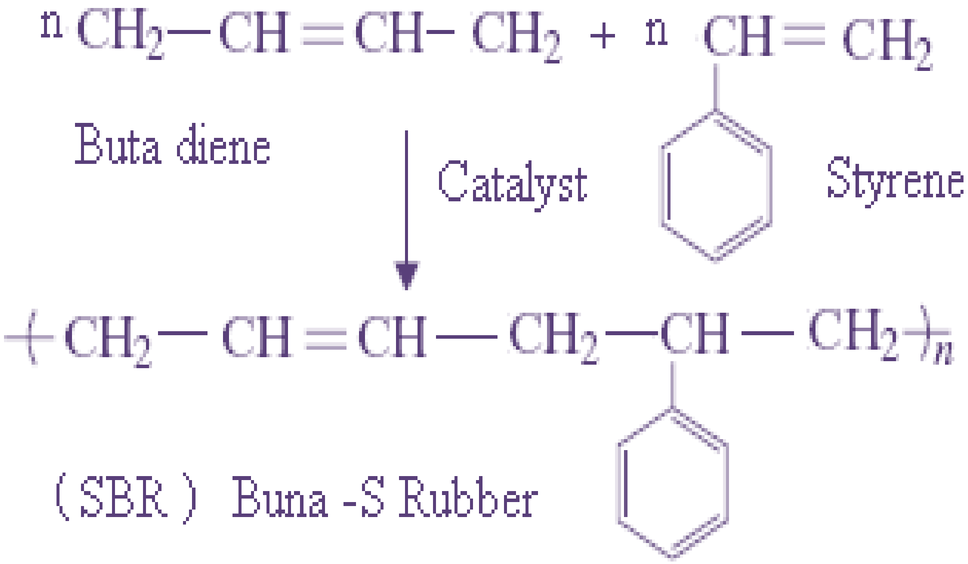
Synthetic rubber

An elastomer (synthetic rubber) is a vulcanisable man made rubber like polymer, which is superior to natural rubber in certain properties.

Ex: 1 Polybutadiene co-styrene polymer or Buna –S rubber (GR-S)

The Buna–S rubber is the first synthetic rubber developed during the time of Second World War by U.S. in order to overcome the scarcity of natural rubber.

It is prepared by the co-polymerisation of butadiene and styrene.

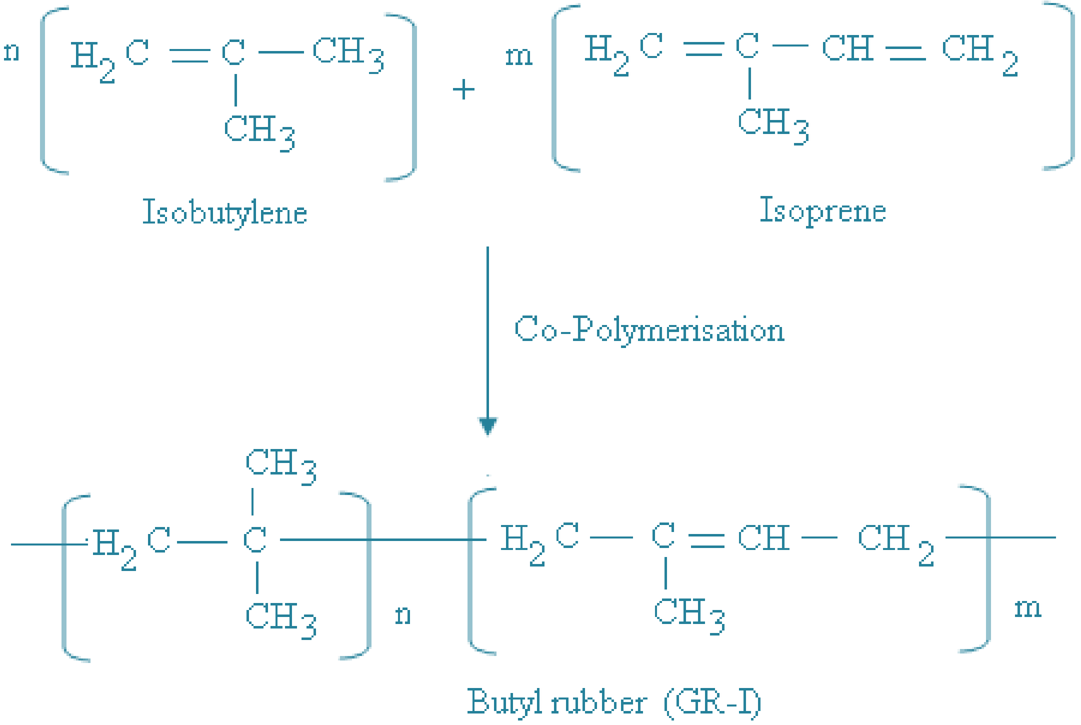


Uses:

1. It is used for the manufacture of motor tyres.
2. It can also be used for foot wear soles, gaskets, cable insulation, tank lining etc.

Ex: 2 Butyl rubber (GR-I)

Butyl rubber is made by the co-polymerisation of isobutylene with small amount of isoprene.



Properties:

1. It shows extremely low permeability to air and other gases.

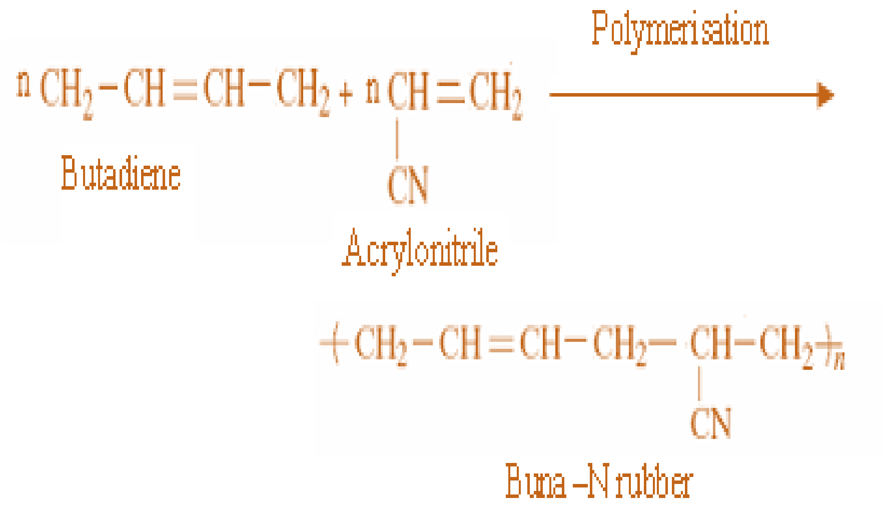
2. It also posses resistance to heat, Mineral acids, Polar solvents etc.

Uses:

1. It is used in making cycle and automobile tubes.
2. It also used for making hoses, Conveyor belts, insulating cables etc.

Ex: 3 Nitrile ruber or Buna –N rubber (GR – A):

The Buna –N rubber is prepared by the co-polymerisation of butadiene with acrylonitrile.



Properties and Uses

1. It has good resistance to heat, sunlight, acids, chemicals, etc.
2. It is mainly used in making conveyor belts, aircraft components, gaskets, hoses, tank linings, automobile parts etc.

Draw backs of raw rubber

✓ It is plastic in nature, i.e., it becomes soft at high temperature and is too brittle at low temperature.

✓ It has poor strength and less durability.

✓ It has large water absorption capacity.

✓ It is non-resistant to non-polar solvents like benzene, vegetable &mineral oils.

✓ It is attacked by oxidation agents like HNO_3 ,H_2SO_4

✓ It swells and disintegrates gradually in organic solvents

Vulcanisation of rubber

Vulcanisation process is discovered by Charles Good in the year 1839. "*The properties of rubber can be improved by compounding it with some chemicals like sulphur, hydrogen sulphide, benzoyl chloride etc. under heat and pressure is called as Vulcanisation. But the most important additive is sulphur*".

Characteristics of vulcanisation

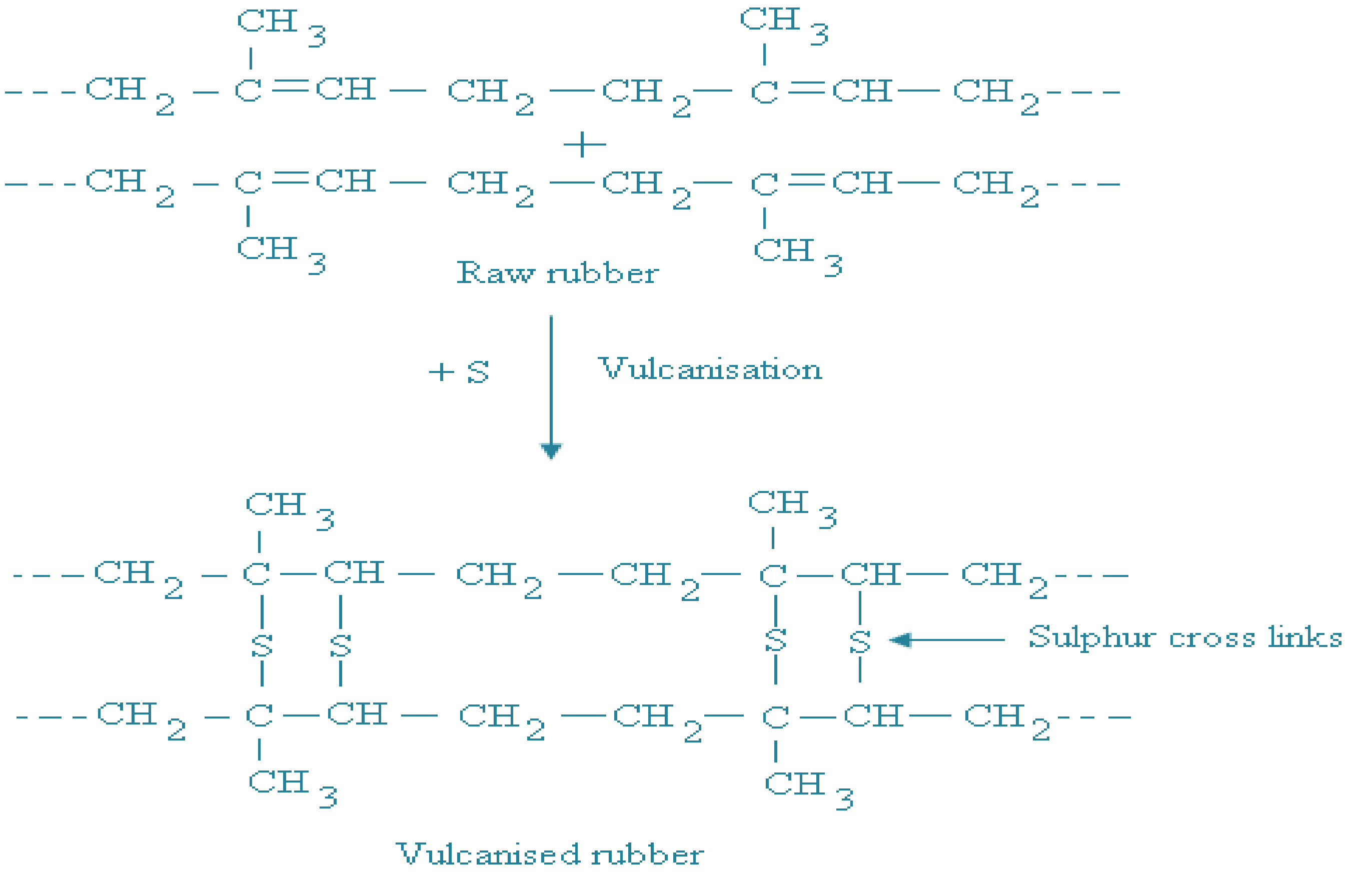
✓ To improve tensile strength, toughness and elasticity.

✓ Excellent resistance to swelling, temperature, chemical and oxidation process etc.

✓ It improves durability and resistance to wear and tear

Process of vulcanisation

The process of vulcanisation involves heating of raw rubber with sulphur about 100-140 ºC. The added sulphur forms cross covalent bond with the double bond of the isoprene units, which prevents intermolecular movement of rubber.



Biodegradable Polymers

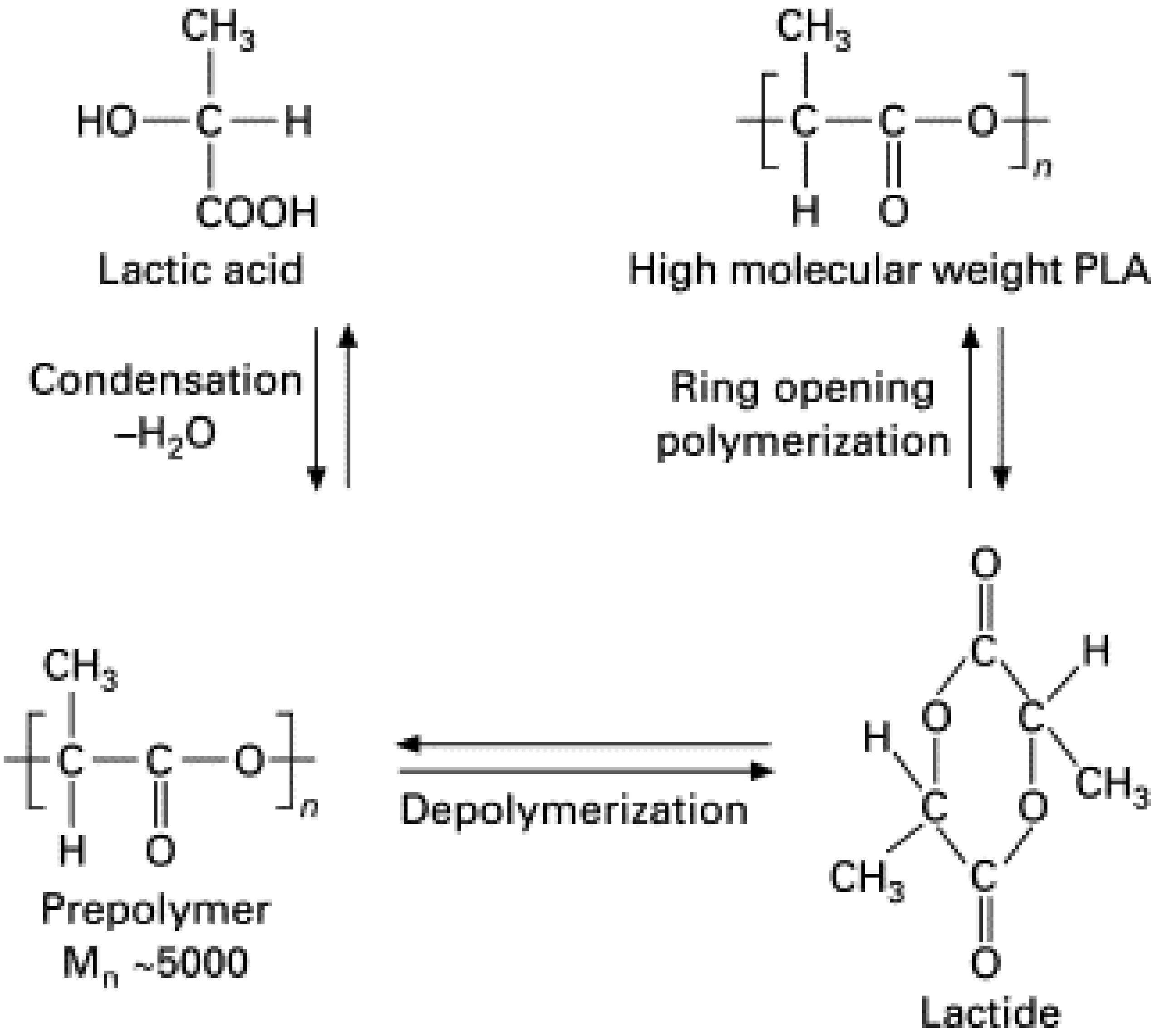
Biodegradable polymers are a special class of polymer that breaks down after its intended purpose by bacterial decomposition process to result in natural byproducts such as gases (CO2, N2), water, biomass, and inorganic salts.

- These polymers are found both naturally and synthetically made, and largely consist of ester, amide, and ether functional groups
- Their properties and breakdown mechanism are determined by their exact structure
- These polymers are often synthesized by condensation reactions, ring opening polymerization, and metal catalysts

Properties of Biodegradable Polymers

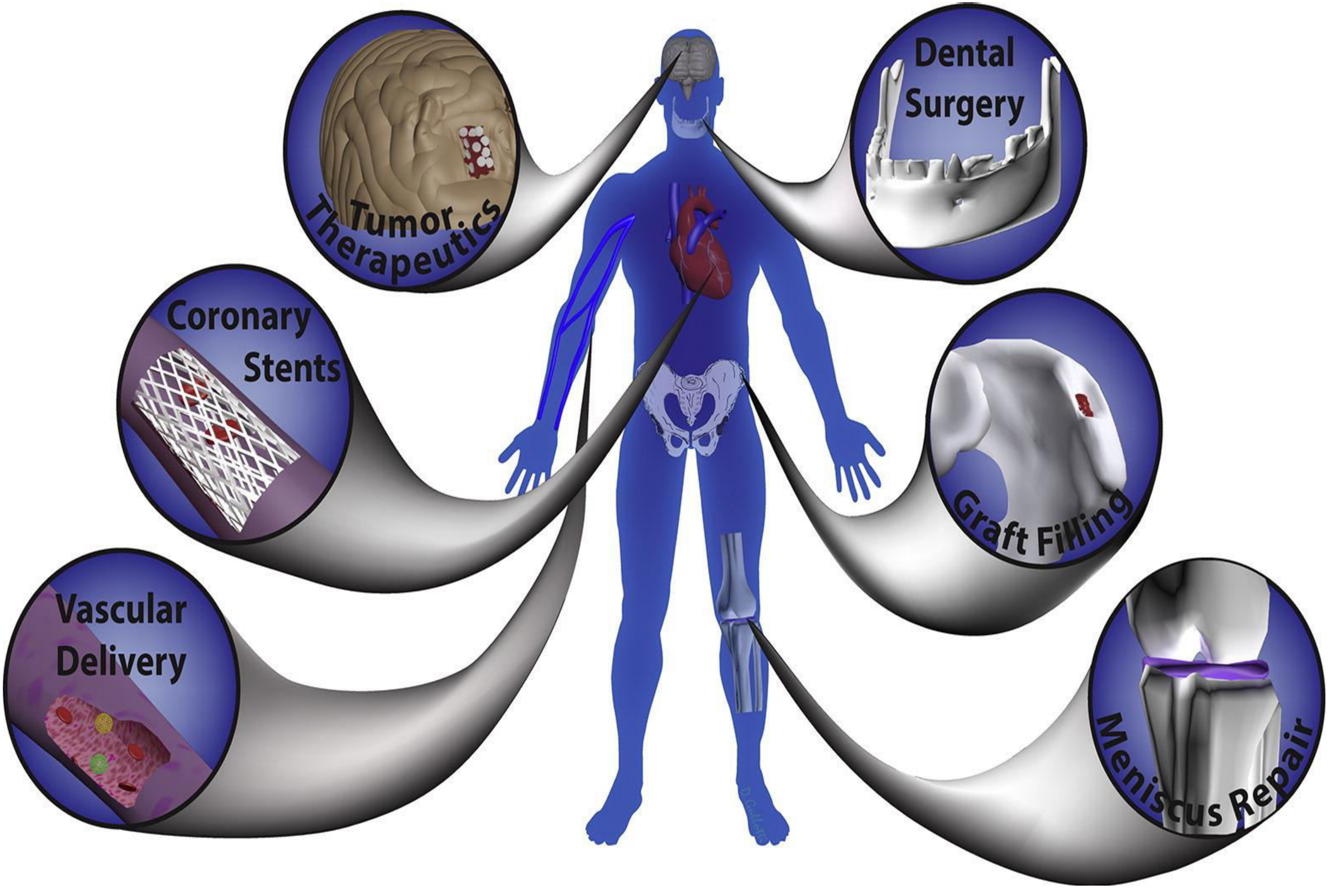
- Biodegradable polymers should be stable and durable enough for use in their particular application
- Its have extremely strong carbon backbones that are difficult to break
- Crystallinity is often low as it also inhibits access to end groups
- non-toxic
- capable of maintaining good mechanical integrity until degraded
- capable of controlled rates of degradation

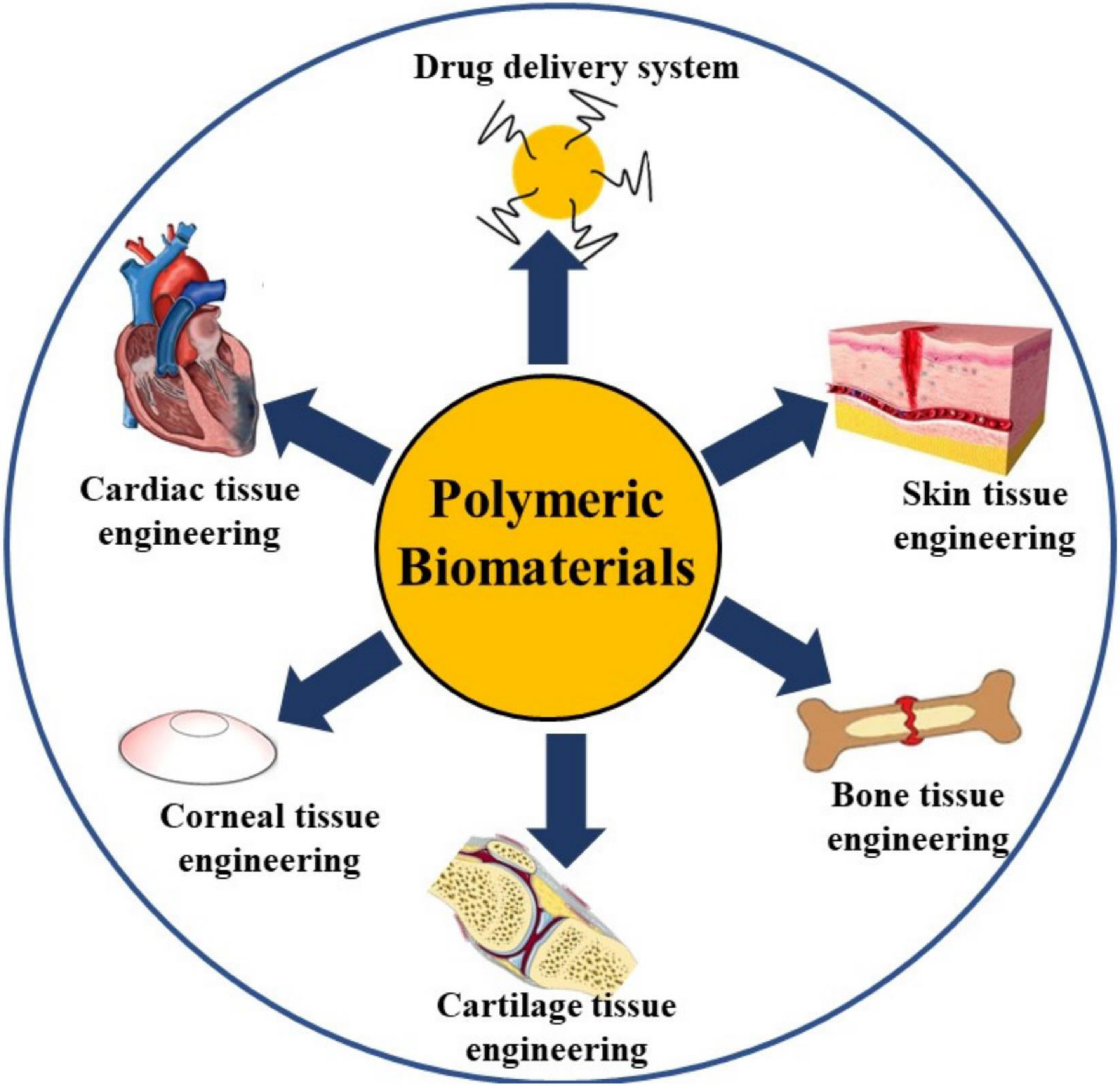
Synthesis of Poly lactic acid



Biomedical Applications of Poly lactic acid

- PLA has shown promise as a biomaterial in a plethora of healthcare applications such as tissue engineering or regenerative medicine, cardiovascular implants, dental niches, drug carriers, orthopedic interventions, cancer therapy, skin and tendon healing, and lastly medical tools / equipment
- It is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh
- PLA has emerged as an important polymeric material for biomedical applications on account of its properties such as biocompatibility, biodegradability, mechanical strength and process ability


Tumor Therapeutics
Dental Surgery
Coronary Stents
Graft Filling
Vascular Delivery
Meniscus Repair


Drug delivery system
Cardiac tissue engineering
Polymeric Biomaterials
Skin tissue engineering
Corneal tissue engineering
Bone tissue engineering
Cartilage tissue engineering

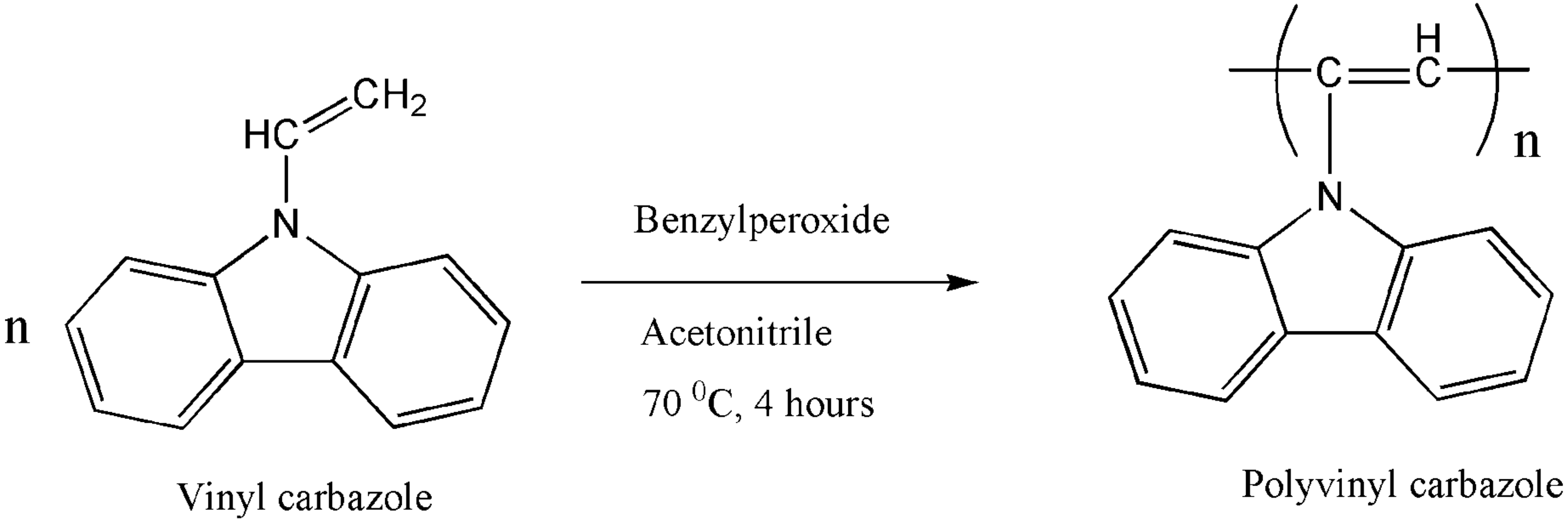
Photoconducting Polymers

Photoconductive polymers absorb electromagnetic radiation and produce an increase of electrical conductivity. Photoconductive polymers have been used in a wide variety of technical applications such as Xerography (electro photography) and laser printing.

There are two essential requirements for photoconductivity:

- The absorbed photons must induce the formation of charge carriers
- The charge carriers must be mobile, i.e. they must be able to move independently under the influence of an external electric field

Synthesis of Polyvinyl carbazole



Physical properties:

- PVK can be used at temperatures of up to 160 - 170 °C and is therefore a temperature-resistant thermoplastic
- The electrical conductivity changes depending on the illumination
- For this reason, PVK is classified as a semiconductor or photoconductor
- The polymer is extremely brittle, but the brittleness can be reduced by copolymerization with a little isoprene

Chemical properties:

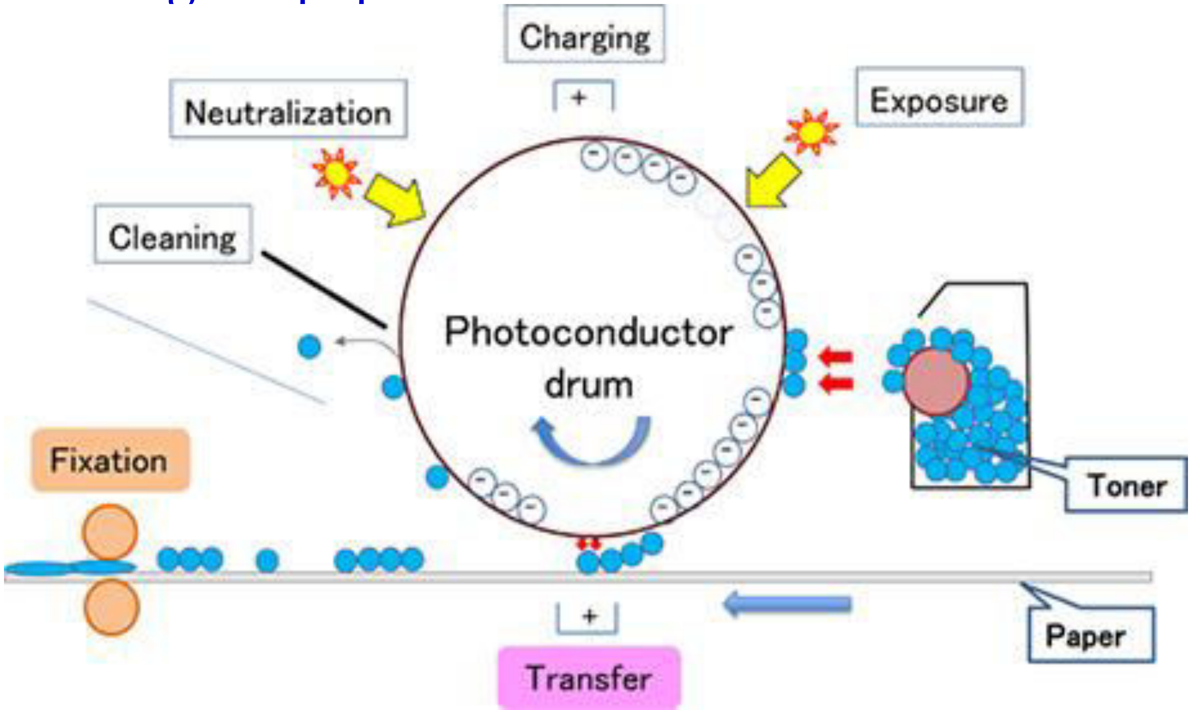
- Polyvinylcarbazole is soluble in aromatic hydrocarbons, halogenated hydrocarbons and ketones
- It is resistant to acids, alkalis, polar solvents and aliphatic hydrocarbons
- The addition of PVC to other plastic masses increases their temperature resistance

Application:

- Due to its high price and special properties, the use of PVC is limited to special areas
- It is used in insulation technology electro photography (e.g. in copiers and laser printers) organic light-emitting diodes and photovoltaic devices
- In addition, PVC is a well researched component in photorefractive polymers and therefore plays an important role in holography
- PVC is also used in laser printing

Photoconducting Polymers in Laser Printing

- Laser printing is an electrostatic digital printing process
- It produces high-quality text and graphics by repeatedly passing a laser beam back and forth over a negatively charged cylinder called a "drum" to get a charged image
- The drum can selectively collect electrically charged powdered ink (toner), and transfers the image to paper



That’s All

UNIT IV

NON CONVENTIONAL ENERGY SOURCES

TYPES OF ENERGY

▪ RENEWABLE ENERGY:

Renewable energy can be generated continuously practically without decay of source.

Some examples are :

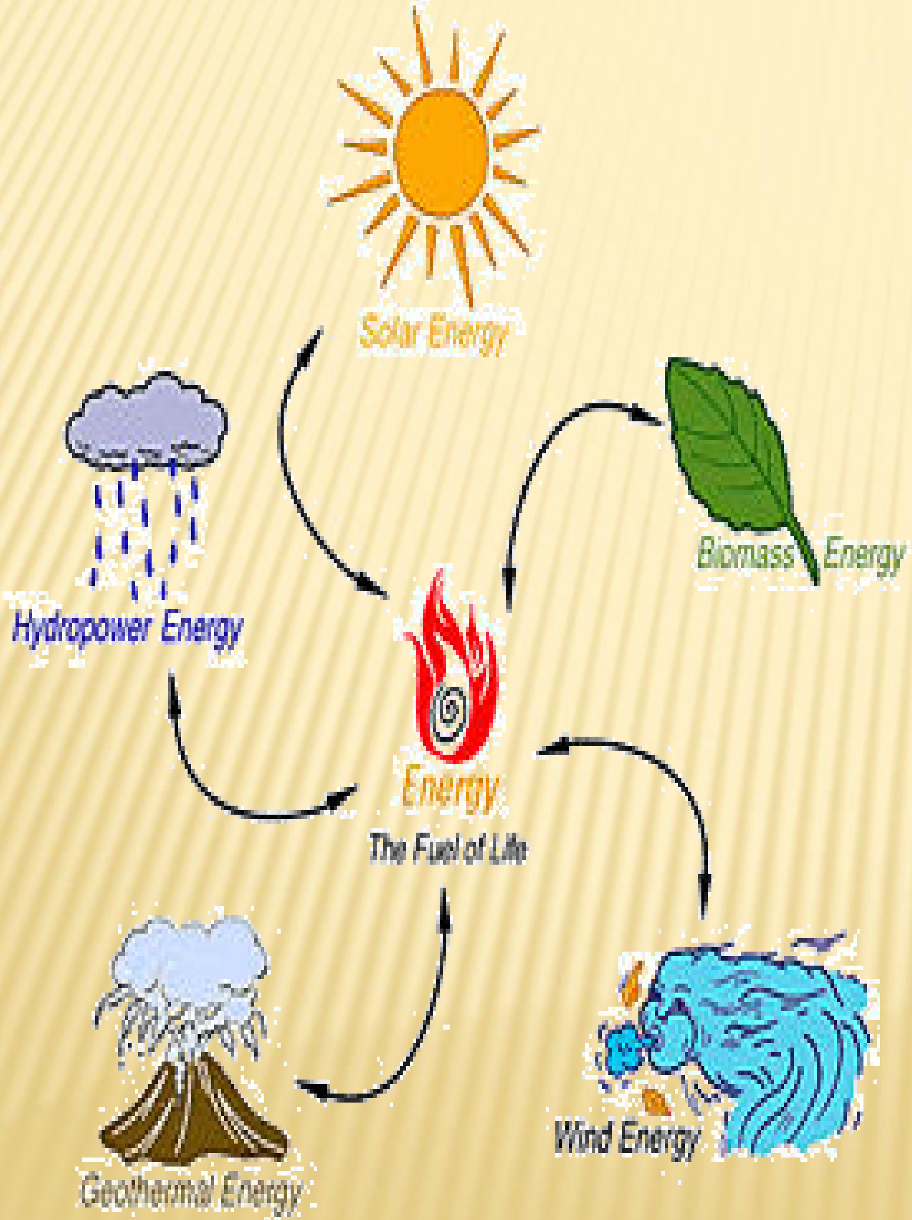
- Solar energy , Wind energy , Geothermal energy , Hydro energy.

NON-RENEWABLE ENERGY:

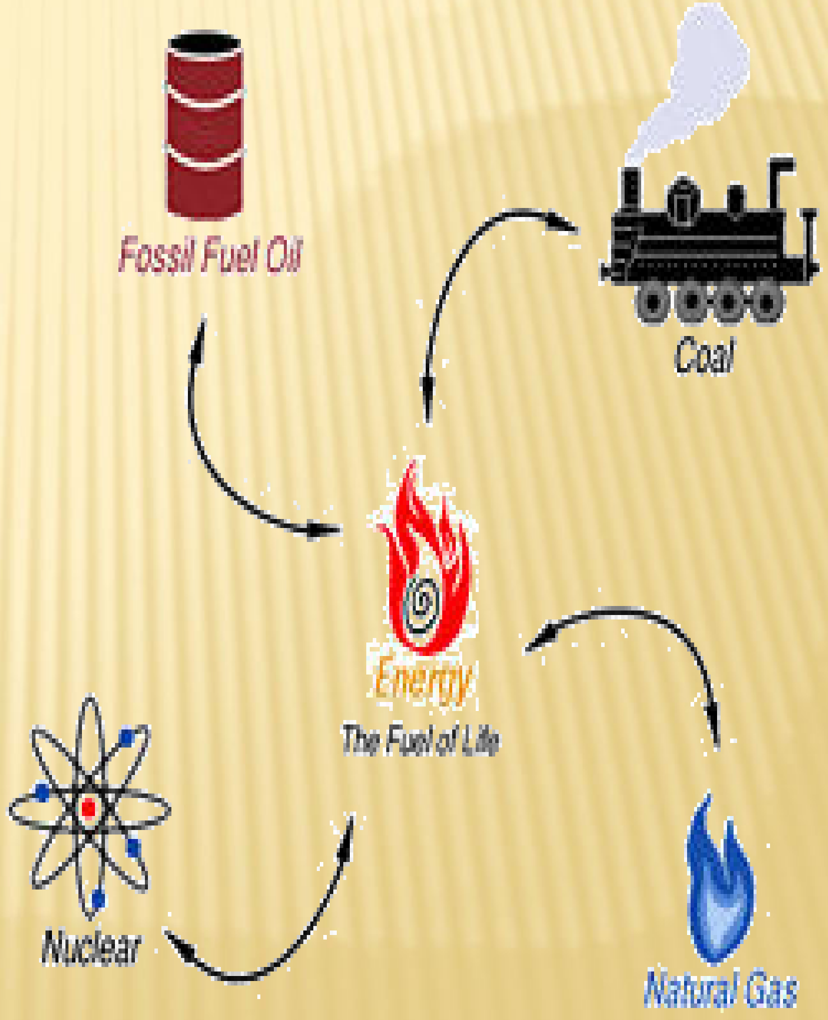
Non-renewable energy is energy that comes from the ground and is not replaced in a relatively short amount of time.

e.g. energy generated from combustion of fossil fuels , coal , gas etc.

Renewable Energy



Non-Renewable Energy



THE GENERATION OF ELECTRICAL POWER

CONVENTIONAL ENERGY

PEAT

OIL

COAL

NATURAL GAS

NUCLEAR ENERGY

ALTERNATIVE ENERGY

WIND POWER

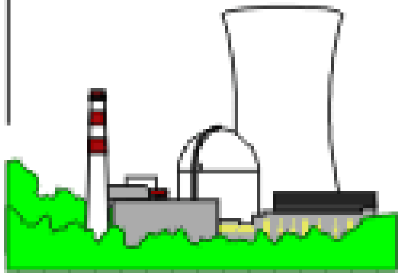
SOLAR POWER

WAVE POWER

TIDAL POWER

HYDRO POWER

BIOFUELS



- **Nuclear Energy** – Energy released during nuclear fission

NUCLEAR FISSION

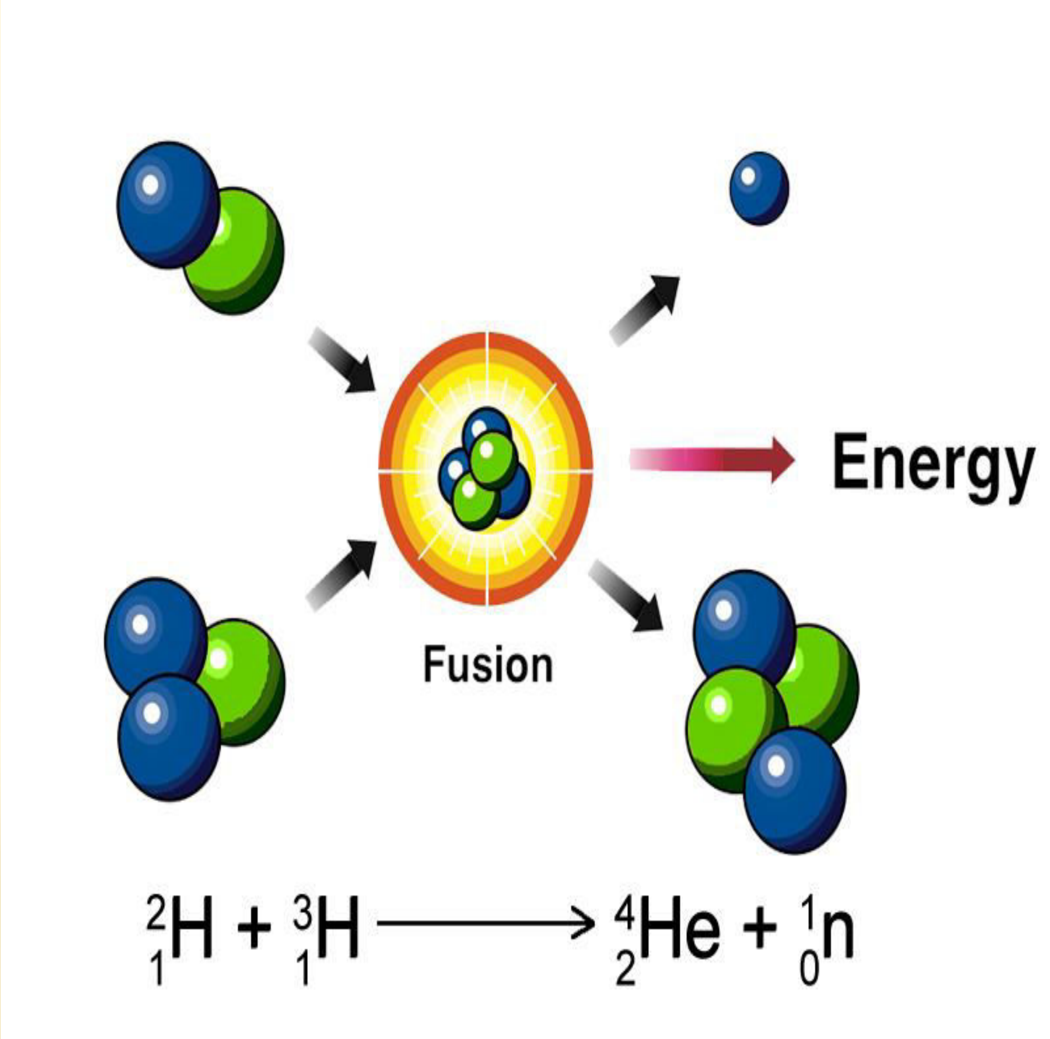
- The process of splitting of heavier nucleus into smaller nuclei with the liberation of large amount of energy by the bombardment of slow moving neutrons.
- During nuclear fission, neutrons are released.

$$ {}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}\mathrm{n} $$

NUCLEAR FISSION

NUCLEAR FUSION

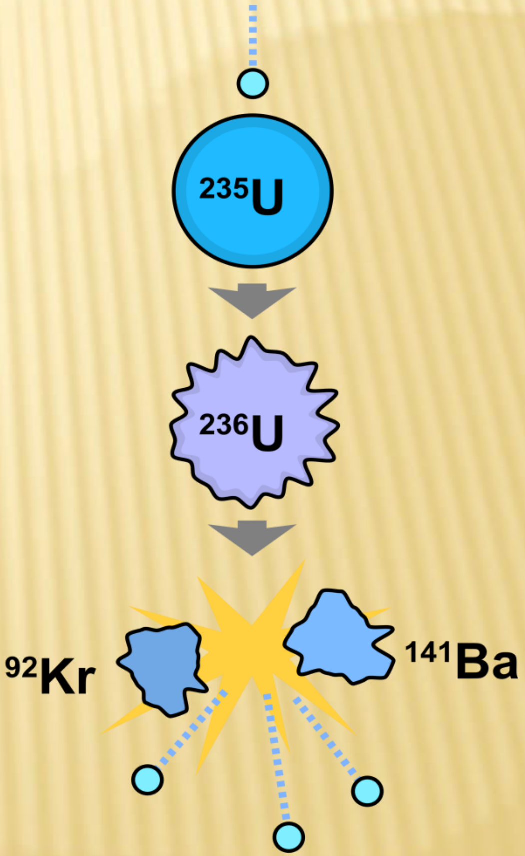
- **Nuclear fusion** is a nuclear reaction in which two or more atomic nuclei collide at a very high speed and join to form a new type of atomic nucleus.



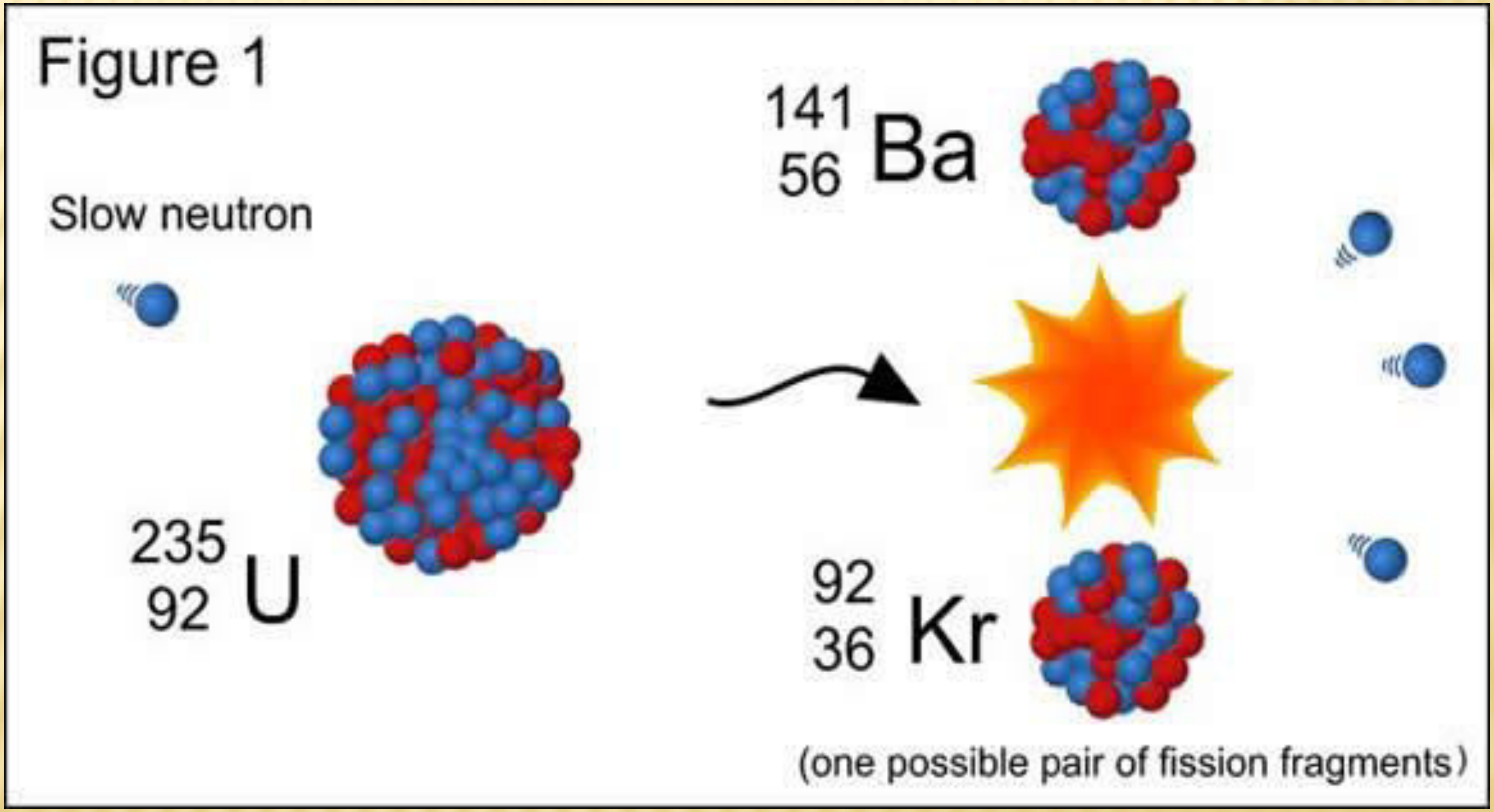
$${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n$$

NUCLEAR FISSION-MECHANISM

- U^{235} – bombarded by thermal slow moving neutrons
- Unstable U^{236} is formed - splits into approx. 2 equal nuclei
- Releases huge amount of energy and neutrons.



NUCLEAR FISSION-PROCESS

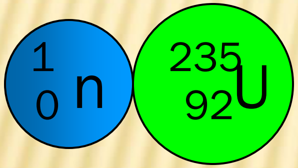


FISSION PROCESS…

- U^{235} – bombarded by thermal slow moving neutrons

FISSION PROCESS…

- The neutron strikes the nucleus which then captures the neutron

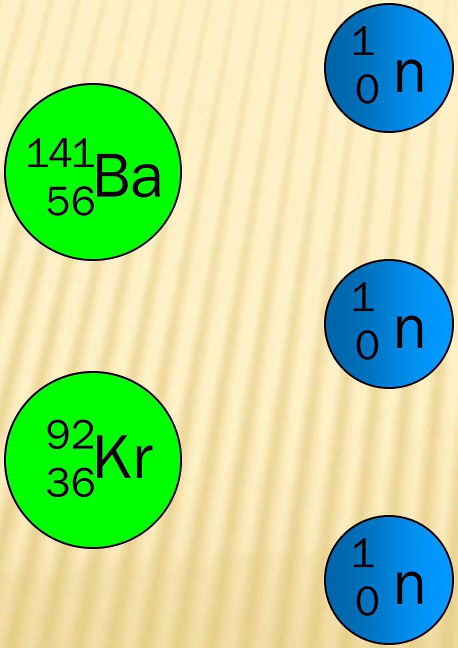


FISSION PROCESS…

- The nucleus changes from being uranium-235 to uranium-236 as it has captured a neutron.
- The uranium-236 nucleus formed is very unstable

FISSION PROCESS…

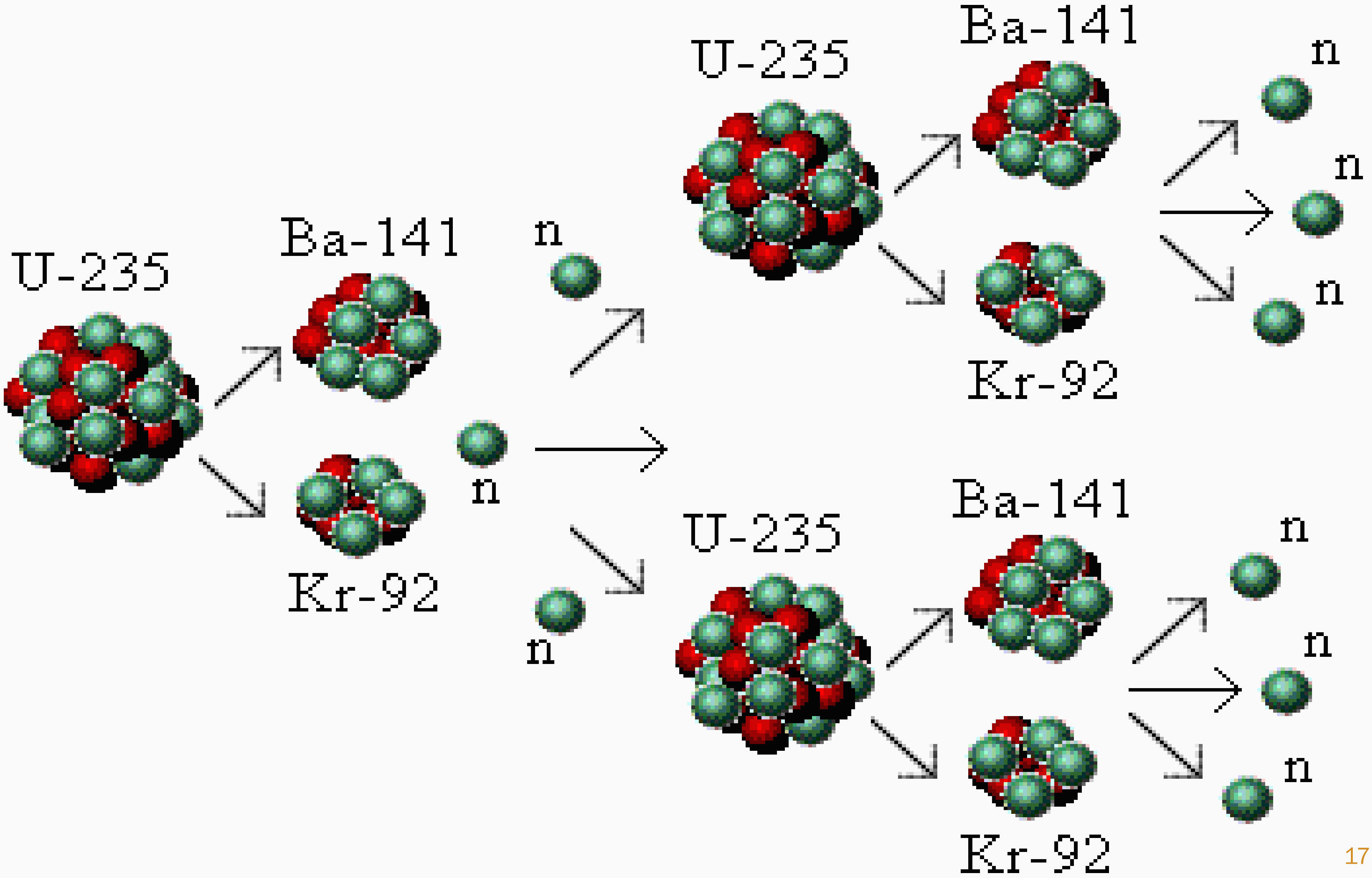
- It then splits into 2 fission fragments and releases neutrons



NUCLEAR FISSION-CHARACTERISTICS

- Heavy nucleus – bombarded with slow moving neutrons.
- **Splits** into approx. 2 or more nuclei
- 2 or more **neutrons** released
- Huge amount of **energy** is released
- Fission fragments are **radioactive** – emits α, β, and γ radiations
- Atomic weight of fission fragments – 70-160
- Fission reactions – **self propagating chain reactions**.

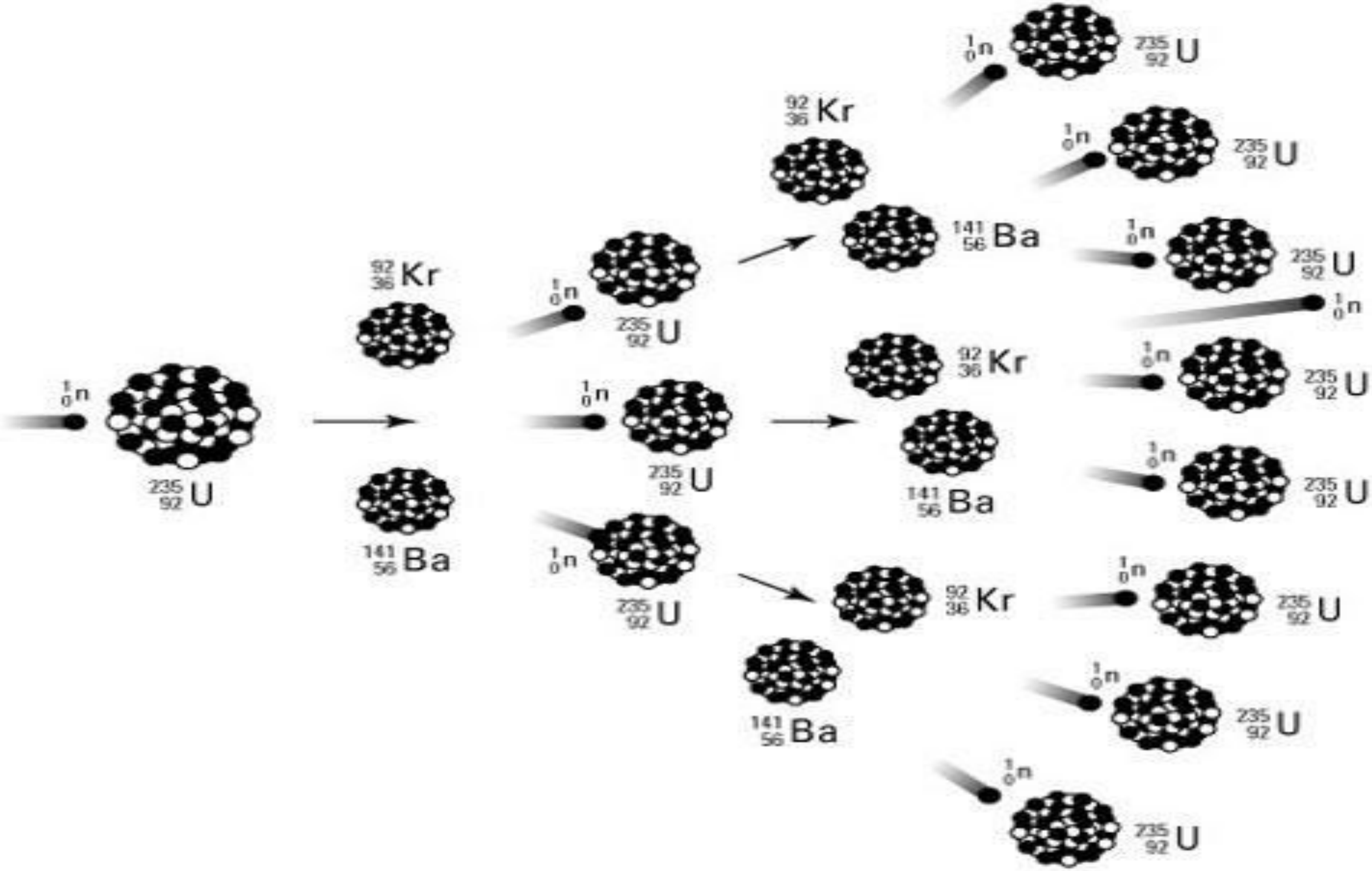
CONTD….



NUCLEAR CHAIN REACTION

- **Self sustaining chain reaction** with the release of huge amount of energy – Nuclear chain reaction
- A chain reaction refers to a process in which **neutrons** released in fission produce an additional fission in another nucleus.
- This nucleus in turn produces neutrons, and the process repeats. The process may be controlled (nuclear power) or uncontrolled (nuclear weapons).

CONTD….



$^{1}_{0}n$
$^{235}_{92}U$
$^{92}_{36}Kr$
$^{141}_{56}Ba$
$^{1}_{0}n$
$^{235}_{92}U$
$^{1}_{0}n$
$^{235}_{92}U$
$^{1}_{0}n$
$^{235}_{92}U$
$^{92}_{36}Kr$
$^{141}_{56}Ba$
$^{92}_{36}Kr$
$^{141}_{56}Ba$
$^{92}_{36}Kr$
$^{141}_{56}Ba$
$^{1}_{0}n$
$^{235}_{92}U$
$^{1}_{0}n$
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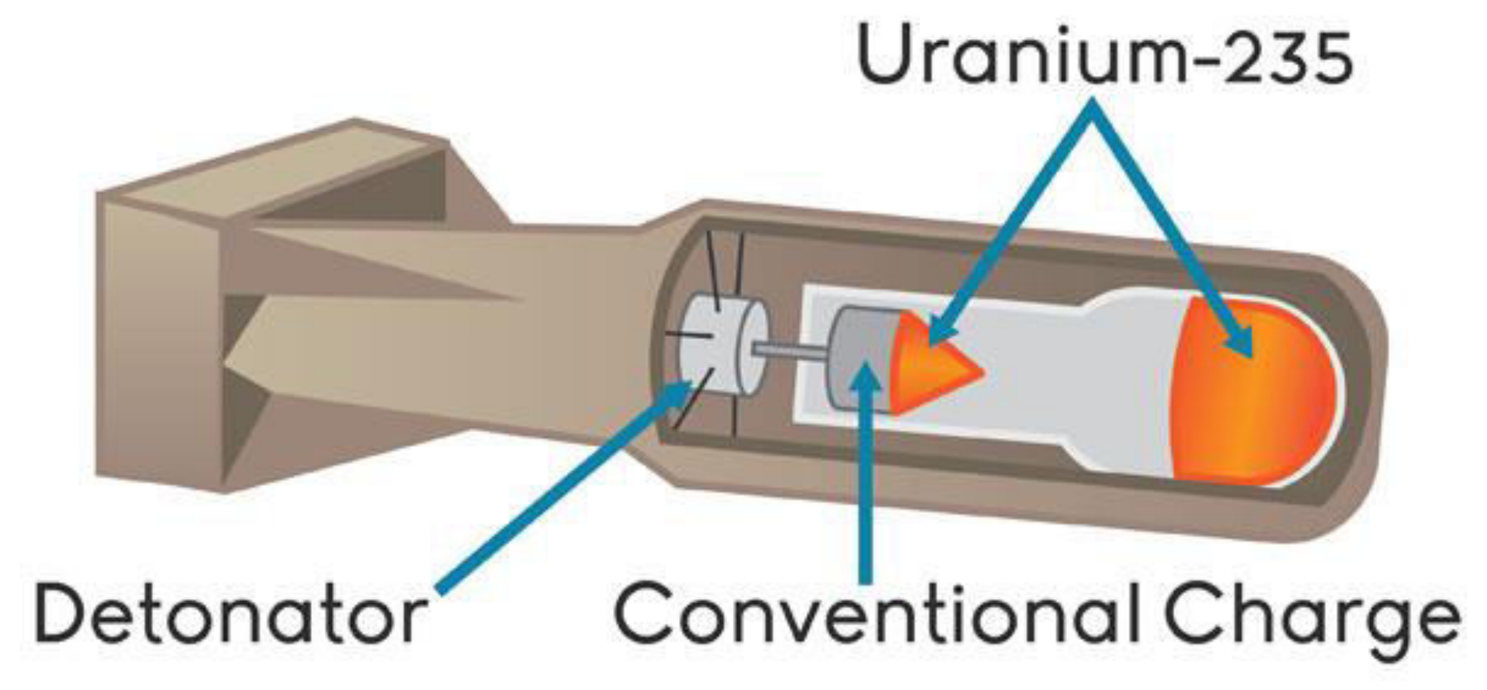
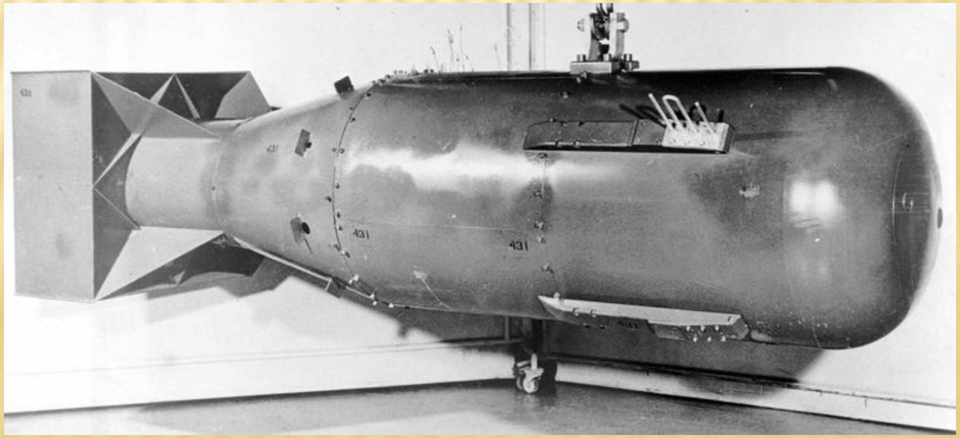
$^{235}_{92}U$
$^{1}_{0}n$
$^{235}_{92}U$
$^{1}_{0}n$
$^{235}_{92}U$
$^{1}_{0}n$
$^{235}_{92}U$
$^{1}_{0}n$
$^{235}_{92}U$

NUCLEAR CHAIN REACTION-CHARACTERISTICS

- Sufficient amount of U^{235} should be present to capture the neutrons
- **Critical Mass**: Min. amount of fissionable material required to continue the chain reaction
- Eg: Critical mass of **U^{235} – 1 kg to 100 kg**
- **Super critical mass** – mass of fissionable material is more than the critical mass
- **Sub-critical mass** – mass of fissionable material is less than the critical mass
- Mass > or < critical mass – hinder the propagation of chain reaction

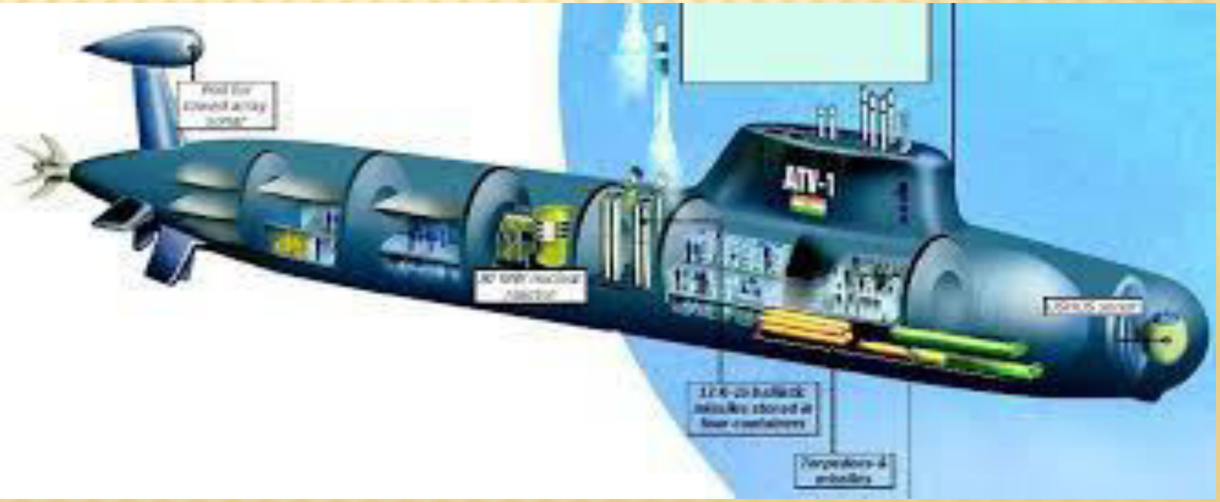
NUCLEAR BOMB





NIMITZ WAR SHIP

NUCLEAR SUBMARINE



WHY HUGE AMOUNT OF ENERGY????

- Due to loss in some mass…..
- Sum of masses of products is slightly < sum of masses of target species and bombarded neutrons.
- This loss in mass gets converted into energy, $E=mc^2$

WHY HUGE AMOUNT OF ENERGY????

1 amu = 1/12 of mass of carbon atom

1 amu = 1/12 * 12/N

(N=Avagadro no. = $6.023*10^{23}$)

1 amu = $1.66 * 10^{-27}$ kg

$$E=mc^2$$

$E = 1.66 * 10^{-27} \text{ kg} * (2.99 * 10^8 \text{ m/s})^2$

$= 1.49 * 10^{-10} \text{ kgm}^2\text{s}^2$

E = 931.47 MeV for 1 amu

WHY HUGE AMOUNT OF ENERGY????

- Loss in mass of U^{235} } = (mass of products– mass of reactants)

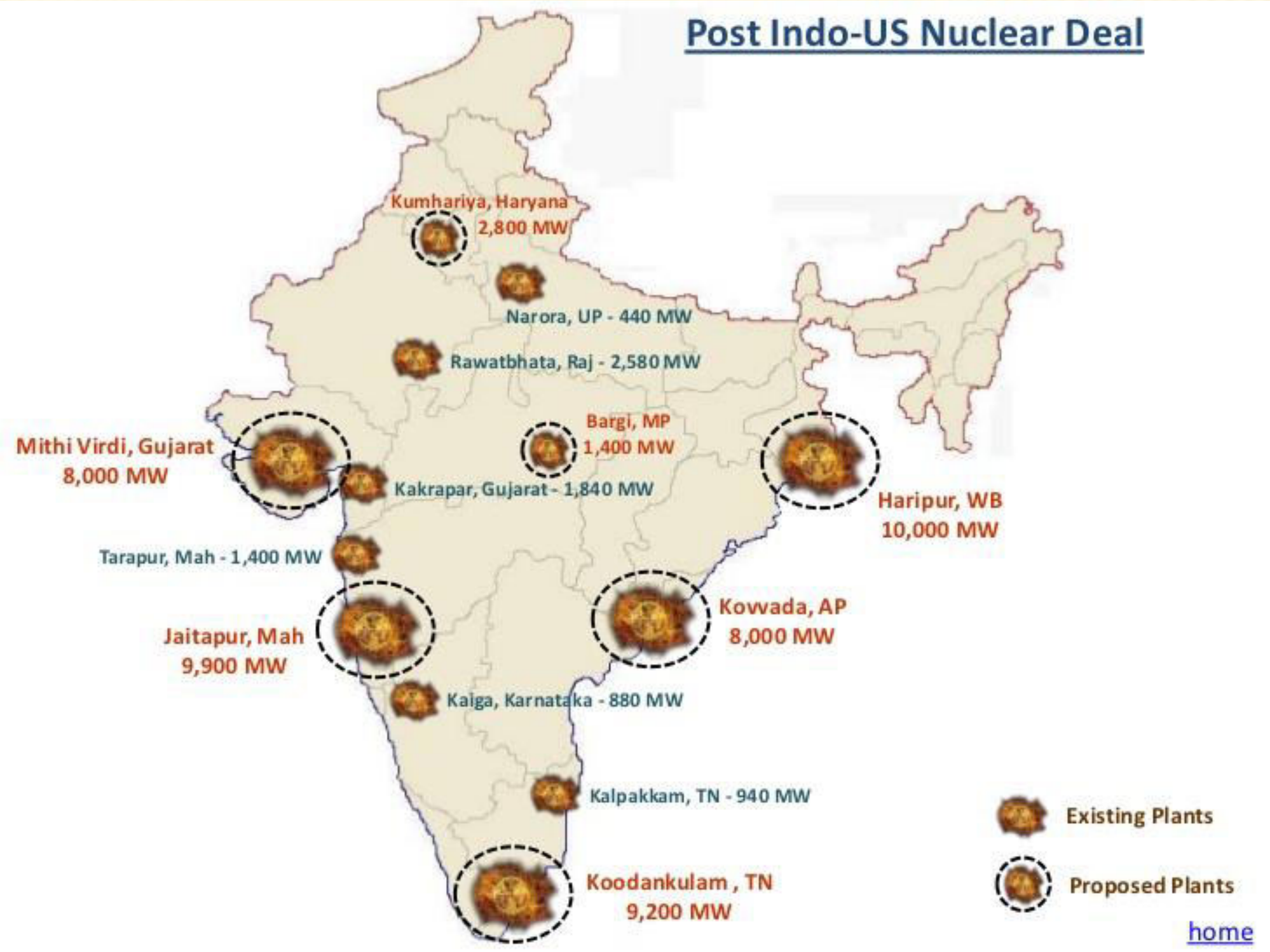
= 236.12 – 235.8

= 0.282 amu

Loss in 1 amu liberates 931.47 MeV

0.282 amu releases = 0.282 * 931.47 MeV

= 262.6 MeV


Post Indo-US Nuclear Deal
Kumhariya, Haryana
2,800 MW
Narora, UP - 440 MW
Rawatbhata, Raj - 2,580 MW
Bargi, MP
1,400 MW
Mithi Virdi, Gujarat
8,000 MW
Kakrapar, Gujarat - 1,840 MW
Haripur, WB
10,000 MW
Tarapur, Mah - 1,400 MW
Kovvada, AP
8,000 MW
Jaitapur, Mah
9,900 MW
Kaiga, Karnataka - 880 MW
Kalpakkam, TN - 940 MW
Koodankulam , TN
9,200 MW
Existing Plants
Proposed Plants
home

NUCLEAR REACTOR

Device used to carry out fission reaction under controlled conditions.

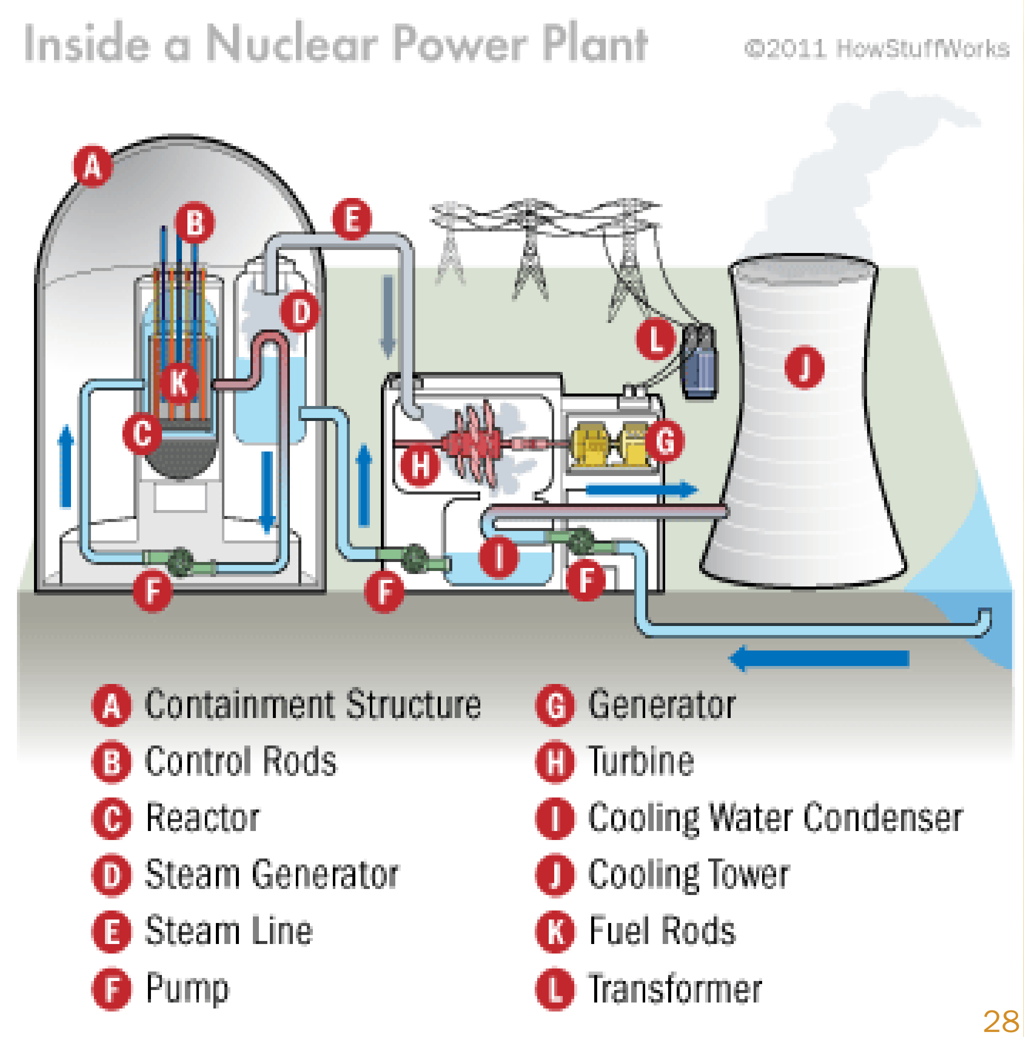
- **Components:**

1. Reactor Core
    - a. Fuel rods
    - b. Moderator
    - c. Coolant
    - d. Control rods
2. Reflector

3.Pressure vessel

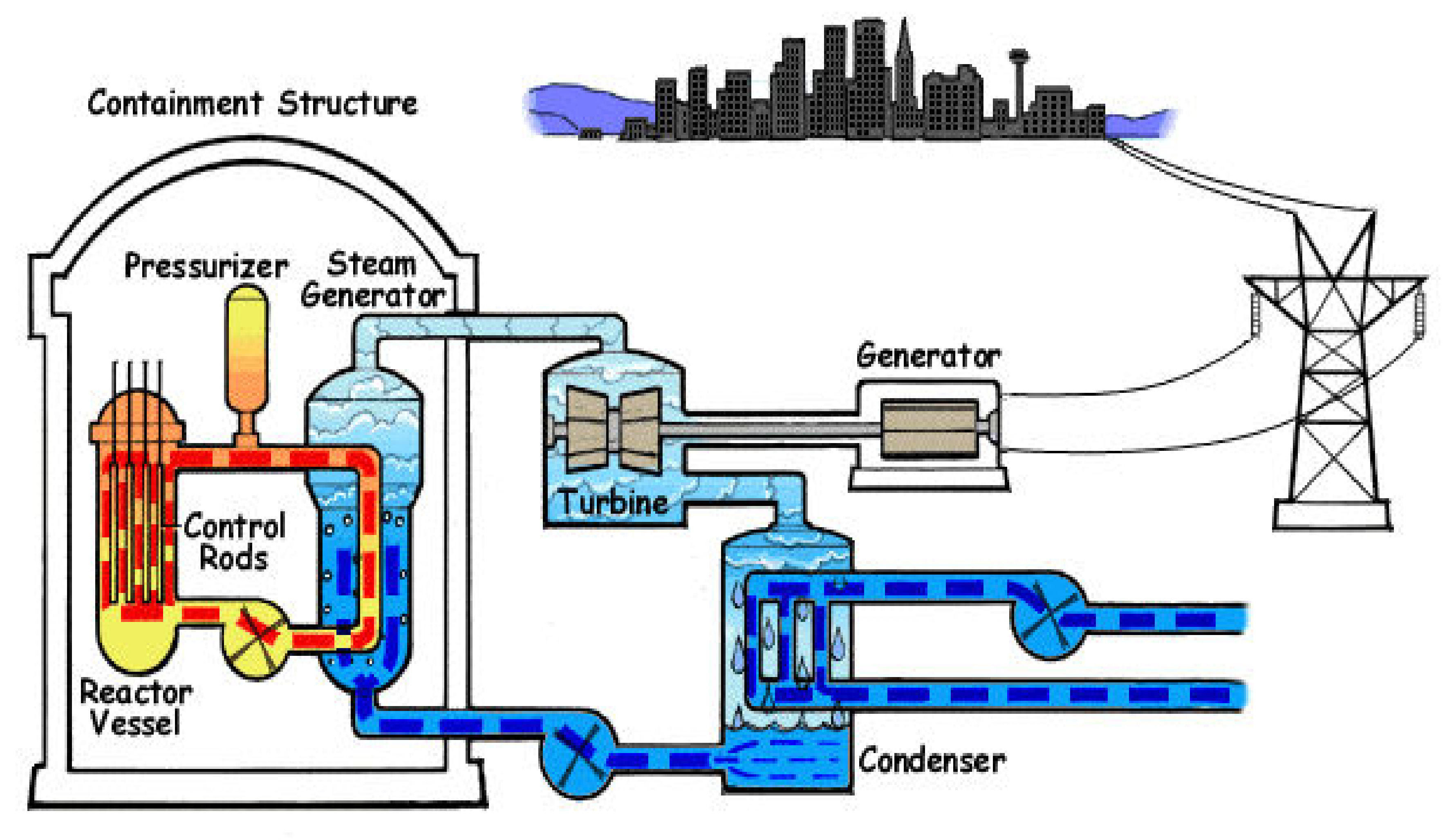
4. Shielding

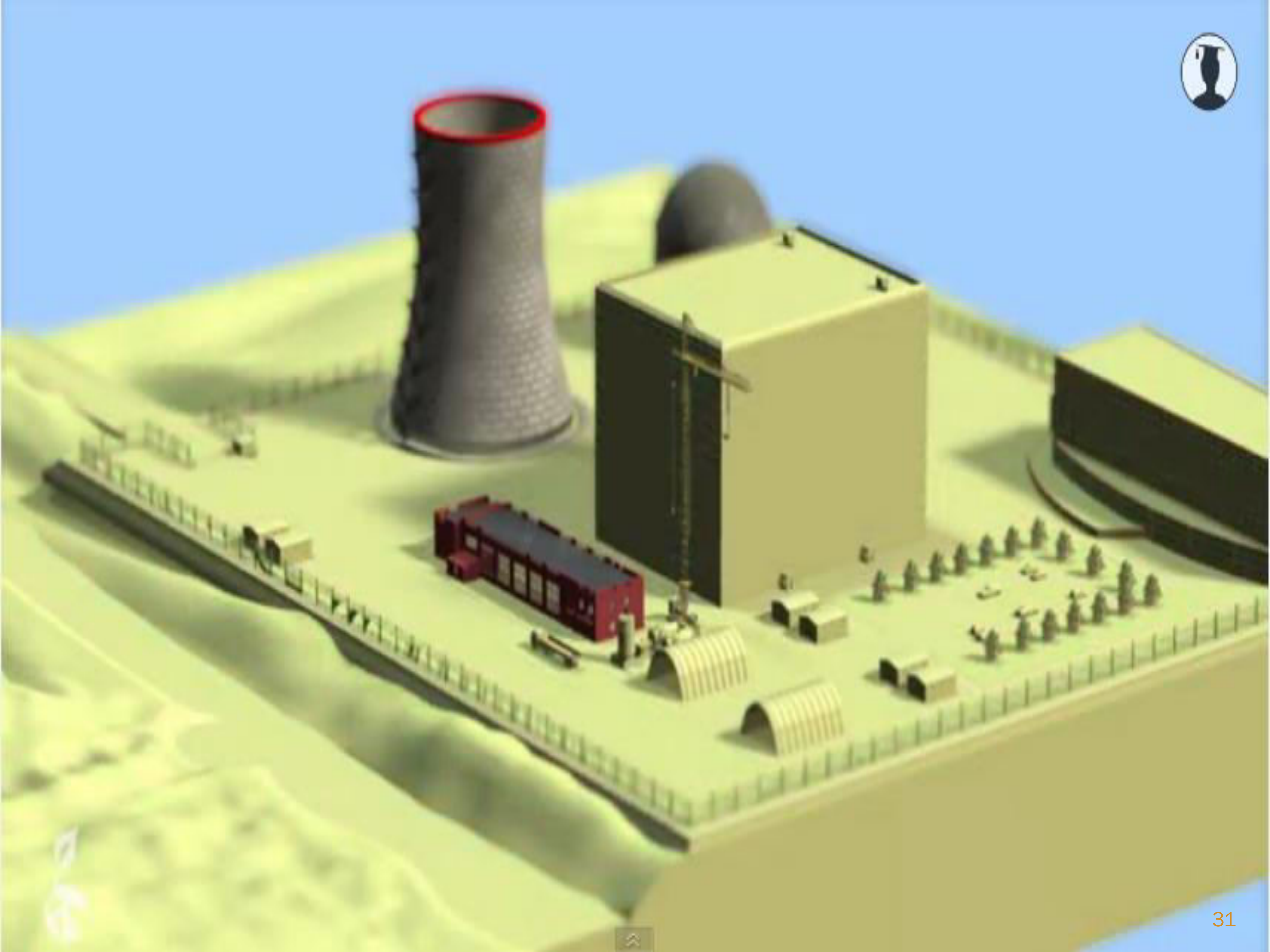
5. Heat exchanger and turbines

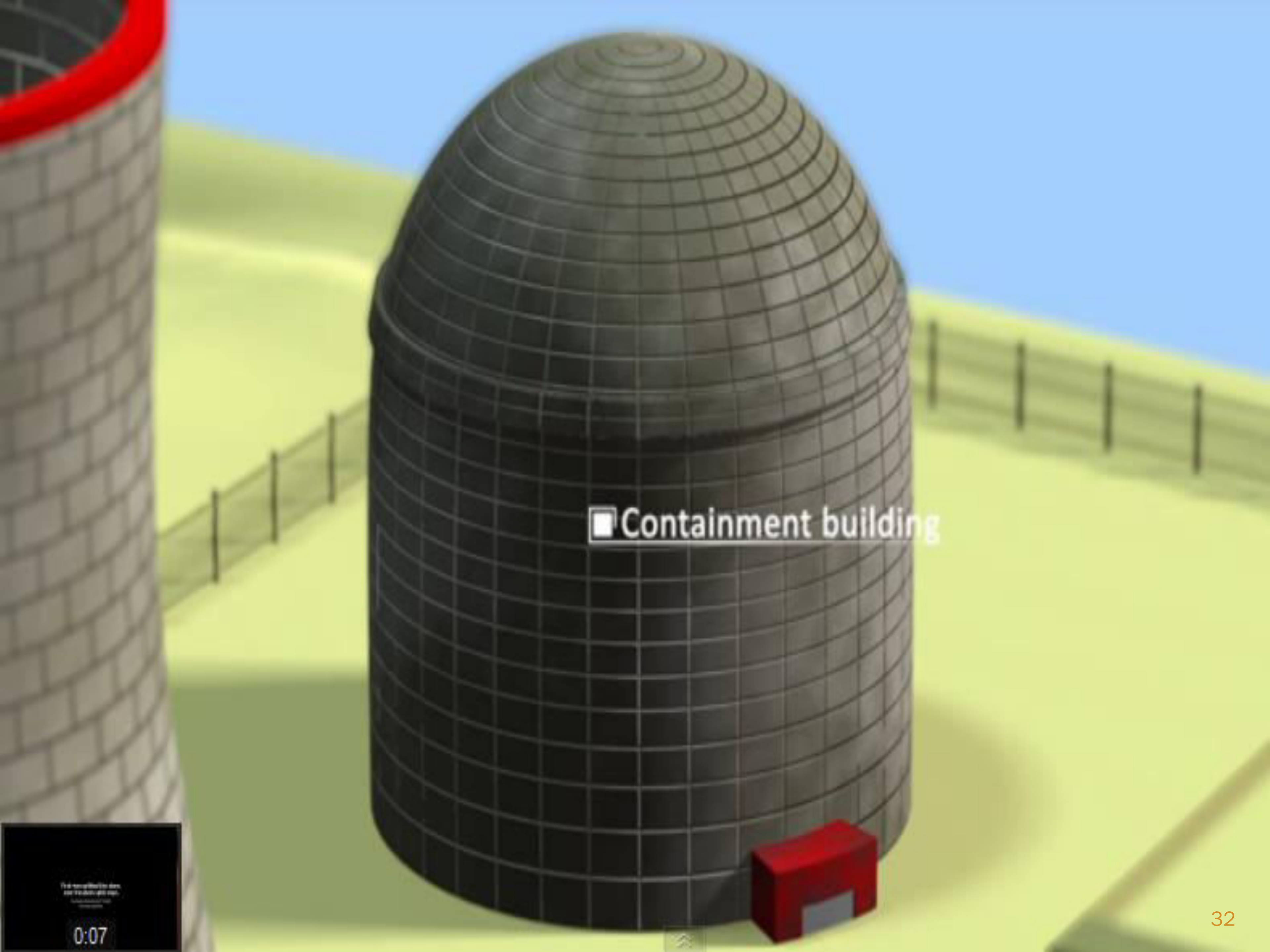


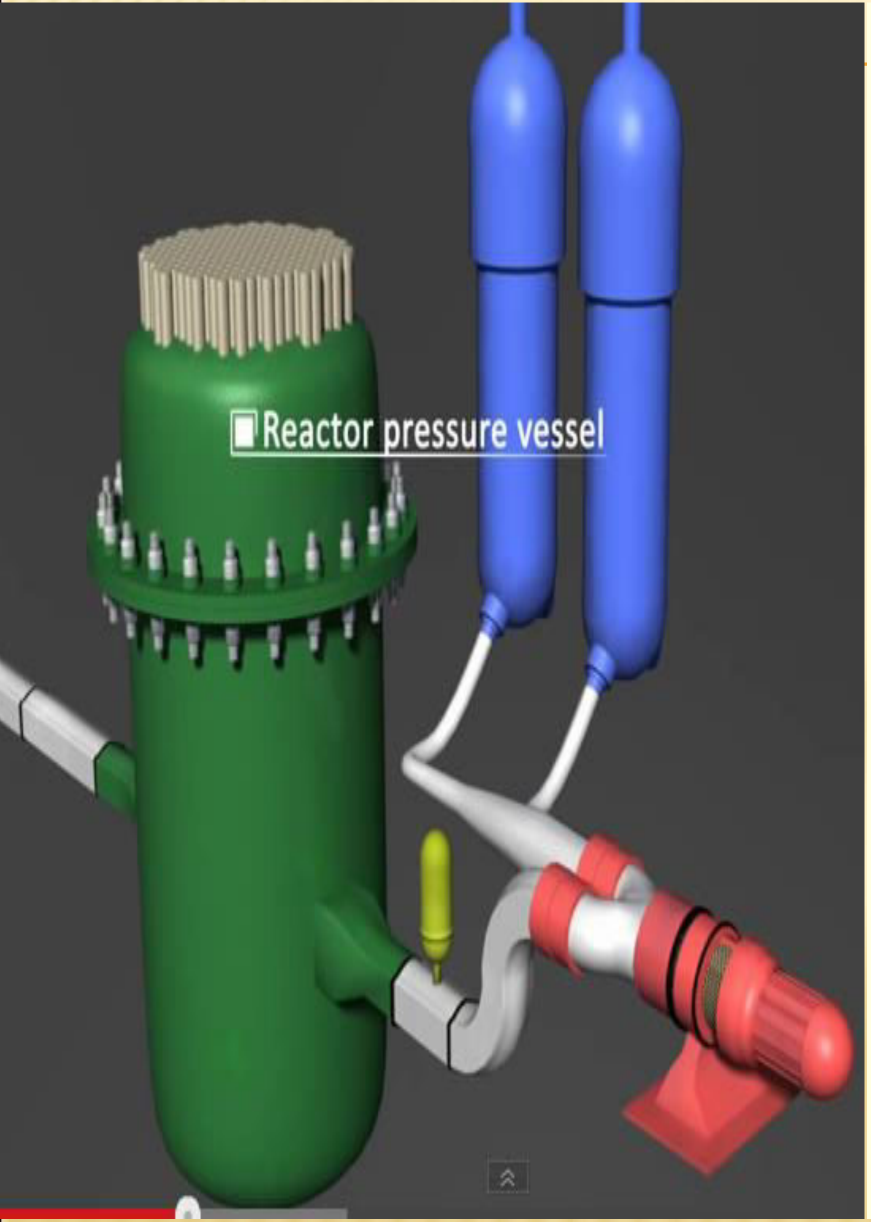
Name of the component	Function	Examples
Fuel rods	Fissionable material enriched with U235	Rods or strips
Moderators	To slow down the neutrons	Ordinary water, heavy water
Coolants	To cool down the intense heat produced	Ordinary water, heavy water
Control rods	Controls the fission reaction; Absorbs excess neutrons	Cd, B rods $_{43}Cd^{113} + _0n^1 \rightarrow _{43}Cd^{114} + \gamma$
Reflector	Reflects the escaping materials	Heavy water, graphite
Pressure vessel	Withstands pressure	-
Shielding	Protects environment and operating persons from destruction	Steel reinforced concrete shield
Heat exchanger and turbines	Steam operates the turbine, rotates the generator – produces electricity	

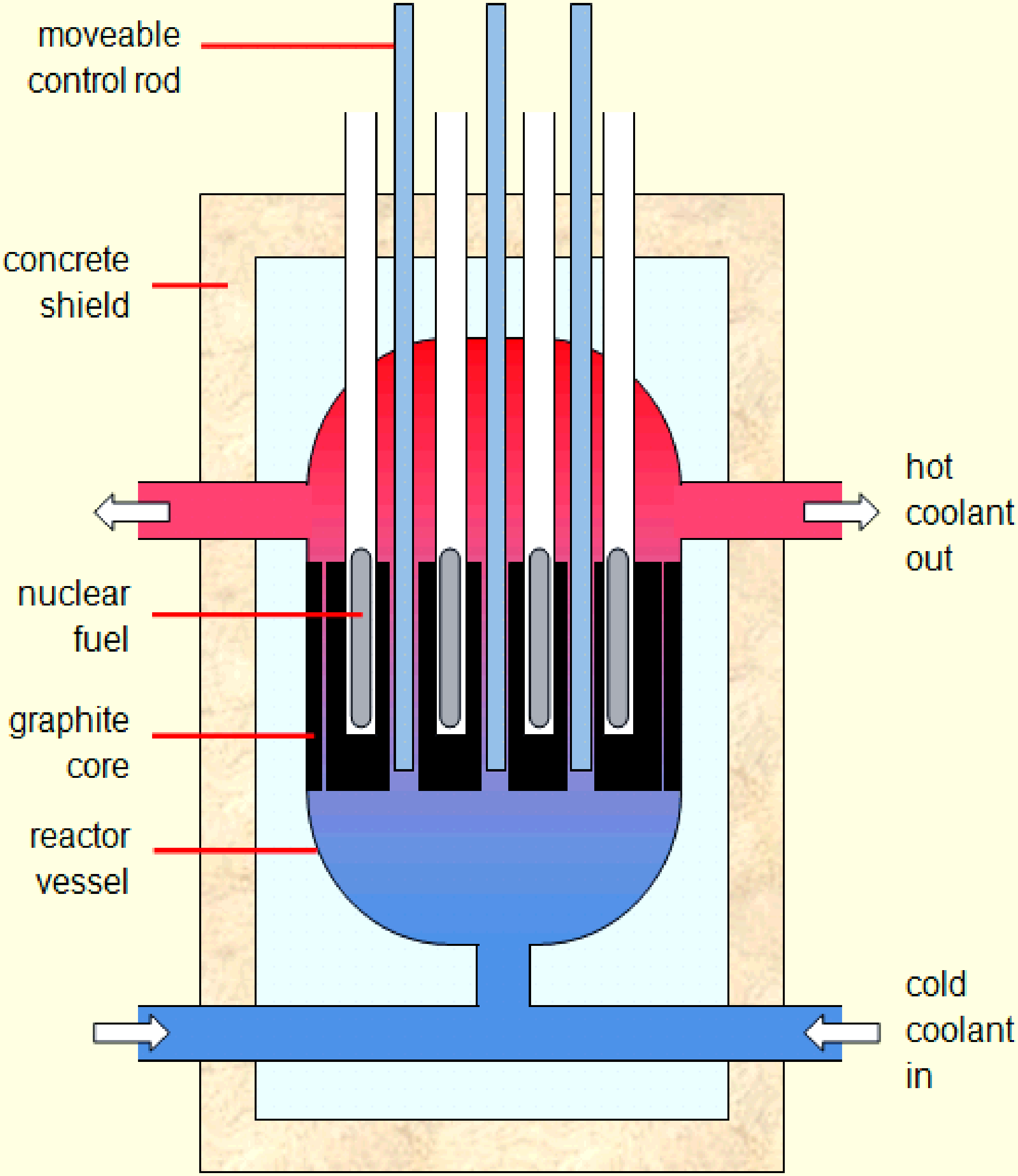
PRESSURIZED WATER REACTOR

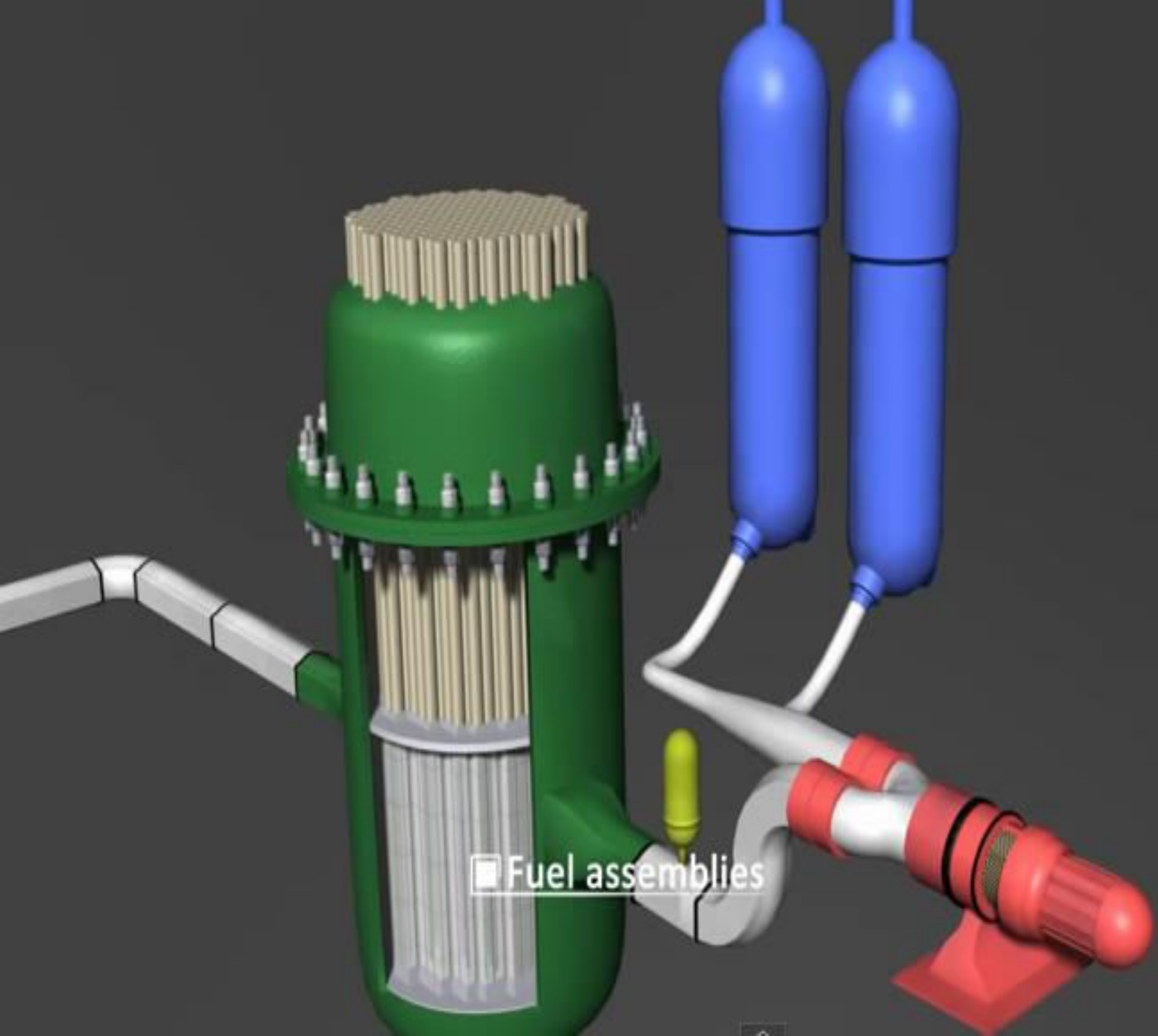


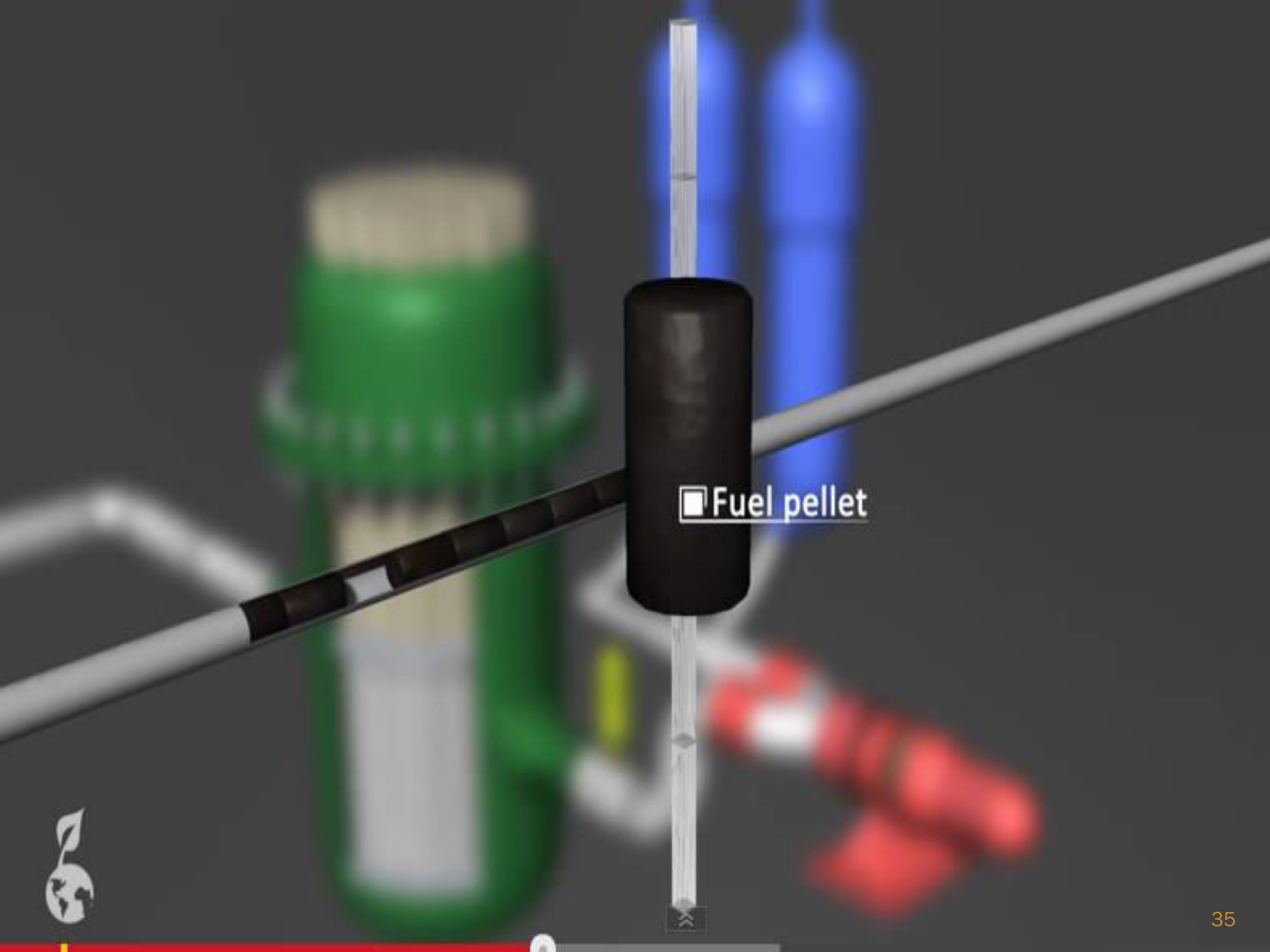


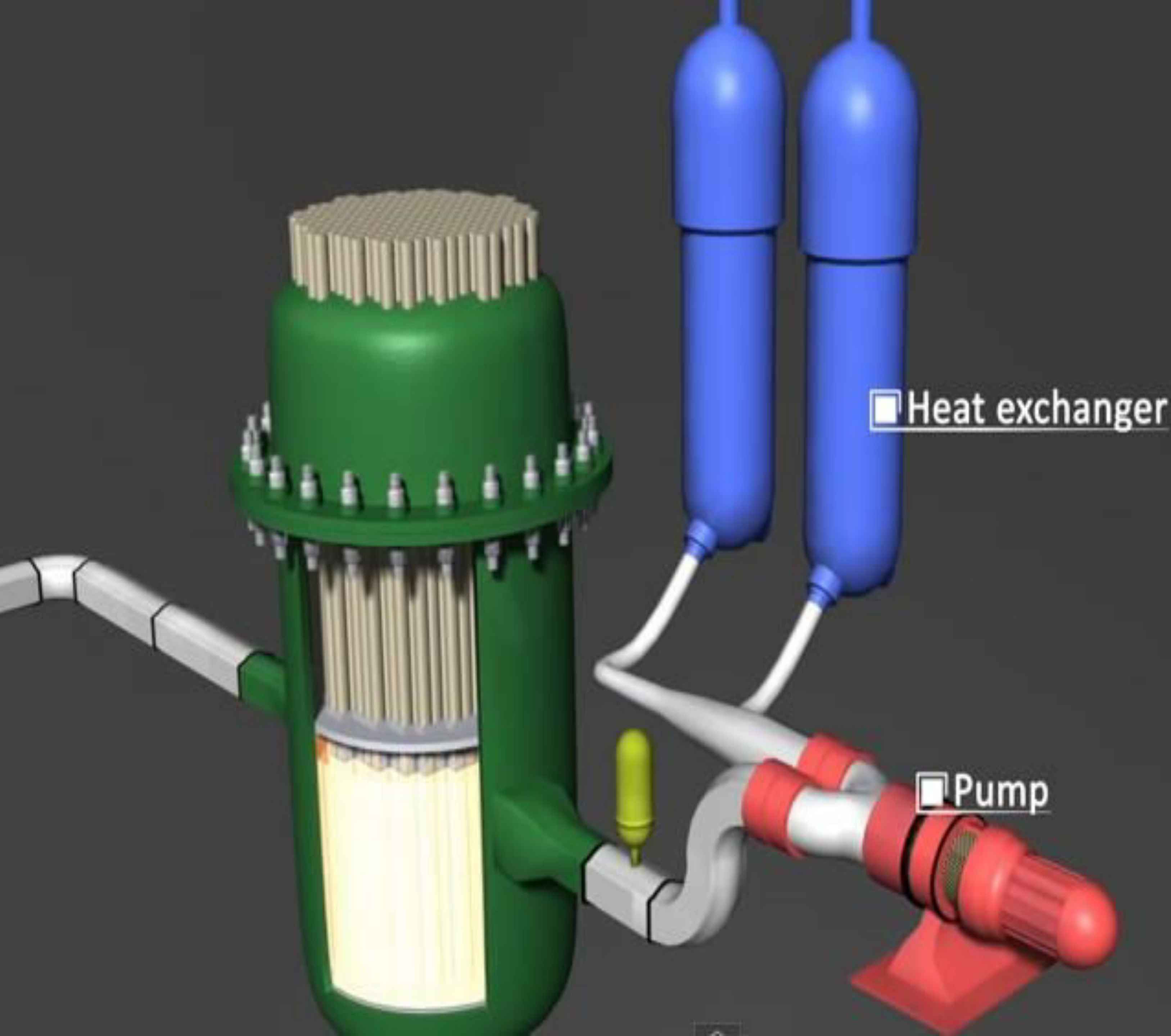

Containment building
0:07


Reactor pressure vessel

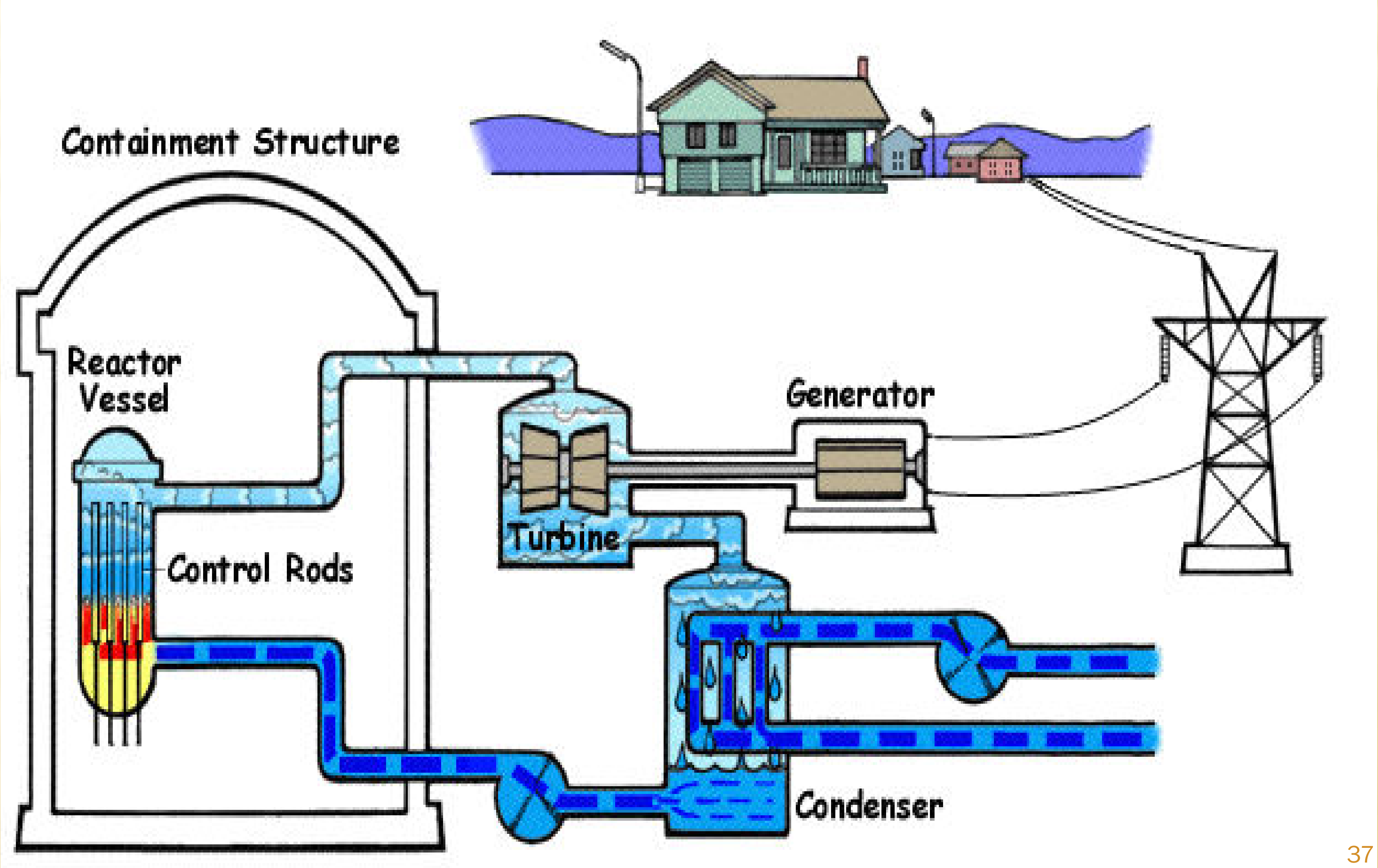

moveable control rod
concrete shield
nuclear fuel
graphite core
reactor vessel
hot coolant out
cold coolant in


Fuel assemblies


Fuel pellet

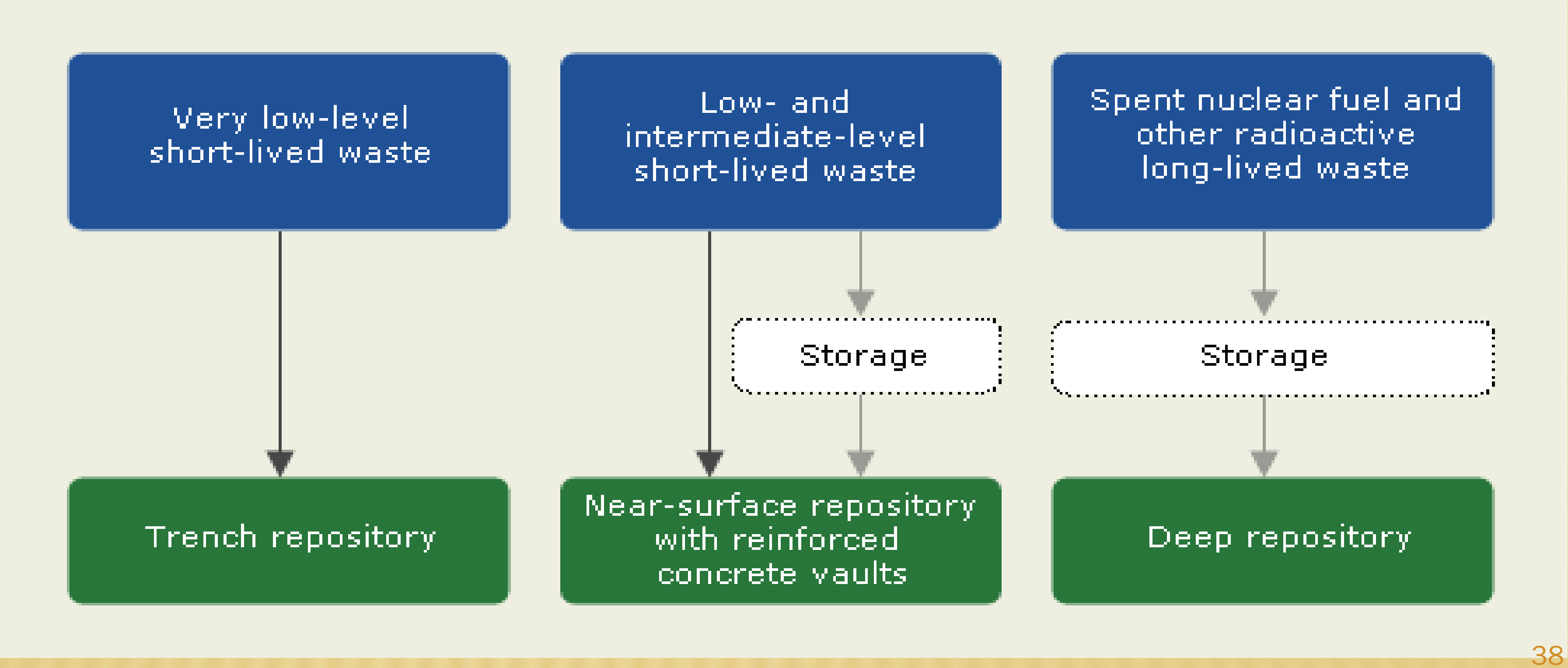

Heat exchanger
Pump

BOILING WATER REACTOR



DISPOSAL OF NUCLEAR WASTES

- Fission products (eg:Ba, Kr) – radioactive
- Emits dangerous radiation



Very low-level short-lived waste

Low- and intermediate-level short-lived waste

Spent nuclear fuel and other radioactive long-lived waste

Storage

Storage

Trench repository

Near-surface repository with reinforced concrete vaults

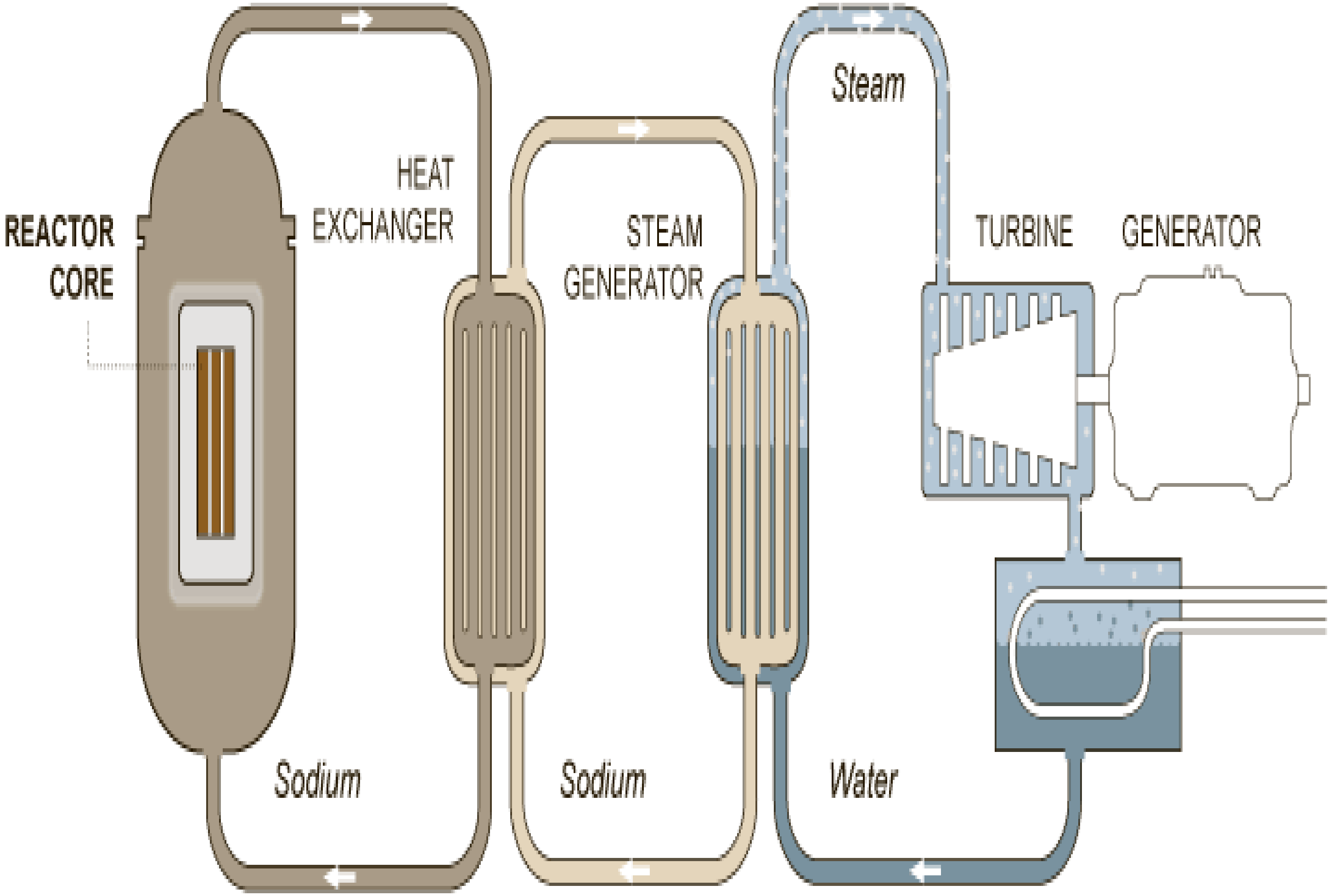
Deep repository

BREEDER REACTOR

- Is a reactor, converts non-fissionable material into fissionable material
- $_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{94}Pu^{239} + 2e^{-}$
- $_{94}Pu^{239} + {}_{0}n^{1} \rightarrow$ fission products + $3{}_{0}n^{1}$
- Non-fissionable – fertile nuclides
- Fissionable – fissile nucleides

1 The core of a breeder reactor contains fissile uranium and plutonium, atoms that split easily and release energy as heat and radiation. Neutrons released during this reaction are absorbed by a "blanket" of fertile uranium surrounding the core. Fertile uranium, harder to split than fissile uranium, turns into plutonium when it absorbs neutrons.

Unlike conventional reactors that use water to transfer heat, a breeder uses liquid sodium. The sodium does not slow the neutrons like water, and high-energy neutrons are more readily absorbed by the fertile uranium to create plutonium.



2 The sodium surrounding the core flows through a heat exchanger, a cluster of thin-walled metal tubes, and transfers its energy to a separate stream of sodium.

3 The heat then passes through a steam generator. If there is a leak and the sodium comes into contact with water or air, the sodium burns. A 1995 fire caused by a sodium leak shut down the Monju breeder reactor for 14 years.

4 The steam drives a turbine, generating electricity.

SOLAR ENERGY

- Energy directly from sun
- Renewable energy

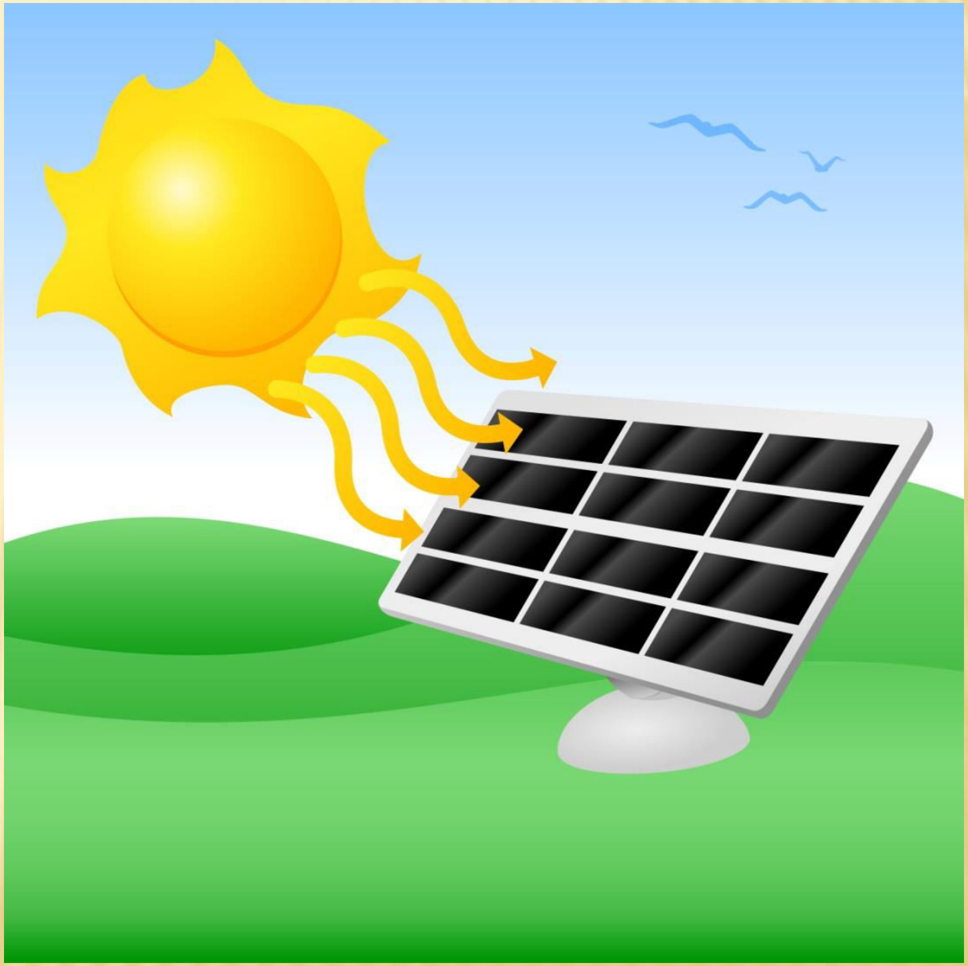


PHOTO VOLTAIC CELL

p-type semiconductor – Boron enriched Silicon

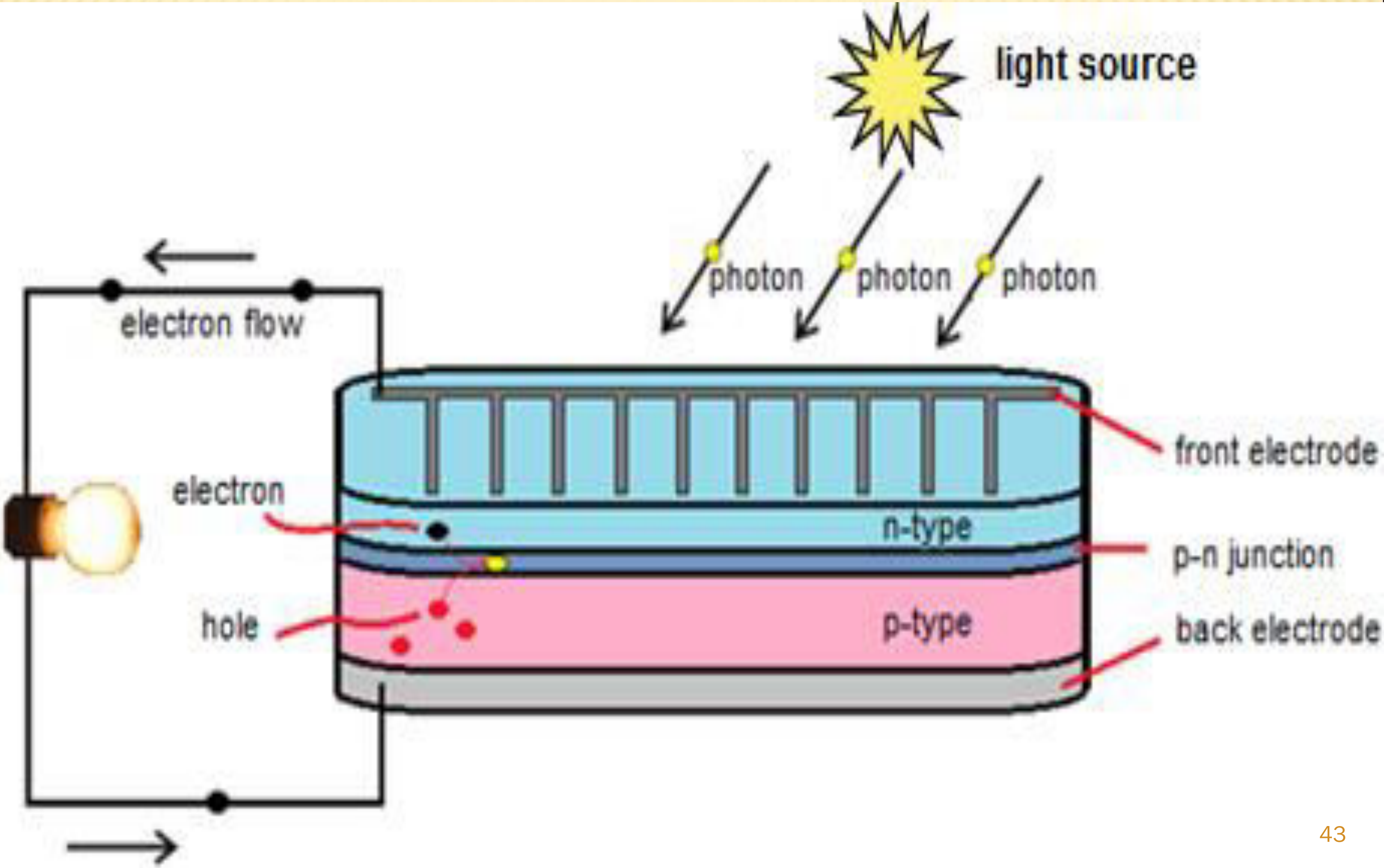
n-type semiconductor – Phosphorus enriched Si

p & n – close contact with each other

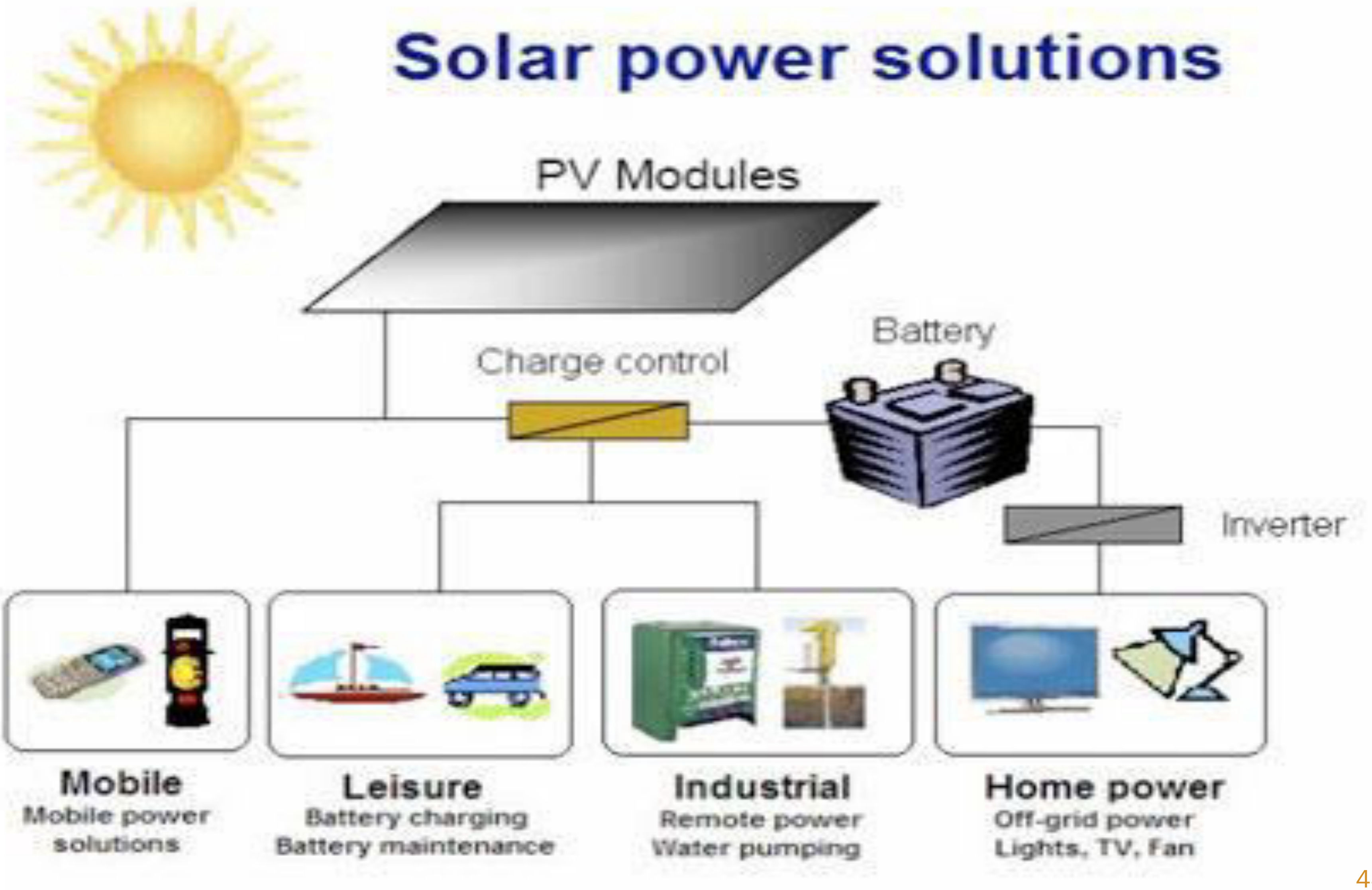
Sun rays falls on the p-type, ens from valence band promoted to conduction band – cross the p-n junction

Potential difference created – causes flow of ens

PHOTO VOLTAIC CELL



APPLICATIONS OF SOLAR ENERGY

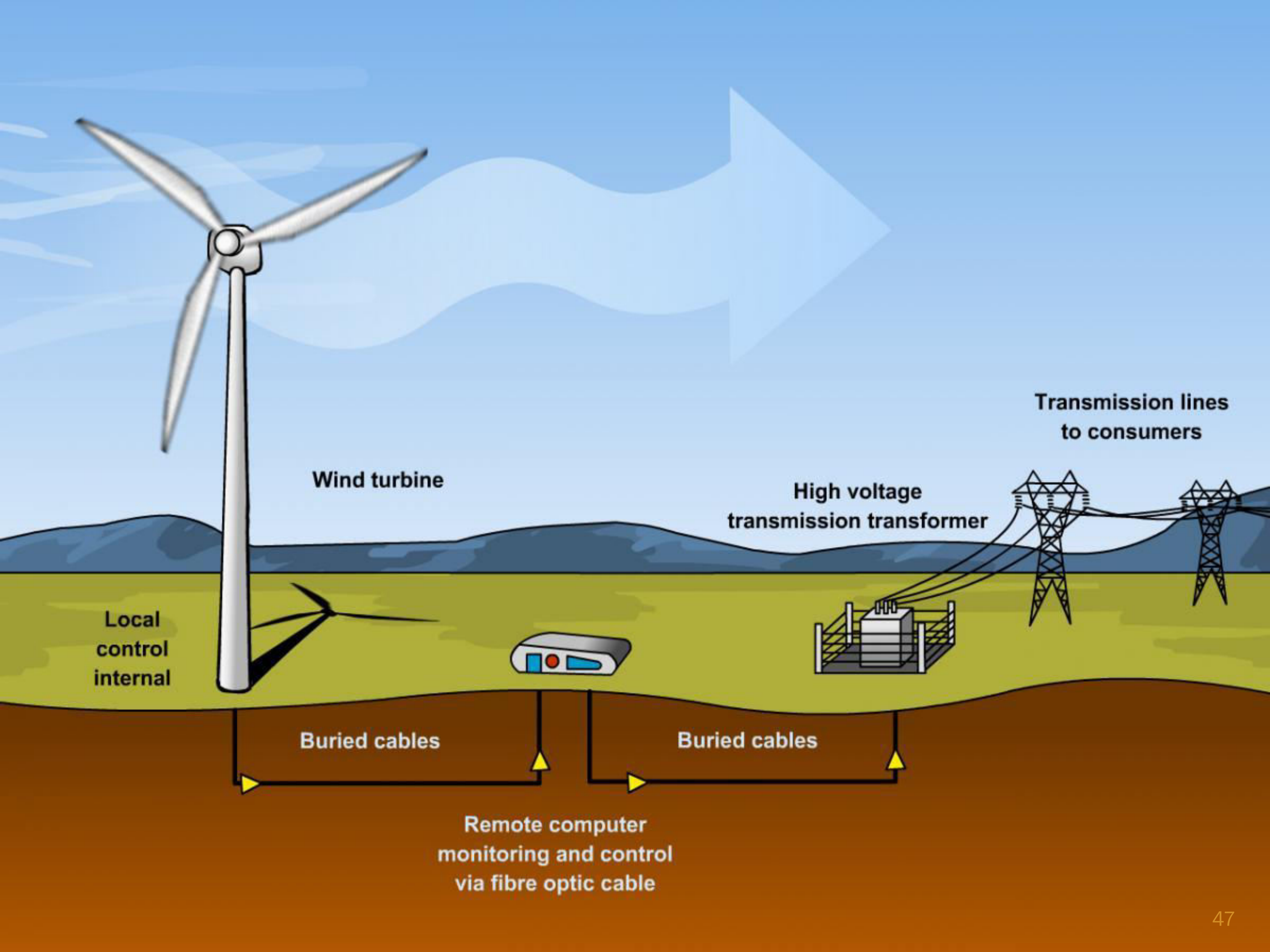


WIND ENERGY

- Renewable energy
- Moving air is called wind

HARNESSING WIND ENERGY

- The process by which the wind is used to generate mechanical power or electricity.
- Wind turbines convert the kinetic energy in the wind into mechanical power.
- This mechanical power can be used for specific tasks (such as grinding grain or pumping water) or a generator can convert this mechanical power into electricity to power homes, businesses, schools, etc..


Transmission lines
to consumers
Wind turbine
High voltage
transmission transformer
Local
control
internal
Buried cables
Buried cables
Remote computer
monitoring and control
via fibre optic cable

UNIT - IV

ENERGY STROAGE DEVICES

BATTERIES & FUEL CELLS

BATTERIES-Electrochemical cell connected in series

Types	Description	Examples
Primary battery/Non-reversible battery	Cell reaction is not reversible Once all the reactants → products, no more electricity is produced. Battery becomes dead. Not chargeable	Dry cell (laclanche cell), alkaline battery
Secondary battery/Reversible battery	Cell reaction can be reversed. Can be recharged – used again and again	Lead-acid battery, lithium battery
Flow battery	Reactants, products and electrolytes all pass thro' the cell produces electricity The cell runs continuously until the reactant's supply is exhausted	H_2-O_2 fuel cell, methanol-O_2 fuel cell

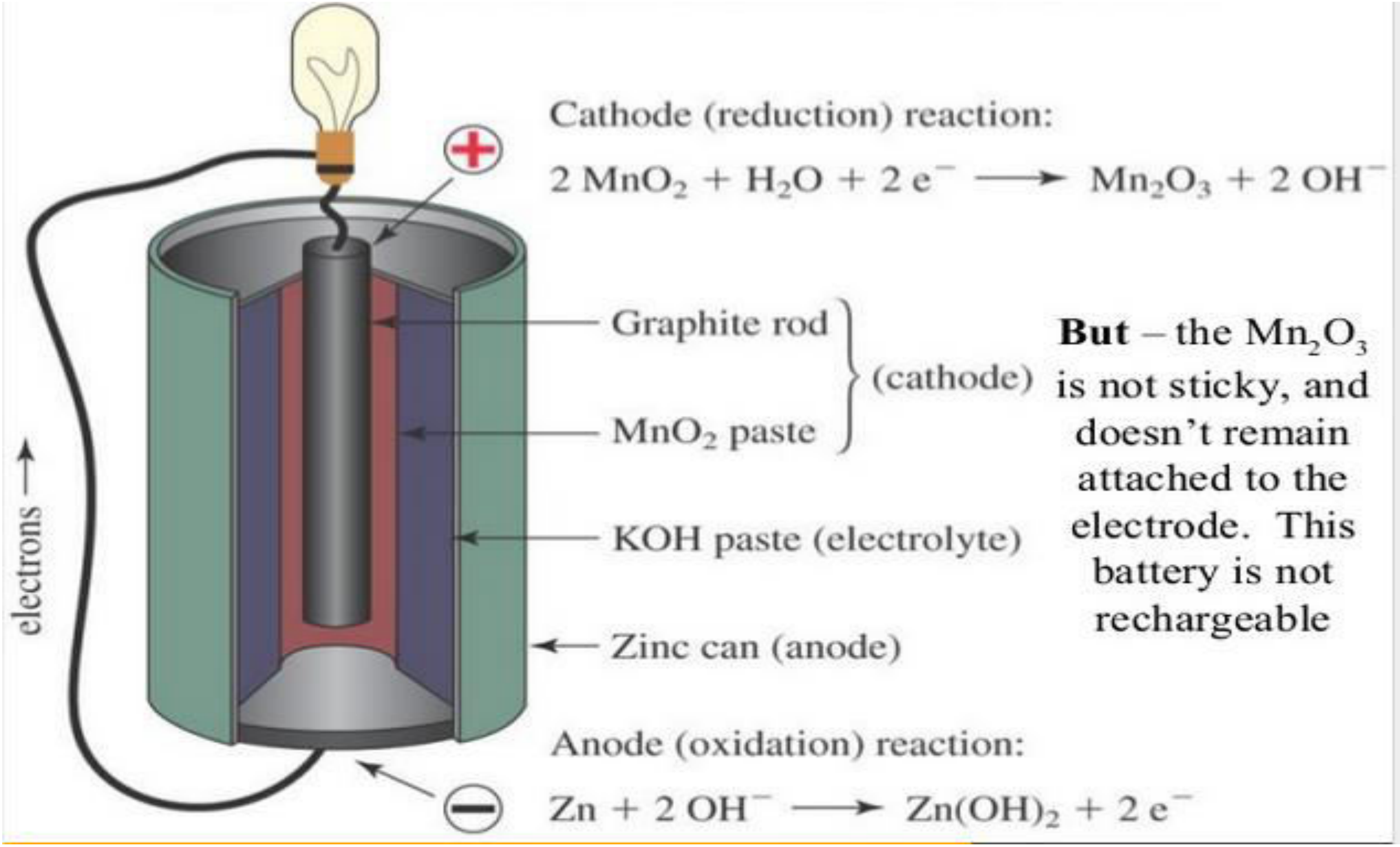
Primary battery

- Cell reaction is not reversible
- Once all the reactants → products, no more electricity is produced.
- Battery becomes dead.
- Not chargeable

Alkaline battery – improved form of dry cell

- Anode – zinc
- Cathode - manganese dioxide
- Electrolyte – KOH

- **Advantages over dry cell:**
- Zinc does not dissolve in basic medium
- Lifetime is longer than dry cell (no corrosion on zinc)
- Maintains its voltage



Cathode (reduction) reaction:

$$2\,MnO_2 + H_2O + 2\,e^- \longrightarrow Mn_2O_3 + 2\,OH^-$$

But – the Mn_2O_3 is not sticky, and doesn't remain attached to the electrode. This battery is not rechargeable

Anode (oxidation) reaction:

$$Zn + 2\,OH^- \longrightarrow Zn(OH)_2 + 2\,e^-$$

Overall reaction:

$$Zn_{(s)} + 2MnO_{2(s)} \rightleftharpoons ZnO_{(s)} + Mn_2O_{3(s)}\ [e^\circ = 1.43\ V]$$

Secondary batteries

- Cell reactions can be reversed.
- Can be recharged – used again and again
- Operates both as voltaic cell and electrolytic cell
- Discharging – acts as voltaic cell;

(chemical energy → electrical energy)

- Recharging – acts as an electrolytic cell

(electrical energy → chemical energy)

Examples:

1. Lead – Acid battery
2. Nickel – Cadmium battery
3. Lithium battery

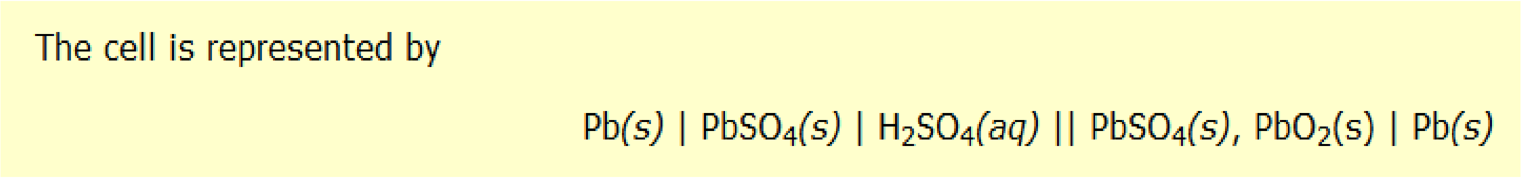
Lead – Acid battery

Also known as lead storage cell, lead accumulators

Anode – lead plates

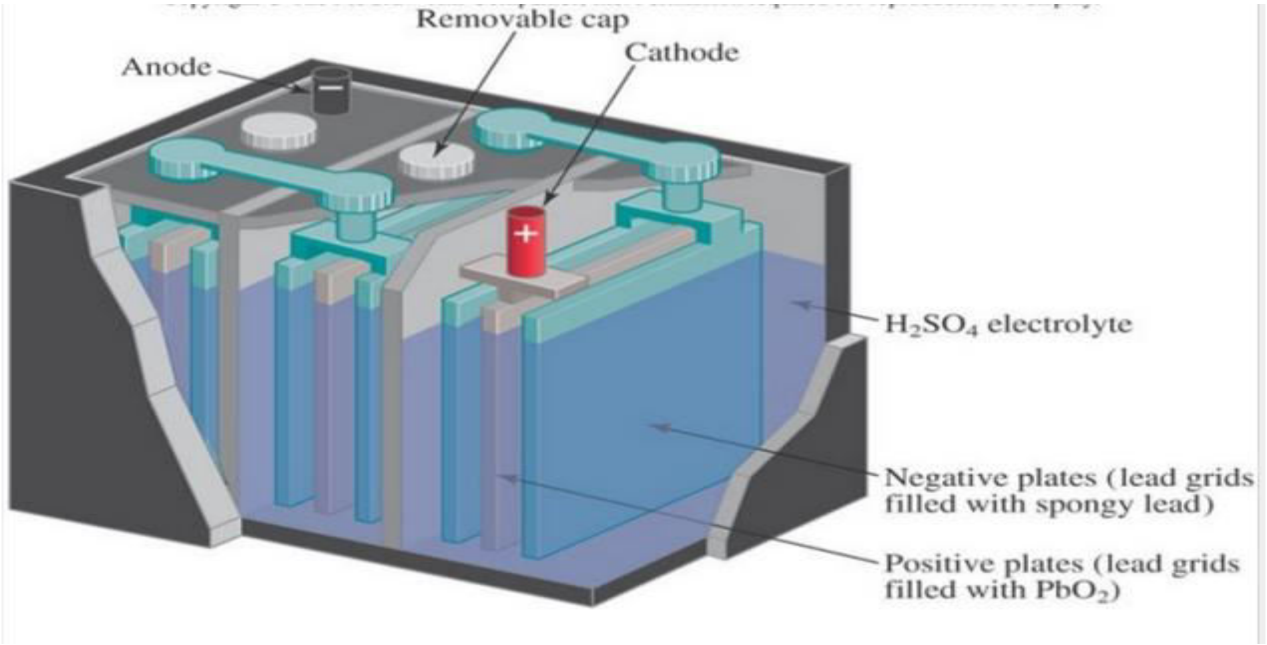
Cathode – lead peroxide plates

Electrolyte – dil. Sulfuric acid(water : acid = 3:1)



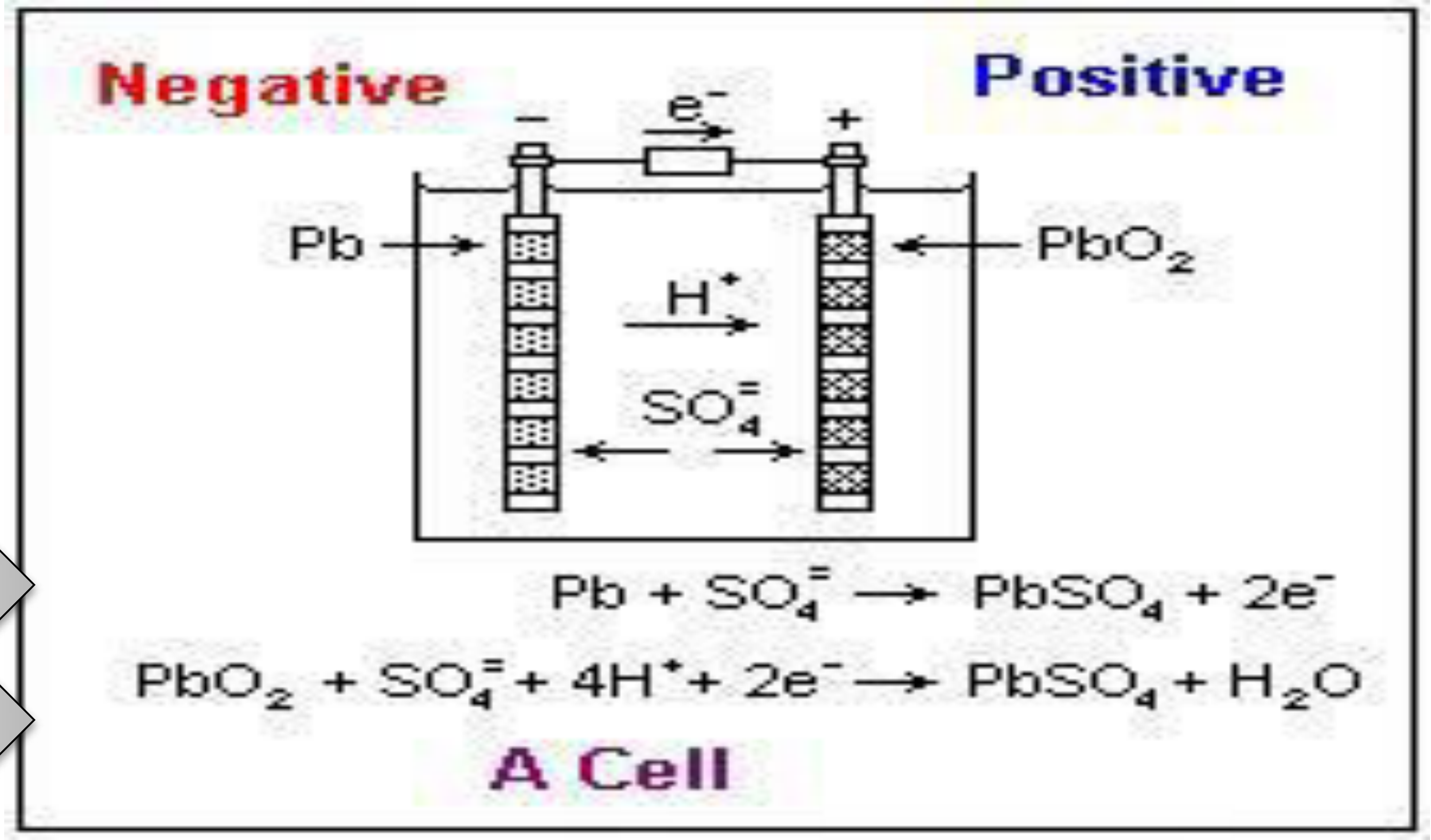
The cell is represented by

$$Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \parallel PbSO_4(s), PbO_2(s) \mid Pb(s)$$




N105 12V105Ah
POWER
HIGH ENERGY
DRY CHARGE LEAD-ACID
BATTERY
JAPANESE STANDARD

Discharging



At Anode

$$Pb + SO_4^= \longrightarrow PbSO_4 + 2e^-$$

At Cathode

$$PbO_2 + SO_4^= + 4H^+ + 2e^- \longrightarrow PbSO_4 + H_2O$$

A Cell

The total reaction can be written as

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

Recharging

- PbSO4 is precipitated at both the electrodes.
- Concentration of sulfuric acid decreases – battery needs recharging.
- By passing electric current in the opposite direction
- Pb deposits on anode, PbO2 on cathode

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

Uses:

In automobiles – cars, buses, trucks, etc.

Large backup power supplies for telephone and computer centers, grid energy storage and household electric power systems

Nickel – Cadmium battery

- Also known as NiCad battery
- Anode – Cadmium
- Cathode – metal grid having NiO2 paste
- Eletrolyte - KOH

At Anode

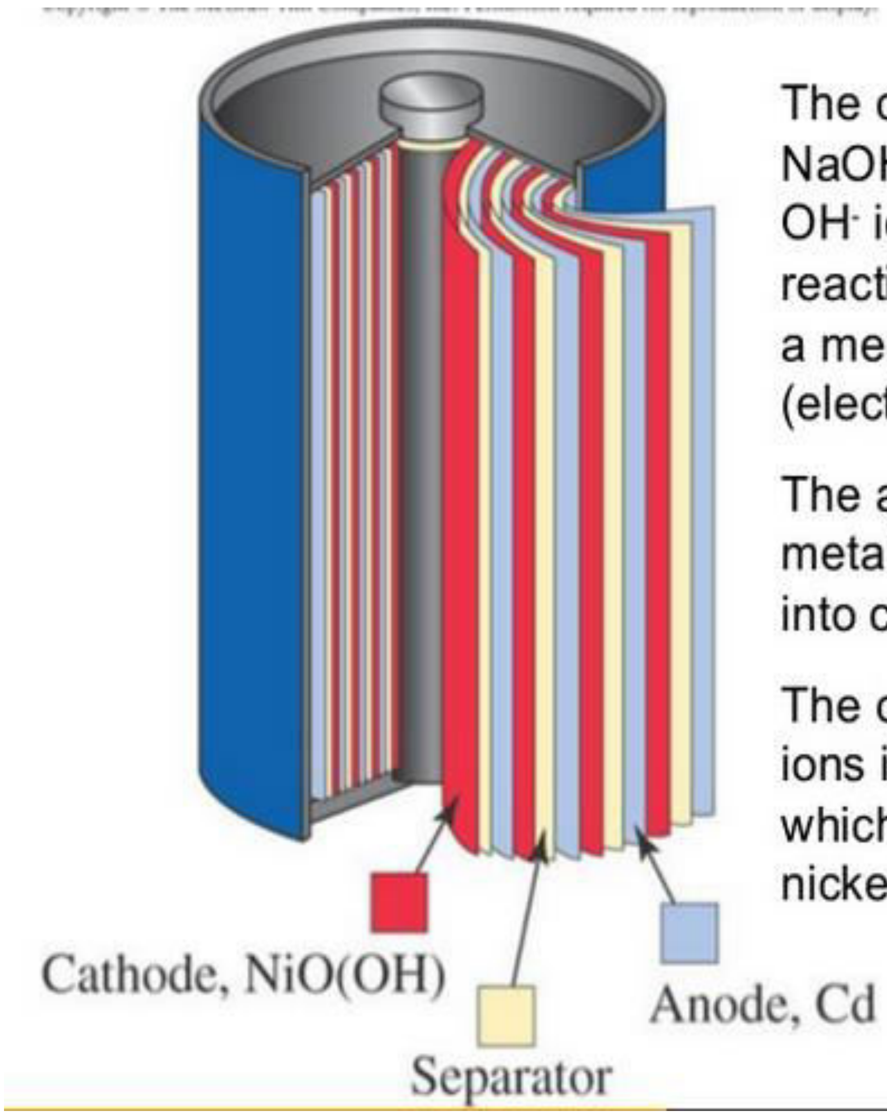
$$Cd + 2(OH)^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$$

At Cathode

$$2NiOOH + 2H_2O + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_2 + 2(OH)^-$$

$$\text{Overall cell reaction: } 2NiOOH + Cd + 2H_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_2 + Cd(OH)_2$$

Nickel – Cadmium battery



The cell contains a paste of NaOH – this provides the OH^- ions needed for the reaction, while also providing a medium to pass charge (electrolyte)

The anode consists of solid metal which is transformed into cadmium hydroxide

The cathode consists of Ni^{3+} ions in a NiO(OH) paste which are transformed into nickel hydroxide

Nickel – Cadmium battery

Uses:

- Small cells are used for portable electronics and toys (such as solar garden lights)
- Miniature button cells are sometimes used in photographic equipment, hand-held lamps (flashlight or torch)
- Specialty Ni–Cd batteries are used in cordless and wireless telephones, emergency lighting.

Disadvantages:

Expensive than lead acid battery

Not as powerful as newer batteries

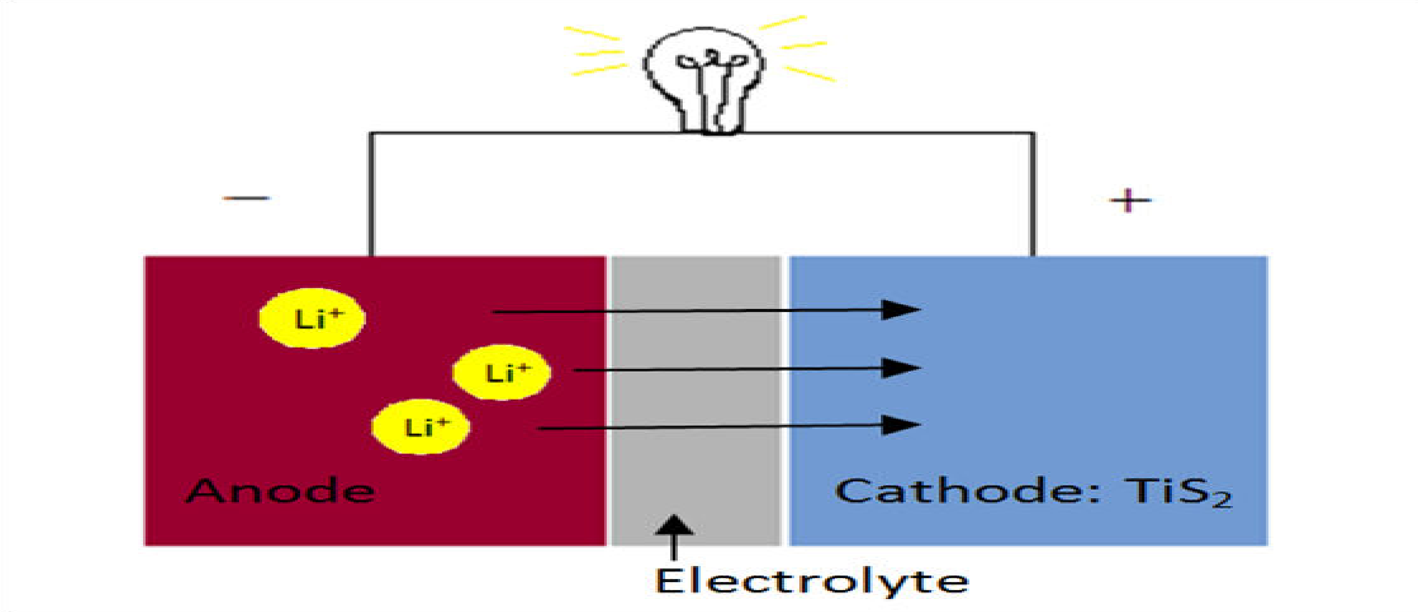
Often self-discharge

Contains toxic metals

Disposal of these batteries is difficult

Lithium batteries

- Solid state battery – since the electrolyte used is solid
- Anode – Lithium
- Cathode – TiS2
- Electrolyte – Polymer (passes the ions not the ens)



Uses

- In portable devices – mobile phones, laptops, tablets, camera, game consoles, torches
- In power tools – cordless drills, garden equipments
- In electric vehicles – model aircraft, electric cars, electric wheel-chairs

Advantages & Disadvantages

- High energy density
- Low self-discharge
- Low maintenance
- All constituents are solid – no leakages
- Can made into any size and shape

- Requires protection from being over charged.
- Ageing – depends upon charging/discharging cycles
- Costly than other batteries
- Restrictions in transportation (particularly in air)- protect from short circuit

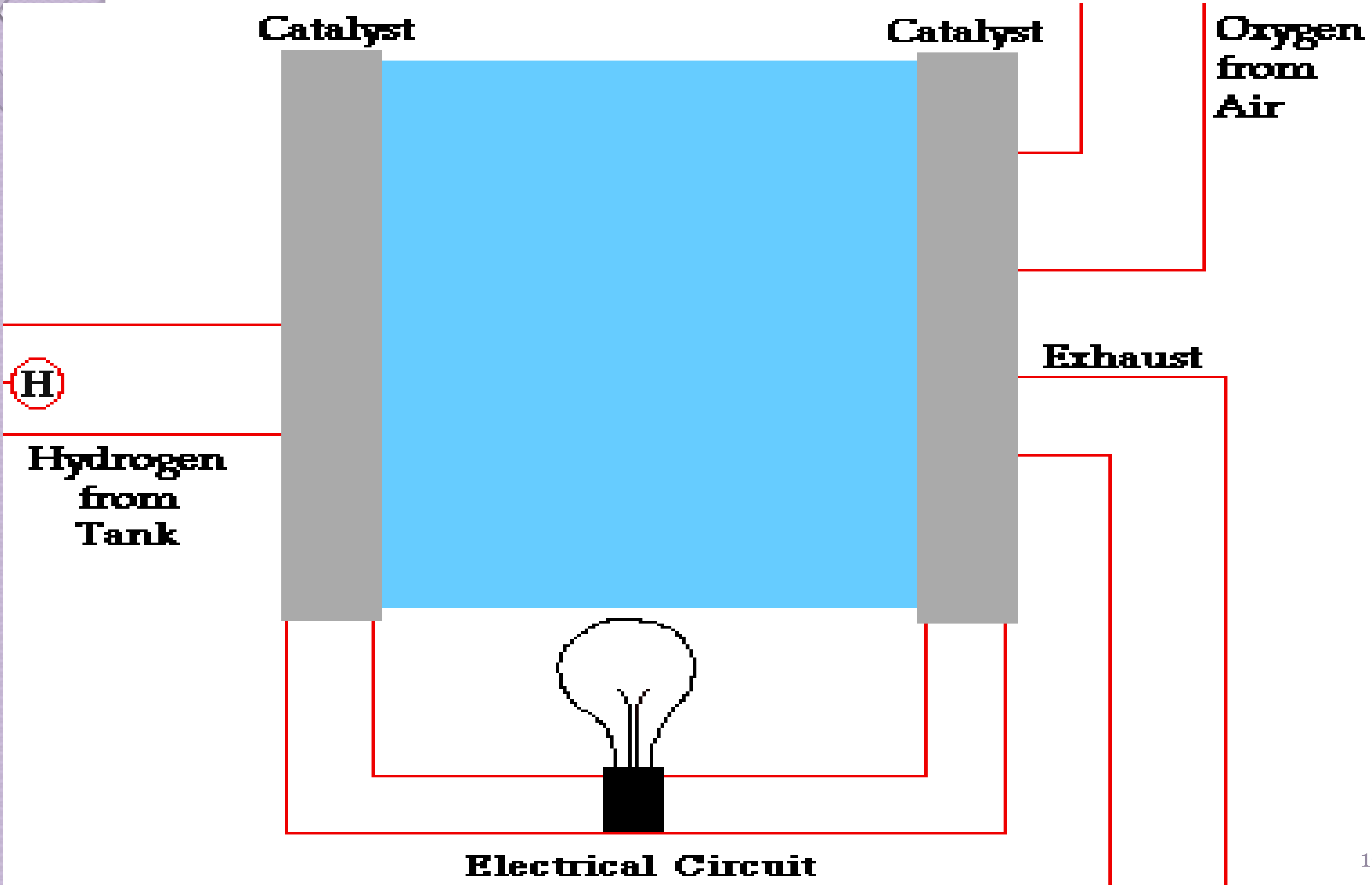
Fuel cells

- Is a voltaic cell – converts chemical energy of the fuels directly into electricity
- Reactants, products and electrolytes all pass thro' the cell
- Fuel + oxygen → oxidation products +electricity
- Examples: H_2-O_2 fuel cell, methanol-O_2 fuel cell
- http://digitalsplashmedia.com/2008/02/hydrogen-fuel-cell-animation/

H_2-O_2 fuel cell

- Fuel – Hydrogen
- Oxidizer – Oxygen
- Electrolyte – KOH or NaOH
- Two porous carbon electrodes with small amount of catalyst (Pt, Pd) – Anode, Cathode
- Between the electrodes – electrolytic solution
- $2H_2$ gas and O_2 gas are bubbled into the electrolyte through the porous carbon electrodes. Thus the overall reaction involves the combination of hydrogen gas and oxygen gas to form water.
- The cell runs continuously until the reactant's supply is exhausted

H_2-O_2 fuel cell



H_2-O_2 fuel cell

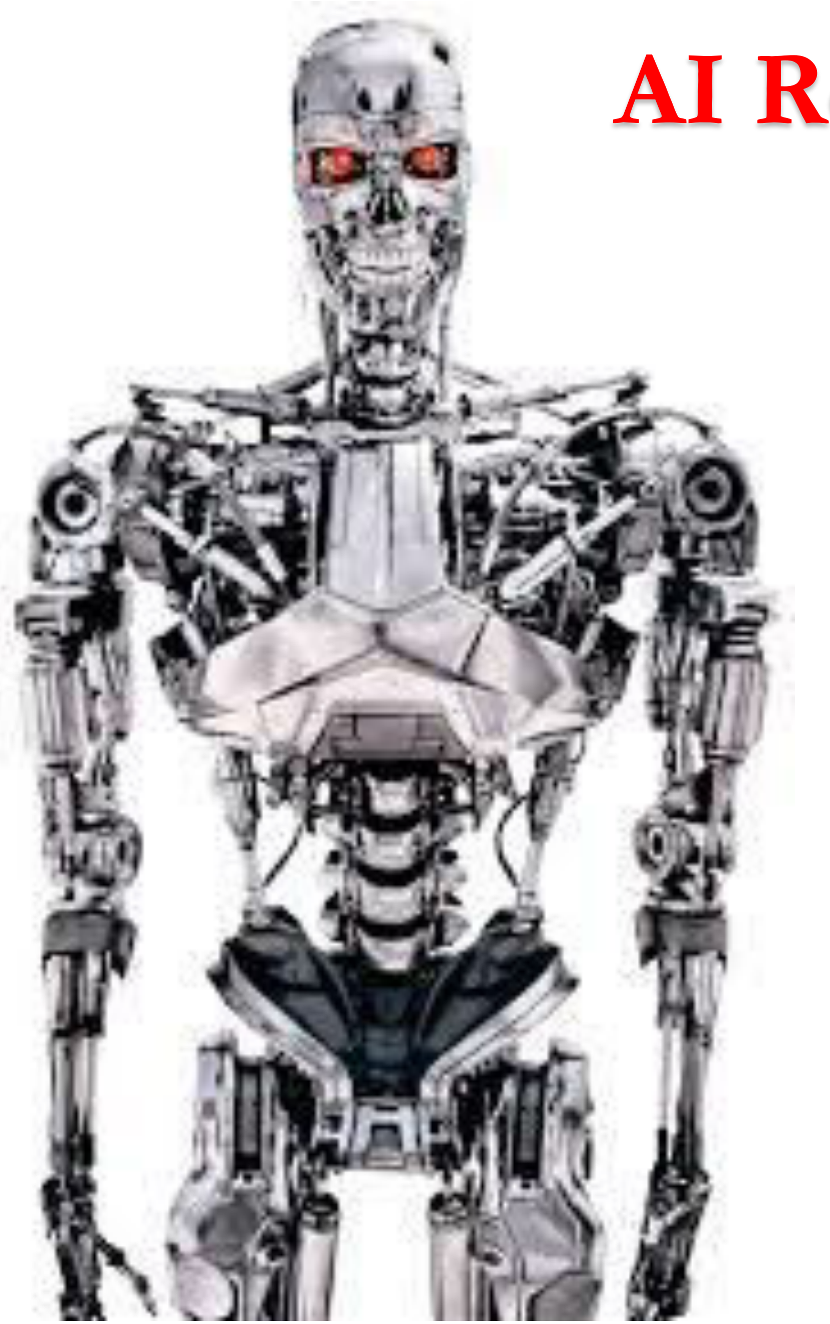
- H_2 (fuel) bubbled thro’ anode – oxidized (liberates ens)
- O_2 (oxidizer) bubbled thro’ cathode – reduced (gains ens)
- $2H_2 + O_2 \rightarrow 2H_2O$
- Emf of the cell = 0.8-1.0 V

Applications:

- Fuel cells are very useful as power sources in remote locations, such as spacecraft, remote weather stations, large parks, communications centers, rural locations including research stations, and in certain military applications

International Space Satiation

AI Robots



Modern Automobiles

H_2-O_2 fuel cell

- **Advantages**:
- High efficiency
- Environment friendly
- Hydrogen is readily available
- No harmful emissions (when used in NASA's spaceships, the burned hydrogen gas leaves behind clean drinking water for the astronauts)

- **Disdvantages**:
- Expensive (to free from other elements)
- Storage (difficult to transport)
- Highly flammable

THAT'S
ALL
ABOUT
UNIT IV

Unit - V

Engineering Materials – Abrasives, Refractories & Glass

Introduction

Abrasives are very hard substances used for grinding, shaping and polishing other materials

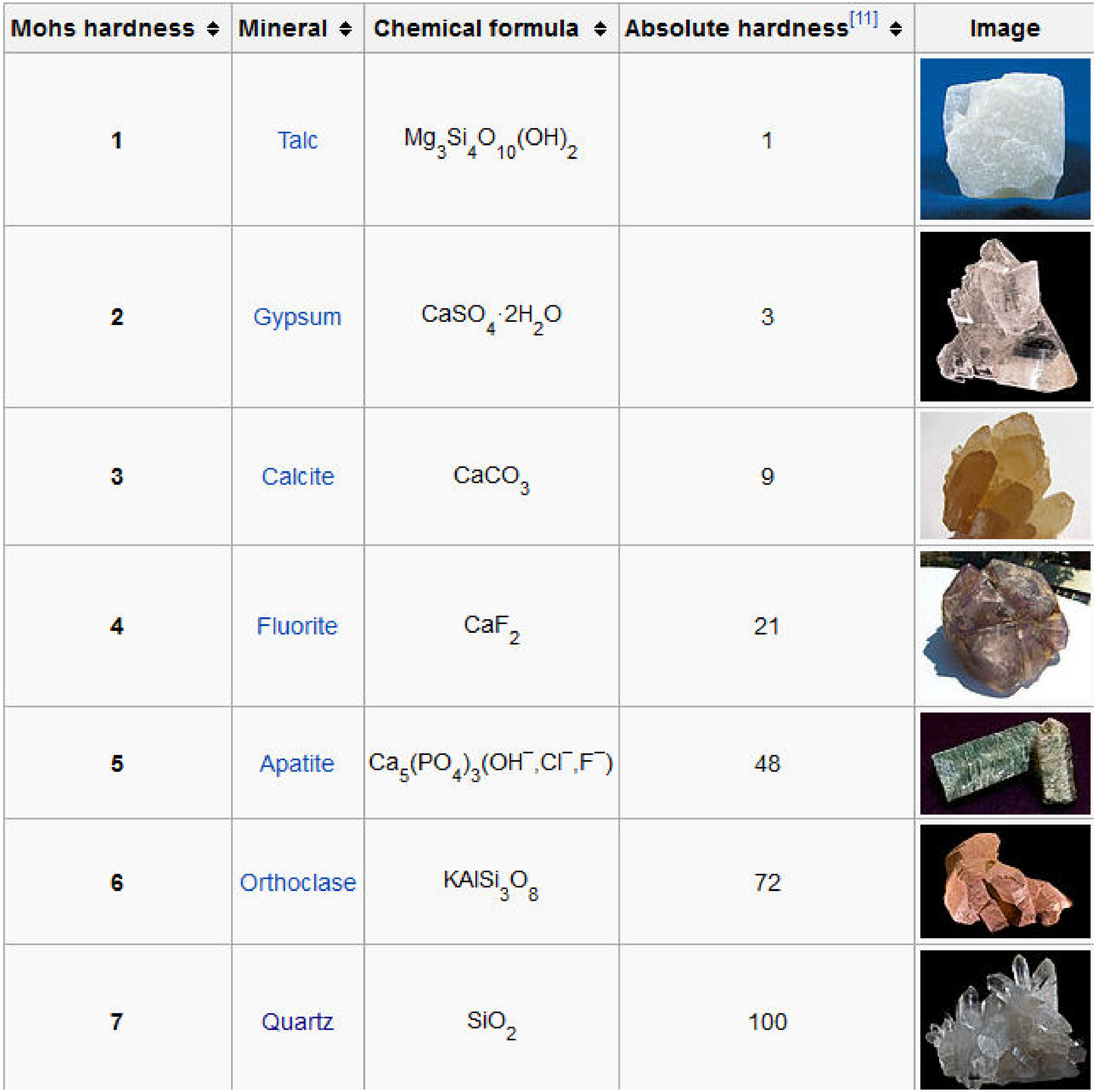
Properties

- ✓ Have very high melting point
- ✓ Chemically inert
- ✓ High abrasive power (ability to scratch away or sharp other materials)
- ✓ Sometimes hard and brittle or soft and flexible

Hardness of Abrasives

"The Moh's scale of mineral hardness is a qualitative ordinal scale which characterizes the scratch resistance of various minerals through the ability of a harder material to scratch a softer material. The hardness of an abrasive material is measured by Moh's scale"

1	TALC	6	FELDSPAR
2	GYPSUM	7	QUARTZ
3	CALCITE	8	TOPAZ
4	FLOURITE	9	CORUNDUM
5	APATITE	10	DIAMOND



Mohs hardness	Mineral	Chemical formula	Absolute hardness[11]	Image
1	Talc	$Mg_3Si_4O_{10}(OH)_2$	1	
2	Gypsum	$CaSO_4 \cdot 2H_2O$	3	
3	Calcite	$CaCO_3$	9	
4	Fluorite	CaF_2	21	
5	Apatite	$Ca_5(PO_4)_3(OH^-,Cl^-,F^-)$	48	
6	Orthoclase	$KAlSi_3O_8$	72	
7	Quartz	SiO_2	100	

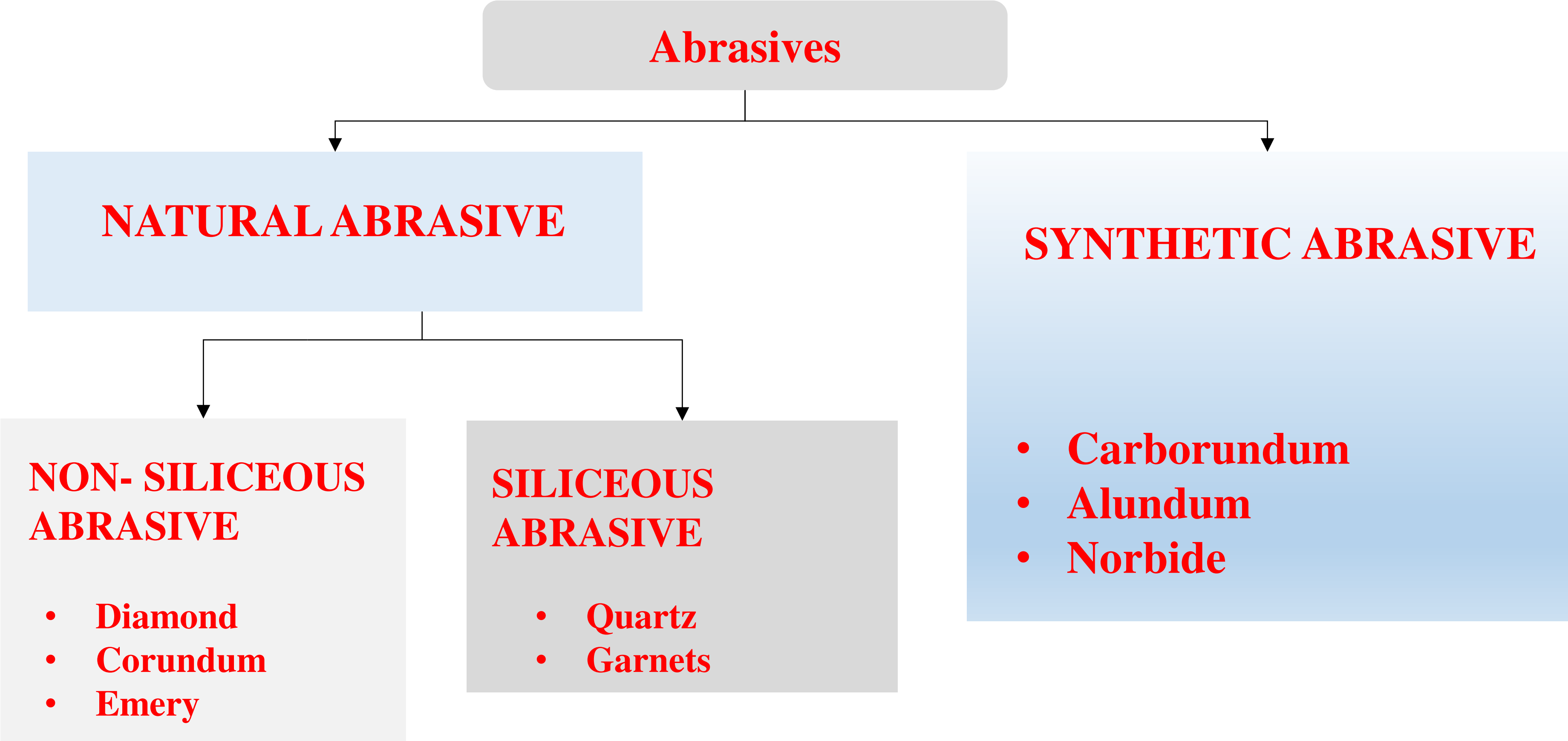
Soft Abrasives

8	Topaz	$Al_2SiO_4(OH^-,F^-)_2$	200	
9	Corundum	Al_2O_3	400	
10	Diamond	C	1600	

Characteristics of Abrasives

- ✓ Hard
- ✓ Resist abrading action
- ✓ Chemically inactive
- ✓ High refractoriness
- ✓ High Melting Point
- ✓ Not affected by frictional heat

Type of Abrasives



Abrasives

NATURAL ABRASIVE

NON- SILICEOUS ABRASIVE

- **Diamond**
- **Corundum**
- **Emery**

SILICEOUS ABRASIVE

- **Quartz**
- **Garnets**

SYNTHETIC ABRASIVE

- **Carborundum**
- **Alundum**
- **Norbide**

Natural Abrasives : Non Siliceous

Diamond

- Crystalline Carbon, hardest substance
- Ranks first in Moh's scale (Hardness 10)
- Chemically insert
- Not affected by Acids & Alkalis
- **Borts** – Off Color Diamond
  Carbando – Black color diamond

Uses :

- Drilling points
- Cutting stones, rocks
- Grinding wheels

Corundum

- Pure Crystalline Alumina (Al_2O_3)
- Transparent material, but can have different color based on the presence of impurities in it. (If red , its called Ruby)
- Ranks second in Moh's scale (Hardness 9)

Uses :

Grinding

- Glass
- Gems
- Metals

Emery

- Fine grained , opaque, black color material
- Aggregate of 55- 75 % crystalline alumina, 20-40 % magnetite, 12 % other materials (tourmaline)
- Ranks third in Moh's scale (Hardness 8)
- Grinding depends on proportion of alumina

Uses :

- Tips of cutting and drilling tools
- Making abrasive papers & cloth

Natural Abrasives : Siliceous

Garnet

- Trisilicates of alumina, magnesia and ferrous oxide.
- General formula : $X_3Y_2(SiO_4)_3$
- **Major varieties:**
  - Grossular : $Ca_3Al_2Si_3O_{12}$
  - Andradite : $Ca_3Fe_2Si_3O_{12}$
  - Spessartine : $Mn_3Fe_2Si_3O_{12}$
- Hardness : 6.5 to 7.5 in Moh's scale

Uses :

- Along with glue to make paper or cloth as it is soft in nature
- Bearing pivots, watches, glass grinding and polishing metal

Quartz

- Pure Crystalline Silica
- General Formula : Si O_2
- Ranks fourth in Moh's scale (Hardness 7)

Uses :

- Grinding pigments in paint industry
- Granules in grinding machines
- Hydrated form used in sand paper

Synthetic Abrasives : Carborumdum or Silicon Carbide

Manufacturing process

- $SiO_2 + 3C \xrightarrow{1500^{o}C} SiC + 2CO$
- Addition of saw dust while burning increases the porosity
- Addition of salt removes iron and other impurities as volatile chlorides, which too increases porosity
- Binded with clay or silicon nitrate

Properties

- High thermal conductivity, intermediate between metals and ceramics
- Low expansion
- High resistance to abrasion and spalling
- Withstands load upto 1650 ^{o}C
- Intermediate between conductors and insulators
- Self bonded product > Silicon nitrite bonded product > Clay bonded product

Strength , Density , Abrasion-resistance , Chemical resistance, softening temperature

Synthetic Abrasives : Norbide or Boron Carbide

Manufacturing process

- $2B_2O_3 + 7C \xrightarrow{2700^{o}C} B_4C + 6CO \uparrow$

Properties

- Hardness is 9 on Moh's scale
- Light weight and black in color
- Resistance to chemical and erosion
- Better than diamond in resisting oxidation

Uses

- Grinding dyes
- Cutting and sharpening of hard high speed tools
- Used to prepare scratch and wear resistance coatings

Synthetic Abrasives : Alundum

Manufacturing process

- Bauxite (Al) + $3O_2 \xrightarrow[C]{\Delta} 2Al_2O_3$

Properties

- Hardness is 9 on Moh's scale
- Resistance to acids
- Stable at high temperature
- Not as hard as carborundum, but less brittle and tougher

Uses

- Grinding hard steel and high tensile strength materials
- Manufacturing of abrasive wheels

Applications of Abrasives

- ✓ As loose powder
  - Example : Quartz and Garnet
- ✓ As abrasive paper or cloth
  - Example : Alumina and Silicon carbide
- ✓ Grinding wheels

Abrasive paper or cloth

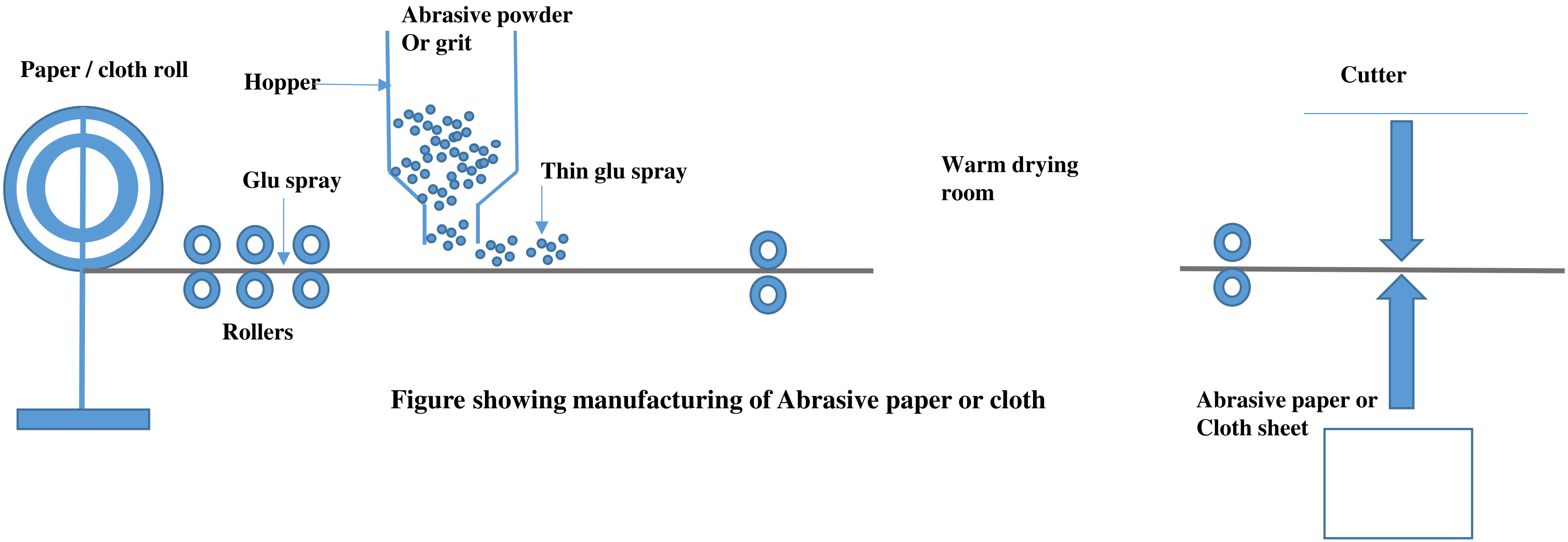


Figure showing manufacturing of Abrasive paper or cloth

Grinding Wheels

Are expandable wheels, composed of an abrasive compound

Characteristics

- ✓ Abrasive Grain

  Actual abrasive is selected according to the intended purpose of the grinding wheel and hardness of the material being cut
- ✓ Grain Size

  Grain size vary from 8 (coarsest) to 1200 (finest) determines the physical size of the abrasive grains
- ✓ Wheel grade

  Grade from A (soft) to Z (hard), determines how tightly the bond holds the abrasive
- ✓ Grain spacing

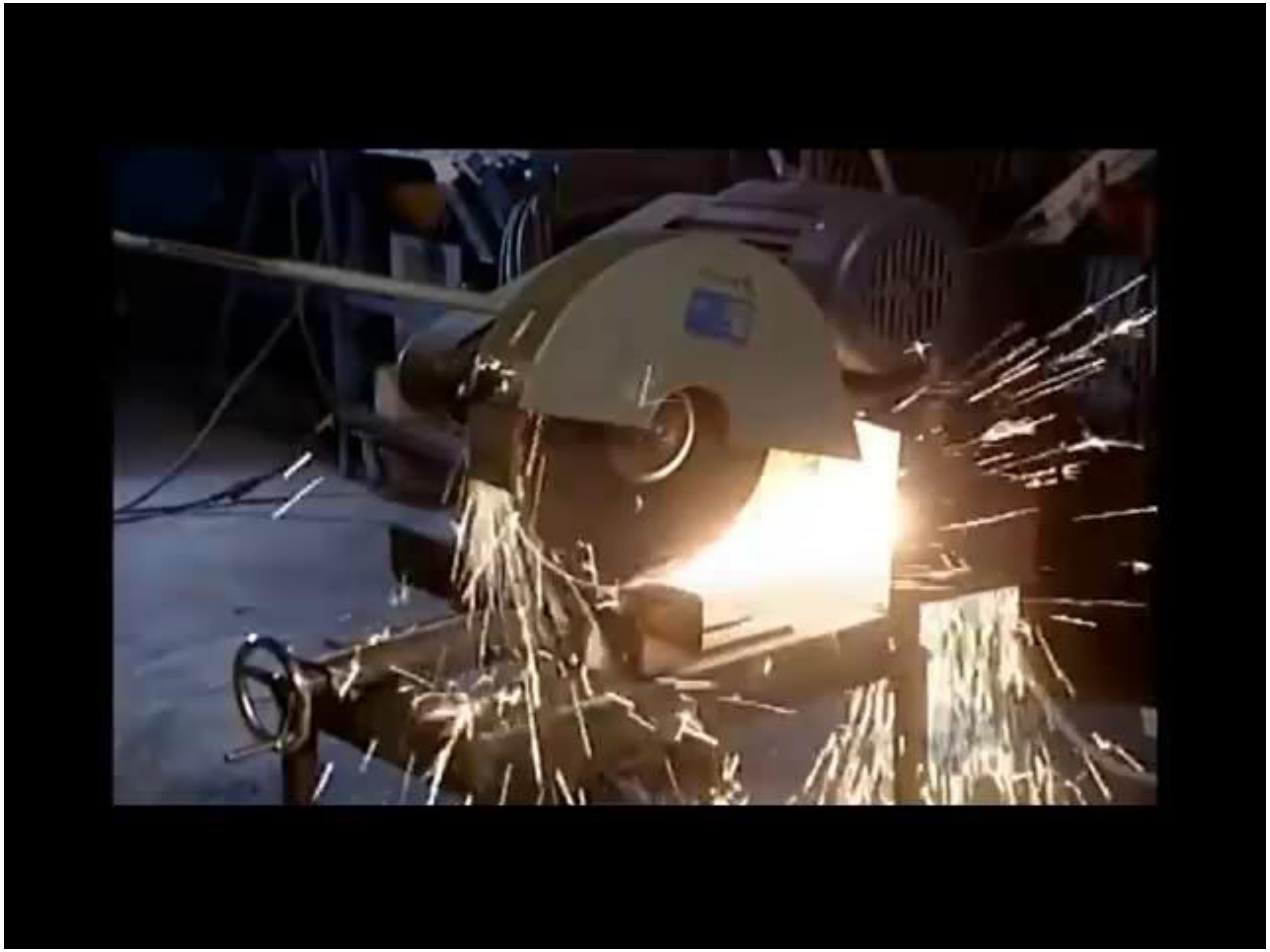
  Varies from 1 (densest) to 16 (least dense)
- ✓ Wheel bond

  It determines how the wheel holds the abrasive

Uses:

- ✓ Removal of scales from the iron surfaces
- ✓ Sharpening cutting tools
- ✓ Sharpen the knives, tools etc.,

Manufacturing of Grinding Wheels



Engineering Materials - Refractories

Refractories

- Materials that can withstand high temp without softening and deformation in their shape.
- Used for the construction of furnaces, converters, kilns, crucibles etc.

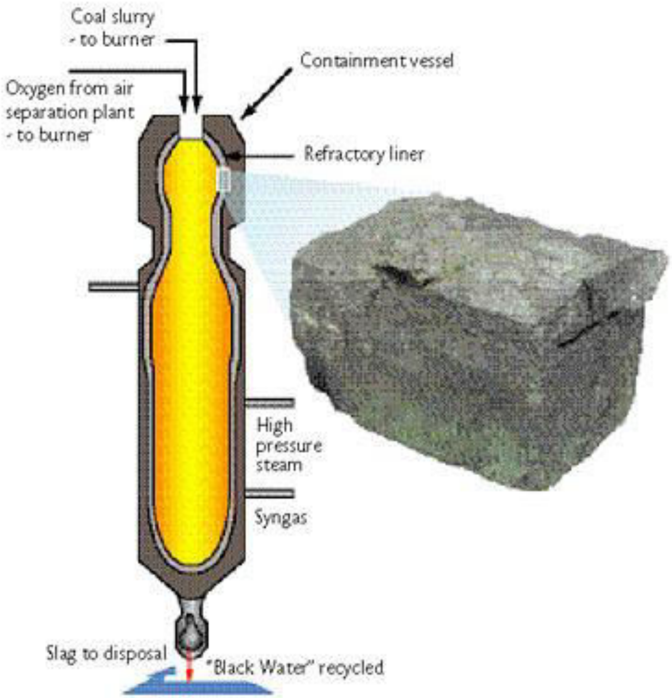


Fig (1) : Schematic of gasifier cross section showing the location of the spent refractory brick

Refractories Examples

Fig (2 & 3) : Various shapes of materials used in refractories

Fig (4 & 5) : Furnace inner lining showing refractory materials

Characteristics of Refractories

- Infusible at operating temperature
- Chemically inert towards corrosive gases, liquids etc.
- Should not suffer change in size at operating temp
- Should have high refractoriness
- Should have high load bearing capacity at operating temp.

Classification of Refractories

Refractories

CHEMICAL NATURE

- Acidic Refractories
  - Silica , Alumina
- Basic Refractories
  - Magnesite, Dolomite
- Neutral Refractories
  - Graphite, Carborundun

REFRACTORINESS

- Low Heat Duty
- Intermediate Heat Duty
- High Heat Duty
- Super Heat Duty

Properties of Refractories contd..

Pyrometric Cone : “Is a refractory specimen of standard dimension (38mm height and 19mm triangular base) and composition. “

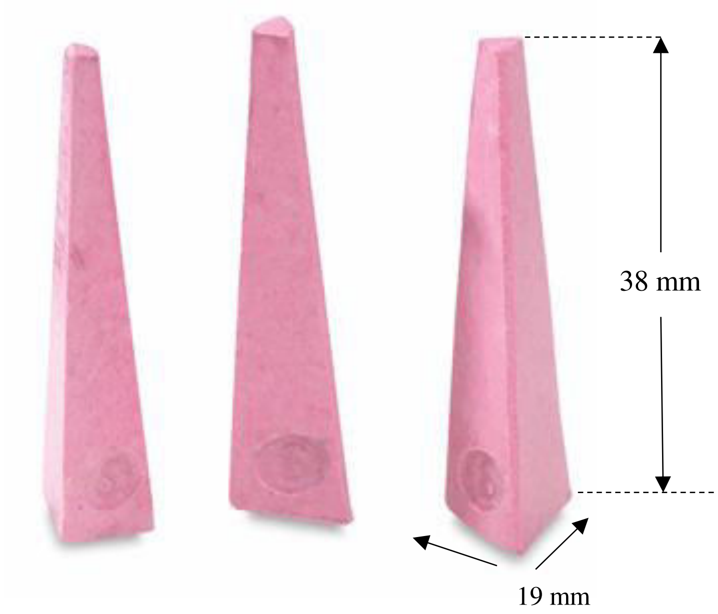
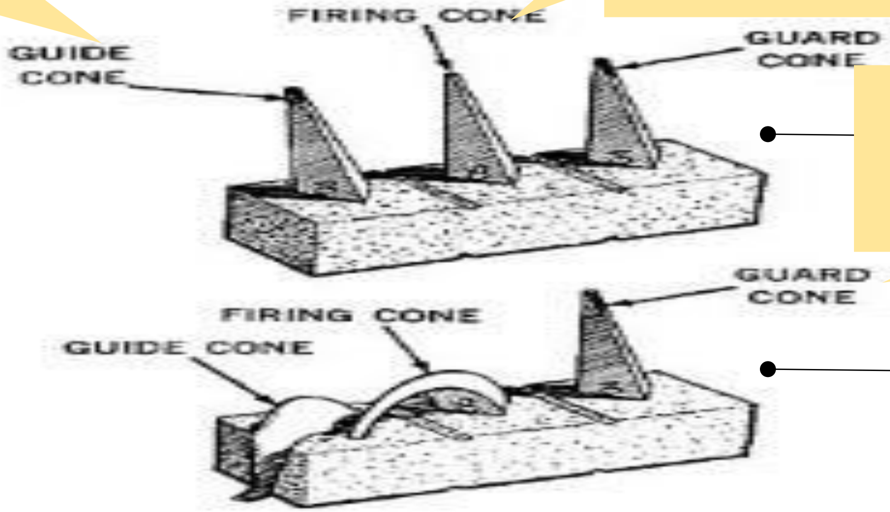


Figure showing Pyrometric Cones

Objectives of PCE Test

- To determine the softening temperature of a test refractory material.
- To classify the refractories
- To determine the purity of the refractories
- To check whether the refractory can be used at particular servicing temperature.



One cone number cooler than firing cone

The desired cone for the ware being tested

One cone number hotter than firing cone

After Firing

Objectives of PCE Test contd…

Seger Cone : "Are pyramid shaped standard refractory of definite composition and dimensions and hence it has a definite softening temperature. "

- Refractoriness is determined by comparing the softening temperature of a test cone with that of a series of seger cones
- A test cone is prepared from a refractory for which the softening temperature to be determined, as the same dimensions of seger cones

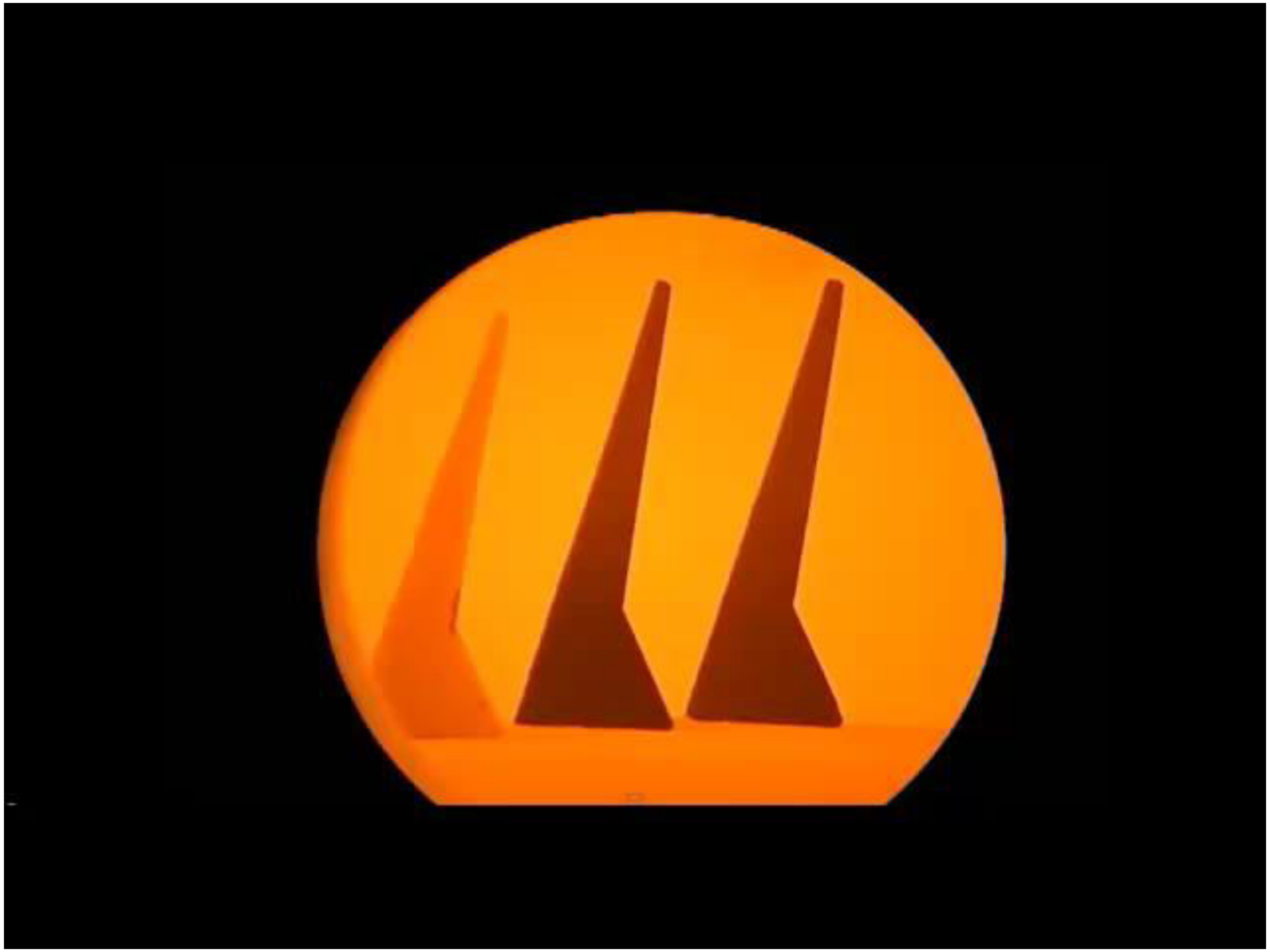
Heat at 10° C / min in electric furnace

Seger Cone bends

Test Cone bends and Seger cone bends more and touches base

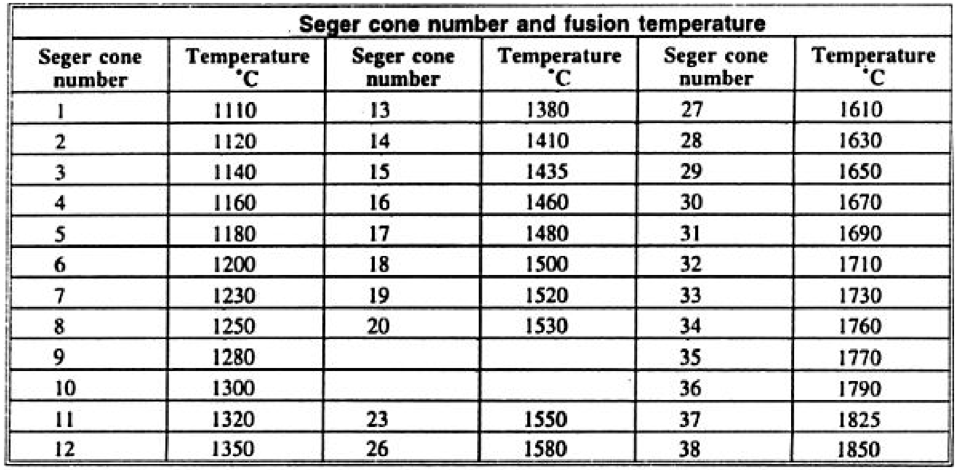
Figure showing PCE Test

Bending of Pyrometric Cones



Pyrometric Cone Equivalent (PCE) Number

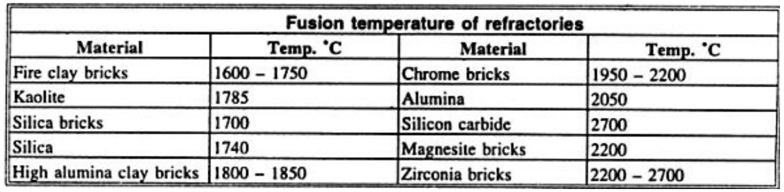
PCE Number: "Value representing the number of standard cones which also fuses with test cone for a given refractory"



Seger cone number and fusion temperature

Seger cone number	Temperature °C	Seger cone number	Temperature °C	Seger cone number	Temperature °C
1	1110	13	1380	27	1610
2	1120	14	1410	28	1630
3	1140	15	1435	29	1650
4	1160	16	1460	30	1670
5	1180	17	1480	31	1690
6	1200	18	1500	32	1710
7	1230	19	1520	33	1730
8	1250	20	1530	34	1760
9	1280			35	1770
10	1300			36	1790
11	1320	23	1550	37	1825
12	1350	26	1580	38	1850

Figure showing Seger Cone Number and fusion temperature



Fusion temperature of refractories

Material	Temp. °C	Material	Temp. °C
Fire clay bricks	1600 – 1750	Chrome bricks	1950 – 2200
Kaolite	1785	Alumina	2050
Silica bricks	1700	Silicon carbide	2700
Silica	1740	Magnesite bricks	2200
High alumina clay bricks	1800 – 1850	Zirconia bricks	2200 – 2700

Figure showing fusion temperature of various refractories

Refractories Under Load (RUL) Test

What ? The temp. at which a std dimensioned specimen of a refractory undergoes 10% deformation with a constant load of 3.5 or 1.75 Kg/cm2
Use ? The load bearing capacity of a refractory can be measured by RUL test

Figure showing Apparatus for RUL Test

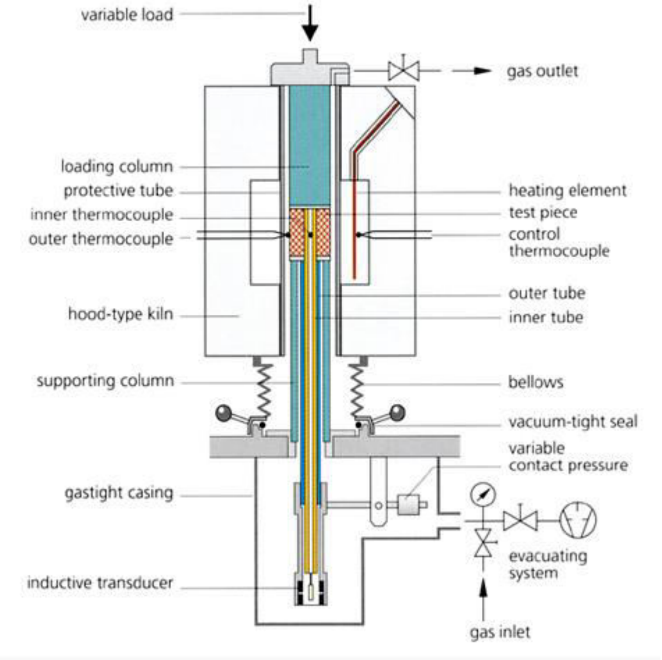
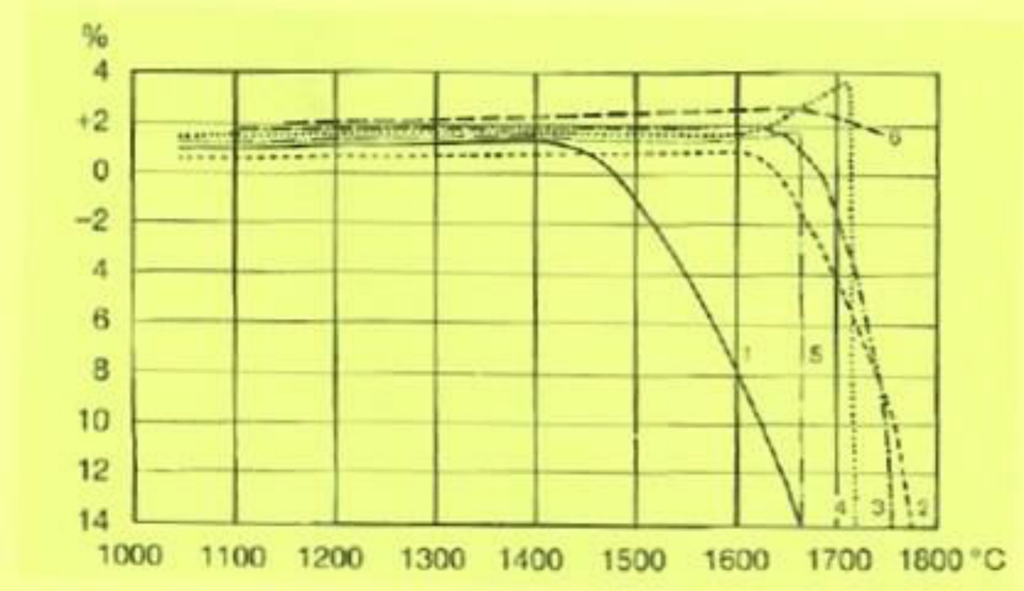


Figure showing Schematic Representation of Apparatus for RUL

Refractories Under Load (RUL) Test contd …

- The RUL test gives only an index of refractory quality, rather than a figure which can be used in a refractory design

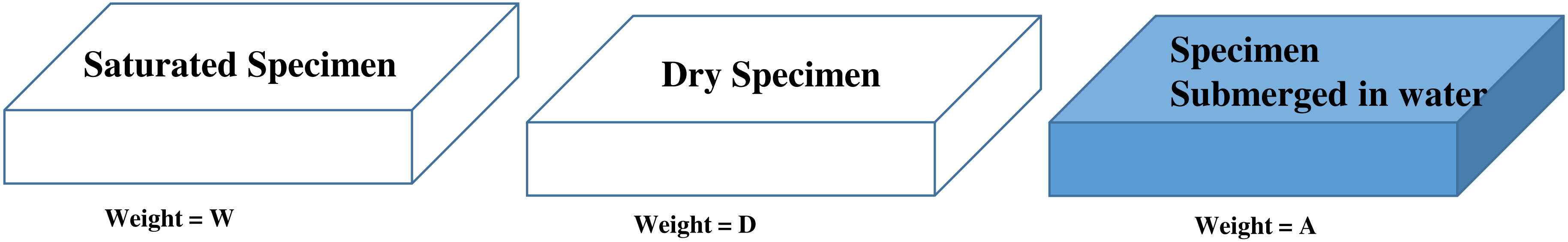


Refractoriness under load curves of refractory bricks
1. Fireclay, 2. Sillimanite, 3. Chrome magnesia, 4. Silica (crown), 5. Silica (Coke oven), 6. Magnesia chrome

Figure showing RUL curves of different refractories

Porosity

- All refractories contain pores, either due to manufacturing methods or deliberately made(by incorporating saw-dust or cork during manufacture).
- Porosity is the ratio of its pore’s volume to the bulk volume.



Saturated Specimen

Weight = W

Dry Specimen

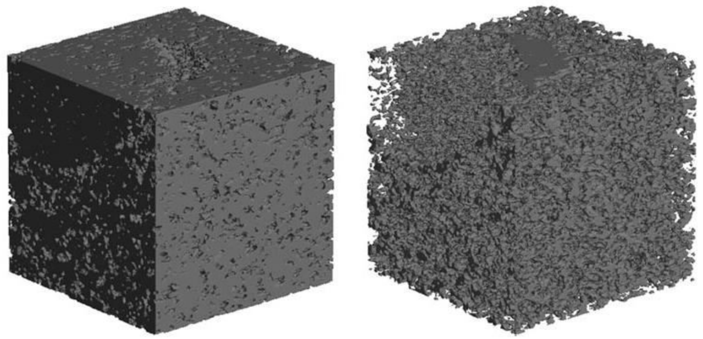
Weight = D

Specimen
Submerged in water

Weight = A

$$P = \left(\frac{W - D}{W - A}\right) X 100$$

Porosity contd…



An important property of refractory bricks as it affects many other refractory characteristics

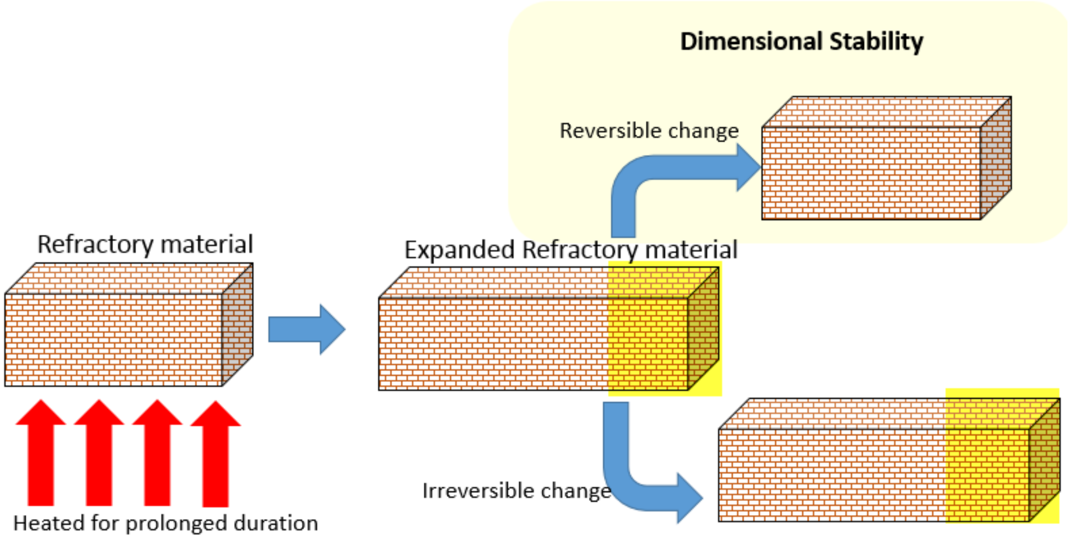
In a porous refractory, molten charge, slags, gases etc. are likely to enter more easily to a greater depth and may react and reduces the life of the refractory material

Porosity Decreases
Strength
Resistance to abrasion
Resistance to corrosion
Penetration by slag / gases etc.

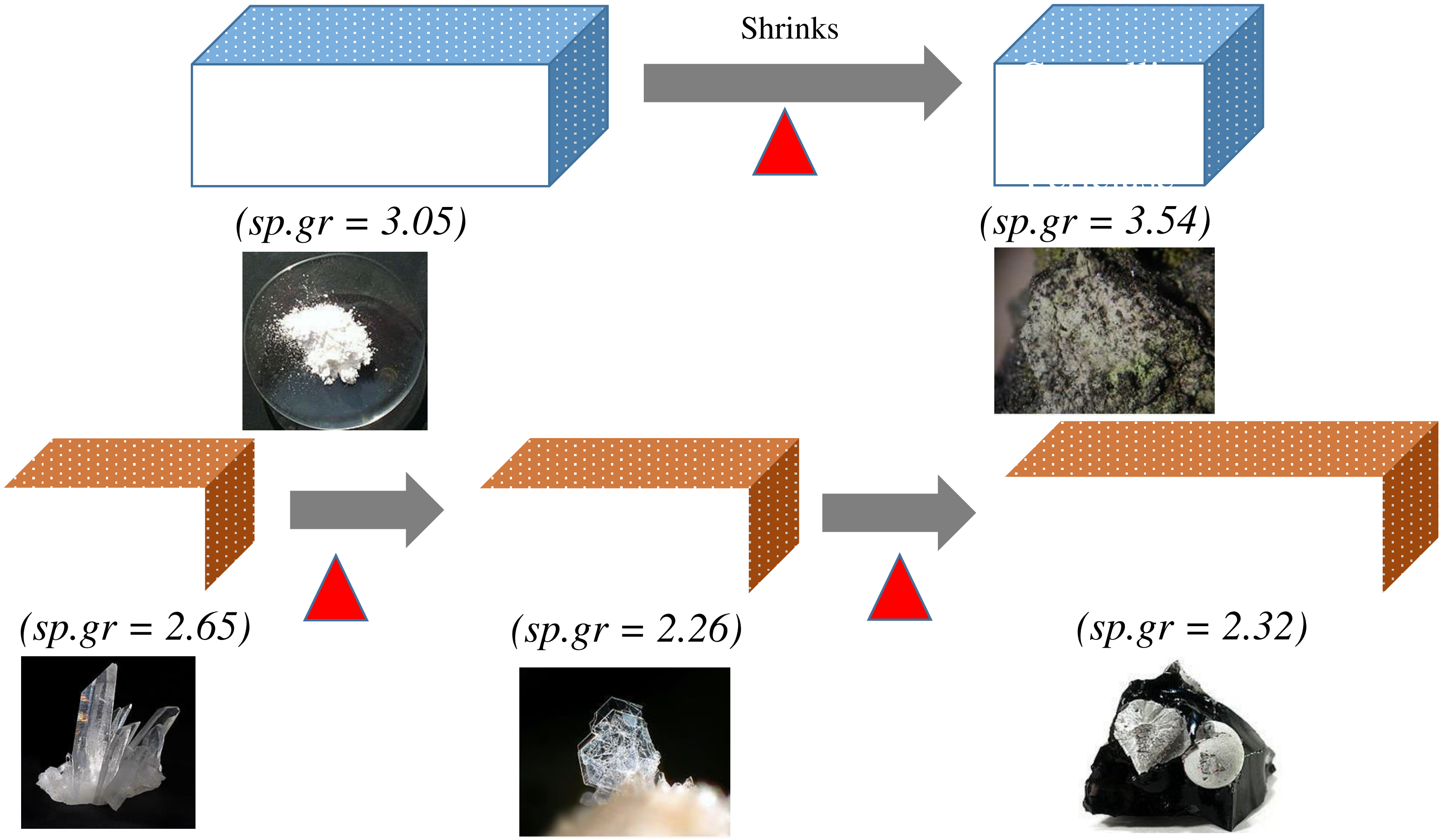
Dimensional Stability

"Resistance of a material to any volume changes, which may occur on its exposure to high temperature, over a prolonged time"

- Dimensional changes can be permanent or reversible
- Irreversible changes may result either in the contraction or expansion of a refractory



Dimensional Stability Examples



Shrinks

(*sp.gr* = 3.05)

(*sp.gr* = 3.54)

(*sp.gr* = 2.65)

(*sp.gr* = 2.26)

(*sp.gr* = 2.32)

Thermal Spalling

“Property of breaking, cracking or peeling of refractory material under high temp”

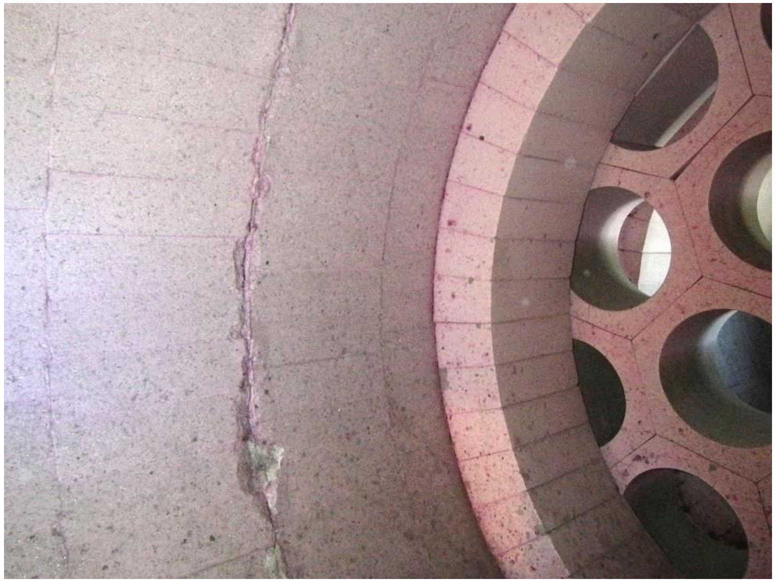


Figure showing crack of refractory material inside furnace

Thermal spalling is mainly due to

a. Rapid Change in temperature

This causes uneven expansion and contraction within the mass of a refractory, and leads to development of uneven stresses and strain

b. Slag penetration

This causes variation in the co-efficient of expansion and leads to spalling.

Thermal spalling can be decreased by

(i) Using high porosity , low co-efficient of expansion and good thermal conductivity refractory.
(ii) A voiding sudden temperature changes.
(iii) By modifying the furnace design

Thermal Expansion

“Expansion of a refractory material , when exposed to heat for a longer duration ”

- Refractory expansion has an impact on the capacity of the furnace lifetime
- Repeated expansion and contraction of refractory materials due to thermal impact causes wear & tear, breakdown etc.,

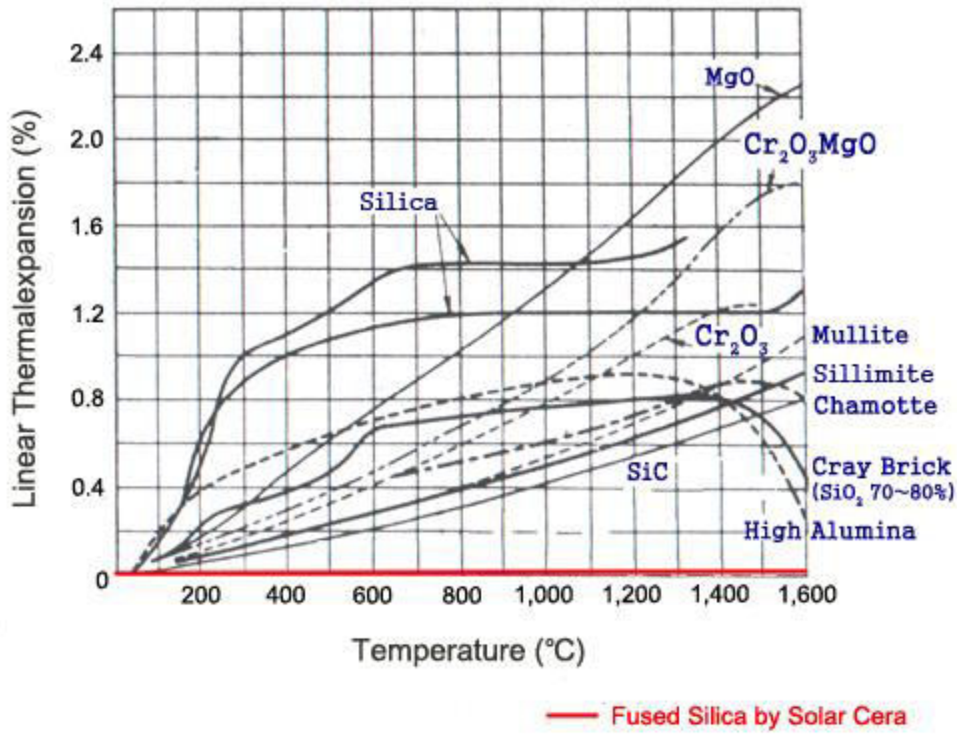
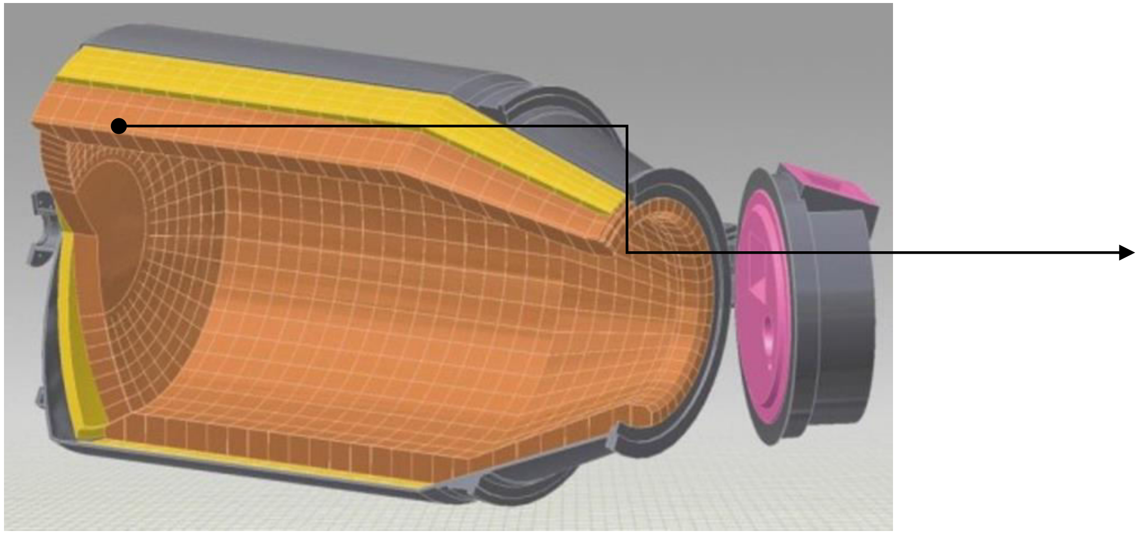


Figure showing thermal expansion % of various refractories

Characteristics of good refractory material

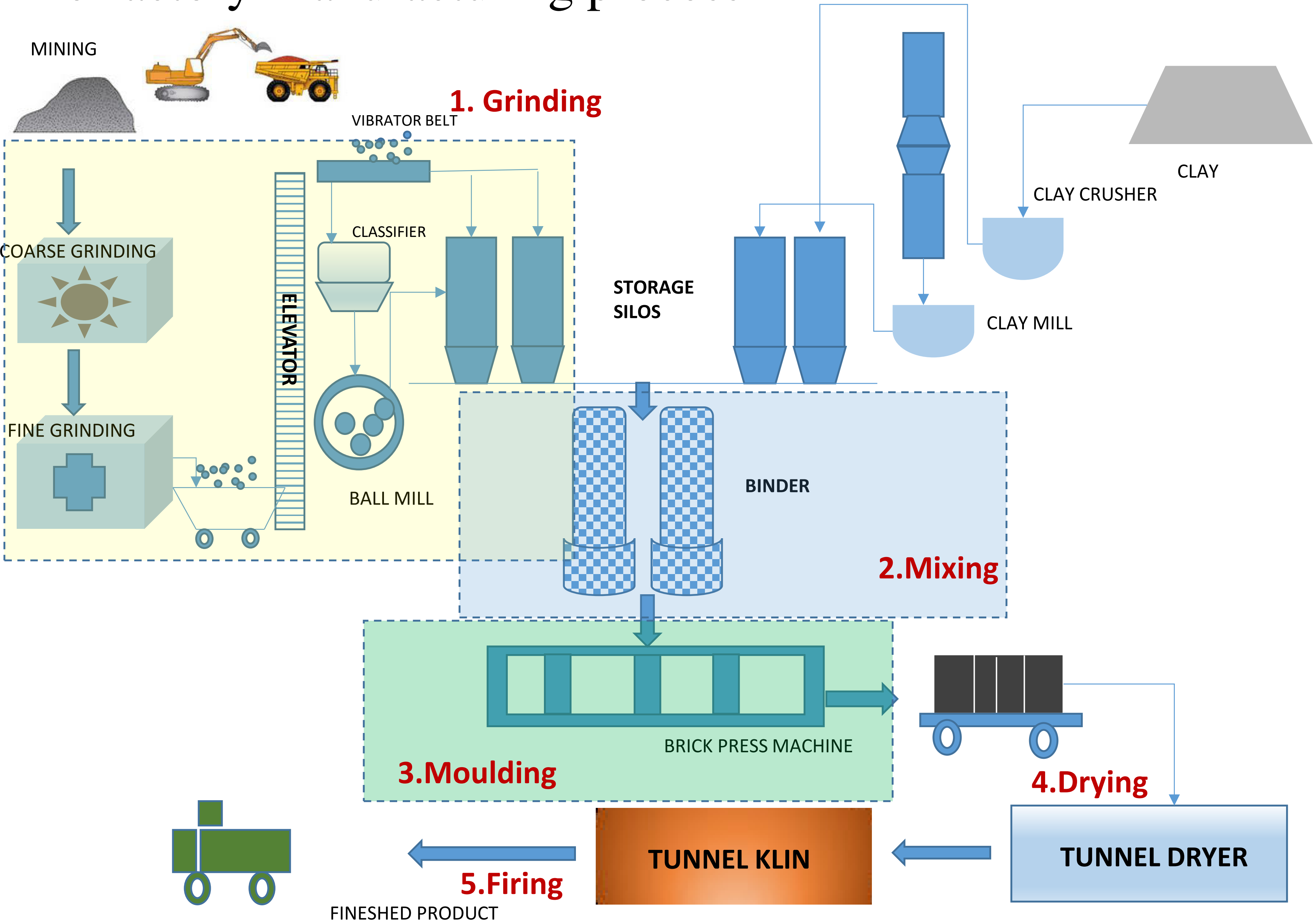


Lining of furnace with Refractory material

- Refractoriness
- RUL
- Dimensional stability

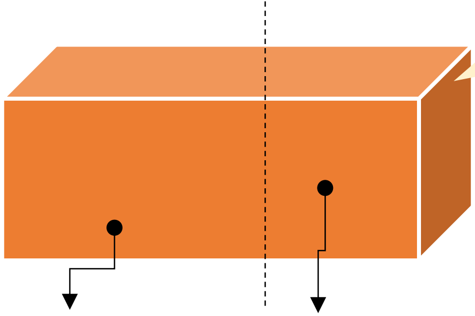
- Porosity
- Thermal Spalling
- Thermal Expansion

Refractory Manufacturing process



Acidic Refractory : Alumina Bricks or fire clay bricks

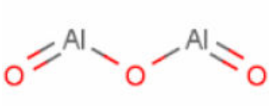
Composition of Alumina Bricks



50 % or more of Calcium Bauxite Al_2O_3

\+

Silica,Grog (fire clay)



\+ WATER

PASTE

Moulding: Machine pressing or slip casting

Drying and Firing at 1200°C to 1400°C (6 to 8 days)

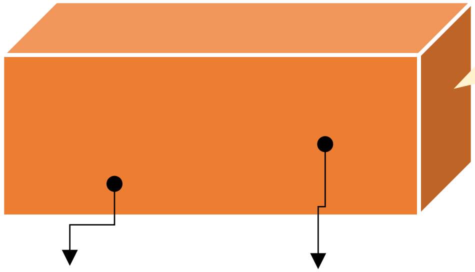
PROPERTIES

- Low coefficient of expansion
- High porosity
- Little tendency to thermal spalling
- Resistance to slag
- Stable and wear resistance
- High temperature load bearing capacity
- Inert to gases lik COl_2 , H_2 and natural gas

- **Medium Duty Bricks :** 50 – 60 % of Al_2O_3
  - Cement rotary klins
  - Soaking pits
  - Reheating furnace
  - Hearths & walls
- **High Duty Bricks** : 75 % of Al_2O_3
  - Hottest zones of cement rotary klins
  - Brass melting reverberatories
  - Aluminium melting furnaces

Basic Refractory : Magnesite bricks

Composition of Magnesite Bricks



more of Calcined Magnsite MgO **+** Castic Magnesia or Iron Oxide, Sulphite Lye

+ WATER

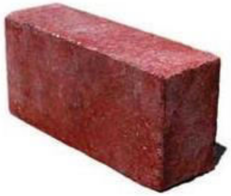
PASTE

Moulding: Machine pressing

Drying and Firing at 1500^{o}C (8 hours)

PROPERTIES

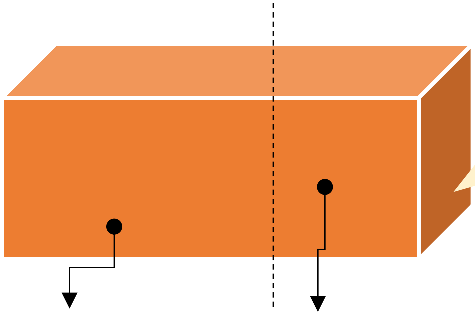
- Withstands 2000 ^{o}C without load and upto 1500 ^{o}C under load of 3.5Kg / cm^{2}
- Good resistance to basic slags
- Little shrinkage and more of spalling
- Poor resistance to abrasion
- Easily combines with Carbon dioxide and water
- Highly sensitive to sudden change to temperature



- **Steel Industry for lining of**
  - Basic Convertors
  - Open – hearth furnace
- **Copper Convertors**
- **Reverberatory furnaces**
- **Refining furnaces for Gold, silver and platinum etc.,**
- **Hot mixture linings**

Neutral Refractory : Caborundum or Silicon Carbide (SiC) Bricks

Composition of Silicon Carbide Bricks



60 % of Sand SiO_2 **+** 40 % Coke (C)

+ SAW DUST, WATER

PASTE

Moulding: Machine pressing

Drying and Firing at 1500°C

PROPERTIES

- High thermal conductivity
- Low thermal expansion
- 'Clay bonded' can be used upto **1750°C**
- 'Silicon nitrate bonded' poses high strength and thermal shock resistance
- 'Self bonded' has high refractoriness, strength , density, abrasion resistance and chemical resistance
- Oxidizes when heated at **900°C - 1000°C** , which can be prevented by coating with zirconium

➢ **Partial Walls of**
  - Chamber klins, coke ovens, muffle furnace

➢ **Floor for**
  - Heat treatment furnace

➢ **Heating elements in forms of**
  - Rods and Bars (globars)

Engineering Materials - Glasses

Introduction

“Glass is an amorphous, hard, brittle, transparent or translucent, ***super-cooled liquid***, obtained by fusing a mixture of a number of metallic silicates, most commonly Na, K,Ca and Pb”. It possesses no sharp melting point, crystalling structure and definite formula

Represented as **$xR_2O\ .\ yMO\ .\ 6SiO_2$**

R = monovalent alkali metals like Na,K

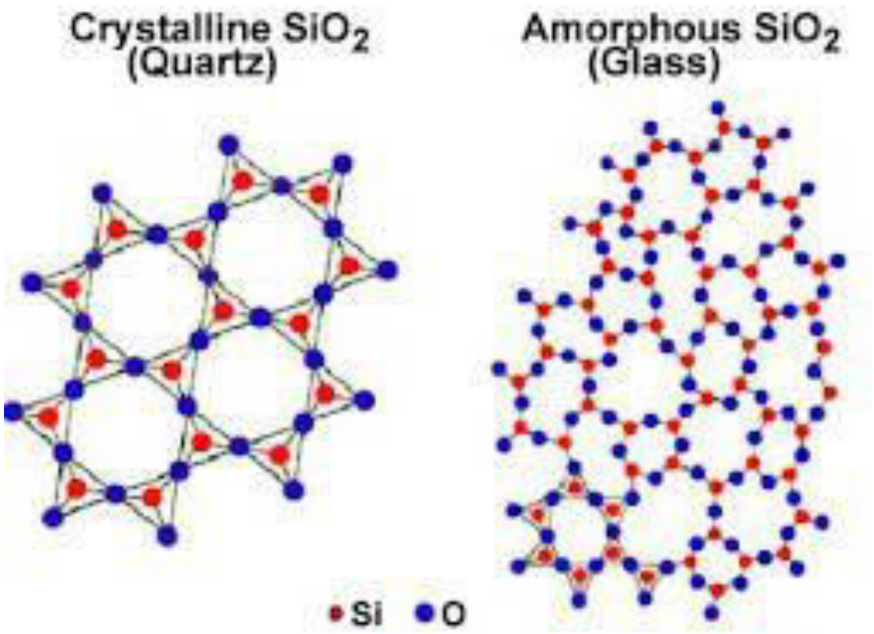
M = Divalent metals like Ca, Pb,Zn, etc

x & y = whole numbers

- Approximate composition of ordinary glass(Soda lime glass) is $Na_2O\ .\ CaO\ .\ 6SiO_2$
- In some glasses, SiO_2 may be replaced by $Al_2O3\ .\ B_2O_3\ .\ P_2O_5$, etc

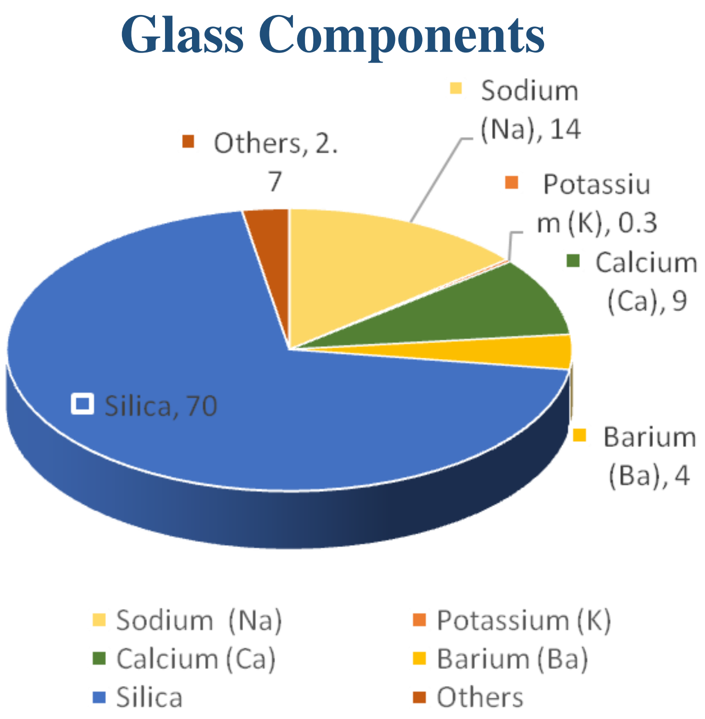
General Properties of glass

- ✓ Amorphous Solid
- ✓ No definite melting point
- ✓ Very brittle
- ✓ Softens on heating
- ✓ Can absorb, reflect and transmit light
- ✓ Good electrical insulator
- ✓ Affected by alkalis



- ✓ Not affected by air, water, acid or chemical reagents . But soluble in HF which converts into SiF_4
- ✓ Possesses high compressive strength and since it doesn’t have any crystalline structure , no slippage between planes can occur
- ✓ Light in weight because it has homogeneous internal structure similar to liquids

Raw materials of glass



Sl.No	Name of the element	Source of the element	Name of the glass produced
1	Sodium (Na)	Na_2CO_3,Na_2SO_4	Soft glass
2	Potassium (K)	Potash, K_2CO_3,KNO_3	Hard glass
3	Calcium (Ca)	Lime, limestone	Glass with high RI
4	Barium (Ba)	$BaCO_3$	Glass with high RI
5	Lead	Litharge, red lead	Flint glass
6	Zinc	Zinc Oxide	Heat & Shock proof glass
7	Borate	Borax, boric acid	Heat & shock proof glass
8	Silica	Sand, quartz	
	Colors Yellow	Ferric Salt	
	Green	Ferrous and chromium	
	Blue	Cobalt salt	

Glass Manufacturing

Manufacturing of glass consists of following high level steps

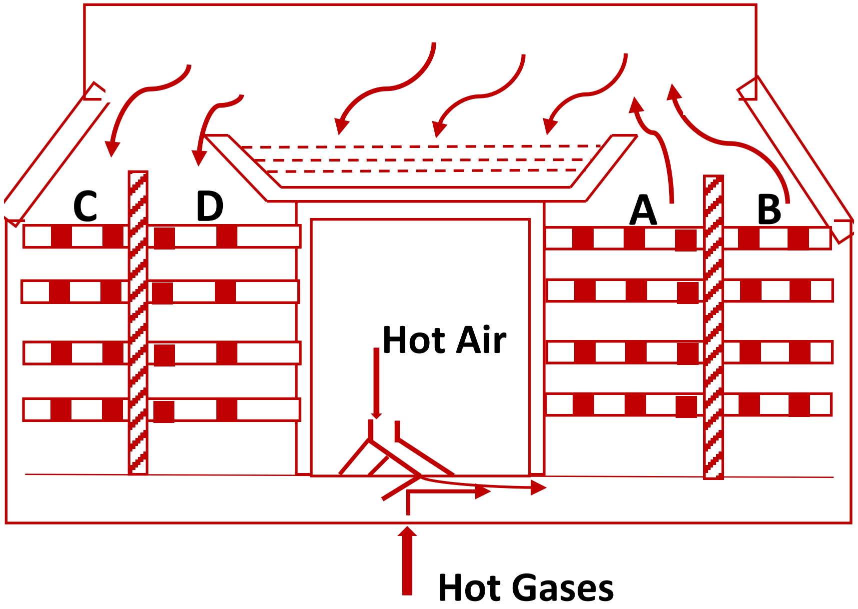
1. Melting
    a. Pot furnace
    b. Tank furnace
2. Forming and shaping
3. Annealing
4. Finishing

Melting

- Raw materials in proper proportions (sand, soda ash and lime stone) are mixed and finely powdered
- The homogenous mixture known as **Batch** is fused with some broken glass , called “**Cullet**” in any of the two types of furnaces
- The homogeneous mixture is melted either in
  a. Pot furnace or
  b. Tank furnace
- The **batch** melts and fuses at 1800°C

Melting: Pot furnace

Figure showing Pot furnace



- ✓ Two types of pots are used
  1. a. Open crucible type pot
  2. b. Closed covered type pot
- ✓ Generally closed covered type pot is used
- ✓ Pot is placed in a circle around a central opening in its bottom
- ✓ Heated by burning producer gas and air
- ✓ Roof of the pot is constructed with refractory material which also reflects the heat
- ✓ Also called as batch process

Melting: Tank Furnace

- The “batch” is melted in the tank using producer gas and air
- It follows “regenerative system of heat economy”
- Air and fuel is passes through A & B
- The burnt gases are deflected by the roof and “batch” gets melted
- Hot waste gas escapes through firebricks C & D
- The direction of the fuel gas & air is reversed through C & D , which absorbs the heat of the waste gas and burns
- The waste gas now escapes through A & B

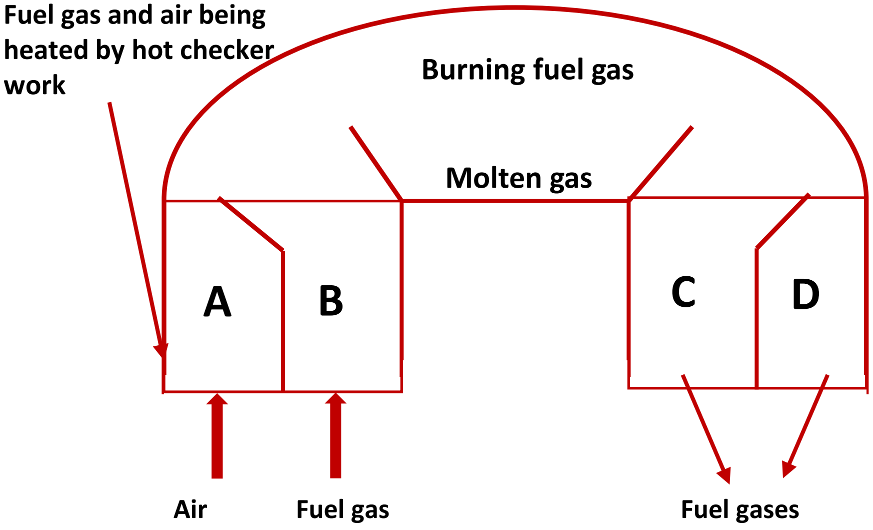


Figure showing tank furnace

Melting : Chemical reactions

- Cullet melts at relatively low temperature and assists in melting of rest of the charge
- During the melting process following reactions occur

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2 \uparrow$$

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

- The molten mass is heated till its free from air bubbles
- For colored gases desired pigment is added
- The molten mass is then cooled at about 800^{o}C at later point of time

Forming & Shaping, Annealing and Finishing

✓ Molten gas is converted to desired shape by blowing or moulding or pressing between rollers - “Forming and Shaping”

✓ Articles are then cooled gradually at room temperature. - “Annealing”

The longer the annealing period better the quality of glass

✓ After annealing, the articles are subjected to cleaning, polishing, cutting, sand blasting etc., - “Finishing”

Types of glasses

1. Soda-lime or soda glass
2. Potash lime or hard glass
3. Lead glass or Flint glass
4. Borosilicate glass or Pyrex glass or Jena glass
5. Alumina silicate glass
6. Optical or Crookes glass
7. Glass wool
8. Quartz glass
9. Opal glass

Soda-lime (or) Soft glass

Composition

Na_2O . CaO . $6SiO_2$

Raw Materials

- Silica
- $CaCO_3$
- Soda ash

Properties

- Low cost
- Resistant to water
- Attacked by acids
- Melts easily
- Moulded easily to any shape
- Poor thermal & chemical resistance

Uses

Window glasses, electric bulbs, bottles, jars, table wares etc.,

Potash-lime (or) Hard glass

Raw Materials

- Silica
- $CaCO_3$
- K_2CO_3

Properties

- High Melting point
- Not attacked by acids, alkali and other solvents
- Costlier than soda-lime glass

Uses

Combustion tubes, chemical apparatus

Composition

$K_2O . CaO . 6SiO_2$

Lead glass (or) Flint glass

Composition

$K_2O . PbO . 6SiO_2$

Raw Materials

- Silica
- Lead Oxide
- Potassium Oxide

Properties

- Bright, lustrous and possesses high specific gravity
- Expensive to manufacture , than ordinary lime-soda glass
- Lower softening temperature than soda-lime glass
- Higher refractive index and excellent electrical properties

Uses

- High quality table wares, neon sign tubings , optical lenses
- High dense glasses are used for windows to protect from X-rays and gamma rays

Pyrex-glass (or) Jena glass

Raw Materials

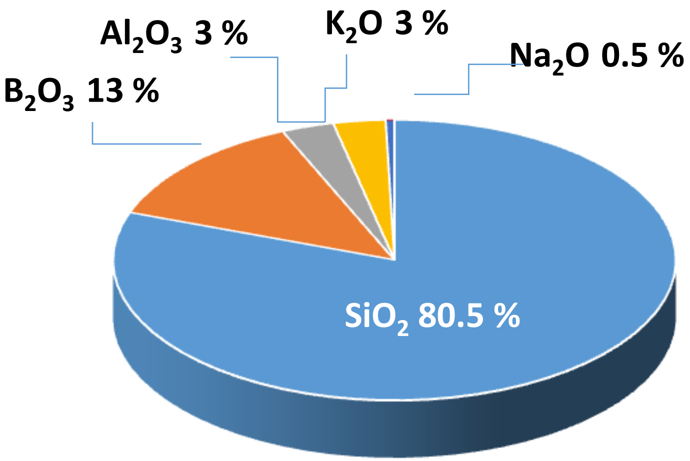
- Silica
- Small amount of alumina
- Some oxides

Properties

- Substitution of alkali (Na_2O) and basic alkaline earth oxides(CaO) of the soda glasses by boron and aluminium oxides results in low thermal co-efficient
- High softening point and excellent resistivity(shock proof)
- High chemical resistance

Uses

Industrial pipeline for corrosive liquids, gauge glasses, superior laboratory apparatus etc.,



Composition

Alumino Silicate glass

Raw Materials

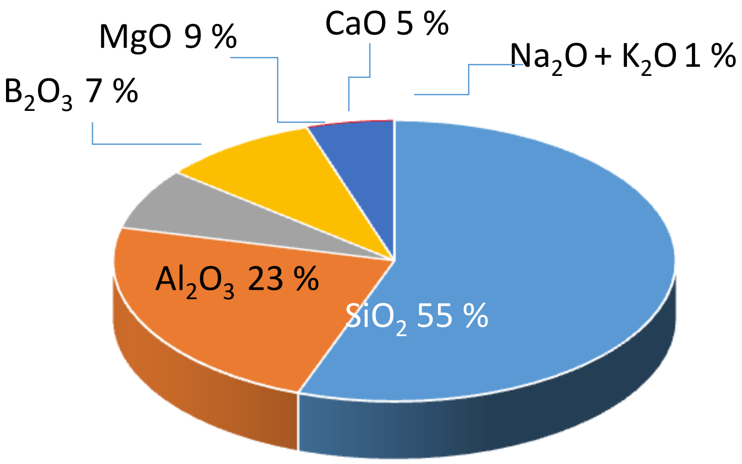
- 5 % more of alumina
- Addition of alumina makes glass heat resistant

Properties

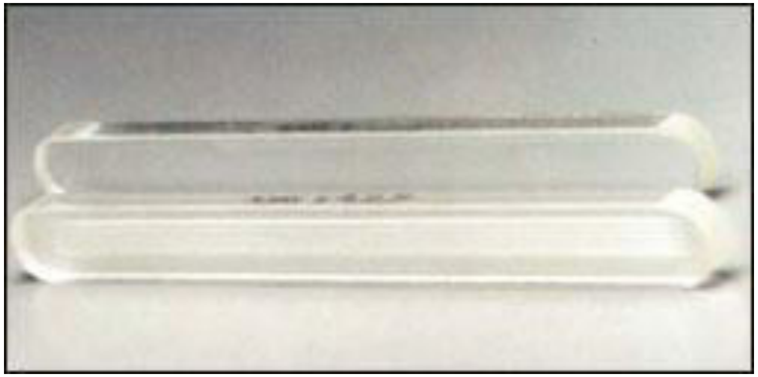
- Exceptionally high softening temperature
- Chemically durable
- Resistance to hydrolysis
- Affected by moisture due to high surface area

Uses

- High pressure mercury discharge tubes, chemical combustion tubes, specific domestic equipments
- Fibre glass



Composition



Optical, Quartz and Opal Glass

Optical glass

Raw Material

- Phosphorous and lead silicate together with small amount of cerium oxide

Properties

- Low melting point
- Soft
- Chemical-resistance
- Durability lesser than ordinary glasses
- Absorbs UV light

Uses

Optical lenses

Quartz glass

Raw Material

- Crystalline silica fused at 1900°C

Properties

- Outstanding resistance to thermal shock and chemicals

Uses

- Special lab-ware
- Crucibles
- Reaction tubes

Opal glass

Raw Material

- NaF (or) CaF_2 (or) $Ca_3(PO_4)_2$ (or) SnO_2

Properties

- Translucent white or milky glasses
- Transparent when in liquid
- Opaque when cooled

Glass wool

- Fibrous wool-like material, composed of intermingled fine threads (or) filaments of glass
- Alkali free
- Glass filaments are obtained by forcing molten glass through small orifices which measures about **0.0005** to **0.0007** mm in diameter

Properties

- Very good fire-proof and heat proof
- Very low electircal conductivity and thermal conductivity
- Resistance to water and most chemicals
- Tensile strength is 8X of steel

Uses

- Heat insulation purpose
- Electrical and sound insulation
- Filtration of corrosive liquids like acids
- Manufacturing fibre-glass, by blending with plastic resins

That's All