

1

Water Technology

Syllabus

Hard water – estimation of hardness by EDTA method – potable water- sterilization and disinfection – boiler feed water – boiler troubles – priming and foaming, scale formation, corrosion, caustic embrittlement, turbine deposits – softening of water – lime soda, zeolite processes – reverse osmosis – electro dialysis, ion exchange process.

Objectives

For prospective engineers, knowledge about water used in industries (boilers etc.) and for drinking purposes is useful. So chemistry of hard water, boiler troubles and modern methods of softening hard water is introduced.

At the conclusion of this unit, a student should able to:

1. Define hardness and know how to estimate the hardness
2. Know standards and specifications for the potable water and obtaining the same after sterilization and disinfection.
3. Know requirements for boiler feed water and about boiler troubles.
4. Understand the conventional and modern methods of processing of water for industrial and domestic use.

1.1 Introduction

Although the problem of water supply is one of the most important of the problems that we face, it continues to draw very little attention from most people because many things are taken for granted. When the engineer is called upon to select a site for the location of a factory, he is sometimes apt to consider all other factors except that of water supply. Yet, it may be a deciding factor in the working of a factory. In some cases, the water requirement is very great. For example, about 30 million litres of water are needed per 1,000 tonnes of steel produced and about half a million litres per tonne of paper and over one and a half lakh litres per automobile. It may be noted that the largest requirement of water is for municipal supply. Besides the quantity of water, the nature and amount of impurities present in the water are of no less importance. Therefore, in selecting a proper site for a factory the following factors have to be taken in to account regarding the water supply: 1. quality and quantity of water available, 2. effect of impurities on the process and 3. quantity of water needed.

Generally, the water available contains a wide range of impurities but only a few of them may affect a process, so one is concerned with the removal, or reduction of concentration of only the few impurities and the rest may be allowed to remain as such, e.g., bacteria, if present, need not be removed from water for use in boilers. It may be noted that the water supplied for a particular industry is generally not 'consumed' in the operation in the sense of the term as electricity is consumed in a process. Almost the total quantity of water appears in one form or another and the engineer has also to deal with the disposal or re-use of waste water. The nature of the impurities in the outgoing water may be such that it is not safe or wise to let it flow out in the river stream or into the sources of water supply. Thus, connected with the water supply is the problem of the disposal of the waste or sewage. Again, in the same industry, water for several purposes is needed, e.g., steam generation, cooling, general needs of the processes and plant services, and for each purpose the specifications may be different.

1.1.1 Sources of Water

Even *rain water*, which is the purest form of water found in nature, contains a considerable amount of dissolved gases and solids – both of organic and inorganic origin. Rain water either flows in to rivers or lakes and ultimately into the sea and is known as *surface water*, or it sinks underground and is available as well or spring water, when it is known as *underground water*. In general, the greater the contact that water has with the soil, or the more soluble the earthy matter with which it has come in contact, the greater is the amount of dissolved impurities. A sufficient quantity of flowing water of low hardness is available from many rivers. Even in any particular river the amount of dissolved mineral matter varies 2 to 3 times during the year. The amount of suspended and organic matter is still more variable. For cooling purposes, river water does not need any special treatment unless the amount of suspended matter is very great. Sometimes even *sea water*, in spite of its causing corrosion, can be used for cooling purposes. Sea water contains about 3.5 percent of dissolved salts, principally sodium chloride (2.7%), and magnesium chloride and sulphate (0.6%). It is an important source of these and other substances.

Lake water has a more constant chemical analysis and the seasonal changes can be predicted quite accurately. It is softer than well water and a big lake can be taken to be a

dependable source of water supply, but attention should be paid to the organic matter present. The quality of water of some of the big lakes is so good that hardly any treatment is needed for industrial uses.

Usually well water is still more constant in its composition. It is clear but contains more of dissolved matter and is harder than surface water. It is more suitable for human consumption because of clarity and freedom from organic matter, harmful bacteria, unpleasant taste and odour. Deep well water is cool and is available at a more constant temperature throughout the year but contains more of dissolved minerals. Usually it is of high organic purity.

1.1.2 The Common Impurities in Water

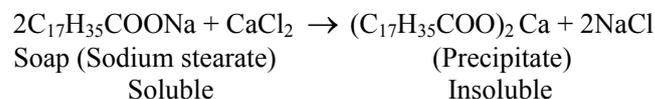
The common impurities present in natural waters may be classified as follows.

1. *Dissolved minerals* – mostly comprise of carbonates, bicarbonates, sulphates and chlorides of calcium, magnesium, sodium and potassium.
2. *Dissolved gases* – mostly air and carbon dioxide.
3. *Suspended matter* – mostly mineral matter, giving turbid or muddy water. Organic matter may also be present.
4. *Microscopic matter* – consists mostly of plant and bacterial life giving colour, taste and odour.

In general, the removal of impurities from water of classes 1, 2 and 3 form the chief problem for industrial usage, and 3 and 4 for municipal supplies.

1.2 Hardness and Causes

From the standpoint of an engineer the dissolved salts of calcium and magnesium are of special interest as they are responsible for some of the common and major boiler troubles and therefore will be considered in greater detail. A simple method of detecting these is by the use of soap (not detergent). **A sample of water that reacts with soap to form a white scum and does not produce lather is known as hard water.** *Soft water* lathers freely with soap. Calcium and magnesium salts are present mostly as bicarbonates, sulphates and also as chlorides. The difficulty in producing lather arises because of the fact that soaps are sodium and potassium salts of higher fatty acids and are soluble in water but when soap is used in water containing calcium and magnesium salts, insoluble soaps of calcium and magnesium are formed and precipitated, thus destroying the soap. A typical reaction may be illustrated as follows:



Such precipitates are not formed with the newer detergents, which are sulphonates of long chain alcohols. Titration of cold water will give total hardness of water sample when the water sample is boiled for 5 min; cooled to room temperature and titrated to the end point it will give the permanent hardness as temporary hardness is removed by boiling.

1.2.1 Types of Hardness

Calcium and magnesium salts are not the only salts that cause hardness. They are mentioned because they are most commonly present. *As a general rule, all soluble salts of heavy metals cause hardness because they form precipitates with soap.* The bicarbonates of calcium and magnesium are decomposed by boiling the water when carbonates are formed which are less soluble. Thus the hardness due to the bicarbonates can be removed by boiling. The hardness due to these salts is called **temporary hardness**. As magnesium carbonate is only partially precipitated, the term **carbonate hardness** is now used instead of temporary hardness. Sulphates and chlorides of calcium and magnesium are not removed by boiling and hardness due to these is called **permanent or non carbonate hardness**.

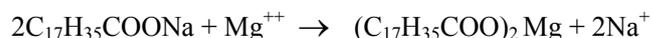
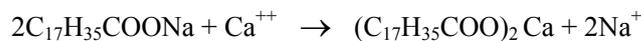
Temporary hardness is precipitated from water when heated and is responsible for the scaling of heating elements and metal pipes and therefore very bad in industrial point of view. Permanent hardness consists of non-carbonate base metal salts, and does not precipitate out of heating.

Carbonate/Temporary hardness is caused by a particular ratio of carbonate to bicarbonate with a certain buffering action in an aquarium or pond and prevents any pH changes, called "pH shock", to aquatic life and livestock. Permanent hardness on the contrary is bad for biota since it interferes with osmotic processes of biota and is not suitable to plants and fish

1.2.2 Estimation of Hardness

In a boiler house, the degree of hardness of feed water forms a simple and important guide to its suitability for boiler feed. Further knowledge of hardness of water helps in proper designing of engineering processes and structures. Two methods are popular in the estimation of hardness.

1. **Soap titration method:** This is a simple but somewhat qualitative method. In a simple test, usually performed for water to be used in a low pressure boiler, 70 ml of water is taken in a 300 ml bottle. A standard soap solution is added from a burette and the bottle is shaken. The volume of soap required to produce lather stable for 5 minutes is noted and hardness is calculated. It is an empirical method but after some experience fairly accurate results can be obtained. It is estimated that if about 2 kg of common soap is added to 100 litres of water of hardness 100 mg per litre it would get precipitated by the salts present in the water. Lather would be produced only if more than this amount of soap is used.



Soap (Sodium stearate)	(Precipitate)
Soluble	Insoluble

2. **EDTA method:** For more accurate results the soap method has been replaced by the complexometric method. This depends upon the fact that when ethylenediamine tetra acetic acid (abbreviated as EDTA) or its sodium salt solution is added to a solution containing certain metals, chelated and soluble complex is formed.

The choice of CaCO_3 in particular is due to its molecular weight being 100 and moreover, it is the most insoluble salt that can be precipitated in water treatment.

The equivalents of CaCO_3

$$= \frac{[\text{Mass of hardness producing substance}] \times [\text{Chemical equivalent of } \text{CaCO}_3]}{\text{Chemical equivalent of hardness producing substance}}$$

For example, 162 parts by weight of $\text{Ca}(\text{HCO}_3)_2$ would react with the same amount of soap as 100 parts by weight of CaCO_3 . Therefore, the weight of $\text{Ca}(\text{HCO}_3)_2$, is multiplied by $100/162$ to give weight in terms of CaCO_3 . Similarly, weights of CaSO_4 , CaCl_2 , MgSO_4 , $\text{Mg}(\text{HCO}_3)_2$ and MgCl_2 actually present are converted in terms of weight of CaCO_3 by multiplying x with

$$\frac{100}{136}, \frac{100}{111}, \frac{100}{120}, \frac{100}{146}; \text{ and } \frac{100}{95} \text{ respectively. } \left(x \times \frac{100}{\text{mol. wt of the compound}} \right)$$

The common unit of expression at present is in terms of parts of the hardness causing impurities in terms of weight of CaCO_3 per million parts (are particle parts) of water. For example, if 6 kg of MgSO_4 , are present in 100,000 kg of water, then in 1,000,000 kg of water 60 kg of it would be present. Therefore, the weight in terms of CaCO_3 , would be $60 \times \frac{100}{120} =$

50 kg. So, the hardness of this sample of water, is 50 parts per million parts of water, which is written as 50 ppm (parts per million). In the French system it is expressed in terms of parts per 100,000 parts. It is said to be **degree French** of °F (one part in 10^5 parts). In the English system, hardness is expressed in terms of grains (1/7000 lb) per gallon (10 lbs) of water, i.e., parts per 70,000 parts. This is also called **degree Clark**, e.g., 14° Clark means impurities equivalent to 14 grains in terms of CaCO_3 are present per gallon of water or 14 parts per 70,000 parts of water. Therefore on ppm scale it is $14 \times \frac{1,000,000}{70,000} = 200$ ppm

Units of hardness:

1. **Parts per million (ppm):** is the parts of calcium carbonate equivalent hardness per 10^6 parts of water i.e 1 ppm = 1 part of CaCO_3 eq. Hardness in 10^6 parts of water.

2. **Milligrams per litre (mg/L):** is the number of milligrams of CaCO_3 equivalent hardness present per litre of water. Thus

$$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq. Hardness of 1 lit of water}$$

$$\text{but } 1 \text{ lit of water weighs} = 1 \text{ kg} = 1,000 \text{ g} = 1000 \times 1000 \text{ mg} = 10^6 \text{ mg}$$

$$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq per } 10^6 \text{ mg of water}$$

$$= 1 \text{ part of } \text{CaCO}_3 \text{ eq. Per } 10^6 \text{ parts of water} = 1 \text{ ppm}$$

3. **Clarke's degree (Cl):** is number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water or it is parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus

$$1^\circ \text{ clarke} = 1 \text{ grain of } \text{CaCO}_3 \text{ eq. hardness per gallon of water}$$

$$1^\circ \text{ Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ eq. hardness per } 70,000 \text{ parts of water}$$

4. **Degree French (Fr):** is the parts of CaCO_3 equivalent hardness per 10^5 parts of water. Thus

$$1 \text{ Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ hardness eq per } 10^5 \text{ parts of water}$$

5. **Milliequivalent per litre (meq/L):** is the number of milli equivalents of hardness present per litre. Thus

$$\begin{aligned} 1 \text{ mg/L} &= 1 \text{ meq of } \text{CaCO}_3 \text{ per L of water} \\ &= 10^{-3} \times 50 \text{ gm of } \text{CaCO}_3 \text{ eq per litre} \\ &= 50 \text{ mg of } \text{CaCO}_3 \text{ eq per litre} \\ &= 50 \text{ mg/h of } \text{CaCO}_3 \text{ eq} = 50 \text{ ppm} \end{aligned}$$

interconversions

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1^\circ \text{ Fr} = 0.07^\circ \text{ Cl} = 0.02 \text{ meq/L}$$

$$1 \text{ mg/L} = 1 \text{ ppm} = 0.1^\circ \text{ Fr} = 0.07^\circ \text{ Cl} = 0.02 \text{ meq/L}$$

$$1^\circ \text{ Cl} = 1.433^\circ \text{ Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/L} = 0.286 \text{ meq/L}$$

$$1^\circ \text{ Fr} = 10 \text{ ppm} = 10 \text{ mg/L} = 0.7^\circ \text{ Cl} = 0.2 \text{ meq/L}$$

$$1 \text{ meq/L} = 50 \text{ mg/L} = 50 \text{ ppm} = 5^\circ \text{ Fr} = 0.35^\circ \text{ Cl}$$

1.3 Potable Water

Perhaps the most important problem of water technology that of municipal water supply, because if the water supplied to the cities and villages is not of the right kind, the results will be disastrous to human lives. The requirements for this purpose are very different from those of the industries. Municipalities have to supply **potable water**. i.e., *water which is safe and good to drink*. Potable water does not mean pure water. Distilled water, for example, is flat and tasteless. At the same time potability cannot be determined merely on the basis of its taste, odour and appearance. Water may have disease producing bacteria which cannot be detected by these means.

Briefly, water supplied by the municipalities should be free from disease-producing bacteria, suspended impurities and excess of dissolved salts or chemicals used for water treatment. It should be clear, colourless, odourless and pleasant to taste. A sample of clear water which has low dissolved salt content but has disease-producing bacteria can be used in a boiler, but would be unfit for drinking. On the other hand, a sample of clear water, free from bacteria, but containing a certain amount of dissolved salts may be unfit for boiler feed, yet fit to drink.

Municipalities draw their water from rivers, wells and lakes. Water so obtained contains dissolved matter which in most cases is harmless for drinking. In general, municipal water treatment is not directed towards removal of the dissolved salts present in water. Water, such as sea water which contains a large amount of dissolved matter is not commonly looked upon as a source of drinking water. But, as good quality water is not uniformly distributed on the surface of the earth, and demand for drinking water is increasing due to increase in population, a considerable amount of research is being done on *conversion of sea water* into drinking water. Some experimental plants, each producing over half a crore litres per day of

potable water from sea water, are functioning in the U S A. Two avenues of approach for obtaining potable water from sea water are distillation, and freezing out pure water as ice, leaving the salt in the mother liquor. Distillation is a well-known process but the salts present in sea water cause severe corrosion of the equipment. Freezing is more expensive but there is less corrosion and is likely to be successful in the cold climates.

The latest approach in converting sea water fit for drinking is the application of *reverse osmosis technique*. On account of low capital cost, low operating cost, reliability and simplicity of operation the reverse osmosis process is becoming the principal method for this purpose. Such plants have been mainly installed in the petroleum rich countries of the Middle East.

Municipalities in general do not soften the water. There are only a few municipalities in the world which partially soften the water because the water available to them is very hard.

The treatments more widely given include: 1. Sedimentation, 2. Filtration, and 3. Sterilization. See Fig. 1.1.

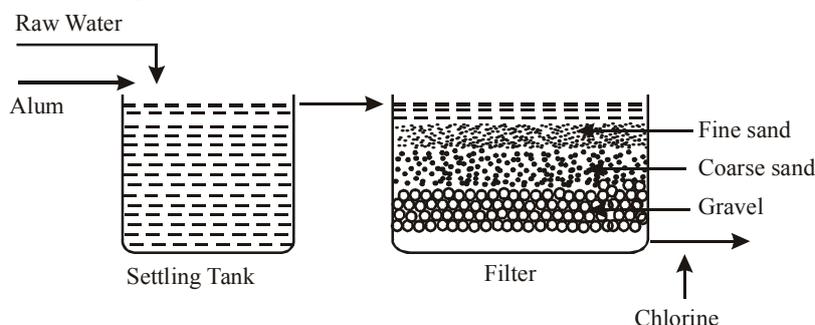


Fig. 1.1 Principle of municipal water treatment.

1.3.1 Sedimentation

Sedimentation means simple settling. It is the process by which the force of gravity acts on particles heavier than water and causes them to move downwards and settle. For this purpose water is kept in huge tanks, called sedimentation tanks (or basins) in which water moves very slowly. The basins have to be designed carefully so that the formation of eddy currents (which cause mixing) or straight channeling of water is avoided.

The time required for sedimentation depends upon the weight, size and shape of particles and the viscosity and frictional resistance of water. Because viscosity changes with temperature, the settling rate varies in different seasons. It has been calculated that the settling rate at 0° is only 45% of the rate at 30° . Consequently turbidity is more easily removed during summer than during winter. Water is kept in sedimentation tanks from 4 to 12 hours.

Finely divided suspended matter does not settle down easily. Generally, only 70% of the suspended matter settles down by plain sedimentation. For better clarification, chemical means have to be used. This is done by the addition of coagulants like alum,

ferrous sulphate, ferric chloride, sodium aluminate, etc. Each of these works best within a particular pH range and has a certain function in addition to clarification. Generally about 95% of the suspended matter is removed by coagulation.

Coagulation reactions are complicated but a simplified explanation can be that the salt hydrolyses and produces a floc of the hydroxide, e.g., $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. The flocculent precipitate so produced has an enormous surface area per unit volume. The floc removes the finely divided and colloidal matter by a variety of mechanisms, e.g., by adsorption, mechanical entanglement and electrical attraction of oppositely charged particles. Thus the smaller particles gather together to form bigger particles which quickly settle down. Some bacteria and colour are also removed. The dosage of the coagulant depends upon turbidity and may be 5 to 100 mg/l.

These years increasingly large quantities of *coagulant aids*, mostly polyelectrolytes, are being used. The polyelectrolytes are high molecular weight water soluble polymers. Some naturally occurring organic flocculants have been used. Polyacrylamides aid materially in the formation of rapidly settling flocs. Other organic polymeric materials which are strongly cationic have been used in place of aluminium or iron salts. These function through hydration. The true polyelectrolytes contain groups which undergo electrolytic dissociation giving highly charged large molecular weight ions which attract other charged particles and help coagulation. They may give anions, cations or may be non-ionic (i.e., provide both positive and negative charges in solution). Considerable research work is being done in this field but the mechanism of their activity has not been well understood.

Each coagulant gives best results in a pH range which is affected by the mineral characteristics of the water. For Example, in pure water, potash alum coagulates best at a pH of 5.5 but for most natural waters the range is 5.5 to 8.0. It should be noted that each ppm of added alum, consumes about 0.5 ppm of natural alkalinity thereby reducing the pH level. So lime or soda needs to be added. The presence of iron and manganese in water introduces additional factors affecting the choice and dosage of coagulant. It is therefore necessary that laboratory tests be made with different coagulants at varied pH levels and varied concentrations. Retention time of 2 to 6 hours is usually provided. Often coagulation can be combined with sedimentation followed by filtration. Potash alum and ferric alum are the most widely used coagulants.

1.3.2 Filtration

Filtration may be defined as 'the process of passing a liquid containing suspended matter through a suitable porous material in such a manner as to effectively remove the suspended matter from the liquid'. Generally, water is filtered after sedimentation and coagulation. In some cases where there is great shortage of space or the water is quite clear, it may be filtered directly thus saving large areas needed for the construction of sedimentation basins. Filtration is primarily a mechanical process. When water flows through a porous material many suspended particles are unable to pass through the interstices (or gaps) in the material because of their size. Thus these particles are removed and clarification takes place.

Filtration removes the suspended matter and to some extent bacteria. True colour is not removed by filtration. It can be removed by the use of coagulants.

Filters are of two types: (a) gravity filters and (b) pressure filters.

(a) *Gravity filters*. In these the water flows through the bed by gravity. These filters are of two types: (i) Slow sand filters and (ii) Rapid sand filters.

(i) *Slow sand filters* are still being used in India by many municipalities. They occupy large areas and the rate of filtration is slow. The filters are like large shallow tanks made of concrete. At the bottom there is an under-drain system through which the filtered water goes to the storage tank. Gravel is placed in the tank above the under-drain system. It consists of several layers of stone of sizes varying from 6 cm to 0.5 cm. On the gravel is placed a bed of coarse sand and above it a layer of fine sand is placed. See Fig. 1.11.

As water percolates through the filters, the suspended particles are retained on the top 5 to 10 cm layer of the fine sand. In fact, the layers of coarse sand and of gravel do not filter at all. They support the fine sand, the top layer of which retains the suspended matter. When the suspended matter has been deposited to such an extent that the rate of filtration becomes very slow, the portion of the top layer is scraped and the bed is used again. After continued use of the bed for a long time, it becomes necessary to replace the layer completely.

(ii) *Rapid sand filters* are coming into greater use primarily because their efficiency for filtration is many times that of slow sand filters, hence, they need much less space. The general arrangement of the sand bed is similar to that of slow sand filters, the distinguishing feature being the backwash system. The chief reason for a slow rate of filtration through the slow sand filter is that as the suspended matter is deposited, the gaps between the sand particles get filled up and the flow is restricted. To overcome this difficulty, the rapid sand filters are provided with backwash system. After filtering for some time the filtration is stopped and a portion of filtered water is *sent up* through the bed. This removes the suspended particles deposited in the pores and cleans the bed. When the suspended matter has been removed, the wash water supply is stopped and the filter bed which is as clean as a freshly made bed, is again ready for filtration. The cycle of filtration and washing is repeated. Thus high filter rates are obtained. The wash water is discarded. The rate of filtration may be 30 times that of the rate of filtration through slow sand filters.

(b) *Pressure filters* have essentially the same arrangement of the filter media as gravity filters. The filter material is kept in a closed cylinder and water is forced through the filter bed under pressure. Pressure filters can be installed in the water supply line, thus repumping of filtered water is avoided. As these are enclosed, they are more suitable for filtering hot water. If hot water is filtered through gravity filters, there is more loss of heat. The pressure filters occupy much less space than the other types of filters. Because of these advantages pressure filters are widely used for industrial water conditioning.

1.3.3 Sterilization and Disinfection

After filtration it becomes necessary to destroy or make inactive the residual bacteria and to prevent their further growth. This is achieved by sterilization and disinfection.

Sterilization is a term referring to any process that eliminates (removes) or kills all forms of microbial life, including fungi, viruses and bacterial spore present on a surface or contained in a fluid. Sterilization can be achieved by applying heat, chemicals, irradiation, high pressure, and filtration or combinations thereof.

Disinfection is the process of elimination of most pathogenic microorganisms (*excluding bacterial spores*) on inanimate objects. Disinfection can be achieved by physical or chemical methods. Chemicals used in disinfection are called disinfectants. Different disinfectants have different target ranges, not all disinfectants can kill all microorganisms. Some methods of disinfection such as filtration do not kill bacteria, they separate them out.

Sterilization is an absolute condition while disinfection is not. The two are not synonymous.

Often ground water is free from disease-producing bacteria but the surface water, which is the main source of municipal water supply, is likely to be contaminated, especially because of the discharge of sewage into streams. Some epidemics, like cholera, plague and also typhoid can be controlled by taking better care of drinking water.

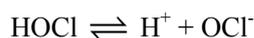
Chlorination is mainly used for killing disease-producing organisms. Further, it reduces (or may even remove) objectionable tastes and odours from drinking water, and oxidizes iron, manganese and hydrogen sulphide, and thereby help their removal. It also causes oxidation, decolourization and destruction of organic matter. Because of wide range of action chlorine, besides its use in water treatment, is injected into sewage and industrial waste before being discharged into streams. In such cases it causes reduction in bacteria, destruction of chemicals that may react with oxygen, such as sulphides, sulphites, ferrous ions, etc. It helps coagulation by destroying organic matter, hence the practice of pre-chlorination. In water used for food processing industries chlorine should be used cautiously. It may spoil the flavour and even corrode the metal container.

Small volumes of water can be sterilized by boiling. For larger volumes chlorine is very widely used.

Bleaching powder is convenient for use on smaller scales. Its disinfecting action is due to the chlorine made available by it. When the chlorine requirement is over about 10 kg per day, it is more economical to use chlorine gas. The reactions of chlorine and water can be represented thus.



At higher pH values hypochlorous acid ionizes thus:



Earlier it was believed that the disinfecting properties of chlorine were due to the nascent oxygen liberated, which oxidizes harmful matter. More recent work has shown that the HOCl molecules (not hypochlorite ion, OCl⁻) combine with an enzyme in the cells of the organisms

and thereby destroy the organisms. Therefore, **chlorine is more effective as a disinfectant at lower pH values (below 6.5)**. A part of the chlorine added is used in combining with or oxidizing some of the impurities. The amount of chlorine added is generally such that about 0.2 mg/L of chlorine is left behind after the reactions.

If the water is exposed to the atmosphere, especially to sunlight, chlorine is dissipated quickly. In order to overcome this disadvantage, ammonia may be added along with the chlorine when chloramines like NH_2Cl and NHCl_2 , are formed. These are not as active as chlorine but are not so easily removed, and are more desirable when water is to be distributed over long distances.

Chloramines require higher concentrations and longer contact time for comparable bacterial reduction. Chloramine tablets are used by the army for sterilizing water. Water is collected in the bottles and chloramine tablets are added followed by sodium thiosulphate tablets which remove excess, of chlorine.

Break point chlorination is a specialized method of chlorination applied to highly polluted water and for the removal of ammonia. In the beginning as chlorine is added to such samples of water there is a proportionate increase in the amount of residual chlorine as is indicated in the Fig. 1.2. Ammonia is converted to monochloramine and then to dichloramine. Further chlorination gives trichloramine or oxidizes ammonia to free nitrogen. At this stage there is a marked decline in the residual chlorine but further addition of chlorine gives a proportionate increase of free available chlorine. Because of the peculiar character of the curve obtained on such chlorination, this practice is known as “break point chlorination”.

Besides its use in the removal of organic matter from highly polluted water, break point chlorination is useful in removing ammonia from boiler feed water.

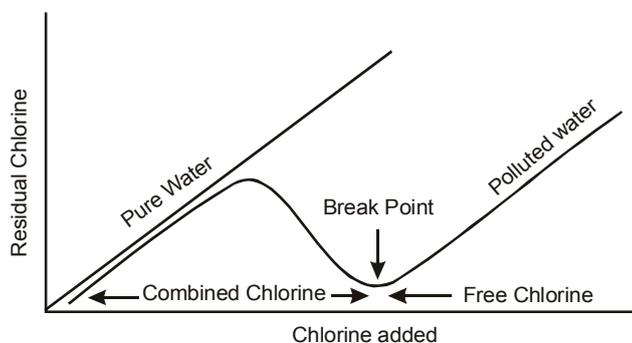


Fig. 1.2 Break point chlorination.

Disinfecting agents other than chlorine are also used. The use of ozone for disinfection has been suggested. It is expensive, hence is only used on a small scale. Bromine has been used in swimming pools. Silver iodide, in soluble form, is a good disinfectant but it is also expensive. In World War II pellets of silver iodide were used by the armed forces. Exposure of clear water to ultra violet rays also destroys the bacteria. None of these methods are adopted for disinfection on a wide scale.

In India well water is still used to a considerable extent. This can be disinfected by adding potassium permanganate solution to the well. Chlorine can also be added.

1.3.4 IS specifications of potable water

Many developed countries specify standards to be applied in their own country. In Europe, this includes the European Drinking Water Directive and in the USA the United States Environmental Protection Agency (EPA) establishes standards as required by the Safe Drinking Water Act. For countries without a legislative or administrative framework for such standards, the World Health Organisation (*WHO*) publishes guidelines on the standards that should be achieved. India has **Indian Standard specifications** for drinking water **IS: 10500**. According to these standards, desirable limits in brief, are

1. Colour 5 hazen units and may be extended up to 50 if toxic substances are suspected
2. Turbidity 10 NTU units and may be relaxed up to 25 in the absence of alternate
3. pH 6.5 to 8.5 and may be relaxed up to 9.2 in the absence of alternate
4. Total hardness 300ppm and may be extended up to 600 in the absence of alternate

1.4 Water for Industries

Although the manufacturing industries need water for a variety of purposes the largest demand for water is for heat transfer. Water is the usual medium for extracting heat. Boilers, cooling towers, heat exchangers, condensers, coolers, refrigerators and air conditioning equipment illustrate the use of water for heat extraction. It is estimated that the large thermal power stations require 800 tons of water per ton of coal consumed.

Water is a *raw material* when it becomes a part of the product as in the beverage industry and some of the chemical industries. In a few cases it is a *reactant* as in the manufacture of acetylene from calcium carbide. Water being the cheapest liquid available is used widely for cleaning and washing in the homes as well as in industry. One is not conscious of its uses in *material handling*, in the pumping of materials like coal in the form of slurry for many kilometers. Harmful effluents from industries are *diluted* by large quantities of water. High pressure water jets for cleaning metal parts or the removal of bark from logs of wood illustrate the use of water for kinetic energy. Since water does not yield radio activities when exposed to neutron flux, it is used for *nuclear shielding*, or as a moderator in nuclear energy reactors.

It is obvious from the above examples that not only the quantity but also the quality of water needed for different uses vary widely. The high pressure boilers require water of very high purity for steam making necessitating very careful and elaborate treatment whereas for ordinary washing no treatment, other than simple settling for highly turbid water is needed.

As it is not possible in a small monograph to discuss the requirements of each industry separately, the treatment of water for steam making has been taken up by way of illustration showing how almost absolutely pure water can be obtained from the sea. Where the requirement is not that stringent the treatment may not be carried out to eliminate all the impurities.

1.4.1 Water for Steam Making, Boiler feed water

In water tube boilers steam is generated on the surface of the tubes which are heated by the hot gases and the flames produced by the combustion of the fuel. The steam travels through the tubes and is delivered to the boiler drums. At this stage the steam is mixed with the boiler water, foam and sludge. The problem of the production of clean-dry steam has been investigated by engineers for the last few decades. In recent times this has become a still more serious problem because boilers working at much higher pressures are being used. Therefore, all the boilers are provided with suspended particle separators, i.e., devices for separating steam from the liquid and the solid particles. This equipment provides purification mainly by changing the direction of steam whereby the heavier particles, i.e., the liquid and the suspended matter, drop out. As a matter of fact, more heat is added to steam so that *superheated* steam is obtained. The properties of superheated steam are almost those of a perfect gas, hence it does better work in steam engines and turbines and the steam consumption is lower. Super heated steam being at higher temperature does not have the problem due to the condensation of water in the pipelines, engines, etc., and so dry steam can be supplied over longer distances.

In water treatment complete elimination of all the impurities is not aimed at. Only those impurities which give rise to certain troubles are eliminated or kept within certain limits. In the modern high pressure boilers water purer than the distilled water used in laboratories has to be supplied. The major boiler troubles, due to the use of unsuitable water, may be classified as 1. Carry over, 2. Corrosion, 3. Scale formation, 4. Caustic embrittlement and 5. Turbine deposits. The total destruction of several large power houses has ultimately been traced to the use of unsuitable water which caused explosion of the boilers.

The maximum permissible hardness of water for boilers operating at different pressures is as follows :

at	0 to 10 kg/cm ²	80 ppm
at	10 to 15 kg/cm ²	40 ppm
at	15 to 30 kg/cm ²	10 ppm
	over 30 kg/cm ²	2 ppm

1.5 Boiler Troubles

Usage of hard water leads to many boiler troubles and heavy industrial losses due to its mal function.

1.5.1 Carry over – priming and foaming

As steam emerges from the surface of the water, it is associated with tiny droplets of water. Such steam is called *wet steam*. The droplets may carry with them suspended matter, besides the dissolved matter present in the boiler water. Such carrying over of water by steam along with the suspended and the dissolved solids is called *carry over*. It is mainly due to priming and foaming.

The liquid contamination in the steam is expressed in percentage, by weight, of the total mixture and is called *steam quality*. If steam contains 0.3 per cent moisture steam quality is 99.7 percent. The impurity due to solids is represented by *steam purity* and is expressed in parts per million (ppm) or milligrams per litre (mg/l) of impurity. If steam contains 1 part by weight (or 1 mg) of solid contamination per million parts by weight of steam (or per litre of water), steam purity is 1 ppm (or 1 mg/l).

Priming is such rapid or violent boiling of water occurring in the boiler that water is carried into the steam outlet in the form of a spray. It may be caused by 1. very higher water level; 2. presence of excessive foam filling the steam space; 3. high steam velocity; 4. sudden steam demand leading to sudden boiling and 5. faulty boiler design.

Control of priming is fundamentally a problem of boiler design. It is controlled by providing proper evaporation and adequate heating surfaces, uniform distribution of fire and of working load, providing anti-priming pipes or dash plates, etc. In a given boiler priming can be minimized by 1. keeping the water level as low as it can safely be kept. Even a slight lowering of the water level greatly reduces priming; 2. avoiding sudden steam demands (by suddenly taking out a quantity of steam the pressure in the boiler is reduced, thus the boiling point of water is lowered and the superheated water is suddenly converted into steam); and 3. minimizing foaming.

Foaming is the formation of small but stable bubbles above the surface of water. It becomes a serious problem when the bubbles are persistent, i.e., do not break easily. These bubbles are carried over along with steam, leading to excessive priming.

Foam formation takes place when the concentration of solids in the surface layer is different from that in the mass of the liquid. This means that the solid must alter (whether increase or decrease) markedly the surface tension. Therefore all those solids which alter markedly the surface tension of water promote foaming. Presence of fatty oil is highly undesirable as it may form soap with the alkalinity. Soaps greatly reduce surface tension of water.

Pure water has little tendency to foam but almost all the impurities cause foaming, especially the dissolved impurities like soap, which reduce the surface tension of water. It may be noted that as the steam is being generated the concentration of the dissolved impurities, especially of sodium and potassium salts is increasing. The general construction of locomotive boilers is such that these have foaming more easily than the stationary boilers have.

To a certain extent foaming can be controlled by the use of anti-foaming chemicals, some of which act by counteracting the reduction in surface tension, and some by mechanical action, like castor oil which spreads on the surface of the water. Castor oil may be used for low pressure boilers. The only satisfactory remedy for foaming is *blow down*, i.e., removal of concentrated boiler water and replacing it by fresh feed water.

Dissolved solids, suspended solids and alkalinity affect carry over. It is believed that, in general, the suspended solids are more responsible for carry over than the dissolved solids. Carry over is undesirable because it not only decreases the efficiency but also results in some practical difficulties in the successful operation of a boiler. Some of these are: 1. a

considerable amount of heat is wasted by the removal of hot boiler water; 2. water reduces superheat of steam in the super heaters; 3. water takes along with it grit which impinges on the surface at high velocity, and damages the walls of the cylinders and valve seats; 4. water contains considerable amount of dissolved solids which gradually get deposited and the deposits restrict the passage in the pipelines, causing corrosion and insulation; 5. water entering the steam engine cylinder causes serious trouble because of its incompressibility and inability to escape quickly through the steam ports; 6. foaming of water makes it difficult to know the exact level of water in the gauge glass.

1.6 Corrosion and Hardness

Corrosion is one of the most serious problems caused by the use of unsuitable water. Boiler tubes, drums, economizers, super heaters and condensers are the most affected parts. The corrosion problem extends even to parts which are not directly in contact with boiler water because gases like oxygen and carbon dioxide are released during heating of water. These gases have corrosive effects. Corrosion can be attributed to the following (i) dissolved oxygen; (ii) mineral acids; (iii) dissolved carbon dioxide and (iv) galvanic cell formation.

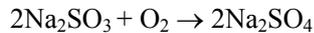
(i) *Dissolved Oxygen*

Oxygen dissolved in water is mainly responsible for corrosion in boilers. Dissolved oxygen in the presence of moisture and at the high temperature prevailing in the boiler readily attacks iron. The higher the pressure, the greater will be the dissolved oxygen content, and the higher the temperature the lesser the oxygen content. The amount of oxygen dissolved is also influenced by the other dissolved matter present. The solubility of oxygen in pure water is greater than in water containing other dissolved matter. In a boiler, oxygen is introduced through the fresh make up water supplied to it and also through infiltration of air into the condensate system. As the water is heated the dissolved oxygen is liberated and iron is corroded, (The mechanism of corrosion has been discussed in detail in the chapter on Corrosion.)

Dissolved oxygen can be removed by :

- (a) ***Mechanical deaerator*** : Various types of deaerators have been designed. The general principle is that in a cylindrical chamber water falls through perforated plates, or is sprayed, so that a larger surface is exposed. The deaerator is connected to a vacuum line which sucks out the gases.
- (b) ***Pre-heating*** : Advantage is taken of the fact that the solubility of a gas decreases with rise in temperature. Air begins to be expelled at a temperature of about 65° and is almost completely removed at the boiling point. For the removal of dissolved oxygen the sample of water is sprayed in cylindrical equipment. It meets steam moving in the opposite direction. Steam heats and carries away with it the gases which have been liberated.
- (c) ***Chemical treatment*** : The above two methods remove most of the oxygen but for a complete removal, chemical treatment is required. This is done by adding a

reducing agent, sodium sulphite being commonly used, which at boiler temperature reacts rapidly as follows :



Ferrous sulphate is also used. It gives precipitate of $\text{Fe}(\text{OH})_2$ which is oxidized to $\text{Fe}(\text{OH})_3$.

In high pressure boilers even traces of oxygen are undesirable. As it is necessary to keep dissolved salts also to a minimum, hydrazine is added in such amounts that after reacting as under, there is a residual hydrazine of about 0.02 mg/l:

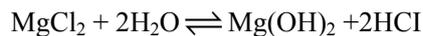


Thus no solid is added to the boiler. Hydrazine should be handled carefully, usually its solutions are used.

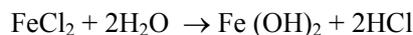
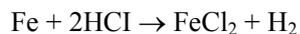
(ii) Mineral acids

Most of the natural waters are alkaline. Waters in the mining areas are often acidic. Sometimes, in industrial areas the water may become acidic because of the discharge of acidic industrial wastes into the surface water.

Some of the inorganic salts may hydrolyse to produce acidity, the most important of such salts being magnesium chloride. Its action may be represented thus:



(As $\text{Mg}(\text{OH})_2$ is insoluble, the forward reaction goes to completion.)

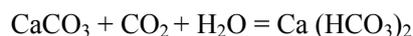


As a result of these reactions even a small amount of MgCl_2 will cause corrosion of a large amount of iron. If the amount of the acid formed is small, it may get neutralized by the alkalinity present in the water, otherwise alkali will have to be added. It has been suggested that except in high pressure boilers, boiler water should have a pH value of about 10.5 so that the acid may not attack iron. High pressure boiler water needs separate consideration.

(iii) Carbon dioxide

Water contains some dissolved carbon dioxide. In case some bicarbonates are present in the boiler water, more carbon dioxide will be produced on heating because of the decomposition of the bicarbonates. Carbon dioxide coming in contact with water produces carbonic acid, H_2CO_3 , which has a corrosive effect on the equipment. If carbon dioxide is released inside the boiler, it will be carried along with steam and H_2CO_3 will be formed where the steam condenses, and corrosion will take place. *Local corrosion caused by carbon dioxide is called pitting.*

Carbon dioxide in water can be removed by the addition of lime. Another method is to filter water through limestone when it not only becomes clear but carbon dioxide is also removed:



Of course, this reaction adds to the hardness of water.

The problem of carbon dioxide present in the steam can be tackled by the use of ammonia. It may be noted that ammonia itself has a corrosive action on copper and copper alloys; therefore its use is being replaced by amines.

(iv) **Galvanic cells**

Corrosion can also be due to simple galvanic cells which iron forms with some of the boiler fittings made of other materials or with impurities. This can be avoided by suspending zinc plates. Zinc is more electropositive than iron hence it is anodic to iron and gets dissolved first and iron is saved.

Galvanic couples set up cells which cause formation of corrosion products. These deposits in themselves lead to further corrosion. This type of damage can be reduced by the use of proper inhibitors. Care has to be taken to see that the surface is clean and the inhibitor film covers the surface completely. Use of organic as well as inorganic inhibitors for protection against corrosion has been discussed in the Chapter on Corrosion. It may be added that in high pressure boilers often chromates are used as inhibitors. These have to be removed from the blow down before discharge otherwise fresh water may get poisoned. The pH is reduced to < 5 and then deionized and finally the pH is increased to 6 and then discharged.

Silicates, amines, polyphosphates, tannins and lignins have been used in recirculated water systems for protection against corrosion.

1.7 Sludge, Scale and Their Formation

From the standpoint of the chemical constituents present in water, a boiler may be considered to be a huge concentrator of impurities. Water containing impurities is fed into the boiler and pure water, in the form of steam, is removed, leaving behind the impurities. In a high pressure boiler, steam equivalent to the total water capacity may be produced within 15 minutes. Boiler tubes completely blocked by deposits and fragments of scales are not very uncommon. Even the pipes feeding water in a boiler are found to have sufficient deposits.

Some of the deposits stick to the metal surface and are known as **scales**. If they are in the form of *soft and muddy deposits, which can be flushed out easily*, or in the form of suspensions, they are known as **sludges**.

Scale formation takes place by two distinct mechanisms. A salt like calcium bicarbonate gives off carbon dioxide and insoluble calcium carbonate is precipitated on the boiler surface giving the scale. This is the principal factor in fire tube boilers. Another important cause is the lower solubility of certain salts, notably calcium sulphate, at elevated temperatures. The data available on the solubility of various salts does not conform to the high temperature and pressure conditions of the boiler. Another complicating factor is that a number of salts are present in water which affects the solubilities of each other. Therefore, it is difficult to calculate the quantity of a salt that will crystallize out in a boiler.

Water near the hot metal surface is at a higher temperature than the main body of water. A salt like calcium sulphate crystallizes out on the metal surface because the solution there becomes super-saturated. Also, as a film of water on the metal surface is converted into steam, it leaves behind a deposit of the salts in spite of the fact that the rest of the water in the boiler is not saturated with those salts. Gradually, more and more salts are deposited giving a layer on the surface which is known as scale. The scales so formed are mostly of calcium sulphate which stick tenaciously to the metal surface and interfere seriously with the flow of heat.

The behaviour of the silicates is not well understood. Even when there are only a few milligrams of silica per litre of water it is likely to deposit silicate of calcium or magnesium or other silicates. The silicate deposits are particularly troublesome as their thermal conductivity is very poor and they stick very firmly to the metal surface making the removal of the scales very difficult.

Broadly speaking, the scales may be considered to be of three types namely, carbonate, sulphate and silicate types, whose formation has been described above. Generally, the scales found in the boilers are of mixed composition and are composed of several salts. Colloidal and suspended matter may get deposited by coagulation or may be trapped in the precipitates of other salts.

1.7.1 Disadvantages of scale formation

Scale formation is objectionable for the following reasons:

- (a) **Waste of fuel.** The scales are bad conductors of heat, therefore, their effect is like that of an insulating material spread over the metal surface. This results in reduction in the rate of heat transfer with the result that a larger quantity of fuel has to be used. It has been reported that 0.25 cm thick scale would increase fuel consumption by about 2 to 3%.
- (b) **Overheating of the boiler tubes.** A more serious effect than the waste of fuel due to overheating of the tubes is explained with the help of Fig. 1.3. The figure on the left shows a section of the boiler tube metal which is completely free from scales. In this case, in order to heat the boiler water to T_1^0 the metal surface towards the source of heat is heated to T_2^0 because of the temperature drop across the metal. The figure to the right represents a similar situation except that there has been scale formation. As the scale is an insulator, there is a greater drop in temperature. Therefore, for heating water to T_1^0 the temperature on the inner surface of the metal is T_3^0 and on the outer surface the temperature is T_4^0 which is considerably higher than the scale-free metal surface temperature of T_2^0 .

At higher temperatures the metal becomes weak and can withstand less pressure. Overheating also causes undue expansion of tubes leading to 'bagging'. This becomes dangerous in modern high pressure boilers.

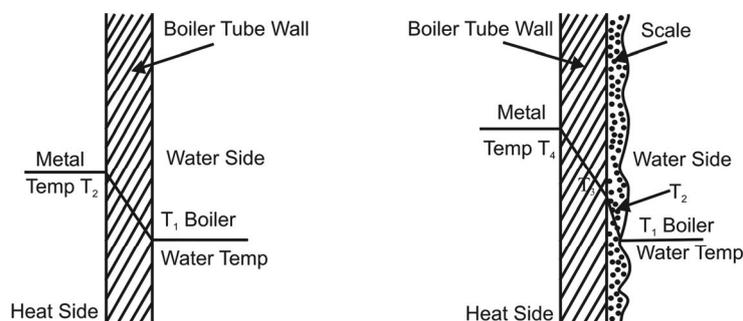


Fig. 1.3 Insulating effect of scales.

- (b) **Corrosion.** At the higher temperature so maintained there is greater corrosion of the boiler tubes.

Thus it is seen that the disadvantages of scale formation are primarily due to the fact that scales are bad conductors of heat.

Scale formation can be prevented by the following means:

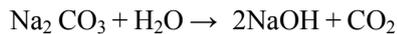
- (i) **External treatment.** This treatment is given outside the boiler before the feed water enters it. Attempt is made to remove or reduce the amounts of that substance, mainly calcium and magnesium salts and silica, which form deposits. This requires an investment on external treatment equipment. In several cases this can be avoided, for example where the water requirement is not very exacting, the plant is small, the water available is of good quality or a combination of these reasons.
- (ii) **Internal treatment.** In spite of the external treatment, some salts often remain in the water. Attempt is made, by adding chemicals to water entering the boiler, to convert the remaining salts into more soluble salts or such salts that the deposits will be in the form of nonstick sludge which can be easily removed. The treatment also aims to prevent corrosion not only inside the boiler but also in the pipe line and equipment handling steam in general and condensate in particular, due to the dissolved gases liberated in the boiler. In the cooling water system it prevents biological growths.
- (iii) **Blow down.** In spite of giving external and internal treatments the concentration of impurities, especially the soluble impurities, goes on increasing as steam generation progresses and the ultimate practical solution available is to make a blow down, i.e., remove a portion of the concentrated water which contains a considerable amount of dissolved matter. Along with it some sludge is also removed. Fresh water is then fed in its place which contains a smaller amount of impurities.

The percentage of blow down is an indication of the efficiency of the water treatment. It should be less than 10%.

1.8 Caustic Embrittlement

It has been found that sometimes the boiler failure takes place because the metal plate has become brittle and inter crystalline cracks have been formed in the metal. This happens in the areas which are under stress.

The alkali metal carbonates and the bicarbonates present in the feed water give rise to caustic alkalinity at the high temperatures and pressures prevailing in the boiler.



On evaporation of water the dissolved caustic soda increases its concentration which attacks the surrounding area, there by dissolving iron of boiler as sodium ferrate. The concentration becomes greater near the rivets because of bad circulation of water and also because of leaks through which steam escapes leaving behind water with a higher concentration of caustic alkalinity. This causes embrittlement of boiler parts such as bends, joints, rivets etc., due to which boiler fails.

Prevention

1. It has been observed that those boilers which were fed with water containing sodium sulphate were free from such troubles and therefore the usual practice has been to keep the ratio of sodium sulphate to sodium hydroxide as 1:1, 2:1 and 3:1 for boilers working at pressures up to 10, 20 and above 20 kg/sq. cm respectively.
2. By maintaining the pH values of water and neutralization of excess alkali.
3. By using sodium phosphate as softening reagents in the external treatment of boilers (details given later).
4. Caustic embrittlement can also be prevented by adding tanning or lining which prevents the infiltration of caustic soda solution by blocking hair-cracks.

1.9 Methods of Boiler Water Treatment – Softening Methods

The objective of boiler feed water treatment is firstly to avoid trouble in the boiler plant and secondly to obtain steam of sufficient purity for the steam turbine. If the steam is not of sufficient purity, there is fouling of the blades of the steam turbine which reduces the capacity of the turbines.

The actual treatment that needs to be given to boiler feed water depends to a great extent on the working pressure. As the boiler pressure goes up, the specifications for feed water become more rigid. Accordingly, a treatment has to be carefully chosen. The common treatments are described below : (i) External treatments (ii) Internal treatments the softening methods fall under class of external treatments.

1.9.1 Preliminary treatments

Preliminary treatments may include simple treatments like sedimentation, coagulation and filtration. These will not be needed for clear water, like well water. An operation like filtration may be postponed for a later stage, say after lime-soda process. Details of these treatments are similar to those given under municipal water supply and need to be studied carefully.

In case a plant is getting some clear water, say, from a well, and some turbid water, say from a river, it is advisable not to mix them but to remove the turbidity of the river water first. Otherwise turbidity will get diluted and will be more difficult to remove. Similar principle applies for other kinds of impurities.

1.9.2 Pre-heating

Pre-heating is heating feed water before it enters the boiler. Very often blow down water and low pressure steam is available at the plant at negligible cost and can be used for heating the feed water. Hot flue gas leaving the boiler furnace is also used for pre-heating. Water may be heated in a heat exchanger. The advantages of pre-heating are:

- Instead of feeding the boiler with water at that atmospheric temperature it is fed with hot water, thus saving fuel.
- A portion of temporary hardness may be removed. The bicarbonates are decomposed precipitating the insoluble carbonates thus :



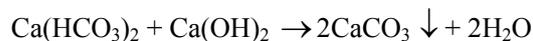
It may be noted that for complete removal of temporary hardness water has to be boiled for 10 to 15 minutes. Usually this does not happen in pre-heaters.

- Dissolved oxygen and carbon dioxide are removed. Initially dissolved gases are removed from water on heating to about 65° and are almost completely removed on boiling. As these gases have a corrosive effect their removal is advantageous.
- Use of hot water while giving chemical treatments, such as lime-soda treatment, greatly helps the operation. The effect of temperature is discussed along with the lime-soda process.

1.9.3 Lime-Soda Process

This process is used for feed water treatment for low and also medium pressure boilers. It is based on converting the soluble impurities into insoluble salts, which get precipitated. The precipitate is allowed to settle and is then filtered off. A calculated amount of milk of lime, generally with about 10% excess, is added to the sample. Its effects are :

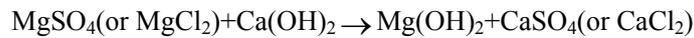
- temporary hardness is removed by the following reactions:



CaCO_3 being comparatively insoluble is readily precipitated. MgCO_3 formed in a similar 1:1 reaction is not so insoluble and is not precipitated. Therefore for the removal of $\text{Mg}(\text{HCO}_3)_2$ twice the amount of lime is needed that produces $\text{Mg}(\text{OH})_2$, an insoluble magnesium salt. Excess $\text{Ca}(\text{OH})_2$ could be removed by addition of NaHCO_3 .

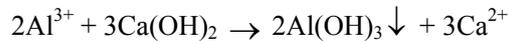
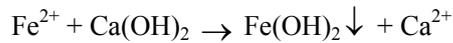
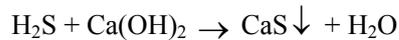
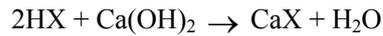
The removal of temporary hardness by the use of lime has an important advantage, namely, that of reduction in total dissolved solids. Generally speaking, a large portion of the hardness in natural water is temporary. The removal of temporary hardness by the use of lime does not introduce any soluble salt in water, as is the case with soda treatment or even zeolite process. This is a distinct advantage especially where water with low total solid content is required. As lime is inexpensive, for obtaining high quality water it may be more economical to give lime treatment to water of high carbonate hardness followed by zeolite or demineralizing treatment.

- (ii) Lime also removes all permanent magnesium-hardness but is not useful to remove permanent calcium hardness.

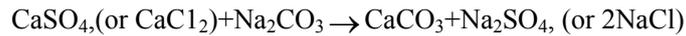


An equivalent amount of permanent calcium hardness is introduced, which has to be removed by soda treatment. Therefore, in spite of almost quantitative precipitation of magnesium, there is no softening.

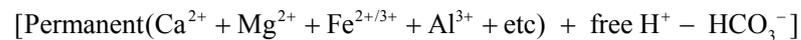
- (iii) Lime also removes free acids, carbon dioxide, hydrogen sulphide and precipitates dissolved iron and aluminium salts as insoluble hydroxides. A large excess of lime should be avoided.



The lime treatment is followed by soda treatment which removes the remaining calcium permanent hardness (including Ca-hardness introduced during the removal of Mg-permanent hardness)



$$\therefore \quad \text{Soda} = \frac{106}{100}$$



The process may be carried on in batches or continuously. In the batch process the chemicals are added in batches in water taken in tanks, agitated for the necessary time and the precipitate allowed to settle and then filtered. Fresh water is again taken into the tank and the operation is repeated. Filtration through sand beds should be avoided as the water is alkaline and will easily dissolve silica. It may be filtered through filter press, coal, coke or even dense iron ore. Silica may also be introduced by the use of lime of inferior quality.

In the continuous process, water together with lime and soda solutions enters a smaller tank continuously at a predetermined rate, bringing the correct amount of materials together. The chemicals and the water to be treated enter a bigger tank or chamber (Fig. 1.4). The second chamber is a tall structure having a larger cross

section at the top than at the bottom. As a solution moves upwards the precipitates formed as a result of the chemical reactions settle down, because towards the upper portion of the chamber the velocity is less due to the larger cross section. Clear water is removed continuously from the top and sludge from the bottom. A part of the sludge is recirculated which not only enables the use of excess chemicals left behind in the sludge but also helps in the precipitation by providing nuclei.

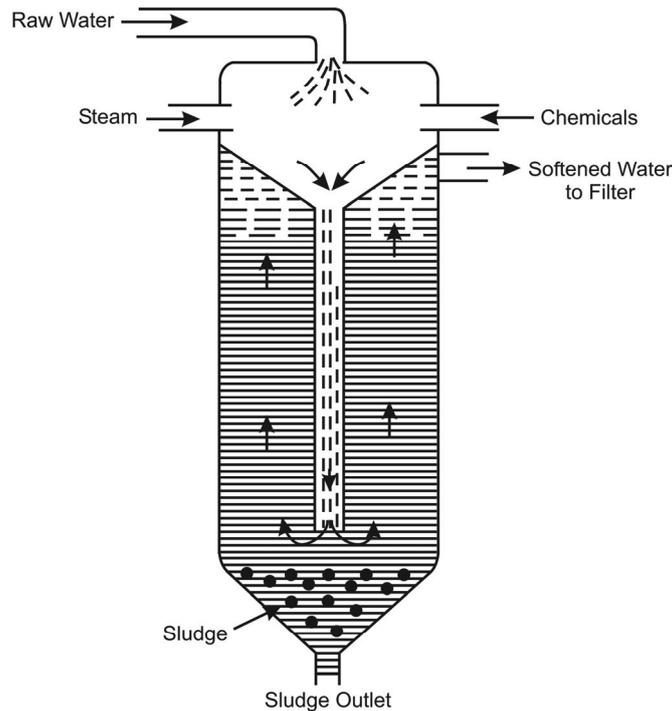


Fig. 1.4 Continuous hot lime-soda process.

When the chemicals are added to water at atmospheric temperature, the process is known as *cold lime soda process*. At this temperature the precipitates are finely divided and do not settle easily, nor can they be easily filtered. It is therefore, necessary to add coagulants like alum, aluminium sulphate, ferrous sulphate, sodium aluminate etc. These get hydrolysed and form flocculent and gelatinous precipitates which entrap the finely divided particles and settle down readily or are easily filtered off. Ferrous sulphate and sodium aluminate are costlier than alum. Ferrous sulphate helps to remove oxygen and sodium aluminate helps the removal of silica and also oil.

When this treatment is given at a higher temperature the process is known as *hot lime soda process*. Water is heated by waste steam or hot gases and a calculated amount of chemicals are added as in the cold process. The distinguishing features are the following :

- (i) As the reactions proceed quickly at higher temperature, the softening reactions are completed in about 15 minutes, whereas in the cold process several hours are needed. This greatly increases the capacity of the plant.

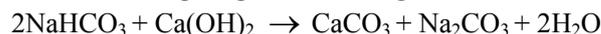
- (ii) Precipitates and sludges formed settle rapidly at higher temperatures, hence coagulants are not needed.
- (iii) Filtration becomes easier because of the bigger size of the particles and the reduced viscosity of solution at the higher temperature; hence the capacity of the filter is also increased.
- (iv) Residual hardness, i.e., hardness of softened water needs careful consideration. Generally, the solubility of substances is lower at lower temperatures but the solubility of calcium salts is very slightly higher. More than this, the time taken for the completion of the reactions at a lower temperature is greater. In the hot process the reactions are completed in much less time with the result that the hot process gives softer water.

In an experiment, a portion of a sample of water was treated with chemicals at 95°C and another portion of the sample of the same water was treated under identical conditions except that the temperature was 10 °C. It was found that the residual hardness of the hot solution at the end of 10 minutes was less than that of the cold solution even after 5 hours. If the cold solution was allowed to stand for a longer period, more of the hardness would have been removed. This difference is chiefly because at higher temperatures the rates of reactions are greater, so more of the hardness is removed in less time.

Residual hardness also depends upon the excess of chemicals used. According to the Law of Mass Action the reaction is more complete and quicker if higher concentrations of the reagents are used, but large excess of the reagents should be avoided as they will appear in the softened water. Excess of chemicals required in the hot process is less than in the cold process. If precipitation is incomplete in the softening plant, salts, will be precipitated in the pipes, storage tanks and boiler.

In practice, cold lime soda process gives water with a residual hardness 50-60 mg/l and the hot lime soda process reduces the hardness to 15-30 mg/L.

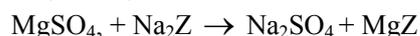
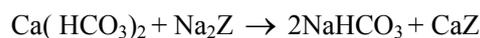
In some places, water is highly alkaline and contains a considerable amount of sodium bicarbonate. The total alkalinity of this type of water is greater than the total hardness. On adding lime, calcium carbonate precipitates forming sodium carbonate.



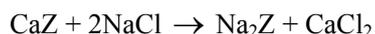
In such a case, soda may not be needed for the removal of permanent hardness. As a matter of fact, cases are known where gypsum has to be added to remove soda so produced.

1.9.4 Permutit or Zeolite Process

Permutits or **zeolites** are natural or synthetic complex compounds, consisting of hydrated sodium aluminium silicates approximately corresponding to the chemical formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$. The artificial zeolites have greater capacities per unit weight for softening water than natural zeolites but are less durable. Zeolites are insoluble. They introduce Na^+ in place of Ca^{++} and Mg^{++} . As these exchange bases, they are also known as *base exchangers*. If Na_2Z represents permutit or zeolite, the reactions taking place may be represented thus :



Permutits or zeolites are kept in cylinders and used as filter beds. Hard water is percolated through them at a certain specified rate. The hardness causing substances (or ions) are retained as insoluble compounds according to the reactions given above. Thus the outgoing water contains sodium salts corresponding to the calcium and magnesium salts present in the incoming hard water. After use for some time the zeolite is converted into calcium or magnesium zeolite and then it ceases to soften water. At this stage it has to be regenerated by treatment with a concentrated sodium chloride solution when the original sodium zeolite is recovered :



The zeolite bed is then washed with water and is again ready for use. See Fig. 1.5.

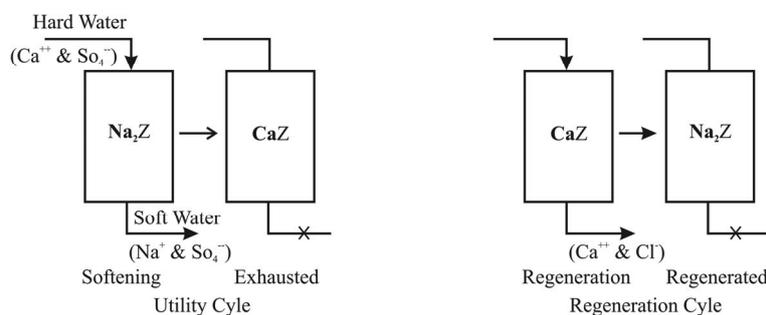


Fig. 1.5 Water softening by zeolite process.

Water having turbidity or excess of acidity or alkalinity or containing dissolved iron or manganese salts should not be fed into a zeolite softener. Turbidity will clog the pores and restrict the flow; excess of acidity or alkalinity will attack the zeolite, therefore the pH value of water to be passed through a zeolite bed should be around 7; iron or manganese salts will produce iron or manganese zeolites from which it cannot be easily regenerated. Therefore, these should be removed before passing water through the zeolite bed. Generally, hot water is not passed through a zeolite bed because zeolite tends to dissolve in hot water.

It is to be further noted that the acid radicals are not removed. The temporary hardness will give water containing NaHCO_3 which dissociates inside the boiler giving high alkalinity:



Alkalinity causes "caustic embrittlement". Carbon dioxide goes along with steam and makes the condensed water acidic, hence corrosive. Thus waters containing a large amount of temporary hardness should not be directly treated by the zeolite process. Such water may be boiled or treated by lime to remove temporary hardness and then softened by this process.

The *advantages* of the zeolite process are several. It removes the hardness completely; the equipment is a compact unit occupying a small space; it automatically adjusts itself to different hardness and can be worked under pressure, therefore the plant can be installed in the water supply line and double pumping is avoided. Moreover, as the impurities are not precipitated, there is no danger of sludge formation at a later stage.

A combination of lime soda process and zeolite process gives better results. Zeolite process has now been superceded by deionization process.

1.9.5 Comparison, Merits and Demerits of Lime-Soda and Zeolite Processes

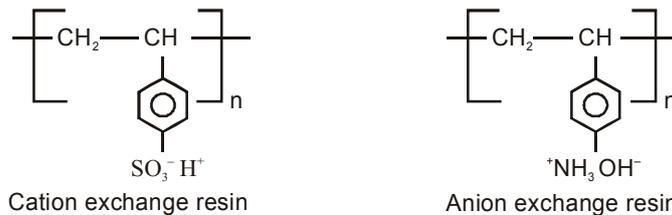
Lime-soda process		Zeolite/Permutit	
1.	Water of generally 15-50 ppm hardness is obtained.	1.	Water of 10-15 ppm residual hardness is obtained.
2.	Treated water contains lesser amount of sodium salts.	2.	Treated water contains larger amount of sodium salts than in original raw water.
3.	Cost of plant is lower.	3.	Cost of plant and material is higher.
4.	Operational expenses are higher	4.	Operational expenses are lower.
Merits of both processes			
It is very economical		It removes the hardness almost completely	
If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.		The equipment used is compact, occupying a small space.	
The process increases the pH value of the treated water, there by corrosion of the distribution pipes is reduced.		No impurities are precipitated, so there is no danger of sludge formation in the treated water at a later stage.	
Besides the removal of hardness, the quantity of minerals in the water are reduced.		The process automatically adjusts itself for variation in hardness of incoming water.	
To certain extent, iron and manganese are also removed from the water.		It requires less time for softening.	
Due to alkaline nature of treated water amount of pathogenic bacteria in water is considerably reduced.		It requires less skills for maintenance as well as operation.	
Demerits of both processes			
For efficient and economical softening, careful operation and skilled supervision is required.		The treated water contains more sodium salts than in lime soda process.	
Disposal of large amounts of sludge (insoluble ppt) possess a problem. However the sludge may be disposed off in raising low-lying areas of the city.		The method only replaces (Ca^{+2} and Mg^{+2} ions by Na^+ ions, but leaves all the acidic ions (like HCO_3^- and CO_3^{2-}) as such in the softened water.	
This can remove hardness only upto 15 ppm, which is not good for boilers.		High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed, there by creating problem for its working.	

1.9.6 Ion-Exchange Process (Deionizers or Demineralizers)

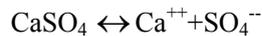
Several organic polymeric-resins, such as polystyrene with functional groups ($-\text{NH}_3\text{OH}^+$, $-\text{SO}_3\text{H}^+$) on benzene rings, are now available which behave in a manner similar to the zeolites.

This process differs from all other processes in the fact that by it all the ions are removed. The cations are replaced by H^+ and anions by OH^- . Water to be treated is generally passed through two cylinders containing the resins, one of which removes cations and the other anions. See Fig. 1.6.

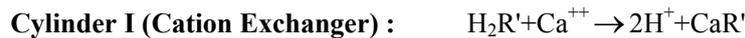
Polystyrene resins :



When the resins get used up, they are regenerated by acid and alkali treatments similar to sodium chloride solution treatment for zeolites. Suppose the first and second cylinders contain resins represented by the formulas H_2R' and $(OH)_2R''$, the reactions may be represented thus :



(Any other hardness causing salt or ionisable substance will behave in a similar manner).



It is easy to see that the water coming out of the cation exchanger is highly acidic. This has to be kept in mind in selecting the materials handling it. Water from natural sources usually contains sufficiently large quantities of carbonates and bicarbonates. These ions like other anions can be removed by passing through the anion exchanger. CO_3^{2-} and HCO_3^- in the presence of H^+ form H_2CO_3 (or $\text{H}_2\text{O} + \text{CO}_2$). The load on anion exchanger is reduce by having a aerator/degasifier (which removes gases like CO_2 by mechanical means like blowing air or suction, as shown in Fig. 1.6). Thus only mineral acidity will have to be removed by the anion exchanger.

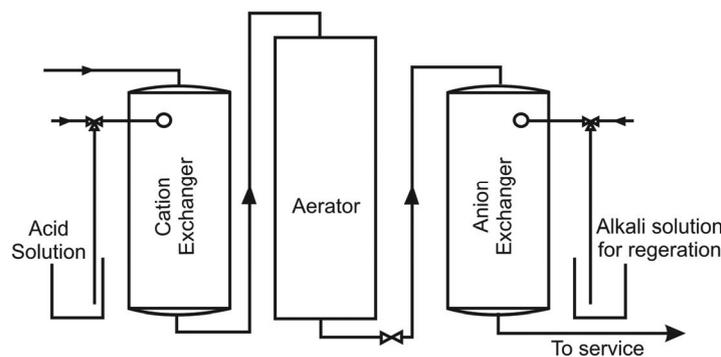
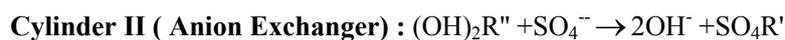


Fig. 1.6 Deionization of water.



H^+ and OH^- unite to form H_2O , thus no solid is added to water. When the plant does not soften any more, the first cylinder is regenerated by passing a dilute acid solution through it and the second cylinder by passing a dilute alkali solution. The reactions during regeneration may be represented thus:



Mixed bed deionizers are also now available. In these the sample of water is passed through only one cylinder and all the ions get removed.

This process can also be used to purify highly acidic or alkaline water. As a matter of fact, it removes all the ionizable substances and the water obtained is like distilled water. Many of the commercial plants give water with total dissolved solids as low as 3 mg/l and silica 0.1 mg/l.

The main disadvantage is that the equipment is costly and more expensive chemicals, as compared with the zeolite process, are needed for regeneration. Another important factor to be considered is the quality of water that is being softened. If it contains turbidity or a large amount of dissolved salts then the output is reduced. Turbidity must be below 10 ppm and has to be removed first by coagulation and filtration. If the water contains sufficient temporary hardness it is advisable to treat it first by lime, which removes hardness without adding dissolved salts, and then remove the remaining hardness by this process.

This process is very good for water for very high pressure boilers. For low pressure boilers, working say below 50 kg/cm^2 , the equipment is rather costly and water may be treated more economically by other processes.

1.9.7 Comparison of Zeolite and Ion-Exchange Processes

Zeolite process or Permutit process	Resin process or ion exchange process
Exchange of only cations takes place	Exchange of both cations and anions takes place
Capital cost is high	Capital cost is very high
Operating expenses are low	Operating expenses are high
Residual hardness q is low (about 0-15 ppm)	Residual hardness is least (0-2 ppm)
The plant occupies less space	The plant occupies more space
Raw water to be treated should not be acidic	Raw water to be treated can be acidic or alkaline

1.9.8 Membrane Processes (Electro Dialysis, Reverse Osmosis)

These processes have now been developed to such an extent that some large plants are using them for treating high dissolved salt containing water prior to the common demineralization. Two of the methods are (i) Electro-dialysis and (ii) Reverse osmosis techniques.

- (i) **Electro dialysis:** In the electro dialysis or E. D. technique the dissolved mineral is driven away from the water. The basic principle is that the water is passed between paired sets of parallel membranes. An electric field is applied perpendicular to the direction of flow of water. The ions move towards the electrodes of the opposite charge. Selectively permeable membranes are chosen. The membrane near the negative electrode allows the cations to pass and the one near the positive electrode allows the anions to pass (Fig. 1.7). A large number of pairs of membranes are assembled. Plastic spacers not only separate the membranes but also direct the flow of water through a winding path across the exposed membrane surfaces. Water is sent at a pressure of about 6 kg/cm^2 . This technique is favoured for water with very high dissolved salt contents and even for sea water.

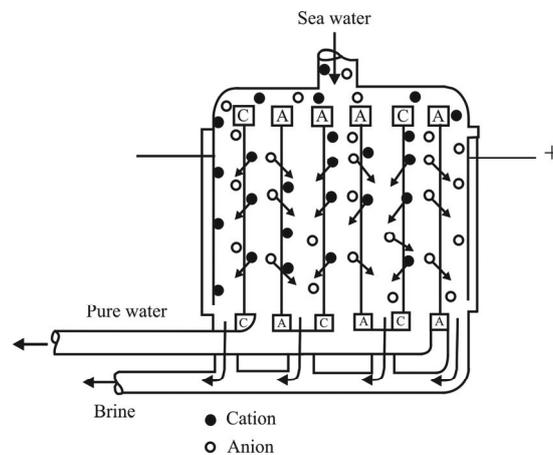


Fig. 1.7 Electro dialysis cell. In brackish water cations are removed through cation permeable membranes (C) and anions are removed through anion permeable membranes (A).

- (ii) **Reverse Osmosis:** Diffusion is the movement of molecules from a region of higher concentration to a region of lower concentration. Osmosis is a special case of diffusion in which the molecules are water and the concentration gradient occurs across a semipermeable membrane. The semipermeable membrane allows the passage of water, but not ions (e.g., Na^+ , Ca^{2+} , Cl^-) or larger molecules (e.g., glucose, urea, bacteria). Diffusion and osmosis are thermodynamically favorable and will continue until equilibrium is reached. Osmosis can be slowed, stopped, or even reversed if sufficient pressure is applied to the membrane from the 'concentrated' side of the membrane. Since reverse osmosis is thermodynamically unfavourable process, it requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases. Reverse Osmosis is a technology that is used to remove a large majority of contaminants from water by pushing the water under pressure through a semi-permeable membrane.

The reverse osmosis process is used in a wide range of applications. This includes waste water treatment, production of pure water for industries [e.g., wafer fabrication], and removal of salts from salty or sea water [desalination].

1.9.9 Functioning of Reverse Osmosis

Let us start with the normal osmosis process. Consider a semi-porous membrane that separates equal volumes of liquid into two compartments. In one compartment is water, and the other dilute salt solution [see Fig. 1.8(a)]. Due to the effect of osmosis, water flows from side containing water to the side with the salt solution. Water flows over because it is trying to dilute the salt solution. This continues until an equilibrium state is reached.

For reverse osmosis, the aim is not to dilute a salt solution, but to purify water by removing salts and other contaminants. This is done by applying a pressure to the side containing the salt solution. It causes water to flow to the other side of the membrane [see Fig. 1.8(b)]. This purifies the water, since the membrane prevents salts and other particles from passing through.

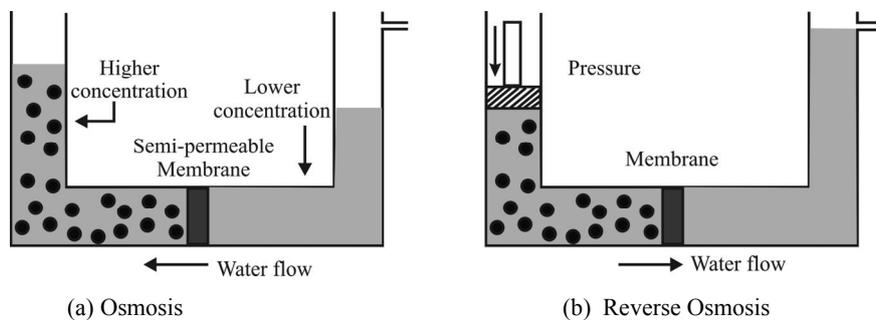


Fig. 1.8 Reverse Osmosis Cell.

Semipermeable membrane : Many synthetic membranes that can withstand high pressures have been developed. A typical reverse osmosis membrane has 2 layers :

- a dense top layer of less than $1\mu\text{m}$ thick
- a porous sublayer of $50\text{-}150\mu\text{m}$ thick, for supporting the top layer

Reverse osmosis is also known as hyperfiltration and is the finest filtration known. Reverse osmosis is not only used to purify water and remove salts but to remove other impurities in order to improve the color, taste or properties of the fluid. Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150-250 daltons. The larger the charge and the larger the particle, the more likely it will be rejected.

Further this process can be used to purify fluids such as ethanol and glycol, which will pass through the reverse osmosis membrane, while rejecting other ions and contaminants present in them.

Reverse osmosis units remove ionizable as well as non-ionizable matter, both colloidal and high molecular weight organic matter. This is a distinct advantage and sounds very attractive in dealing with the problem of colloidal silica, which is not removed by demineralization, for water for supercritical boilers. Electro dialysis units require more skilled labour who can handle the electrical and mechanical auxiliary units. Their initial cost for low dissolved solid range is slightly lower than the R.O. units. Cellulose acetate affixed to either

side of perforated tube is a popular membrane. Plants giving several million litres of water are available. At the present R.O. units are being preferred. Suppliers claim efficiencies from 85 to 99%.

The E.D. and R.O. units have attained prominence during the last few years and are particularly useful when feed water has a large amount of dissolved solids. When used before demineralization the chemical requirement for demineralization is reduced and the life of the resin is increased.

In the reverse osmosis process the maintenance cost is almost entirely on the replacement of the membrane. It is reported that in a plant the life of the membrane is quite high, about three years. When the conductivity measurement indicates that excess dissolved solids are going in the water, the module can be replaced within a few minutes thus giving an almost uninterrupted supply.

In the reverse osmosis process there are certain problems connected with the fouling of the membrane and design is yet to be perfected, but the results are very encouraging and it seems that in the future R.O. technology will be used in conjunction with mixed bed demineralization for very high pressure and super-critical boilers, where the impurities are measured in parts per billion instead of parts per million.

Just to give a rough idea it may be mentioned that in one case the dissolved salt decreased in the feed water from about 4500 ppm to about 350 ppm, conductivity from about 6000 μmho to about 500 μmho and silica from 7 ppm to 2 ppm after passing through a spirally wound polyamide reverse osmosis unit. The water now becomes suitable for treatment by demineralization.

An interesting case is that of a two-unit 800 MW power station at Cadafe, Venezuela, S. America. The plant was nearing completion in 1973 but public water supply was not ready. Alternative sources considered were well and sea water. Treatment methods for water from the sea—which provides uninterrupted water supply—considered were waste-heat desalination, distillation and reverse osmosis technique. The deciding factors were capital cost, operating cost, reliability, simplicity of operation, ease with which capacity could be expanded in the future and delivery time. In that area well water was not considered a reliable source for the large quantities of water needed.

In 1978 the capital investment required for a 12 million litre per day plant was estimated to be 4.5 crore rupees for reverse osmosis technique and 3.8 crore for multistage distillation; operating costs were almost similar, the distillation being slightly costlier. In spite of higher investment costs the reverse osmosis was preferred because the energy costs are rapidly increasing and it was felt that distillation cost would increase considerably.

In the Cadafe plant the sea water is treated with chlorine and ferrous sulphate, to destroy biological growth and to coagulate, filtered twice to remove fine particles, excess chlorine removed, pH adjusted and then pumped at 60 kg/cm^2 pressure through the reverse osmosis unit which has a number of modules of the semi-permeable membranes. The primary unit reduces the total dissolved solids from 38,000 ppm of the sea water to 1,000 ppm which is treated in the secondary unit that gives water with 100 ppm of the total dissolved solids. Necessary quantity of water is taken for supply as potable water and the remaining passed through demineralizers giving high quality water for the high pressure boilers.

1.10 Solving of Water Treatment Problems

- I. *Calculation of Hardness.* It has already been explained, with examples, under the Degree of Hardness that the hardness is expressed in terms of CaCO_3 . The weights of the substances are converted in terms of weight CaCO_3 and then the results are expressed in units of milligrams per litre of water (or parts per million or degree Clark, etc.).
- II. *Lime-Soda Requirement.* In Water Chemistry, by lime is meant Ca(OH)_2 and not CaO , and by soda is meant Na_2CO_3 . The weights of the substances should be converted into weight of CaCO_3 .

The following should be noted for lime requirement:

- (i) Lime is required for $\text{Ca(HCO}_3)_2$
- (ii) Lime requirement for temporary magnesium hardness is *double* that required for temporary calcium hardness.
- (iii) Lime removes permanent magnesium hardness, *but it* introduces an equivalent amount of permanent calcium hardness.

As 100 parts of CaCO_3 are equivalent to 74 parts of Ca(OH)_2 , the lime needed for softening = $\frac{74}{100} \times (\text{temporary Ca hardness} + 2 \times \text{temporary Mg hardness} + \text{permanent Mg hardness})$.

(*Note:* the hardness is in terms of CaCO_3).

In case the water analysis shows the presence of acidic substances, e.g. H_2SO_4 , etc., lime has to be calculated for these also. It should be noted that the result of this would be the introduction of the corresponding calcium salts, e.g. CaSO_4 , which will cause permanent hardness and soda requirement for this will also have to be calculated.

Soda is needed for the removal of permanent calcium hardness. In the process of the removal of permanent magnesium hardness an equivalent amount of calcium hardness is introduced which also needs soda for its removal.

As 100 parts of CaCO_3 are equivalent to 106 parts of Na_2CO_3 ,

the soda requirement = $\frac{106}{100} \times (\text{permanent Ca hardness} + \text{permanent Mg hardness})$.

Of course provision has to be made for calcium hardness that may be introduced by other reactions with lime, e. g. with acids.

Example 1.

Calculate the amount of lime-soda needed for softening water containing the following per litre:

Ca(HCO ₃) ₂	...	162 mg;	Mg (HCO ₃) ₂	...	73 mg;
MgCl ₂	...	95 mg;	CaSO ₄	...	136 mg;
NaCl	...	585 mg;			

What is the temporary and total hardness of the sample?

Solution: NaCl neither causes hardness nor has any reaction with lime-soda. The other substances on conversion in terms of CaCO₃ give the following results :

$$\text{Ca (HCO}_3)_2 \quad \dots \quad 162 \times \frac{100}{162} = 100 \text{ mg.}$$

$$\text{Mg (HCO}_3)_2 \quad \dots \quad 73 \times \frac{100}{146} = 50 \text{ mg.}$$

$$\text{MgCl}_2 \quad \dots \quad 95 \times \frac{100}{95} = 100 \text{ mg.}$$

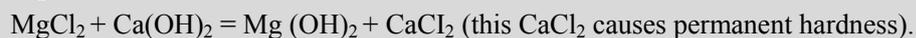
$$\text{CaSO}_4 \quad \dots \quad 136 \times \frac{100}{136} = 100 \text{ mg.}$$

- (i) Temporary hardness is due to the bicarbonates which are $100 + 50 = \mathbf{150 \text{ mg/l}}$.
- (ii) Total hardness is the sum of all the hardness causing constituents which are $100 + 50 + 100 + 100 = \mathbf{350 \text{ mg/l}}$.
- (iii) Lime requirement is (for temporary Ca hardness + 2 × temporary magnesium hardness + permanent Mg hardness).

$$\begin{aligned} \therefore \text{Wt. of lime needed} &= \frac{74}{100} (100 + 2 \times 50 + 100) \\ &= \frac{74}{100} \times 300 = \mathbf{222 \text{ mg/l}} \end{aligned}$$

- (iv) Soda is needed for permanent Ca hardness + permanent Mg hardness,

(Note : Permanent magnesium hardness appears under soda requirement also, because in the lime treatment permanent calcium hardness is introduced in place of magnesium hardness. Since the amount of calcium hardness introduced is equivalent to the hardness originally present, the weights in terms of CaCO₃ remain the same for calculations:



$$\begin{aligned} \therefore \text{Wt. of soda needed} &= \frac{106}{100} \times (100 + 100) = \frac{106}{100} \times 200 \\ &= \mathbf{212 \text{ mg/l.}} \end{aligned}$$

Example 2.

In example 1 calculate the amounts of lime soda needed per 10,000 litres of water if the sample of lime is 85% pure and soda is 98% pure and 10% excess of the chemicals are to be added in order to complete the reactions quickly.

Solution : The quantities of pure lime and soda needed will remain the same but as 100 parts of the sample of lime contain only 85 parts of the pure substance the weight of the sample of lime = $222 \times \frac{100}{85}$ mg/l.

Further, 10% excess chemical is added, i.e., 110 parts are added for 100 parts are added for 100 parts of the calculated.

$$\therefore \text{Actual requirement} = 222 \times \frac{100}{85} \times \frac{110}{100} = 287.3 \text{ mg/l.}$$

$$\begin{aligned} \therefore 10,000 \text{ litres of water needs } & 287.3 \times \frac{10,000}{1,000} \\ & = 2873 \text{ g or } 2.87 \text{ kg of lime.} \end{aligned}$$

Similarly soda requirement per 10,000 litres

$$= 212 \times \frac{100}{98} \times \frac{110}{100} \times \frac{10,000}{1,000} = 2380 \text{ g or } 2.38 \text{ kg.}$$

Example 3.

Calculate the amounts of lime-soda needed for the treatment of 1,000 litres of water containing the following:

CaCO₃ - 120 mg/l; MgCO₃ - 42 mg/l; Mg(NO₃)₂ - 148 mg/l;

CaCl₂ - 111 mg/l and KCl - 50 mg/l.

Solution : CaCO₃ and MgCO₃ should be regarded as being present in the form of their bicarbonates and that their weights have been expressed in terms of CaCO₃ and MgCO₃. Permanent hardness will be caused by Mg(NO₃)₂. KCl will not react with lime and soda. On converting the weights in terms of the weight of CaCO₃ the following results are obtained :

$$\text{CaCO}_3 \dots 120 \text{ mg/l; } \quad \text{Mg(NO}_3)_2 \dots 148 \times \frac{100}{148} = 100 \text{ mg/l}$$

$$\text{MgCO}_3 \dots 42 \times \frac{100}{84} = 50 \text{ mg/l; } \quad \text{CaCl}_2 \dots 111 \times \frac{100}{111} = 100 \text{ mg/l.}$$

Lime is required for CaCO₃ and MgCO₃ (present as bicarbonates) and for Mg(NO₃)₂.

$$\text{Lime requirement} = \frac{74}{100} \times (120 + 2 \times 50 + 100) = 236.8 \text{ mg/l.}$$

$$1000 \text{ litres of the sample needs } 236.8 \times \frac{1000}{1000} = \mathbf{236.8 \text{ g of lime}}$$

Soda is required for CaCl_2 and for $\text{Mg}(\text{NO}_3)_2$ (Now present as $\text{Ca}(\text{NO}_3)_2$ as a result of reaction with $\text{Ca}(\text{OH})_2$).

Soda required for 1000 litres of the sample

$$= \frac{106}{100} \times (100 + 100) \times \frac{1000}{1000} = \mathbf{212 \text{ g of soda.}}$$

Example 4.

A sample of polluted water on analysis gave the following results:-

Suspended matter –200 mg/l; CaSO_4 –250 mg/l; MgSO_4 –240 mg/l; MgCl_2 –190 mg/l; H_2SO_4 –98 mg/l and organic matter –750 mg/l. Calculate the amounts of lime soda needed per litre for its treatment if the purity of lime is 90% and that of soda is 98%. What is the hardness of the sample?

Solution : The suspended and organic matter does not need lime and soda. Sulphuric acid does not cause hardness but reacts with the alkali added for softening. Let it be assumed that lime is first added followed by soda treatment. In such a case lime will react with H_2SO_4 producing CaSO_4 which will cause permanent hardness for which soda will be needed.

Expressing the weights, in terms of equivalents of CaCO_3 the following results are obtained ;-

$$\begin{aligned} \text{CaSO}_4 & \dots 250 \times \frac{100}{136} = 184 \text{ mg/l} \\ \text{MgSO}_4 & \dots 240 \times \frac{100}{120} = 200 \text{ mg/l} \\ \text{MgCl}_2 & \dots 190 \times \frac{100}{95} = 200 \text{ mg/l} \\ \text{H}_2\text{SO}_4 & \dots 98 \times \frac{100}{98} = 100 \text{ mg/l} \end{aligned}$$

Lime is needed for MgSO_4 , MgCl_2 and H_2SO_4 .

$$\therefore \text{Weight of pure lime needed} = \frac{74}{100} \times (200+200+ 100) = 370 \text{ mg/l.}$$

As the sample is 90% pure, the weight of the sample of lime needed $370 \times \frac{100}{90}$
= 411mg/l.

Soda is needed for CaSO_4 and for the calcium salts produced during the removal of MgSO_4 , MgCl_2 and H_2SO_4 by lime treatment.

\therefore Wt. of 98% pure soda

$$= \frac{106}{100} \times (184 + 200 + 200 + 100) \times \frac{100}{98} = 740 \text{ mg/l}$$

Hardness is produced by CaSO_4 , MgSO_4 and MgCl_2 only

$$\therefore \text{Hardness} = 184 + 200 + 200 = 584 \text{ mg/l.}$$

Example 5.

In an experiment to determine the hardness of a sample of water 25 ml of N/50 Na_2CO_3 solution was added to 100 ml of the sample of water. After the completion of the precipitation of the insoluble carbonates, the unreacted Na_2CO_3 was titrated against N/50 H_2SO_4 solution when 10 ml of the acid was required. Calculate the degree of hardness and comment on the nature of the hardness so determined.

Solution: Na_2CO_3 will precipitate the calcium hardness as CaCO_3 . Hardness due to magnesium salts will not be precipitated because MgCO_3 is comparatively soluble. Therefore this method does not report the magnesium hardness.

$$\begin{aligned} \text{Volume of N/50 } \text{Na}_2\text{CO}_3 \text{ solution left unreacted} \\ = \text{volume of N/50 acid solution used for titration} = 10 \text{ ml.} \end{aligned}$$

$$\begin{aligned} \text{Volume of N/50 } \text{Na}_2\text{CO}_3 \text{ solution used in precipitation} \\ = 25 - 10 = 15 \text{ ml} \end{aligned}$$

$$1 \text{ litre of N solution} = 50 \text{ g of } \text{CaCO}_3$$

$$\begin{aligned} \therefore 15 \text{ ml of N/50 } \text{Na}_2\text{CO}_3 \text{ solution} \\ = \frac{50}{50} \times \frac{15}{1000} = 0.015 \text{ g of } \text{CaCO}_3 \end{aligned}$$

\therefore Hardness equivalent to 0.015 g CaCO_3 was present in 100 ml sample.

$$\text{Hardness of the sample is } 0.015 \times \frac{1000}{100} \text{ g/l}$$

$$\text{OR } 0.015 \times \frac{1000}{100} \times 1000 = 150 \text{ mg/l.}$$

Example 6.

The hardness of 10,000 litres of a sample of water was completely removed by passing it through a zeolite softener. The zeolite softener required 200 litres of sodium chloride solution containing 20,000 mg/l of NaCl for regeneration. Calculate the hardness of the sample of water.

Solution : As 200 litres of sodium chloride solution containing 20,000 mg/l of NaCl was needed to regenerate the zeolite through which 10,000 litres of hard water had been passed, the hardness of 10,000 litres of the sample of hard water is equivalent to $200 \times 20,000$ mg of NaCl.

Since 58.5 parts of NaCl \equiv 50 parts of CaCO_3 ,

The hardness of 10,000 litres of the sample

$$= 200 \times 20,000 \times \frac{50}{58.5} \text{ mg of CaCO}_3$$

or the hardness of 1 litre of the sample

$$= 200 \times 20,000 \times \frac{50}{58.5} \times \frac{1}{10,000} \text{ mg of CaCO}_3$$

$$= 341.9 \text{ mg of CaCO}_3$$

Hardness of the sample of water is 341.9 mg/l.

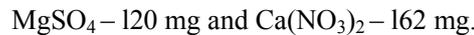
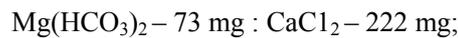
Examples

1. A sample of water contains the following $\text{Ca}(\text{HCO}_3)_2$ – 162 mg/L; $\text{Mg}(\text{HCO}_3)_2$ – 146 mg/L; CaSO_4 – 68 mg/L; MgCl_2 – 95 mg/L, and KCl – 745 mg/L.

Calculate (a) temporary hardness, (b) permanent hardness and (c) amounts of lime and soda needed for the softening of 1 litre of the sample of water.

(Answer : (a) 200 mg/l; (b) 150 mg/l; (c) 296 mg and 159 mg.)

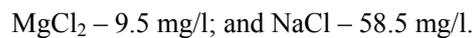
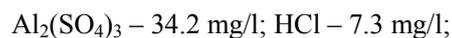
2. A sample of water contains the following impurities per litre :



The sample of lime available is 74% pure and soda is 90% pure. 10% excess chemicals have to be added. Calculate the amounts of lime and soda required for the treatment of 5,000 litres of water.

(Answer : 1100 g; 2591 g).

3. Calculate the amounts of lime and soda needed for the treatment of 10,000 litres of water containing the following:



(Lime treatment is given first, followed by soda treatment.)

[Hint. Al = 27. Try to solve this question by writing chemical equations also.]

(Answer : 37 mg/l, 53 mg/l).

4. A sample of water contains the following $\text{Ca}(\text{HCO}_3)_2$ – 162 mg/l; $\text{Mg}(\text{HCO}_3)_2$ – 146 mg/l; CaSO_4 – 68 mg/l; MgCl_2 – 95 mg/l, and KCl – 745 mg/l.

Calculate (a) temporary hardness, (b) permanent hardness and (c) amounts of lime and soda needed for the softening of 1 litre of the sample of water.

(Answer : (a) 200 mg/l; (b) 150 mg/l; (c) 296 mg and 159 mg.)

5. A sample of water contains the following impurities per litre :

$\text{Mg}(\text{HCO}_3)_2$ – 73 mg : CaCl_2 – 222 mg;

MgSO_4 – 120 mg and $\text{Ca}(\text{NO}_3)_2$ – 162 mg.

The sample of lime available is 74% pure and soda is 90% pure. 10% excess chemicals have to be added. Calculate the amounts of lime and soda required for the treatment of 5,000 litres of water.

(Answer : 1100 g; 2591 g).

6. Calculate the amounts of lime and soda needed for the treatment of 10,000 litres of water containing the following:

$\text{Al}_2(\text{SO}_4)_3$ – 34.2 mg/l; HCl – 7.3 mg/l;

MgCl_2 – 9.5 mg/l; and NaCl – 58.5 mg/l.

(Lime treatment is given first, followed by soda treatment.)

[Hint. $\text{Al} = 27$. Try to solve this question by writing chemical equations also.]

(Answer : 37 mg/l, 53 mg/l).

7. In an experiment to determine the hardness of a sample of water the following results were obtained;

Volume of the sample of water to be tested = 50 ml.

N/50 Na_2CO_3 solution added to the sample = 12 ml.

N/50 H_2SO_4 solution used to titrate = 7 ml.

Calculate the hardness of water in grains per gallon and mg/l

(Answer : 7 gr/gal.; 100 mg/l).

8. 100 ml of a sample of water was titrated against a N/10 acid solution using phenolphthalein as indicator when 6 ml of the acid solution was required for discharging the colour. Then on the addition of methyl orange 4 ml of the acid solution was further required for neutralization. Calculate the hydroxyl and carbonate alkalinities in terms of mg/l of CaCO_3 .

(Answer : 100; 400).

9. 100 ml of a sample of water required 5 ml of N/10 acid solution for titration while using phenolphthalein as indicator. 100 ml of the sample of water was again taken and methyl orange was used as indicator when 15 ml of the same acid solution was required for neutralization. Interpret the results of alkalinities in mg/l.

(Answer : Carbonate alkalinity 500 mg/l; bicarbonate alkalinity 250 mg/l.)

10. A zeolite softener was completely exhausted and was regenerated by passing 100 litres of a sodium chloride solution containing 120 g/l of sodium chloride. How many litres of a sample of water of hardness of 500 mg/l can be softened by the softener before regenerating it again?

(Answer : 20,513 litres).

1.11 Questions

1. Among chloramine and bleaching powder, which is the powerful disinfectant?
2. Name the indicator used in the EDTA method.
3. Why demineralization process preferred over zeolite process.
4. Write the general formula of zeolite.
5. Differentiate between sludge and scale
6. What is reverse osmosis? Explain its functioning.
7. Convert 219 ppm of $\text{Mg}(\text{HCO}_3)_2$ to CaCO_3 equivalent.
8. Treating boiling water with soda will remove what type of hardness.
9. What is meant by caustic embrittlement.
10. Explain Break point chlorination.
11. (a) Explain the scale and sludge formation in boilers.
 (b) What problems are caused by these?
 (c) Calculate the total hardness in $^{\circ}\text{Fr}$ and $^{\circ}\text{Clarke}$ for a sample of water obtained from a well in Khammam which showed the followed analysis:

$\text{MgCl}_2 = 9.5$ mg/litre;	$\text{CaCl}_2 = 11.11$ mg/litre
$\text{Mg}(\text{HCO}_3)_2 = 14.6$ mg/litre;	$\text{NaCl} = 5.84$ mg/litre
$\text{Ca}(\text{HCO}_3)_2 = 16.2$ mg/litre;	Organic impurities = 20 mg/litre
12. (a) Outline the lime-soda process for the softening of hard water.
 (b) A sample of water from Nalgonda showed the following

$\text{NaOH} = 4.0$ ppm;	$\text{MgSO}_4 = 24$ ppm
$\text{MgCl}_2 = 94$ ppm;	$\text{Ca}(\text{HCO}_3)_2 = 16.2$ ppm
$\text{Ca}(\text{NO}_3)_2 = 16.4$ ppm;	$\text{KCl} = 7.45$ ppm

Calculate the amount of lime and soda required (in kgs) to soften 10,000 litres of this water.
13. (a) What are boiler troubles and how they can be avoided?
 (b) Describe the ion-exchange process for softening of hard water.
14. (a) How is the softening of water carried out using the Zeolite process?
 (b) A sample of water from a well in Adilabad gave the following analysis:-

$\text{NaCl} = 5.85$ mg/litre	;	$\text{MgSO}_4 = 12.0$ mg/litre
$\text{Ca}(\text{HCO}_3)_2 = 8.1$ mg/litre	;	$\text{CaSO}_4 = 13.6$ mg/litre
$\text{Mg}(\text{HCO}_3)_2 = 14.6$ mg/litre	;	Organic matter = 4.0 mg/litre

Calculate the quantities (in kgs) of lime and soda required to soften 12,000 litres of this water.

15. (a) Discuss the permutit process of softening of hard water
 (b) Calculate in kgs the amount of lime and soda required to soften 10,000 litres of water from a bore well in Medak which showed the following analysis:-
- $\text{KOH} = 0.0056 \text{ gm/litre} ; \text{MgSO}_4 = 0.024 \text{ gm/litre}$
 $\text{Ca(NO}_3)_2 = 0.0164 \text{ gm/litre} ; \text{Mg Cl}_2 = 0.094 \text{ gm/litre}$
 $\text{Ca(HCO}_3)_2 = 0.0162 \text{ gm/litre} ; \text{KCl} = 0.0745 \text{ gm/litre}$
16. Write a note on Boiler troubles
17. (a) Explain the processes of scale and sludge formation in boilers.
 (b) What is caustic embrittlement and how it can be prevented?
 (c) Determine the temporary, permanent and total hardness in ppm units for a water sample from Kurnool which showed the following analysis:-
- $\text{Ca(CO}_3)_2 = 32.4 \text{ mg/litre} ; \text{Mg(HCO}_3)_2 = 29.2 \text{ mg/litre}$
 $\text{NaCl} = 5.85 \text{ mg/litre} ; \text{CaCl}_2 = 22.2 \text{ mg/litre}$
 $\text{Mg SO}_4 = 1.2 \text{ mg/litre} ; \text{Organic matter} = 15.5 \text{ mg/litre}$
18. Discuss the hot and cold lime-soda processes for the softening of hard water.
19. (a) How is the softening of hard water carried out using Zeolite process?
 (b) A sample of water from a tank in Narsapuram showed the following analysis :
- $\text{CaCl}_2 = 11.1 \text{ mg/litre} ; \text{KCl} = 40 \text{ mg/litre}$
 $\text{Organic matter} = 30 \text{ mg/litre} ; \text{MgCl}_2 = 9.5 \text{ mg/litre}$
 $\text{Ca(HCO}_3)_2 = 16.2 \text{ mg/litre} ; \text{Mg (HCO}_3)_2 = 14.6 \text{ mg/litre}$
- Calculate the amount of lime and soda required in kg to soften 50,000 litres of this water.
20. Write a short note on potable water
21. (a) Describe the ion-exchange process for softening of hard water.
 (b) One litre of water from a well in Garividi Town, near Vijayanagaram, gave the following analysis:-
- $\text{Suspended matter} = 100 \text{ mg} ; \text{Ca(HCO}_3)_2 = 81 \text{ mg};$
 $\text{Mg (HCO}_3)_2 = 146 \text{ mg} ; \text{MgSO}_4 = 120 \text{ mg}$
 $\text{Ca(SO}_4) = 136 \text{ mg}; ; \text{NaCl} = 58.5 \text{ mg}.$
- Calculate the total hardness in $^{\circ}\text{Fr}$ and $^{\circ}\text{Clarke}$ of this sample of water.
22. Define sterilization and Write a note on Sterilization of drinking water.

23. (a) Describe the lime-soda process for softening of hard water.
 (b) Sample of water from an underground reservoir in Anantapuram town gave the following analyses:-
- | | | | | |
|-----------------------------|----------------|---|-----------------|------------------|
| $\text{Ca}(\text{HCO}_3)_2$ | = 81 mg/litre | ; | NaCl | = 5.85 mg/litre. |
| Organic matter | = 25 mg/litre | ; | MgSO_4 | = 120 mg/litre. |
| $\text{Mg}(\text{HCO}_3)_2$ | = 146 mg/litre | ; | CaSO_4 | = 136 mg/litre. |
- Calculate the quantities (in kgs) of lime and soda required to soften 20,000 litres of this water.
24. Differentiate between lime-soda and zeolite processes for softening of water giving merits and demerits of the two processes.
25. How is the hardness of water expressed? What are the various units employed? Explain their interconversion.
26. What are the factors that lead to caustic embrittlement in boilers? How can this be prevented?
27. Distinguish between zeolite process and Ion-exchange process.
28. Write a note on complexometric titration used for estimation of hardness of water by EDTA.
29. Explain the process of electro dialysis.
30. (a) Why is hard water harmful to boilers?
 (b) Describe the causes and harmful effects of scale formation.
31. One liter of water from Krishna District in Andhra Pradesh showed the following analysis: $\text{Mg}(\text{HCO}_3)_2 = 0.0256$ g, $\text{Ca}(\text{HCO}_3)_2 = 0.0156$ g, $\text{NaCl} = 0.0167$ g, $\text{CaSO}_4 = 0.0065$ g, and $\text{MgSO}_4 = 0.0054$ g. Calculate the lime and soda required for softening of 10,000 litres of water.

1.12 Fill in the Blanks

1. NaCl causes _____ hardness
2. _____ water contains highest organic impurity.
3. Temporary hardness is caused by _____.
4. Formation of _____ causes caustic embrittlement.
5. $\text{Ca}(\text{HCO}_3)_2$ causes _____ hardness.
6. Equivalent weight of CaCO_3 is _____.
7. Hardness of water is measured in _____.
8. One ppm of hardness is equal to _____ °Cl.
9. Dissolved oxygen in water is removed by _____.

10. Dissolved carbon dioxide in water is removed by _____.
11. Caustic embrittlement is avoided by adding _____ softening agent
12. Phosphate conditioning of water is done by using _____ salt.
13. Radio active conditioning prevents formation of _____.
14. $MgCO_3$ forms _____ (scale/sludge)
15. $CaCO_3$ forms _____ (scale/sludge)
16. _____ forms hardest scale.
17. In Hot-Lime soda process the function of lime is to remove _____ type of hardness.
18. Alkalinity in water cannot be due to the simultaneous presence of _____
19. The process of removing extra common salt from water is called as _____
20. When $P = M$ the alkalinity is due to the presence of _____ ions.
21. A water sample contains 136 mg of calcium sulphate per liter. The hardness of water in terms of calcium carbonate _____
22. The hardest scale is formed from _____ ions.
23. _____ act as coagulant simultaneously as softening agent.
24. Chlorine is used in purification of drinking water for _____.
25. Removal of micro organisms in water is called as _____.
26. _____ is the indicator used in EDTA method.
27. EDTA is _____ acetic acid.
28. Sterilization of water is done to remove _____.
29. The best sterilization agent is _____.
30. Powerful disinfectant is _____.
31. Removal of microorganisms in water is called as _____.
32. O_3 can act as _____.