

Unit 1 Chemistry of Water Analysis

Introduction:

Water is the most useful, wonderful and abundant compound on earth. It's a vital component of the life forms. It's a proven theory that one can live without food for many number of days but one cannot live without water. Water is the important constituent of all the body fluids, without which all the cells or organisms are in crystalline or dead state. (For example, the human body contains 70%, land plants 50 – 75% and aquatic plants 95 – 99%). Water is not only essential for the lives of animals and plants, but also occupies a unique position in industry.

- Water is used in power generation. As steam in steam turbines and as coolants.
- Blasting and water jet cutters. Very high pressure water guns are used for precise cutting. It is also used in the cooling of machinery to prevent over-heating, or prevent saw blades from over-heating.
- Industry requires pure water for many applications and utilizes a variety of purification techniques both in water supply and discharge.
- Water plays many critical roles within the field of food science.
- Water is widely used in the production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air conditioning, drinking, bathing, sanitary, washing, irrigation and fire-fighting etc.

Sources of water:

The chief sources of water supply for industrial use are:

- Rain water.
The purest form of water, collected on the roofs. Yet this method is seldom adopted in industry.
- Surface waters.
Flowing waters, such as rivers, streams etc.
- Still waters,
such as lakes, ponds etc.
- Ground water
Water from springs

Water from shallow wells. In the case of shallow wells, the boring is done only through one geological stratum.

Water from deep wells. Here the boring is done through many geological strata.
- Sea water. Its use is very limited as its uses entails very great problems of chemical engineering.

Common Impurities of Water

Water is a very good solvent; therefore, it dissolves a large number of substances in it. The common impurities present in water are as follows

A. *Dissolved impurities*

- These may be dissolved salts like carbonates, bicarbonates, nitrates, sulphates and chlorides of calcium, magnesium, sodium, potassium, iron, manganese, aluminium, etc.
- Dissolved gases like O₂, CO₂, SO₂, NH₃, N₂ and oxides of nitrogen also fall in this category.

B. *Colloidal impurities* These are those impurities whose particle size varies from 1 to 100 nm. It consists of finely divided silica, clay, aluminium hydroxide, ferric hydroxide, organic waste products, coloring matter, etc.

C. *Suspended impurities* These are impurities with particle size greater than 100 nm and can be removed by filtration or settling. They may be organic, inorganic or microorganism.

- ***Organic impurities*** consist of animal and vegetable matter, wood pieces, leaves, oil globules, etc.
- ***Inorganic impurities*** include clay, silica, sand, etc.
- ***Microorganisms*** include various types of algae, protozoa, bacteria and fungi.

Suspended impurities give turbidity and color to water. Microorganisms are the main cause of water-borne diseases.

WATER PURIFICATION:

Impurities are removed from water by skimming, sedimentation, filtration, chlorination or irradiation. Aeration removes odours and tastes caused by decomposing organic matter, industrial wastes and some gases. Various salts and metals cause hardness in water. Hardness may be removed by boiling, by adding sodium carbonate and lime or by filtering through natural or artificial zeolites. Water is also purified by processes such as desalination, reverse osmosis, electrolysis etc.

CHARACTERISTICS OF WATER

The water quality parameters or characteristics for which analysis is carried out generally fall into three groups:

1. Physical characteristics
2. Chemical characteristics
3. Biological characteristics

Physical characteristics

These are characteristics that respond to touch, taste, sight, etc. These include turbidity, temperature, odor, color and taste.

(a) ***Color:*** Clean water should be colorless. The presence of color in water indicates the presence of various minerals, decomposed organic matter like leaves, roots, organic and inorganic wastes, wastes from textile mill, paper pulp industries, foodprocessing industries, domestic wastes, wastes from laundry, dyeing, dairy products, etc.

(b) ***Taste and odor:*** Water should be odorless and should have a fairly good taste.

There are no specific units to measure these parameters, but generally decaying organic matter imparts odor and bad taste to water. The minimum odor that can be detected is called threshold odor number (TON). The value of TON is determined as follows:

$$\text{TON} = \frac{A+B}{A}$$

A = Volume of sample in mL; B = Volume of distilled water (i.e., odor-free water in mL).

(c) **Temperature:** It is an important water quality parameter. High temperature indicates thermal pollution and disturbs aquatic ecosystem by reducing the dissolved oxygen in water.

(d) **Electrical conductivity:** It gives an idea about the dissolved solids in water. Greater the amount of dissolved solids, higher will be the conductivity. It can be measured easily with the help of conductivity meter. The average value of conductivity for potable water should be less than 2 $\mu\text{mho/cm}$ ($\mu\text{S/cm}$).

(2) Chemical characteristics

Some important chemical characteristics are pH, hardness, alkalinity, total dissolved solids, chlorides, fluorides, sulphates, phosphates, nitrates, metal, etc.

(a) **pH** The pH of normal drinking water is 6.5–8.5. It can be measured with the help of pH meter using a combined electrode (a glass electrode and a calomel electrode as reference electrode). pH scale ranges from 0 to 14. pH 7 indicates neutral solution, less than 7 is acidic, whereas greater than 7 signifies alkaline or basic water.

(b) **Hardness:** It expresses the concentration of calcium and magnesium ions in water in terms of equivalent of CaCO_3 . The maximum acceptance limit is 500 ppm.

(c) **Total dissolved solids (TDS):** The maximum permissible limit is 500 mg/L. TDS includes both organic and inorganic dissolved impurities. It can be measured by evaporating a sample to dryness and then weighing the residue.

(d) **Total solids:** This includes both the dissolved solids as well as suspended impurities.

(e) **Dissolved oxygen:** It is an important water quality parameter. Higher the amount of DO better is the quality of water. Normal water contains 4.7 mg/L of DO. Lesser amount of DO in water indicates pollution in water. Winkler or iodometric methods using membrane electrode is used for measuring DO in water.

(f) **Chlorides** Its amount in water should be less than 250 ppm. High percentage of chloride in water harms metallic pipes as well as agriculture crops.

(g) **Fluorides** Maximum permissible limit is 1.5 ppm. The amount of fluoride in water sample can be determined using an ion meter. Excess of fluoride causes discoloration of teeth, bone fluorosis and skeletal abnormalities.

(h) **Sulphates** Permissible limit is 250 ppm. These are generally found associated with calcium, magnesium and sodium ions. It leads to scale formation in boilers, causes boiler corrosion and imparts odor to water.

(i) **Nitrates** Its concentration in drinking water should not exceed 45 mg/L. Excessive nitrates in drinking water causes 'methemoglobinemia' or blue baby syndrome in infants. Nitrates dissolve in water because of leaching of fertilisers from soil and nitrification of organic matter.

(3) **Biological characteristics**

should be free from all types of bacteria, viruses, protozoa and algae. The coliform count in any sample of 100 mL should be zero.

a) Bacteriological standards

(i) **Water entering the distribution system** Coliform count in any sample of 100 mL should be zero. A sample of water entering the distribution system that does not confirm to this standard calls for an immediate investigation into both the efficacy of the purification process and the method of sampling.

(ii) **Water in the distribution system** It shall satisfy these three criteria:

- (a) *E. coli* count in 100 mL of any sample should be zero.
- (b) Coliform organism should not be more than 10 per 100 mL of any sample.
- (c) Coliform organism should not be present in 100 mL of any two consecutive samples or more than 5% of the samples collected for the year.

b) **Virological standards** 0.5 mg/L of free residual chlorine for 1 h is sufficient to inactivate virus, even in water that was originally polluted. This free residual chlorine should be present in all disinfected supplies in area suspected of infectious hepatitis to inactivate virus and also bacteria. For water supply in such areas, 0.2 mg/L of free residual chlorine for half an hour should be insisted.

As per the suggestion given by World Health Organisation (WHO) and by Indian Council of Medical Research (ICMR), the following are the important characteristics of potable water.

1. It should be clear, colourless and odourless.
2. It should be cool and pleasant to taste.
3. It should be free from harmful bacteria and suspended impurities.
4. It should be free from dissolved gases like CO₂, H₂S, NH₃, etc., and poisonous minerals like lead, arsenic, manganese, etc.,
5. Hardness should be less than 500 ppm.
6. Chloride ion content should be less than 250 ppm.
7. Fluoride ion content should be less than 1.5 ppm.
8. Total Dissolved Solids (TDS) content should be less than 500 ppm.
9. pH of the potable water should be 6.5 – 8.5.

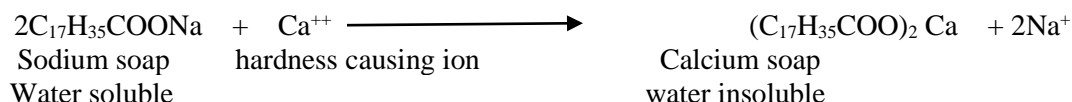
10. Nitrate ion content should not exceed 45 mg/L.
11. Sulphate ion content should not exceed 250 ppm.

HARDNESS

Hardness is caused by the soluble salts of calcium, magnesium, iron, manganese, sodium, sulphates, chlorides and nitrates. The degree of hardness depends on the type and amount of impurities present in the water. Hardness also depends on the amount of carbon-di-oxide in solution. Carbon-di-oxide influences the solubility of the impurities that cause hardness. The hardness caused by carbonates and bicarbonates is called carbonate hardness. The hardness caused by all others (chlorides, sulphates, nitrates) is called non-carbonated hardness.

HARD WATER

Water which does not produce lather with soap solution, but produces white precipitate (scum) is called hard water. In other words, water that contains mineral salts (an calcium and magnesium ions) that limit the formation of lather with soap. This is due to the presence of dissolved Ca and Mg salts.



SOFT WATER

Which produces lather, readily with soap solution is called soft water. This is due to the absence of Ca and Mg salts. Water that is not hard (ie. does not contain mineral salts that interfere with the formation of lather with soap)

HARDNESS OF WATER

How to detect hardness?

Hardness of water can be detected in two ways.

- When the water is treated with soap solution, if it prevents lathering and forms white scum, the water contains hardness.
- Water containing hardness, gives wine red colour with Eriochrome Black –T indicator. The total water hardness (including both Ca^{2+} and Mg^{2+} ions) is read as parts per million (ppm) or weight / volume (mg/L) of Calcium Carbonate (CaCO_3) in the water. Although water hardness usually measures only the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminum and manganese may also be present at elevated levels in some geographical locations. The predominant source of magnesium is dolomite ($\text{CaMg}(\text{CO}_3)_2$).

TYPES OF HARDNESS

Depending upon the types of dissolved salts present in water, hardness of water can be classified into two types:

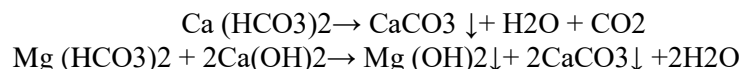
- Temporary Hardness
- Permanent Hardness
-

Temporary Hardness (or) Carbonate Hardness (CH) (or) Alkaline Hardness

Temporary hardness is caused by a combination of calcium and magnesium bicarbonate ions in the water. It can be removed by

- boiling water
- by the addition of lime (Ca(OH)₂)

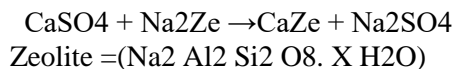
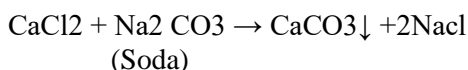
Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.



Permanent Hardness (or) Non – Carbonate Hardness (NCH) (or) Non – alkaline Hardness

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulphates and /or chlorides which become more soluble as the temperature rises. Despite the name, permanent hardness can be removed using water – softener or ion-exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column. It can be removed by

- Lime – Soda process
- Zeolite process



Hard water causes scaling, which is the left- over mineral deposits that are formed after the hard water had evaporated. This is also known as lime scale.

UNITS OF HARDNESS

1. Parts per million (ppm)

It is defined as the number of parts of CaCO₃ equivalent hardness per 10⁶ parts of water.

2. Milligrams per litre (mg/lit)

It is defined as the number of milligrams of CaCO₃ equivalent hardness per 1 litre of water.

3. Degree Clarke's (°Cl)

It is defined as the number of parts of CaCO₃ equivalent hardness per 70,000 parts of water.

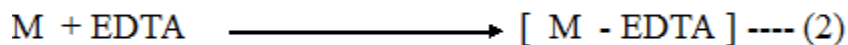
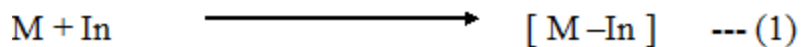
4. Degree French (°Fr) It is defined as the number of parts of CaCO₃ equivalent hardness per 10⁵ parts of water.

Relationship between various units

$$1\text{ppm} = 1\text{ mg/lit} = 0.1\text{ }^\circ\text{Fr} = 0.07\text{ }^\circ\text{Cl}$$

ESTIMATION OF TOTAL HARDNESS OF WATER BY EDTA METHOD

The hardness of water is estimated by EDTA method using Eriochrome Black –T [EBT]. Principle: The calcium ion in the water is capable of forming complex with Indicator EBT and also with the EDTA in the pH range 8- 10. To keep the solution at this pH range , a buffer [mixture of ammonium chloride and ammonium hydroxide] is used . The complex between EDTA and indicator is more stable than that of between the metal ion and indicator



(2) is more stable than (1)

Experiment :

1.Preparation of Standard hard water :

Hard water is prepared in such a way that 100 ml of containing 100 mg of Calcium carbonate; So , 1 ml of Std. hard water = 1mg

2.Standadisation of EDTA :

EDTA is taken in the burette; 20 ml of Std. hard water is pipette out in beaker; 5ml of buffer solution and 2 a few drops of indicator are added ; now the solution becomes wine –red colour because the colour of the complex between calcium and indicator [M- In] is wine –red. Then it is titrated against EDTA; at the end point the colour changes to Pale blue, which is colour of the free indicator. Since the complex between metal ion -EDTA is more stable that of between the metal ion and indicator , the Metal moves from [M-In] towards EDTA and forms complex with that , which is colourless; now the indicator is freed and the solutions attains steel blue colour , which is the colour of the free indicator. Let the titre value be V1.

1ml of Std. hard water = 1mg of CaCO_3

20 ml of Std. hard water = 20 mg of CaCO_3

V_1 ml of EDTA = 20 of Std. hard water

= 20 mg of CaCO_3

1 ml of EDTA = $20 / V_1 \times 20$ mg of CaCO_3

= $\frac{1}{V_1}$ mg of CaCO_3

3. Determination of Total hardness of water :

20 ml of the given sample of water is taken and titration is conducted as before; let the titre value be V_2 ;

20ml of Sample of water = V_2 ml of EDTA

= $V_2 \times \frac{1}{V_1}$ mg of CaCO_3

= $\frac{V_2}{V_1}$ mg of CaCO_3

1000 ml of sample = $V_2 / V_1 \times 1000$ mg of CaCO_3

The weight in milligrams of calcium carbonate in 1000 ml of the sample of water

= $V_2 / V_1 \times 1000$ mg of CaCO_3

Total hardness of the given water = $V_2 / V_1 \times 1000$ ppm

PREPARATION OF SOLUTIONS;

1. **Standard hard water:** 1 gm of dry CaCO_3 is dissolved in minimum quantity of HCl and evaporate the solution to dryness on a water bath, and then diluted to 1 lit with water. Each ml of this solution then contains 1 mg of CaCO_3 hardness.
2. **EDTA solution:** 4 gm of EDTA crystals + 0.1 gm MgCl_2 in 1lit
3. **Indicator:** 0.5 gm of EBT in 100 ml of alcohol.
4. **Buffer solution:** 67.5 gm NH_4Cl + 570 ml of Con. Ammonia solution diluted with distilled water to 1 lit.
5. **Titration of permanent hardness of water:** Take 250 ml of the water sample in a large beaker. Boil till the volume is reduced to 50 ml. Filter, wash the precipitate with distilled water collecting filtrate and. Finally make the volume to 250 ml with distilled water. Then titrate 50 ml of the boiled water sample just as in step (5).

Let volume used by V_3 ml Calculations:

50 ml of standard hard water = V_1 ml of EDTA \therefore

50 x 1 mg of CaCO_3 = V_1 ml of EDTA \therefore

1 ml of EDTA = $50/V_1$ mg of CaCO_3 eq.

50 ml. of given hard water = V_2 ml EDTA = $V_2 \times 50/V_1$ mg of CaCO_3 eq.

\therefore 1 L (1,000 mL) of given hard water = $1000 V_2/V_1$ mg of CaCO_3 eq. \therefore

Total hardness of water = $1000 V_2/V_1$ mg/L = $1000 V_2/V_1$ ppm

Now 50 ml of boiled water = V_3 ml of EDTA $\therefore V_3 \times 50/V_1$ mg of CaCO_3 eq

$\therefore V_3 \times 50/V_1$ mg of CaCO_3 eq 1000 ml (= 1 L) of boiled water = $1000 V_3/V_1$ mg of CaCO_3 eq 1000 V_3

Permenent hardness = = . . . ppm

And Temporary hardness = Total hardness – Permanent hardness = ppm =

Advantages of EDTA method:

This method is definitely preferable to the other methods, because of the

(i) Larger accuracy; (ii) Convenience; (iii) Rapid procedure

ALKALINITY

Alkalinity is a chemical measurement of water's ability to neutralize acids.

Alkalinity is classified as

Depending up on the anions that are responsible for the alkalinity of water, there are three types of alkalinity:

1. Hydroxide alkalinity – due to hydroxide ions
2. Carbonate alkalinity - due to carbonate ions
3. Bicarbonate alkalinity - due to bicarbonate ions

The alkalinity due hydroxide and carbonate can be detected by Phenolphthalein indicator and so they are collectively called as Phenolphthalein Alkalinity, represented by P.

The alkalinity due hydroxide, carbonate and bicarbonate can be detected by Methyl orange indicator and so it is called as in Methyl orange Alkalinity, represented by M.

1.Determination of Phenolphthalein Alkalinity, P :

100 ml of given water sample is taken in the conical flask, a few drops of Phenolphthalein indicated are added and titrated against N/50 H₂SO₄, let the titre value when the solution becomes colourless, be V₁.

2.Determination of Methyl orange Alkalinity, M :

The in the same solution a few drops of Methyl orange indicator are added and titrated against the same acid until the colour changes from yellow to red ; let the titre value be V₂ .

Calculations:

$$\text{Phenolphthalein alkalinity (P) (ppm)} = \frac{V_1 \times \text{Normality of HCl} \times 50000}{\text{Volume of water sample taken}}$$

$$\text{Methyl orange alkalinity (M) (ppm)} = \frac{V_2 \times \text{Normality of HCl} \times 50000}{\text{Volume of water sample taken}}$$

Relation between P & M	Phenomenal Condition	Alkalinity (ppm) Hydroxide (OH ⁻)	alkalinity Carbonate (CO ₃ ²⁻)	alkalinity Bicarbonate (HCO ₃ ⁻) alkalinity
P = 0	If phenolphthalein end point is zero, then alkalinity is due to only bicarbonate.	-----	-----	M
P = M	If methyl orange end point is zero & only there is phenolphthalein end point, then the alkalinity is due to hydroxide alone.	P	-----	-----
P = ½M	If phenolphthalein end point is exactly half the total titration, then only carbonate alkalinity is present.	-----	2P	-----
P > ½M	If phenolphthalein end point is greater than half the total titration, then alkalinity is due to both carbonate & hydroxide.	2P – M	2(M – P)	-----

$P < \frac{1}{2} M$	If phenolphthalein end point is less than half the total titration, then alkalinity is due to both carbonate & bicarbonate.	-----	$2P$	$M - 2P$
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BOILER TROUBLES

SCALE AND SLUDGE FORMATION IN BOILERS

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When their concentrations reaches saturation point, they are thrown out of water in the form of precipitates which stick to the inner walls of the boiler. If the precipitation takes place in the form of loose or slimy precipitate it is called sludge. On the other hand, if the precipitated matter forms a hard adhering crust/ coating on the inner walls of the boiler, it is a scale. Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludge can be easily scrapped off with a wire brush. It is formed at comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow at bends. Sludges are formed by substances which have greater solubilities in hot water than in cold water. Examples are $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

Differences between scale and Sludge.

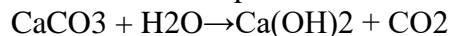
S.No.	Scale	Sludge
1.	Scale is hard and adherent .	Sludge is loose , slimy and non –adherent.
2.	formed by the salts like Calcium bicarbonate , Calcium sulphate , etc.	formed by the salts like magnesium Sulphate magnesium carbonate , etc,
3.	Scale formation can be prevented by dissolving scale using dilute acids like HCl , H_2SO_4 .	formation of sludge can be prevented by i periodically removing the concentrated water by fresh water ii. taking soft water

Formation of scales may be due to

1. Decomposition of calcium bicarbonate



However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low pressure boilers. But in high pressure boilers $CaCO_3$ is soluble.



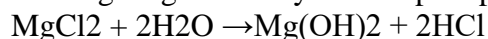
2. Decomposition of calcium sulphate:

The solubility of calcium sulphate in water decreases with increase in temperature. Thus, solubility of calcium sulphate is 3,200 ppm at 15 oC and it reduces to 55 ppm at 230 oC and

27 ppm at 320 oC. In other words, calcium sulphate is soluble in cold water, but almost completely insoluble in superheated water. Consequently calcium sulphate gets precipitated as hard scale on the heated portions of the boiler. This is the main cause in the high pressure boilers.

3. Hydrolysis of magnesium salts:

Dissolved magnesium salts undergo hydrolysis at prevailing high temperatures in the boiler forming magnesium hydroxide precipitate, which forms a soft type of scale.



4. Presence of silica (SiO_2), even if present in small quantities, deposits as calcium silicate (CaSiO_3) and/ or magnesium silicate (MgSiO_3). These deposits stick very firmly to the inner walls of the boiler surface and are very difficult for removal. One important source of silica in water is the sand filter used.

Disadvantages of scale formation:

Sludge is poor conductors of heat, so they tend to waste a portion of heat used. If sludge is formed along with scales, the former get entrapped in the later and both get deposited as scales. Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge glass connection thereby causing even chocking of the pipes.

1. Wastage of fuels: Scales have a low thermal conductivity, so the rate of transfer of heat from boiler to inside water is largely decreased. In order to provide a steady supply of heat to water, excessive or over heating is done which causes unnecessary increase in fuel consumption.

2. Lowering of boiler safety:

Due to scale formation, over-heating of the boiler has to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of the boiler tube and makes the boiler tube unsafe to bear the pressure of the steam especially in high-pressure boilers.

3. Decrease in efficiency:

Scales may sometimes get deposited in the valves and condensers of the boiler and choke them partially or totally. This results in decrease the efficiency of the boiler.

4. Danger of explosion:

When thick scales crack due to uneven expansion, the water comes in contact with the overheated iron plates. This causes a release of a large amount of steam suddenly, developing a high pressure, which may cause explosion in the boiler.

Prevention of sludge formation:

1. By using well softened water.

2. By a frequent blow down operation, i.e., drawing off a portion of the concentrated water. Scales are hard deposits, which stick very firmly to the inner surface of the boiler. Scales are very difficult to remove even with the help of hammer and chisel. Scales are the main source of boiler troubles.

Removal of scales:

1. With the help of scraper or piece of wood or wire brush, if they are loosely adhering.
2. By giving thermal shocks like heating the boiler and suddenly cooling it with cold water.
3. Dissolving scales by adding suitable chemicals, if they are adherent and hard. Thus calcium carbonate scales can be dissolved by the addition of 5% HCl. Calcium sulphate scales can be dissolved by the addition of EDTA (ethylene diamine tetra acetic acid), with which they form complexes.
4. By frequent blow down operation, if the scales are loosely adhering.

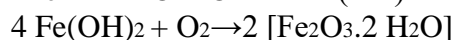
BOILER CORROSION

Boiler corrosion is the decay of boiler material (iron) either by chemical or electro chemical attack of its environment.

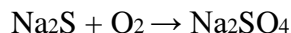
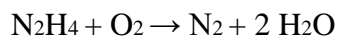
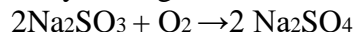
Main reasons for the boiler corrosion are:

Dissolved oxygen:

Water usually contains 8 mg of dissolved oxygen per liter at room temperature. Dissolved oxygen in water in the presence of prevailing high temperature of the boiler, attacks the boiler material as

**Removal of the dissolved oxygen:**

- a. By adding calculated amount of sodium sulphite or hydrazine or sodium sulphide.



- b. Mechanical de-aeration:

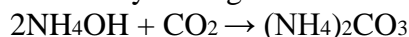
In this process water is sprayed in to a tower fitted with perforated plates (Fig), heated from sides and connected to vacuum pump. High temperature, low pressure and large exposed surface area reduce the dissolved oxygen in water.

Dissolved carbon dioxide:

Carbon dioxide dissolved in water forming carbonic acid, has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler, if water, containing bicarbonates is used for steam generation



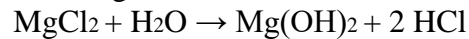
Removal of dissolved carbon dioxide: a. By adding calculated amount of ammonia



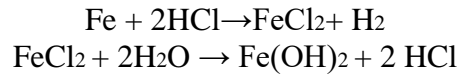
- b. By mechanical de-aeration process along with oxygen (described above)

Acids from dissolved salts:

Water containing dissolved salts of magnesium liberates acids on hydrolysis.



The liberated acid reacts with the iron material of the boiler in chain like processes, producing HCl again and again.



Consequently, presence of even small amount of magnesium chloride will cause corrosion to a large extent and may cause damage to the boiler material. Removal of acids: a) Softening boiler water to remove magnesium chloride, if any. b) By frequent blow down operation of removal of concentrated water with fresh soft water. c) Addition of inhibitors as sodium silicate/sodium phosphate/sodium chromate, which protect the boiler material against acid attack.

PRIMING AND FOAMING

When a boiler is producing steam rapidly, some particles of the condensed liquid water are carried along with the steam. The process of wet steam formation is called priming. Priming is caused by

1. The presence of large amounts of dissolved solids
2. High steam velocities
3. Sudden boiling
4. Improper boiler design
5. Sudden increase in the steam production rate.

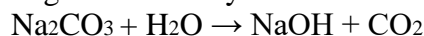
Foaming is the production of persistent foam or bubbles in boilers, which do not break easily.

Foaming is due to the presence of substances like oils in water, which reduce the surface tension of water. Priming and foaming usually occur together. They have to be eliminated because

- Dissolved salts in boiler water are carried by the wet steam to super heater and turbine blade, where they get deposited as water evaporates. This deposit reduces the efficiency of the boiler.
- Dissolved salts may enter the other parts of the machinery, where steam is being used, thereby decreasing the life of the machinery
- Actual height of the water column cannot be judged properly making the maintenance of the boiler pressure difficult.
- Priming can be avoided by fitting mechanical steam purifiers, avoiding the rapid change in steaming rate, maintaining low water levels in boilers, efficient softening and filtration of the boiler feed water. Foaming can be avoided by adding anti foaming chemicals like castor oil, or removing oil from boiler water by adding compounds like sodium aluminate.

CAUSTIC EMBRITTLEMENT

Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. During softening process by lime- soda process, free sodium carbonate is usually present in small proportion in the softened water. In high pressure boilers, sodium carbonate decomposes to give sodium hydroxide and carbon dioxide, and their presence makes the boiler water caustic.



The water containing sodium hydroxide flows into the minute hair cracks always present, by capillary action in to the inner sides of the boiler. Here as water evaporates the dissolved caustic

soda concentration increases progressively. This concentrated caustic soda attacks the surrounding area dissolving inner iron side of the boiler by forming sodium ferroate. This causes the embrittlement of the boiler parts, particularly stressed parts such as bends, joints, rivets etc., causing even failure of the boiler operations. Caustic cracking can be explained by the following concentration cell Iron at Bends, rivets and joints

The iron surrounded by the dilute NaOH becomes the cathodic surface and the iron present with the high concentration of NaOH becomes anodic which is consequently dissolved or corroded.

Caustic embrittlement can be avoided by

1. By using sodium phosphate as a softening agent instead of sodium carbonate.
2. By adding tannin or lignin to the boiler water, since these substances block the hair cracks, thereby preventing the infiltration of the caustic soda solution in to these.
3. By adding sodium sulphate to boiler water: Sodium sulphate blocks the hair cracks preventing the infiltration of caustic soda solution in to these. It has been observed that caustic cracking can be prevented, if sodium sulphate is added to the boiler in the ratio of $\text{Na}_2\text{SO}_4 : \text{NaOH}$ as 1:1; 2:1; 3:1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

EXTERNAL TREATMENT OR SOFTENING METHODS

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. It should, therefore, be freed from hardness- producing salts before it is being put to use. The process of removing hardness-producing salts from water is known as softening of water. In industry three methods are mainly employed for softening of water.

Lime soda process:

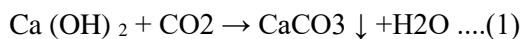
In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$.

Calcium carbonate $[\text{CaCO}_3]$ and magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ are precipitated and removed.

Lime-Soda Softening Soda Softening

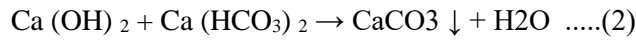
In this process Calcium and Magnesium ions are precipitated by the addition of lime $(\text{Ca}(\text{OH})_2)$ and soda ash (Na_2CO_3) . Following are the reactions that takes place in this process:

- As slacked lime is added to a water, it will react with any carbon dioxide present as follows:



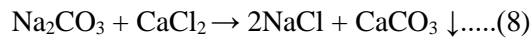
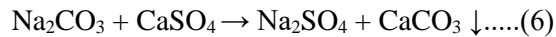
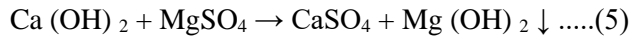
- The lime will react with bi carbonate hardness as follows:

- Removal of temporary hardness



The product magnesium carbonate in equation 3 is soluble. To remove it, more lime is added:

- Removal of permanent magnesium hardness



- Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:

• Lime addition removes only magnesium hardness and calcium carbonate hardness. In equation 5 and 7 magnesium hydroxide is precipitated, however, an equivalent amount of calcium is added. The water now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5 and 7. Soda ash is added to remove calcium non-carbonate hardness

To precipitate CaCO_3 requires a pH of about 9.5; and to precipitate Mg(OH)_2 requires a pH of about 10.8, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.

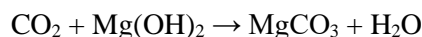
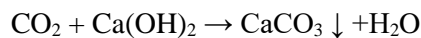
- **The amount of lime required:**

lime (meq/l) = carbon dioxide (meq/l) + carbonate hardness (meq/l) + magnesium ion (meq/l) + 1.25 (meq/l)

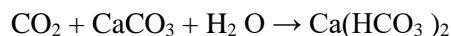
- **The amount of soda required:**

soda ash (meq/l) = non-carbonate hardness (meq/l)

After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate. Recarbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:



Further recarbonation, will bring the pH to about 8.5 and stabilize the calcium carbonate as the following:



It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness

- **Lime**

Lime is commercially available in the forms of:

- quicklime
- hydrated lime

- **Quicklime**

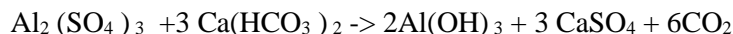
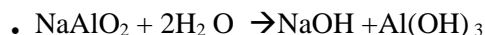
- available in granular form
- contains minimum of 90% CaO
- magnesium oxide is the primary impurity

- **Hydrated Lime**

- contains about 68% CaO
- Slurry lime is written as Ca(OH)₂.

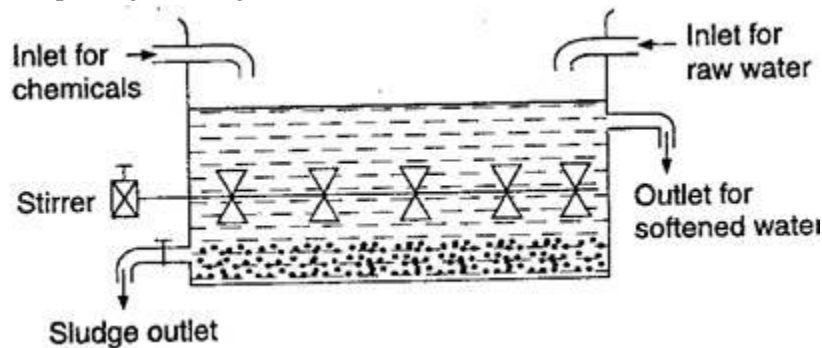
A) COLD LIME-SODA PROCESS:

In this Method, Calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (Like Alum, aluminum sulphate, sodium aluminate, Etc.) Which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminate as coagulant, also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.



Method:

Raw water and calculated quantities of chemicals (Lime+soda+coagulant) are fed from the top into the inner vertical circular chambers, fitted with a vertical rotating shaft carrying a number of paddles , As the raw water and chemicals flow down there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer chamber of the lime the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn off occasionally.

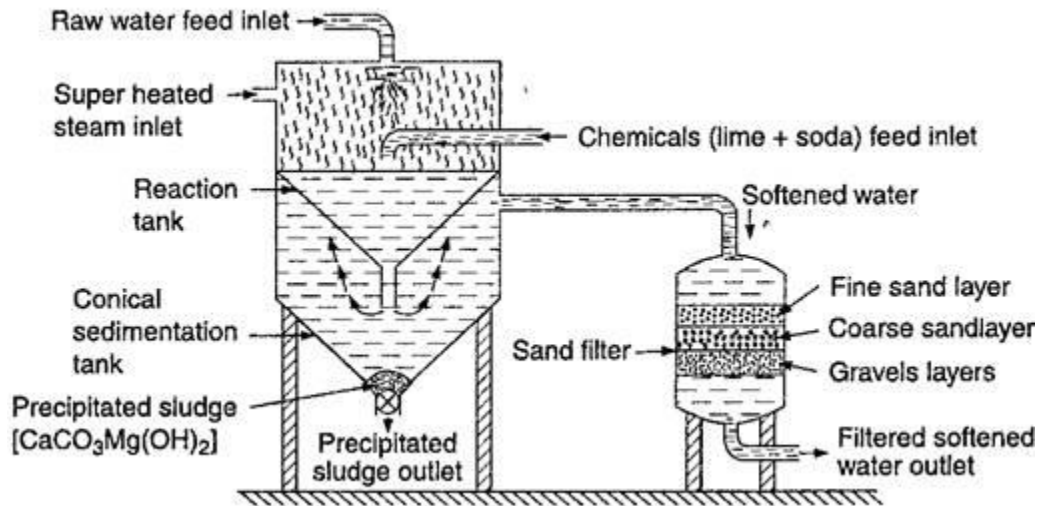


HOT LIME-SODA PROCESS:

Involves in treating water with softening chemicals at a temperature of 80 to 150°C. Since hot process is operated at a temperature close to the boiling point of the solution, so

- (a) The reaction proceeds faster.
- (b) The softening capacity of hot process is increased to may fold
- (c) The precipitate and sludge formed settle down rapidly and hence, no coagulants are needed;
- d) Much of the gases (Such as CO₂ and air) Driven out of the water
- (e) Viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters.
- (f) Hot Lime-Soda Produces water of comparatively lower residual hardness of 15 to 30ppm.

Hot lime-soda plant consists essentially of three parts (a) a 'reaction tank' in which raw water, chemicals and steam are thoroughly mixed; (b) a 'conical sedimentation vessel' in which sludge settles down, and (c) a 'Sand filter' which ensures complete removal of sludge from the softened water.



Advantages of Lime Soda Process:

- (i) It is a very economical
- (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed
- (iii) The process increased the pH value of the treated water, thereby corrosion of the distribution pipes is reduced
- (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced
- (v) To certain extent, iron and manganese are also removed from the water.
- (vi) Due to alkaline nature of treated- water, amount of pathogenic bacteria's in water is considerably reduced

Disadvantages of Lime Soda Process:

For efficient and economical softening, careful operation and skilled supervision is required

- (i) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (ii) This can remove hardness only up to 15ppm, which is not good for boilers.

Limitation of Soda Lime Process:

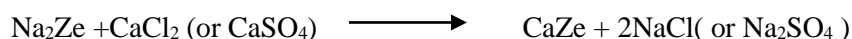
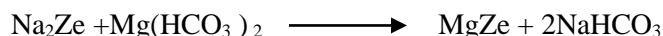
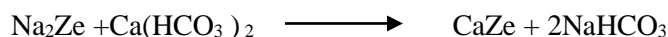
Lime soda softening cannot produce a water at completely free of hardness because of the solubility (little) of CaCO_3 and Mg(OH)_2 . Thus the minimum calcium hardness can be achieved is about 30 mg/L as CaCO_3 , and the magnesium hardness is about 10 mg/L as CaCO_3 . We normally tolerate a final total hardness on the order of 75 to 120 mg/L as CaCO_3 , but the magnesium content should not exceed 40 mg/L as CaCO_3 (because a greater hardness of magnesium forms scales on heat exchange elements).

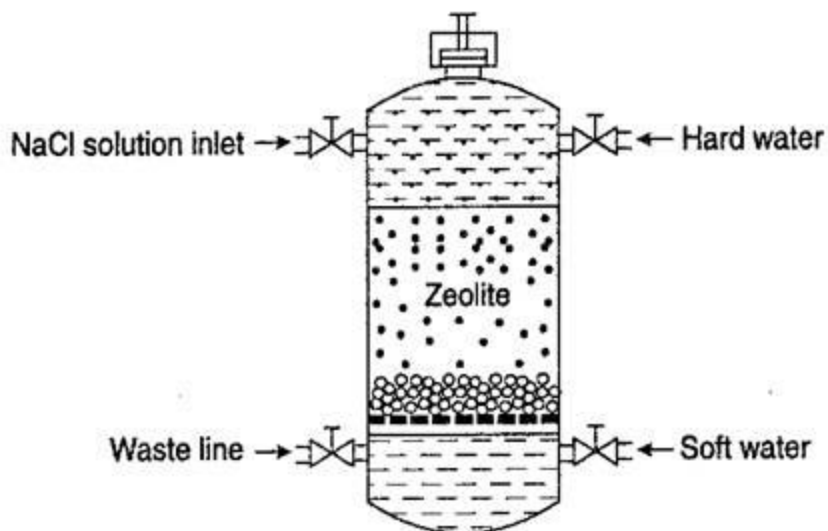
2) ZEOLITE PROCESS:

Chemical structure of sodium zeolite may be represented as $\text{Na}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x=2-10$ and $y=2-6$. Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness, producing ions in water. Zeolites are two types,

- (i) Natural zeolites are non porous for Ex; Natrolite $\text{Na}_2\text{Al}_3\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- (ii) Synthetic zeolites possess gel structure. Synthetic Zeolites possess higher exchange capacity than natural Zeolites

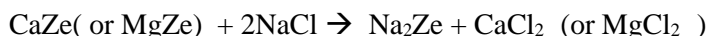
Process: - For Softening of water by Zeolite process, hard water is percolated at a specified rate through a bed of zeolite; kept in a cylinder. The Hardness causing ions (Ca^{+2} , Mg^{+2} etc.) are retained by the zeolite as CaZe and MgZe ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are





REGENERATION:

After Some time the zeolite is completely converted into calcium and magnesium Zeolites and it ceases to soften water i.e.; it gets exhausted. At this stage the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated NACL solution



The washings are led to drain and the regenerated zeolite bed thus obtained is used again for softening process

Limitations:

- (i) If the supply of water is turbid in will clog the pores of zeolite bed
- (ii) Water contains large quantities of colored ions such as Mn^{+2} and Fe^{+2} they may be removed first because these ions produce Mn and Fe Zeolites ,which can't be easily regenerated
- (iii) Mineral acids destroy the zeolite bed

ADVANTAGES:

- (i) It removes the hardness almost completely
- (ii) Equipment occupying a small space
- (iii) Requires less time
- (iv) It is quite clean

DISADVANTAGES:

- (i) Treated water contains more sodium salts than in time soda process
- (ii) The method only replaces Ca^{+2} and Mg^{+2} ions by Na^{+} ions leaves all the acidic ions

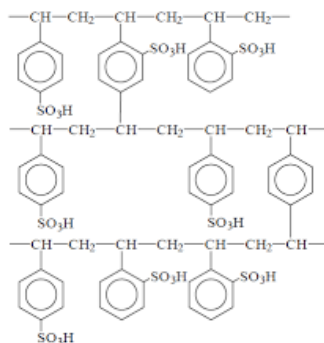
Ion Exchange Process – Deionisation or Demineralisation of Water

Ion exchange process is defined as the reversible exchange of ions in the structure of an ion exchanger to ions in solution that is brought in contact with it. The resins used for the purpose are called ion exchange resins. They are porous, insoluble, cross linked, long chain organic polymers capable of exchanging ions.

Two types of resins are employed for the softening of water.

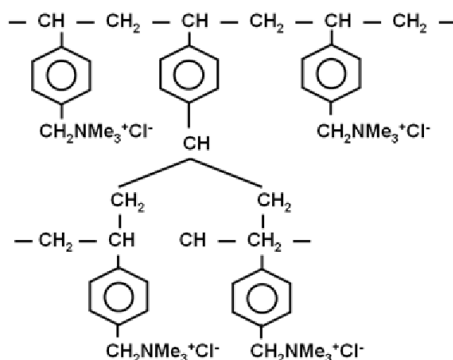
(i) *Cation exchange resin*

They are materials capable of exchanging a cation in their structure to the cation in solution. For softening of water, the resins used should be capable of exchanging H^+ ions in their structure to other cations in solution. Commonly used resins are styrene divinyl benzene copolymers, which on sulphonation or carboxylation become capable of exchanging hydrogen ions with the cations in water. They are represented as $R-H^+$ (R represents insoluble polymer matrix and H is the exchangeable ion). Amberlite IR-120 and Dowex-50 are examples of commercially available cation exchange resins.



Anion exchange resin

They are materials capable of exchanging an anion in their structure (for water softening the exchangeable anion should be OH^- ion) to anion in solution. Anion exchangers employed for water softening are styrene divinyl benzene or amine formaldehyde copolymers, which contain basic functional group such as amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These after treatment with dilute $NaOH$ solution become capable of exchanging OH^- ions with the anions in water. They are represented as R^+OH^- (where R^+ is the insoluble polymer matrix and OH^- is the exchangeable ion). Amberlite 400 and Dowex-3 are examples of commercially available anion exchange resins.



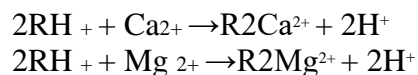
Ion exchange or de-ionization or de-mineralization process:

Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a micro porous structure, and the “functional groups” attached to the chains are responsible for the ion exchanging properties. Resins containing acidic functional groups (-COOH, -SO₃H etc.) are capable of exchanging their H⁺ ions with other cations, which come into their contact; whereas those containing basic functional groups (-NH₂=NH as hydrochloric acid) are capable of exchanging their anions with other anions, which come into their contact.

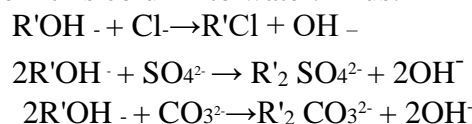
The ion-exchange resins may be classified as: (i) Cation exchange resins (RH⁺) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation become capable to their hydrogen ions with the cations present in the raw water

(ii) Anion exchange resins (R'OH⁻) are styrene-divinyl benzene amineformaldehyde copolymers, which contains amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH⁻ anions with anions present in the raw water.

Process: The hard water is passed first through cation exchange column, which removes all the cations like Ca²⁺, Mg²⁺, etc., from it and an equivalent amount of H⁺ ions are released from this column to water. Thus: 2



The water which is now free from cations, is passed through anion exchange column, which removes all the anions like SO₄²⁻, Cl⁻ etc., present in the water and equivalent amount OH⁻ ions are released from this column to water. Thus:



H⁺ and OH⁻ ions (released from cation exchange and anion exchange columns respectively) combine to produce water.



Thus the water coming out from the exchanger is free from all cations as well as anions. Ion-free water is known as de ionized or de mineralized water.

Regeneration: When capacities of cation and anion exchangers to exchange H⁺ and OH⁻ ions respectively are lost, they are then said to be exhausted

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or H₂SO₄. The regeneration can be represented as:



The column is washed with deionized water and such washing (which containing Ca²⁺, Mg²⁺, etc. and cation SO₄²⁻) is passed into sink or drain. The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as:



The column is washed with deionized water and such washing (which contains Na^+ and SO_4^{2-} or Cl^- ions) is passed into sink or drain.

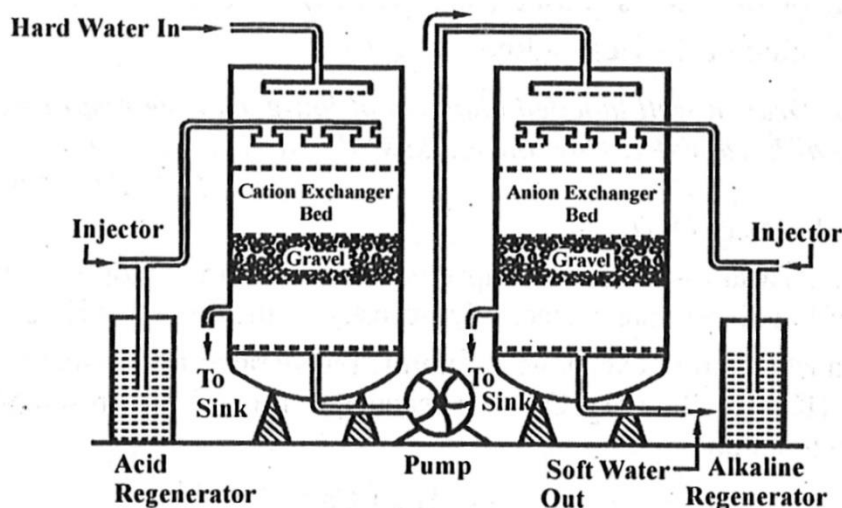
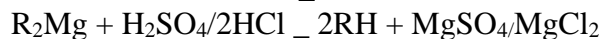
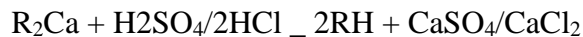


Fig. Demineralization of Water

Regeneration

After sometime the resin loses all its H^+ and OH^- ions and then its capacity to exchange ions is lost. In such a condition they are said to be exhausted. The exhausted cation exchange resin is regenerated by passing a solution of HCl or H_2SO_4 .



The column is then rinsed with distilled water to remove the salts formed. Ideally, HCl is used for regeneration as CaCl_2 and MgCl_2 are more soluble. The anion exchange resin is regenerated by passing a dilute solution of NaOH and then washing with distilled water



NaCl , Na_2SO_4 are removed by washing with distilled water.

Advantages:

1. The process can be used to soften highly acidic or alkaline waters.
2. It produces water of very low hardness (2 ppm).
3. Unlike zeolite process the soft water does not contain sodium ions.
4. It removes all cations and anions other than H^+ and OH^- ions.
5. All ionisable impurities are removed.

Disadvantages

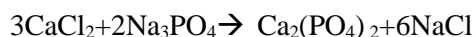
1. The equipment is costly and expensive chemicals are needed.
2. If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation followed by filtration.

INTERNAL TREATMENT:

In this process; an ion is prohibited to exhibit its original character by converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to the boiler water either to precipitate the scale forming impurities in the form of sludge, which can be removed by blow down operations, or to convert them into compounds, which will stay in dissolved form in water and they do not cause any harm

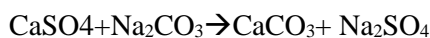
Important Internal treatment methods are:

- (i) **Colloidal conditioning:** In low pressure boilers, scale formation can be avoided by adding organic substances like Kerosene, tannin, agar-Agar etc; which get coated over the scale forming precipitates, thereby yielding coated non sticky and loose deposits
- (ii) **Phosphate conditioning:** In High pressure boilers, scale formation can be avoided by adding sodium phosphate which reacts with hardness of water forming non-adherent and easily removable soft sludge



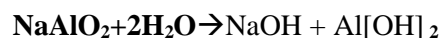
The main phosphates employed are (a) NaH_2PO_4 (b) Na_2HPO_4 (c) Na_3PO_4

- (iii) **Carbonate Conditioning:** In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water, then CaSO_4 converted into CaCO_3 in equipment CaCO_3 forms loose sludge

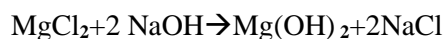


- (iv) **Calgon Conditioning:** Involves in adding calgon $[(\text{NaPO}_3)_6]$ to boiler water then it forms soluble complex compound with CaSO_4
 $\text{Na}_2 [\text{Na}_4(\text{PO}_3)_6] \rightarrow 2\text{Na}^+ + [\text{Na}_4\text{P}_6\text{O}_{18}]^{2-}$
 $2\text{CaSO}_4 + [\text{Na}_4\text{P}_6\text{O}_{18}]^{2-} \rightarrow [\text{CaP}_6\text{O}_{18}] + 2$

- (v) **Treatment with sodium aluminate (NaAlO_2).** Sodium aluminate gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminium hydroxide



The NaOH , so formed precipitation some of the magnesium as $\text{Mg}(\text{OH})_2$ i.e.;



The precipitate of $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ produced inside the boiler entraps finely suspended and Colloidal impurities including oil drops and silica.

Potable water

The water which is fit for human consumption is known as potable water. Municipalities have to supply potable water, i.e., water which is safe to human consumption should satisfy the following essential requirements

1. It should be sparkling clear and odourless.
2. It should be pleasant in taste
3. It should be perfectly cool
4. Its turbidity should not exceed 10 ppm
5. It should be free from objectionable dissolved gases like hydrogen sulphide.
6. It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
7. Its alkalinity should not be high. Its pH should not be above 8.0
8. It should be reasonably soft
9. Its total dissolved solids should be less than 500 ppm
10. It should be free from disease-producing micro-organisms.

Purification of domestic water for domestic use:

For removing various types of impurities in the natural water from various sources, the following treatment process is employed;

Removal of suspended impurities :

The treatment water for municipal supply involves the following steps:

1. Screening :

It is a process of removing the floating materials like , leaves , wood pieces ,etc., from water. Here water is passed through a screen having a number of holes .

2. Aeration :

The process of mixing air with water is called aeration; here the gases like CO₂, H₂S and other volatile impurities responsible for the bad taste and odour, are removed; further ferrous and manganese salts are converted into insoluble ferric and manganic salts .

3. Sedimentation :

In this process suspended impurities are removed by keeping the water undisturbed for 2 – 6 hours in a tank. This removes only 75 % of the suspended *impurities*.

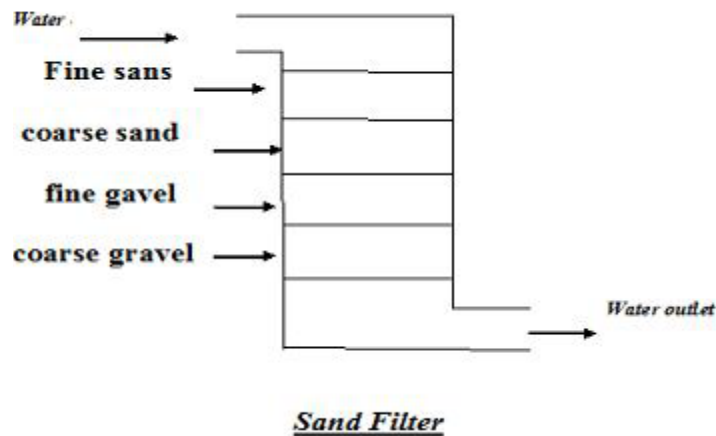
4. Coagulation :

In this method by adding coagulants like aluminium sulphate, the colloidal impurities like finely divided clay, silica, etc., are also removed. The aluminium sulphate hydrolysed to give gelatinous precipitate Al(OH)₃ ; The suspended impurities adhere to the precipitate and settle down at the bottom.



5. Filtration :

The bacteria, colour, taste ,odour and suspended impurities are removed by passing the water through the layers of fine sand , coarse sand and fine gravel and coarse gravel successively placed in a filter tank.



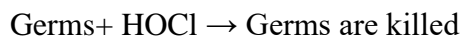
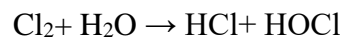
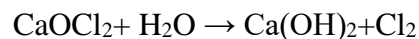
After a long time the rate of filtration is ceased as the holes in the filter are blocked by the impurities; so filtration is stopped and the top concentrated sand layer is scrapped off and replaced by fresh sand .

Removal of micro-organisms:

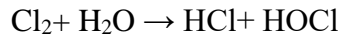
The process of destroying /killing the disease producing bacteria, micro-organisms, etc., from the water and making it safe for the use, is called disinfection.

a. Boiling: By boiling water for 10-15 minutes, all the disease producing bacteria is killed and the water becomes safe for use.

b. Adding bleaching powder: In small water works, about 1 kg of bleaching powder per 1000 kiloliter of water is mixed and allowed to stand undisturbed for several hours. The chemical action produces hypochlorous acid (a powerful germicide)



c. Chlorination: Chlorination (either gas or in concentrated solution form) produces hypochlorous acid, which is a powerful germicide.



Break point chlorination (or) or free residual chlorination

It involves addition of sufficient amount of chlorine to oxidize: (a) organic matter (b) reducing substance and (c) free ammonia in raw water; leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing bacteria. The addition of chlorine at the

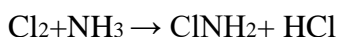
dip or break is called “break point” chlorination. This indicates the point at which free residual chlorine begins to appear..

Advantages:

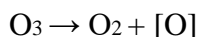
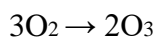
1. It oxidizes completely organic compounds, ammonia and other reducing compounds.
2. It removes color, odor and taste of water.
3. It removes completely all the disease causing bacteria/micro-organism.
4. It prevents the growth of any weeds in water.

Using Chloramine (ClNH₂)

When chlorine and ammonia are mixed in the ratio of 2:1 by volume, Chloramine is formed. Chloramine is a better bactericidal than chlorine.

**Disinfection by Ozone**

Ozone gas is an excellent disinfectant, which is produced by passing silent electric discharge through cold and dry oxygen.

**Desalination of brackish water**

The process of removing common salt (NaCl) from the water is known as desalination. Water containing high concentration of dissolved salts with a peculiar salty taste is called brackish water. Sea water is an example containing 3.5% of dissolved salts. The common methods for the desalination of brackish water are;

Electrodialysis

It is a method in which the ions are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair. An Electrodialysis cell consists of a large number of paired sets of rigid plastic membranes. Hard water is passed between the membrane pairs and an electric field is applied perpendicular to the direction of water flow. Positively charged membrane and negatively charged membrane repel positively charged ions and negatively charged ions respectively to pass through. So, in one compartment of the cell, the salt concentration decreases while in the adjacent compartment it increases. Thus we get alternative stream of pure water and concentrated brine. Advantages: 1. It is most compact unit

Reverse osmosis

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrate sides, due to osmosis. If, however a hydrostatic pressure in excess to osmotic pressure is applied on the concentrated side, the solvent flow is reversed, i.e, solvent is forced to move from concentrated side to dilute side across the

membrane. This is the principle of reverse osmosis (RO). Thus in reverse osmosis method, pure solvent is separated from its contaminants, rather than removing contaminants from the water. The membrane filtration is sometimes also called super filtration or hyper filtration.

METHOD

In this process, pressure is applied to the sea water or impure water to force the pure water content of it out the semi-permeable membrane, leaving behind the dissolve solids. The principle of reverse osmosis as applied for treating saline/sea water The membrane consists of very thin film of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

ADVANTAGES

1. Reverse osmosis possesses distinct advantages of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization.
3. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.
4. The life time of membrane is quite high, about 2 years,
5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
6. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining grounds at present for converting sea water into drinking water and for obtaining water for very high –pressure boilers.

Analysis of Water

Dissolved Oxygen (DO)

Oxygen is important to all lives. Dissolved oxygen is the form of oxygen in water that is freely available to aquatic plants and animals. Dissolved oxygen is vital to fish and other aquatic life and for the prevention of odors. Oxygen is transferred from the atmosphere into surface waters, as well as being produced by aquatic plants, algae and phytoplankton as a by-product of photosynthesis. Once dissolved in water, oxygen diffuses throughout a water body very slowly since distribution depends on the movement of aerated water by turbulence and currents, water flow and thermal upwelling. Oxygen, in water, is measured as dissolved oxygen (D.O). One unit of measure of dissolved oxygen in water is parts per million (ppm) which is the number of oxygen (O) molecules per million total molecules in a sample. It is also defined as the number of moles of molecular oxygen (O₂) dissolved in a litre of water at a temperature, expressed as mg O₂/L.

A high percentage of dissolved oxygen is conducive to supporting aquatic flora and fauna, such as algae, plants, fish, mollusks and invertebrates. A low percentage or depleted of dissolved oxygen indicates a negative impact on a body of water, which results in an abundance of worms and fly larvae. Aquatic life uses oxygen that is dissolved in the water and is in much smaller quantities than in the air. If more oxygen is consumed than is produced, dissolved oxygen levels decline and some sensitive animals may move away, weaken or die.

Dissolved Oxygen Levels are affected by

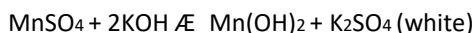
1. Water temperature: when temperature decreases, more oxygen dissolves in water; when temperature increases, dissolved oxygen decreases.
2. Aquatic plant populations
3. Stream flow
4. Altitude/atmospheric pressure
5. Human activities
6. Organic waste (such as leaves, sewage, industrial waste, agricultural/ fertilizer runoff and faecal matter) build up when it increases and dissolved oxygen decreases

Weather, temperature and salinity affect amounts of dissolved oxygen (DO). Cold and fresh water holds more oxygen than warm or salty water. If DO levels are severely low, large quantities of fish may die

Theory of Winkler's Method for DO Determination

The Winkler method (1888), otherwise known as the iodometric technique, is the most precise and reliable titrimetric procedure for DO analysis. The chemistry of this test is based on the addition of a manganese solution followed up by a strong alkali solution. The DO present rapidly forms hydroxide salts with the manganese. The colour of the precipitate formed is an initial indicator of how much DO is present. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts back to the divalent state and the liberated iodine is equivalent to the original DO content. This iodine is then titrated with a standard thiosulphate solution. The redox chemistry of Winkler's method is as follows:

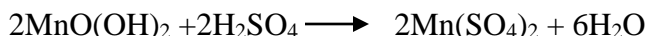
Manganous sulphate reacts with the potassium hydroxide-potassium iodide to produce a white flocculent precipitate of manganous hydroxide:



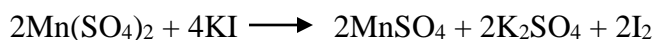
If there is any DO in the water, a second reaction between the Mn(OH)_2 and DO occurs immediately to form a brownish manganic oxide precipitate.



When the samples are ready to be titrated, requisite amount of H_2SO_4 (1:1 sulphuric acid) is added to each and the bottles are inverted several times in order to completely re-dissolve the brownish precipitate. Manganic sulphate ($\text{Mn(SO}_4)_2$) is yielded as the product of this reaction:



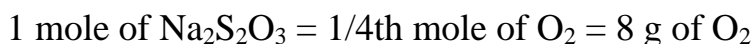
The $\text{Mn(SO}_4)_2$ immediately reacts with the potassium iodide (KI) added, liberating the number of moles of iodine exactly equivalent to the number of moles of oxygen present in the sample. The release of iodine (I_2) imparts a brown colouration to the water typical of iodine.



Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) then reacts with the released I_2 to give an accurate estimate of the DO in the original sample. The sample is then titrated to a pale, straw colour before the starch

indicator is added. This will change the solution blue. The titration end-point is when the blue colour disappears.

Calculation of DO



Therefore,

$$\text{DO of water sample} = \frac{8 \times V \times 0.005 \text{ N}}{25} \text{ at } t \text{ } ^\circ\text{C}$$

Biochemical Oxygen Demand (BOD)

The BOD is an important measure of water quality. It is a measure of the amount of oxygen needed (in milligrams per litre or ppm) by bacteria and other microorganisms to oxidize the organic matter present in a water sample over a period of 5 days.

Biochemical oxygen demand (BOD) is defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. When organic matter decomposes, microorganisms (such as bacteria and fungi) feed upon this decaying material and eventually it becomes oxidized. Microorganisms such as bacteria are responsible for decomposing organic waste. When organic matter such as dead plants, leaves, grass clippings, manure, sewage or even food waste is present in water supply, the bacteria will begin the process of breaking down this waste. When this happens, much of the available dissolved oxygen is consumed by aerobic bacteria, robbing other aquatic organisms of the oxygen they need to live.

BOD directly affects the amount of dissolved oxygen in rivers and streams. The more rapidly oxygen is depleted in the stream, the greater the BOD. This means less oxygen is available. The detriment of high BOD is same as low dissolved oxygen; aquatic organisms become stressed, suffocate and die.

Sources of BOD include leaves and woody debris, dead plants and animals, animal manure, effluents from pulp and paper mills, wastewater treatment plants, feedlots and food-processing plants, failing septic systems and urban storm water runoff.

Determination of BOD

The 5-day biochemical oxygen demand (BOD₅) assay is a standardized assessment of the amount of oxidizable, or respirable, organic matter in water. It is the amount of oxygen (in mg/L) required by bacteria to oxidize the organic molecules aerobically. Oxygen consumed by inorganic compounds is also measured by this test which is why it is referred to as biochemical oxygen rather than just biological oxygen demand. It is used as an index of the amount of organic pollution of the water and is routinely employed to measure the efficiency of wastewater treatment plants in removing organic matter from wastewater or in assessing the effect of effluents on the tropic status of natural waters.

Any wastes, such as municipal sewage, abattoir discharge and some industrial wastes with high BOD, must be treated to remove or lower the BOD before release into the receiving water. This removal of BOD by the wastewater treatment plant is inevitably biological but may be either aerobic or anaerobic.

Introduction

A sample of the water of interest is placed in a BOD bottle and its dissolved oxygen (DO) concentration is measured. The bottle is sealed and incubated in the dark for 5 days at 20 C at the end of the incubation time the DO is measured again. The drop in DO over the incubation period is the amount of oxygen used by bacteria to oxidize the organic material in the sample. BOD is high in organically polluted waters and low in pristine water. It is very high in wastewater, some industrial effluents and slaughterhouse wastes.

Dilution

Waters with high concentrations of organic material will not contain sufficient dissolved oxygen for complete oxidation. In this case an undiluted sample will become anaerobic sometime during the five-day incubation period and no useful information will be gained from the procedure. It is necessary to dilute such samples so that there will be sufficient oxygen present to oxidize all the organic matter, with a little oxygen left over.

The amount of dilution required by any given sample must be determined by trial and error method or past experience. It is customary to prepare multiple dilutions, usually three, of each sample to assure finding one that is usable. Although the best dilutions to use must be determined by trial and error, the following guidelines can be used to approximate the correct dilution.

Dilution water

Bacterial growth requires inorganic nutrients as well as organic compounds and these must be added to the dilution water to ensure their presence. The dilution water is also buffered to ensure a pH suitable for bacterial growth.

Seeding

After dilution, the sample must be seeded with a bacterial source to ensure the presence of bacteria capable of degrading the organic material in the sample. Non-chlorinated treatment plant secondary effluent or raw sewage may be used for this but it is preferable to use commercial preparations of lyophilized bacteria such as polyseed®.

BOD measurements

The following procedure applies to both total BOD₅ and soluble BOD₅ determinations.

No dilution is required for samples whose 5-day BOD is less than 6 mg/L. Standard dilution technique should be applied to samples with DO depletion greater than 6 mg/L. The analyst has to decide what dilution should be set for determination of BOD. In most instances, three dilutions will be sufficient to cover the possible range of a sample with unknown strength.

The BOD value is not affected by oxygen concentrations greater than 0.5 mg/L. Dilutions that produce a depletion of oxygen less than 2 mg/L should not be used. Hence, it is customary to base calculations of BOD on samples that produce a depletion of at least 2 mg/L and have at least 0.5mg/L of dissolved oxygen remaining at the end of the incubation period. This restriction usually means a DO range of 2 to 6 mg/L.

Table presents suitable dilutions prepared by direct pipetting into bottles of about 300 mL capacity. It is customary to estimate the BOD of a sample and set one dilution based upon the estimate. Two other dilutions, one higher and one lower, are also set up. For example, a sample is estimated to have a BOD of 1000 mg/L. From Table 2, a 0.5% mixture should be used. If a 0.2 and a 1.0% mixture are included, the

range of measurable BOD is extended from 200 to 3000 mg/L and should compensate for any errors in the original estimate.

Table BOD measurable with various dilutions of samples.

Using percent mixtures		By direct pipetting into 300 mL bottles	
% mixture	Range of BOD (mg/L)	mL	Range of BOD (mg/L)
0.01	20,000 - 60,000	0.02	30,000 - 90,000
0.02	10,000 - 30,000	0.05	12,000 - 36,000
0.05	4,000 - 12,000	0.10	6,000 - 18,000
0.1	2,000 - 6,000	0.20	3,000 - 9,000
0.2	1,000 - 3,000	0.50	1,200 - 3,600
0.5	400 - 1,200	1.0	600 - 1,800
1.0	200 - 600	2.0	300 - 900
2.0	100 - 300	5.0	120 - 360
5.0	40 - 120	10.0	60 - 180
10.0	20 - 60	20.0	30 - 90
20.0	10 - 30	50.0	12 - 36
50.0	4 - 12	100	6 - 18
100.0	0 - 6	300	0 - 6

In the direct-pipetting technique, preliminary dilutions should be made of all samples that require less than 0.5 mL of the sample, so that amounts added to the bottles can be measured without serious error. The volumes of all bottles must be known in order to allow calculation of the BOD when this method is used.

Procedure for Standard Dilution Technique

- (i) Prepare dilution water by adding the following per litre of required dilution water, then aerate to oxygen saturation (approx. 1 hour),
 - 1 mL phosphate buffer,
 - 1 mL magnesium sulfate solution,
 - 1 mL calcium chloride solution,
 - 1 mL ferric chloride solution,
 - 2 mL of settled raw sewage seed.
- (ii) Set up three seeded dilution water blanks. Always siphon dilution water into BOD bottles to avoid entrapping air bubbles.
 Note, BOD₅ of seeded dilution water should range between 0.6~1.0 mg/L.
- (iii) Prepare three dilutions for each sample.
- (iv) Measure the initial DO of each diluted sample and blank using a calibrated DO probe.
- (v) Incubate blanks, the remaining samples at 20°C for five days.
- (vi) After five days incubation, measure DO in each bottle by DO probe, and calculate BOD₅ as follows:

$$\text{BOD}_5 \text{ as mgO}_2 / \text{L} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

where: D1 = initial DO of sample, mg/L

D2 = Final DO of incubated sample after 5 days, mg/L

B1 = DO of seed control before incubation, mg/L

B2 = DO of seed control after incubation, mg/L

P = Decimal volumetric fraction of sample used

Note: Only consider dilutions where:

(1) depletion is ≥ 2.0 mg/L, and

(2) final DO ≥ 1.0 mg/L.

If more than one dilution satisfies (1) and (2) above, selects dilution with greatest DO depletion.

Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is another parameter used widely to measure the pollutional strength of domestic and industrial wastewaters. COD is defined as the amount of oxygen required to oxidize organic matter chemically. Potassium dichromate ($K_2Cr_2O_7$) is generally chosen for this purpose due to its strong chemical oxidizing capability. Almost all organic compounds (except for ammonia, aromatic hydrocarbons, pyridine and their related compounds) can be oxidized by dichromate under heated acidic and Ag_2SO_4 -catalysed conditions, equivalent to 95 – 100% of the theoretical values. 2 One of the main limitations of the COD test is its inability to differentiate between biologically oxidizable and biologically inert organic matter. Nor can it provide any evidence of the biological decomposition rate that proceeds either in natural or man-made conditions. The major advantage of COD test is the short time required for evaluation. The determination can be made in about 3 hr rather than the usual 5 days required for the measurement of BOD.

In the test of COD, potassium dichromate is used to oxidize the organic matter. In order for the potassium dichromate to oxidize organic matter completely, the solution must be strongly acidic and is refluxed with a silver catalyst at an elevated temperature.

Principle

A known volume of the wastewater sample is refluxed with a known excess of $K_2Cr_2O_7$ solution in H_2SO_4 medium containing $HgSO_4$ (catalyst) and Ag_2SO_4 [which retains halides] for about $1\frac{1}{2}$ hours for the oxidation to be completed. A part of the $K_2Cr_2O_7$ is used up for the oxidation of impurities. Remaining $K_2Cr_2O_7$ determined by titration with standard FAS solution

using ferroin as an indicator. The end-point is the change of colour from blue green to reddish brown.

A blank is performed by titrating known volume of the acidified $K_2Cr_2O_7$ with the same FAS using the same indicator.

$$\text{COD of water sample} = \frac{(A - B) \times M \times 8000 \text{ ml}}{\text{volume of the sample}} \text{ mg/L}$$

where

A = Blank titre value of $K_2Cr_2O_7$ versus FAS and

B = volume of FAS consumed for unreacted $K_2Cr_2O_7$ of the solution.

M = molarity of FAS. solution.

Procedure

25 mL of wastewater is pipetted out into a round bottomed flask. 10 mL of $K_2Cr_2O_7$ is pipetted out into the

same flask along with one test tube full of 1:1 H_2SO_4 containing $HgSO_4$ and Ag_2SO_4 . The flask is filled with a reflux water condenser and the mixture is refluxed for 2 hours. The contents are cooled and transferred to a conical flask. Five drops of ferroin indicator is added to it and titrated against FAS taken in the burette till

the colour changes from blue green to reddish brown. Same volume of $K_2Cr_2O_7$ is pipetted out, mixed with sulphuric acid and ferroin and titrated against same FAS to get blank titre value.

Calculation

$$\text{Chemical oxygen demand COD of water sample} = \frac{(A - B) \times M \times 8000 \text{ ml}}{V} \text{ mg/L}$$

where

A = FAS (mL) used for blank.

B = FAS (mL) used for sample.

M = Molarity of FAS

V = Volume of sample (mL).

