Unit 1: Water treatment

❖ **Water Hardness:** The hardness of water arises due to the high mineral content.

✓ Hard water is formed when water percolates through deposits of limestone, chalk, or gypsum, which are largely made up of calcium and magnesium carbonates, bicarbonates, and sulfates.

✓ Hard water does not lather with soap but instead forms a precipitate i.e. soap scum.

$$2C_{17}H_{35}COONa \; + \; CaCl_2/MgCl_2 \; \rightarrow \; (C_{17}H_{35}COO)_2 \, Ca/Mg + 2NaCl$$

soap (soluble)   salts (soluble)   insoluble scum

✓ Long-term use of hard water causes the formation of limescale in vessels e.g., kettles and water heaters for domestic purposes. However, it can create critical problems in industrial settings, where water hardness is monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment that handles water.

✓ Rainwater and distilled water are soft because they contain comparatively fewer ions.

❖ **Representative chemical explanation of the origin of hardness of water:**

The following equilibrium reaction describes the dissolving and formation of calcium carbonate and calcium bicarbonate (on the right):

$$CaCO_3 \text{ (s)} + CO_2 \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons Ca^{2+} \text{ (aq)} + 2 \, HCO_3^- \text{ (aq)}$$
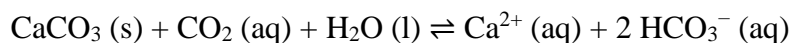
The reaction can proceed in either direction. Rain containing dissolved carbon dioxide can react with calcium carbonate and carry calcium ions away with it. The calcium carbonate may be re-deposited as calcite as the carbon dioxide is lost to the atmosphere, sometimes forming stalactites and stalagmites.

❖ **Types of Hardness:** The hardness of water can be classified into two types:

➤ **Permanent hardness:**

The permanent hardness of water is determined by the concentration of multivalent cations in the water. Usually, the cations have a charge of 2^+. Common cations found in hard water include Ca^{2+} and Mg^{2+}. In general, when the soluble salts of magnesium and calcium are present in the form of carbonates, chlorides, and sulfides in water, it is called permanent hardness because this hardness cannot be removed by boiling. These ions enter in a water supply by leaching from minerals within an aquifer. Common calcium-containing minerals are Calcite and Gypsum. A common magnesium mineral is Dolomite (which also contains calcium as part of the ore).

➤ **Temporary hardness:**

Temporary hardness is caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these types of minerals yield calcium and magnesium cations (Ca^{2+}, Mg^{2+}) and carbonate and bicarbonate anions (CO_3^{2-} and HCO_3^-). However, unlike permanent hardness, the "temporary" hardness can be reduced either by boiling the water or by the addition of lime (calcium hydroxide) through the process of lime softening. Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of the solution, leaving water that is softer upon cooling.

❖ **Disadvantages of hard water:**

✓ When hard water is heated, limescale forms and is deposited in particular places. As a result, appliances for heating water and water pipes both have furring. The build-up of deposits in pipes and appliances can result in blockages, and in appliances, it can reduce energy efficiency and shorten life.

✓ Use of hard water can create critical problems in industrial settings, where water hardness can cause costly breakdowns in boilers, cooling towers, and other equipment that handles water.

✓ Washing garments in hard water can make them appear dull and grey, losing all of their original colors.

✓ With soap or detergents, lathering is challenging. Additionally, using hard water increases the likelihood of scum build-up, which wastes soap.

✓ Hard water can cause dry skin and hair in people, among other effects.

❖ **Water softening processes:**

❖ **Water softening-lime-soda process:**

The soda lime process was used earlier in water treatment to remove hardness from water. This process is now obsolete but was very useful for the treatment of large volumes of hard water. Addition of lime (CaO) and soda (Na_2CO_3) to the hard water precipitates calcium as the carbonate, and magnesium as its hydroxide. The amounts of the two chemicals required are can be calculated from the analysis of the water and stoichiometry of the reactions.
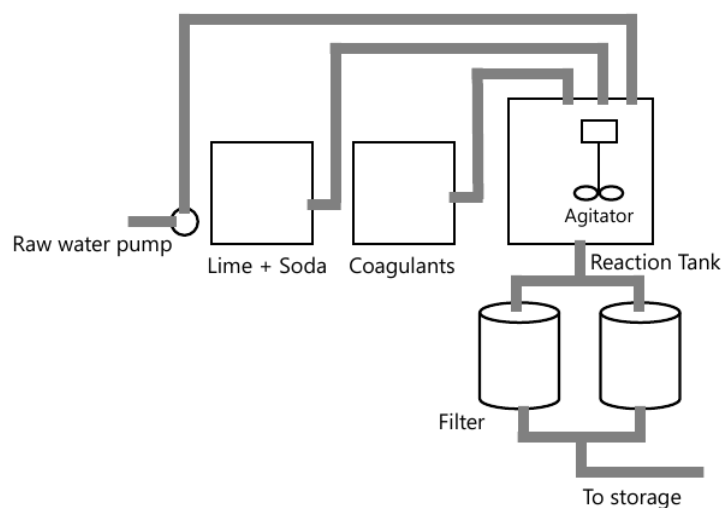
Set-up of Lime-Soda Process for the removal of water-hardness

The stepwise reactions that take place in this process can be attributed as follows:

➢ As slacked lime is added to water, it will react with any carbon dioxide present to ppt calcium carbonate: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$....(1)

➢ The lime will react with bicarbonates to precipitate corresponding carbonates:
$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$.....(2)
$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3\downarrow + 2H_2O$.....(3)

- Since the magnesium carbonate formed in the medium is soluble in nature, more lime is added to remove it via its conversion into insoluble magnesium hydroxide: $Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3\downarrow + Mg(OH)_2\downarrow$.....(4)
- Magnesium non-carbonate hardness, such as magnesium sulfate is removed via its conversion into insoluble hydroxide by lime: $Ca(OH)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(OH)_2\downarrow$.....(5)
- Lime addition removes only magnesium hardness and calcium carbonate hardness but additionally produces calcium non-carbonate hardness e.g., calcium sulfate as shown in equation 5.
- Soda ash is added to remove calcium non-carbonate hardness by precipitating insoluble carbonate: $Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3\downarrow$.....(6)
- pH of about 9.5 and 10.8 are required to precipitate $CaCO_3$ and $Mg(OH)_2$ respectively. Therefore, an excess lime of about 1.25 meq/l is required to raise the pH.
- The amount of lime required can be calculated as: lime (meq/l) = carbon dioxide (meq/l) + carbonate hardness (meq/l) + magnesium ion (meq/l) + 1.25 (meq/l)
- The amount of soda ash required: soda ash (meq/l) = non-carbonate hardness (meq/l)

➜ **Problems associated with the process:**
- ✓ After the process of softening, the water will have high pH and will contain the excess lime and magnesium hydroxide, and calcium carbonate that did not precipitate.
- ✓ Recarbonation (adding carbon dioxide) is used to stabilize the excess lime and magnesium hydroxide, which also reduces pH from 10.8 to 9.5 as the following: $CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$ and $CO_2 + Mg(OH)_2 \rightarrow MgCO_3 + H_2O$
- ✓ Further recarbonation will lower the pH to about 8.5 and stablize the calcium carbonate as the following: $CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2$
- ✓ Thus it is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

➜ **Limitation of Soda Lime Process:**
- ✓ Lime soda softening cannot produce water completely free of hardness because of the partial solubility of $CaCO_3$ and $Mg(OH)_2$. Thus, the minimum calcium hardness that can be achieved is about 30 mg/L as $CaCO_3$, and the magnesium hardness is about 10 mg/L as $CaCO_3$. We normally tolerate a final total hardness on the order of 75 to 120 mg/L as $CaCO_3$, but the magnesium content should not exceed 40 mg/L as $CaCO_3$ (because a greater hardness of magnesium forms scales on heat exchange elements).
- ✓ Disposal of large amounts of sludge (insoluble precipitate) poses a problem.

❖ **Ion exchanger polished water:**
   Ion exchangers exchange one ion for another, hold it temporarily, and then release it to a regenerant solution. In an ion exchange system, undesirable ions in the water supply are replaced with more acceptable ions.

❖ **Sodium zeolite softener:**
➜ **Zeolite:** Zeolites are hydrated sodium alumina silicates having a porous structure with molecular formula $Na_2O.Al_2O_3.xSiO_2.yH_2O$ (x = 2 to 10 and y = 2 to 6). They

are represented as Na_2Ze where Ze represents the insoluble framework and Na are the loosely held sodium ions.

➜ **History of the development of zeolite:**

✓ In 1905, Gans, a German chemist, used synthetic aluminosilicate materials known as zeolites in the first ion exchange water softeners. Although aluminosilicate materials are rarely used today, the term "zeolite softener" is commonly used to describe any cation exchange process.

✓ The synthetic zeolite exchange material was soon replaced by a naturally occurring material called Greensand. Greensand had a lower exchange capacity than synthetic material, but its greater physical stability made it more suitable for industrial applications. Capacity is defined as the amount of exchangeable ions a unit quantity of resin will remove from a solution. It is usually expressed in kilograms per cubic foot as calcium carbonate.

Microscopic view of cellular resin beads (20-50 mesh) of a sulfonated styrene-divinylbenzene strong acid cation exchanger
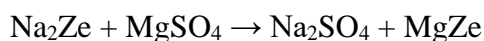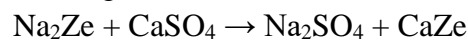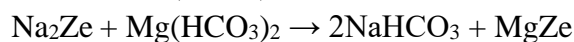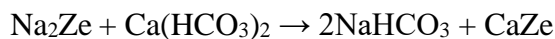
✓ The development of a sulfonated coal cation exchange medium, referred to as carbonaceous zeolite, extended the application of ion exchange to hydrogen cycle operation, allowing for the reduction of alkalinity as well as hardness.
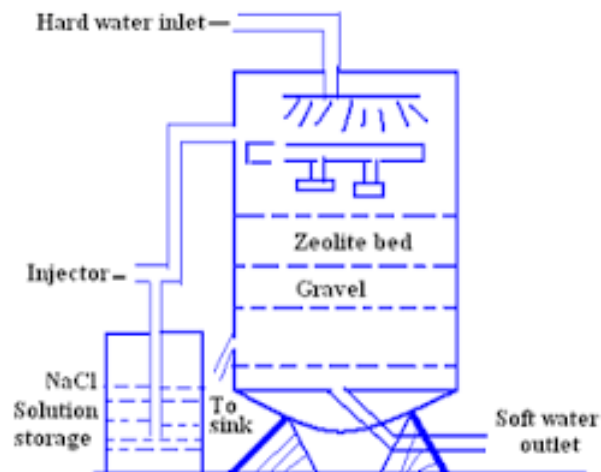

➜ **Principle of zeolite process:** They are capable of exchanging their loosely bound sodium ions reversibly with the hardness-producing cations in water (Ca^{2+} and Mg^{2+}).

➜ **Working:** It involves two steps:

- **Water softening:** When Ca^{2+} and Mg^{2+} ions containing hard water is passed through a bed of sodium zeolite, the sodium ions are replaced by the calcium and magnesium ions.

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow 2NaHCO_3 + CaZe$$
$$Na_2Ze + Mg(HCO_3)_2 \rightarrow 2NaHCO_3 + MgZe$$
$$Na_2Ze + CaSO_4 \rightarrow Na_2SO_4 + CaZe$$
$$Na_2Ze + MgSO_4 \rightarrow Na_2SO_4 + MgZe$$

- **Regeneration:** When all sodium ions are replaced by calcium and magnesium ions, the zeolite becomes inactive and thus needs to be regenerated in order to continue to the second cycle of working. Brine solution is passed through the bed of inactivated zeolite where the following reactions are taken place and form Na_2Ze is regenerated.

$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$
$$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$$
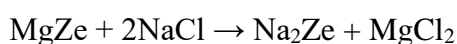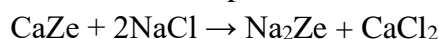
➔ **Advantages of the zeolite process:**
✓ It produces water with about 10 ppm hardness left behind.
✓ There is no danger of sludge formation.
✓ Requires less time and operation is clean.
✓ Process automatically adjusts itself for variation in the hardness of incoming water.
✓ Equipment is compact, and maintenance and operation are easy.

➔ **Disadvantages of the zeolite process:**
✓ This method only replaces cationic impurities; anions are left behind in the water.
✓ Treated water contains more sodium salts, so this water cannot be used in boilers else it will cause caustic embrittlement.

➔ **Limitations of the zeolite process:**
✓ Turbid water cannot be fed as it will clog the pores of the zeolite.
✓ Acidic water cannot be fed as it will destroy the zeolite bed.
✓ Hot water cannot be used as zeolite tends to dissolve in it.

❖ **Ion exchange resin softener:**

➔ **History of the development of ion exchange resin:**
✓ Gradually, an anion exchange resin (a condensation product of polyamines and formaldehyde) was developed. The new anion resin was used with the hydrogen cycle cation resin in an attempt to demineralize (remove all dissolved salts from) water. However, early anion exchangers were unstable and could not remove such weakly ionized acids as silicic and carbonic acid.
✓ In the middle 1940's, ion exchange resins were developed based on the copolymerization of styrene cross-linked with divinylbenzene. These resins were very stable and had much greater exchange capacities than their predecessors. The polystyrene-divinylbenzene-based anion exchanger could remove all anions, including silicic and carbonic acids. This innovation made the complete demineralization of water possible.
✓ Polystyrene-divinylbenzene resins are still used in the majority of ion exchange applications. Although the basic resin components are the same, the resins have been

modified in many ways to meet the requirements of specific applications and provide a longer resin life. One of the most significant changes has been the development of the macro reticular, or macroporous, resin structure.

✓ Standard gelular resins have a permeable membrane structure. This structure meets the chemical and physical requirements of most applications. However, in some applications, the physical strength and chemical resistance required of the resin structure is beyond the capabilities of the typical gel structure. Macroreticular resins feature discrete pores within a highly cross-linked polystyrene-divinylbenzene matrix. These resins possess a higher physical strength than gels, as well as a greater resistance to thermal degradation and oxidizing agents. Macroreticular anion resins are also more resistant to organic fouling due to their more porous structure. In addition to polystyrene-divinylbenzene resins, there are newer resins with an acrylic structure, which increases their resistance to organic fouling.
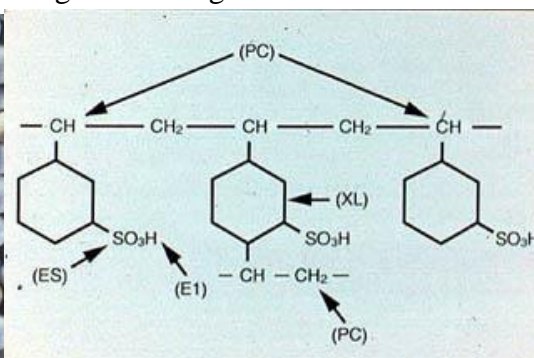


Macroreticular anion resin   **Polystyrene-divinylbenzene resin**

✓ In addition to a plastic matrix, ion exchange resin contains ionizable functional groups. These functional groups consist of both positively charged cation elements and negatively charged anion elements. However, only one of the ionic species is mobile. The other ionic group is attached to the bead structure. Ion exchange occurs when raw water ions diffuse into the bead structure and exchange for the mobile portion of the functional group. Ions displaced from the bead diffuse back into the water solution.

➢ **Classifications of ion exchange resins:**

• **Cation Exchange Resins (RH+):** These are phenol-sulphonic acid-formaldehyde resin and styrene-divinylbenzene copolymers that exchange their H^+ ions with the cations present in the water i.e., Ca^{2+} and Mg^{2+}.
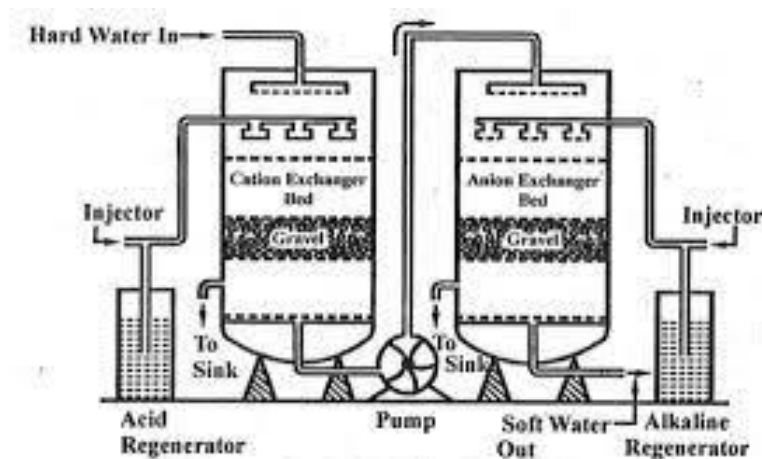

cation exchange resin
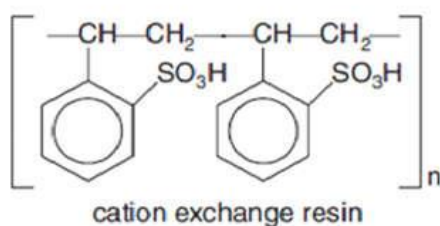
• **Anion Exchange Resins (ROH):** These are basically styrene-divinyl benzene or amine-formaldehyde copolymers containing quaternary ammonium

tertiarysulphonium or amino group in the resin. The resin upon treatment with hard water is capable of exchanging different anions like Cl^- or SO_4^{2-} with its OH^-.

Anion exchange resin
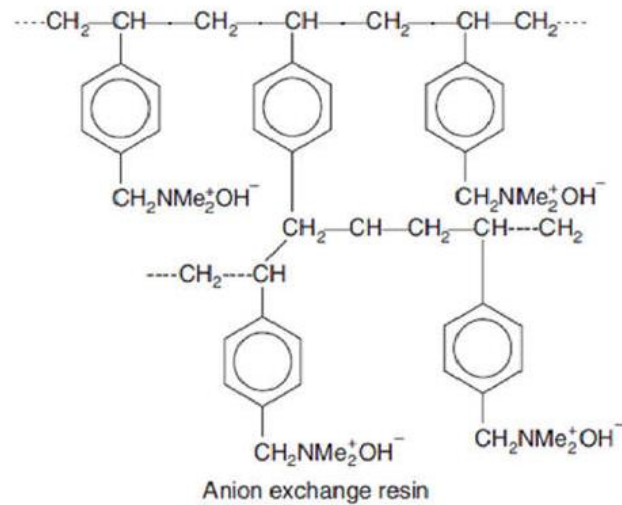
➢ **Purification of water by ion exchange process:**

✓ The ion exchange process consists of two columns- The cation exchanger column and the anion exchanger column.

✓ First hard water is passed through a cation exchanger which exchanges hardness causing
cations like Ca^{2+}, Mg^{2+}, Fe^{2+}, etc in water with H^+ ions held loosely on the porous cation exchange resin.

✓ Then hard water is passed through an anion exchanger which exchanges hardness causing
anions like SO_4^{2-}, Cl^- etc in water with OH^- ions held loosely on the porous anion exchange resin.

✓ The H^+ and OH^- ions thus released in water by the cation and anion exchangers respectively combine to form a water molecule.

✓ The water coming out of the columns will be free from hardness causing cations as well as anions and thus it is known as deionized or demineralized water.
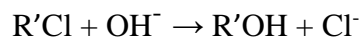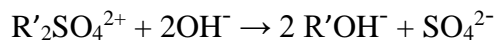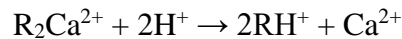

Set-up of the ion-exchange resin process

> **Reactions:**
> **Step 1:** Cation exchanger - $2R-H + Ca^{+2} \rightleftharpoons R_2-Ca + 2H^+$ (R = insoluble matrix)

Anion exchanger – $R'-OH + Cl^- \rightleftharpoons R'Cl + OH^-$ (R = insoluble matrix)

> **Step 2:** After some time, these two exchanges are exhausted when all their H^+ and OH^- ions are replaced by hardness-causing ions. At this stage, the hard water supply is stopped and cation and anion exchangers are regenerated by treating with acid and base respectively.

$$R_2Ca^{2+} + 2H^+ \rightarrow 2RH^+ + Ca^{2+}$$
$$R'_2SO_4^{2+} + 2OH^- \rightarrow 2\ R'OH^- + SO_4^{2-}$$
$$R'Cl + OH^- \rightarrow R'OH + Cl^-$$

❖ **Boiler feed water:**

> **Boiler:** A boiler is a device for generating steam, which consists of two principal parts: the furnace, which provides heat, usually by burning fuel, and the boiler proper, a device in which the heat changes water into steam. The steam or hot fluid is then recirculated out of the boiler for use in various processes in heating applications.
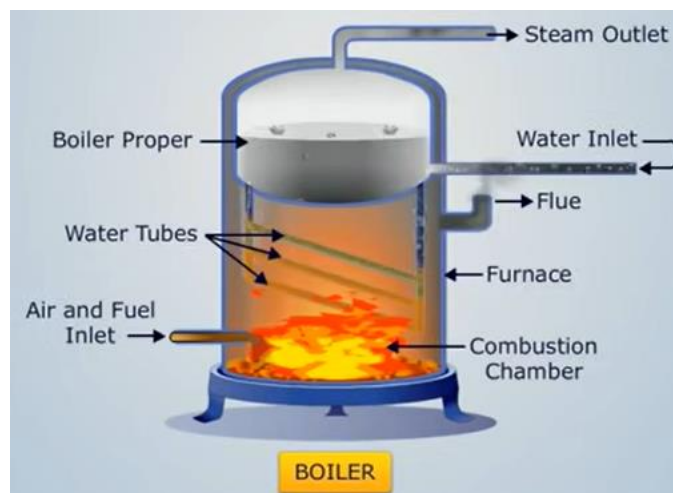
> **Boiler-feed water** is specially conditioned water that is fed into the boiler to generate Steam or Hot water.

> **Composition of Boiler-feed water:** The boiler receives the feed water, which consists of a varying proportion of recovered condensed water (return water) and fresh water, which has been purified in varying degrees (make-up water). The make-up water is usually natural water either in its raw state or treated by some process before use. Feed-water composition, therefore, depends on the quality of the make-up water and the amount of condensate returned to the boiler.

Heat Economy System : Block Diagram

BOILER FEED WATER = RETURN WATER + MAKE-UP WATER
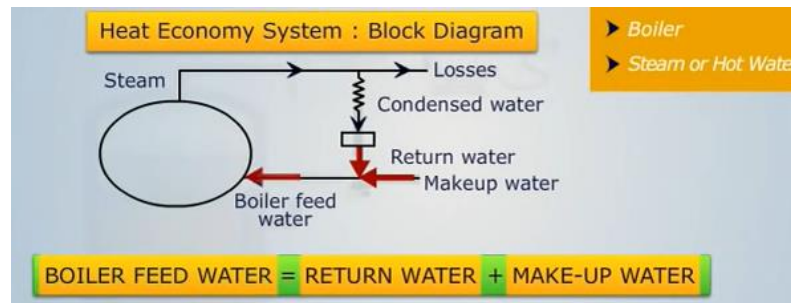
> **Treatment of boiler-feed water and maintenance of boiler:** The steam, which escapes from the boiler, frequently contains liquid droplets and gases. The water remaining in liquid form at the bottom of the boiler picks up all the foreign matter from the water that was converted to steam. The impurities must be blown down by the discharge of some of the water from the boiler to the drains. The permissible percentage of blown down at a plant is strictly limited by running costs and initial outlay. The tendency is to reduce this percentage to a very small figure.

Proper treatment of boiler feed water is an important part of operating and maintaining a boiler system. As steam is produced, dissolved solids become concentrated and form deposits inside the boiler. This leads to poor heat transfer and reduces the efficiency of the boiler. Dissolved gasses such as oxygen and carbon dioxide will react with the metals in the boiler system and lead to boiler corrosion. In order to protect the boiler from these contaminants, they should be controlled or removed, through external or internal treatment. For more information check the boiler water treatment web page.

Specifications of Boiler Feed Water:

HARDNESS < 0.2 ppm

0.15 ppm < CAUSTIC ALKALINITY < 0.45 ppm

0.45 ppm < SODA ALKALINITY < 1 ppm

Should be free from:
- Turbidity
- Sediments
- Organic Matter
- Oil
- Grease
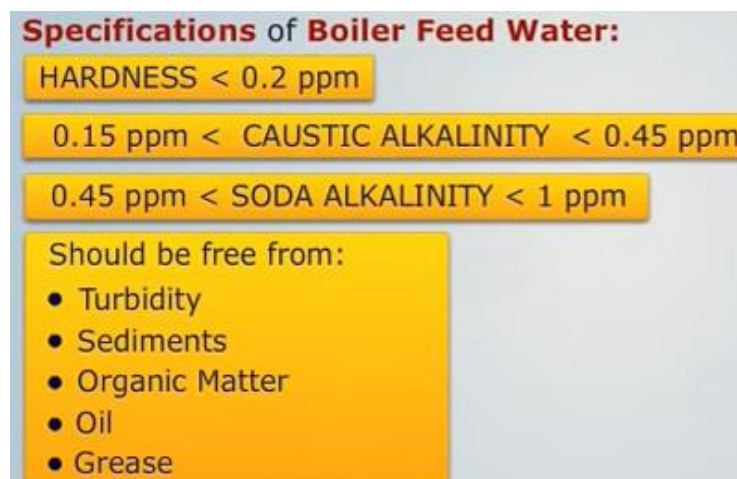
❖ **Boiler Problems:** If the water used for steam making in the boiler does not satisfy the specified requirements for the boiler feed water, the development of boiler problems occurs. There are many types of boiler problems. They are:

> **Carryover:** The process of carrying of water by steam along with the impurities is called carryover. The phenomenon occurs due to priming and foaming.

➔**Priming:** When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along with the steam. This process of 'wet steam' formation is called priming**.**

➢ **Causes of Priming:**
1. Presence of a large amount of dissolved solids;
2. High steam velocities,
3. Sudden boiling;
4. Improper boiler design;
5. Sudden increase in steam-production rate.

➔**Foaming:** It is the production of persistent foam or bubbles in boilers, which do not break easily. Foaming is due to the presence of substances like oils (which greatly reduce the surface tension of the water).

➢ **Priming and foaming, usually, occur together. They are not acceptable because;**
❖ dissolved salts in boiler water are carried by the wet steam to the super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency,
❖ dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery;
❖ actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

➢ **Priming can be avoided by:**
(i) fitting mechanical steam purifiers;
(ii) avoiding rapid changing steaming rate;
(iii) maintaining low water levels in boilers,
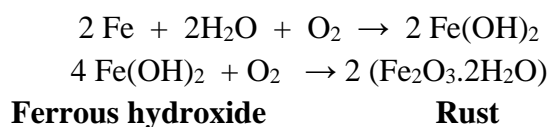(iv) efficient softening and filtration of the boiler-feed water.

➢ **Foaming can be avoided by:**
(i) Adding anti-foaming chemicals like castor oil,
(ii) Removing oil from boiler water by adding compounds like sodium aluminates.
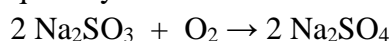
❖ **Boiler Corrosion**
Boiler corrosion is the decay of boiler material by a chemical or electrochemical attack by its environment. The main reasons for boiler corrosion are:

➢ **Dissolved oxygen**: Water usually contains about 8 ml of dissolved oxygen per litre at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:

$$2\,Fe \ + \ 2H_2O \ + \ O_2 \ \rightarrow \ 2\,Fe(OH)_2$$
$$4\,Fe(OH)_2 \ + O_2 \ \rightarrow 2\,(Fe_2O_3.2H_2O)$$
Ferrous hydroxide   Rust

➢ **Removal of dissolved oxygen:**
By adding the calculated quantity of sodium sulfite or hydrazine or sodium sulfide.
$$2\,Na_2SO_3 \ + \ O_2 \rightarrow 2\,Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2\,H_2O$$
$$Na_2S + 2\,O_2 \rightarrow Na_2SO_4$$
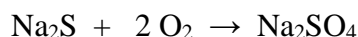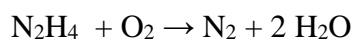
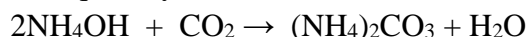➢ **Dissolved carbon dioxide**: Dissolved CO_2 has a slow corrosion effect on the boiler material. CO_2 is also released inside the boiler if the water used for steam generation contains bicarbonates.
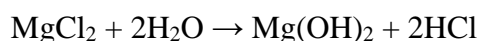
$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$$

➢ **Removal of CO_2**:
(1) By adding the calculated quantity of ammonia. Thus,
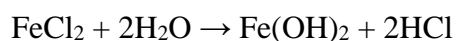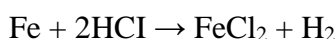$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$
(2) By mechanical-aeration process along with oxygen.
(3) Acids from dissolved salts: Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,
$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$
The liberated acid reacts with iron (of the boiler) in chain-like reactions producing HCI again and again.
$$Fe + 2HCI \rightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$
Consequently, the presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent

❖ **Caustic embrittlement:**

Caustic embrittlement is the phenomenon, during which the boiler material becomes brittle due to the accumulation of caustic substances.

It is a type of boiler corrosion, caused by using highly alkaline water in the boiler. During softening process by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water. In high-pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide,
$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$
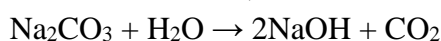
This makes the boiler water basic ["caustic"]. The NaOH-containing water flows into the minute hair cracks, always present in the inner side of the boiler, by capillary action. Here, water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving the iron of the boiler as sodium ferrate this causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.

➢ **Caustic embrittlement can be avoided:**
1. By using sodium phosphate as softening agent, instead of sodium carbonate;
2. By adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these;

3. By adding sodium sulfate to the boiler water. Na_2SO_4 also blocks hair cracks, thereby preventing the infiltration of caustic soda solutions. It has been observed that caustic cracking can be prevented if Na_2SO_4 is added to the boiler water.
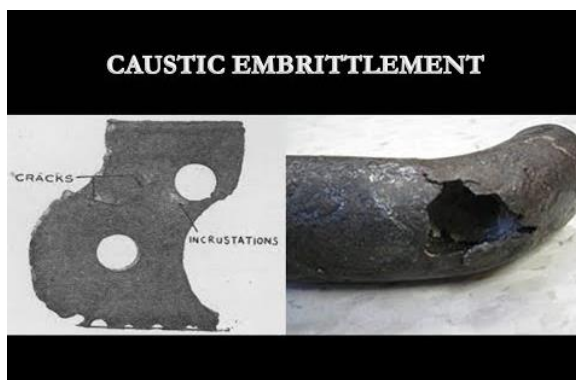
❖ **Expressions and mathematical problems:**

➢ **Expression of Hardness:**

Both temporary and permanent hardness are expressed in ppm (parts per million) as $CaCO_3$. The choice of $CaCO_3$ is due to the fact that its molecular weight is 100 and its equivalent weight is 50 and it is a very less soluble salt in water (around 15-20 mg/l).

Equivalent of $CaCO_3$ =

$$\frac{\text{(Mass of hardness-producing substance) X (Chemical equivalent of } CaCO_3)}{\text{Chemical equivalent of hardness producing substance}}$$

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

➢ **Units of hardness**

1. Parts per million (ppm)

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

2. French degree (°Fr)

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

3. Clarke's degree (°Cl)

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

4. Milligrams per litre (mg/l)

It is defined as the number of milligrams of $CaCO_3$ equivalent hardness per 1 litre of water.

➢ **Relationship between various units:**

1 ppm	= 1 mg/L	= 0.1° Fr	= 0.07° Cl
1 mg/L	= 1 ppm	= 0.1° Fr	= 0.07° Cl
1 ° Cl	= 1.433° Fr	= 14.3 ppm	= 14.3 mg/L
1 ° Fr	= 10 ppm	= 10 mg/L	= 0.7° Cl

> **Problems:**
Problem-1: A sample of water is found to contain the following dissolving salts in milligrams per liter $Mg(HCO_3)_2$ = 73, $CaCl_2$ = 111, $Ca(HCO_3)_2$ = 81, $MgSO_4$ = 40 and $MgCl_2$ = 95. Calculate temporary and permanent hardness and total hardness.

Name of the hardness-causing salts	Amount of the hardness causing salts (mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	73	146	73×100/146 = 50
$CaCl_2$	111	111	111×100/111 = 100
$Ca(HCO_3)_2$	81	162	81×100/162 = 50
$MgSO_4$	40	120	40×100/120 = 33.3
$MgCl_2$	95	95	95×100/95 = 100

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ = 50 + 50 = 100mg/Lit.
Permanent hardness = $CaCl_2$ + $MgSO_4$ + $MgCl_2$ = 100 + 33.3 + 100 = 233.3mg/Lit.
Total hardness = Temporary hardness + Permanent hardness = 100 + 233.3
=333.3mg/Lit.

Problem-2: A sample of water is found to contain the following dissolving salts in milligrams per litre $Mg(HCO_3)_2$ = 16.8, $MgCl_2$ = 12.0, $MgSO_4$ = 29.6 and NaCl = 5.0. Calculate temporary and permanent hardness of water.

Name of the hardness-causing salts	Amount of the hardness-causing salts(mg/Lit)	Molecular weight of the hardness-causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	16.8	146	16.8×100/146 = 11.50
$MgCl_2$	12.0	95	12.0×100/95 = 12.63
$MgSO_4$	29.6	120	29.6×100/120 = 24.66
NaCl	5.0	NaCl does not contribute any hardness to waterhence it is ignored.	

Temporary hardness = $Mg(HCO_3)_2$ = 11.50mgs/Lit.
Permanent hardness = $MgCl_2$ + $MgSO_4$ = 12.63 + 24.66 = 37.29mgs/Lit.

Problem-3: A sample of water is found to contain following analytical data in milligrams per litre $Mg(HCO_3)_2$ = 14.6, $MgCl_2$ = 9.5, $MgSO_4$ = 6.0 and $Ca(HCO_3)_2$ = 16.2. Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.

Name of the hardness-causing salts	Amount of the hardness-causing salts(mg/Lit)	Mol. weight of the hardness-causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	14.6	146	14.6×100/146 = 10
$MgCl_2$	9.5	95	9.5×100/95 = 10
$MgSO_4$	6.0	120	6.0×100/120 = 5
$Ca(HCO_3)_2$	16.2	162	16.2×100/162 =10

Temporary hardness [Mg $(HCO_3)_2$ + Ca $(HCO_3)_2$] = 10 + 10 = 20mg/Lit

$$= 20ppm$$
$$= 20 \times 0.07°Cl = 1.4°Cl$$
$$= 20 \times 0.1°Fr = 2°Fr$$

Permanent hardness [$MgCl_2$ + $MgSO_4$] = 10 + 5 = 15mg/Lit

$$= 15ppm$$
$$= 15 \times 0.07°Cl = 1.05°Cl$$
$$= 15 \times 0.1°Fr = 1.5°Fr$$

Problem-4: Calculate the amount of temporary and permanent hardness of a water sample in Degree Clarke's, Degree French, and Milligrams per Litre which contains the following impurities.

Ca$(HCO_3)_2$ = 121.5 ppm, Mg$(HCO_3)_2$= 116.8 ppm, $MgCl_2$ = 79.6 ppm and $CaSO_4$ = 102 ppm.

Name of the hardness-causing salts	Amount of the hardness causing salts(ppm)	The molecular weight of hardness-causing salts	Amounts equivalent to $CaCO_3$ (ppm)
Ca$(HCO_3)_2$	121.5	162	121.5×100/162 = 75
Mg$(HCO_3)_2$	116.8	146	116.8×100/146 = 80
$MgCl_2$	79.6	95	79.6×100/95 = 3.37
$CaSO_4$	102	136	102×100/136 = 75

Temporary hardness [Mg $(HCO_3)_2$ + Ca $(HCO_3)_2$] = 75 + 80 = 155 ppm

$$= 155 \times 0.07°Cl = 10.85°Cl$$
$$= 155 \times 0.1°Fr = 15.5°Fr$$
$$= 155 \times 1mg/Lit = 155 \ mg/Lit$$

Permanent hardness [$MgCl_2$ + $CaSO_4$] = 10 + 5 = 15mg/Lit = 15ppm

$$= 15 \times 0.07°Cl = 1.05°Cl$$
$$= 15 \times 0.1°Fr = 1.5°Fr$$

Problem-5: 50 ml of standard hard water containing 1 gram of pure $CaCO_3$ per liter consumed 20 ml of EDTA. 50 ml of hard water consumed 25 ml of the same EDTA solution EBT indicator. Calculate the total hardness of the water sample in ppm.

Strength of standard hard water sample ($CaCO_3$ solution) M1=

$$\frac{\text{Weight of } CaCO_3 \times 1000}{\text{Mol. wt of} CaCO_3 \quad 1000}$$
$$= \frac{1 \ gm \times 1000}{100 \quad 1000}$$
$$= 0.01M$$

Strength of EDTA solution M2 = $\frac{V_1 \ M_1}{V_2}$ = $\frac{50 \times 0.01}{20}$ = 0.025 M

V_1 = Volume of standard hard water (50 ml), M_1 = Strength of standard hard water (0.01M)

V_2 = Volume of EDTA solution (20 ml), M_2 =Strength of EDTA solution =?

Calculation of Total hardness $M_3 = \dfrac{V_2\,M_2}{V_3} = \dfrac{25 \times 0.025}{50} = 0.0125$ M

V_2 = Volume of EDTA solution (25 ml), M_2 =Strength of EDTA solution= 0.025M

V_3 = Volume of sample hard water (50 ml), M_3 = Strength of sample hard water =?

Total Hardness = 0.0125×10^5 ppm

$\qquad$ = 0.0125×100 (Mol. Wt of CaCO3) $\times 1000$ (ml)ppm

$\qquad$ = 1250 ppm.

Problem-6: 0.28 grams of $CaCO_3$ were dissolved in HCl and the solution was made up to one liter with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hardwater sample consumed 33 ml of the same EDTA solution EBT indicator. 100 ml of this water after boiling cooling and filtering required 10 ml of EDTA solution in titration. Calculate the permanent and temporary hardness of water sample in ppm.

Strength of standard hard water sample ($CaCO_3$ solution) M

= $\dfrac{\text{Weight of CaCO3}}{\text{Mol. wt of CaCO3}} \times \dfrac{1000}{1000}$

= $\dfrac{0.28\text{gm}}{100} \times \dfrac{1000}{1000} = 0.0028$ M

Strength of EDTA solution $M_2 = \dfrac{V_1\,M_1}{V_2} = \dfrac{100 \times 0.0028}{28} = 0.01$ M

V_1 = Volume of standard hard water (100 ml), M_1 = Strength of standard hard water (0.0028M)V_2 = Volume of EDTA solution (28 ml), M_2 = Strength of EDTA solution=?

Calculation of Total hardness $M_3 = \dfrac{V_2\,M_2}{V_3} = \dfrac{33 \times 0.01}{100} = 0.0033$ M

V_2 = Volume of EDTA solution (33 ml), M_2 = Strength of EDTA solution (0.01M)
V_3 = Volume of sample hard water (100 ml), M_3 = Strength of sample hard water =?

Total Hardness = 0.0033×10^5 ppm

$\qquad$ = 0.0033×100 (Mol. Wt of CaCO3) $\times 1000$ (ml)ppm

$\qquad$ = 330 ppm

Calculation of Permanent hardness $M_4 = \dfrac{V_2\,M_2}{V_4} = \dfrac{10 \times 0.01}{100} = 0.001$ M

V2 = Volume of EDTA solution (10 ml), M2 = Strength of EDTA solution (0.01M)

V4 = Volume of sample hard water after boiling cooling and filtering (100 ml)

M4 = Strength of sample hard water after boiling cooling and filtering =?

Permanent Hardness = 0.001×10^5 ppm

$$= 0.001 \times 100 \text{ (Mol. Wt of } CaCO_3) \times 1000 \text{ (ml)ppm}$$
$$= 100 \text{ ppm}$$

Calculation of Temporary hardness = Total hardness - Permanent hardness

$$= 330 - 100 = 230 \text{ ppm}$$

Problem-7

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

Solution:

1 litre of NaCl contains = 20 gm of NaCl

∴ 15 litres of NaCl contains = 20 × 15 = 300 gm of NaCl

Now 58.5 gm NaCl = 50 gm of $CaCO_3$ equivalent

∴   300 gm NaCl = $\dfrac{300 \times 50}{58.5}$

= 256.41 gm

Total quantity of water = 77,500 litres

77,500 litres of water = 256.41 gm $CaCO_3$ emits

1 litre of water = 0.0033 gm = 3.30 ppm

Hardness of water = 3.30 ppm

Problem - 8

Calculate the carbonate and non-carbonate hardness of a sample of water:

cont ai ning the dissolved salt s as given below in mgs/li t . **M** $g(HCO_3)_2 = 7.3$; $Ca(HCO_3)_2$ = **40.5**; $CaSO_4 = 13.6$; $MgCl_2 = 21.75$ **and** $NaCl = 50$.

Solution: Given:

(i)   Hardness producing salt $Mg(HCO_3)_2$ (Mol. Wt = 146), Amount in mgs/lit = 7.3

$$= \dfrac{73 \times 100}{146} = 5 \text{ mgs/lit.}$$

(ii) $Ca(HCO_3)_2$ (Mol. Wt = 162), Amount in mgs/lit = 40.5

$$= \dfrac{40.5 \times 100}{162} = 25 \text{ mgs/lit.}$$

(iii) $CaSO_4$ (Mol. Wt. = 136), Amount in mgs/lit = 13.6

$$= \frac{13.6 \times 100}{136} = 10 \text{ mgs/lit.}$$

(iv) $MgCl_2$ (Mol. Wt. = 95), Amount in mgs/lit = 21.75

$$= \frac{21.75 \times 100}{95} = 22.9 \text{ mgs/lit.}$$

(v) $NaCl$, Amount in mgs/lit = 50.

But Nacl does not contribute any hardness to water, hence it is ignored.

Carbonate hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$

$$= 5 + 25 = 30 \text{ mgs/lit}$$

Non-Carbonate hardness = $CaSO_4 + MgCl_2$

$$= 10 + 22.9 = 32.9 \text{ mgs/lit.}$$

Total hardness = Carbonate Hardness + Non-Carbonate Hhardness

$$= 30 + 32.9 = 62.9 \text{ mgs/lit.}$$

Problem-9

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

Solution:

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

50 litres of NaCl solution contain = 50×250 = 12,500 gm of NaCl as

$$CaCO_2 = 2 \text{ NaCl}$$
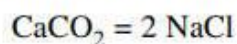
$$100 = 2(58.5)$$

$$50 = 58.5$$

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

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

∴ $12500 \times \dfrac{50}{58.5}$ gm will be present in

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

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

Problem-10

Calculate the quantity of lime and soda required for softening 10,000 litres of H_2O containing the following impurities per litre

$$Ca(HCO_3)_2 = 7.8 \text{ mg} \qquad Mg(HCO_3)_2 = 8.00 \text{ mg}$$
$$CaSO_4 = 12.2 \text{ mg} \qquad MgSO_4 = 10.6 \text{ mg}$$
$$NaCl = 5.5 \text{ mg} \qquad SiO_2 = 2.1 \text{ mg}$$

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

$NaCl$ and SiO_2 are not hardness causing substances. Hence, they do not consume lime and soda.

Molecular weight of the impurities are,

(i) $Ca (HCO_3)_2 = 40 + 2 [1 + 12 + 3 \times 16] = 162$
(ii) $Mg (HCO_3)_2 = 24 + 2 [1 + 12 + 3 \times 16] = 162$
(iii) $CaSO_4 = 40 + 32 + (4 \times 16) = 136$
(iv) $MgSO_4 = 24 + 32 + (4 \times 16) = 120$
(v) Molecular weight of $CaCO_3 = 100$

Impurity	Amount	Molecular weight	Multiplication factor	$CaCO_3$ equivalent in ppm
$Ca(HCO_3)_2$	7.8	162	100/162	$7.8 \times 100/162 = 4.8$
$Mg(HCO_3)_2$	8.00	146	100/146	$8 \times 100/146 = 5.4$
$CaSO_4$	12.2	136	100/136	$12.2 \times 100/136 = 8.9$
$MgSO_4$	10.6	120	100/120	$10.6 \times 100/120 = 8.8$

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

$$= \frac{74}{100} [4.8 + (2 \times 5.4) + 8.8] \text{ mg/lit.}$$

$$= 18.05 \text{ mg/lit}$$

For 10, 000 litres of water lime required

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

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

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

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

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

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

$$= 182340 \text{ mg}$$

Problem-11

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

$$Ca^{+2} = 160 \text{ ppm}$$
$$Mg^{+2} = 72 \text{ ppm}$$
$$HCO_3^- = 73.2 \text{ ppm}$$
$$CO_2 = 44 \text{ ppm}$$
$$Al_2(SO_4)_3 = 34.2 \text{ ppm}$$
$$HCl = 36.5 \text{ ppm}$$

Solution: Conversion into $CaCO_3$ equivalents.

Iron or salt	Amount present (ppm)	Conversion	$CaCO_3$ equivalent (ppm)
Ca^{+2}	160	$\dfrac{100}{40}$	$160 \times \dfrac{100}{40} = 400$
Mg^{+2}	72	$\dfrac{100}{24}$	$72 \times \dfrac{100}{24} = 300$
HCO_3	73.2	$\dfrac{100}{122}$	$73.2 \dfrac{100}{122} = 60$
CO_2	44	$\dfrac{100}{44}$	$44 \times \dfrac{100}{44} = 100$
$NaAlO_2$	16.4	$\dfrac{100}{164}$	$16.4 \times \dfrac{100}{164} = 10$
$Al_2(SO_4)_3$	34.2	$\dfrac{100}{342}$	$34.2 \times \dfrac{100}{342} = 10$
HCl	36.5	$\dfrac{100}{36.5}$	$36.5 \times \dfrac{100}{36.5} = 100$

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

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

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

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

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

$$= 7.84 \text{ kg}$$

Soda required $= \dfrac{106}{100} [400 + 300 + 3(10) + 1/2(100) - 60 - 10]$

$\qquad = \dfrac{106}{100} [400 + 300 + 30 + 50 - 70]$

$\qquad = 752.6$ mg/lit

$\qquad = 752.6 \times 20.000 \times \dfrac{1}{10^6}$

$\qquad = \textbf{15.05 kg}$

Problem-12

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

$$Ca(HCO_3)_2 = 30.2 \text{ ppm} \qquad Mg(HCO_3)_2 = 20.8 \text{ ppm}$$
$$CaCl_2 = 28.1 \text{ ppm} \qquad MgCl_2 = 8.7 \text{ ppm}$$
$$CaSO_4 = 35.00 \text{ ppm} \qquad MgSO_4 = 6.7 \text{ ppm}$$

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

Impurity	Amount in ppm	Molecular weight	Multiplication factor	$CaCO_3$ equivalent in ppm
$Ca(HCO_3)_2$	30.2	162	100/162	$30.2 \times 100/162 = 18.64$
$Mg(HCO_3)_2$	20.8	146	100/146	$20.8 \times 100/146 = 14.24$
$CaCl_2$	28.1	111	100/111	$28.1 \times 100/111 = 25.31$
$MgCl_2$	8.7	95	100/95	$8.7 \times 100/95 = 9.15$
$CaSO_4$	35.00	136	100/136	$35 \times 100/136 = 25.73$
$MgSO_4$	6.7	120	100/120	$6.7 \times 100/120 = 5.58$

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

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

$\qquad = 45.769 \text{ ppm}$

$$\text{Soda required} = \frac{106}{100} [(25.31 + 25.73) + (9.15 + 5.58)]$$

$$= 69.71 \text{ ppm}$$

Lime is 70%

∴ for 100,000 lit. of water.

$$\text{Lime required} = \frac{100}{70} \times (100,000 \times 45.769) \text{ mg} \times \frac{1}{106}$$

$$= 65.384 \text{ kg}$$

$$\text{Soda required} = \frac{100}{85} \times (100,000 \times 69.71) \text{ mg} \times \frac{1}{106}$$

$$= 82.01 \text{ kg}$$

Problem-13

A sample of water was found to contain the following analytical data in mgs/lit

$Mg(HCO_3)_3 = 14.6$; $MgCl_2 = 9.5$; $MgSO_4 = 6.0$; $Ca(HCO_3)_2 = 16.2$. Calculate the temporary and Permanent hardness of the sample of water.

Solution: Given: Hardness producing salt.

(i) $Mg(HCO_3)_2$ (Mol. Wt. = 146), Amount in mgs/lit. = 14.6

$$= \frac{14.6 \times 100}{146} = 10 \text{ mgs/lit.}$$

(ii) $MgCl_2$ (Mol. Wt. = 95), Amount in mgs/lit. = 9.5

$$= \frac{9.5 \times 100}{95} = 10 \text{ mgs/lit.}$$

(iii) $MgSO_4$ (Mol. Wt. = 120), Amount in mgs/lit = 6.0

$$= \frac{6.0 \times 100}{120} = 5 \text{ mgs/lit.}$$

(iv) $Ca(HCO_3)_2$ (Mol. Wt. = 162), Amount in mgs/lit = 16.2

$$= \frac{16.2 \times 100}{162} = 10 \text{ mgs/lit.}$$

Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$

$$= 10 + 10 = 20 \text{ mgs/lit.}$$

Permanent hardness = $MgCl_2 + MgSO_4$

$$= 10 + 5 = 15 \text{ mgs/lit.}$$