

2.1 INTRODUCTION

Water plays a vital role in our life. It is most abundant, wonderful and useful solvent. Although it is the most abundant commodity in nature it is the most misused one also. 80% of the earth's crust is covered with water. The quantity available for actual use in the form of rivers, lakes, wells and ponds is hardly 0.5% of the world's water resources. This is because more than 96% of water is locked in oceans which is too saline to drink or to be used directly for agricultural, industrial or domestic purposes. 2% of the water is locked up in polar ice caps and glaciers. About 1% is deeply underground and not accessible. Due to rapid industrialisation, urbanisation and growth in population man has successfully polluted most of the water available on earth. Industrial and domestic waste has caused significant—pollution of the aquatic ecosystem (Trivedi and Goel 1986). Hence monitoring and control of pollution is essential for better future.

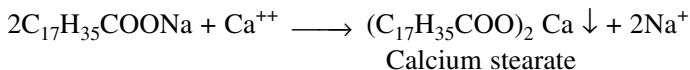
2.2 SOURCES OF WATER

- (i) **Surface waters:** (Rivers, lakes, seawater, etc.) Water present on the surface is called surface water. River water, stream water (flowing water, moorland surface drainage) as well as water in the ponds, lakes and reservoirs (low land surface drainage) is called surface water.
- (ii) **Underground water:** (Wells) Some part of rain water penetrates through the soil. It goes down and down till it reaches impermeable rocks. If the top of this rock is flat, it stays there. If the layers of rock have slope, water will flow the slope down. We get this water in the form of well or spring water. Water from lower measures of coal mines is also underground water.
- (iii) **Rainwater:** It is purest form of water obtained by natural distillation process.

2.3 IMPURITIES IN NATURAL WATER

When rainwater reaches the earth and flows on the earth, it becomes impure because of absorption of impurities. The absorbed impurities are of the following types.

But compounds of fatty acids with other metals do not dissolve in water. If water contains other metal ions like calcium and magnesium ions, they react with sodium salts of long chain fatty acids to form insoluble soap which we observe as curd.



These other metals ions are responsible for the hardness of water. Most important metal ions which cause hardness to water are calcium and magnesium ions. The hardness of water can be calculated from the amounts of calcium and magnesium ions present in water along with bicarbonates, sulphates, chlorides and nitrates.

The relation between the type of water and degree of hardness is as given below.

Type of water	Hardness as ppm of CaCO_3
Soft	0 – 75
Moderately hard	75 – 150
Hard	150 – 300
Very hard	above 300

Standards of water for drinking

As per Indian Standards (IS: 10500-1983)

Sr. No.	Characteristics	Desirable limit
1.	pH value	6.5 to 8.5
2.	Odour	unobjectionable
3.	Colour (Hazon unit), maximum	10
4.	Test	Agreeable
5.	Turbidity (NTU) maximum	5
6.	Total dissolved solids (TDS) ppm	500
7.	Total hardness maximum as (CaCO_3 ppm)	300
8.	Calcium (ppm)	75 – 200
9.	Magnesium (ppm)	30 – 150
10.	Iron as Fe (ppm)	0.1 – 1.0
11.	Chloride (as Ci) ppm	200 – 600
12.	Nitrate (as NO_3^-) ppm	45
13.	Sulphate as (SO_4) ppm	200 – 400
14.	Phosphate as (PO_4) ppm	10 – 15
15.	Organic matter (ppm)	0.2 – 1.0

2.5 TYPES OF HARDNESS

Hardness due to the presence of calcium and magnesium bicarbonates is called hardness.

3. In sugar industry presence of calcium magnesium salt interfere with the crystallisation of sugar.
4. In paper industry smooth finish and proper colour cannot be obtained if hard water is used.
 - (a) **Pharmaceutical industry:** If hard water is used for preparing pharmaceutical products like drugs, injections, lotions, syrups, etc., then the hardness causing ions in water may react with them to produce undesirable products. Which may reduce efficiency of the material or create adverse action.
 - (b) **Concrete making:** If the water containing chlorides, sulphates, etc. is used may affect the hydration of compounds in cement and final strength of concrete will be affected.

2.7 UNITS OF HARDNESS

Hardness in water is expressed in terms calcium carbonate equivalents as:

2.7.1 Parts Per Million (ppm)

It expresses the concentration of hardness causing salt as the number of parts of substance by weight in million parts by weight of water.

One part per million, i.e., 1 ppm hardness means one part of CaCO_3 equivalent hardness is present in one million parts of water. For calculation, the units of weight used should be same for the substance and water. $1 \text{ ppm} = 1 \text{ mg/litre}$.

2.7.2 Degree Clark ($^{\circ}\text{Cl}$)

It is the number of grains of CaCO_3 equivalent hardness per gallon of water. It is also expressed as parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus, 1°Clark is equal to one grain of CaCO_3 equivalent hardness in one gallon of water which is same as 1 part of CaCO_3 equivalent hardness per 70,000 parts of water.

2.7.3 French Unit ($^{\circ}\text{F}$)

It is the part of CaCO_3 equivalent hardness per 10^5 parts of water.

The various units of hardness are inter-convertible and by using the following information, hardness in one unit can be expressed in other units.

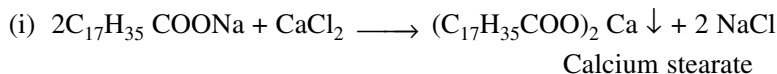
1 ppm	≡	1 mg/litre	≡	0.1°F	≡	0.07°Cl
1 mg/litre	≡	1 ppm	≡	0.1°F	≡	0.07°Cl
1°Cl	≡	14.3 ppm	≡	14.3 mg/litre	≡	1.43°F
1°F	≡	10 ppm	≡	10 mg/litre	≡	0.7°Cl

2.8 ESTIMATION OF HARDNESS

Hardness of water can be determined by two methods:

2.8.1 Soap Titration Method

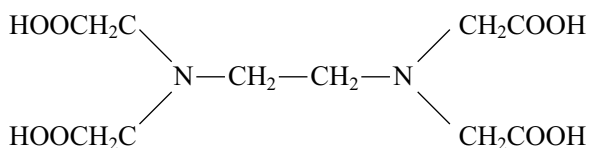
Total hardness of water can be determined by titrating a fixed volume of water sample (100 ml) against standard alcoholic soap solution. Formation of stable lather which persists for two minutes is the end point of titration. In the beginning sodium soap will precipitate all hardness causing ions as their respective stearates.



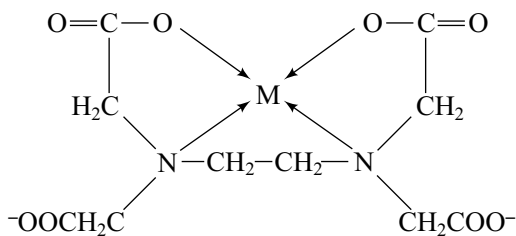
(Thus, water which readily lathers with soap is called soft water whereas water which forms scum or precipitate and does not form lather immediately is called hard water.)

2.8.2 EDTA Method (Complexometric Titration)

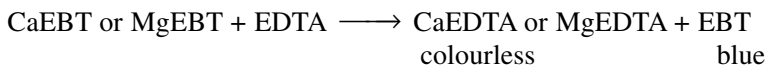
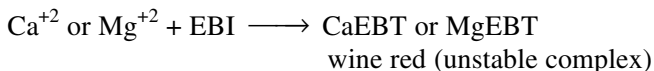
Principle: It is based on the fact that hardness causing ions like Ca^{++} , Mg^{++} form unstable complexes with the indicator Eriochrome Black T. However, when such a complex is treated with EDTA, since EDTA has more affinity to form stable complexes with metal ions, it extracts the metal ions from the metal ion-dye complex to form stable metal EDTA complex. The colour of dye-metal complex and dye are different. However, the change in colour is sharper at pH 10.0 than at other pH ranges. The metal-dye complex has wine red colour at pH 10.0 where the dye itself has blue colour at pH 10.0. Hence, by observing the sharp change in colour, the exact end point of reaction involving complete extraction metal ions by EDTA can be determined. The results obtained by this method are more accurate than those obtained by soap titration method.



EDTA (Ethylene diamine tetra acetic acid)



Metal complex of EDTA



The various steps involved in estimation of hardness by EDTA method are given below.

Preparation of Solutions

1. Standard hard water

1.0 gm of pure CaCO_3 dissolved in minimum quantity of conc. HCl and diluted to a one litre with distilled water. Each ml contains 1 mg CaCO_3 .

2. EDTA solution

4 gm of pure EDTA (disodium salt) is dissolved in one litre of water.

3. Eriochrome Black T Indicator

0.5 gm of the dye is dissolved in 100 ml of pure alcohol 2 to 3 drops of indicator is usually sufficient. Freshly prepared solutions are more suitable in order to obtain more accurate results.

4. Buffer of pH = 10.0

67.5 of NH_4Cl is mixed with 570 ml of liquor ammonia, and diluted upto a litre with distilled water.

Estimation of Hardness

1. 50 ml of standard hard water is pipetted out a clean 250 ml conical flask. Add 5 to 10 ml pH 10.0 buffer and mix well. Add 3 to 4 drops of Eriochrome Black T. The colour of solution is wine red.
2. Fill the burette with EDTA solution and titrate against standard hard water in flask. Let the volume of EDTA required be 'A' ml when the color changes to blue.
3. Pipette out 50 ml of sample of hard water add 5 to 10 ml buffer and 3 to 4 drops of indicator and titrate against EDTA from burette. Let the volume be 'B' ml.
4. Boil 50 ml of sample of hard water. Cool and filter, add 5 to 10 ml pH 10.0 buffer, 3 to 4 drops of indicator and titrate against EDTA till the colour changes to blue. Let the volume of EDTA consumed be 'C' ml.

Calculations

Since standard hard water contains 1 mg/ml of CaCO_3 hardness equivalent,
 50 ml of standard hard water \equiv 50 mg of CaCO_3 hardness
 50 ml of standard hard water requires \equiv A ml of EDTA

$$\begin{aligned} &\equiv \frac{50}{10} \text{ mg of CaCO}_3 \\ &\equiv 5 \text{ mg of CaCO}_3 \\ 50 \text{ ml of water sample} &\equiv 10 \text{ ml of EDTA solution} \\ &\equiv 10 \times 5 \text{ mg of CaCO}_3 \\ &\equiv 50 \text{ mg of CaCO}_3 \\ 50 \text{ ml of water sample} &\equiv 50 \text{ mg CaCO}_3 \\ 1000 \text{ ml of water sample} &\equiv 50 \times \frac{1000}{50} \\ &\equiv 1000 \text{ mg CaCO}_3 \end{aligned}$$

Hardness of water sample \equiv 1000 ppm.

Problem 2.2: In the determination of hardness by EDTA method, 50 ml of standard hard water (containing 1 mg of CaCO_3 hardness per ml of solution) required 30 ml of EDTA solution while 50 ml of the sample of hard water consumed 20 ml of EDTA solution. After boiling 50 ml of the same sample required 10 ml of EDTA solution. Calculate the various hardnesses in ppm.

Solution:

$$\begin{aligned} 1 \text{ ml of std. hard water} &\equiv 1 \text{ mg of CaCO}_3 \\ 50 \text{ ml of std. hard water} &\equiv 50 \text{ mg of CaCO}_3 \\ 50 \text{ ml of std. hard water} &\equiv 30 \text{ ml of EDTA} \\ &\equiv 50 \text{ mg of CaCO}_3 \\ \therefore 1 \text{ ml of EDTA} &\equiv \frac{50}{30} \text{ mg of CaCO}_3 \\ \text{Now 50 ml of sample water} &\equiv 20 \text{ ml of EDTA solution} \\ &\equiv 20 \times \frac{50}{30} \text{ mg of CaCO}_3 \\ 1000 \text{ ml of sample water} &\equiv 20 \times \frac{50}{30} \times 20 \text{ mg of CaCO}_3 \\ \text{Total hardness} &\equiv 664 \text{ mg of CaCO}_3 \\ &\approx 664 \text{ ppm.} \\ 50 \text{ ml of boiled water sample} &\equiv 10 \text{ ml of EDTA solution} \\ &\equiv 10 \times \frac{50}{30} \text{ mg of CaCO}_3 \\ \therefore 1000 \text{ ml of boiled water sample} &\equiv 10 \times \frac{50}{30} \times 20 \text{ mg of CaCO}_3 \\ &\equiv 332 \text{ mg of CaCO}_3 \\ \text{i.e. permanent hardness} &\equiv 332 \text{ ppm.} \\ \text{i.e. temporary hardness} &\equiv \text{Total} - \text{Permanent} \\ &\equiv 664 - 332 = 332 \text{ ppm.} \end{aligned}$$

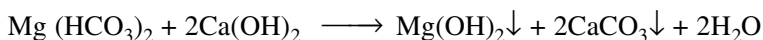
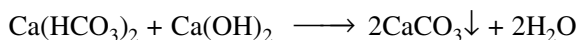
2.9 SOFTENING OF WATER

Softening of water means removal of hardness. Since hardness is mainly due to the presence of soluble salts of calcium and magnesium, softening methods aim at removal of these components from water. The lime soda process involves converting soluble impurities into insoluble precipitates by treatment with lime and washing soda. The precipitates are then removed by sedimentation and filtration. Other softening methods involving replacing the calcium and magnesium by harmless ions through exchange as in zeolite and ion exchange processes, are more effective and efficient in removal of hardness. These methods are discussed in detail below.

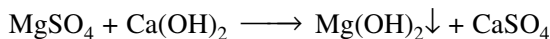
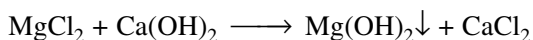
2.9.1 Lime Washing Soda Method

Principle: Calculated quantities of lime and soda (10% excess) are added to hard water to convert soluble impurities into insoluble one which can be easily removed by filtration. Reactions are as follows. If process is carried out at room temperature it is called cold lime soda process.

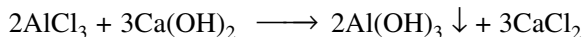
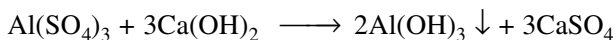
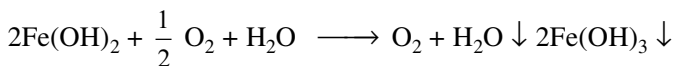
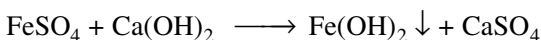
- **Removal of temporary hardness**



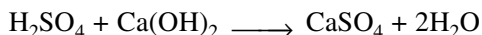
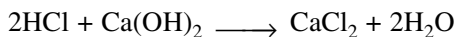
- **Removal of permanent hardness causing magnesium compounds**



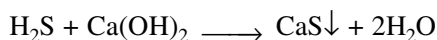
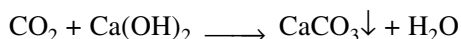
- **Removal of ions like iron, aluminium, manganese**



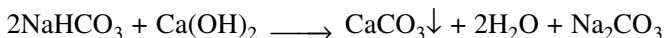
- **Neutralisation free acids**



- **Removal of dissolved gases**



- **Reaction with bicarbonate ions**



The above reactions also enable us to calculate the lime requirement on quantitative basis assuming that purity of lime is 100% pure.

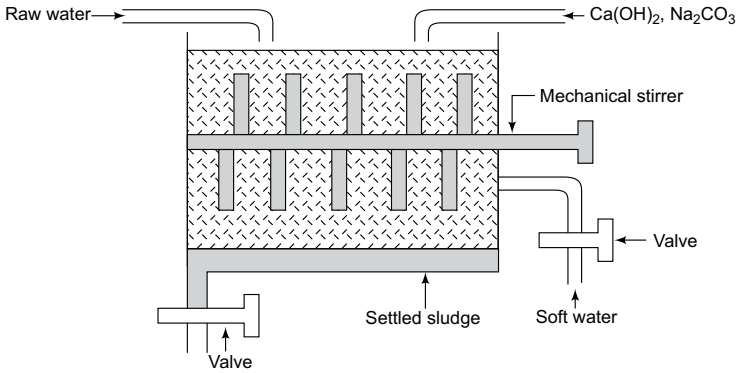


Fig. 2.1 Batch process.

Continuous Lime Soda Process

In order to obtain soft water on large scale, continuous treatment methods are used. This involves treating raw water with chemicals in continuous manner and removing the precipitated material partly by settling and by filtration. The equipment consists of two concentric vertical chambers. The inner chamber is provided with stirrer whose action not only mixes the chemicals and raw water intimately but also helps to gather the precipitated matter at the bottom in the conical portion. The treated water containing some floating particles of precipitate passes through a filter pad provided through which water passes. The treated water flows out from the top of outer chamber and is filtered and used.

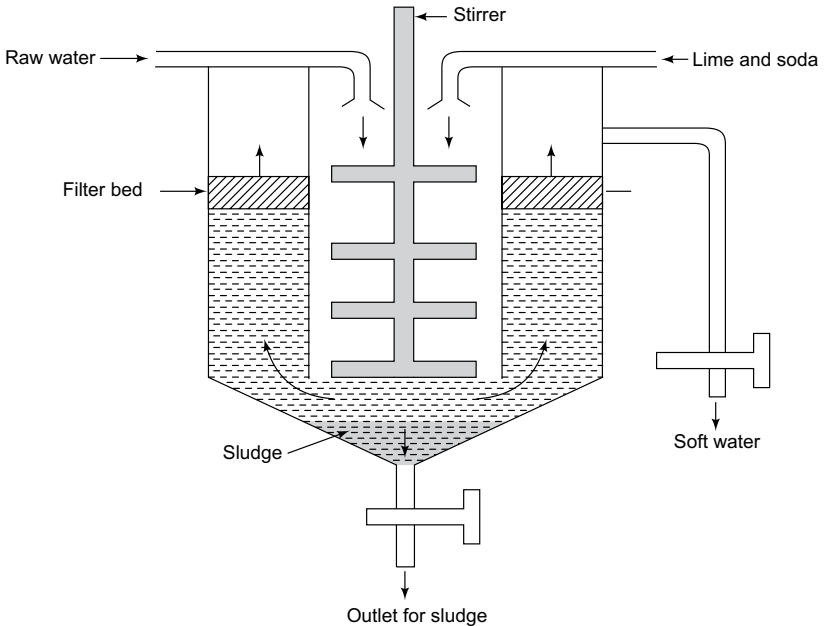


Fig. 2.2 Soda lime softening continuous process.

Hot Lime Soda Process

The shortcomings of cold lime soda process like incomplete precipitation, slow reaction and reduction of residual hardness only to 30-50 ppm are overcome by carrying out the reaction at higher temperature 50-60°C.

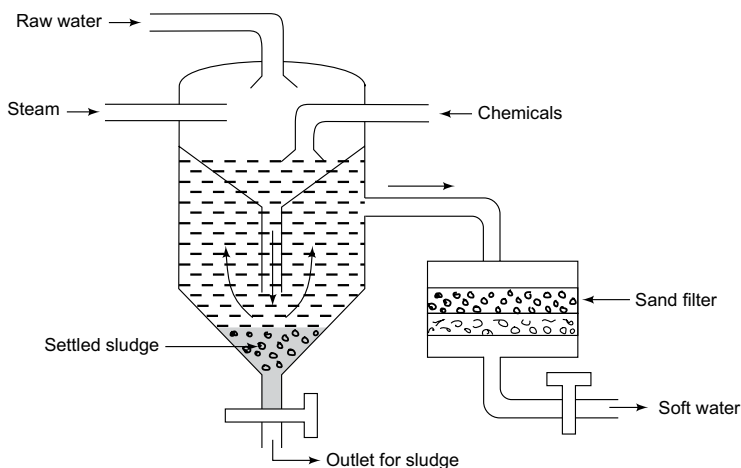


Fig. 2.3 Hot lime soda softener.

The softening is carried out in large steel tanks having two chambers. The upper chamber is separated from lower chamber by funnel shaped inlet. The raw water and chemicals flow into upper chamber where they are heated directly by high pressure steam. The treated water passes down the funnel. The precipitated matter settles down in the conical portion of chamber and are periodically removed. The softened water is removed from an opening at top lower chamber and passed through filter bed to remove any suspended impurities still remaining in water.

The main advantages of this method are:

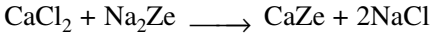
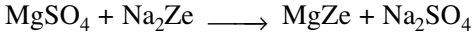
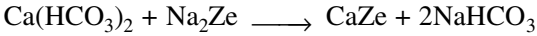
- (a) The time required for treatment is reduced considerably so that larger volumes of water can be treated. Thus, it is more economical.
- (b) The chemical reactions take place faster, the precipitate settles faster. The amount of coagulant if added is very low.
- (c) Higher temperature of water, coupled with alkaline conditions reduce the bacterial count to minimum.
- (d) Iron and manganese salts are precipitated out and their content in water is also reduced.
- (e) The final hardness of water after treatment is between 20-25 ppm which is almost 50% of the value obtained by the cold process.
- (f) The solubility of gases like oxygen, carbon dioxide is reduced at higher temperature and hence corrosion of boilers due to dissolved oxygen and carbon dioxide is reduced.

Though there are many advantages, use of steam for heating will add on to cost of production. Treating large volumes of water will also generate large volumes

of sludge material which has to be disposed of simultaneously. The residual hardness of 20-30 ppm is high and such water cannot be used in high pressure boilers.

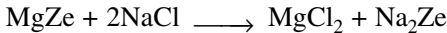
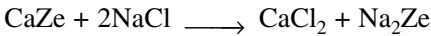
2.9.2 Zeolite Process of Softening (Permutit's Process)

Zeolites are naturally occurring (hydrated) sodium aluminium silicates, having different amounts of water of crystallisation. They are represented as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$, where x varies from 2 to 10 and y from 2 to 6. The naturally occurring mineral though more durable, is non-porous and has lower exchange capacity. Synthetic zeolites, on the other hand, are porous and have more exchange capacity per unit weight. Whether natural or synthetic, zeolite have the property of exchanging their Na ions for hardness causing ions like Ca^{++} and Mg^{++} . Calcium and magnesium zeolite on treatment with a solution of NaCl can replace Ca^{++} and Mg^{++} ion with Na^+ ions, thereby regenerating the zeolite. The reactions taking place during the process of softening are presented below:



where Ze represents zeolite.

The zeolite mineral gets exhausted when all the Na^+ ions are replaced by Ca^{++} and Mg^{++} ions. This indicates such an exhausted zeolite no longer has the capacity to exchange any more Ca^{++} and Mg^{++} ions. Under such situation, the hardness of incoming water and outlet will be same. Zeolite can be regenerated by passing NaCl solution.



The regenerated zeolite can now be used for replacing Ca^{++} and Mg from hard water.

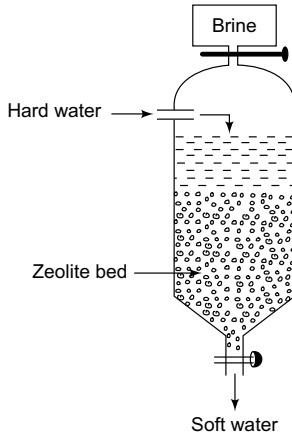


Fig. 2.4 Zeolite soften.

Advantages of Zeolite Process

1. By careful monitoring it will be possible to achieve very low hardness of less than 5 ppm.
2. The zeolite bed gets adjusted to any hardness of incoming water, i.e., variation in hardness of raw water does not affect the exchange process. The rate at which regeneration has to be carried out will vary.
3. The equipment is compact and materials used are cheap and easily available. Suitably trained people can handle the equipment without any problem.
4. The process can be operated under pressure also.
5. Since the reaction involves only replacement of Ca^{++} and Mg^{++} ions with Na^+ ions, there is no chance of sludge formation after precipitation at later stage.

2.9.3 Demineralisation or Ion Exchange Process

Ion exchange resins are used for softening of water. Ion exchange resins are organic polymers with long chains with cross links and having functional groups through which various ions are exchanged. The resins are porous and insoluble in water.

There are two types of ion exchange resins-cationic exchange resins which exchange their H^+ ions for cations present in water. These resins have functional groups like $-\text{SO}_3^-\text{H}^+$, $-\text{COO}^-\text{H}^+$, OH (phenolic) where the H^+ ion get replaced with other cations present in water. The anion exchange resins have functional groups like $-\text{NH}_2$, $=\text{NH}$, OH which can be exchanged with anions present in water.

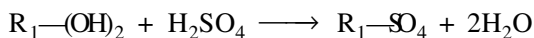
The principle of ion exchange method is based on ability of the ion exchange resins to exchange their functional group like H^+ with cations like Ca^{++} , Mg^{++} , Na^+ and $(\text{OH})^-$ with all anions present. The process of softening in the ion exchange process involves passing raw water through cationic exchange resin and followed by passing it through the anion exchange resin. The equipment consists of two cylinders which contain the cation exchange resin and the anion exchange resin. The outlet from cation exchange resin is connected to anion exchange cylinder. Separate outlets are provided for draining purposes. Tanks provided at the top of cylinders contain the regeneration chemicals.

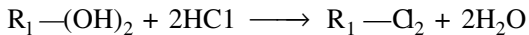
As the raw water passes through the cation exchange resin, Ca^{++} , Mg^{++} and other ions are exchanged with H^+ ions of the resin.



Thus, sulphates, chlorides, bicarbonates, get converted into sulphuric, hydrochloric and carbonic acids.

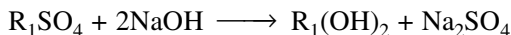
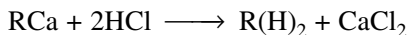
The acidic water emerging from the cation exchange bed is passed through the anion exchange bed where the anions are exchanged for the OH ions of resin.





The water emerging from the anion exchange bed is free from both cations and anions and hence completely demineralised. It means it does not have any hardness at all. However water may contain some dissolved gases. In order to remove the dissolved gases, water is passed through degassifiers where the water is heated, the escaping gases are removed by applying vacuum.

The cation exchange resin and the anion exchange resin are regenerated when they get saturated with cations and anions. Cation exchange resins are regenerated by passing dilute acids and anion exchange resins by passing alkali.



The regenerated resins can be used for treating further fresh raw water. Thus, the same amount of resins can be used over and again after regeneration.

Water obtained from ion exchange softening process has very low residual hardness of less than 2 ppm. It can be safely used for high pressure boilers.

Limitations due to presence of certain impurities

As in the case of zeolites, ion exchange resins do not function effectively in the presence of turbidity or suspended matter as they tend to cover the surface of resin and prevent easy exchange of ions. Similarly, very high total solid content in raw water will mean frequent regeneration of the resin. Hence, for efficient performance, raw water is pretreated to reduce the total dissolved solid content.

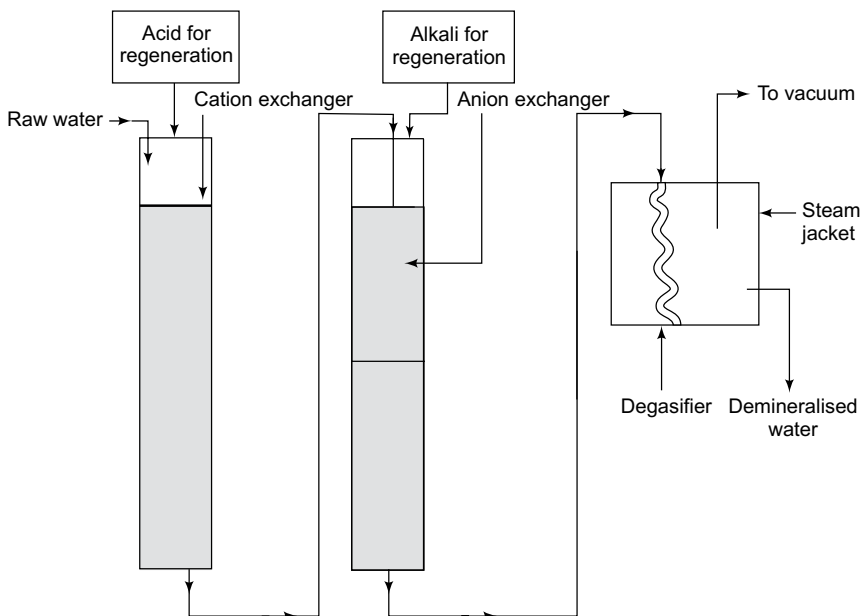


Fig. 2.5 Ion exchange method of softening of water.

Advantages of Ion Exchange Process

1. The process can be used for softening acidic or alkaline waters.
2. Where mineral free water is required as in the case of some pharmaceutical, cosmetics and explosives and other manufacturing processes, ion exchange process of softening is the only process available for getting such pure water.
3. The residual hardness after treatment is less than 2 ppm and this makes water suitable for high pressure boilers.
4. Continuous supply of softened water can be made available by providing storage facilities and two columns of each resins.

Disadvantages of the Ion Exchange Process

1. The resins used are costly, the regeneration chemicals like acids and alkalis are costlier.
2. The initial investment in equipment is more.
3. Where water is highly turbid and contains a large amount of dissolved matter, pretreatment of such water is essential to get the best results from the ion exchange method.

2.9.4 Calculation of Water Softening Reagents

1. Calculation of hardness

Hardness should be expressed in terms of weight of CaCO_3 i.e. in milligrams per litre (mg/l) or parts per million (ppm) or degree clark ($^\circ\text{Cl}$).

2. Lime requirements

Lime, i.e. $\text{Ca}(\text{OH})_2$ is required for

- (a) Temporary calcium hardness $\text{Ca}(\text{HCO}_3)_2$.
- (b) Temporary magnesium hardness, $\text{Mg}(\text{HCO}_3)_2$. Lime requirement for temporary Mg hardness is double that required for Ca hardness.
- (c) Lime eliminates permanent magnesium hardness but introduces an equivalent permanent calcium hardness.
- (d) Lime also reacts with dissolved CO_2 , iron and aluminium salts, free acids and introduces an equivalent Ca hardness.
- (e) Lime also reacts with bicarbonates of Na and K to form carbonates.

Since 100 parts of CaCO_3 is equivalent to 74 parts of $\text{Ca}(\text{OH})_2$.

Lime required for softening,

$$= \frac{74}{100} \left[\begin{array}{l} \text{Temp. Ca hardness} + 2 \times \text{temp. Mg hardness} \\ + \text{perm. (Mg + Fe + 3Al) hardness} \\ \frac{1}{2} \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- + \text{CO}_2 \blacklozenge \text{NaAlO}_2 \\ \text{all in terms of CaCO}_3 \text{ equivalents} \end{array} \right]$$

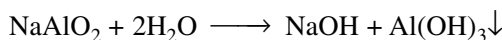
3. Washing soda requirement

Washing soda is required for eliminating salts of calcium other than temporary hardness.

Since 100 parts of CaCO_3 is equivalent to 106 parts of sodium carbonate, Washing soda requirement

$$= \frac{106}{100} \left[\begin{array}{l} \text{Perm. Ca hardness} + \text{Perm. (Me + Fe + 3Al) hardness} \\ \frac{1}{2} \text{HCl} + \text{H}_2\text{SO}_4 - \text{HCO}_3^- - \text{NaAlO}_2 \\ \text{all in terms of CaCO}_3 \text{ equivalents} \end{array} \right]$$

- Above mentioned formulae are used when CaCO_3 equivalents are calculated directly. When it is calculated by using multiplication factor with respect to chemical reaction then HCl, Aluminium equivalents are to be added directly.
- If NaAlO_2 is present in water, it undergoes hydrolysis to NaOH and Al(OH)_3 as follows:



NaAlO_2 does not need lime or soda, but since one equivalent of it produces one equivalent of $(\text{OH})^-$ ion it can be considered equal to one equivalent of lime. Hence, in calculation involving NaAlO_2 , the corresponding CaCO_3 equivalent should be deduced from lime and soda requirement. The conversion factor for

$$\text{CaCO}_3 \text{ equivalent is } \frac{100}{82 \times 2}.$$

- When aluminium salt present in water is other than $\text{Al}_2(\text{SO}_4)_3$ then multiplication factor will be with respect to the reaction with lime.

2.10 WATER POLLUTION

One of the serious problems in the world as practically whole quantity of water available on the earth is polluted which has caused adverse effects in plants and animal life. These pollutants enter in water from industrial effluent, drainage systems, pesticides, radioactive sources, etc. Animals like fish and plants are contaminated by pollutants, these are used as food by man. Pollutants enter in our body and create problems. Arsenic poisoning in Japan was mainly from fishes where the industrial effluent was going in the sea containing arsenic. Fishes can store more quantity of Pb, Hg and As in their body. In order to avoid these problems, industrial waste is treated properly and the BOD and COD of the wastewater is brought to the normal level and it can be reused again. Most of the industries have started wastewater treatment plant thereby large quantity of water can be saved. At the same time water pollution is minimised.

2.11 TYPES OF WATER POLLUTANTS

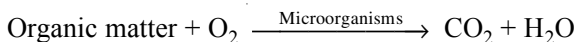
1. **Pathogenic micro organisms:** Disease producing or pathogenic micro organisms originate from domestic wastewater. Wastewater released from

sanitaria, municipalities, tanning and slaughtering plants are the sources of bacteria or other micro-organisms causing disease to intestinal tract in human and animals. The intestinal discharges of infected individuals contain billions of the pathogen, which if allowed to mix with water supply source, may result in epidemic. Some of these diseases according to their causative agents are:

Infectious hepatitis, poliomyelitis	→	Viruses
Cholera, bacterial dysentery, typhoid	→	Bacteria
Amoebic dysentery	→	Protozoa
Hookworm, guinea worm	→	Helminth

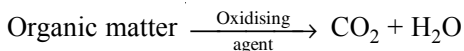
The presence of the coliform group of bacteria in water indicates contamination with sewage.

- 2. Organic pollutants:** The colour and odour of water is due to dissolved organic matter. Dissolved oxygen (DO) is an essential requirement of aquatic life. Its optimum value in natural water is 4-6 ppm. Decrease in this DO concentration indicates water is polluted due to organic matter. The common parameters of characterisation of organic matter are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Micro-organisms mainly bacteria, utilize various types of waste organic matter as their food to obtain energy. They decompose organic matter into carbon dioxide and water in the presence of oxygen. This oxygen is taken from water.



The amount of oxygen consumed is taken as a measure of quantity of organic matter is called biochemical oxygen demand (BOD). The BOD test is the most important parameter to assess the pollution of water bodies by organic matter and its effect on the oxygen resources of streams and lobes. The disappearance of plant and animal life is a result of the oxygen depletion of water.

The organic matter present in wastewater is of two types—biologically oxidisable as well as biologically inert. This total organic content of water is determined by another parameter, chemical oxygen demand (COD).



It is the amount of oxygen required by organic matter present in water for its oxidation by strong oxidant like $\text{K}_2\text{Cr}_2\text{O}_7$. COD values are always higher than BOD values.

- 3. Plant nutrients:** There are chemicals containing elements such as Ca, PK, S, N, Fe, Mn, B, they are essential for the growth of plants. Some are required in small quantities (micronutrients). Plants require relatively large amount of carbon, nitrogen and phosphorus. Carbon is taken in the form of carbon dioxide from air, while nitrogen and phosphorus are taken from soil. Run-off from agricultural lands provides plants nutrient to marine plants.

In the first stage of sewage treatment, solid wastes and scum are removed by screening and then settling of the sludge. In the second stage, biological degradation of organic material is done by aerobic or anaerobic micro organisms.

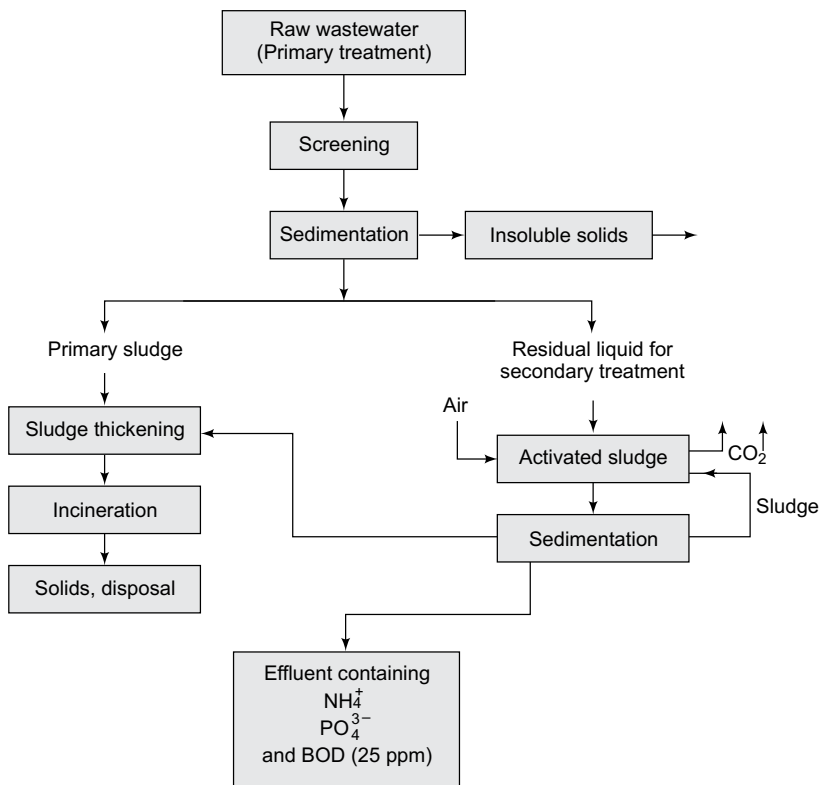
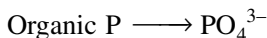
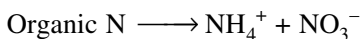
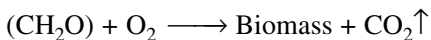


Fig. 2.6 Flow diagram for primary and secondary municipal wastewater treatment plant.

2.14 AEROBIC TREATMENT (ACTIVATED SLUDGE PROCESS)

It is based on biological oxidation of soluble organic material by bacteria.



Activated sludge process involves extensive aeration of the sewage water and the process of aerobic oxidation being enhanced by the addition of part of sludge from previous oxidation process, into sewage water. The added sludge is known as activated sludge, as it contains large number of aerobic bacteria and other micro organisms. Mixture of sewage water and activated sludge is sent to aeration tank where it is aerated and agitated for several hours. During the process organic matters oxidised. After completion of the process the effluent is sent to a

sedimentation tank, where sludge is deposited and water free from organic matter is drawn off. A part of the settled sludge is sent back for settling fresh batch of sewage. The effluent from secondary treatment has much lower organic load. This water after chlorination is discharged into lakes, streams, rivers and seas.

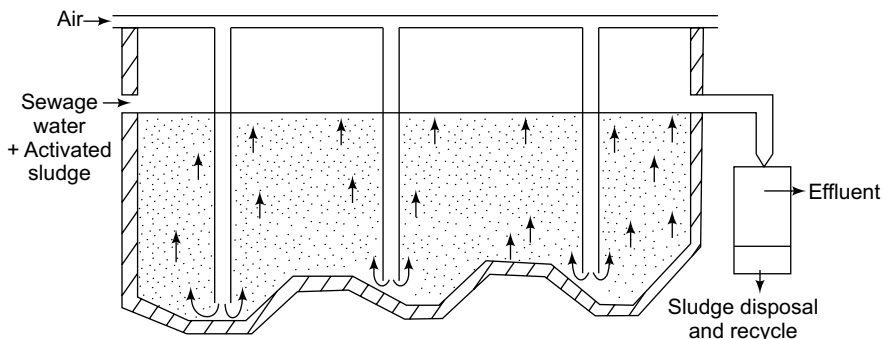
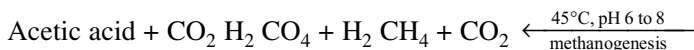
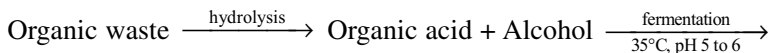


Fig. 2.7 Activated sludge process.

By this process about 50% of biodegradable carbon present in wastewater is converted into biomass and remaining 50% into carbon dioxide. This process has major problem of sludge disposal. Sludge can be used as a fertilizer. Incineration or anaerobic digestion of the sludge can be done, but it creates new environmental problems.

2.14.1 Anaerobic Treatment

In this method, degradation of organic waste is carried under anaerobic conditions.



biogas

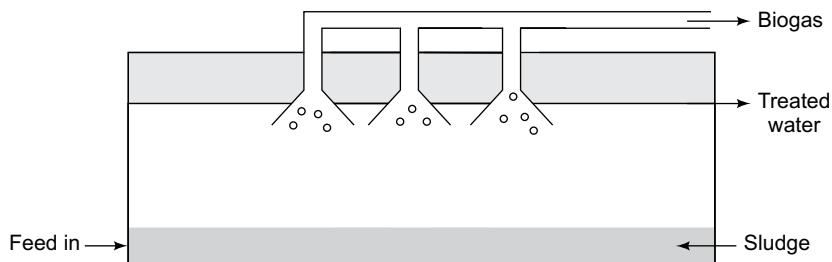


Fig. 2.8 Unflow anaerobic sludge blanket reactor.

2.15.1 Trickling Filters

When volume of effluent treated is not large, another method of reducing the organic content of sewage is adopted. Trickling filters consist of large rectangular circular tanks, 2 metres in depth, packed with broken stone pieces or coals or bricks. The tanks are provided with sprinkler system on the top and arrangement of collecting the drainage and circulating it again and outlet for treated effluent.

The process involves spraying the sewage at the top of tank and recirculating the drainage till active biomass is built on the surface of stones or bricks. As the sewage trickles down the bed, the micro organisms present, attach themselves to the surface and start using the organic matter present in sewage. In this process, a layer of actively growing organisms is held on to the surface of packed material. These organisms consume the organic impurities present in sewage and thereby bring about reduction in BOD. When the required reduction is obtained, the water can be drained out after ensuring that it is properly disinfected by treating with chlorine or bleaching powder.

This method is slow as compared to activated sludge process but is convenient and cheaper. Another disadvantage is as the microorganisms built up, they block the passage and flow rate drops considerably. Hence, periodic cleaning is necessary to remove excess sludge and maintain efficiency of the process.

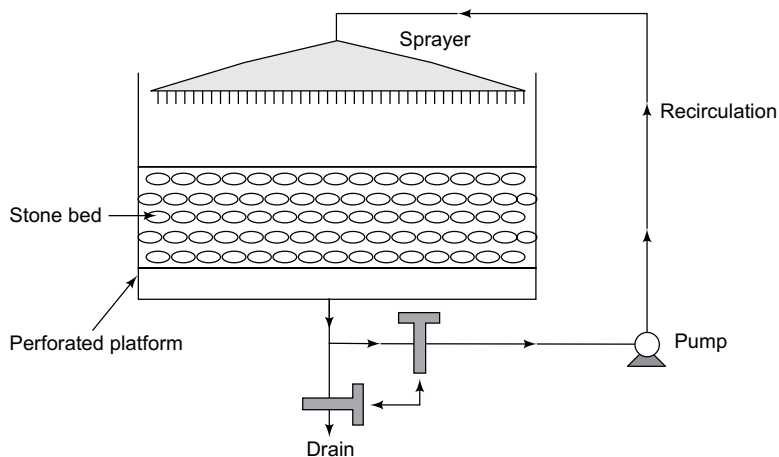


Fig. 2.9 Trickling filters.

The sludge obtained from activated sludge process and trickling filter is dewatered by filtering through sand beds. Dried sludge can be used as fertiliser.

2.15.2 Removal of Odour

The unpleasant odour of water is due to the presence of phenols, hydrogen sulphide, chlorine, organic sulphur compounds. Pesticides and detergents impart peculiar odour to water. Decaying organic matter in water also produces bad smell.

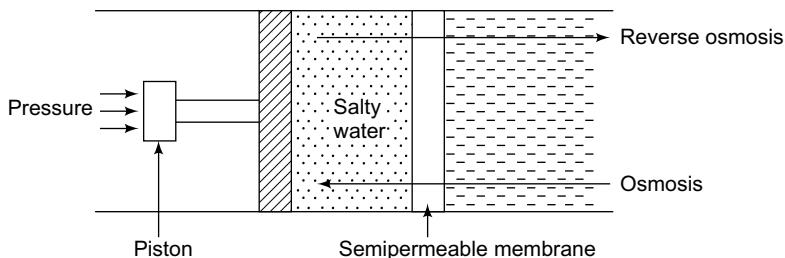


Fig. 2.10

This natural tendency of water may be reversed by applying a higher pressure on the salty water part. This tends to flow water from higher concentrations to lower one. This reverse process of osmosis is called as reverse osmosis. The membranes used are cellulose acetate, cellulose butyrate, etc. This method is also known as superfiltration. This is a single and continuous process, involves no phase changes and needs low energy. This technique is also used for the separation of toxic ions from plating wastes, concentration of radioactive waste and removal of organics from vegetable and animal wastes.

2.17 ULTRAFILTRATION

Some of the toxic chlorinated organisms are removed by filtering industrial waste with activated charcoal as follows.

Aldrin, Dieldrin, Endrin, DDT, etc. are removed nearly 99%.

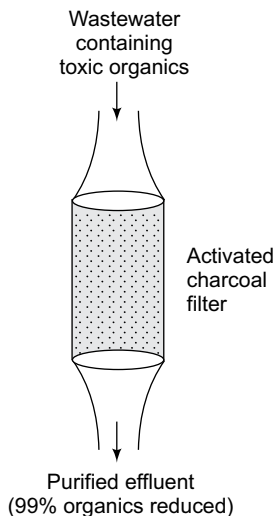
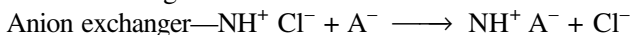
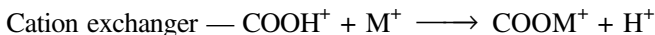


Fig. 2.11 Filtration of industrial wastes with activated charcoal.

Synthetic organic ion exchange resins are very useful for removal of industrial waste chemicals. Styrene-divinyl-benzene copolymer can remove chlorinated pesticides by adsorption at the surface. Ionic dyes from textile mill wastewater can be eliminated by using cation and anionic ion exchange resins.



The ion exchange membrane finds an important application in the removal of toxic wastes by ultrafiltration. In ultrafiltration, the solution is pushed under pressure through a membrane which contains pores of size 2 to 10,000 nm ($20 \times 10^5 \text{ \AA}$) whereby big molecules are retained and the effluent that passes off is free of the big molecules. In reverse osmosis, the membrane pores are smaller—0.04 to 600 nm—in size. Both these techniques have found extensive application in purification of industrial wastewater in metal, textile, protein isolation, paper and pulp and food industries.

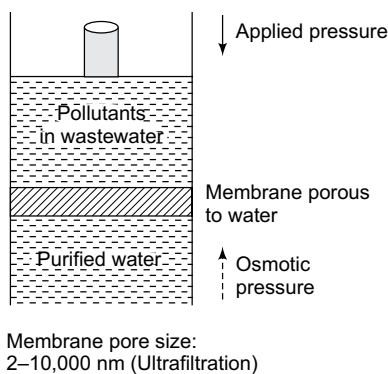


Fig. 2.12 Industrial wastewater purification by ultrafiltration.

2.18 CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand (COD) is the amount of oxygen used while oxidising organic matter by means of strong oxidising agent. All organic matters are converted into CO_2 and H_2O . In chemical oxidation both biologically oxidisable organic matter like starch, sugar, inert materials like cellulose, etc. are oxidised and hence COD values are always higher than BOD. COD can be determined in 3 hours.

The wastewater sample is refluxed with a known excess of potassium dichromate in a dilute sulphuric acid in the presence of silver sulphate as a catalyst or HgSO_4 . The organic matter of the sample is oxidised to water, carbon dioxide and ammonia. The unreacted excess of dichromate remaining is titrated with standard solution of ferrous ammonium sulphate.

$$\text{COD} = \frac{(V_1 - V_2) \times N \times 8}{x} \times 100 \text{ mg/L}$$

the degree of pollution hence it has special significance is pollution control. BOD values are useful generally in process design and loading calculations, measurement of treatment efficiency and operation, steam pollution control and in determination of self purifying capacity of a stream.

2.20 MONITORING AND CONTROL OF WATER POLLUTION

Pollutant enters into the water system by following ways:

- (i) Direct discharge of domestic and industrial wastes
- (ii) Run-off and seepage.
- (iii) River-flow transport
- (iv) Reactions and transport across the air water interface and water sediments interface.

Apart from the direct discharge, the major transport of pollutants from land surface to water system takes place by runoff water which picks up the soluble as well as suspended materials from the soil and transport them to the receiving waters. A large quantity of soils itself can move with the run-off called soil erosion causing silting. Monitoring is an essential part. In India, the monitoring of water quality on a national level is being carried out by the Central Pollution Control Board as

- (i) Global Environmental Monitoring System (GEMS)
- (ii) Monitoring of Indian National Aquatic Resources (MINARS)
- (iii) Ganga Action Plan (GAP)

Recently, there are about five hundred Automatic Water Quality Monitoring Stations (AWQMS) which continuously monitor temperature, DO, pH, conductivity and turbidity of water.

The Central Pollution Control Board and Department of Ocean and Environments has also established 173 stations over the entire coastline of the country to assess the quality of coastal and estuarine waters.

2.20.1 Monitoring of Lake Pollution

Pollutants are distributed unevenly in the lake water with a depth, hence several signals are usually required for a worthwhile monitoring of lake. Any monitoring programme may include the following parameters.

- (i) Physical: Temperature, colour, solid, turbidity, conductivity
- (ii) Chemical: pH, DO, COD, BOD, alkalinity, NH_3 , NO_3 , NO_2 chloride, sulphate, phosphate, calcium magnesium hardness, pesticides, heavy metals, detergents, etc.
- (iii) Biological: Microinvertebrates, pathogens, coliforms, etc.

Example 2.2 Calculate quantities of lime and soda required for softening of 20,000 litres of water containing following salts in ppm (16.4 ppm NaAlO_2 used as a coagulant)

$$\text{Ca}^{+2} = 160 \text{ ppm}$$

$$\text{Mg}^{+2} = 72 \text{ ppm}$$

$$\text{HCO}_3^- = 73.2 \text{ ppm}$$

$$\text{CO}_2 = 44 \text{ ppm}$$

$$\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ ppm}$$

$$\text{HCl} = 36.5 \text{ ppm}$$

Solution: Conversion into CaCO_3 equivalents.

<i>Iron or salt</i>	<i>Amount present (ppm)</i>	<i>Conversion</i>	<i>CaCO_3 equivalent (ppm)</i>
Ca^{+2}	160	$\frac{100}{40}$	$160 \times \frac{100}{40} = 400$
Mg^{+2}	72	$\frac{100}{24}$	$72 \times \frac{100}{24} = 300$
HCO_3	73.2	$\frac{100}{122}$	$73.2 \times \frac{100}{122} = 60$
CO_2	44	$\frac{100}{44}$	$44 \times \frac{100}{44} = 100$
NaAlO_2	16.4	$\frac{100}{164}$	$16.4 \times \frac{100}{164} = 10$
$\text{Al}_2(\text{SO}_4)_3$	34.2	$\frac{100}{342}$	$34.2 \times \frac{100}{342} = 10$
HCl	36.5	$\frac{100}{36.5}$	$36.5 \times \frac{100}{36.5} = 100$

$$\text{Lime required} = \frac{74}{100} [300 + 3(10) + 1/2(100) + 100 + 60 - 10]$$

$$= \frac{74}{100} [300 + 30 + 50 + 100 + 60 - 10]$$

$$= \frac{74}{100} [530]$$

$$= 392.2 \text{ mg/lit}$$

$$= 392.2 \times 20000 \times \frac{1}{10^6}$$

$$= \mathbf{7.84 \text{ kg}}$$

$$\begin{aligned}
 \text{Soda required} &= \frac{106}{100} [400 + 300 + 3(10) + 1/2(100) - 60 - 10] \\
 &= \frac{106}{100} [400 + 300 + 30 + 50 - 70] \\
 &= 752.6 \text{ mg/lit} \\
 &= 752.6 \times 20.000 \times \frac{1}{10^6} \\
 &= \mathbf{15.05 \text{ kg}}
 \end{aligned}$$

Example 2.3 A water sample contains the following impurities per litre.

Ca(HCO ₃) ₂	–	81 mg
Mg(HCO ₃) ₂	–	73 mg
CaSO ₄	–	68 mg
MgSO ₄	–	60 mg
KCl	–	100 mg

Calculate (a) temporary and permanent hardness in water.

(b) Quantity of lime and soda required in kg for softening 50,000 litres of water if the purity of lime and soda are 80% and 90% respectively.

Solution: 1. Conversion of the impurities into CaCO₃ equivalents.

Substance	Quantity mg per/ litre	Conversion factor	CaCO ₃ equivalent mg/litre
Ca(HCO ₃) ₂	81	$\frac{100}{162}$	$\frac{100}{162} \times 81 = 50$
Mg(HCO ₃) ₂	73	$\frac{100}{146}$	$\frac{100}{146} \times 73 = 50$
CaSO ₄	68	$\frac{100}{136}$	$\frac{100}{136} \times 68 = 50$
MgSO ₄	60	$\frac{100}{120}$	$\frac{100}{120} \times 60 = 50$

KCl does not react with lime or soda and its presence can be ignored.

$$\begin{aligned}
 2. \text{ Lime requirement} &= \frac{74}{100} [\text{Temp. Ca H} + 2 \times \text{Temp. Mg H} + \text{Perm. Mg H}] \\
 &= \frac{74}{100} \left[\begin{array}{ccc} 50 & + & 2 \times 50 & + & 50 \\ \text{Ca(HCO}_3)_2 & & \text{Mg(HCO}_3)_2 & & \text{MgSO}_4 \end{array} \right]
 \end{aligned}$$

Salt	Amount present ppm	Conversion factor	CaCO ₃ equivalents ppm
Ca(HCO ₃) ₂	162	$\frac{100}{162}$	$162 \times \frac{100}{162} = 100$
MgCl ₂	9.5	$\frac{100}{95}$	$9.5 \times \frac{100}{95} = 10$
Fe ₂ O ₃	100 ppm	Does not contribute hardness	—
NaCl	58.5 ppm		—
SiO ₂	25 ppm		—
H ₂ SO ₄	98	$\frac{100}{49}$	$98 \times \frac{100}{49} = 200$
MgSO ₄	60	$\frac{100}{120}$	$60 \times \frac{100}{120} = 50$
CaCQ ₃	100	$\frac{100}{100}$	$100 \times \frac{100}{100} = 100$

$$\begin{aligned}
 \text{Amount of lime required} &= \frac{74}{100} [200 + 10 + 50 + 100] \\
 &= \frac{74}{100} [360] \times 50,000 \times \frac{1}{10^6} = 266.4 \text{ mg/lit} \\
 &= 13.32 \text{ kg} = \text{Rs. } 70.59
 \end{aligned}$$

$$\begin{aligned}
 \text{Amount of soda required} &= \frac{106}{100} [10 + 50 + 100] \\
 &= \frac{106}{100} [160] \times 50,000 \times \frac{1}{10^6} \\
 &= 169.6 \text{ mg/lit} \\
 &= \mathbf{8.48 \text{ kg}} \\
 &\text{Cost } 38.16 \text{ Rs.}
 \end{aligned}$$

$$\text{Total cost} = 70.59 + 38.16 = \mathbf{\text{Rs. } 108.6}$$

Although water quality studies have been taken for many years on some rivers, CPCB is now operating water quality monitoring networks on major rivers under Global Environmental Monitoring System (GEMS) and Monitoring of National Aquatic Resources (MINARS) through State Pollution Control Boards (SPCB). The Central Water Commission (CWC) is monitoring water quality at large number of stations on almost all the major rivers.

2.21 NUMERICAL PROBLEMS

2.21.1 Numerical Problems based on EDTA Method

- Calculate the hardness in a given hard water sample having the following data. 50 ml of standard hard water containing 1 mg of CaCO_3 per ml consumed.
 - 50 ml of standard hard water consumed 25 ml EDTA using eriochrome black T as indicator.
 - 50 ml water sample consumed 40 ml EDTA using the same indicator.
 - 50 ml water sample after boiling consumed 25 ml of EDTA using the same indicator.

$$(i) \text{ 50 ml standard hard water} \quad \equiv 25 \text{ ml EDTA}$$

$$(50 \times 1) \text{ mg CaCO}_3 \equiv 25 \text{ ml EDTA}$$

$$\therefore \quad 1 \text{ ml EDTA} \equiv \frac{50}{25} \text{ mg CaCO}_3 = 2 \text{ mg CaCO}_3$$

$$(ii) \text{ 50 ml water sample} \quad \equiv 40 \text{ ml EDTA}$$

$$\equiv 40 \times 2 \text{ mg CaCO}_3 \equiv 80 \text{ mg CaCO}_3$$

$$\therefore \text{ 1000 ml water sample contains } \left(\frac{80}{50} \times 1000 \right) \times \text{ mg CaCO}_3$$

$$= 1600 \text{ ppm}$$

$$(iii) \text{ 50 ml boiled water sample} = 25 \text{ ml EDTA}$$

$$\equiv (2.5 \times 2) \text{ mg CaCO}_3 = 50 \text{ mg CaCO}_3$$

$$\therefore \text{ 1000 ml boiled H}_2\text{O sample contain } \left(\frac{50}{50} \times 1000 \right) \text{ mg CaCO}_3$$

$$= 1000 \text{ mg CaCO}_3$$

$$\therefore \quad \text{Permanent hardness} = 1000 \text{ ppm}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= (1600 - 1000) \text{ ppm}$$

$$= 600 \text{ ppm}$$

- 50 ml of a hard water sample required 8 ml of 0.05 N EDTA solution for titration. 30 ml of the same water sample after boiling required 5 ml of 0.02 N EDTA solution for titration. Calculate the hardness of water.

$$1000 \text{ ml 1 N EDTA} \equiv 50 \text{ gm CaCO}_3$$

$$1 \text{ ml 1 N EDTA} \equiv 50 \text{ mg CaCO}_3$$

$$\text{Now 50 ml hard water sample} \equiv 8 \text{ ml 0.05 N EDTA}$$

$$\equiv (8 \times 0.05) \text{ ml (1 N) EDTA}$$

$$\equiv (8 \times 0.05 \times 50) \text{ mg CaCO}_3$$

$$= 20 \text{ mg CaCO}_3$$

$$\therefore 100 \text{ ml hard water sample contains } \left(\frac{20}{50} \times 1000 \right) \text{ mg CaCO}_3$$

$$= 400 \text{ mg CaCO}_3$$

$$\therefore \text{Total hardness} = 400 \text{ ppm}$$

$$20 \text{ ml boiled water sample} \equiv 5 \text{ ml } 0.02 \text{ EDTA}$$

$$\equiv (5 \times 0.02) \text{ ml } 1 \text{ N EDTA}$$

$$\equiv 5 \text{ mg CaCO}_3$$

$$\therefore 1000 \text{ ml boiled water sample contains}$$

$$\left(\frac{5}{30} \times 1000 \right) \text{ mg CaCO}_3 = 166.6 \text{ mg CaCO}_3$$

$$\text{Permanent hardness} = 166.6 \text{ ppm}$$

$$\text{Temporary hardness} = [\text{Total hardness} - \text{Permanent hardness}]$$

$$= 400 - 166.6$$

$$= 234 \text{ ppm}$$

3. A standard hard water sample contains 0.20 mg of CaCO_3 per ml. 100 ml of this water consumed 25 ml 0.02 N EDTA. 25 ml sample H_2O consumed 12 ml of 0.05 N EDTA. The sample water is boiled and filtered, 50 ml of this boiled water sample consumed 4 ml of 0.01 N EDTA. Calculate the hardness of water.

Solution:

$$(i) 100 \text{ ml standard hard water } (0.20 \text{ mg/ml CaCO}_3)$$

$$\equiv 25 \text{ ml } 0.02 \text{ N EDTA}$$

$$(ii) 25 \text{ ml sample water} \equiv 12 \text{ ml } 0.02 \text{ N EDTA}$$

$$(iii) 50 \text{ ml boiled sample} \equiv 4 \text{ ml } 0.01 \text{ N EDTA.}$$

$$\therefore (i) 25 \text{ ml } 0.02 \text{ N EDTA} = (100 \times 0.20) \text{ mg CaCO}_3$$

$$1 \text{ ml } 1 \text{ N EDTA} = \frac{100 \times 0.20}{25 \times 0.02}$$

$$= 40 \text{ mg CaCO}_3$$

$$(ii) 25 \text{ ml sample H}_2\text{O} \equiv 12 \text{ ml } 0.02 \text{ N EDTA}$$

$$= (12 \times 0.02) \text{ ml } 1 \text{ N EDTA}$$

$$= (12 \times 0.02 \times 40) \text{ mg CaCO}_3$$

$$= 9.60 \text{ mg CaCO}_3$$

$$\therefore \text{Total hardness} = 9.60 \times \frac{100}{25} \text{ mg/lit.}$$

$$= 384 \text{ mg/lit}$$

(iii) 50 ml boiled sample = 4 ml 0.01 N EDTA

$$(4 \times 0.01) \text{ ml IN EDTA}$$

$$= 4 \times 0.01 \times 40 \text{ mg CaCO}_3$$

$$= 1.6 \text{ mg CaCO}_3$$

$$\therefore \text{Permanent hardness} = \left(1.6 \frac{1000}{50}\right) \text{ mg/lit.}$$

$$= 32 \text{ mg/lit.}$$

$$\text{Temporary hardness} = (384 - 32) \text{ mg/lit.}$$

$$= 352 \text{ mg/lit.}$$

2.21.2 Additional Problems based on Lime-Soda Process

1. Calculate the quantity of lime and soda required for softening 1,00,000 litres of water containing the following impurities.

$$\text{Ca(HCO}_3)_2 = 30.2 \text{ ppm}$$

$$\text{Mg(HCO}_3)_2 = 20.8 \text{ ppm}$$

$$\text{CaCl}_2 = 28.1 \text{ ppm}$$

$$\text{MgCl}_2 = 8.7 \text{ ppm}$$

$$\text{CaSO}_4 = 35.00 \text{ ppm}$$

$$\text{MgSO}_4 = 6.7 \text{ ppm}$$

The purity of lime is 70% and the purity of soda 85% [At. wt. for H = 1, C = 12, O = 16, Na = 23, Mg = 24]

Impurity	Amount in ppm	Molecular weight	Multiplication factor	CaCO ₃ equivalent in ppm
Ca(HCO ₃) ₂	30.2	162	100/162	30.2 × 100/162 = 18.64
Mg(HCO ₃) ₂	20.8	146	100/146	20.8 × 100/146 = 14.24
CaCl ₂	28.1	111	100/111	28.1 × 100/111 = 25.31
MgCl ₂	8.7	95	100/95	8.7 × 100/95 = 9.15
CaSO ₄	35.00	136	100/136	35 × 100/136 = 25.73
MgSO ₄	6.7	120	100/120	6.7 × 100/120 = 5.58

$$\text{Lime required} = \frac{74}{100} [\text{Temp Ca}^{2+} + 2 \times \text{Temp mg}^{2+} + \text{Perm mg}^{2+}]$$

$$\frac{74}{100} [18.64 + (2 \times 14.24) + 9.15 + 5.58]$$

$$= 45.769 \text{ ppm}$$

$$\begin{aligned}\text{Soda required} &= \frac{106}{100} [(25.31 + 25.73) + (9.15 + 5.58)] \\ &= 69.71 \text{ ppm}\end{aligned}$$

Lime is 70%

∴ for 100,000 lit. of water.

$$\begin{aligned}\text{Lime required} &= \frac{100}{70} \times (100,000 \times 45.769) \text{ mg} \times \frac{1}{106} \\ &= 65.384 \text{ kg}\end{aligned}$$

$$\begin{aligned}\text{Soda required} &= \frac{100}{85} \times (100,000 \times 69.71) \text{ mg} \times \frac{1}{106} \\ &= 82.01 \text{ kg}\end{aligned}$$

2. Calculate the quantity of lime and soda required for softening 10,000 litres of H₂O containing the following impurities per litre

$$\text{Ca(HCO}_3)_2 = 7.8 \text{ mg} \quad \text{Mg(HCO}_3)_2 = 8.00 \text{ mg}$$

$$\text{CaSO}_4 = 12.2 \text{ mg} \quad \text{MgSO}_4 = 10.6 \text{ mg}$$

$$\text{NaCl} = 5.5 \text{ mg} \quad \text{SiO}_2 = 2.1 \text{ mg}$$

(Atomic weights for H = 1, C = 12, O = 16, Na = 23, Mg = 24)

Solution:

NaCl and SiO₂ are not hardness causing substances. Hence, they do not consume lime and soda.

Molecular weight of the impurities are,

(i) $\text{Ca(HCO}_3)_2 = 40 + 2 [1 + 12 + 3 \times 16] = 162$

(ii) $\text{Mg(HCO}_3)_2 = 24 + 2 [1 + 12 + 3 \times 16] = 162$

(iii) $\text{CaSO}_4 = 40 + 32 + (4 \times 16) = 136$

(iv) $\text{MgSO}_4 = 24 + 32 + (4 \times 16) = 120$

(v) Molecular weight of CaCO₃ = 100

Impurity	Amount	Molecular weight	Multiplication factor	CaCO ₃ equivalent in ppm
Ca(HCO ₃) ₂	7.8	162	100/162	7.8 × 100/162 = 4.8
Mg(HCO ₃) ₂	8.00	146	100/146	8 × 100/146 = 5.4
CaSO ₄	12.2	136	100/136	12.2 × 100/136 = 8.9
MgSO ₄	10.6	120	100/120	10.6 × 100/120 = 8.8

$$\begin{aligned}\text{Lime required} &= \frac{74}{100} [\text{Temp Ca}^{2+} + 2 \times \text{Temp Mg}^{2+} + \text{Perm Mg}^{2+}] \\ &= \frac{74}{100} [4.8 + (2 \times 5.4) + 8.8] \text{ mg/lit.} \\ &= 18.05 \text{ mg/lit}\end{aligned}$$

For 10, 000 litres of water lime required

$$= (18.5 \times 10,000) \text{ mg}$$

$$= 18050 \text{ mg.}$$

$$\text{Soda required} = \frac{106}{100} [\text{perm Ca}^{2+} + \text{Perm mg}^{2+}]$$

$$= \frac{106}{100} [8.9 + 8.8]$$

$$= 18.23 \text{ mg/lit}$$

For 10, 000 litres of water soda required ($18.23 \times 10, 000$) mg

$$= 182340 \text{ mg}$$

3. Calculate the amount of lime (90% pure) and soda (95% pure) required to soften one million litres of water which contains the following impurities.

$$\text{CaCO}_3 = 15 \text{ ppm} \quad \text{MgCO}_3 = 9 \text{ ppm}$$

$$\text{CaCl}_2 = 20 \text{ ppm} \quad \text{MgCl}_2 = 8 \text{ ppm}$$

$$\text{CO}_2 = 30 \text{ ppm} \quad \text{HCl} = 9.2 \text{ ppm}$$

<i>Impurity</i>	<i>Amount in ppm</i>	<i>Molecular weight</i>	<i>Multiplication factor</i>	<i>CaCO₃ equivalent in ppm.</i>
CaCO ₃	15.0	100	100/100	15 × 100/100 = 15
MgCO ₃	9.00	84	100/84	9 × 100/84 = 10.7
CaCl ₂	20.0	111	100/111	20 × 100/111 = 18.0
MgCl ₂	8	95	100/95	8 × 100/95 = 8.42
CO ₂	30.0	44	100/44	30 × 100/44 = 68.18
HCl	9.2	36.5	100/(2 × 36.5)	9.2 × 100/73 = 12.6

$$\text{Equivalent weight of HCl} = 36.5$$

$$\text{Equivalent weight of CaCO}_3 = 50$$

$$\text{Multiplication factor} = \frac{50}{36.5} = \frac{100}{73}$$

$$\text{Lime required} = \frac{74}{100}$$

[Temp Ca²⁺ + 2 × Temp Mg²⁺ + Perm Mg²⁺ + CO₂ + HCl]

$$= \frac{74}{100} [15 + 2(10.7) + 8.42 + 68.18 + 12.6] \times 100,000 \times \frac{100}{90}$$

$$= 103.27 \text{ kg}$$

$$\begin{aligned}\text{Soda required} &= \frac{106}{100} [\text{Perm Ca}^{2+} + \text{Perm Mg}^{2+} + \text{HCl}] \\ &= [18 + 8.42 + 12.6 - 17.6] \\ &= 39.02 \text{ kg}\end{aligned}$$

For 1 million litres of water 95% pure soda required

$$\begin{aligned}&= \frac{100}{95} \times 39.02 \times 10^6 \text{ mg} \\ &= 41.07 \text{ kg.}\end{aligned}$$

Additional problems based on lime soda process

- (1) Calculate amount of lime and soda required for softening of 50,000 litres of water containing following salts. (Purity of lime = 95% and soda = 93%)
 $\text{CaCO}_3 = 34.1 \text{ mg/lit}$, $\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ mg/lit}$, $\text{Mg}(\text{NO}_3)_2 = 29.6$,
 $\text{MgSO}_4 = 36.0 \text{ ms/lit}$, $\text{CaSO}_4 = 27.2 \text{ mg/lit}$, $\text{MgCl}_2 = 47.5 \text{ mg/lit}$, $\text{SiO}_2 = 105 \text{ mg/lit}$,
 $\text{NaCl} = 52 \text{ mg/lit}$, $\text{H}_2\text{SO}_4 = 9.8 \text{ mg/lit}$.

Calculations for CaCO_3 equivalents:

Impurity	Amount	Mol.wt.	$\text{CaCO}_3 \text{ equts.} = \frac{\text{Amt} \times 100}{\text{Mol.wt}}$
CaCO_3	35.0	100	35
$\text{Mg}(\text{HCO}_3)_2$	29.2	146	20
$\text{Mg}(\text{NO}_3)_2$	29.6	148	20
MgSO_4	36.0	120	30
CaSO_4	27.2	136	20
H_2SO_4	9.8	98	10
SiO_2	}		
NaCl			

$$\text{Amt. of lime required} = \frac{74}{100} [\text{Temp Ca}^{+2} + 2 \times \text{Temp Mg}^{+2} +$$

$$\text{Perm Mg} + \text{H}_2\text{SO}_4] \times 50,000 \times \frac{1}{10^6} \times \frac{100}{95}$$

$$= \frac{74}{100} [35 + 2 \times 20 + 100 + 10] 50,000 \times \frac{1}{10^6} \times \frac{100}{95}$$

$$= 7.205 \text{ kg}$$

$$\text{Soda required} = \frac{106}{100} [\text{Perm}(\text{Ca} + \text{Mg}) + \text{H}_2\text{SO}_4 \times 50,000 \times \frac{1}{10^6} \times \frac{100}{93}]$$

$$= \frac{106}{100} [20 + 100 + 10] \times 50,000 \times \frac{1}{10^6} \times \frac{100}{93}$$

$$= 7.408 \text{ kg}$$

- (2) Calculate amount of lime and soda required for softening of 20,000 litres of water containing following salts in ppm. $\text{CaSO}_4 = 13.6$, $\text{Ca}(\text{HCO}_3)_2 = 16.2$, $\text{MgCO}_3 = 16.8$, $\text{HCl} = 36.5$, $\text{AlCl}_3 = 13.5$, $\text{KCl} = 5.1$

Calculations for CaCO_3 equivalents.

Impurity	Amount	Mol.wt.	CaCO_3 equts
CaSO_4	13.6	136	10
MgCO_3	16.8	84	20
AlCl_3	13.3	133.5	10
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	10
HCl	3.65	36.5	10
KCl	5.1	Do not contribute hardness.	
Reaction \rightarrow	$2 \text{AlCl}_3 + 3 \text{Ca}(\text{OH})_2 \rightarrow 2 \text{Al}(\text{OH})_3 \downarrow + 3 \text{CaCl}_2$		

$$\begin{aligned} \text{Amount of lime required} &= \frac{74}{100} [\text{Temp Ca} + 2 (\text{Temp Mg}) + \text{Perm } 1.5 \text{ Al} + 1/2 \text{ HCl}] \\ &\times 20,000 \times \frac{1}{10^6} \\ &= \frac{74}{100} [10 + 2 \times 20 + 1.5 \times 10 + 1/2 \times 10] \times 20,000 \times \\ &\frac{1}{10^6} = 1.036 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Amount of soda required} &= \frac{106}{100} [\text{Perm Ca} + \text{Perm } (1.5 \text{ Al}) + 1/2 \text{ HCl}] \\ &\times 20,000 \times \frac{1}{10^6} \\ &= \frac{106}{100} [10 + 1.5 \times 10 + 1/2 \times 10] \times 20,000 \times \frac{1}{10^6} \\ &= 0.636 \text{ kg} \end{aligned}$$

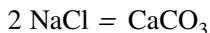
2.21.3 Zeolite

1. 1000 litres of hard H_2O is softened by zeolite process. The zeolite was regenerated by passing 20 litres of sodium chloride solution containing 1500 mg/lit. of NaCl. Calculate hardness of H_2O .

Solution:

20 litres of NaCl contain = $1.5 \times 20 = 30$ gm of NaCl

We have to convert it in terms of CaCO_3 equivalent.



$$2 \times 58.5 \text{ gm} = 100 \text{ gm}$$

$$58.5 = 50 \text{ gm}$$

Thus, 30 gm of NaCl equivalent to $30 \times \frac{50}{58.5}$ gm of CaCO_3

10,000 litres of H_2O contains $30 \times \frac{50}{58.5}$ gm of NaCl as CaCO_3

1 litre of H_2O contains $\frac{30}{1000} \times \frac{50}{58.5}$ gm of NaCl as CaCO_3

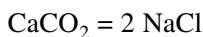
Thus, 1 litre water contains = $\frac{30}{1000} \times \frac{50}{58.5} \times 1000$ mg of NaCl as CaCO_3
 = 25.64 mg 1 litres or ppm

2. By passing 50 litres of NaCl solution containing 250 gm/litre of NaCl, a exhaust zeolite softener bed was regenerated. Calculate the litres of hard H_2O sample (hardness equal to 200 ppm as CaCO_3) which can be softened by regenerated bed of zeolite softener.

Solution:

First, we have to calculate total NaCl in terms of CaCO_3 equivalent, used for the regeneration of zeolite.

50 litres of NaCl solution contain = $50 \times 250 = 12,500$ gm of NaCl as



$$100 = 2(58.5)$$

$$50 = 58.5$$

\therefore CaCO_3 equivalent would be = $12,500 \times \frac{50}{58.5}$ gm

As the hardness is 200 ppm, i.e., 200 mg/lit. of CaCO_3 of 0.2 gm/lit. of CaCO_3 are present.

\therefore $12500 \times \frac{50}{58.5}$ gm will be present in

$$\frac{1200 \times 50}{0.2 \times 58.5} = 53,418.80 \text{ lit. of water.}$$

The zeolite bed can soften 53,418.80 lit. of H_2O .

3. An exhausted zeolite softener was regenerated by passing 100 litres, of NaCl. Solution containing 150 gm per lit. of NaCl. How many lit. of a sample of H₂O of hardness 300 ppm can be softened by this softener? (Given at wts. for C = 12, O = 16, Na = 23, Cl = 35.5, Ca = 40)

Solution:

150 lit. of NaCl solution contains (100 × 150) i.e. 15000 gm of NaCl (2 × 58.5) gm NaCl required by a hardness of 100 gm CaCO₃.

$$\therefore 15,000 \text{ gm NaCl required by a hardness of } \frac{100 \times 15,000}{2 \times 58.5} \text{ gm CaCO}_3$$

If 'X' lit. of hard water is softened by the zeolite softener. Then amount of

$$\text{CaCO}_3, \text{ present} = (300 \times 'X') \text{ mg} = \left(\frac{300 \times X}{1000} \right) \text{ gm}$$

$$\therefore = \frac{100 \times 15,000}{2 \times 58.5}$$

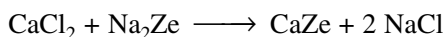
$$\therefore X = \frac{100 \times 15,000}{58.5} \text{ lit.} = 25,641 \text{ lit.}$$

\therefore The softener can soften 25,641 lit. of hard H₂O.

4. A hard H₂O sample containing 4.5 gm/lit. of CaCl₂ is passed through a permutit softener, what is the amount of NaCl present per lit. of the soft H₂O? (at wts. Na = 23, Cl = 35.5, Ca = 40)

Solution:

The softening reaction is,



Mol. wt. of

$$\text{CaCl}_2 = 40 + (2 \times 35.5) = 111$$

$$\text{NaCl} = 23 + 35.5 = 58.5$$

\therefore 111 gm CaCl₂ leaves 2 × 58.5 gm. NaCl in soft water.

$$\therefore 4.5 \text{ gm CaCl}_2 \text{ leave } \left(\frac{2 \times 58.50}{111} \times 4.5 \right) \text{ gm NaCl} = 4.7 \text{ gm/lit. of NaCl.}$$

Thus, the soft water will contain 4.7 gm/lit. of NaCl.

5. How many litres of 10% Brine solution will be required to regenerate an exhausted zeolite bed after softening of 10 litres of hard water of 750 ppm hardness.

Solution:

Hardness of water 750 ppm

Total quantity 10 litres = 750 × 10

= 7500 mg of CaCO_3 equivalent.

NaCl used is 10%, i.e., 10 gm/100 ml of 100 gm/1000 ml

58.5 g NaCl = 50 gm CaCO_3

$$\therefore 100 \text{ gm NaCl} = \frac{100 \times 50}{58.5}$$

$$= \frac{5000}{58.5} = 85.47 \text{ gm/lit.}$$

$$= 85.47 \text{ mg/ml}$$

85.47 mg CaCO_3 equivalent \longrightarrow one ml of NaCl

$$\therefore 7500 \text{ mg } \text{CaCO}_3 \text{ equivalent} \longrightarrow \frac{7500}{85.47}$$

$$= 87.75 \text{ ml of NaCl}$$

\therefore Volume of NaCl required = 87.75 ml

6. Hardness of 77500 litres of water was completely removed by zeolite method. The exhausted zeolite softener then required 15 litres of NaCl (2%). For regeneration calculate hardness of water sample.

Solution:

1 litre of NaCl contains = 20 gm of NaCl

\therefore 15 litres of NaCl contains = $20 \times 15 = 300$ gm of NaCl

Now 58.5 gm NaCl = 50 gm of CaCO_3 equivalent

$$\therefore 300 \text{ gm NaCl} = \frac{300 \times 50}{58.5}$$

$$= 256.41 \text{ gm}$$

Total quantity of water = 77,500 litres

77,500 litres of water = 256.41 gm CaCO_3 emits

1 litre of water = 0.0033 gm = 3.30 ppm

Hardness of water = 3.30 ppm

QUESTIONS

1. Define soft and hard water.
2. What are temporary hardness and permanent hardness?
3. Distinguish between soft and hard water.
4. Distinguish between temporary and permanent hardness.
5. What is the principle involved in the estimation of hardness of water by EDTA titration method?

6. Why water is required to be softened? Mention the methods available for softening.
7. What are zeolites? Discuss the zeolite process of softening of hard water.
8. Explain in detail the demineralisation process. State advantages and disadvantages.
9. Give the comparison between ion exchange process and zeolite process.
10. Describe the process of lime-soda method of softening of water. Mention its advantages and disadvantages.
11. Explain with the help of chemical reactions the principle of softening of water by lime-soda process.
12. What is reverse osmosis? Explain it in detail.
13. What is ultrafiltration? Write its industrial applications.
14. What are the different methods to determine extent of water pollution? Explain anyone in detail.
15. Write notes on:
 - (i) BOD (ii) COD
 - (iii) Effect of hard water in the manufacturing sector.
16. What are the different methods to control water pollution. Explain activated sludge method in detail.
17. Describe the recycling issues in detail.

NUMERICAL PROBLEMS FOR PRACTICE

1. Calculate the hardness of a water sample whose 100 ml required 20 ml EDTA 20 ml of calcium chloride solution (whose strength is equivalent to 4.5 gm of calcium carbonate per litre) required 30 ml of the same EDTA.
(Ans. 600 ppm)
2. 0.5 gm of CaCO_3 are dissolved in dilute HCl and diluted to 500 ml, 25 ml of this solution required 24.0 ml of EDTA using Eriochrom black T indicator. 50 ml of a hard water sample required 22.5 ml of the same EDTA. 100 ml of the water sample after boiling required 12.0 ml of the said EDTA. Calculate the hardness in the sample.

[Total hardness = 468.75 ppm, Permanent hardness = 125 ppm]

3. Calculate the quantity of lime and soda required for softening one million litre of the following sample of water. If the purities of lime and soda are 80% and 85% respectively. The impurities are

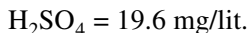
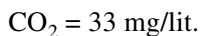
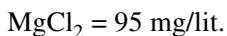
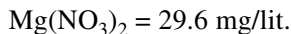
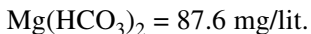
Silica = 75 mg/litre $\text{MgCl}_2 = 19$ mg/lit.

$\text{MgSO}_4 = 30$ mg/lit. $\text{CaSO}_4 = 68$ mg/lit.

$\text{MgCO}_3 = 884$ mg/lit. $\text{CaCO}_3 = 120$ mg/lit.

[Lime = 337 kg, Soda = 118.847 kg]

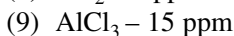
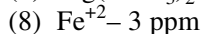
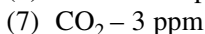
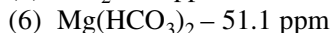
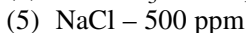
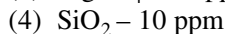
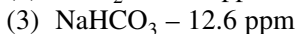
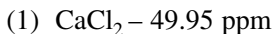
4. Calculate the quantity of lime and soda required for softening one million litres of hard water which on analysis was found to contain the following impurities.



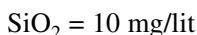
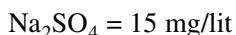
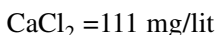
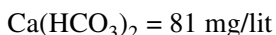
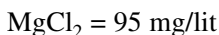
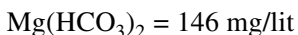
[Lime = 247.9 kg Soda = 127.2 kg]

5. A sample of water has hardness 304 ppm CaCO_3 equivalent. Find the hardness in terms of degree clark, degree French and mg/lit.
6. Calculate the quantities of lime (85% pure) and soda (95% pure) for softening one million litres of water if it has analysis as follows:

(Dec. 2006)



7. Calculate lime (90% pure) and soda ash (90% pure) to soften 1,00,000 litres of water containing:



8. 50 ml of standard hard water (1.2 g CaCO_3 /lit) requires 32 ml of EDTA solution. 100 ml of water sample consumes 14 ml EDTA solution. 100 ml of boiled and filtered water sample consumes 8.5 ml EDTA solution. Calculate temporary hardness of this sample from above experimental data.
9. Calculate quantity of lime (90% Pure) and Soda (95% Pure) required for softening of one million litres of water containing $\text{CaCO}_3 = 140$ ppm, $\text{CaSO}_4 = 136$ ppm, $\text{MgCO}_3 = 8.4$ ppm, $\text{MgSO}_4 = 60$ ppm, $\text{MgCl}_2 = 38$ ppm, $\text{SiO}_2 = 25$ ppm.

(Ans. 180.9 kg lime, 178.5 kg)

10. A sample of water was found to contain following impurities in mg/lit $\text{Mg}(\text{HCO}_3)_2 = 7.3$ mg, $\text{CaCl}_2 = 22.2$ mg, $\text{HCl} = 3.65$ mg, $\text{H}_2\text{SO}_4 = 9.8$ mg, $\text{Ca}(\text{NO}_3)_2 = 16.4$ mg, $\text{MgSO}_4 = 12.0$ mg, $\text{FeSO}_4 = 15.2$ mg, $\text{Al}_2(\text{SO}_4)_3 = 340$ mg
Calculate amount of lime and soda required for softening of 10,000 litres of water.

MUMBAI UNIVERSITY QUESTIONS

May 2004

- What are advantages of hot limesoda process? (2)
- Explain boiler corrosion. (5)
- Explain ion exchange resins for softening of water. (4)

- Explain phosphate conditioning as an internal treatment method. (3)
- Explain caustic embrittlement in boilers. (6)

Dec. 2004

- Explain the theory of limesoda process with special reference to the different functions of lime and soda. (6)
- What is the degree of hardness in water? How is it expressed? (2)
- What are scales and sludges? What are their disadvantages? How scales can be prevented by phosphate conditioning? (6)
- What are zeolites? Explain theory, procedure and limitations of zeolite process with the help of neat diagram. (6)

May 2005

- Why hydrazing is preferred over $\text{Na}_2\text{S}, \text{Na}_2\text{SO}_3$? (2)
- How dimineralisation of water is carried out? (7)
- Draw labelled diagram of hot lime-soda process and give only advantages of the method. (6)

Dec. 2005

- Name the indicator used in EDTA titration. What is the colour change at the end point titration? (3)
- Explain reactions of lime and soda used for softening. (6)
- Give an account of phosphate conditioning. (4)

May 2006

- What are zeolites? Explain the zeolite process of softening of water. (6)
- Write short notes on (i) caustic embrittlement (ii) phosphate conditioning. (6)
- What is hardness of water? Distinguish between alkaline and non-alkaline hardness of water. (4)

Dec. 2006

- How hardness of water is determined by EDTA method? Explain with the help of following points.

(i) Principle	(ii) Chemical reactions
(iii) Structure	(iv) Calculations

 (9)
- Distinguish clearly between scale and sludge. (3)
- Write short note on BOD and COD. (4)
- What is pollution? Name the primary pollutants. (3)
- Write note on caustic embrittlement. (3)

May 2007

- Explain boiler corrosion due to dissolved oxygen? How it can be prevented. (3)
- What is demineralisation? Explain with reference to

(i) Principle	(ii) Ingradient used
(iii) Chemical equations	(iv) Advantages and disadvantages
- Explain BOD and COD stating its applications. (5)
- Explain principle and reactions involved in limesoda method for softening of water. (5)

Dec 2007

- What do you mean by hardness of water? Distinguish between alkaline and non-alkaline hardness of water. (2)
- Explain theory of lime-soda process with reference to the different reactions. (5)
- Explain the terms with significance, BOD and COD. (3)
- 800 litres of raw water was softer by zeolite softener. After it got exhausted, required 40 litres of NaCl solution containing 110 gm per litres of NaCl for its regeneration. Calculate the hardness of water. (4)
- Calculate lime (90%) pure and soda (95%) pure required for softening of 20000 litres of water containing following impurities:

(i) $\text{Ca}(\text{HCO}_3)_2 = 81$ mg per litre
(ii) $\text{MgCO}_3 = 42$ mg per litre
(iii) $\text{NaAlO}_2 = 4.1$ mg per litre
(iv) $\text{HCl} = 3.65$ mg per litre
(v) $\text{Ca}(\text{NO}_3)_2 = 82$ mg per litre
(iv) $\text{NaCl} = 4.5$ mg per litre

(At Wt. Ca = 40, H = 1, C = 12, O = 16, Mg = 24, Na = 23, Al = 27, Cl = 35.5, N = 14) (5)

May 2008

- Explain theory, procedure and limitations of zeolite process. (6)
- Explain carbonate and noncarbonate hardness. (3)
- Give brief account of reverse osmosis. (3)
- Write note on activated sludge process. (5)
- A water sample contains:

(i) $\text{Ca}(\text{HCO}_3)_2 = 32.4$ mg/L
(ii) $\text{Mg}(\text{HCO}_3)_2 = 29.2$ mg/L
(iii) $\text{CaSO}_4 = 13.5$ mg/L

- 0.5 gm of CaCO_3 was dissolved in HCl and the solution made upto 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water. (5)

Dec. 2009

- Calculate temporary and total hardness of a water sample containing: $\text{Mg}(\text{HCO}_3)_2 = 7.3$ mg/L, $\text{Ca}(\text{HCO}_3)_2 = 16.2$ mg/L, $\text{mgCl}_2 = 9.5$ mg/L, $\text{CaSO}_4 = 13.6$ mg/L. (3)
- Calculate amount of lime and soda needed to soften 50,000 litres of water containing the following impurities per litres of water
 $\text{CaCl}_2 = 222$ mg, $\text{Mg}(\text{NO}_3)_2 = 296$ mg,
 $\text{Ca}(\text{HCO}_3)_2 = 324$ mg, $\text{H}_2\text{SO}_4 = 196$ mg and organic matter. (7)
- Explain the ion exchange process of softening of hard water. What are the advantages and disadvantages? (7)
- Name the different methods to control water pollution. Explain activated sludge method in detail. (8)
- What are the advantages and disadvantages of lime soda process? (5)