

Natubhai V. Patel College of Pure & Applied Sciences
S. Y. B.Sc. Semester-4
Industrial chemistry/ IC (Vocational)
US04CICV01/US04CICH02: Chemical Plant Utilities
UNIT – 1

SYLLABUS

Water- Impurities and hardness of natural water, Water for steam making and industrial processes, Boiler water treatments, Calculations on water treatments.

1.0 INTRODUCTION

Water is nature's most wonderful, abundant and useful compound. Without water human and plant cannot survive. Water is one of the most essential compounds like air, food, and shelter for humans. It also occupies a unique position in industries too. The most important use is in steam generation. Water is also widely used in the production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, fire-fighting etc.

1.1 SOURCES OF WATER

1.1.1 Surface waters

1.1.1.1 Rain water

It is probably the purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards through the atmosphere, it dissolves a considerable amount of industrial gases (like CO₂, SO₂, NO₂, etc.) and suspended solid particles, both of organic and inorganic origin.

1.1.1.2 River water

Rivers are fed by rain and spring waters. Water from the sources flows over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. In general, the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water. River water thus contains dissolved minerals of the soil such as chlorides, sulfates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains organic matter, derived from the decomposition of plants, and small particles of sand and rock in suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

1.1.1.3 Lake water

It has a more constant chemical composition. It, usually, contains much lesser amounts of dissolved minerals than even well water, but quantity of organic matter present in it is quite high.

1.1.1.4 Sea water

It is the most impure form of natural water. Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water, from the surface of sea, makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulfate of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

Surface water, generally, contains suspended matter, which often contains the disease-producing (or pathogenic) bacteria. Hence, such waters as such are not considered to be safe for human consumption.

1.1.2 Underground waters

A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it

meets a hard rock, when it retreads upwards and it may even come out in form of 'spring'.

1.1.3 Spring and well water or underground water

In general, is clearer in appearance due to the filtering action of the soil, but contains more of the dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

1.2 COMMON IMPURITIES PRESENT IN NATURAL WATER

Dissolved minerals: These are carbonates, bicarbonates, sulfates and chlorides of calcium, magnesium, sodium and potassium.

Dissolved gases: mainly air and Carbon dioxide

Suspended matter: consists of mineral matter, giving turbid or muddy water, Organic matter may also be present.

Microscopic matter: of plant and bacterial life giving colour, taste and odour.

From above, class 1, 2 and 3 form chief problem for industries and 3 & 4 for municipal supplies.

1.3 EFFECT OF WATER ON ROCKS AND MINERALS

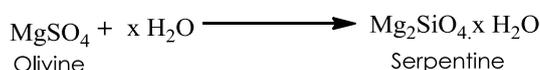
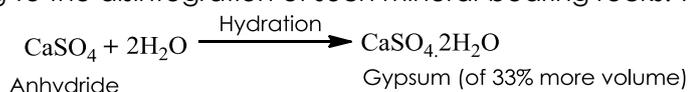
When water flow over/percolates through the ground rocks or solid, it gets contaminated due to the following physical and chemical changes:

1.3.1 Dissolution of mineral

Mineral constituents of rocks like sodium chloride, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), etc., readily dissolve in water.

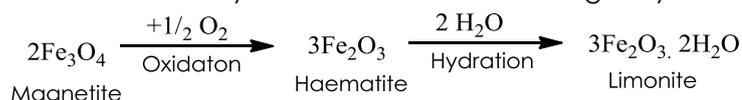
1.3.2 Hydration

Some minerals like anhydrite (CaSO_4), olivine (Mg_2SiO_4), etc., readily undergo hydration, leading to the formation of products of increased volume; and consequently, leading to the disintegration of such mineral-bearing rocks. Thus:



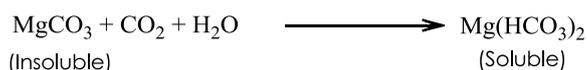
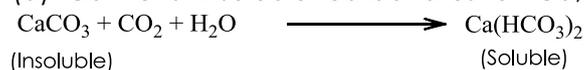
1.3.3 Action of dissolved oxygen

Oxidation and hydration reactions are brought by dissolved oxygen,

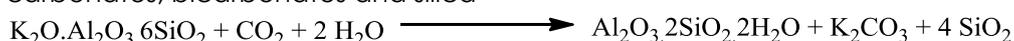


1.3.4 Action of dissolved carbon dioxide

(a) Converts insoluble carbonates of Ca, Mg and Fe into soluble bicarbonates



(b) Converts rock-forming silicates and aluminosilicates of Na, K, Ca and Fe into soluble carbonates, bicarbonates and silica



Dissolved salts, fine clay and silica finally collect in water.

When the formation of complex with the free ions is completed, EDTA extracts the ions from dye and solution turns blue. This is the end point. Hardness is calculated in parts per million (ppm) from the reading obtained and ml. of water taken.

$$\begin{aligned} \text{Total hardness (X)} &= \frac{\text{Burette reading} \times 10^6}{\text{ml. of water taken}} \\ &= X \text{ ppm} \end{aligned}$$

1.5.3 Degree of Hardness or Equivalents of calcium carbonate

The weight of all the substances is expressed in terms of a weight equivalent to the weight of CaCO₃, since this mode permits the multiplication and division of concentrations, when required. The choice of CaCO₃ in particular is due to its molecular weight is 100 (equivalent weight = 50) and moreover, it is the most insoluble salt that can be precipitated in water treatment.

Thus, equivalent of CaCO₃

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

$$= \frac{\text{Mass of hardness - producing substance} \times 50}{\text{Chemical equivalent of hardness - producing substance}}$$

For example 162 parts by weight of Ca(HCO₃)₂ would react with the same amount of soap as 100 parts by weight of CaCO₃. Therefore, the weight of Ca(HCO₃)₂ is multiplied by 100/162 to give weight in terms of CaCO₃.

Dissolved salt/ ion	Molar mass	Chemical equivalent	Multiplication factor for converting into equivalents of CaCO ₃
Ca(HCO ₃) ₂	162	81	100/162
Mg(HCO ₃) ₂	146	73	100/146
CaSO ₄	136	68	100/136
CaCl ₂	111	55.5	100/111
MgSO ₄	120	60	100/120
MgCl ₂	95	47.5	100/95
CaCO ₃	100	50	100/100
MgCO ₃	84	42	100/84
CO ₂	44	22	100/44
Mg(NO ₃) ₂	148	74	100/148
HCO ₃ ⁻¹	61	61	100/122
OH ⁻	17	17	100/34
CO ₃ ⁻²	60	30	100/60
NaAlO ₂	82	82	100/164
Al ₂ (SO ₄) ₃	342	57	100/114
FeSO ₄ .7H ₂ O	278	139	100/278
H ⁺	1	1	100/2

Table: 1 Calculation of equivalents of calcium carbonate

1.6 UNITS OF HARDNESS

1.6.1 Parts per million (ppm)

It is the parts of calcium carbonate equivalent hardness per 10⁶ parts of water, i.e. 1 ppm = 1 part of CaCO₃ eq. hardness in 10⁶ parts of water.

1.6.2 Milligrams per liter (mg/L)

It is the number of milligrams of CaCO₃ equivalent hardness present per liter of water.

Thus,

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

But 1 L of water weighs

$$= 1 \text{ kg} = 1,000 \text{ g} = 1,000 \times 1,000 \text{ mg} = 10^6 \text{ mg.}$$

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

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

1.6.3 Clarke's degree (°Cl)

It is number of grains (1/7000lb) of CaCO₃ equivalent hardness per gallon (10lb) of water. Or it is parts of CaCO₃ equivalent hardness per 70,000 parts of water. Thus,

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

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

1.6.4 Degree French (°Fr)

It is the parts of CaCO₃ equivalent hardness per 10⁶ parts of water. Thus,

$$1^\circ \text{ Fr} = 1 \text{ part of CaCO}_3 \text{ hardness eq. per } 10^6 \text{ parts of water.}$$

1.6.5 Relationship between various units of hardness

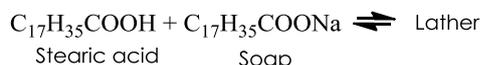
1 ppm	= 1 mg/L	= 0.1° Fr	= 0.07° Cl
1 mg/L	= 1 ppm	= 0.1° Fr	= 0.07° Cl
1° Cl	= 1.43° Fr	= 14.3 ppm	= 14.3 mg/L
1° Fr	= 10 ppm	= 10 mg/L	= 0.7° Cl

1.7 DISADVANTAGES OF HARD WATER

1.7.1 Domestic use

1.7.1.1 Washing

Hard water, when used for washing purposes, does not lather freely with soap. On the other hand, it produces sticky precipitates of calcium and magnesium soaps. The formation of such insoluble, sticky precipitates continues, till all calcium and magnesium salts present in water are precipitated. After that, the soap (eg., sodium stearate) gives lather with water. Thus,



This causes wastage of lot of soap being used. Moreover, the sticky precipitate (of calcium and magnesium soaps) adheres on the fabric/cloth giving spots and streaks. Also presence of iron salts may cause staining of cloth.

1.7.1.2 Bathing

Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is depressed and a lot of it is wasted.

1.7.1.3 Cooking

Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an unpleasant taste and muddy-looking extract. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

1.7.1.4 Drinking

Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

1.7.2 Industrial use

1.7.2.1 Textile industry

Hard water causes much of the soap (used in washing yarn, fabric, etc.) to go as waste, because hard water cannot produce good quality of lather. Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed latter on, do not produce exact shades of colour. Iron and manganese salts-containing water may cause coloured spots on fabrics, thereby spoiling their beauty.

1.7.2.2 Sugar industry

Water containing sulfates, nitrates, alkali carbonates, etc., if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

1.7.2.3 Dyeing industry

The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitates, which yield impure shades and give spots on the fabrics being dyed.

1.7.2.4 Paper industry

Calcium and magnesium salts tend to react with chemicals and other materials employed to provide a smooth and glossy (i.e., shining) finish to paper. Moreover, iron salts may even affect the colour of the paper being produced.

1.7.2.5 Laundry

Hard water, if used in laundry, causes much of the soap used in washing to go as waste. Iron salts may even cause coloration of the clothes.

1.7.2.6 Concrete making

Water containing chlorides and sulfates is used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

1.7.2.7 Pharmaceutical industry

Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.,) may produce certain undesirable products in them.

1.7.3 Steam generation in boilers

For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as

1. Carry over
2. Corrosion
3. Scale formation
4. Caustic embrittlement
5. Turbine deposits

1.8 MAJOR BOILER TROUBLES

1.8.1 Carry over

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 carryover of water by steam along with suspended and the dissolved solids are called carry over. It is mainly due to priming and foaming.

1.8.1.1 Priming

It is such rapid or violent boiling of water occurring in the boiler that water is carried into the steam outlet in the form of spray.

Priming is because of

- Very high water level
- Presence of excessive foam filling the steam space
- High steam velocity
- Sudden steam demand leading to sudden boiling
- Faulty boiler design

Priming is controlled by

- Keeping the water level as low as possible. Slight lowering of water level greatly reduces priming
- Avoid sudden steam demands, (by suddenly taking out a quantity of steam from boiler, the pressure in the boiler is reduced, the boiling point of water is reduced and super heated water is suddenly converted into steam minimizing foaming)

1.8.1.2 Foaming

It is the formation of small but stable bubbles above the surface of water. These are carried over along with steam, leading to excessive priming.

Foam formation takes place when the concentration of solid in the surface layer is different from that in the mass of the liquid. This means that the solid must change the surface tension of water and promote foaming. Presence of fatty oil may form soap with the alkalinity. Soap greatly reduces surface tension of water.

Foaming can be controlled by the use of anti-foaming chemicals. e.g. Castor oil, which spreads on the surface of the water. This oil is used for low-pressure boilers. Only satisfactory way for foaming is blow down, i.e. removal of concentrated boiler water and replacing it by fresh feed water.

Carry over is undesirable because

- A considerable amount of heat is wasted by the removal of hot boiler water (i.e. in case of blow down).
- Water reduces superheat of steam in the super heaters.
- water takes along with it grit which strikes on the surface at high velocity and damages the walls
- Water contains large amount of dissolved solids which gradually get deposited and restrict the passage in the pipelines, causing corrosion and insulation,
- Water entering the steam engine cylinder causes serious trouble because of its incompressibility and inability to escape quickly through the steam parts.
- Foaming of water makes it difficult to know the exact level of water in the gauge glass.

1.8.2 Corrosion

It 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 O₂ and CO₂ are released during heating of water.

These gases have corrosive effects corrosion is because of:

- Dissolved oxygen
- Mineral acids
- Dissolved CO₂
- Galvanic cell formation

1.8.2.1 Dissolved oxygen

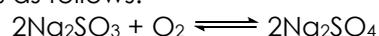
Dissolved oxygen in water is mainly responsible for corrosion in boilers. Dissolved O₂ in presence of moisture and at high temperature readily attacks iron. At high pressure, O₂ will dissolve more and high temperature reduces O₂ content. Solubility of O₂ in pure water is more than in the impure water.

Dissolved oxygen can be removed by

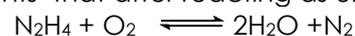
(a) Mechanical deaerator: Various types of deaerators have been designed. In a cylindrical chamber, water falls through perforated plates or is sprayed, so that larger surface is exposed. The deaerator is connected to a vacuum line, which sucks out the gases.

(b) Pre-heating: Solubility of a gas decreases with rise in temperature. Air begins to be expelled at temperature of about 65°C and is completely removed at the boiling point. Water is sprayed in a cylindrical equipment and steam moving in opposite direction. Steam heats and carries away the gases, which have been liberated.

(c) Chemical treatment: for complete removal of O₂ chemical treatment is required. This is done by adding a reducing agent, sodium sulphite being commonly used, which reacts as follows:



Ferrous sulfate is also used. It gives precipitate of Fe(OH)₂ which is oxidized to Fe(OH)₃. In high-pressure boiler, even traces of O₂ are undesirable hydrazine is added in such amounts that after reacting as under, residual hydrazine is about 0.02 mg/litre.



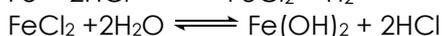
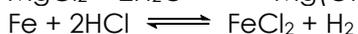
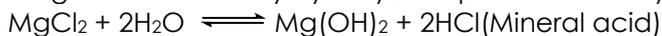
Thus no solid is added to the boiler. Hydrazine should be handled carefully; usually its

solutions are used.

1.8.2.2 Mineral acids

Natural waters are alkaline. Waters in the mining areas are often acidic. In industrial areas the water may become acidic due to acidic industrial waste discharge into water.

Magnesium salts may hydrolyze to produce acidity as follows:



Thus small amount of MgCl_2 will cause corrosion of a large amount of iron by producing HCl. Boiler water should have a pH value of about 10.5 so that acid may not attack iron.

1.8.2.3 Carbon dioxide

Water contains some dissolved CO_2 . If bicarbonates are present into the water, on heating they will decompose and produce more CO_2 . CO_2 with water gives carbonic acid, H_2CO_3 , which has a corrosive effect. Local corrosion caused by CO_2 is called pitting.



CO_2 can be removed by addition of limestone.



CO_2 can also be removed by NH_3 but NH_3 is corrosive to copper and its alloys, therefore amines are used.

1.8.2.4 Galvanic cells

Galvanic cells which iron forms with some of the boiler fittings made of other materials or with impurities, which cause corrosion. Zn is more electropositive than iron hence it is anodic to iron and gets dissolved first and iron is saved.

1.8.3 Scale formation

Water containing impurities is fed into the boiler and pure water is removed in the form of steam leaving behind the impurities.

Some of the deposits stick to the metal surface and are known as scale. If they are in the form of soft and muddy deposits, which can be removed easily, are known as sludges.

Scale formation takes place because of salt like $\text{Ca(HCO}_3)_2$ which gives off CO_2 and insoluble CaCO_3 is precipitated on boiler surface giving the scale.

Some salts having lower solubility at high temperature cause crystallization, e.g. CaSO_4 crystallizes out on the surface at high temperature.

Silicate of Calcium and magnesium or other silicates deposit cause trouble because they are poor thermal conductor.

1.8.3.1 Disadvantages of scale formation

Waste of Fuel: The scales are bad conductors of heat, therefore they act as an insulator on the surface. This results in reduction in the heat transfer rate hence large quantity of fuel is required to maintain the rate of heat transfer.

Overheating of the boiler tubes: This is explained by following figure

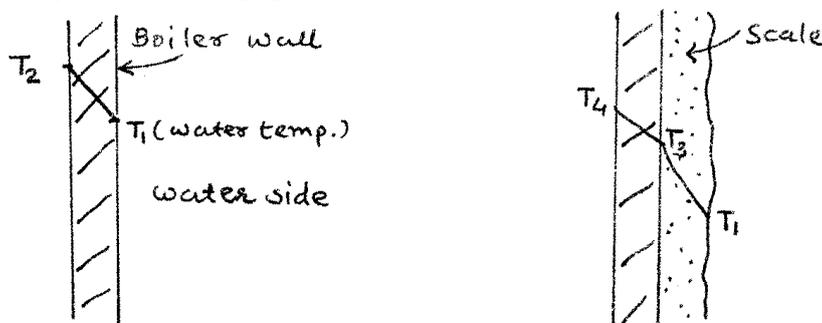


Figure: 1 Insulating effect of scales

The figure to the right represents surface with scale. Therefore, heating the water to $T_1^\circ\text{C}$ the metal surface in the heat source side is heated to $T_4^\circ\text{C}$ which is higher than $T_2^\circ\text{C}$.

At high temperature metal becomes weak and cannot withstand high pressure. This becomes dangerous.

1.8.3.2 Prevention of scale formation

External treatment: It is given outside the boiler to remove the calcium and magnesium salts and silica from water which forms scale. For this, external equipment is needed which requires an investment.

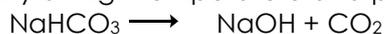
Internal treatment: Chemicals are added into the water entering the boiler, to convert the remaining salts into more insoluble salts that will be in form of nonstick sludge. This can be easily removed.

Blow down: In spite of giving external and internal treatment, concentration of impurities goes on increasing and practical solution is to make a blow down, i.e. remove the portion of the concentrated water which contains a large amount of dissolved matter. Along with it some sludge is also removed.

1.8.4 Caustic embrittlement

Sometimes boiler failure is due to metal plate becoming brittle and cracks having been formed in the metal. This happens in areas which are under stress.

Alkali metal carbonates and bicarbonates present in water give rise to caustic alkalinity at high temperature and pressure,



Alkali metal Caustic
Bicarbonate

The concentration becomes greater near the rivets because of bad circulation of water and also the leaks through which steam escapes leaving behind water with a higher concentration of caustic alkalinity.

1.8.5 Turbine deposits

To avoid or to minimize the turbine deposit, chemical analysis throughout the steam and water line is carried out. Chemicals are added properly and mixed properly. Operate demineralization plant properly to avoid the dissolved mineral matters.

1.9 METHODS OF BOILER WATER TREATMENT

The common treatments given to the boiler water to overcome from the troubles are described below

1.9.1 Preliminary treatments

They may include simple treatments like sedimentation, coagulation and filtration.

1.9.1.1 Sedimentation and Coagulation

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 in which water moves very slowly. Time required for sedimentation depends on the weight, size and shape of particles and the viscosity and fractional resistance of water. Because viscosity varies with temperatures the settling rate varies in differ at season. Sedimentation requires 4-12 hours.

Generally, only 70% of suspended matter settles down by plain sedimentation.

Further removal of matter is done by addition of coagulants like, alum, ferrous sulfate, ferric chloride, sodium aluminate etc. Generally about 95% suspended matter is removed by coagulation.

Coagulation reactions are salt hydrolyses and produce a flow of the hydroxide e.g. $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. The flocculent precipitate so produce has a large surface area and the floe removes the finally divided matter by adsorption or electrical attraction of oppositely charged particles, which quickly settle down.

1.9.1.2 Filtration

It is 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 liquid. Two types of filters are used viz., gravity filters and pressure filters

1.9.2 Pre-heating

It is heating feed water before enters the boiler. Very often blow down and low pressure steam is available. Hot fuel gas also is used for pre-heating. Water may be heated in a heat exchanger.

Advantages

- Save fuel
- Removes temporary hardness

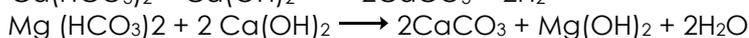
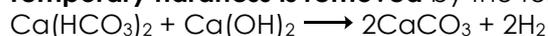
$$\text{Ca (HCO}_3)_2 \longrightarrow \text{CaCO}_3(s) + \text{CO}_2 + \text{H}_2\text{O}$$
- Removes dissolved $\text{O}_2 + \text{CO}_2$. Initially at 65°C dissolved gases are removed from water and almost completely removed at boiling point. Thus removal of corrosive gases is advantageous.
- Use of hot water in chemical treatments such as lime-soda process, greatly helps in the process

1.9.3 Lime-soda process

It is used for feed water treatment for low and medium pressure boilers. Lime and soda convert the soluble impurities, into insoluble salts, which get precipitated and after settling they are filtered off.

Lime is generally 10% excess is added to water. Its advantages are

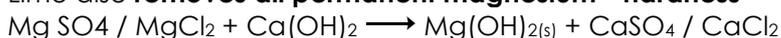
Temporary hardness is removed by the following reactions:



CaCO_3 & Mg(OH)_2 are precipitated.

The removal of temporary hardness by lime does not introduce any soluble salt in water and reduce the total dissolve solids.

Lime also **removes all permanent magnesium - hardness**



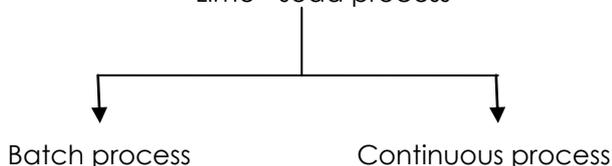
An equivalent amount of permanent calcium hardness is introduced, which has to be removed by soda treatment. Here, there is no softening.

Lime also **removes free acids, CO_2 and H_2S**

Soda Treatment: It removes the remaining calcium permanent hardness.



Lime - soda process



1.9.3.1 Batch process

In this process chemicals are added in batches in water taken in tanks, agitated for necessary time and the precipitate allowed to settle and then filtered. Fresh water is again taken into the tank and the operation is repeated.

1.9.3.2 Continuous process

Water together with lime and soda solutions enters a smaller tank continuously at a predetermined rate.

The chemicals and water to be treated enter a bigger tank or chamber (see the figure). The second chamber is tall structure having a larger cross section at the top than at the bottom. As chemical reactions settle down, because towards the upper portion of chamber the velocity is less due to larger cross section, clear water is removed continuously from the top and sludge from the bottom. A part of sludge is recycled which helps in reuse of excess chemicals left behind in the sludge and also helps in precipitation by providing nuclei.

1.9.3.3 Cold 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 precipitate is finely divided and do not settle easily, nor can it be easily filtered. Therefore it is necessary to add coagulants like alum, aluminum sulfonate, sodium aluminate etc.

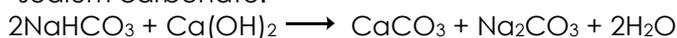
Coagulants get hydrolyzed and form flocculent and gelations precipitated which entraps the finely divided particles and settle down readily or are easily filtered off. Ferrous sulfate and sodium aluminate are costlier than alum. Ferrous sulfate helps to remove oxygen and sodium aluminate helps the removal of silica and also oil.

1.9.3.4 Hot lime soda process

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 calculated amount of chemicals is added as in cold process.

Advantages

- As reactions proceed, quickly at higher temperature, the reactions are completed in about 15 min., whereas in the cold process, several hours are needed. This greatly increases the capacity of the plant.
- Precipitate and sludge formed settle rapidly at higher temperature; hence coagulants are not needed.
- 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.
- Residual hardness, i.e. hardness of softened water needs careful consideration. Solubility of calcium salts is very slightly higher at low temperature. More than this, the time taken for the completion of the reaction at a lower temperature is greater. In the hot process the reaction time is less with the result that the hot process gives softer water. In some places, water is highly alkaline, and contains considerable amounts of sodium bicarbonates. On adding lime, calcium carbonate precipitates forming sodium carbonate.



In such a case, soda may not be heated 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.

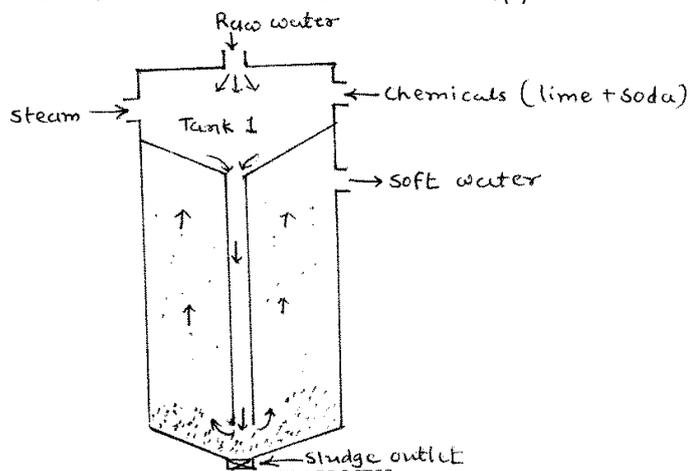


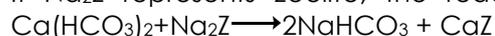
Figure: 2 Hot lime soda process

1.9.4 Permutit or zeolite process

Zeolites are natural or synthetic complex compounds, consisting of hydrated sodium aluminum silicates approximately corresponding to the chemical formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$. Zeolites are insoluble.

They introduce Na^+ in place of Ca^{+2} and Mg^{+2} . As these exchange bases, they are also known as base exchangers.

If Na_2Z represents Zeolite, the reactions taking NaCl may be represented thus:



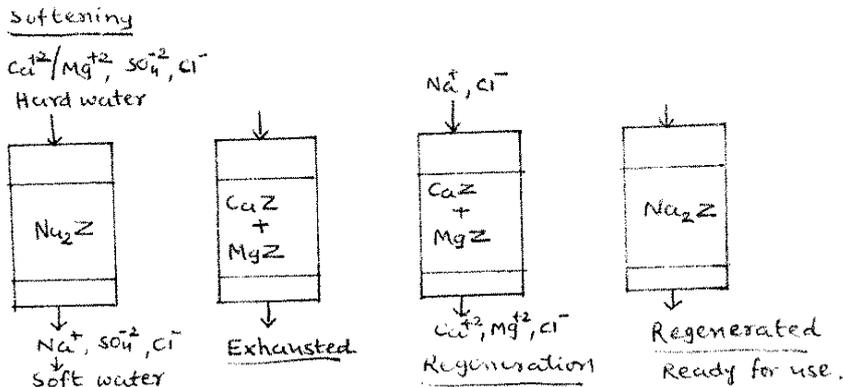


Figure: 3 Water softening by Zeolite process.

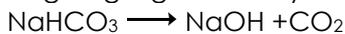
Zeolites are kept in cylinders, which act as filter beds. Hard water is passed through them. The hardness causing substances are retained as insoluble compounds according to the reactions given above. After use for some time the zeolite is converted into Calcium or magnesium zeolite and then it stop to soften water. At this stage it has to be regenerated by treatment with a conc. sodium chloride solution. When the original sodium zeolite is recovered



The Zeolite bed is again ready for use.

Turbidity will clog the pores and restrict the flow, excess acidity alkalinity will attack the zeolite, therefore pH value 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 zeolite bed. Hot water is not passed through zeolite bed because zeolite tends to dissolve in hot water.

The temporary hardness will give water containing NaHCO_3 which dissociates inside the boiler giving high alkalinity



Alkalinity causes caustic embrittlement. CO_2 with steam makes condensed water acidic, hence corrosive. Thus it is necessary to remove temporary hardness as far as possible before using zeolite.

Advantages

- It removes the hardness completely.
- Equipment is a compact unit occupying a small space
- It automatically adjusts itself to different hardness and can be worked under pressure, therefore plant can be installed in the water supply line and avoid double pumping
- Impurities are not precipitated; there is no danger of sludge formation at a later stage.

1.9.5 Deionizer or Demineralizers

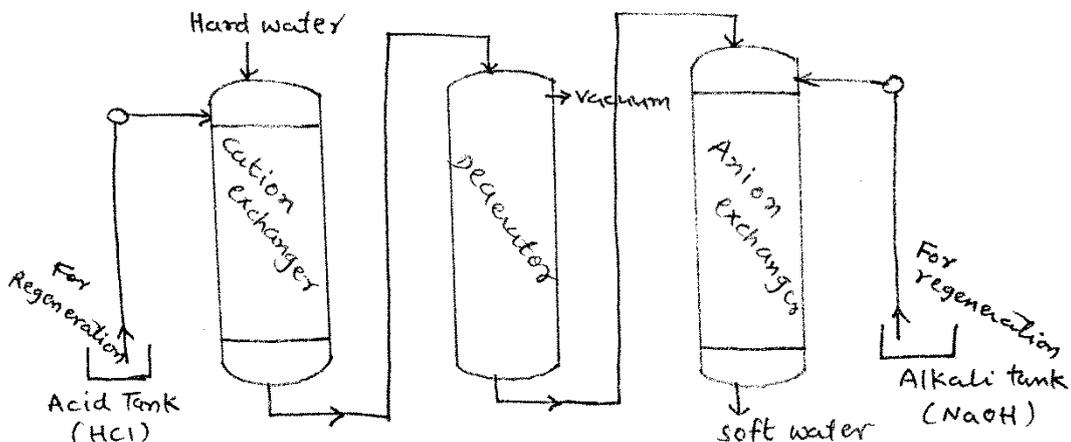
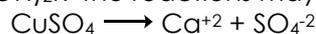


Figure: 4 Water softening by deionizer or demineralizer process

Several organic substances - resins of complex chemical structures - which behave similar to the zeolites. By this process all the ions are removed. The cations are replaced by OH⁻. Water is treated in two cylinders containing the resins, one of which removes cations and other anions.

When resins get used up, they are regenerated by acid and alkali treatment

Suppose the first and second cylinders contain resins represented by the formulas H₂R' and (OH)₂R'' the reactions may be represented thus :



Cylinder I: $\text{H}_2\text{R}' + \text{Ca}^{+2} \longrightarrow 2\text{H}^+ + \text{CaR}'$

Water coming out from cation exchanger is highly acidic. Water from nature contains large amount of carbonates and bicarbonates. These ions like other anion can be removed by passing through union exchanger. CO₃⁻² & HCO₃⁻ in presence of H⁺ form H₂CO₃⁻ (or H₂O + CO₂). The loud on anion

Exchanger is reduces by having a deaerator which will remove CO₂.

Cylinder II: $(\text{OH})_2\text{R}'' + \text{SO}_4^{-2} \longrightarrow 2\text{OH}^- + \text{SO}_4\text{R}''$

H⁺ and OH⁻ unite to form H₂O, thus not solid is added to water. When the plant does not soften any more, the first cylinder is regenerated by passing a dil. Solution through it and second cylinder by passing dilute alkali.

Reactions for regeneration



Mixed bed deionizers are also now available. The main disadvantage of process is the equipment is costly and more expensive chemicals are needed for regeneration. If water contains turbidity or large amount of dissolved salts then the output is reduced.

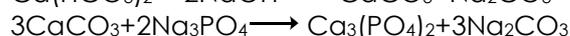
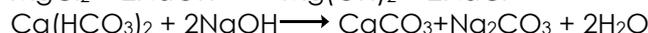
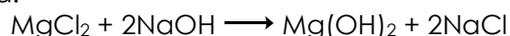
This process is very good for water for very high pressure boilers. For low pressure boiler, the equipment is rather costly and water may be treated more economically by other processes.

1.10 FEED WATER CONDITIONING

It is treatment given to correct undesirable tendencies.

1.10.1 Phosphate treatment

In the lime- soda process, calcium is precipitated as CaCO₃, which is quite insoluble. However a small amount remains in solution. This can be removed by sodium phosphate (Na₃PO₄) which precipitates the less soluble Ca₃(PO₄)₂, thus hardness is further reduced. For the best results, the pH value of water should not be less than 9.5. For this purpose NaOH is added.



Na₃PO₄ and NaOH precipitate magnesium as hydroxide and calcium as phosphate. These reagents are costlier than lime and soda.

Na₃PO₄ treatment also helps to control pH value of water. Na₃PO₄ gives alkaline reaction and can be used to increase the pH value.

This treatment is often given after lime-soda treatment. It has disadvantage of causing "after precipitation", that is gradual precipitation in pipes, equipment, etc.

1.10.2 Sodium aluminate treatment

Sodium aluminate precipitates calcium and magnesium as insoluble aluminates NaAlO₂ hydrolyses also, giving NaOH and Al(OH)₃. NaOH so produced precipitates some of the magnesium as Mg(OH)₂. Flocculent precipitates of Al(OH)₃ and Mg(OH)₂ are produced which remove finely suspended and colloidal impurities., including silica and oil droplets, which are ordinarily difficult to remove. Sodium aluminate is cheaply available from bauxite refineries.

1.10.3 Treatment for microbiological growth

The growth of greenish matter may be commonly observed in stagnant waters. Similar growth may take place in heat exchangers, condensers and cooling systems. They restrict

the flow of water and also retard the heat transfer. Sometimes they may come out suddenly in large masses and clog the pipe or the pump. Algae and slime are present in such water.

Bacteria produce gas which can attack stainless steel and cause pitting.

Chlorine is very effective to remove algae and slime. CuSO_4 is more effective for algae than for slime. It cannot be used if pH value is above 8.5 as copper hydroxide will be precipitated. Chromates are used for corrosion control and for control of algae and slime.

Chloramine is also used. Bleaching powder mixed with NH_3 and when NH_3 and Cl_2 combine to form Chloramine which destroys the microbiological growth.

1.10.4 Fe and Mn Removal

These are present in small amounts in water in absence of dissolved O_2 . Fe and Mn give red and black precipitates, respectively, when water comes in contact with air. They are highly undesirable in water for dye and tanning industries and for laundries. They also give metallic taste to water. They are removed in forms of insoluble $\text{Fe}(\text{OH})_3$ & $\text{Mn}(\text{OH})_2$ by oxidation, followed by coagulation and filtration. The oxidation may be by blowing of air in water.

1.10.5 Silica Removal

About 5-8 mg/lit silica is present in natural water. After lime-soda process because of alkalinity of water, during filtration through sand bed silica dissolves in water. Calcium and Magnesium silicates act as cements and bind together other particles into a hard scale.

Soluble silica is removed by the use of magnesium compounds like MgO . For high pressure boiler silica is removed by strongly basic anion exchangers.

1.10.6 Oil removal

Generally, natural waters are free from oil but small amounts are likely to come from the oils used for lubrication of the pumps.

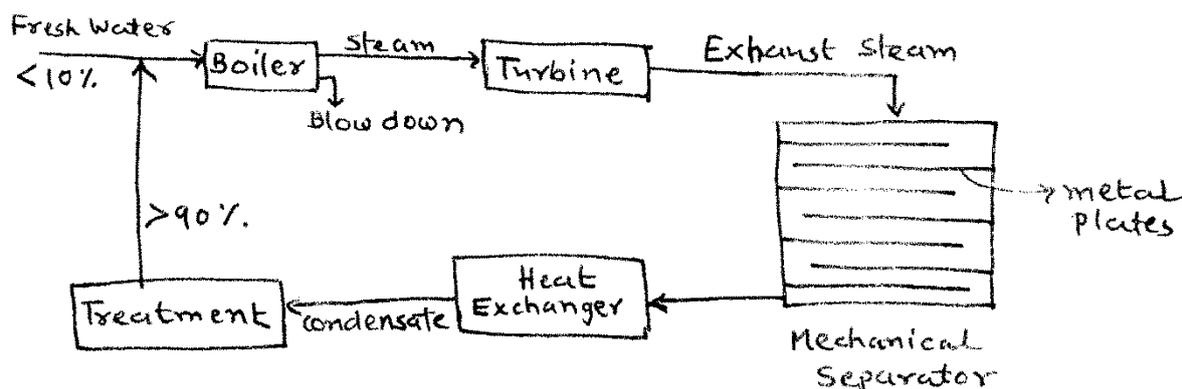


Figure: 5 Oil removals by mechanical separator

For removal of oil the exhaust steam is passed through mechanical oil separators, which consists of a chamber with a number of metal plates. As the steam with droplets of oil passes over the plates, droplets of oil are retained on the metal surface. Thus most of the oil is removed. Sodium aluminate is added to the condensate, which removes remaining oil.

If oil is vegetable or animal oil, it may get hydrolysed producing fatty acids, which may have corrosive action.

Fatty acids may combine with the alkalinity, producing soap, which forms sticky coating on the metal surface. These will attract other impurities and form thicker deposits.

1.10.7 O_2 removal

Write down about preheating, deaerator and reducing agents in this topic, which you previously studied.

1.10.8 Boiler compounds

The inorganic constituents of boiler compounds precipitate the scale forming salts and also help to control the corrosion. The organic constituents are characterized by high molecular weights. These form large particles, which are adsorbed on the metal surface and then prevent the formation of hard scale.

Boiler compounds are more expensive than the ingredients brought separately.

Example 1: Calculate the amount of lime-soda needed for softening water containing the following per liter.

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.

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

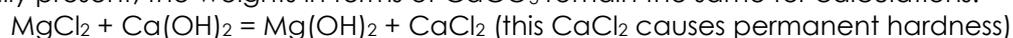
$$\text{CaSO}_4 \dots 136 \times \frac{100}{136} = 100 \text{mg}$$

- i. Temporary hardness is due to the bicarbonates which are 100+50 = 150 mg/L.
- ii. Total hardness is the sum of all the hardness causing constituents which are 100+50+100+100 = 350 mg/L.
- iii. Lime requirements are for temporary Ca hardness + 2x temporary magnesium hardness + permanent Mg hardness.

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

- iv. Soda is needed for permanent Ca hardness+ permanent Mg hardness.

Permanent magnesium hardness appears under soda requirements 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.



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

Example 2: In example 1 calculate the amounts of lime-soda needed per 10,000 liters 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

$$= 222 \times \frac{100}{85} \text{ mg / L}$$

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

$$\therefore \text{Actual lime requirements} = 222 \times \frac{100}{85} \times 110 = 287.3 \text{mg / L}$$

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

Similarly soda requirements per 10,000 liters

$$= 222 \times \frac{100}{98} \times \frac{110}{100} \times \frac{10,000}{1,000} = 2380 \text{ g or } 2.38 \text{kg}$$

Example 3: Calculate the amounts of lime-soda needed for the treatments of 1,000 liters of water containing the following:

CaCO₃- 120 mg/l; MgCO₃- 42mg/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 CaCO_3 and MgCO_3 . Permanent hardness will be caused by $\text{Mg}(\text{NO}_3)_2$. KCl will not react with lime and soda. On converting the weights in terms of the weight of CaCO_3 the following results are obtained.

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

$$\text{MgCO}_3 \quad \dots 42x \frac{100}{84} = 50 \text{ mg / L} \quad \text{CaCl}_2 \dots 111x \frac{100}{111} = 100 \text{ mg / L}$$

Lime required for CaCO_3 and MgCO_3 (present as bicarbonates) and for $\text{Mg}(\text{NO}_3)_2$.

$$\text{Lime requirement} = \frac{74}{100} x (120 + 2x50 + 100) = 236.8 \text{ mg / L}$$

$$1000 \text{ liters of the sample needs} = 236.8x \frac{1000}{100} = 236.8 \text{ g of lime}$$

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 liters of the sample.

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

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 liter for its treatments if the purity of lime 90% and that of soda 98%. What is the hardness of the sample?

Solution

The suspended and organic matters do not need lime and soda. Sulfuric 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.

$$\text{CaSO}_4 \quad \dots 250x \frac{100}{136} = 184 \text{ mg / l}$$

$$\text{MgSO}_4 \quad \dots 240x \frac{100}{120} = 200 \text{ mg / l}$$

$$\text{MgCl}_2 \quad \dots 190x \frac{100}{95} = 200 \text{ mg / l}$$

$$\text{H}_2\text{SO}_4 \quad \dots 98x \frac{100}{98} = 100 \text{ mg / l}$$

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

As the sample is 90% pure, the weight of the sample of lime needed

$$370x \frac{100}{90} = 411 \text{ mg / l.}$$

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

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

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 10ml 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.

Volume of N/50 Na_2CO_3 solution left unreacted

\equiv volume of N/50 acid solution used for titration = 10 ml.

Volume of N/50 Na_2CO_3 solution used in precipitation = 25-10 = 15 ml

1 liter of N solution \equiv 50 g of CaCO_3

\therefore 15 ml of N/50 Na_2CO_3 solution

$$\equiv \frac{50}{50} \times \frac{15}{1000} = 0.015 \text{ g of } \text{CaCO}_3$$

\therefore Hardness equivalent to 0.015 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 liter of a sample of water was completely removed by passing it through a zeolite softener. The zeolite softener required 200 liter of sodium chloride solution containing 20,000 mg/l of NaCl for regeneration. Calculate the hardness of the sample of water.

Solution

As 200 liter of sodium chloride solution containing 20,000 mg/l of NaCl was needed to generate the zeolite through which 10,000 liter of the sample of hard water is equivalent to 200 x 20,000 mg of NaCl.

Since 58.5 parts of NaCl \equiv 50 parts of CaCO_3

The hardness of 10,000 liters of the sample

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

or the hardness of 1 liter of the sample

$$\equiv 200 \times 20,000 \times \frac{50}{58.5} \times \frac{1}{1000} \text{ mg of } \text{CaCO}_3$$

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

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