

Notes 1. Water Technology & Green Chemistry

Information technology (Pimpri Chinchwad College of Engineering)

UNIT-I

Water Technology & Green Chemistry

Introduction

Impurities in water

i) Suspended Impurities

The impurity particles like soil, sand, organic waste in water having size of particles greater than 1000\AA and visible are the suspended impurities.

Removal Method-They can be separated from water by simple filtration or the sedimentation or settlement methods.

ii) Colloidal Impurities

Finely divided organic or inorganic matter of the colloidal particle size 10 to 1000\AA makes water turbid.

Removal Method-The colloidal particles in water are negatively charged. They are separated by coagulation followed by sedimentation or filtration.

The coagulants are like FeSO_4 , alums, pulv floors, sodium aluminum, aluminum sulphate.

iii) Dissolved Impurities

Various metal salts are water soluble. Gases like O_2 , SO_2 , NH_3 , H_2S , CO_2 etc are soluble in water. Organic solids like sugars alcohols carboxylic acids, urea etc are soluble in water. Under ground and surface water due to contact with soil, rocks, contains cations like Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Fe^{+2} , Mn^{+2} , Al^{+3} etc. and anions like Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} etc.

Removal Method

The inorganic dissolved impurities are removed by chemical treatment.

Dissolved gases are removed by warming the water or mechanical deaeration method.

The organic dissolved impurities are removed by oxidation or biochemical oxidation.

iv) Biological Impurities

These impurities in water include bacteria, algae, fungi, and other small size aquatic animals.

Removal Method:

They are removed by first filtration and killed by sterilization.

The sterilization can be done by using chemicals like bleaching powder, sodium hypochlorite, chlorine, chloramines, ozone etc. and by physical methods like boiling of water, UV light.

Hardness of water:

The water which does not produces foam with soap , this water is known as hard water.

Soft water produces foam with soap. Hard water does not produces foam with soap because hard water contains impurities of hardness causing salts. These salts precipitates with soap.

Carbonates, bicarbonates of calcium & magnesium, chlorides, sulphates, nitrates of heavy metal are the hardness causing salts.

On the basis of these salts, hardness is divided in to two main types

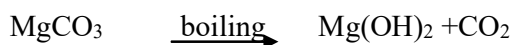
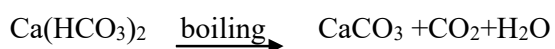
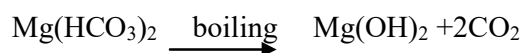
1. Temporary Hardness/Carbonate Hardness

2. Permanent/Non carbonates Hardness

1. Temporary Hardness/Carbonate Hardness:

The hardness comes in water due to presence of carbonates & bicarbonates of heavy metal salts. This hardness is called temporary Hardness/Carbonate Hardness.e.g. CaCO_3 , MgCO_3 , $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, Fe_2CO_3 etc

This hardness can be removed by boiling the water i.e. CO_2 is removed.



2. Permanent/Non carbonate Hardness:

The hardness comes in water due to presence of dissolved salts other than carbonates & bicarbonates. This hardness is called as permanent/Non carbonate Hardness.

Such salts are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 etc.

These salts cannot removed by boiling method but can removed by chemical treatment method.

Total Hardness: The hardness due to all hardness causing salts is known as total hardness.

i.e. Total hardness= Temporary Hardness +Permanent Hardness

Unit of Hardness:

The hardness of water is always expressed in terms of calcium carbonate equivalent because calcium carbonate is insoluble in water as compared to other salts and it's molecular weight is average 100.

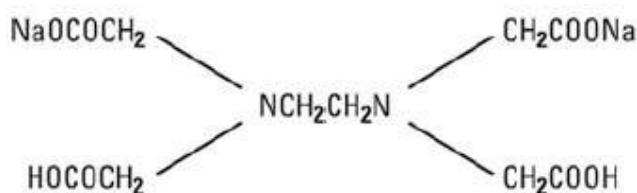
$$\text{mg CaCO}_3 \text{ eq. of any salt} = \frac{\text{Weight of that chemical} \times 50}{\text{Equivalent weight of chemical}}$$

- i) mg CaCO₃ eq.per lit
- ii) ppm CaCO₃ eq.per lit
- iii) ppb CaCO₃ eq.per lit
- iv) degree clerk & degree French

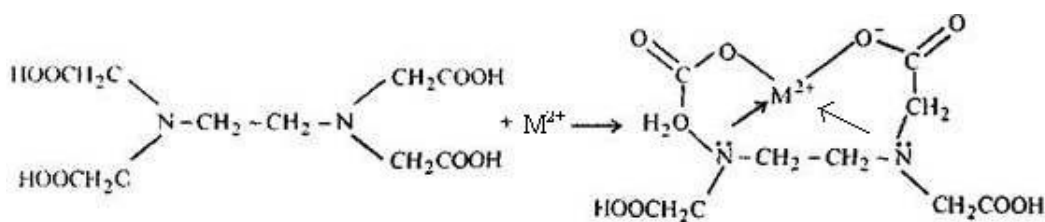
Determination of hardness of water by EDTA method.

Theory:

- ❖ Disodium EDTA reacts quickly with the hardness causing metal ions in water, even in very low conc. of salts.
- ❖ During the reaction H⁺ ions are formed & decrease the pH of reaction mixture.
- ❖ Therefore buffer solution of pH about 10 is necessary during titration .so that it will not allow the decrease of pH, otherwise the reaction is reversible.
- ❖ The reaction between disodium EDTA & heavy metal ion, forms cyclic co-ordination complex & hence the titration is known as complexometric titration.
- ❖ Generally organic dyes such as Erichrome black-T (EBT),Calcon, etc act as indicators for the EDTA titrations.
- ❖



DiSodium EDTA



Principle:

- ❖ The hardness causing ions like Ca^{++} & Mg^{++} present in water form unstable complexes (M-EBT) with indicator EBT, having pink red colour.
- ❖ EDTA then reacts with all hardness causing metal ion present in water to form stable complexes. (EDTA – metal complex).
- ❖ EDTA then reacts with metal ions from M-EBT complex to form stable EDTA metal complex with the regeneration of blue color of EBT.

Reactions:**Procedure : Titration part I Standardization of EDTA solution:**

- ❖ Fill a burette with disodium EDTA solution & pipette out 25 ml std. MgSO_4 solution in a conical flask.
- ❖ Add about 15 ml buffer solution of pH about 10 & 4-5 drops of EBT indicator in it.
- ❖ Titrate the pink red coloured mixture against the EDTA solution till it changes to sky blue.
- ❖ Let the titration reading be V_1 ml.

Part II: Hardness of water sample

- ❖ Take 50 ml water sample in a conical flask.
- ❖ Take about 15 ml of buffer solution of pH 10 & 4-5 drops of EBT indicator solution in it.
- ❖ Titrate this pink-red mixture against the EDTA solution till the color change to sky blue. Let the titration reading be y ml.

Calculations:**Part I: Standardization of EDTA**

$$M_1 V_1 = M_2 V_2$$

$$\text{EDTA} = \text{MgSO}_4$$

Part II: Total hardness of water sample:

$$\text{Hardness of water sample} = (Y \times Z \times 100 \times 1000) / V \text{ ppm CaCO}_3 \text{ equivalent.}$$

Where Y= Volume of EDTA

Z= Molarity of EDTA

V= Volume of Water sample

Temporary & permanent hardness by EDTA:

1. First total hardness of a water sample is found out, by using above formula.
2. Then hardness of the boiled & filtered water sample is found out.
3. The boiled & filtered water sample contains only permanent hardness.
4. Permanent hardness is subtracted from total hardness to get temporary hardness.

Advantages:

1. Suitable indicators available for accurate reading.
2. Color change at the end point of titration is sharp.
3. The EDTA titration method is convenient, fast, and easy.

Q. 100 ml of water requires 18.5 ml of 0.02 M disodium EDTA for end point in titration. 100 ml of the same water sample after boiling and filtration takes 10.7 ml of the disodium EDTA for end point in titration. Calculate Temporary & permanent hardness of water sample in ppm CaCO_3 equivalent.

Solution:- Volume of water sample titrated (V) = 100 ml

Molarity of EDTA (Z) = 0.02 M

Volume of EDTA (V_1) = 18.5 ml = Total hardness

Volume of EDTA (V_2) = 10.7 ml = permanent hardness

Total hardness = $(V_1 \times Z \times 100 \times 1000) / V$ ppm CaCO_3 equivalent.

$$= (18.5 \times 0.02 \times 100 \times 1000) / 100$$

$$= 370 \text{ ppm } \text{CaCO}_3 \text{ equivalent}$$

Permanent hardness = $(V_2 \times Z \times 100 \times 1000) / V$ ppm CaCO_3 equivalent.

$$= (10.7 \times 0.02 \times 100 \times 1000) / 100$$

$$= 214 \text{ ppm } \text{CaCO}_3 \text{ equivalent.}$$

Temporary hardness = Total hardness - permanent hardness

$$= 370 - 214$$

$$= 156 \text{ ppm CaCO}_3 \text{ equivalent.}$$

Q. 50 ml of a water sample requires 12.7 ml of 0.02M EDTA during titration. Calculate total hardness of the water.

Soln: $V = \text{Volume of water sample titrated} = 50 \text{ ml}$

$Y = \text{volume of EDTA} = 12.7 \text{ ml}$

$Z = \text{molarity of EDTA} = 0.02\text{M}$

Total hardness = $(Y \times Z \times 10^5) / V$ ppm CaCO₃ equivalent

$$= (12.7 \times 0.02 \times 10^5) / 50$$

$$= 508 \text{ ppm CaCO}_3 \text{ equivalent}$$

Alkalinity of water sample

Water sample is alkaline due to presence of hydroxides, bicarbonates & carbonates compounds dissolved in water.

Composition of alkaline water

Hydroxides: NH_4OH , $\text{Ca}(\text{OH})_2$

Bicarbonates: $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Fe}(\text{HCO}_3)_2$

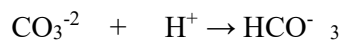
Carbonates: MgCO_3 , FeCO_3

Alkalinity of water sample:

Theroy:

- ❖ When an alkaline water is titrated with strong acid, first all OH^- get neutralized, then all the CO_3^{2-} ions are half neutralized to HCO_3^- .
- ❖ Till this stage PH of mixture decreases to about 8.2 & completion of this stage is indicating by change in colour of phenolphthalein.
- ❖ On continued addition of acid during titration ,all the HCO_3^- in the titration mixture get neutralized & completion of this stage ,is indicated by methyl orange colour change at 4 to 5 pH.

❖ **Reactions:**



Procedure:

- ❖ The alkalinities in water can be easily determined by neutralization titration against a standard strong acid titrant.
- ❖ Take V ml of alkaline water sample in a conical flask & add 2 drops of phenolphthalein indicator in it.
- ❖ Titrate this sample against std. strong acid solution (Z N) from burette ,till pink color changes to colourless . Let the burette be V₁ ml.
- ❖ Add few drops of methyl orange indicator into the same titrating mixture & continue the titration till the yellow colour of mixture changes to orange. Note the burette reading as V₂ ml.

Phenolphthalein alkalinity (P):

$$= (V_1 \times Z \times 50 \times 1000) / V \text{ ppm of CaCO}_3 \text{ equivalents.}$$

Methyl orange alkalinity OR Total alkalinity (M):

$$= (V_2 \times Z \times 50 \times 1000) / V \text{ ppm of CaCO}_3 \text{ equivalents.}$$

Types of alkalinities:

- i) Only OH⁻ ii) Only CO₃²⁻
- ii) Only HCO₃⁻ iv) OH⁻ & CO₃²⁻ together
- v) CO₃²⁻ & HCO₃⁻ together.

The amount of alkalinities due to OH⁻, CO₃²⁻, HCO₃⁻ types are calculated from the relation between value of P & M

Alkalinity	Quantity of OH ⁻	Quantity of CO ₃ ²⁻	Quantity of HCO ₃ ⁻
P =0	0	0	M
P =1/2M	0	2P	0
P = M	P	0	0
P < 1/2M	0	2P	M-2P
P > 1/2M	(2P-M)	2(M-P)	0

Numerical

Q. 50 ml of a water sample requires 9.2 ml of N/50 HCl up to phenolphthalein end point and total 13.1 ml of the acid for complete neutralization. Find the types and amount of alkalinity in the water sample.

Soln: $V_1 = 9.2$ ml

$V_2 = 13.1$ ml

$Z = N/50 = 0.02$ N

V = volume of water sample = 50 ml

P = phenolphthalein alkalinity

$$= V_1 \times Z \times 50 \times 1000 / V$$

$$= 9.2 \times 0.02 \times 50 \times 1000 / 50$$

$$= 184 \text{ ppm CaCO}_3 \text{ equivalent}$$

$$M = (V_2 \times Z \times 50 \times 1000) / V$$

$$= (13.1 \times 0.02 \times 50 \times 1000) / 50$$

$$= 262 \text{ ppm CaCO}_3 \text{ equivalent}$$

Type of alkalinity = $P > 1/2 M$

Quantity of $[\text{OH}]^- = (2P - M) = 106$ ppm CaCO_3 equivalent

And quantity of $[\text{CO}_3]^{2-} = 156$ CaCO_3 equivalent

III effect of hard water in boiler.

Large scale use of boiler water in industries is for:

- i) Steam generation
- ii) coolant

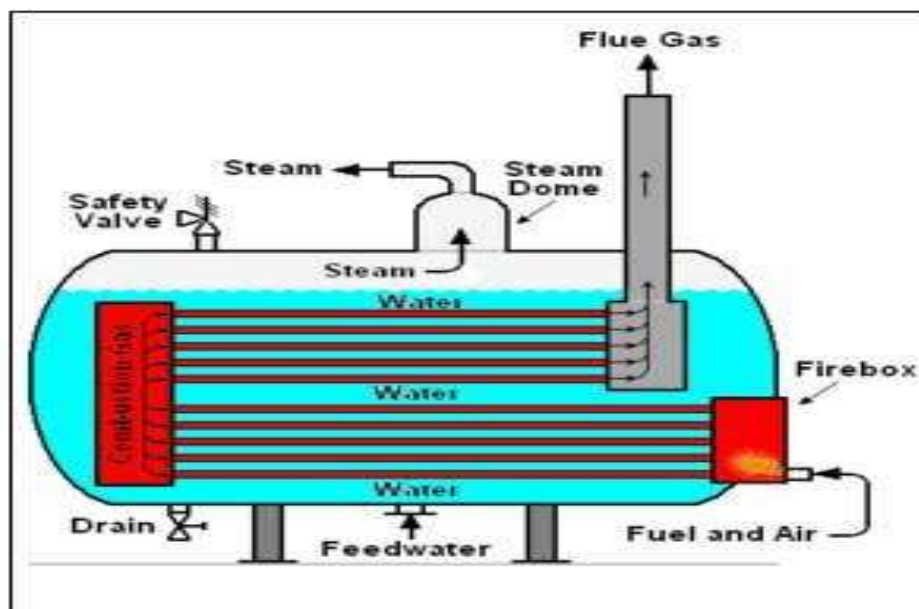
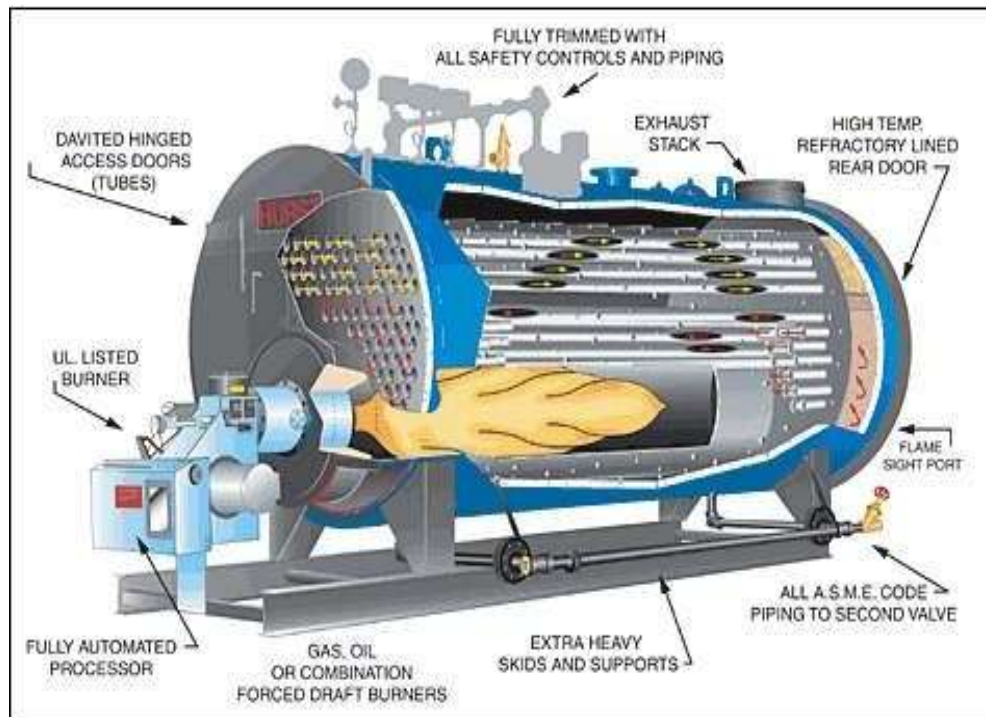
But due to use of hard water some problems are created known as ill effect. Which are discussed below.

Depending upon the operating pressure of boiler, the feed water should satisfy the following requirements of hardness:

Types of boiler, Steam pressure	Permitted hardness of feed water
Low pressure: Below 15 Kg/cm ²	25-50 ppm CaCO_3 equivalent
Medium pressure: 15-30 Kg/cm ²	10-25 ppm CaCO_3 equivalent
High pressure: Greater than 30 Kg/cm ²	0-10 ppm CaCO_3 equivalent

There are main four factors affecting boiler;

- A) Boiler Corrosion
- B) Priming & foaming
- C) Sludge & scale formation
- D) Caustic embrittlement



A) Boiler Corrosion:

The metal of boiler tube is mild steel, it get corrode if hard water is used for steam generation.

Disadvantages of corrosion:

1. Reducing the life of boiler

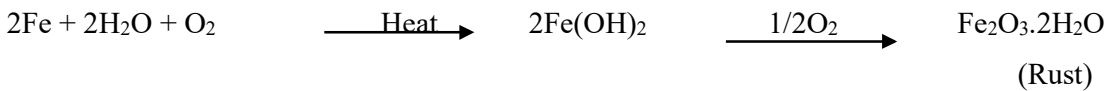
2. Leakage of joints and rivets
3. Increased cost of repairs & maintenance.



Reasons of corrosion in boiler:

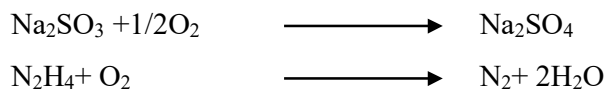
a) Dissolved oxygen:

If boiler feed water contains dissolved oxygen, then it corrodes boiler metal as follows:



Removal of oxygen:

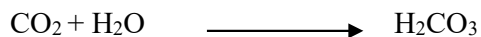
i) The dissolved oxygen is removed by adding some quantity of Na_2SO_3 (Sodium Sulphite) or hydrazine (N_2H_4)



ii) Dissolved oxygen can be removed by mechanical deaerator.

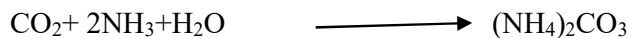
b) Dissolved CO_2

i) If boiler feed water contains dissolved CO_2 , then it forms carbonic acid (H_2CO_3) hence corrosion takes place.



Removal of CO_2 :

CO_2 can be removed by adding suitable amount of NH_3

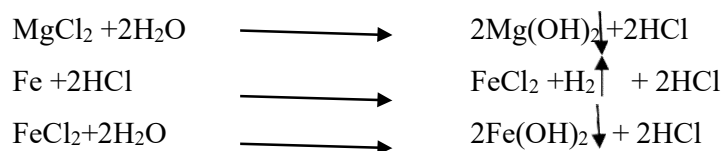


To avoid corrosion due to ammonia, its conc. is maintained to 10 ppm.

ii) Dissolved CO_2 can be removed by mechanical deaerator.

c) Hydrolysis of salts:

If water contains weak base- strong acid salts like MgCl_2 , CaSO_4 etc, then they are hydrolysed at high temp. & form strong acid. This acid corrodes boiler metal



To prevent corrosion due to acid formation in boiler the pH of water is adjusted to 8.5-9.0.

d) Galvanic Cells:

Galvanic cells are formed due to two different metals in water

If water contains impurities of metal which acts as a cathode then boiler metal acts as anode & corrode.

Galvanic corrosion can be avoided by dipping zinc plates in boiler feed water, which acts as sacrificial anode & boiler metal acts as cathode & does not corrode the boiler metal.

Assignment:

1. How is Alkalinity in a water sample determined? State the type of Alkalinities.
2. Explain boiler corrosion as ill effects of using hard water in boilers. State their causes and preventive measures.
3. 50 ml of a water sample requires 9.2 ml of N/50 HCl up to phenolphthalein end point and total 13.1 ml of the acid for complete neutralization. Find the types and amount of alkalinity in the water sample.

Ill effect of hard water in boiler:

B. Priming and Foaming:

Priming: "When a boiler produces steam rapidly, some water droplets are carried along with steam. This process of "Wet" steam formation is called priming."

Causes: 1. Very high level of boiler feed water

2. Presence of excessive foam
3. High speed of steam generation.
4. Faulty boiler design

Foaming: "It is the formation of continuous foam or bubbles on the surface of water."

Causes:

1. High conc. of dissolved salts in boiler feed water.
2. Presence of oil droplets and alkalies.
3. Presence of Finely dispersed suspended material
4. Violent agitation of boiler feed water

Disadvantages of priming and foaming:

1. Because of foaming actual height of water column cannot be judged well.
2. Because of priming, the salts present in the droplets enter in the part of machineries where steam is being used, thereby decreasing life of machineries.

3. The dissolved salts in droplet of wet steam get deposited on evaporation of water, which reduces efficiency of machine parts.
4. Foaming causes wet steam formation.

Prevention of Priming and foaming:

1. Foaming can be prevented by adding antifoaming agents like castor oil or by adding chemical like sodium aluminate and followed by blow down operation.
2. Priming can be prevented by use of well softened and filtered water
3. Maintaining low water level in boiler prevent priming
4. Rapid changes in steam rate should be avoided.
5. Steam purifier can be used.

C) Sludge & scale formation

Definition: The slimy and loose deposit of precipitated salts in boiler tube, depositing at the bends and valves, affecting free flow of water, is known as sludge.

Sludge formation:

In boiler water evaporate continuously & the concentration of salt left behind, goes on increasing after the saturation point they get precipitated .If the ppt. remains in boiler tubes as loose and slimy matter.

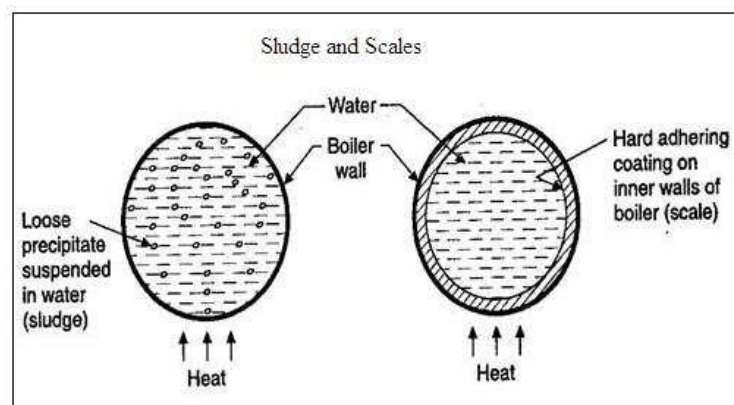
They are generally formed at cooler portions of boiler and the parts of boiler where flow rate is slow.

Disadvantages:-

1. They waste some portion of heat.
2. It disturbs working of boiler and sometimes may choke up the pipe
3. It reduces the flow rate of water in boiler.

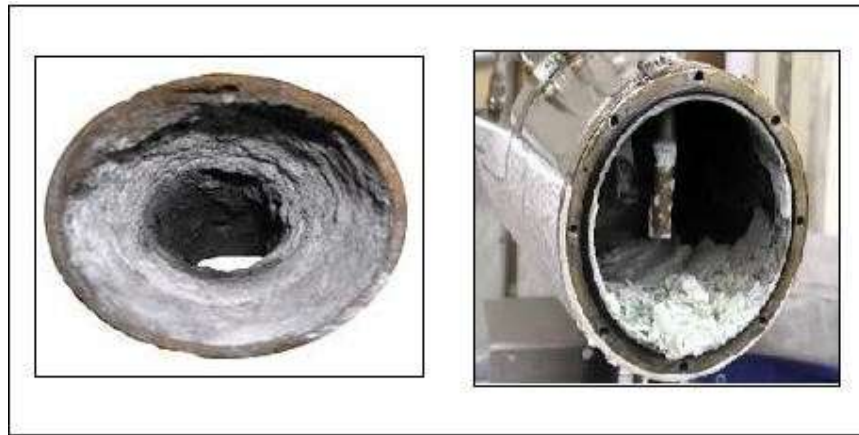
Prevention:-

1. Use of water containing very low quantity of total dissolved solids.
2. Frequently making blow down operation.



Scale formation:-

Definition: The hard and strong coating formed inside boiler tube by chemical reactions, which is bad conductor of heat, is called as scales.



Causes-

i) Decomposition of bicarbonates:

At high temp, bicarbonates decompose into sticky water insoluble material.



ii) Hydrolysis of magnesium salts: at higher temperature, magnesium salt undergoes hydrolysis, to form sticky.



iii) Presence of silica: Silica in the form of colloidal particles can deposit as calcium silicate or magnesium silicate as strong adhering material.

iv) Decreased solubility of CaSO_4 :

CaSO_4 has lesser solubility at higher temperature. Hence at high temp. CaSO_4 present in boiler will precipitate as hard scale forming material.

Disadvantage of Scales:

- ❖ **Wastage of Fuel:** Scales are bad conductors of heat & result in the reduction of heat transfer to the boil.
- ❖ **Over heating of boiler:** Scale reduces transfer of heat from boiler to boiler water, hence overheating is required to keep the required steam pressure.
- ❖ **Boiler Safety:**

Overheating of boiler is done due to scale formation. To maintain constant steam supply with required pressure boilers are overheated. Overheating makes boiler metal soft & weak which causes distortion of boiler tube & becomes dangerous in high pressure boiler.

- ❖ **Danger of explosion:**

When thick scale cracks due to uneven expansion, the water comes in contact with overheated boiler metal which causes large amount of steam formation & develops sudden high pressure. Due to this boiler metal may burst with explosion.

Removal of scales:

- ❖ The scale can be dissolved by use of suitable chemicals like EDTA, sodium phosphate, calgon etc & removed by blow down operation.
- ❖ Thin scales can be removed by use of scraper or wire brush.
- ❖ Thick scales can be removed by hammer & chisel.
- ❖ To remove hard & brittle scale thermal shocks techniques is used.

Prevention of scales:

- ❖ Use of softened water.
- ❖ Adding sodium phosphate to the water. (Phosphate conditioning).
- ❖ Frequent blow down operations to remove the sludge & precipitate rich water from boiler.
- ❖ Adding sodium aluminates, which can trap the scale forming particles.
- ❖ Adding organic chemicals like tannin which forms coating on the scale forming particles. This matter becomes easily removable by blow down operation.

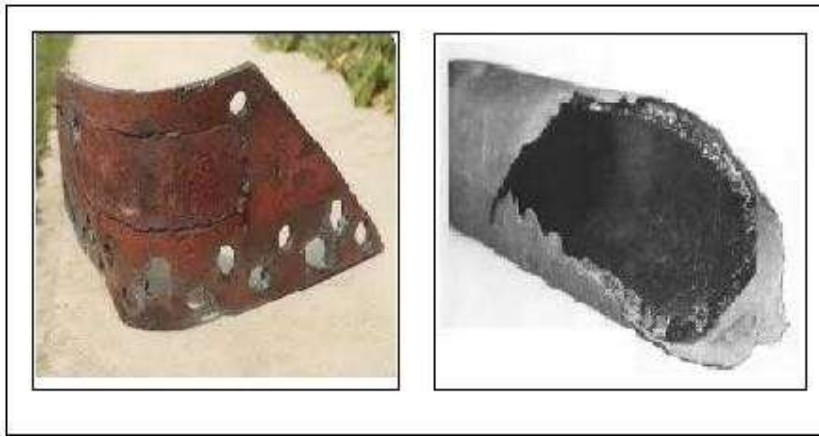
Differentiate between sludge and scale in boiler

Sr.No	Sludge	Scale
1.	Sludge is a loose deposit or slimy matter	Scale is hard coating
2	Sludge is less adherent on boiler metal and can be removed easily by brushes, detergents.	Scale is strongly adhered to boiler metal and difficult to remove
3	Sludge is form at the cooler parts & where flow rate is slow.	Scale is form at the hotter parts.
4	Sludge may lead to chocking	Scale may lead to bulging of metal tube
5	Sludge formation is due to an increase in concentration of salts in boiler water	Scales are formed due to CaSO_4 , CaCO_3 , $\text{Mg}(\text{OH})_2$, MgSiO_3 , CaSiO_3 ...etc.

D. Caustic embrittlement:

It is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances.

Definition: it is the fast corrosion of boiler caused by highly alkaline condition of water, during steam generation, especially in those boilers which generate high pressure steam.



Causes of Caustic embrittlement:

- ❖ Sodium carbonate (Na_2CO_3) is used for softening of water, but slight quantity of Na_2CO_3 is remained in unreacted state then it gets hydrolysed to form hydroxide.
 - ❖ That hydroxide makes the water alkaline and attacks at the bends, valves and edges of boiler tube.
- $$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{CO}_2\uparrow$$

Disadvantages:

- ❖ The hydroxide formed, comes in contact with boiler metal through cracks or grain boundaries' in boiler metal and formed sodium ferrite. it decreases strength of boiler metal.
- $$\text{Fe} + \text{NaOH} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NaFeO}_2 + \text{H}_2\uparrow$$
- sodium ferrite
- ❖ Sodium ferrite is brittle in nature; if attack of NaOH is continuous then whole boiler becomes brittle and cannot be used further.
 - ❖ In this type of corrosion two types of cell are formed.
 - ❖ A) Galvanic cell: stressed part of boiler metal acts as anode and gets corrode while unstressed part of boiler metal acts as cathode and remains protected.
 - ❖ B) Concentration cell: Higher conc. Of NaOH in cracks of stressed part acts as anode and gets corrode while lower conc. Of NaOH in unstressed part of boiler metal acts as cathode and remains protected.

Prevention:

- ❖ Use Sodium phosphate for water softening instead of Na_2CO_3 .
- ❖ Add some Tannin or Lignin to boiler water which blocks the cracks.
- ❖ Adjust pH 8-9 of boiler water.
- ❖ Add Na_2SO_4 to boiler water to keep the ratio of Na_2SO_4 to NaOH as 1:1, 2:1, 3:1 at pressure 10,20 and above 20 Kg /cm² respectively.

Zeolite process

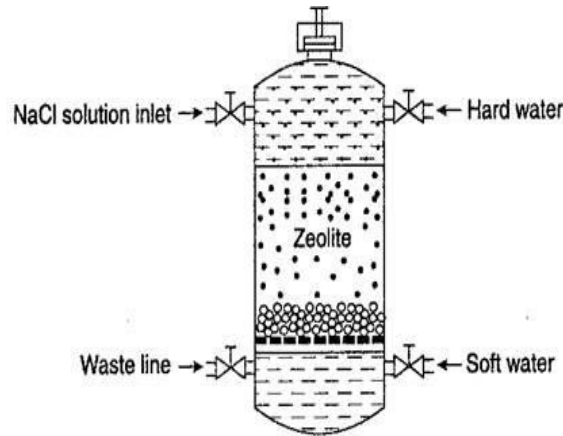
Principle : Sodium Zeolite has the property of capturing the heavy metal ions from water & in exchange released the Na^+ due to removal of heavy water ions (Ca^{++} , Mg^{++} , etc) from water ,the hard water is converted into soft water,by zeolite.

Zeolite structure representation: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$

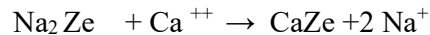
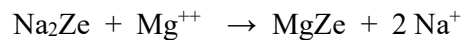
Process:

- ❖ The zeolite softener consists of cylindrical pot in which powder of sodium zeolite is placed over a perforated plate.
- ❖ There is an inlet on the top for or hard water & an outlet for collecting soft water from bottom.
- ❖ There is another inlet for adding 10%NaCl solution to regenerate the exhausted Zeolite bed.

Fig:-



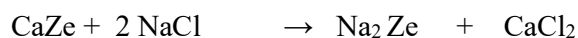
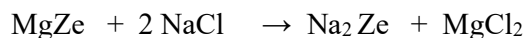
- ❖ When hard water percolates downwards through the zeolite bed, the hardness causing Ca^{++} , Mg^{++} , etc. Cation is retained in the bed & Na^+ ions are released in exchange .
- ❖ The soft water obtained and it contains equivalent quantity of sodium salts.
- ❖ There is reaction during treatment :



Regeneration:

When a large quantity of hard water is passed through the zeolite bed , the sodium zeolite bed completely gets changed to calcium & magnesium zeolite & there is no exchangeable Na^+ ion in it. Such zeolite is said to be exhausted & need's regeneration

The regeneration can be done by passing suitable volume of 10% NaCl (Brine) solution.



Advantages:

1. Easy process to operate.
2. Low cost operating process.
3. Process adjusts with water of any hardness & there is no need to analyse water before softening

4. The zeolite bed is whether active or exhausted, a be easily tested with soap solution.
5. The softener occupies small space.

Limitations:

1. Warm water should not be softened as it may decompose sodium zeolite slowly.
2. Mn^{++}, Fe^{+2} like ions get permanently captured by Zeolite bed .
3. The output water has almost zero hardness but contains equivalent quantities of sodium salts.

Applications:

1. Used for removing hardness causing ions from water.
2. Used for removing toxic metal ions & dye cations from polluted water.

Numericals:

Q.A zeolite bed exhausted by softening 4000 liters of a water sample requires 10 liters of 15% NaCl solution for regeneration. Calculate the hardness of water sample.

Solution:- 15% Nacl = 15gmNaCl/100ml
=150gm NaCl/lit

i)Amount of NaCl in mg =gm/lit x lit x 1000
=150 x 10 x 1000
=1.5 x 10⁵mg of NaCl.

ii) Amount of NaCl in terms of CaCO₃ = (amount x 50)/58.5
=(1.5 x 10⁶ x 50) /58.5
=1.28 x 10⁶ mg of CaCO₃ equivalent.

iii)Hardness of water per liter of water =1.28 x 10⁶
Hardness =1.28 x 10⁶ /4000
=320.51ppmCaCO₃ equivalent.

Q.A zeolite bed exhausted by softening 3500 litres of a water sample, requires 10 liters of 10% NaCl solution for regeneration. Calculate the hardness of water sample.

Solution:-

10% Nacl = 10gmNaCl/100ml
=100gm NaCl/lit

i)Amount of NaCl in mg =gm/lit x lit x 1000
=100 x 10 x 1000
=1 x 10⁶ mg of NaCl.

ii)Amount of NaCl in terms of CaCO₃ = (amount x 50)/58.5
=(1 x 10⁶ x 50)/58.5

$$= 8.5 \times 10^5 \text{ mg of CaCO}_3 \text{ equivalent}$$

iii) Hardness of water per liter of water $= 8.5 \times 10^5$

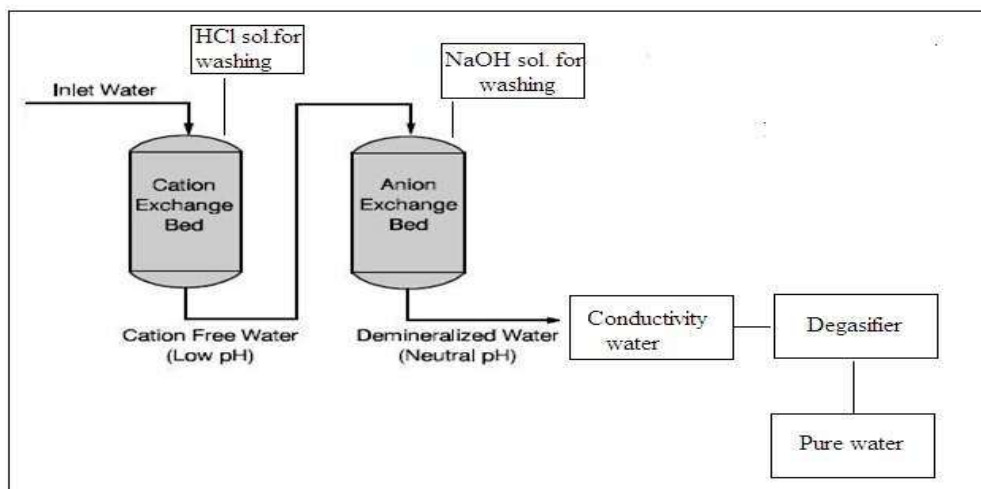
$$\text{Hardness} = 8.5 \times 10^5 / 3500$$

$$= 242.857 \text{ ppm CaCO}_3 \text{ equivalent.}$$

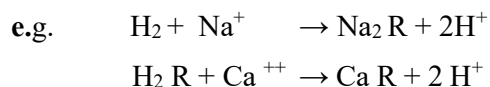
Demineralization process / Ion Exchange Process:

Principle : When water containing cation & anions, is passed through the resins, cation exchange resin captures all cation & anion exchanger resin captures all anions, to give pure & all ions free water.

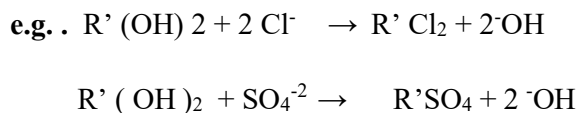
Process: The flow sheet of the treatment is shown in fig.



i) The water to be treated first enters in porous cation exchanger resin, where all cations are captured by the resin & H^+ is released in exchange.

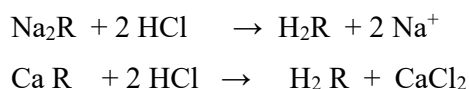


ii) Then the acidic output water from first resin enters in the porous anion exchanger resin where all anions in water are captured & OH^- is released in exchange.

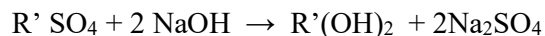


Regeneration:

i) The exhausted cation exchanger is regenerated by washing with dil. HCl solution.



ii) Cation exhausted anion exchanger resin is generated by washing with NaOH solution.



iii)Thus the water flowing out from second exchanger resin contains equivalent amount of H^+ & OH^- ions which combines to form H_2O & there is no ionic impurity in the final water . This method is also called as deionization or demineralization process.

Advantages:

1. The method gives water of zero hardness & no ionic impurities.
2. If the output water is passed throw degassifier, then the gaseous impurities like O_2 , CO_2 also get expelled, to get water for drinking purpose.
3. Equipment occupies small space.
4. Process is easy to operate, with negligible running cost.

Desalination of brackish water:

The water contains high concentration of dissolved salts is called brackish water.

Desalination is the process of removing common salts (mostly $NaCl$) from water

Commonly used Membrane techniques for Desalination are

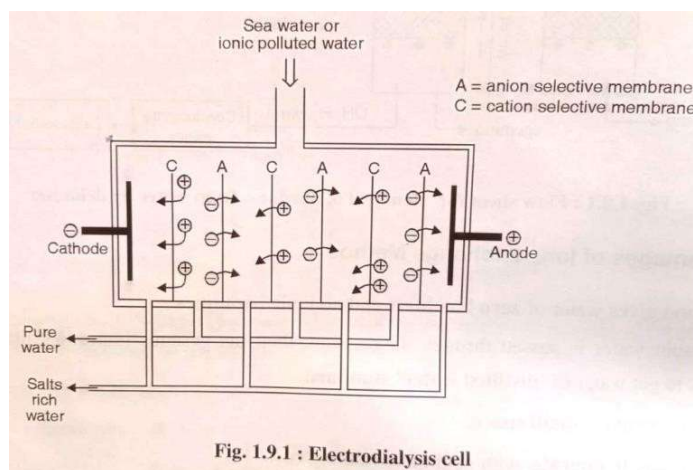
- i) Electrodialysis
- ii) Reverse Osmosis

Electrodialysis:-The process of removing ionic pollutants from water using membranes and electric field is known as Electro dialysis.

Construction and working:-

- ❖ An Electro dialysis cell consists of a large number of paired sets of plastic membranes.
- ❖ The membranes are ion selective. E.g. Cation selective membrane will allow only cation to pass through it, as this membrane consists of negatively charged fixed groups which repel anions and do not allow going it.
- ❖ The anion selective membrane will allow only anions to pass through it, as this membrane consists of positively charged fixed groups which repel cation and do not allow to go it.
- ❖ When an electric field is applied ,perpendicular to the direction of flow of water the anion move towards positively charged electrode throw the anion selective membrane in neighboring compartment but after the there is cation selective membrane & the movement stopped.

Diagram:



- ❖ Similarly cation move in the direction of negatively charged electrode & go in neighboring compartment .they cannot move further because next is anion selective membrane.
- ❖ The result will be alternate compartments to them with negligible concentration of ionic substances. Thus we get alternate stems of pure water from the electrodialysis cell.

Applications:-

1. Removal of ionic pollutants (Toxic, salts, ionic dyes, etc.) from treated industrial waste.
2. Removal of salt from tree water, to get pure water.
3. Removal of limited quantity of salts from sea water to get drinking (mineral) water.

Reverse Osmosis:

Membrane technique selectively separates the solutes or impurities on the basis of pore size.

Membrane technique involves;

- a) Reverse osmosis
- b) Hyper filtration
- c) Ultra filtration

Reverse osmosis is commonly used.

Principle:

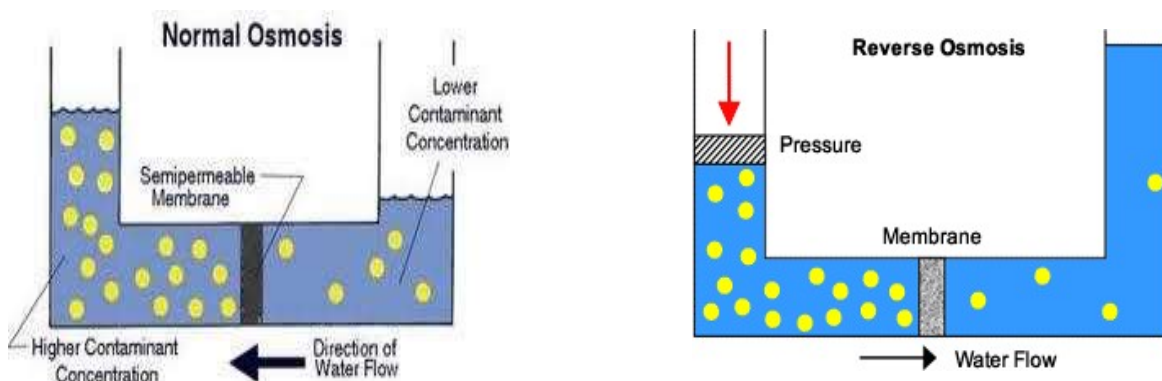
“The flow of solvent from higher concentration to lower concentration solution through semipermeable membrane by applying slightly higher external pressure than osmotic pressure of higher conc. Solution.”

This is the reverse process than normal osmosis. In normal osmosis, solvent flows from lower conc. To higher conc. through semi permeable membrane.

In the reverse osmosis, we apply external pressure on the higher conc. solution, thus solvent (water) flows from higher conc. solution to lower conc. solution and impurities remained behind.

Thus, water separate from the impurities.

Diagram:



Process:

Semi permeable membrane made up from polymeric materials like acrylics, polyamides, aramids etc.

Hard water or sea water is filled in reverse osmosis cell.

When pressure 200psi is applied on it, the water passed through Semi permeable membrane and impurities remains on Semi permeable membrane. Pure water collected from lower outlet.

Advantages:

- Ionic, colloidal, non-ionic impurities remove from water.
- Pure water for high pressure boiler can be obtained.
- It is used to obtain drinking mineral water.
- Simple to operate.
- Low cost process.

Green chemistry

Definition:

Green chemistry is use of chemistry for prevention by designing proper processes that reduce of element the generation of pollution of hazardous by products.

Goals of green chemistry

- To reduce adverse environmental impacts.
- To develop process based on renewable feed.
- To minimize by products (by higher % atom economy)
- To develop relations evolving less toxic materials.
- To develop process which is hazards free.
- To use environment friendly solvents & extractants rather than organic solvents.
- To improve energy efficiency by developing low temperature, low pressure processes using improved catalysts.
- To develop reliable methods to monitor & control processes.

Efficiency parameters for Reactions:

1. **Atom economy** =
$$\frac{\text{Molecular wt of desired product} \times 100}{\text{Molecular wt of all products}}$$

It can be alternatively stated as,

Atom Economy =
$$\frac{\text{Molecular wt. of desired product} \times 100}{\text{Molecular wt of all reactant}}$$

Desirable is the high atom economy. Addition reactions have economy = 100

2. **Conversion (%)** =

$$\frac{\text{Amount of reactant taken} - \text{Amount of reactant unconsumed}}{\text{Amount of reactant taken}} \times 100$$

= Amount of reactant reacted * 100/ amount of reactant taken

3. **Reaction yield:**

Yield (%) =
$$\frac{\text{Amount of product formed}}{\text{Expected amount of Product}} \times 100$$

High yield % is desirable

4. **Reaction selectivity:**

Selectivity (%) =
$$\frac{\text{Amount of desired product formed}}{\text{Amount of product expected on the basis of amount of reactant consumed}} \times 100$$

5.

Environmental load factor (E) :

$$E = \frac{\text{Total mass of effluent generated}}{\text{Mass of desired product}}$$

E is the effluent generated per kg of the desired product .it should be minimum.

6. **Mass intensity:**

It is the ratio of mass reactant used to mass of desired product.

Mass intensity (MI) = Mass of reactants used /mass of product desired.

(Mass of reactants excludes mass of water solvent, catalyst

It is related to environmental load factor (E) as **E= MI-1**

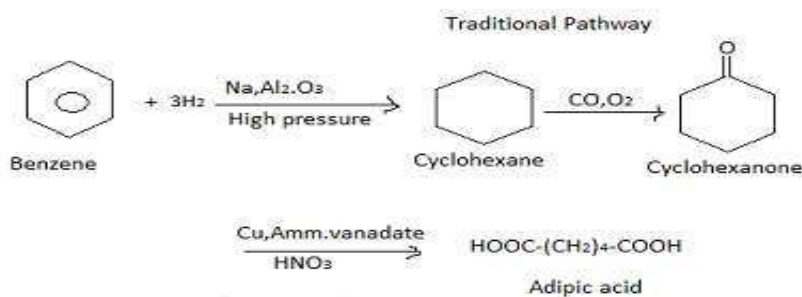
Ideally, MI should be 1, so that maximum mass of reactant is utilized in product formation.

Synthesis of Adipic Acid (For study only)

Traditional pathway of synthesis:

A) Synthesis of Adipic acid: Adipic acid is required for the manufacture of **nylon 66** .It is prepared by traditional & green pathway as below.

Traditional pathway:



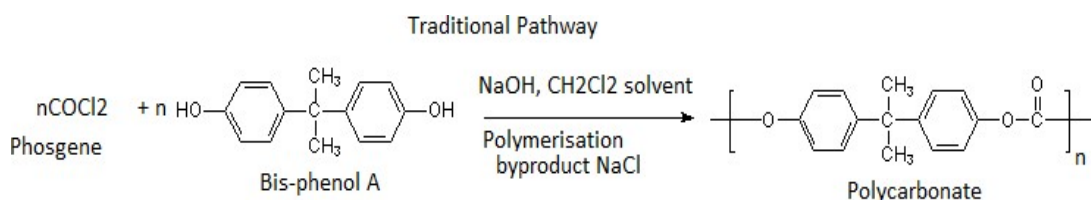
The problems or disadvantages of the traditional route are,

- Non renewable feedstock
- Carcinogenic feedstock
- Energy consuming
- More step & derivatives
- Higher temperature & pressure process
- The nitrous oxide emission from this process measurably contributes to global warming and ozone depletion.

Synthesis of Polycarbonate:

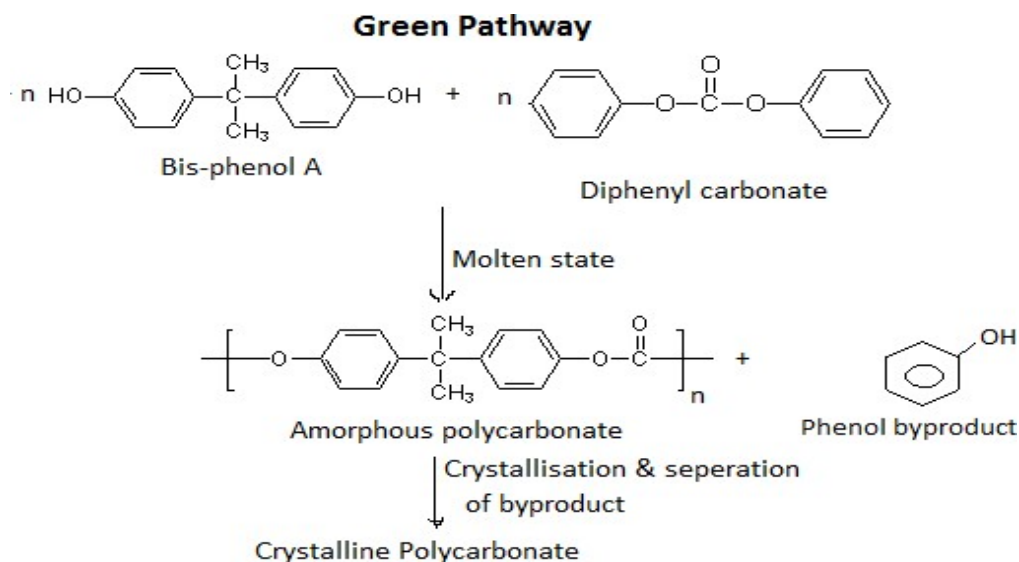
Polycarbonate is a very high impact polymer .It is a transparent polymer. It is used as bulletproof material, also for making CD, DVDs.

Traditional Route:



Disadvantages of traditional route of polycarbonate:

1. Uses poisonous starting material Phosgene
2. Use non-renewable CH₂Cl₂ solvent which is difficult to separate from product.
3. Solvent is also poisonous.



Green Route:

Green pathway reaction is developed by Komiya et al and his team of Asahi Chemicals, Japan in molten state.

Advantages of Green pathway:

1. Does not require solvent, reaction carried out in molten state.
2. Avoids use of poisonous starting material.

Principles of green chemistry:

Paul Anastas & John Warner has suggested **twelve principles** of green chemistry and is well accepted by chemists all over the world.

1. Prevention of waste.
2. High atom economy
3. Less hazardous chemical synthesis.
4. Designing safer chemicals
5. Use of safer solvents & auxiliaries.
6. Design for energy efficiency.
7. Use of renewable feed stock.
8. Reducing derivatives.
9. Catalysis
10. Design for degrading products.
11. New analytical methods.
12. Accident prevention.

1. Prevention Of waste

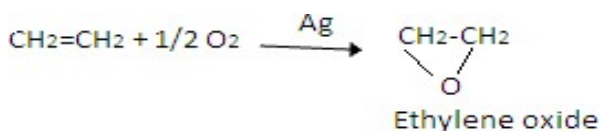
- It is better to prevent waste than to treat or clean up after it is formed.
- The waste produced if dumped on land or in water or released in air, it results in the pollution of soil /water/air.
- If stringent laws are imposed on industries for treatment or disposal, it adds to the cost of process & product.
- Green chemistry suggests the chemical synthesis pathway for products without forming waste.

2. High Atom Economy –

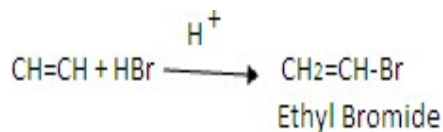
The concept of Atom Economy was given by the scientist Trost. The reaction of synthesis of product is suggested by green chemistry such that all the reactant involved is converted to products without byproducts i.e. high atom economy. All the atoms in reactant are incorporated in the final product, in the high atom economy reaction.

Addition Reactions, Diels –Alder reactions are having economy 100%

Eg. 1.



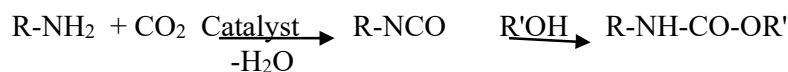
2.



3. Less Hazardous Chemical Synthesis

Whenever practically possible that Synthesis method should be selected which use are generate little or no toxicity to human health & environment

Route 1 : Non –phosgene urethane Synthesis (green path)



Route 2: Traditional Path



The traditional route involves use of poisonous phosgene chemical use, hence not green path.

4. Designing safer chemicals

“Chemical products must be designed to affect their desired function while minimizing their toxicity.” For example .Insecticides like DDT, aldrin, gamexane etc.are toxic to human & alternatively biological pesticides is green to use.

Another example is, some antibiotics have more side effects are green to use.

5. Safer solvent & Auxillaries

- The use of auxiliary substances like solvent, separating agents, should be avoided whenever possible.
- For example: Use of highly inflammable solvents, carcinogenic solvents like CCl_4 , benzene Chloroform should be avoided for dry cleaning fabrics, use of petrol should be avoided & Supercritical solvent CO_2 as alternative solvent should be preferred .water is best solvent but water is not usable then more ecofriendly solvents like Supercritical solvent like Carbon die oxide or ionic solvent should be used.
- Examples of ionic solvents are;
Cations: NH_4^+ , S^+ ,
Anions: BF_4^- , SbF_6^- , CH_3SO_3^- , FeCl_4^-

Examples of ionic solvents are :

- Excellent solvent for wide range of Organic, inorganic & Organometalic reagents.
- Highly polar
- Non- Volatile.
- Immiscible with many Organic solvent which help for biphasic separation
- Acidity or basicity can be changed
- Thermally stable.
- Easy to handle & environment friendly.

As far as possible synthesis should be possible without any solvent or if not, water should be used & last alternative being supercritical CO_2 is non –toxic, renewable & non & non-inflammable.

The order of preferential selection of solvent is given below,

No solvent > Water> Aq Alcohol > Alcohol > ionic solvent > super critical CO_2 > Organic solvent > Halogenated or aromatic organic solvent.

6. Design for energy efficiency:

Energy requirement of a reaction should be minimum considering the environmental & economical impacts. The chemical synthesis should be carried out at ordinary temperature & pressure conditions.

This can be achieved by

- Use of proper catalyst, enzymes.
 - Use of micro organisms for organic synthesis.
 - Use of renewable starting materials instead of fossil matter like naphtha, petrol NG etc.
- Energy efficiency i.e amount of product formed per unit amount of energy.

7. Use of renewable feed stock :

A raw material or feed stock should be renewable rather than reflecting whenever possible .e.g.

I) Adipic acid can be prepared from D-glucose rather than from costly ,non renewable ,poisonous benzene.

- Lactic acid monomer for polylactic acid polymer can be obtained by fermentation of starch by a species of bacteria rather than from propylene non –renewable material.

8. Reduce derivatives

Unnecessary derivatisation i.e use of blocking groups, temporary modifications etc. should be minimized or avoided because such steps require additional reagent, generate waste, consume time, add to the cost of product i.e a chemical preparation should be carried out in lesser number of steps.

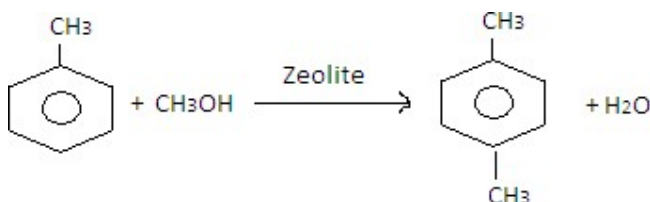
For example in preparation of ibuprofen from isobutyl benzene by Boots route involves five intermediates (six steps) & by BHC route, using catalysis involve two intermediates (three steps). Hence BHC route is greener path.

More Derivatives involve

- Additional reagents
- Generate more waste products.
- More time, higher cost of product.

9. Catalysis

- The catalytic reagent (as selective as possible) is superior for the process rather than stoichiometric reagents.
- For ex : Toluene can be exclusively converted to P- xylene (avoiding O-xylene & m- xylene) by shape selective Zeolites catalyst.



- The O-xylene & m-xylene are trapped inside the pores of the shape selective zeolite until they isomerise to p-xylene.
- Catalysis makes the reaction faster, decrease the energy requirement & if selective, can produce single desired product, minimize waste.

10. Design for degrading product:

The chemical product should be designed such that they undergo degradation after use & do not persist in environment for long.

For ex : i) polyethylene, polystyrene like packaging is not degradable polymer like like Bipol (PHBV) is degradable after use.

ii) Synthesis insecticides remain in food grains & vegetables & do not degraded after use but natural insecticides get easily degraded.

11. New analytical methods:

They have to be developed to allow monitoring & control prior to the formation of hazardous substances. for ex. In the prevention of ethylene glycol, if the reaction condition is not monitored perfectly, then toxic substances are produced.

12. Safer chemistry for Accident prevention:

The reagent & reaction condition should be risk free, in a chemical process, to minimize the chemical accident, explosion, fire & gas release. Eg. preparation of p-nitro aniline.

Bhopal gas tragedy was caused in Dec 1984 claiming thousands of lives, due to leakage of poisonous gas Methyl Isocyanate (CH₃NCO) from union Carbide industry.

Applications of green Chemistry:

The green chemistry approach is useful for developing the safer pathway of syntheses of chemical products, green fuel & green propellants for rocket (H₂O₂), Zeolites for catalysis, biological (enzymatic) processes, safer solvents, energy efficient process, etc.