CHAPTER-2

WATER TECHNOLOGY

Introduction: Water quality parameters - Contamination of water by arsenic, lead, fluoride, mercury and their removal. Hardness: Types - Expression - Units. Estimation of hardness of water by EDTA method - Problems. Estimation of iron, calcium and magnesium: AAS method. Water softening: Zeolite process – Demineralization process. Desalination: Reverse osmosis - Electrodialysis.

2.1   INTRODUCTION

Water is one of nature's most important gifts to mankind which is a key component in determining the quality of our lives. Water reacts with minerals in the soil and rocks and dissolves numerous substances in large amounts thus pure water rarely occurs in nature. The surface and groundwater may contain many different dissolved substances which are normally used for industries, agriculture and domestic households. Industries that produce metals, wood, paper, chemicals, gasoline, oils, and most other products all use water in some part of their production process. Industrial water usage composes around 88% of water consumption worldwide. This chapter mainly deals with various qualities and quantities of impurities present in water and technologies used to eliminate them from water.

2.2   SOURCES OF WATER

There are three main sources of water:

2.2.1   RAIN

Rain is the prime source of all water. A part of the rain water sinks into the ground to form ground water, part of it evaporates back into atmosphere and some runs off to form streams and rivers which flow ultimately into the sea. Rain water is the purest water in nature. Physically it is clear, bright and sparkling. Chemically it is very soft water containing only traces of dissolved solids (0.0005 percent). Rain water tends to become impure as it passes through the atmosphere. It picks up suspended impurities from the atmosphere such as dust, particulates, microorganisms and gases such as carbon dioxide, nitrogen oxides, sulphur oxides, oxygen and ammonia.

2.2.2   SURFACE WATER

Surface water originates from rain water. It is the main source of water supply in many areas. Examples of surface water include rivers, streams, tanks, lakes, ponds, man-made reservoirs and sea water. Surface water picks up the characteristics of the surface over which it passes.

Rivers:
River water contains dissolved and suspended impurities of all kinds such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron, small particles of sand and organic matter. Certain amount of self-purification occurs in river water by natural forces of

purification such as dilution, sedimentation, aeration, oxidation, sunlight, plant and animal life. These agencies are not sufficient to render the water potable. Thus river water needs purification before it can be used for drinking purposes.

Seawater:
Though this source is plentiful it has many limitations. It contains 3.5 percent of dissolved salts such as sulphates, chlorides and bicarbonates of sodium, calcium, magnesium and potassium. Desalting of sea water involves heavy expenditure. Thus it is adopted in places where sea water is the only source available.

2.2.3   GROUND WATER

Rain water percolating into ground constitutes ground water. Ground water is the cheapest and most practical means of providing water to small communities. Ground water is superior to surface water, because the ground itself provides an effective filtering medium. It is likely to be free from pathogenic agents and less subject to contamination than surface water. Ground water is high in mineral content such as salts of calcium and magnesium which increase the hardness of water. Examples of ground water are springs, shallow and deep wells.

2.3   IMPURITIES IN WATER
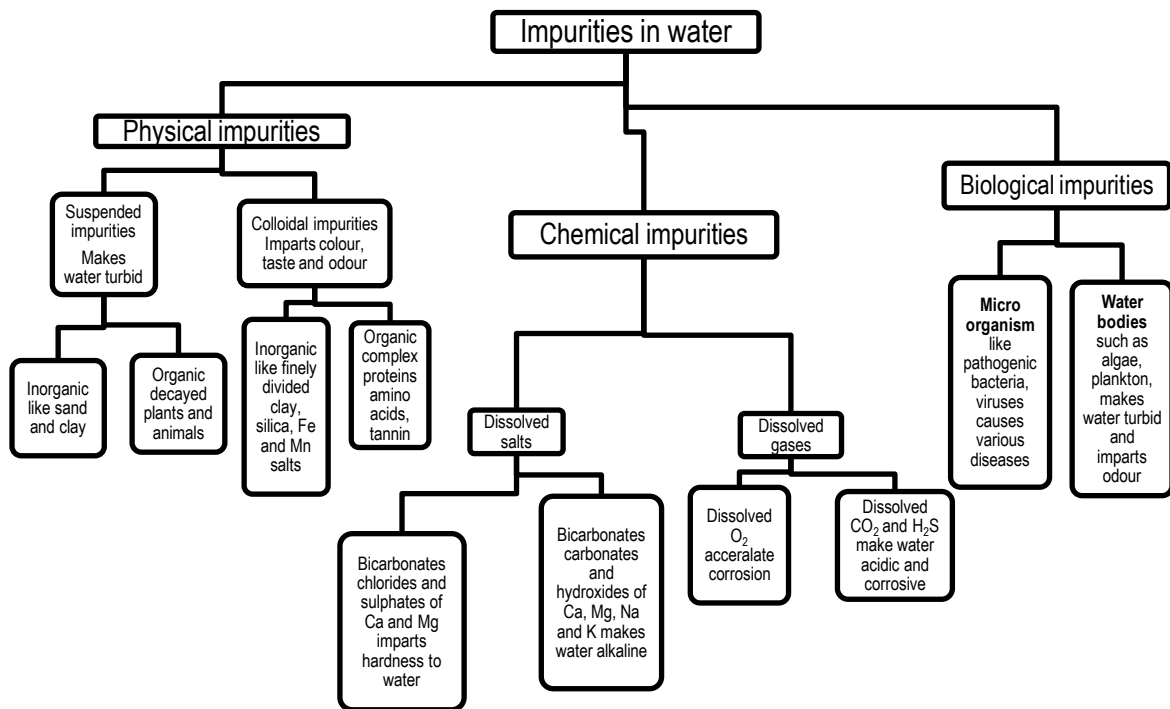
2.4   ACTION OF WATER ON ROCK FORMING MINERALS

HYDRATION: When water comes in contact with the rocks, the minerals undergo hydration, expand in volume and result in rock deformation.

$$CaSO_4 + 2\,H_2O \rightarrow CaSO_4.2\,H_2O$$
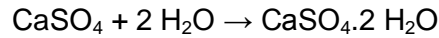
Gypsum

OXIDATION: Dissolved oxygen in water oxidizes the minerals in rocks. The oxidation is more active in presence of water and results in formation of hydrated oxides.

$$2\,Fe_3O_4 + \tfrac{1}{2}\,O_2 \rightarrow 3\,Fe_2O_3 \rightarrow 3\,Fe_2O_3.2\,H_2O$$
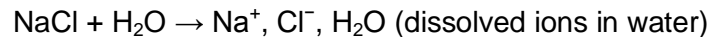
Magnetite   Haematite   Limonite

DISSOLUTION: Minerals like sodium chloride, gypsum present in rocks is readily soluble in water and goes into solution.

$$NaCl + H_2O \rightarrow Na^+, Cl^-, H_2O \text{ (dissolved ions in water)}$$

CARBONATION: When water containing dissolved CO_2 flows through rocks, especially limestone it causes carbonation. The carbonic acid formed by dissolved CO_2 in water reacts with limestone and brings into solution as soluble bicarbonates.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Carbonic acid

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$
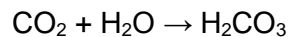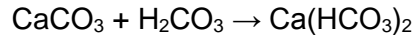
Limestone   Calcium bicarbonate

2.5   EFFECT OF IMPURITIES ON CHARACTERISTICS OF WATER

2.5.1 PHYSICAL IMPURITIES:

1. Turbidity: Turbidity refers to the cloudiness of the water. The materials causing the cloudiness can be inorganic such as clay and sand or organic such as algae and plankton. These colloidal impurities scatter light. Turbidity is normally tested using nephelometer that passes a light through the water and measure the light refraction at a 90° angle from the light source. Surface waters usually have higher turbidity than groundwater. The turbidity in the water may shield bacteria and prevents disinfection chemicals from attacking and destroying the cells. Unit of turbidity: Nephelometric turbidity unit (NTU). Means of treatment: coagulation, settling and filtration.

2. Colour: Colour of water is due the dissolved and colloidal substance present in water like tannin, peat, algae, humus material, iron and manganese salts etc. Soluble iron salts produce red, chromium salts give yellow and algae produce green colour to water. Colour of water is usually measured using tintometer. Unit of colour: Hazen units. Means of treatment: aeration, coagulation, adsorption and filtration.

3. Taste and Odour: Pure water is tasteless and odourless. Taste and odour is imparted to water by the dissolved salts and organic matter. Iron and chlorine gives characteristic taste to water. Water contaminated with algae and other dead and decayed vegetable matter impart grassy odour. Presence of sulphides produces rotten egg smell to water. Means of treatment: aeration and cation exchange process

2.5.2 CHEMICAL IMPURITIES:

1. Alkalinity: Bicarbonates (HCO_3^-), carbonates (CO_3^{2-}), and hydroxides (OH^-) of calcium, magnesium, sodium and potassium makes water alkaline. Alkanity is classified depending on the anion present into bicarbonate alkalinity, carbonate alkalinity and hydroxide alkalinity. The possible combinations of ions causing alkalinity are i) Hydroxide only, ii) Carbonate only, iii) Bicarbonate only, iv) Hydroxide and carbonate and v) Carbonate and bicarbonate. The possibility of combination of hydroxide and bicarbonate is ruled out as they form carbonates ($OH^- + HCO_3^- \rightarrow CO_3^{2-}$). Means of treatment: lime-soda softening, zeolite softening, demineralization anion exchange.

2. Acidity: The acidity of water due to the presence of dissolved CO_2 is called carbon dioxide acidity and due to the presence of mineral acid obtained by hydrolysis of Fe and Al salts is called mineral acidity. Acidity in water promotes corrosion due to the carbonic acid and mineral acids present. Means of treatment: Neutralization with alkalies.

3. Hardness: Hardness of water is caused by calcium and magnesium salts. It is the chief source of scale in heat exchange equipment, boilers, pipe lines and forms curds with soap, interferes with dyeing, etc. Means of treatment: softening; demineralization, internal boiler water treatment.

4. Dissolved gases:

Dissolved CO_2: Surface water contain dissolved CO_2 derived from the atmosphere or biological oxidation of organic matter. The dissolved CO_2 in water changes carbonates in rocks into soluble bicarbonates and makes water alkaline. Action of CO_2 on aluminosilicates produce suspended clay and silica particles in water. Means of treatment: Aeration, deaeration and neutralizing by lime or alkali.

Dissolved O_2: Water contains dissolved oxygen is essential for aquatic life. If the concentration of dissolved O_2 is high it causes corrosion in steam and condenser pipelines. Means of treatment: Deaeration, sodium sulphite treatment and cathodic protection.

2.5.3 BIOLOGICAL IMPURITIES:

Biological contamination of the water is caused by the presence of living organisms, such as algae, bacteria, fungi, protozoan or viruses. Algae are quite abundant in a surface water source and especially if the water contains nutrients that encourage their growth. Algae may cause taste and odor problems, clog filters, and produce nuisance slime growths on intake pipes and equipment. Disease-causing bacteria are called pathogenic bacteria which may cause typhoid fever, dysentery, cholera, and gastroenteritis. Their presence is determined by testing for the

presence of an indicator organism, usually coliform bacteria. Presence of coliform bacteria indicates general bacterial contamination. Some bacteria, although not harmful, may cause taste and odor problems. For example sulphur bacteria which produce hydrogen sulphide and crenothrix iron bacteria which can produce disagreeable taste, odors and stains.

2.6 CONTAMINATION OF WATER BY ARSENIC, LEAD, FLUORIDE AND MERCURY

2.6.1 Mercury

Mercury is a liquid non-essential trace metal. It is usually found in natural deposits such as cinnabar (HgS) or embedded in igneous rocks.

Uses:
- Mercury is used in the chlor-alkali industries (Preparation of Chlorine and NaOH)
- It is also used in batteries, fluorescent tubes, mercury lamps,gear switches etc
- It finds applications in paper, pulp, pharmaceutical and plastic industries

Source: Mercury is discharged into water bodies both by natural and man-made sources.

- The main sources of mercury pollution by natural sources are weathering processes and terrestrial and submarine volcanic activity.
- The main source of mercury pollution by man-made sources are
  - Effluents from the chlor-alkali industries, electrical and electronic industries, plastic industries etc
  - Organomercurials in fungicides used for seed dressing in agriculture
  - Organic mercury fumigants used for preservation of food grains
  - Anthropogenic activities such as burning of coal and crude oil, dental amalgams, mercury containing ointments etc

Mercury poisoning:

Permissible limit: MCL is the maximum contaminant level set by EPA. It is the level of contaminants in drinking water at which no adverse health effects are likely to occur. The MCL given by US Environmental Protection Agency for mercury in drinking water is 0.002 mg/L.

Adverse health effects:

Short term effects: Mercury can cause adverse health effects when exposed to levels higher than MCL for short period of time.
- Mercury exposure for a few hours to 1-3 mg/L causes pulmonary irritation and destruction of lung tissue and central nervous system disorders.
- The two main effects of acute mercury poisoning are neurological and renal disturbances. The former is caused by methyl mercury and ethyl mercury salts and latter by inorganic mercury.
- Dermal exposure to alkylmercurials may give rise to acute toxic dermatitis and eczematous changes.

Long term effects:
- Chronic exposure to mercury concentrations above 0.1 mg/L causes tremors, mental disturbances and gingivitis.

➢ Long term exposure of lower mercury levels causes non-specific neurological and physiological symptoms.
➢ Chronic exposure of mercury above MCL leads to kidney damage.

Biochemical effects: The toxicity of mercury is based on the nature of chemical species is exist. Table (1) shows the various chemical species of mercury.

Table 1   Various chemical species of mercury

S. No	Chemical species	Biochemical properties
1.	Elemental Mercury (Hg)	Relatively inert and non-toxic but its vapour is highly toxic when inhaled
2.	Mercurous ion (Hg_2^{2+})	Insoluble and low toxicity
3.	Mercuric ion (Hg^{2+})	Toxic but does not transported across biological membranes
4.	Organomercurials (RHg^+)	Highly toxic and cause irreversible nerve and brain damage. Easily transported across biological membranes
5.	Diorganomercurials (R_2Hg)	Low toxicity but can be converted to RHg^+ in acidic medium
6.	Mercuric sulphide (HgS)	Highly insoluble and non-toxic

Biochemical effects of organomercurials:
➢ Methyl mercury is a teratogen which is capable of crossing the placenta and causing embroyo toxic effects and abortions. Teratogens are chemical.

➢ Organomercurials such as methyl mercury (CH_3Hg^+) are more soluble in fats, cell membranes and brain tissue. The Hg-C bond is not easily broken and thus retained in the cells for prolonged period of time. Thus they can cross placental barrier and cause irreversible damage to the central nervous system in babies.

➢ Minamita disease: A disease originated in Japanese fishing port of Minamita caused by methyl mercury poisoning which affects the central nervous system. A factory nearby bay synthesised aldehyde using HgCl₂ and HgSO₄ as catalyst. The effluent from factory continuously discharged catalyst into the bay which is biomethylated by bacteria to form methyl mercury. This is gradually bioconcentrated by the fish in the bay which provides the seafood for the people live near the bay. People consumed seafood are affected by various neurological disorder.

Antidote to mercury poisoning: Commonly used mercury-binding chemotherapeutic antidotes for mercury poisoning are
➢ Sodium formaldehyde sulfoxide as local antidote
➢ Intramuscular injection of dimercaprol or penicillamine is administrated as chelating agents which chelate with mercury and excreted in urine.
➢ Isotonic NaCl to protect kidney from higher concentration of mercury

2.6.2 Lead
Lead is a non essential trace element which is toxic and found as deposits in rocks as galena (PbS).

Uses:
- ➢ Lead is used in household plumbing materials or in water service lines used to bring water from the main to the home.
- ➢ It is used in acid stotage batteries, solder and casting materials.
- ➢ It also finds application in the manufacture of leaded-porcelain enamel for protection against radiation in nuclear power reactors and in lead coated steel sheets used in construction of buildings.
- ➢ Lead salts are used in anti-corrosive and highway traffic safety paints

Source: The main source of lead in water is corrosion of household pipes, solder, fixtures, fittings etc. The amount of lead leaching into water depends on the water's acidity and temperature. The other sources of lead poisoning are
- ➢ Smelting of lead ores
- ➢ Emissions from automobile exhaust containing tetra ethyl lead (TEL)
- ➢ Effluents from acid storage batteries
- ➢ Lead containing paints
- ➢ Lead coated steel sheets used for sound attenuation in buildings

Lead poisoning:

Permissible limit: The MCL given by US Environmental Protection Agency for lead is zero. EPA has set this level based on the fact that there is no safe level of exposure to lead.

Adverse health effects:

Short term effects: Lead can cause adverse health effects when exposed to levels higher than MCL for short period of time. Lead in drinking water leads to delayed physical and mental development in babies and children. High blood lead levels in children cause learning disabilities, behavioural problems and mental retardation. Lead accumulates in the bones and interferes with the metabolism of calcium and vitamin D. In adults, it can cause kidney problems or high blood pressure. At very high levels, lead can cause convulsions, coma and death.

Long-term effects: Lead has the potential to cause stroke, kidney disease and cancer from a lifetime exposure at levels higher than MCL.

Biochemical effects:
1. Biochemical effects of Inorganic lead:
   - ➢ Inorganic lead is absorbed by food or inhalation of particulate lead.
   - ➢ Lead interferes with the heme synthesis and disturbs the synthesis of haemoglobin and respiratory pigments such as cytochromes.
   - ➢ Inorganic lead replaces calcium in bones and accumulates in soft tissues such as liver and kidneys.
2. Biochemical effects of Organic lead:
   - ➢ Organic lead such as tetra ethyl lead (TEL) and tetra methyl lead (TML) are more acutely poisonous than inorganic lead.
   - ➢ It is absorbed by inhalation or through the skin.
   - ➢ TEL attacks the central nervous system and cause severe mental disorder.
   - ➢ Organo lead compounds are suspected to cause genetic modifications.

Antidote to Lead poisoning:

➢ Inorganic lead poisoning can be cured by treatment with calcium EDTA chelate in which lead replaces calcium in Ca-EDTA complex and the formed Pb-EDTA complex is excreted in urine. This treatment is called the Chelation therapy. Intramuscular dimercaprol also serves as antidote to lead poisoning.
➢ Organic lead does not form complex with chelating agents and this lead poisoning can be cured by sedative, anti-convulsant and fluid & electrolyte therapy.

2.6.3 Arsenic

Arsenic is a non-essential metalloid element which is toxic and occurs in nature as sulphide ores.

Uses:
➢ Elemental arsenic is used in the manufacture of glass, electronics, semiconductors and photoconductors.
➢ Arsenic compounds are also used as wood preservative, fungicides, preservatives, insecticides, pesticides and herbicides.
➢ It finds applications in paints, dyes, metals, drugs, soaps and drugs.

Source:
The main source of arsenic pollution is from smelting of arsenic containing ores and burning of coal. The other sources of arsenic poisoning are
➢ Arsenic compounds in fungicides, preservatives, pesticides, insecticides and herbicides
➢ Arsine (AsH_3) which is a byproduct of many industrial processes involving arsenic and action of fungi in sewage plants
➢ Arsenic release from metal refining, etching, soldering, galvanising and lead-plating operations.

Arsenic poisoning:

Permissible limit: The MCL given by US EPA for arsenic is 0.010 mg/L.

Adverse health effects:

Short term effects:
➢ Arsenic harms the central and peripheral nervous systems, heart and blood vessels.
➢ It also causes birth defects and reproductive problems.

Long-term effects:
➢ Chronic exposure of arsenic poisoning causes problems in circulatory system.
➢ Long term exposure of arsenic level higher than 0.050 mg/L can cause skin, lung, kidney and bladder cancer.

Biochemical effects:
➢ The major biochemical effects of arsenic poisoning are
  • **Complexation of coenzymes:** As (III) forms complex with enzymes and exerts its toxic therby inhibiting enzyme action
  • **Uncoupling of phosphorylation:** Arsenic interferes in phosphorylation reaction which is the vital step in the generation of ATP

- **Coagulation of proteins:** High concentration of arsenic compounds denatures the secondary and tertiary structures and coagulates protein.
- Arsenic is cumulative protoplasmic poison which can cross placental membrane and thus is a teratogen.

Antidote to arsenic poisoning:

Arsenic poisoning can be cured by the treatment with 2,3-dimercaproproponal (BAL) which is capable of bonding to As(III). This is followed by restoration of fluid and electrolyte balance.

2.6.4 Fluoride

Fluoride is an essential non metal that doesnot occur in the elemental state in nature because of its high reactivity and combines with minerals in soil or rocks.

Uses:
- Fluoride is added to water in small concentration to protect the teeth from decay and to build bone strength.
- Inorganic fluoride compounds are used in Al production and glass fibre industries.
- Fluoride is also used in the production of phosphate fertilizers, bricks, tiles and ceramics.

Source:
- The main source of fluoride is drinking water contaminated from natural geological sources. Most of water bodies contain naturally occurring fluoride.
- It enters water sources from the effluents of fertilizers and aluminium factories.
- Fluoride compounds such as sodium fluoride and fluorosilicates easily dissolves into water flowing through rocks.
- Fluoride is added to drinking water to promote dental health.
- Burning of fluoride rich coal.

Fluoride poisoning or Fluorosis:

Permissible limit: The MCL set by US EPA for fluoride is 4 mg/L. Small amounts of fluoride (1 ppm) are good for teeth and it is added to toothpaste and drinking water.

Adverse Health effects:
- High concentration of fluoride can cause pitting of teeth and severe skeleton problems such as crippling, stiff joints and restricted movement.
- Fluorosis is a major health problem resulting from long term exposure of high fluoride content.
- Fluorosis is characterised by dental mottling and skeleton manifestations such as crippling deformities, osteoporosis and osteosclerosis.
- Fluoride can rapidly cross the cell membrane and is distributed in skeletal and cardiac muscle, liver, skin and erythrocytes.

Antidote to Fluoride poisoning:

Fluorosis is not treatable but it is preventable. Defluoridation is difficult and expensive, so the best option for dealing with excess levels is pursuing alternative water sources if they are available. The goals of therapy in patients with fluoride toxicity are to reduce toxicity and prevent complications. No antidote for fluoride toxicity exists and activated charcoal does not adsorb fluoride. Electrolytes may be used to correct imbalances resulting from fluoride toxicity. The

appearance of the fluorosis teeth can be improved by treatments such as tooth whitening, crowns, porcelain veneers, microabrasion, bonding with coats etc.

### 2.6.5 Removal of Lead, Mercury, Arsenic and Fluoride from water

It is essential to removal the hazardous pollutants such as mercury, lead, arsenic, fluoride etc from water to prevent public from adverse health defects caused by these. There are various methods to remove these pollutants from water. They are reverse osmosis, electrodialysis, coagulation/filtration, adsorption, ion exchange method, electrocoagulation etc. The removal of pollutants by Electrocoagulation method is described below. The other methods mentioned above are explained in different sections of the chapter.

Electrocoagulation Method:

Definition: Electrocoagulation is the process of destabilising suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium.

Principle: Electrocoagulation is an electrochemical process that produces destabilising agents which neutralizes the electrical charge of the pollutant, coagulates and removes them. The cations (Fe^{2+} and Al^{3+}) produced from iron or aluminium anodes are responsible for the increasing of the coagulation of contaminants from an aqueous medium.

Electrocoagulation unit consists of an electrolytic cell with one anode (called sacrificial anode) and one cathode. When an electric current is applied it generates gas bubbles and coagulating agents which is capable of attracting oppositely charged pollutants and neutralizes them. The cations (Al^{3+}, Fe^{2+}) produced at the anode react with OH^- ions and form their respective hydroxides. These hydroxides undergo polymerization and condensation reactions and forms polymeric complexes.

$$Al(OH)_3 + Al(OH)_3 \rightarrow (OH)_2Al - O - Al(OH)_2 + H_2$$

$$Fe(OH)_2 + Fe(OH)_2 \rightarrow (OH)Fe - O - Fe(OH) + H_2O$$
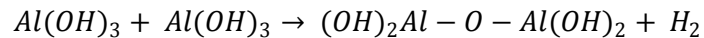
The polymeric complexes [$Al_2(O)(OH)_4$] and [$Fe_2(O)(OH)_2$] remove pollutants from water mainly by either adsorption, surface complexation or by co-precipitation. In general, polymeric aluminium or iron complexes can have both positive and negative charges which are capable of attracting the oppositely charged pollutants, agglomerate to form floc and remove them from water by filtration.

However, if electrocoagulation-flotation apparatus, is used the particulates would float to the top of the tank by means of hydrogen bubbles formed during the reaction from the anode. The floated particulates can be skimmed from the top of the tank.
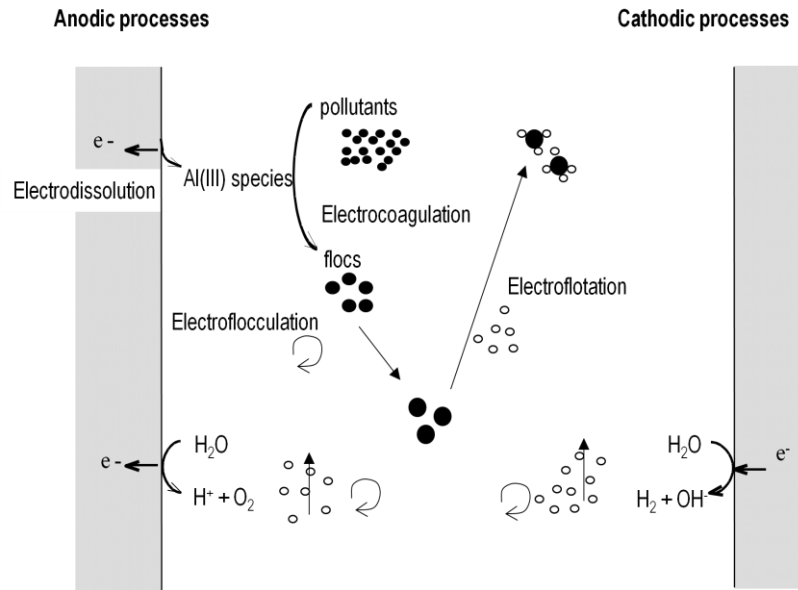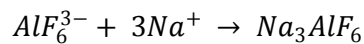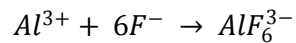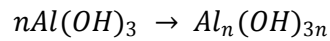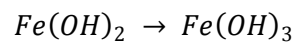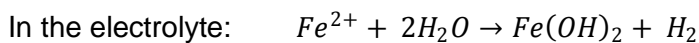
Figure 2.1   Electrocogulation Unit

Mechanism:

Removal of Fluoride by Electrocoagulation

At the cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At the anode: $Al \rightarrow Al^{3+} + 3e^-$

In the electrolyte: $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n}$$

$$Al^{3+} + 6F^- \rightarrow AlF_6^{3-}$$

$$AlF_6^{3-} + 3Na^+ \rightarrow Na_3AlF_6$$
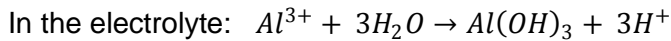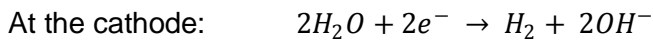
Removal of Arsenic by Electrocoagulation

At the cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At the anode: $Fe \rightarrow Fe^{2+} + 2e^-$

In the electrolyte: $Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + H_2$

$$Fe(OH)_2 \rightarrow Fe(OH)_3$$

$$As + Fe(OH)_3 \rightarrow Fe - As\ (Complex) + H_2O$$

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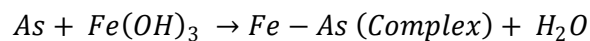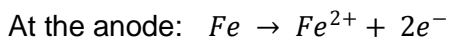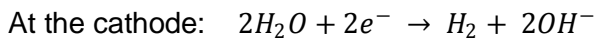
Removal of Heavy metals (Pb and Hg) by Electrocoagulation

At the cathode: (Stainless Steel)
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
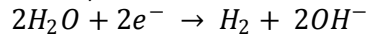
At the anode: (Mild Steel) $Fe \rightarrow Fe^{2+} + 2e^-$

In the electrolyte:
$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + H_2$$

$$Fe(OH)_2 \rightarrow Fe(OH)_3$$
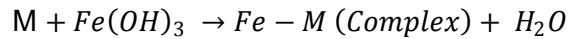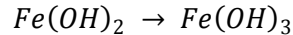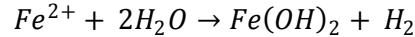
$$M + Fe(OH)_3 \rightarrow Fe - M \ (Complex) + H_2O$$
Where M= Pb,Cr,Hg, etc.,

Advantages:
1. Electrocoagulation requires simple equipment and is easy to operate.
2. Electrocoagulation requires low installation and operating cost.
3. It does not require any chemicals thus no problem of neutralizing excess chemicals.
4. There is no possibility of secondary pollution caused by chemical substances.
5. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be collected and removed.

Disadvantages:
1. Due to oxidation, sacrificial anode dissolved in the water, so need to be regularly replaced.
2. The use of electricity may be expensive in some cases.

2.7   HARDNESS OF WATER

Hardness in water is the characteristic property which prevents the lathering of soap. This is caused by bicarbonates, chlorides and sulphates of calcium and magnesium. When hard water is treated with soap it does not produce lather but forms white scum or precipitate of insoluble calcium and magnesium soaps.

2 $C_{17}H_{35}COONa$ + $CaCl_2$ → $(C_{17}H_{35}COO)_2Ca$ + 2 $NaCl$
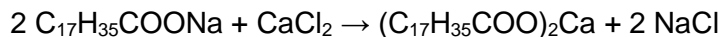
Sodium soap   Insoluble Calcium soap

2 $C_{17}H_{35}COONa$ + $MgSO_4$ → $(C_{17}H_{35}COO)_2Mg$ + Na_2SO_4
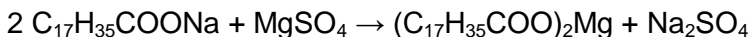
Sodium soap   Insoluble Magnesium soap

Lather is not produced until all the hardness causing Ca^{2+} and Mg^{2+} ions are completely removed as insoluble soap. Hence a large quantity of soap is consumed to produce lather with hard water.

2.7.1   HARD WATER AND SOFT WATER

Water which does not produce lather with soap but forms a white precipitate is called as **hard water**. It contains dissolved salts of calcium and magnesium. Common hardness causing

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impurities are $CaCl_2$, $MgCl_2$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaSO_4$ and $MgSO4$. Water which gives lather readily with soap is called as **soft water**. This water does not contain dissolved calcium and magnesium salts in it.

2.7.2 TYPES OF HARDNESS

Hardness is classified into temporary hardness and permanent hardness.

Temporary or carbonate hardness

Temporary hardness is due to the presence of dissolved bicarbonates of calcium and magnesium and thus referred as carbonate hardness. This hardness can be removed by boiling which converts the bicarbonates into insoluble carbonates or hydroxides.

$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + CO_2 + H_2O$

Insoluble

$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 \downarrow + 2CO_2$

Insoluble

Permanent or non-carbonate hardness

Permanent hardness is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. Permanent hardness cannot be removed by boiling. Since this hardness is caused by salts other than carbonates they are also called as non-carbonate hardness.

2.7.3 EXPRESSION OF HARDNESS OR EQUIVALENTS OF CaCO$_3$

Hardness caused by various dissolved salts is expressed in terms of $CaCO_3$ equivalents. $CaCO_3$ is chosen as standard because its molecular weight is 100 (equivalent weight=50) and it is the most insoluble salt that can be precipitated in water treatment.

$$Hardness\ of\ CaCO_3 eq\ = \frac{Mass\ of\ hardness\ producing\ substance\ (\frac{mg}{L}) \times Molecular\ weight\ of\ CaCO_3}{Molecular\ weight\ of\ hardness\ producing\ substance}.$$

Calculation of hardness of various salts in CaCO$_3$ equivalents

Dissolved salt	Molecular weight	Equivalent weight	Multiplication factor
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
CaCO3	100	50	100/100
MgCO3	84	42	100/84
CaSO4	136	68	100/136

MgSO4	120	60	100/120
$CaCl_2$	111	55.5	100/111
$MgCl_2$	95	47.5	100/95

2.7.4 UNITS OF HARDNESS

Parts per million (ppm) is the number of parts of calcium carbonate equivalent hardness per 10^6 parts of water.

1 ppm = 1 part of $CaCO_3$ eq hardness per 10^6 parts of water.

Milligrams per litre (mg/L) is the number of milligrams of calcium carbonate equivalents per litre of water.

1 mg/L = 1 mg of $CaCO_3$ eq hardness per litre of water.

Clarke's degree (ºC) is the number of parts of calcium carbonate equivalents per 70,000 parts of water.

Degree French (ºFr) is the number of parts of calcium carbonate equivalents per 10^5 parts of water.

Relationship between ppm and mg/L

1 mg/L = 1 mg of $CaCO_3$ eq hardness per litre of water.

But 1 litre of water weighs = 1 Kg = 1000 g =1000 x 1000 mg = 10^6 mg.

1 mg/L =   1 mg of $CaCO_3$ eq hardness per 10^6 mg of water.

1 mg/L =   1 part of $CaCO_3$ eq hardness per 10^6 parts of water

[But 1 ppm = 1 part of $CaCO_3$ eq hardness per 10^6 parts of water]

1 mg/L = 1 ppm

2.7.5 PROBLEMS: CONVERSION OF HARDNESS PRODUCING SALTS INTO $CaCO_3$ EQUIVALENTS

Note:

 1. When hardness causing impurities are given as $CaCO_3$ and $MgCO_3$ they are to be treated as Ca $(HCO_3)_2$ and Mg $(HCO_3)_2$

2. NaCl, KCl, Na_2SO_4, SiO_2, Fe_2O_3 etc. do not make water hard. Therefore they should not be taken into account while calculating hardness.

Hardness producing salts and their CaCO$_3$ equivalents.

S.No	Mole equivalents	Weight equivalents
1.	$1Ca(HCO_3)_2 \equiv 1\ CaCO_3$ 162 parts $\equiv$ 100 parts X parts $\equiv$?	(100/162) x X parts
2.	$1\ Mg(HCO_3)_2 \equiv 1\ CaCO_3$ 146 gm $\equiv$ 100 gm X gm $\equiv$?	(100/146) x x gm
3	$1\ CaCl_2 \equiv 1\ CaCO_3$ 111mg $\equiv$ 100 mg X mg $\equiv$?	(100/111) x X mg
4	$1\ CaSO_4 \equiv 1\ CaCO_3$ 136 parts $\equiv$ 100 parts X parts $\equiv$?	(100/136) x X parts
5	$1MgCl_2 \equiv 1\ CaCO_3$ 95parts $\equiv$ 100 parts X parts $\equiv$?	(100/95) x X parts
6	$1\ MgSO_4 \equiv 1\ CaCO_3$ 120 parts $\equiv$ 100 parts X parts $\equiv$?	(100/120) x X parts
7	$1\ FeSO_4.\ 7H_2O \equiv 1\ CaCO_3$ 278 parts $\equiv$ 100 parts X parts $\equiv$?	(100/278) x X parts

1) Calculate temporary and permanent hardness in terms of caco$_3$ for a water sample containing the following. i) Ca(HCO$_3$)$_2$ = 16.2 mg/L   ii) Mg(HCO$_3$)$_2$ = 14.6 mg/L   iii) MgCl$_2$ = 19 mg/L   iv) CaSO$_4$ = 68 mg/L   v) NaCl = 58.5 mg/L

Solution:

i) 162 mg/L of Ca(HCO$_3$)$_2$ $\equiv$ 100 mg /L of CaCO$_3$

16.2 mg/L of $Ca(HCO_3)_2 \equiv (100 / 162) \times 16.2$ mg of $CaCO_3$

$$\equiv 10 \text{ mg /L of } CaCO_3$$

ii) 146 mg/L of $Mg(HCO_3)_2 \equiv 100$ mg /L of $CaCO_3$

14.6 mg/L of $Mg(HCO_3)_2 = (100 / 146) \times 14.6$ mg /L of $CaCO_3$

$$= 10 \text{ mg /L of } CaCO_3$$

iii) 95 mg /L of $MgCl_2 \equiv 100$ mg /L of $CaCO_3$

19 mg/L of $MgCl_2 = (100/95) \times 19$ mg /L of $CaCO_3$

$$= 20 \text{ mg/L of } CaCO_3$$

iv) 136 mg/L of $CaSO_4 \equiv 100$ mg /L of $CaCO_3$

68 mg/L of $CaSO_4 = (100/ 136) \times 68$ mg /L of $CaCO_3$

$$= 50 \text{ mg /L of } CaCo_3$$

v) NaCl does not produce hardness.

Temporary hardness = $Ca(HCO_3)_2 + Mg(HCO_3)_2 = 10+10 = 20$ mg/L or ppm

Permanent hardness = $MgCl_2 + CaSO_4 = 20 +50 = 70$ mg /L or ppm

2) Calculate carbonate and non carbonate hardness caused by the following salts in water. i) Ca(HCO$_3$)$_2$ = 20 mg/L   ii) Mg(HCO$_3$)$_2$ = 18 mg/L   iii) MgSO$_4$ = 19 mg/L   iv) CaCl$_2$ = 40 mg/L   v) NaCl = 30.5 mg/L

Solution:

Hardness producing salt	Molecular weight	Hardness in terms of $CaCO_3$ eq (mg/L)	Carbonate/non carbonate hardness
$Ca(HCO_3)_2$	162	$(100/ 162) \times 20 = 12.35$	Carbonate hardness
$Mg(HCO_3)_2$	146	$(100/ 146) \times 18 = 12.33$	Carbonate hardness
$MgSO_4$	120	$(100/ 120) \times 19 = 15.83$	non carbonate hardness
$CaCl_2$	111	$(100/ 111) \times 40 = 36.04$	non carbonate hardness
NaCl	Does not produce hardness		

Carbonate hardness = $Ca(HCO_3)_2$ + $Mg(HCO_3)_2$ = 12.35 + 12.33 = 24.68 mg/L or ppm

Non carbonate hardness = $CaCl_2$ + $MgSO_4$ = 36.04 + 15.83 = 51.87 mg /L or ppm

3) Find out the sample which is more hard.

Water sample 1	Water sample 2
$Ca(HCO_3)_2$ = 16.2 ppm	$Mg(HCO_3)_2$ = 16.2 ppm
$CaCl_2$ = 55.5 ppm	$MgCl_2$ = 55.5 ppm
$CaSO_4$ = 13.6 ppm	$MgSO_4$ = 13.6 ppm
NaCl = 58.5 ppm	KCl = 58.5 ppm

Solution:

i) Water sample 1:

 Hardness = $Ca(HCO_3)_2$ + $CaCl_2$ + $CaSO_4$ + NaCl

=[(100/162) x 16.2] + [(100/111) x 55.5] + [(100/136) x13.6] + 0

= 10+50+10+ 0 = 70 ppm

ii) Water sample 2:

 Hardness = $Mg(HCO_3)_2$ + $MgCl_2$ + $MgSO_4$ + KCl

= [(100/146) x 16.2] + [(100/95) x 55.5] + [(100/120) x13.6] +0

= 11+ 58.4 + 11.3 = 80.7 ppm

Therefore, the water sample which is more hard is '2'

2.8   ESTIMATION OF HARDNESS

The EDTA method is a complexometric titration which is more preferred and accurate than soap titration method. In this method usually disodium salt of ethylene diamine tetra acetic acid is used because it is more soluble in water. The eriochrome black –T is an organic azo dye which is used as an indicator. The structure of disodium salt of EDTA is given below.

$$Na^{+\ -}OOC.H_2C \qquad CH_2.COO^-H^+$$
$$N-CH_2-CH_2-N$$
$$H^{+\ -}OOC.H_2C \qquad CH_2.COO^-Na^{+}$$
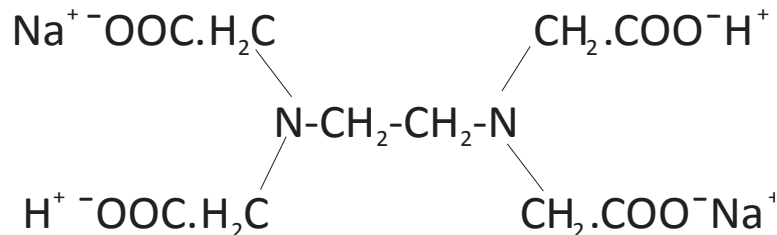
Figure 2.2 Structure of disodium salt of EDTA

Principle: In this method a sample of hard water is titrated against disodium salt of EDTA in presence of a buffer using eriochrome black-T (EBT) as an indicator. The buffer (NH_4OH-NH_4Cl buffer) provides a pH = 9-10 required for the complex formation. The indicator forms an unstable wine red coloured complex [M-EBT] with M^{2+} {Ca^{2+} and Mg^{2+}} ions present in the hard water sample.
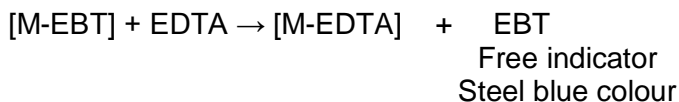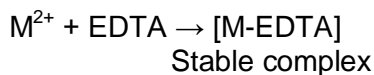
$$M^{2+} + EBT \rightarrow [M\text{-}EBT]$$
$$\text{Unstable Complex}$$
$$\text{Wine red colour}$$
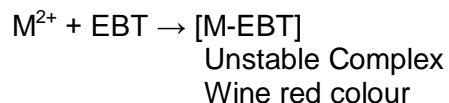
EDTA added forms a stable metal EDTA complex [M-EDTA] with free M^{2+} ions remaining in the water. Further addition of EDTA forms a stable [M-EDTA] complex releasing EBT from the unstable [M-EBT] complex.
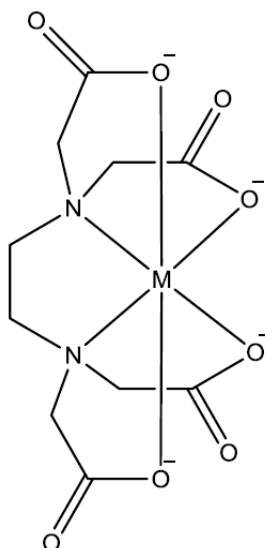
Figure 2.3   Metal-EDTA complex [M-EDTA] where M= Ca^{2+} or Mg^{2+} ion

When all the M^{2+} ions are complexed by EDTA the free indicator released gives steel blue colour. Thus the end point is change of wine red colour to steel blue.

$$M^{2+} + EDTA \rightarrow [M\text{-}EDTA]$$
$$\text{Stable complex}$$

$$[M\text{-}EBT] + EDTA \rightarrow [M\text{-}EDTA] \quad + \quad EBT$$
$$\text{Free indicator}$$
$$\text{Steel blue colour}$$

Steps involved in EDTA method

1. Reagents required for EDTA titration

Preparation of standard hard water: Dissolve 1 g of pure $CaCO_3$ minimum quantity of dilute HCl and then evaporated to dryness. Dissolve the residue in distilled water and make up to 1000 ml. Thus

1 ml of standard hard water = 1 mg of $CaCO_3$ equivalent hardness

Preparation of EDTA solution: Dissolve 4 g of EDTA crystals + 0.1 g of $MgCl_2$ in 1000 ml of distilled water.

Preparation of EBT: Dissolve 0.5 g of EBT in 100 ml of alcohol.

Preparation of buffer solution: Add 67.5 g of NH_4Cl to 570 ml of concentrated ammonia and dilute with distilled water to 1000 ml.

2. Standardization of EDTA solution:

Pipette out 50 ml of standard hard water into a clean conical flask. Add 5 ml of NH_4OH-NH_4Cl buffer and a few drops of EBT indicator. This solution is titrated against EDTA taken in a burette till the colour changes from wine red to steel blue. Let volume of EDTA consumed for 50 ml of standard hard water is V_1 ml.

1 ml of standard hard water = 1 mg of $CaCO_3$ equivalent hardness ------------ 1

50 ml of standard hard water = 50 mg of $CaCO_3$ equivalent hardness ------------ 2

50 ml of standard hard water consumes = V_1 ml of EDTA ------------ 3

From equation 1 and 2

V_1 ml of EDTA = 50 mg of $CaCO_3$ equivalent hardness

1 ml of EDTA $= \frac{50}{V_1}\ mg\ of\ CaCO_3\ equivalent\ hardness$

3. Estimation of Total hardness

Pipette out 50 ml of sample hard water into a clean conical flask. Add 5 ml of NH_4OH-NH_4Cl buffer and a few drops of EBT indicator. This solution is titrated against EDTA taken in a burette till the colour changes from wine red to steel blue. Let volume of EDTA consumed for 50 ml of sample hard water is V_2 ml.

50 ml of sample hard water consumes = V_2 ml of EDTA

50 ml of sample hard water $= V_2$ x 1 ml of EDTA

50 ml of sample hard water $= V_2 \times \frac{50}{V_1}\ mg\ of\ CaCO_3\ equivalent\ hardness$

1000 ml of sample hard water $= V_2 \times \frac{50}{V_1} \times \frac{1000}{50} \, mg \, of \, CaCO_3 \, equivalent \, hardness$

Total hardness of water sample $= \frac{V_2}{V_1} \times 1000 \, ppm$

4. Estimation of permanent hardness

Take 250 ml of water sample in a beaker and boil it to convert temporary hardness causing Ca and Mg bicarbonates into insoluble $CaCO_3$ and $Mg(OH)_2$. Filter the precipitate and wash with distilled water and make upto 100 ml in a standard flask.

Pipette out 50 ml of this boiled sample into a clean conical flask. Add 5 ml of NH_4OH-NH_4Cl buffer and a few drops of EBT indicator. This solution is titrated against EDTA taken in a burette till the colour changes from wine red to steel blue. Let volume of EDTA consumed for 50 ml of boiled sample hard water is V_3 ml.

50 ml of boiled sample hard water consumes $= V_3$ ml of EDTA

50 ml of boiled sample hard water $\qquad = V_3$ x 1 ml of EDTA

50 ml of boiled sample hard water $\quad = V_3 \times \frac{50}{V_1} \, mg \, of \, CaCO_3 \, equivalent \, hardness$

1000 ml of boiled sample hard water $\quad = V_3 \times \frac{50}{V_1} \times \frac{1000}{50} \, mg \, of \, CaCO_3 \, equivalent \, hardness$

Permanent hardness of water sample $= \frac{V_3}{V_1} \times 1000 \, ppm$

5. Temporary hardness of water sample

Temporary hardness of water sample = Total hardness – Permanent hardness

$$= \frac{V_2 - V_3}{V_1} \times 1000 \, ppm$$

2.8.1   PROBLEMS BASED ON EDTA METHOD

Note:

1 Ca or 1 Mg combines with 1 EDTA molecule

i.e 1 Ca ≡ 1 Mg ≡ 1 EDTA

1 ml of 1 M $CaCO_3$ ≡ 1 ml of 2 N $CaCO_3$

$\qquad\qquad$ ≡ 1 ml of 1M EDTA

$\qquad\qquad$ ≡ 1 ml of 2N EDTA

$\qquad\qquad$ ≡ 100 mg of $CaCO_3$

1 ml of N/50 EDTA ≡ 1 ml of M/100 EDTA

1 ml of N/50 EDTA ≡ 1 mg of $CaCO_3$

1) 0.5 gm of CaCO₃ was dissolved in dil.Hcl and diluted to 500 ml. 50ml of this solution required 48 ml of EDTA for titration. 50 ml of a hard water required 15 ml of the EDTA for titration. 50 ml of the same water sample after boiling and filtering required 10 ml of EDTA solution. Calculate the total hardness in ppm.

Solution:

500 ml of std. hard water contains 0.5 g of $CaCO_3$

1 ml of standard hard water = 1 mg of $CaCO_3$ equivalent hardness

50 ml of standard hard water = 50 mg of $CaCO_3$ equivalent hardness

50 ml of standard hard water consumes = 48 ml of EDTA

From equation 1 and 2

48 ml of EDTA= 50 mg of $CaCO_3$ equivalent hardness

1 ml of EDTA $= \frac{50}{48} \, mg \, of \, CaCO_3 \, equivalent \, hardness$

$= 1.041$ mg of $CaCO_3$ equivalent hardness

Estimation of total hardness

50 ml of sample hard water consumes = 15 ml of EDTA

50 ml of sample hard water $= 15 \times 1$ ml of EDTA

50 ml of sample hard water $= 15 \times \frac{50}{48} \, mg \, of \, CaCO_3 \, equivalent \, hardness$

1000 ml of sample hard water $= 15 \times \frac{50}{48} \times 1000 \, mg \, of \, CaCO_3 \, equivalent \, hardness$

Total hardness of water sample $= \frac{15}{48} \times 1000 \, ppm = 312.5 \, ppm$

Estimation of permanent hardness

50 ml of sample hard water consumes = 10 ml of EDTA

50 ml of sample hard water $= 10 \times 1$ ml of EDTA

50 ml of sample hard water $= 10 \times \frac{50}{48} \, mg \, of \, CaCO_3 \, equivalent \, hardness$

1000 ml of sample hard water $= 10 \times \frac{50}{48} \times 1000 \, mg \, of \, CaCO_3 \, equivalent \, hardness$

Permanent hardness of water sample $= \frac{10}{48} \times 1000 \, ppm = 208.2 \, ppm$

Temporary hardness of water sample = Total hardness – Permanent hardness

$$= \frac{V_2 - V_3}{48} \times 1000 \, ppm$$

$$= \frac{15-10}{48} \times 1000 \ ppm \ = 104.2 \ ppm$$

2) 50 ml of a standard hard water containing 1.1 mg of CaCO$_3$ per ml consumed 45ml of EDTA. 50 ml of a water sample consumed 25 ml of EDTA and 50 ml of boiled off water sample consumed 18 ml of EDTA.   Calculate total, permanent and temporary hardness of water.

Solution:

1 ml of standard hard water = 1.1 mg of CaCO$_3$ equivalent hardness

50 ml of standard hard water = 55 mg of CaCO$_3$ equivalent hardness

50 ml of standard hard water consumes = 45 ml of EDTA

From equation 1 and 2

45 ml of EDTA= 55 mg of CaCO$_3$ equivalent hardness

1 ml of EDTA $= \frac{55}{45} \ mg \ of \ CaCO_3 \ equivalent \ hardness$

$= 1.222$ mg of CaCO$_3$ equivalent hardness

Estimation of total hardness

50 ml of sample hard water consumes = 25 ml of EDTA

50 ml of sample hard water   = 25 x 1 ml of EDTA

50 ml of sample hard water $= 25 \times \frac{55}{45} \ mg \ of \ CaCO_3 \ equivalent \ hardness$

1000 ml of sample hard water $= 25 \times \frac{55}{45} \times \frac{1000}{50} \ mg \ of \ CaCO_3 \ equivalent \ hardness$

Total hardness of water sample = 611.11 ppm

Estimation of permanent hardness

50 ml of sample hard water consumes = 18 ml of EDTA

50 ml of sample hard water   = 18 x 1 ml of EDTA

50 ml of sample hard water $= 18 \times \frac{55}{45} \ mg \ of \ CaCO_3 \ equivalent \ hardness$

1000 ml of sample hard water $= 18 \times \frac{55}{45} \times \frac{1000}{50} \ mg \ of \ CaCO_3 \ equivalent \ hardness$

Permanent hardness of water sample = 440 ppm

Temporary hardness of water sample = Total hardness – Permanent hardness

$= 171.11$ ppm

3) Calculate permanent hardness from the following: 250 ml of a water sample is boiled for one hour. It is then cooled and filtered to remove precipitate. The filtrate is made upto

250 ml again with distilled water. 50 ml of this solution required 4 ml of N/50 EDTA with NH₄OH buffer and EBT indicator.

Solution:

We know that

1 ml of N/50 EDTA ≡ 1 mg of $CaCO_3$

4 ml of N/50 EDTA ≡ 4 mg of $CaCO_3$

50 ml of boiled off water sample consumes = 4 ml of EDTA ≡ 4 mg of $CaCO_3$

1000 ml of boiled off water sample = $\frac{4}{50}$ x 1000 = 80 ppm

Permanent hardness of water sample = 80 ppm.

4) 50 ml of sample water consumes 13 ml of 0.02 M EDTA before boiling and 8 ml of the same EDTA after boiling. Calculate the degree of total hardness, permanent and temporary hardness.

Solution:

Estimation of Total hardness

50 ml of sample hard water (before boiling) ≡ 13 ml of 0.02 M EDTA

(1 ml of 0.01 M EDTA ≡ 1 mg of $CaCO_3$)

1 ml of 0.02 M EDTA ≡ 2 mg of $CaCO_3$

13 ml of 0.02 M EDTA ≡ 13 x 2 mg of $CaCO_3$

50 ml of sample hard water (before boiling) = 13 x 2 mg of $CaCO_3$

1000 ml of sample hard water (before boiling) = $13 \times 2 \times \frac{1000}{50}$ $mg\ of\ CaCO_3$

Total hardness of water sample = 520 ppm.

Estimation of permanent hardness

50 ml of sample hard water (after boiling) ≡ 8 ml of 0.02 M EDTA

(1 ml of 0.01 M EDTA ≡ 1 mg of $CaCO_3$)

1 ml of 0.02 M EDTA ≡ 2 mg of $CaCO_3$

8 ml of 0.02 M EDTA ≡ 8 x 2 mg of $CaCO_3$

50 ml of sample hard water ((after boiling) = 8 x 2 mg of $CaCO_3$

1000 ml of sample hard water (after boiling) = $8 \times 2 \times \frac{1000}{50}$ $mg\ of\ CaCO_3$

Permanent hardness of water sample = 320 ppm.

Temporary hardness of water sample = 520 – 320 = 200 ppm.

2.9   ATOMIC ABSORPTION SPECTROMETRY (AAS)

Atomic Absorption Spectrometry is one of the most widely used methods for quantitative elemental analysis. There are a number of situations where elemental composition is important such as iron content in an ore sample, lead in drinking water, calcium in intracellular fluids etc. An obvious application of the determination of calcium and magnesium in water is testing for hardness in hard water.

Principle and Working

➢ Atomic absorption spectrometry is based on the absorption of light by free metallic atoms.

➢ Monochromatic light for a particular element (to be analyzed) is produced by means of a hollow cathode lamp. It is constructed of a metal cathode composed of the metal element to be analyzed and contained in a transparent tube filled with an inert gas.

➢ Calcium and magnesium are both determined with a combination hollow cathode lamp but iron requires a separate lamp and different operating wavelength.

➢ In AAS, a substance is vaporized and decomposed into gaseous atoms in a flame, furnace, or plasma. Concentrations of atoms are measured by absorption or emission of specific wavelengths of radiation.

➢ This monochromatic light is passed through a long flame into which the solution to be analyzed is aspirated.

➢ The heat energy dissociates the molecules and converts the components into atoms.

➢ These atoms absorb the particular wavelength of light as in the hollow cathode lamp.

➢ The amount of light absorbed varies directly with metal ion concentration in the flame.

➢ The transmitted light that is not absorbed reaches the monochromator and strikes the detector.

➢ The decrease in transmitted light is directly proportional to the measure of metal ion concentration in the solution.

Instrumentation

➢ A simple atomic absorption spectrophotometer consists of a source emitting radiation (Hollow cathode lamp), Flame and spray chamber, monochromator, detector (Photomultiplier) and Recorder (Figure 2.4).
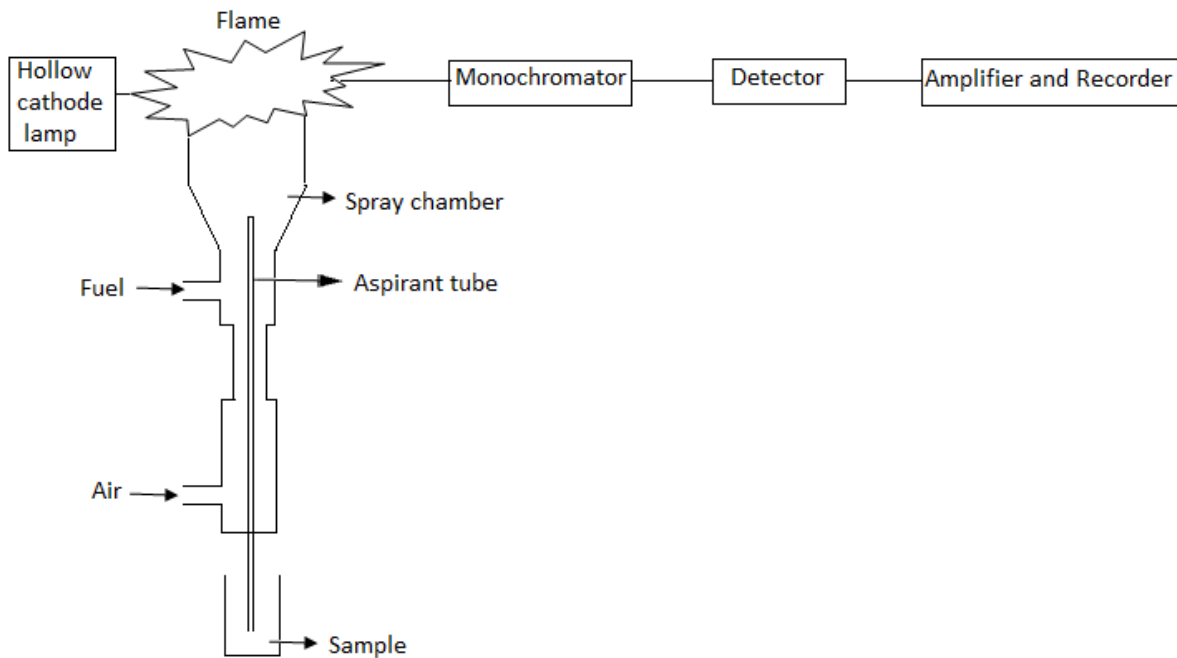
Figure 2.4   Atomic Absorption Spectrophotometer

Light source (Hollow Cathode Lamp)

➢ The hollow cathode lamp (electric discharge lamp) is widely used as light source in AAS.

➢ It is designed to emit the atomic spectrum of a particular element.

Flame

➢ For the vaporization of sample, the sample is sprayed into the burner system.

➢ The flame is produced using one of the gaseous mixture namely Air-acetylene (gives flame temperature of about 2400°K), air-propane (1900°K) and nitrous oxide-acetylene (2900°K).

Monochromator

➢ The monochromator is used to disperse several wavelengths of lights that are emitted from the light source to isolate a particular line of interest.

Detector and Amplifier

➢ The detector produces an electrical current that is dependent on the light intensity.

➢ This electrical current is amplified and processed to produce a signal.

➢ It is a measure of the light attenuation occurring in the sample cell. This signal is further processed to generate readout in concentration units.

Limitations

✓ The sample to be analyzed must be prepared in the form of solution.

✓ Individual source lamp and filters are needed for each element. This is because each and every metal has its own characteristic absorption.

Applications

✓ AAS is the most widely used technique for the quantitative determination of various metals at trace levels (0.1 to 100 ppm).

✓ AAS is extensively used in:

- Water analysis (e.g: Ca, Mg, Fe, Si, Al, Ba content).

- Analysis of animal feedstuffs (e.g: Mn, Fe, Cu, Cr, Se, Zn).

- Analysis of additives in lubricating oils and greases (Ba, Ca, Na, Li).

- Analysis of contaminated soils.

- Clinical analysis (blood samples: whole blood, plasma, serum; Ca, Mg, Li, Na, K, Fe).

2.9.1 Estimation of Calcium, Magnesium and Iron by Atomic Absorption Spectroscopy

Principle

➢ In AAS, the sample is first converted into an atomic vapour and then it is absorbed with a suitable hollow cathode lamp and measured at a selected wavelength which is the characteristic of each individual element.

➢ The measured absorbance is proportional to the concentration of the solution.

Preparation of Standard Stock Solution

➢ **Calcium stock solution:** Accurately weigh about 0.252g of dry primary standard calcium carbonate. Dissolve in a minimum amount of 6 M HCl then dilute to 100 mL in a standard flask with deionized water

➢ **Magnesium stock solution:** Accurately weigh out about 0.1g of dry magnesium oxide. Dissolve in a minimum amount of 6 M HCl then dilute to 1000-mL in standard flask with deionized water.

➢ **NaCl stock solution:** Accurately weigh about 0.510g of NaCl and make up to 200 mL in standard flask with deionized water.

➢ **Standard iron solution:** Accurately weigh out about 0.1g FAS and dissolve it with about 10 mL of 2 M H_2SO_4 and make up to 500 mL with deionized water.

Preparation of calcium/magnesium/iron Calibration Solutions

➢ Prepare a series of standard calcium and magnesium ion solution in the concentration range 3-12 ppm.

Preparation of Given Unknown Solution

➢ Transfer the given unknown solution into a 100 ml standard measuring flask.

➢ Dilute carefully to the mark with de-ionized water and mix thoroughly.

Procedure

➢ Switch on AAS and warm up for about 10 minutes.

➢ Appropriate hollow cathode lamp is chosen based on the analyte to de estimated.

➢ Fix the wavelength and then adjust the meter to zero absorbance or 100% transmittance.

➢ Now the standard solutions are aspirated (introduced) into the air-acetylene flame one by one.

➤ A part of the light from hollow cathode lamp is absorbed by the excited metal atoms, resulting in a proportionate decrease of the light intensity.

➤ The decrease of the light intensity is measured as absorbance.

➤ The absorbance values for different concentrations are used to construct the calibration curves.

➤ The unknown solution is also aspirated into the flame and the absorbance is measured as performed with standard solutions.

➤ With the help of calibration curve, the calcium and magnesium content of test solution is measured (Figure 2.5).
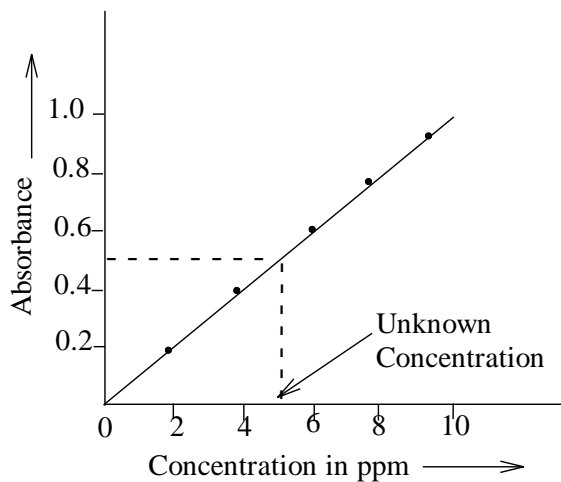
Figure 2.5   Absorbance versus Concentration

2.10   DISADVANTAGES OF HARD WATER IN DOMESTIC USE

1. Washing and bathing: Hard water does not lather with soap but forms sticky white precipitate of calcium and magnesium soaps. After complete removal of Ca^{2+} and Mg^{2+} ions from water sodium soap gives lather with water. This causes wastage of soap. Presence of iron produce yellowish red colour to fabrics.

2. Cooking: Presence of dissolved salts elevate boiling point of water thereby increasing fuel and time required for cooking. The dissolved salts deposit as scales on the inner walls of the utensils. Pulses and peas are not cooked soft in hard water.

3**. Drinking**: Hard water is not suitable for drinking purpose. The dissolved salts cause the formation of calcium oxalate crystals in urinary track. These crystals form stones in kidney and urinary tract.

2.10.1 SPECIFICATION OF WATER FOR INDUSTRIES

Industry	Requisites of water	Disadvantages/Troubles
Textile	i. Soft water	Hardness in water causes wastage of soap. It also affects dyeing of fabrics
	ii. Free from Fe and Mn salts	Causes stains on fabrics
Paper	i. Free from alkalinity	Alkaline water consume more alum thereby increasing cost of production
	ii. Free from Hardness	Ca and Mg salts increase ash content of Paper
	iii. Free from Fe and Mn salts	Affects brightness and colour of paper
Boiler feed water	i. Free from dissolved gases	Causes boiler corrosion
	ii. free from dissolved salts and silica	Causes scales and sludges
Laundry	i. Soft water	Hardness in water consumes lot of soap
	ii. Free from colour, Fe and Mn salts	Impart grey or yellow colour to fabric
Beverages	Should not be alkaline	Alkalinity neutralize the fruit acids an modifies the taste
Sugar industry	Free from sulphates, nitrates and alkali carbonates	Causes difficulties in crystallization of sugar

2.11 BOILER FEED WATER

The major use of water in industries is for steam generation in boilers. There are three types of boilers commonly used in industries.

1. Low pressure boilers (1.76×10^4 Kg m^{-2})
2. Medium pressure boilers (42.2×10^4 Kg m^{-2})
3. High pressure boilers (126.5×10^4 Kg m^{-2})

2.11.1 REQUISITES FOR BOILER FEED WATER:

The boiler feed water for steam generation should be free from

1. Dissolved salts like $CaSO_4$, $Ca(HCO_3)_2$, $MgSO_4$, Na_2CO_3 etc.
2. Dissolved gases like O_2, CO_2 and H_2S
3. Suspended impurities
4. Silica
5. Oil

2.11.2 BOILER TROUBLES

If the raw water containing the above impurities is directly fed into the boilers leads to the following boiler troubles

1. Formation of Scales and sludges

2. Boiler corrosion

3. Caustic embrittlement

4. Priming and foaming (carry over)

1. SCALES AND SLUDGES

When water is continuously converted into steam in boilers, there is increase in the concentration of dissolved salts. If the concentration reaches the saturation point, the salts separate out from solution in order of their decreasing solubility and the least soluble first. Adherent deposits formed are known as scales and soft slimy deposits formed are known as sludges.

Slugde is a soft, loose and slimy precipitate formed within the boiler which can be easily removed by a wire brush. Sludges are formed by $MgCO_3$, $MgSO_4$, $CaCl_2$, etc. These salts have higher solubility in hot water than in cold water thus are formed in comparatively colder regions of boiler where flow rate is slow and in bends.

Disadvantages of sludge formation:

1. Sludge is a poor conductor of heat so they waste a portion of heat generated.

2. Sludges settle in regions of poor water circulation like pipe connection, plug opening and clogs the pipes.

3. Sludges get entrapped in the scales and they both deposit as scales.

Prevention of sludge formation:

1. By using softened water

2. **Blow down operation:** During the blow down operation a portion of concentrated water containing dissolved impurities and suspended sludge is blown off and replaced with fresh water. This process is done periodically.

Scales are hard adherent deposits formed on inner walls of the boiler which are difficult to remove even with hammer and chisel. The principal scale formers are $CaCO_3$, $Ca(HCO_3)_2$, $CaSO_4$ and $MgCl_2$, $CaSiO_3$ and $MgSiO_3$

Types of scales

There two types of scales they are

    i.   **Soft scales:** $Mg(OH)_2$ obtained by hydrolysis of $MgCl_2$ at high temperature and $CaCO_3$ in low pressure boiler forms soft scales.

ii.   **Hard scales:** $CaSO_4$, calcium silicate and magnesium silicate in high pressure boilers forms hard scales.

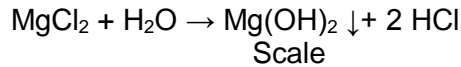**Formation of scales**

i. Calcium carbonate scale:

$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \downarrow$
                    Scale
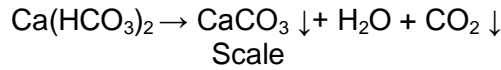
$CaCO_3$ forms hard scale in low pressure boilers. In high pressure boilers it forms water soluble calcium hydroxide.

$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2 \uparrow$
                    Soluble
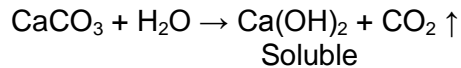
ii. Hydrolysis of $MgCl_2$

$MgCl_2$ undergoes hydrolysis at high temperature into $Mg(OH)_2$ which forms a soft scale.

$MgCl_2 + H_2O \rightarrow Mg(OH)_2 \downarrow + 2\ HCl$
                    Scale

iii. Deposition of $CaSO_4$

The solubility of $CaSO_4$ decreases with increase in temperature. Thus $CaSO_4$ is soluble in cold water but almost completely insoluble in super heated water. In high pressure boilers $CaSO_4$ precipitate as hard scale in the hotter regions. $CaSO_4$ is quite adherent and very difficult to remove even with hammer and chisel.

Temperature	$CaSO_4$ solubility
15ºC	3200 ppm
230 ºC	55 ppm
320 ºC	27 ppm

iv. Presence of silica

Small quantity of silica present in water at high temperature reacts with Ca^{2+} and Mg^{2+} ions and forms calcium silicate ($CaSiO_3$) and magnesium silicate ($MgSiO_3$). These are deposited as hard scale on the inner surface of the boiler.
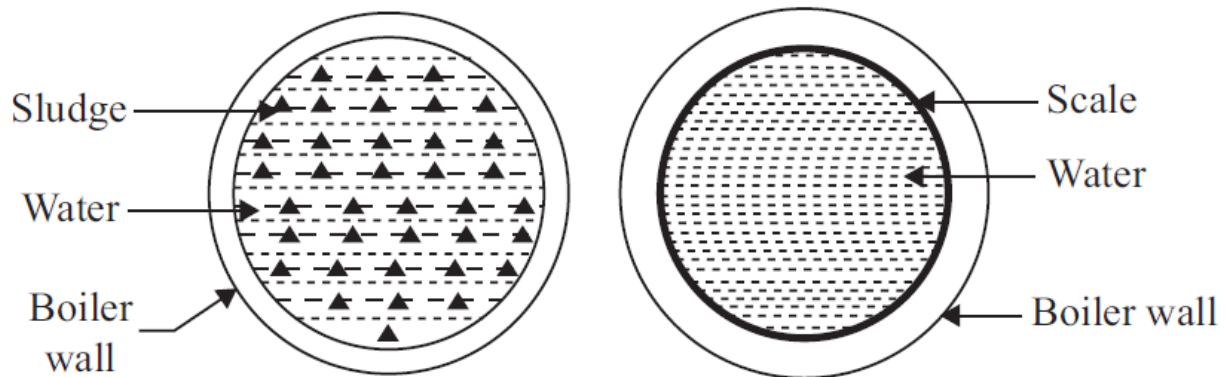
Figure 2.6   a) Sludge   b) Scale

Disadvantages of scale formation:

1. Scale has a low thermal conductivity, thus the heat supplied to boiler is not efficiently transferred to water. To maintain steady supply of steam over heating is done and thus fuel is wasted. The wastage of fuel depends on the thickness of scale. 10 % of fuel is wasted when the thickness of scale is 0.329 mm and it increases to 150 %, if the thickness of the scale increases to 12 mm.

2. The overheating of boiler done to maintain constant supply of steam leads to distortion of boiler parts which makes it unsafe in high pressure boilers.

3. Due to overheating uneven expansion of scales takes place. It leads to the formation of cracks in the scales. When water enters into the cracks and comes in contact with overheated boiler iron plate, it produces a large amount of steam suddenly. This creates a high pressure inside the boiler which may cause sudden explosion of the boiler.

4. Scales may deposit in tubes and valves of the boiler and choke them which decrease the efficiency of boiler.

Prevention of scale formation
Scale formation can be prevented by

1. **External treatment**
External treatment involves the removal of hardness causing calcium, magnesium salts and silica from water before feeding the boiler. The various external treatment methods are lime-soda process, zeolite process and demineralization process.

2. **Internal treatment**
Internal treatment is a corrective treatment which involves addition of chemicals directly to boiler water to remove the scale forming substance that are not removed by external treatment. The various internal treatment methods are

i. Phosphate conditioning: In high pressure boilers to avoid scale formation sodium phosphate is added to boiler water. This reacts with calcium and magnesium ions and forms soft sludge of

calcium phosphate and magnesium phosphate which can be easily removed by blow down operation.

$$3 \ CaCl_2 + 2 \ Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6 \ NaCl$$
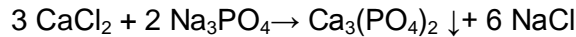
Commonly sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4) and trisodium phosphate (Na_3PO_4) are used for phosphate conditioning.

ii. Calgon conditioning: In this method the scale forming salts are converted into highly soluble complexes which are not precipitated during steam generation. Calgon {sodium hexa meta phosphate $Na_2[Na_4(PO_3)_6]$} added reacts with $CaSO_4$ to form highly soluble calcium hexa meta phosphate

$$Na_2[Na_4(PO_3)_6] \leftrightarrow 2 \ Na^+ + [Na_4(PO_3)_6]^{2-}$$

$$CaSO_4 + [Na_4(PO_3)_6]^{2-} \rightarrow [Ca_2(PO_3)_6]^{2-} + 2 \ Na_2SO_4$$
$$\text{Soluble complex}$$
$$\text{ion}$$
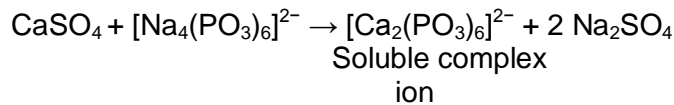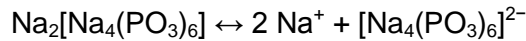
The other important internal treatments are colloidal conitioning, carbonate conditioning, complexometric method etc.

2. BOILER CORROSION

Boiler corrosion is the decay of boiler material by a chemical or electrochemical attack of its environment. It occurs due to the presence of dissolved gases like O_2, CO_2, H_2S and acids formed by the hydrolysis of salts like $MgCl_2$. The main reasons for boiler corrosion are;

1. **Dissolved oxygen:** Dissolved oxygen in water attacks boiler material at high temperature and high pressure and corrodes boiler.

$$2 \ Fe + H_2O + O_2 \rightarrow 2 \ Fe \ (OH)_2 \downarrow$$
(Boiler iron)

$$4 \ Fe(OH)_2 \downarrow + O_2 \rightarrow 2 \ [Fe_2O_3.2H_2O] \downarrow$$
$$\text{Rust}$$
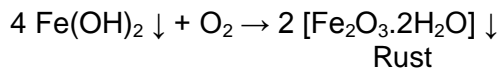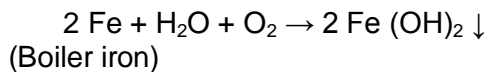
Prevention: Dissolved O_2 should be removed before put in use in boilers. This can be done by

i. By mechanical deaeration: The principle of mechanical deaeration is reducing the solubility of dissolved O_2 and expels it from water. The solubility of any gas is directly proportional to pressure and inversely proportion to temperature. In deaerator, water is sprayed in a tower containing perforated plates, heated from sides and connected to vacuum pump. This provides high temperature, low pressure and increased exposed area (Perforated plates) which decreases the dissolved O_2 in water.
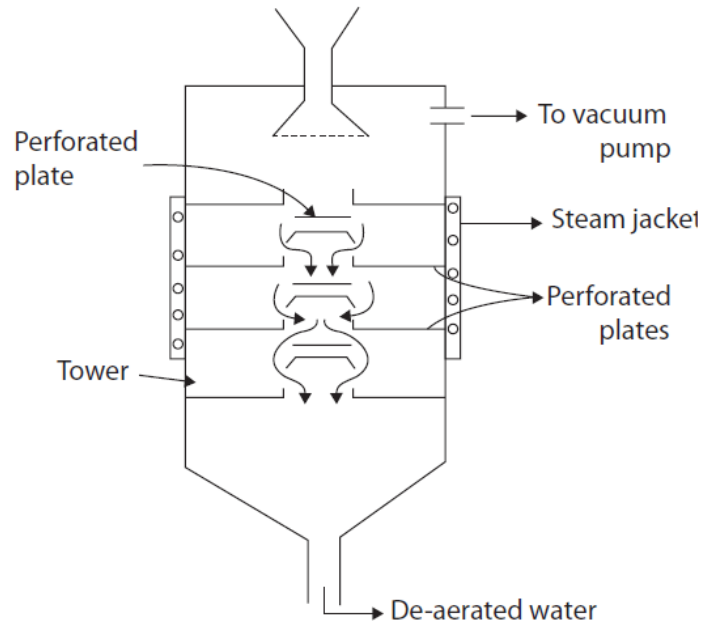
Figure 2.7 Mechanical deaerator

ii. Chemical treatment: For complete removal of dissolved O_2 a calculated quantity of sodium sulphite, sodium sulphide or hydrazine is added.

$Na_2SO_3 + \frac{1}{2} O_2 \rightarrow Na_2SO_4$

$Na_2S + 2 O_2 \rightarrow Na_2SO_4$

$N_2H_4 + O_2 \rightarrow N_2 + 2 H_2O$
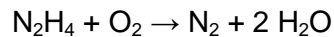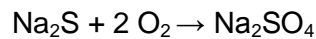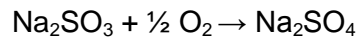
If the concentration of sodium sulphite exceeds 10 ppm it decomposes into SO_2 in high pressure boilers. The SO2 enters the steam pipes and condenses into H_2SO_3.

2. Dissolved CO_2: Dissolved CO_2 forms carbonic acid which has a slow corrosive effect on the boiler material. Water containing bicarbonates release CO_2 on heating which forms carbonic acid with water.

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$\text{(Carbonic acid)}$$

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + \{CO_2 + H_2O\}$$
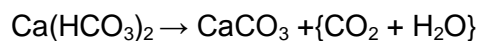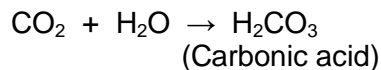
Prevention: Dissolved CO_2 is removed by

i. Chemical treatment: By adding a calculated quantity of ammonia

$$2 NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$
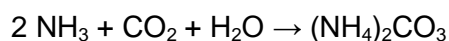
ii. CO_2 is removed by mechanical deaeration along with O_2.

3. Acids from Hydrolysis of salts:

Water containing dissolved magnesium chloride liberates HCl on hydrolysis

$$MgCl_2 + H_2O \rightarrow Mg(OH)_2 \downarrow + HCl$$
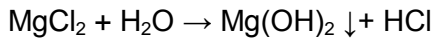
HCl formed reacts with boiler iron and produce HCl again and again in a chain reaction.

$$Fe + 2\ HCl \rightarrow FeCl_2 + H_2 \uparrow$$

$$FeCl_2 + 2\ H_2O \rightarrow Fe(OH)_2 + HCl$$
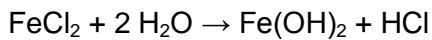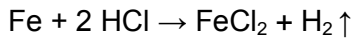
Thus even a small amount of $MgCl_2$ can cause corrosion of iron to a large extent.

Prevention: The HCl formed is neutralized with alkalies.

3. CAUSTIC EMBRITTLEMENT:

In high pressure boilers sodium carbonate is hydrolyzed to NaOH and CO_2. The NaOH containing water flows into hair line cracks in boiler parts due to capillary action. As the water evaporates the NaOH concentration increases and it dissolves the boiler iron and forms sodium ferroate. This leads to embrittlement of stressed parts of boiler like bends, rivets, and joints. Thus the pH of boiler feed water should not be highly alkaline.

Prevention: By adding tannin or lignin or sodium sulphate to boiler water which blocks the hair-cracks and prevent infiltration of NaOH.

4. PRIMING AND FOAMING (CARRY OVER):

Foaming is due presence of oil in water which forms persistent bubbles in boilers. These bubbles do not break easily thus actual height of water column cannot be judged properly.

Prevention: By using soft water and adding anti foaming chemicals like castor oil

Priming is the formation of wet steam. This is due to sudden increase in steam production and presence of large amount of dissolved salts. The carrying of water along with dissolved particles by steam is called wet steam.

Prevention: By using soft water, avoiding rapid change in steaming rate and maintaining low water level in boilers.

2.12 WATER SOFTENING

Water used for steam generation must be free from dissolved salts to minimize troubles like scale formation in boilers and industries such as textiles, laundries, paper, distilleries etc essentially require soft water. Thus water should be freed from the hardness producing salts before use. The process of removing of hardness producing salts from water is known as softening of water. There are three main methods used in industries for water softening. They are i) Lime-soda process, ii) Zeolite process and iii) Demineralization process.

2.12.1 LIME-SODA PROCESS:

The hardness causing Ca and Mg salts are converted into insoluble precipitate by calculated amounts of lime $Ca(OH)_2$ and soda Na_2CO_3 and the precipitate formed is filtered.

2.12.2 ZEOLITE or PERMUTIT PROCESS:

Zeolites are crystalline microporous aluminosilicates built up of three dimensional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked by sharing of oxygen atoms. . The linking of these tetrahedra results in pores of the zeolite which permits the movement of water molecules and ions. Zeolite contains weakly bonded (readily exchangeable) cations (Na^+) in pores of the structure. They are capable of exchanging reversibly its Na^+ ions for hardness causing Ca^{2+} and Mg^{2+} ions in hard water. The cation exchange capacity (CEC) is a measure of number of cations per unit weight available for exchange which depends on the Al content (i.e. more Na^+ needed to balance the charge). Zeolites are of two types;

i)   Natural zeolites are non-porous. Example: Natrolite $Na_2O.Al_2O_3.4SiO_2.2H_2O$

ii)   Synthetic zeolites are porous and possess gel structure. They are synthesized by heating together china clay, feldspar and soda ash. They possess higher exchange capacity per unit weight than natural zeolites.
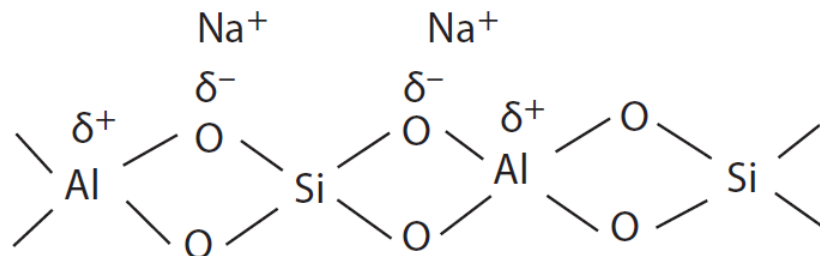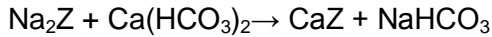

Figure 2.8 Structure of zeolite

Principle:

Sodium zeolite is hydrated sodium aluminosilicate having general formula $Na_2O.Al_2O_3.xSiO_2.yH_2O$ where x=2-10 and y=2-6. Sodium zeolite is represented as Na_2Z where Z stands for insoluble zeolite framework. They are capable of exchanging reversibly its Na^+ ions for hardness causing Ca^{2+} and Mg^{2+} ions in hard water.
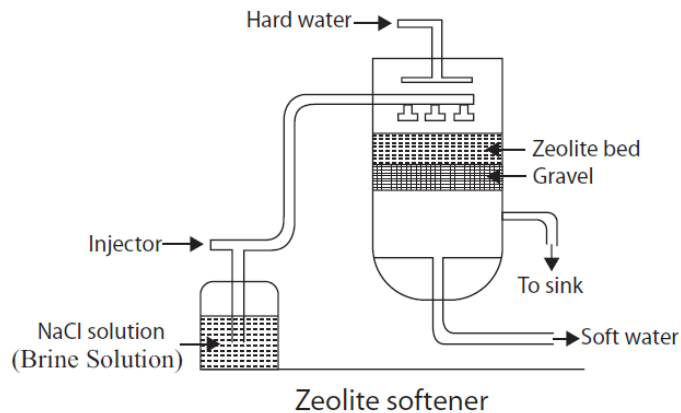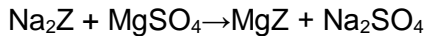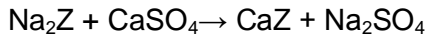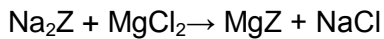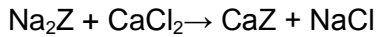

Figure 2.9   Zeolite softener

Softening process: When hard water is passed through the bed of zeolite, the hardness causing Ca^{2+} and Mg^{2+} ions are retained in the zeolite bed as CaZ and MgZ and an equivalent amount of Na^+ ions are released in the outgoing water. The exchange reactions taking place during the softening process are

Removal of Carbonate hardness

$Na_2Z + Ca(HCO_3)_2 \rightarrow CaZ + NaHCO_3$

$Na_2Z + Mg(HCO_3)_2 \rightarrow MgZ + NaHCO_3$
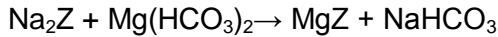
Removal of Non-carbonate hardness

$Na_2Z + CaCl_2 \rightarrow CaZ + NaCl$

$Na_2Z + MgCl_2 \rightarrow MgZ + NaCl$

$Na_2Z + CaSO_4 \rightarrow CaZ + Na_2SO_4$

$Na_2Z + MgSO_4 \rightarrow MgZ + Na_2SO_4$

Regeneration process: When the zeolite is completely exhausted it loses its exchange capacity and thus has to be regenerated. This is indicated by an increase in hardness of the softened water obtained. The exhausted zeolite is regenerated by treating with 10% brine (NaCl) solution and reused. The washing containing $CaCl_2$ and $MgCl_2$ are led to drain.

$CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$

$MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$
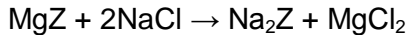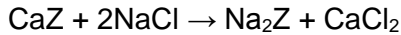
Advantages of zeolite process

1. Water softened by zeolite process has residual hardness of 10 ppm.

2. Equipment is compact and requires less time for softening.

3. Process does not involve any precipitate or sludge.

4. Requires less skill for maintenance and operation.

Disadvantages of zeolite process:

1. Water softened contains large amount of sodium salts which is not suitable for boilers as it leads to boiler corrosion.

2. Turbid water cannot be treated. Turbidity clogs the pores of zeolite and the rate of flow decreases. Thus turbidity of water should be removed by coagulation and filtration before subjecting to softening.

3. It is a base exchange process and therefore anions (CO^{3-}, SO_4^{2-}, Cl^-, etc.) are not removed by zeolite process.

4. Brackish water (salt water containing NaCl) cannot be treated by this method.

5. If water contains Fe and Mn salts they form irreversible iron and manganese zeolite which cannot be easily regenerated.

2.12.3 DEMINERALIZATION PROCESS or ION EXCHANGE PROCESS:

Demineralization process is an ion exchange process in which porous, insoluble, cross linked long chain high molecular weight synthetic resins are used as ion exchangers. The functional groups attached to the polymers are responsible for Ion exchange property. Resins containing acidic groups are capable of exchanging their H+ ions with cations in water where as those containing basic groups are capable of exchanging their OH- ions with anions in water. The organic ion exchange resins are:

Cation exchange resin: These are cross linked styrene - divinyl benzene copolymers containing sulphonic acid group (SO_3H) or carboxylic acid group (COOH) which is capable of exchanging reversibly its H^+ ions for cations in water. It is represented as RH^+.

Anion exchange resin: These are cross linked styrene - divinyl benzene copolymers containing amino, substituted amino or quaternary ammonium group as integral part of resin. This copolymer on treatment with dilute NaOH becomes capable of exchanging reversibly its OH^- ions for anions in water. It is represented as $R'OH^-$
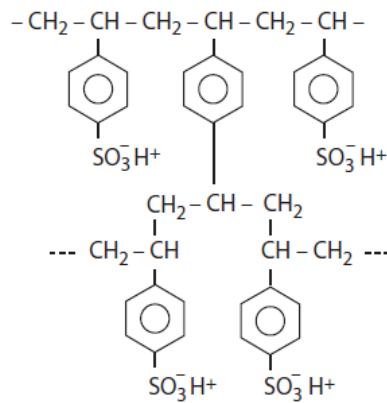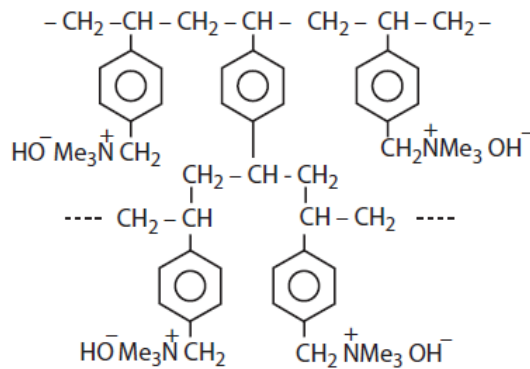

Figure 2.10a Structure of Cation exchange resin

Figure 2.10b Structure of Anion exchange resin

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Softening Process

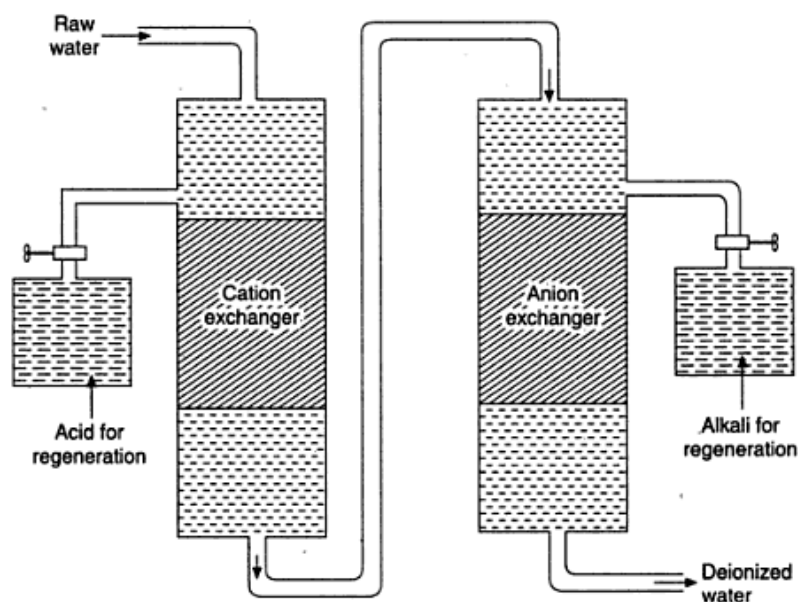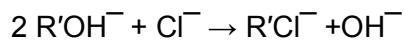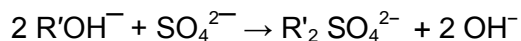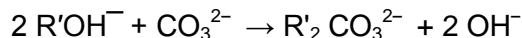The cation and anion exchange resins are kept in two vertical exchangers.

**Figure 2.11   Demineralization cation and anion exchanger**

Cation exchange reaction: : Hard water is first percolated through cation exchange resin where the cations are retained in the resin and an equivalent amount of H^+ ions are released in the outgoing water.

$2\ RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$

$2\ RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$

$RH^+ + Na^+ \rightarrow RNa^+ + H^+$
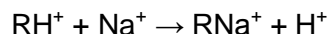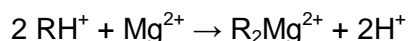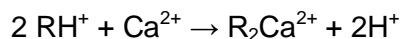
Anion exchange reaction: The water from cation exchange resin is passed through anion exchange resin which retains the anions and releases an equivalent amount of OH^- ions in the water.

$2\ R'OH^- + CO_3^{2-} \rightarrow R'_2\ CO_3^{2-} + 2\ OH^-$

$2\ R'OH^- + SO_4^{2-} \rightarrow R'_2\ SO_4^{2-} + 2\ OH^-$

$2\ R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-$

H^+ and OH^- ions from cation exchange and anion exchange resins combine to form deionized water which is free from cations and anions.

$H^+ + OH^- \rightarrow H_2O$
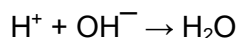
The order of exchange process should not be interchanged as water coming out from cation exchange resin is acidic which does not affect the anion exchange resin. Whereas when the order is changed the water coming from the anion exchange resin is alkaline this harms the cation exchange resin in the subsequent step.

Regeneration Process: When the resin is completely exhausted it loses its ion exchange capacity and are regenerated and reused.

Cation exchange resin: The exhausted cation exchange resins are regenerated by passing dilute HCl or H_2SO_4.
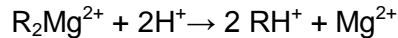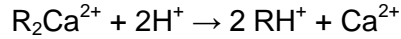
$R_2Ca^{2+} + 2H^+ \rightarrow 2\ RH^+ + Ca^{2+}$
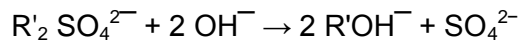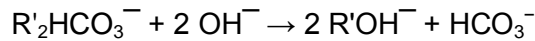
$R_2Mg^{2+} + 2H^+ \rightarrow 2\ RH^+ + Mg^{2+}$

Anion exchange resin: The exhausted cation exchange resins are regenerated by passing dilute NaOH.

$R'_2HCO_3^- + 2\ OH^- \rightarrow 2\ R'OH^- + HCO_3^-$

$R'_2\ SO_4^{2-} + 2\ OH^- \rightarrow 2\ R'OH^- + SO_4^{2-}$

Advantages of Demineralisation process

1. Water obtained from demineralisation process contain residual hardness of 2ppm. This can be used in high pressure boilers.
2. Acidic and alkaline waters can be softened by this method.

Disadvantages of Demineralisation process

1. The cost of equipment and resins are expensive.
2. Fe and Mn containing water cannot be treated by this method as they are irreversibly exchanged.
3. Turbid water cannot be treated as they reduce the efficency of the process.

Mixed-bed deionizer

This consists a mixture of cation and anion exchange resins in the same cylinder. Water passing through this bed comes in contact with the two type of exchangers alternatively which is equivalent to passing water through a series of several cations and anions exchangers. The outgoing water contains less than 1ppm of dissolved solids.

Regeneration

When the resins are exhausted the mixed bed is washed by forcing water in the upward direction. The light anion resin moves to the upper layer and heavier anion resin moves to the bottom layer. The anion resin is regenerated by dilute NaOH from the top. The lower cation resin is regenerated by dilute H_2SO_4. The two resins are mixed again by forcing compressed air.
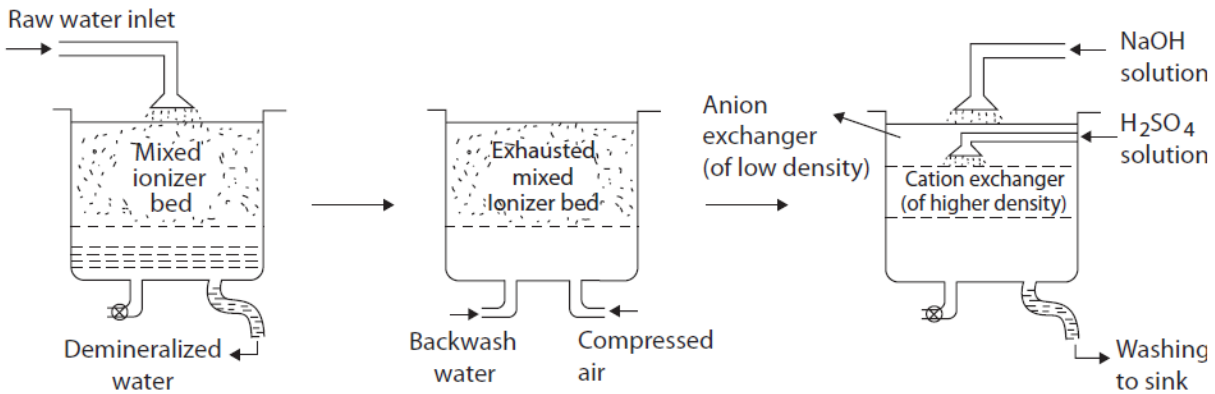
Figure 2.12 Mixed bed deionizer

2.13 DESALINATION

The process of removal of dissolved solids (mainly NaCl) from sea water or brackish water is known as **desalination.**

This is done by two ways

1. Separation of water from brackish water
   Methods: Reverse osmosis, distillation, evaporation, freezing.
2. Separation of salt from brackish water
   Methods: Electrodialysis

2.13.1 OSMOSIS

Osmosis is a natural process. When two liquids of different concentration are separated by a semi-permeable membrane, the solvent has a tendency to move from lower to higher solute concentration for chemical potential equilibrium. This phenomenon is known as **Osmosis.** The driving force for osmosis is called as osmotic pressure.
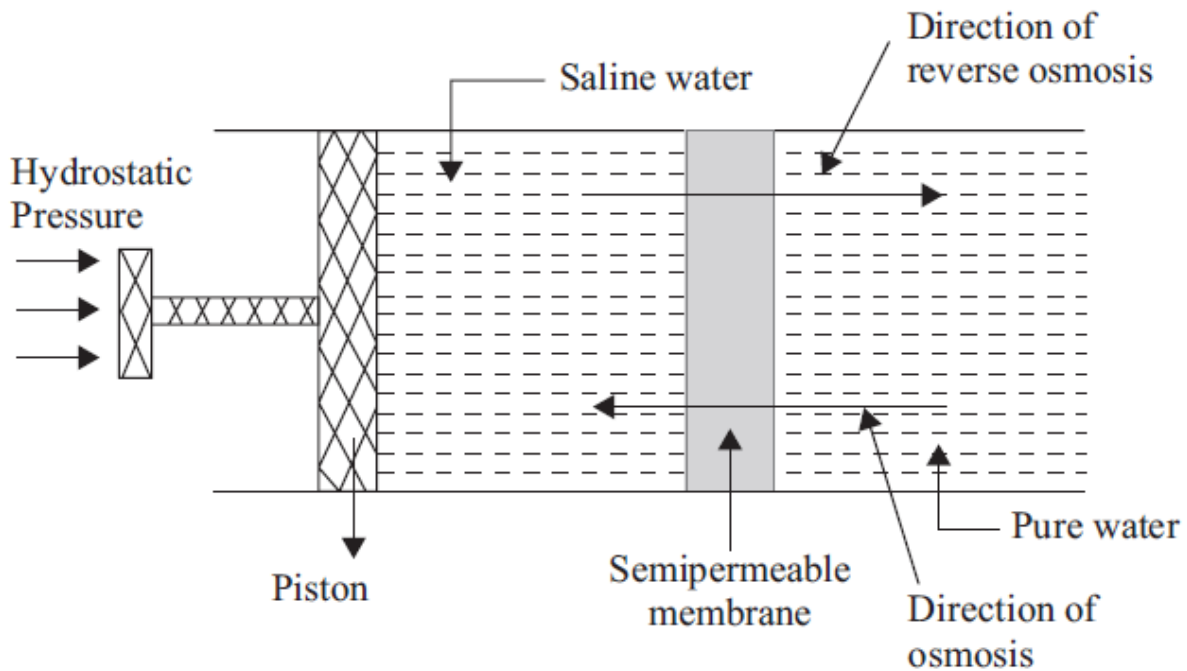
Figure 2.13 Reverse osmosis process

2.13.2 REVERSE OSMOSIS

Reverse osmosis is the process of forcing a solvent from a region of higher solute concentration to a region of lower solute concentration through a semi-permeable membrane by applying a hydrostatic pressure in excess of the osmotic pressure on higher concentration side. The semi-permeable membrane used for reverse osmosis has a dense layer in the polymer matrix containing cellulose acetate, methyl acrylate or polyamides etc.

The largest and most important application of reverse osmosis is the separation of pure water from seawater and brackish water. This process requires a high pressure to be exerted on the higher concentration side of the membrane, usually 2–17 bars for fresh and brackish water and 40–82 bar for seawater. The thickness of the cellulose acetate membrane should be of 100 to 150 microns to withstand the pressure applied. The hydrostatic pressure is applied on the seawater or brackish water side to force the pure water out through the semi-permeable membrane leaving behind the ionic and non ionic dissolved solids. Thus potable drinking water emerges out from the pure water side.

Advantages

1. The life of the membrane is high and it can be replaced with in few minutes.
2. It removes ionic as well as non –ionic and colloidal impurities.
3. Due to low capital cost and simplicity, it is highly reliable for converting seawater to fresh water.

Disadvantages

1. Reverse osmosis is a costlier process since the rigid plastic membranes are expensive.
2. Thin plastic membrane cannot withstand very high pressure therefore it has to be replaced frequently.
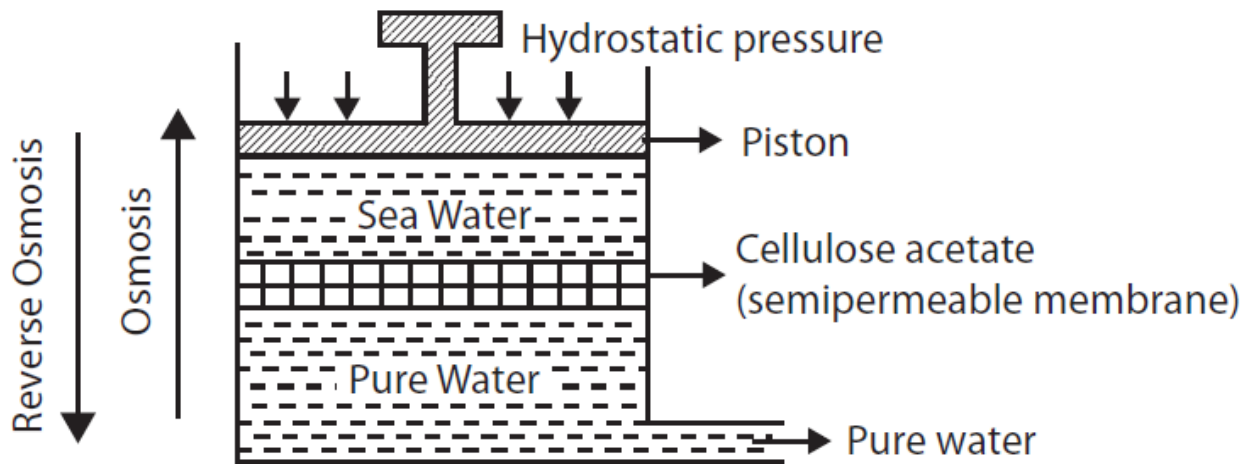3. Frequent fouling of membrane occurs due to the deposition of impurities.

Figure 2.14 Direction of flow of Osmosis and Reverse osmosis

2.13.3 ELECTRODIALYSIS

Definition: *Electrodialysis* is a desalination method used to transport ions from salt solution through ion-selective membranes to another solution in an applied electric field.

Principle: Electrodialysis is related to the principle of electrolysis. In this process the ions in salt water are attracted to opposite electrodes in an applied electric field. The electrical potential acts as the driving force for the movement of ions. When an electric field is applied to saline water, cations such as Na^+, Ca^{2+}, Mg^{2+} moves towards cathode and anions such as Cl^-, SO_4^{2-} moves towards anode through ion-selective membranes. Subsequently the concentration of saline water decreases in the middle compartments and that of the adjacent compartments increases.

Ion-selective membrane: The ion-selective membrane allows either cations or anions to pass through it and not both simultaneously. Thus cation selective membrane (C) is permeable only to cations and not anions whereas anion selective membrane (A) is permeable to anions but not cations. These membranes are made of polystyrene backbone with charged groups. Sulphonated polystyrene is an example for cation selective membrane and polystyrene with quaternary ammonium group is an example for anion selective membrane.

Description and working: An electrodialysis unit consists of a series of compartments made of anion selective and cation selective membranes alternating each other. The outermost

compartments are connected to charged electrodes. Care should be taken to connect (C) to cathode and (A) to anode. All the compartments are filled with saline water and an electric field is applied perpendicular to the direction of flow of saline water. Now cations move towards cathode and anions move towards anode through the membranes. From compartments 2, 4 and 6 the cations pass through cation selective membrane and anions pass through anion selective membrane to the adjacent compartments. Thus in compartments 1, 3, 5 and 7 the concentration of salt increases (brine) whereas in compartments 2,4 and 6 pure water is obtained. The concentrated brine and pure water are collected from the outlets.

Advantages

1. Electrodialysis unit is compact.
2. If electricity is easily available the process can be extended to sea water.
3. The cost of installation is economical.

Disadvantages

1. Electrodialysis process is costly.

Applications

1. Electrodialysis is used in the brackish water and sea water desalination.
2. It finds applications in waste water reduction or recovery.
3. It is also very useful to reduce salt contents of process streams with high amounts of salts.
4. It is used in salt production.
5. This method is effective for small and medium scale drinking water production.

Electrodialysis Unit

A - Anion selective membrane
B - Cation selective membrane
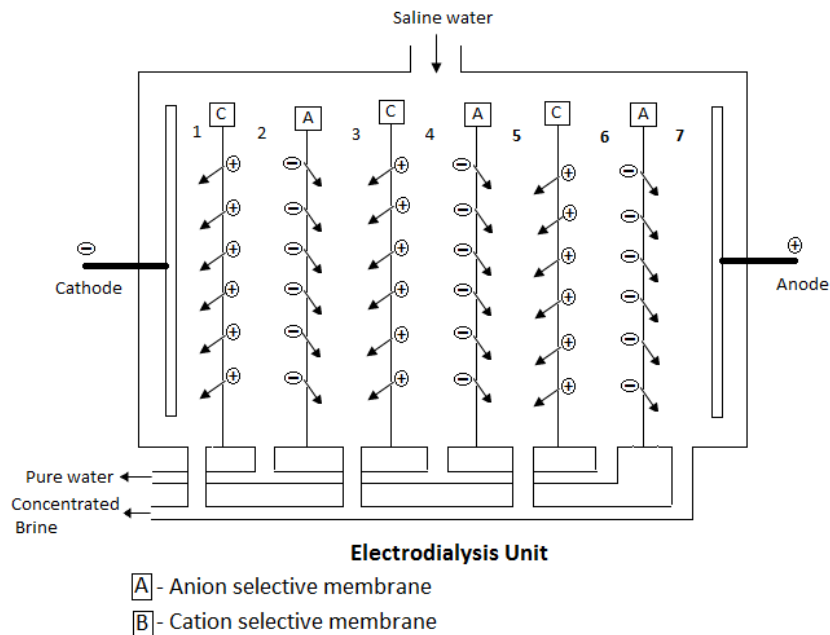
Figure 2.15 Electrodialysis Unit

2.14   PURIFICATION OF WATER FOR DOMESTIC SUPPLY

2.14.1 REQUIREMENTS OF DRINKING WATER

The essential requirements for potable or drinking water are

1. It should be clear, odourless and pleasant in taste.
2. It should be free from dissolved gases like H_2S and minerals such as lead, arsenic, chromium and manganese salts.
3. It should be free from pathogenic microorganisms.
4. pH of water should be 7 - 8.5
5. Total hardness of water should be less than 125 ppm.
6. Total dissolved solids in water should be less than 500 ppm.
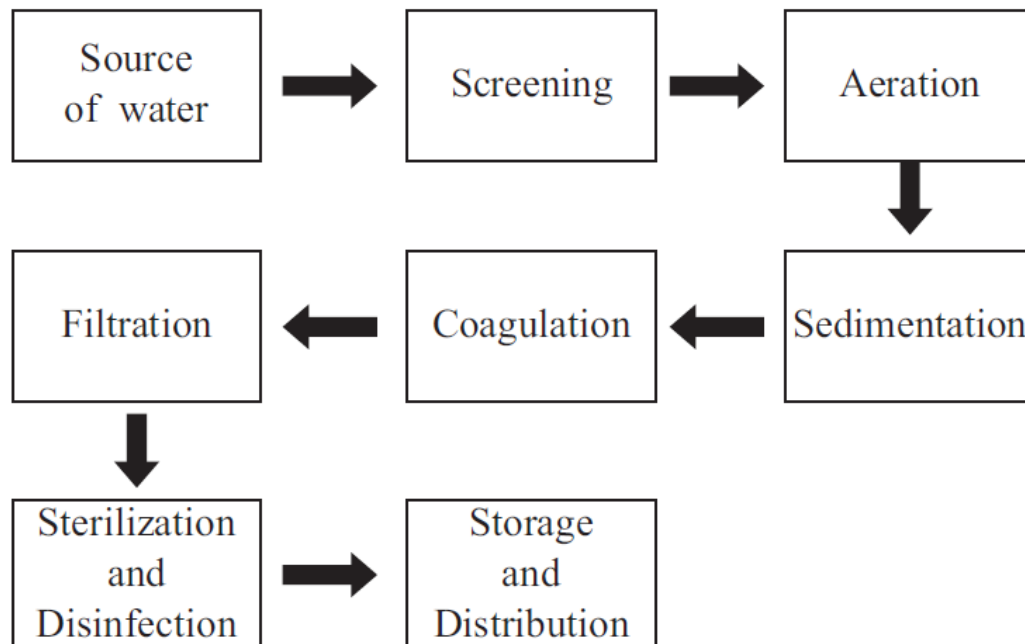
Figure 2.16 Flow chart for stages involved in treatment of water for domestic supply

The various stages in the treatment of water can be indicated as in the flow chart

1. Source of water
2. Screening
3. Aeration
4. Sedimentation
5. Filtration
6. Sterilization and Disinfection
7. Storage and Distribution

Source of water

Municipalities receive water from various sources such as rivers, lakes and canals etc.,

Screening

The raw water is passed through screens having large number of holes or pores which retain the floating materials like wood, metal pieces, plastics etc.

Aeration

Process of mixing the atmospheric (fresh) air with screened water

- To increase the oxygen content in water
- To expel the harmful gases like H_2S, CO_2 etc.
- To oxidize Fe^{2+} and Mn^{2+} ions into their hydroxides (precipitate)

Sedimentation

The process of allowing water to stand without any disturbance for about 2 - 6 hours is known as sedimentation. Most of the suspended (Coarse like) particles settle down at the bottom of the tank due to the force of gravity.

Sedimentation with Coagulation

It is the process of removing finely divided suspended and colloidal impurities by the addition of required amount of chemicals (coagulants) to water before sedimentation.

Due to the mutual repulsion of the negatively charged colloidal particles in water, they do not combine to form larger particles to settle down. By adding coagulants like alum or ferrous sulphate provide highly positively charged Al^{3+} or Fe^{3+} ions which neutralize the negatively charged colloidal clay particles. After losing their charge, the tiny clay particles come nearer to one another and combine to form a bigger floc and settle down under the force of gravity. The coagulants used in water treatment plants depend upon the nature of raw water to be treated.

If the water is **slightly alkaline (pH = 7-9)**

Alum is used in water treatment plants

$$Al_2(SO_4)_3 + 3\ Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2$$
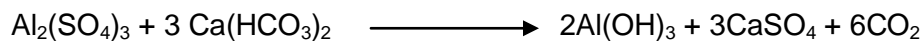
If the water is **slightly acidic (pH < 7)**

Sodium aluminate is used in water treatment plants

$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

The sodium hydroxide so produced, precipitates magnesium salts as $Mg(OH)_2$

$$MgSO_4 + NaOH \longrightarrow Mg(OH)_2 + Na_2SO_4$$

If the water is **highly alkaline**

Ferrous sulphate is used in water treatment plants

$FeSO_4 +Mg(HCO_3)_2 \longrightarrow Fe(OH)_2 +MgCO_3 + CO_2 +H_2O$

$4Fe(OH)_2 +O_2 + 2H_2O \longrightarrow 4 Fe(OH)_3$

$Al(OH)_3$ & $Fe(OH)_3$ forms heavy floc with colloidal particles which causes quick sedimentation.

Filtration

Process of removing colloidal matter and bacteria by passing water through a bed of fine sand, coarse sand and gravel. Filtration is carried out using a sand filter.

Operation of sand filter

A sand filter consists of a thick top layer of fine sand placed over coarse sand and gravels. It is provided with an inlet for water and an under drain channel at the bottom for exit of filtered water. The sedimented water is uniformly distributed over the fine sand bed. After some time, the rate of filtration becomes slow due to clogging of the pores of filter bed by the impurities. At this stage, filtration is stopped and about 2 – 3 cm of the top fine sand layer is scrapped off and replaced with clean fresh sand and the filter is put back into use again. The scrapped sand is washed with water, dried and stored for reuse.
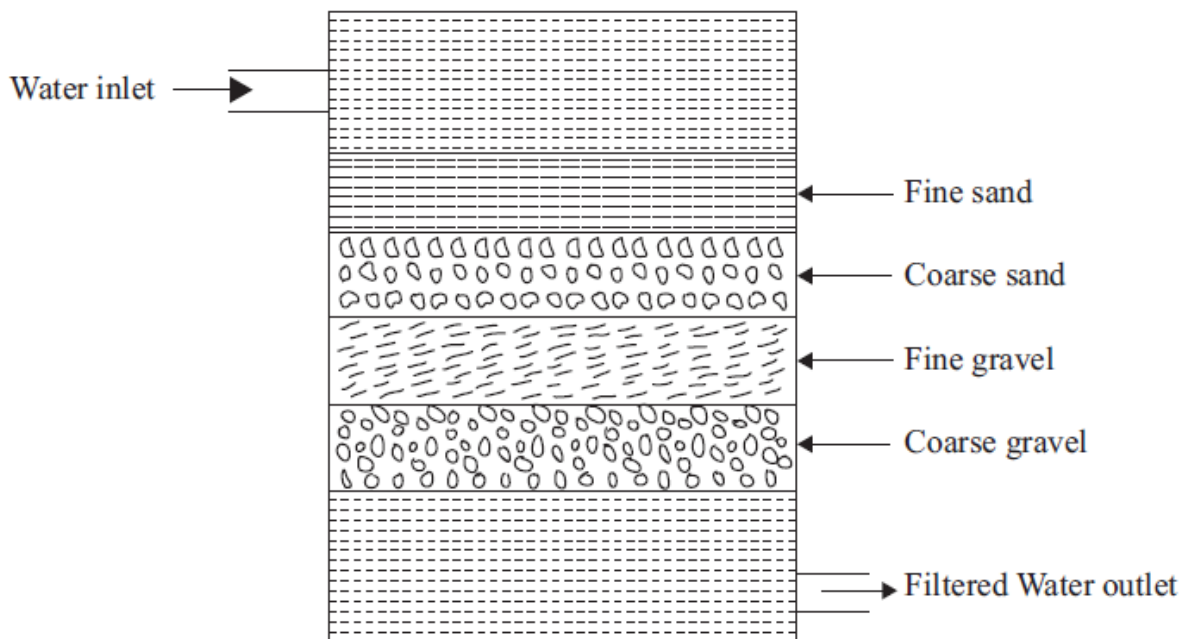
Diagram: Slow sand filter

Figure 2.17 Slow sand filter

Removal of microorganisms

Water used particularly for drinking must be free from disease producing bacteria. The process of destroying or killing of disease producing microorganisms from the water and making it safe for drinking is known as **Disinfection.** The chemical or substances which are used for killing the pathogenic microorganisms are known as **Disinfectant.**

The disinfection of water can be carried out by following methods.

1. Disinfection by boiling:

By boiling water for 10-15 minutes, all the disease producing bacteria are killed and make water safe for drinking.

Drawback:

- This process kills bacteria only at the time of boiling, but does not provide any protection against future possible contaminations.
- Very costly, impossible for large treatment of plant
- Boiling changes taste of water

2. Disinfection by chlorination

The process of adding calculated amount of chlorine to water to kill the bacteria and to make the water safe for drinking is known as **Chlorination.**
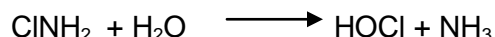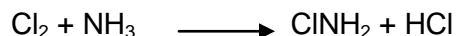
By adding bleaching powder:

It is a compound of chlorine and contains about 30% chlorine. When it dissolves in water it liberates chlorine gas. This liberated chlorine in turn dissolves in water to form hypochlorous acid (powerful germicide).

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$HOCl + Bacteria \longrightarrow Bacteria\ are\ killed$$

By adding chloramines:

When chlorine and ammonia are mixed in the ratio 2:1 by volume, chloramine is formed. They produce hypochlorous acid in water which acts as a powerful germicide.
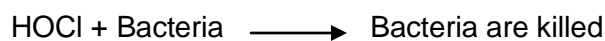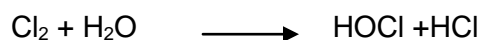
$$Cl_2 + NH_3 \longrightarrow ClNH_2 + HCl$$

$$ClNH_2 + H_2O \longrightarrow HOCl + NH_3$$

$$HOCl + Bacteria \longrightarrow Bacteria\ are\ killed$$

Advantages:

- Its excess does not produce any irritating odour.
- It imparts a good taste to treated water.

By adding Liquid chlorine:

Liquid chlorine produces hypochlorous acid which is a powerful germicide kills the bacteria.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$HOCl + Bacteria \longrightarrow Bacteria\ are\ killed$$

The hypochlorous acid formed inactivates the enzyme in the cell wall and kills the microorganisms.

Break point chlorination:

It involves addition of sufficient amount of chlorine to water to oxidize i) organic matter, ii) reducing substances and iii) free ammonia leaving behind free chlorine for disinfecting disease producing bacteria.When chlorine is passed, it first kills the bacteria. Further addition of chlorine will appear as residual chlorine due to the formation of chloro compounds. After a certain point, the residual chlorine suddenly decreases with the evolution of bad smell and objectionable taste. This indicates that chlorine is being used for oxidizing or destroying the organic impurities or ammonia. The sudden increase in residual chlorine indicates the completion of oxidation of impurities. The point at which both the demands are satisfied and residual chlorine increases is called break point. Beyond the break point, chlorine gets accumulated. The process of adding chlorine beyond the break point is called break point chlorination. The residual chlorine in water should not exceed 0.4 ppm.
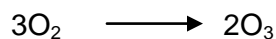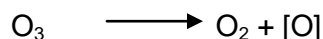
Diagram:
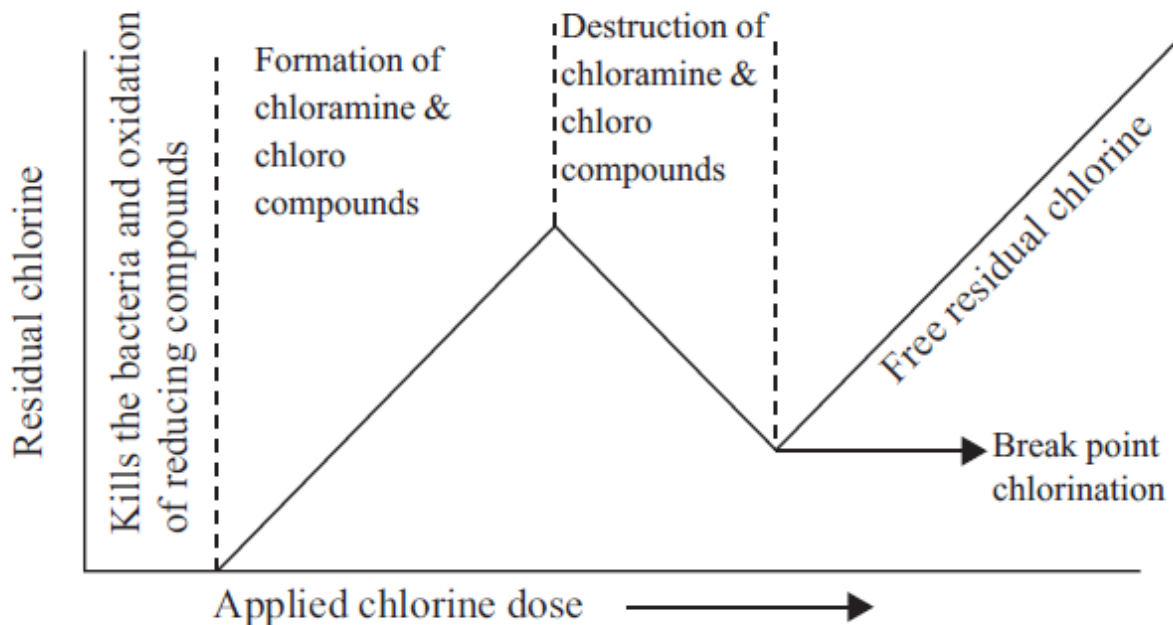
Figure 2.18 Break point chlorination

Disinfection by Ozone:

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

$$3O_2 \longrightarrow 2O_3$$

Ozone is highly unstable and breaks down, liberating nascent oxygen

$$O_3 \longrightarrow O_2 + [O]$$

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The nascent oxygen is very powerful oxidizing agent and kills the bacteria as well as oxidizes the organic matter present in water.

Process:

Ozone is released into the water and the two are allowed to come in contact in a sterilizing tank. The disinfected water is removed from the top. The contact period is about 10-15 minutes and the usual dose strength is 2-3ppm

Disadvantage:

- Quite expensive, impossible for large treatment plant

Advantage:

- Removes color and odour without giving any residue.
- Its excess is not harmful, since it is unstable and decomposes into oxygen.

UV treatment:

Ultraviolet rays are powerful disinfectants. They are produced by passing electric current through mercury vapor lamp. When water is allowed to flow in thin layer, UV rays from the lamp destroys bacteria completely.

Disadvantage:

- Quite expensive
- Ineffective when turbidity is greater than 15 ppm.

EXERCISES

1) Calculate temporary and permanent hardness in terms of $CaCO_3$ for a water sample containing the following. i) $CaCl_2$ = 11.1 mg/L   ii) $MgSO_4$ = 12 mg/L   iii) $MgCl_2$ = 9.5 mg/L v) NaCl = 60 mg/L

2) Calculate carbonate and non carbonate hardness in terms of $CaCO_3$ for a water sample containing the following. i) $Ca(HCO_3)_2$ = 252 mg/L   ii) $Mg(HCO_3)_2$ = 200 mg/L   iii) $MgCl_2$ = 30 mg/L   iv) $CaSO_4$ = 76 mg/L.

3) A water sample contains 29 mg/L of $CaSO_4$. Calculate the hardness caused in terms of $CaCO_3$ equivalents.

4) 2 g of $CaCO_3$ was dissolved in 500 ml of distilled water. 20 ml of this solution consumed 12 ml of EDTA. 20 ml of hard water sample consumed 6 ml of EDTA. 20 ml of the same hard water sample after boiling and filtering consumed 2 ml of EDTA. Calculate the total, permanent and temporary hardness of the given water sample.

5) 0.25 g of $CaCO_3$ was dissolved in 250 ml of distilled water. 25 ml of this solution consumed 16 ml of EDTA. 25 ml of hard water sample consumed 9 ml of EDTA. 25 ml of the same hard water sample after boiling and filtering consumed 4 ml of EDTA. Calculate the carbonate and non carbonate hardness of the given water sample.

6) 50 ml of sample of hard water consumed 15 ml of 0.03 M EDTA. Calculate the hardness of the water sample.

PART-A QUESTIONS
1. Define hardness of water.
2. Give a chemical test to detect hardness in water.
3. Distinguish between carbonate and non carbonate hardness.
4. How is hardness expressed?
5. Establish the relationship between ppm and mg/L.
6. What are teratogens?
7. Mention different methods of removal of pollutants from water.
8. What are the requistes of boiler feed water?
9. Differentiate between scale and sludge.
10. What is sodium zeolite? Give its significance.
11. How are resins regenerated in demineralization process.
12. Distinguish soft water and deionised water.
13. Define reverse osmosis.
14. Define Electrodialysis.
15. Mention the advantages and disadvantages of electrodialysis.
16. Write any two disadvantages of hard water in domestic use.
17. What are the units of hardness?
18. How is boiler corrosion prevented by mechanical deaeration method?
19. Give any four requirements of potable water?
20. Mention the various steps involved in domestic water treatment.
21. Write the advantages and disadvantages of reverse osmosis.
22. Why is water softened before using in boilers? Or what are troubles caused by using raw water without softening.
23. Write the advantages and disadvantages of zeolite process.
24. Write the advantages and disadvantages of demineralization process.
25. Why zeolite processs process cannot be used for softening brackish water.
26. What is break point chlorination?
27. Distinguish hard water and soft water.
28. What are disinfectants? Give examples.
29. What are coagulants? Give examples.
30. Why turbid water cannot be treated by zeolite process?
31. Softened water obtained from zeolite process is not suitable for boilers.Give reason.
32. How are scale formation prevented in boilers?
33. What is blow down operation?
34. Mention the disadvantages of scale formation in boilers.
35. In demineralisation process water is first passed through cation exchange resin followed by anion exchange resin. Justify.

PART B QUESTIONS.
1. How is total hardness of water estimated by EDTA method?
2. Explain the estimation of iron, calcium and magnesium by AAS method.
3. Describe the principle and instrumentation of atomic absorption spectrometry.
4. Describe the demineralization process of water softening with a neat labelled diagram.
5. What is sodium zeolite? Explain the water softening by zeolite process.

6. Write short notes on reverse osmosis.
7. Explain the principle and working of Electrodialysis unit.
8. Discuss the source, biochemical effects and removal of mercury from water.
9. Write notes on the contamination of water by arsenic and fluoride.
10. Briefly explain the source, adverse effects and removal of lead poisoning.
11. Explain the various steps involved in the domestic water treatment.
12. Explain the causes and prevention of boiler corrosion.
13. Briefly explain the causes disadvantages and prevention of scales and sludges.
14. Compare zeolite process and demineralizaion process.
15. Write short notes on impurities in water.
16. Write short notes on specifications and disadvantages of hard water for industries.

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