Unit 1: Impurities in Water

Types of Impurities present in Water:

1. **Dissolved Impurities:** Cations like Ca^{++}, Mg^{++}, Na^+, Zn^{++}, Cu^{++} and anions like Cl^-, SO_4^{--}, NO_3^-, HCO_3^-, F^- (of Inorganic salts), Gases such as CO_2, O_2, N_2, oxides of N_2, NH_3, H_2S and Organic salts

2. **Suspended Impurities:** Clay & Sand (Inorganic), leaves, twigs etc

3. **Colloidal Impurities:** oil globules, animal and vegetable matter (Organic)

4. **Bacterial Impurities:** Bacteria, microorganisms & other forms of animal and plant life

Types of Water: Hard Water & Soft water

Unit 1: Dissolved Mineral Matter in Water

Most Important dissolved mineral matter in water

from **Industrial application** point of view): **Hardness & Alkalinity**

Hardness: Defined as **soap consuming capacity** of a water sample (mainly due to the presence of Ca & Mg ions)

What are Soaps?

Soaps are sodium salts of long chain fatty acids such as oleic acid, palmitic and stearic acid

Ca & Mg ions react with sodium salts of long chain fatty acids present in the soap to form insoluble scums of calcium and magnesium soaps which do not possess any detergent value

(does not produce lather or foam)

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$$
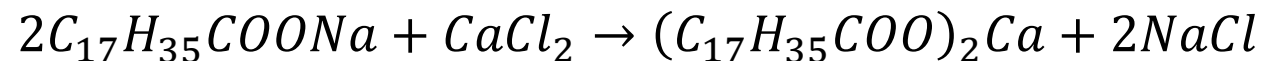
Water hardness is classified by the **U.S. Department of Interior and the Water Quality Association** as follows:

Classification   mg/1 or ppm

- Soft   0 - 17.1
- Slightly hard   17.1 - 60
- Moderately hard   60 - 120
- Hard   120 - 180
- Very hard   180 & over

S.No.	Parameters	Drinking water IS 10500 : 2012	
		Permissible Limit	Maximum Limit
1	Odor	Agreeable	Agreeable
2	Taste	Agreeable	Agreeable
3	pH	6.5 to 8.5	No relaxation
4	TDS (mg/l)	500	2000
5	Hardness (as CaCO3) (mg/l)	200	600
6	Alkalinity (as CaCO3) (mg/l)	200	600
7	Nitrate (mg/l)	45	No relaxation
8	Sulfate (mg/l)	200	400
9	Fluoride (mg/l)	1	1.5
10	Chloride (mg/l)	250	1000
11	Turbidity (NTU)	5	10
12	Arsenic (mg/l)	0.01	0.05
13	Copper (mg/l)	0.05	1.5
14	Cadmium (mg/l)	0.003	No relaxation
15	Chromium (mg/l)	0.05	No relaxation
16	Lead (mg/l)	0.01	No relaxation
17	Iron (mg/l)	0.3	No relaxation
18	Zinc (mg/l)	5	15
19	Fecal Coliform (cfu)	0	0
20	E. Coli (cfu)	0	0

Unit 1: Hardness of Water

Hard Water: **Does not produce lather with soap solution, forms precipitate**
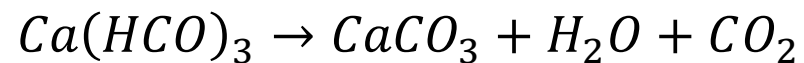
Soft water: **Lathers easily with soap solution**

Types of Hardness:

1. **Temporary Hardness (Carbonate Hardness or Alkaline Hardness)**

   Due to the presence of dissolved impurities in water like bicarbonates of Ca, Mg, Fe, Al, Mn that can be removed from water by merely boiling followed by filtration.

   When natural water is boiled, the soluble bicarbonate ions present get decomposed and form insoluble carbonates or hydroxides.

$$Ca(HCO)_3 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO)_3 \rightarrow Mg(OH)_2 + 2CO_2$$

Thus, temporary hardness causing impurities can be easily removed by boiling and filtration

Unit 1: Hardness of Water

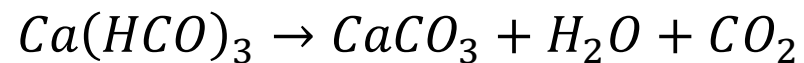**Hard Water:** **Does not produce lather with soap solution, forms precipitate**

Soft water: **Lathers easily with soap solution**

Types of Hardness:

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   When natural water is boiled, the soluble bicarbonate ions present get decomposed and form insoluble carbonates or hydroxides.

$$Ca(HCO)_3 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO)_3 \rightarrow Mg(OH)_2 + 2CO_2$$

Thus, temporary hardness causing impurities can be easily removed by boiling and filtration

Unit 1: Hardness of Water

Types of Hardness:

2. Permanent Hardness (Non-Carbonate Hardness or Non-Alkaline Hardness)

Due to the presence of dissolved impurities in water like chlorides, sulphates and nitrates of Ca, Mg, Fe, Al, Mn etc.

These salts cannot be removed by merely boiling, needs special water softening methods to remove permanent hardness of water.

Temporary and permanent hardness together called as total hardness of water.

Total Hardness = Temporary Hardness + Permanent Hardness

Unit 1: Hardness of Water

Degree of Hardness:

- Total hardness present in water is because of different salts of calcium and magnesium with different molecular weights.

- Hence, **hardness of water** is conveniently **expressed in terms of calcium carbonate equivalence**.

- The weights of different salts causing hardness are converted to weight equivalent to that of calcium carbonate.

- If a water sample contains 2 or more salt their quantities are converted to calcium carbonate equivalence and the sum will give total hardness in terms of calcium carbonate equivalence.

Unit 1: Hardness of Water

Degree of Hardness:

- Degree of hardness is defined as the number of parts by weight of calcium carbonate hardness per particular number of parts of water, depending upon the unit employed.

- Though the hardness does not always arise due to calcium carbonate in water, it is a standard practice to express it in terms of **equivalents of CaCO$_3$.** **WHY ?????**

- Calcium carbonate is selected for expression of degree of hardness because:
  - its molecular weight is exactly 100 which makes calculation convenient
  - it is the most insoluble salt that can be precipitated out of water

Unit 1: Hardness of Water

Degree of Hardness:

The $CaCO_3$ equivalent for any dissolved salt in water can be calculated as:

$CaCO_3$ equivalent of any salt = Weight of salt present (mg/l) $\times \dfrac{Equivalent\ weight\ of\ CaCO_3}{Equivalent\ weight\ of\ salt}$

$CaCO_3$ equivalent of bivalent salt = Weight of salt present (mg/l) $\times \dfrac{Molecular\ weight\ of\ CaCO_3}{Molecular\ weight\ of\ salt}$

Unit 1: Hardness of Water

Units of Hardness:

1. Parts per Million (ppm): It is the number of equivalent parts of $CaCO_3$ present per million parts (10^6) parts of water by weight

2. Milligram per liter (mg/l): It is the number of mg of $CaCO_3$ dissolved in 1 litre of water.

3. Degree Clarke (^0Cl): It is the number of equivalent parts of $CaCO_3$ present per 70,000 parts of water or 1 gallon of water

4. Degree French (^0Fr): It is the number of equivalent parts of $CaCO_3$ present per 10^5 parts of water
   1 mg/l = 1 ppm (Prove)

Alkalinity of water

Alkalinity is a measure of the ability of water to neutralize the acids

- The alkalinity of water is normally due to the presence of **bicarbonates, carbonates** and **hydroxides** of sodium, potassium, calcium and magnesium.

- Some of the salts, which cause alkalinity, also cause hardness, but not all. (However, the presence of other bases such as borates, silicates, phosphates can also contribute to the total alkalinity, though to a small extent)

Alkalinity of water

Classification of Alkalinity: Alkalinity based on the anions present in the water is classified as:

1. Caustic Alkalinity (due to Hydroxide and Carbonate ions)

2. Bicarbonate Alkalinity (due to Bi-carbonate ions)

Alkalinity of a water sample due to different ions can be **determined by neutralization titration** using a **standard acid** and making selective use of indicators. The indicators used are **Phenolphthalein** and **Methyl orange**.

Alkalinity of water

Reactions: The determination is based on following reactions

i. $OH^- + H^+ \dashrightarrow H_2O$

ii. $CO_3^{--} + H^+ \dashrightarrow HCO_3^-$

iii. $HCO_3^- + H^+ \dashrightarrow H_2CO_3$

➢ Reaction 1 and 2 corresponds to Phenolphthalein (P) end point i.e. complete neutralization of OH^- and half neutralization of CO_3^{--}

➢ Reaction 1 to 3 corresponds to Methyl Orange (M) end point i.e. complete neutralization of OH^-, CO_3^{--} and HCO_3^- ions.

Alkalinity of water

Alkalinity may be due to presence of following combinations:

1) Alkalinity due to HCO_3^- only

2) Alkalinity due to, CO_3^{--} only

3) Alkalinity due to, OH^-, only

4) Alkalinity due to, CO_3^{--} and HCO_3^- ions

5) Alkalinity due to, OH^- and CO_3^{--}

The possibility of OH^- and HCO_3^- together is ruled out, they combine instantaneously to form CO_3^{--} ions, thus all ions cannot exist together.

Thus, on the basis of Phenolphthalein alkalinity and methyl orange alkalinity, the alkalinity in water due to different ions can be calculated.

Alkalinity of water

Procedure:

- Pipette out 100 mL of the water sample in a clean titration flask.

- Add 2–3 drops of phenolphthalein indicator.

- Run in N/50 H_2SO_4 or HCl (from a burette), till the pink color is just discharged. This is the first end point.

- Let the volume of acid used until phenolphthalein end point = V_1 mL.

- Then to the same solution, add 2 to 3 drops of methyl orange. Continue titration, till the yellow colour changes to orange/red. This is the second end point.

- Let *volume* of acid used to methyl orange end point = V_2 mL.

Alkalinity of water

OBSERVATIONS:

Volume of water sample (unknown alkalinity) selected = _ ml

For Phenolphthalein end point

- Burette: HCl solution of _____N
- Indicator: Phenolphthalein
- End point: Pink turns colourless
- Volume of titrant (HCl) consumed, V_1 = _____ml

For Methyl orange end point

- Burette: HCl solution of _____N
- Indicator: Methyl Orange
- End point: Yellow turns orange/red
- Volume of titrant (HCl) consumed, V_2 = _____ml

Alkalinity of water

CALCULATIONS:

$$Phenolphthalein\ Alkalinity\ (P) = \frac{50 \times Volume\ of\ acid\ consumed\ (ml) \times Normality\ of\ acid \times 1000}{Volume\ of\ water\ sample(ml)}$$

$$Methyl\ Orange\ Alkalinity\ (M) = \frac{50 \times Volume\ of\ acid\ consumed\ (V2) \times Normality\ of\ acid \times 1000}{Volume\ of\ water\ sample}$$

From the measurement of Phenolphthalein alkalinity and methyl orange alkalinity, it is possible to calculate the magnitude of various forms of alkalinity present in water sample,

Alkalinity of water

Sr. No.	Alkalinity	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
1	$P = 0$	NIL	NIL	M
2	$P = \frac{1}{2}M$	NIL	2P	NIL
3	$P < \frac{1}{2}M$	NIL	2P	(M- 2P)
4	$P > \frac{1}{2}M$	(2P – M)	2 (M-P)	NIL
5	$P = M$	P = M	NIL	NIL

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Alkalinity of water

(i) When **P = 0**,   both OH^- and CO_3^{2-} are absent and alkalinity in that case is due to **HCO_3^-** alone.

(ii) When **P = M**   neither CO_3^{2-} nor HCO_3^- ions are present, only OH^- ions are present, Thus alkalinity due to **OH^-** = P = M.

(iii) When **P = 1/2 M** or $V_1 = V_2/2$, only CO_3^{2-} is present,

since half of carbonate neutralisation (ie $CO_3^{2-} + H^+ \rightarrow HCO_3^-$) takes place with phenolphthalein, while complete carbonate neutralisation ($CO_3^{2-} + H^+ \rightarrow HCO_3^-$; $HCO_3^- + H^+ \rightarrow H_2O + CO_2$) occurs when methyl orange indicator is used. Thus, alkalinity due to **CO_3^{2-}** = 2P.

Alkalinity of water

(iv) When **P>1/2 M** or $V_1 > V_2/2$ In this case, besides CO_3^{2-}, OH^- ions are also present.

Now half of CO_3^{2-} (i.e., $HCO_3^- + H^+ \rightarrow H_2O + CO_2$) is equal to (M – P), so alkalinity due to complete **CO_3^{2-}** = 2(M–P) and

alkalinity due to **OH^-** = M–2(M–P) = (2P–M).

(v) When **P<1/2 M** or $V_1 < V_2/2$, in this case, besides CO_3^{2-}, HCO_3^- ions are also present, now alkalinity due to **CO_3^{2-}** = 2P and alkalinity due to **HCO_3^-** = (M – 2P).

Numericals on Alkalinity of water

1. 50 mL of a sample of water required 5 mL of N/50 H_2SO_4 using methyl orange as indicator but did not give any coloration with phenolphthalein. What type of alkalinity is present? Express the same in ppm. **(P=0, Only HCO_3^-)**

2. 200 mL of water sample on titration with N/50 H_2SO_4 using phenolphthalein as indicator gave the end point when 10 mL of acid were run down. Another lot of 200 mL of the sample also required 10 mL of the acid to obtain methyl orange end point. What type of alkalinity is present in the sample and what is its magnitude? **(P=M/2, Only CO_3^{--})**

3. 500 mL of a water sample on titration with N/50 H_2SO_4 gave a titre value of 29 mL to phenolphthalein end point and another 500 mL sample on titration with same acid gave a titre value of 58 mL to methyl orange end point. Calculate the alkalinity of the water sample in terms of $CaCO_3$ and comment on the type of alkalinity present.

Numericals on Alkalinity of water

- A sample of water was alkaline to both phenolphthalein and methyl orange. 100 mL of this water sample required 30 mL of N/50 H_2SO_4 for phenolphthalein end point and another 20 mL for complete neutralisation. Determine the type and extent of alkalinity present.

- **(P = 300 ppm, M = 500 ppm;** Since P > M/2, *OH^- alkalinity = 100 ppm CO_3^{2-} alkalinity = 400 ppm*)

- A water sample is alkaline to both phenolphthalein as well as methyl orange. 200 mL of this water sample on titration with N/50 HCl required 9.4 mL of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and titration is further continued, the yellow color of the solution just turned red after addition of another 21 mL of the acid solution. Elucidate on the type and extent of alkalinity present in the water sample.

- **(P = 47 ppm, M = 152 ppm,** P < M/2 , *HCO_3^- alk. = 58 ppm & CO_3^{2-} alk.= 94 ppm*)

Boiler Problems with Hard Water

Boiler feed water should correspond with the following composition

   (i) Its hardness should be below 0.2 ppm

   (ii) Its caustic alkalinity (due to OH^-) should lie in between 0.15 and 0.45 ppm

   (iii) Its soda alkalinity (due to Na_2CO_3) should be 0.45–1 ppm

Excess of impurities, if present, in boiler feed water generally cause the following problems

       (i)   Boiler corrosion

       (ii)   Priming and foaming

       (iii) Caustic embrittlement
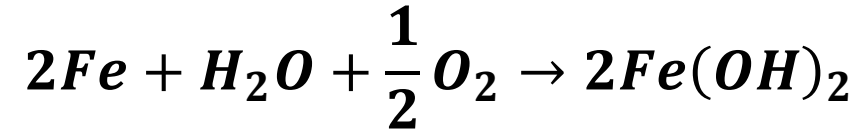
       (iv)   Scale and sludge formation

Boiler Corrosion

What it is???? Why it occurs???? How it can be prevented????

Causes for the Corrosion in boiler are as follows:

• **Dissolved Gases: A) Dissolved Oxygen:**

It corrodes the boiler metal as follows : Iron first produces ferrous hydroxide which eventually gets further oxidised to form rust.

$$2Fe + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow (Fe_2O_3 \cdot H_2O)$$
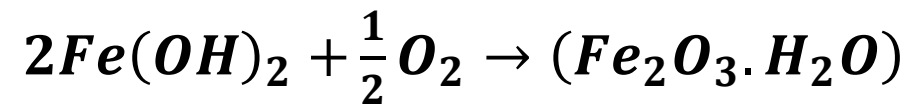
Prevention: Dissolved Oxygen can be removed by adding calculated quantity of sodium sulphite **Na$_2$SO$_3$** or **hydrazine N$_2$H$_4$** (best method) Why?? Or by Mechanical de-aeration
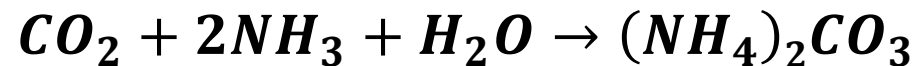
Boiler Corrosion

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

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$
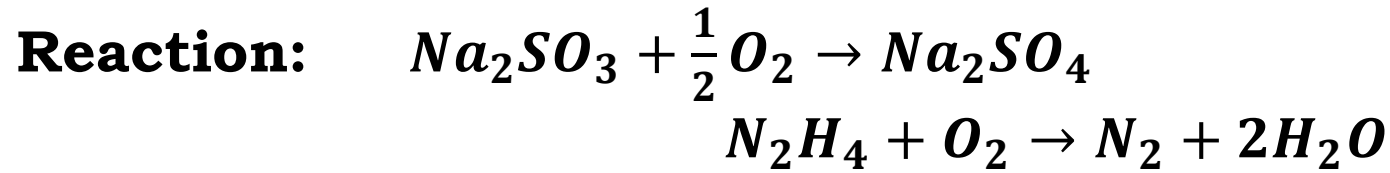
B) Dissolved CO_2:

Gaseous CO_2 is acidic in nature. Water with CO_2 corrodes the boiler slowly as CO_2 in water forms Carbonic acid H_2CO_3. Carbonic acid has a **slow corrosive effect** on the boiler material.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2$$
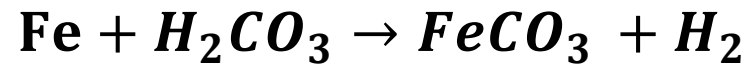
Prevention: Dissolved CO_2 can be removed by adding suitable quantity of NH_3
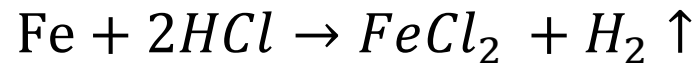
$$CO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2CO_3$$

Or by Mechanical de-aeration: The process consists of spraying water over preheated perforated plates stacked in tower. Removal of dissolved O2 is ensured by applying high temperature and vacuum.

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2.   Hydrolysis of salts:

Water containing weak base-strong acid salts like $MgCl_2$ and $CaSO_4$ results in the formation of strong acid at high temperature in the boiler which attacks the inner surface of boiler, decreasing the strength and life of boiler.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 \downarrow + \textbf{2HCl}$$

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

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 \downarrow + \textbf{2HCl}$$ Formation of acid in boiler is **cyclic**

Prevention:

Corrosion can be prevented by **adjusting the pH of boiler water in 8-9** range

Boiler feed water **should not contain salts of weak base-strong acid**

Boiler Corrosion

3.   Formation of Galvanic Cells:

Galvanic Cells gets formed in the boiler fittings which are made up of different metals or due to impurities (2 different metals in contact with water)

Prevention: Galvanic Cell formation can be avoided by suspending **sacrificial plates (anodes) in boiler water like Zinc plates**. Zn being more electropositive than iron, it undergoes corrosion (anode) and protects the boiler metal (cathode)

Caustic Embrittlement

- It is the phenomenon in which the boiler material becomes brittle due to the accumulation of **excess alkali** in the boiler.

- Caustic embrittlement is a form of **stress corrosion** taking place in boilers operating at **high temperature** and **pressure**.

- It is caused by **high alkalinity of water in the boiler**, particularly at those places which are under stress such as rivets, joints and bends with the result that the metal plates become brittle.

- When water is softened by lime – soda process, the **excess sodium carbonate** undergoes decomposition in high pressure boilers leading to the formation of **NaOH**. $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$
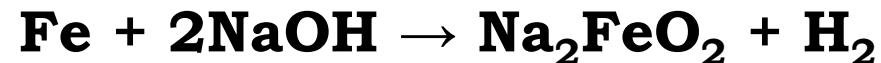
Caustic Embrittlement

This NaOH makes the water alkaline.

The alkaline water penetrates into the minute cracks and crevices between the rivets and joints by capillary action.
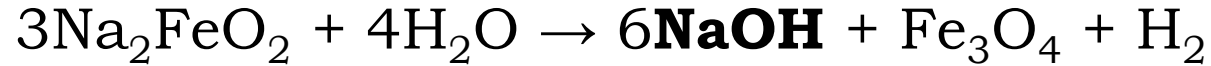
Inside the cracks, the water evaporates and the concentration of NaOH increases on these sites due to poor circulation of water.

NaOH attacks the iron in boiler material converting it to **sodium ferroate (Na_2FeO_2).** A small quantity of **sodium ferrite ($NaFeO_2$)** is also formed.

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2$$

Caustic Embrittlement

$$3Na_2FeO_2 + 4H_2O \rightarrow 6\textbf{NaOH} + Fe_3O_4 + H_2$$

$$6Na_2FeO_2 + 6\ H_2O + O_2 \rightarrow 12\textbf{NaOH} + 2Fe_3O_4$$

$$Fe_3O_4 + 4NaOH \rightarrow 2NaFeO_2 + Na_2FeO_2 + 2H_2O$$

It can be seen that **NaOH is regenerated** in the process and its concentration keeps on increasing maintaining the required environment.

- The caustic embrittlement of the boiler may be explained by assuming the formation of a concentration cell as shown below:

Iron at bends, rivets joints (stressed areas) **|** Concentrated NaOH solution **||**
Dilute NaOH solution **|** Iron at plane surface (stress free)

The iron in the anodic area undergoes corrosion and dissolves making the boiler material brittle.

Caustic Embrittlement

Prevention:

- By adding tannin or lignin to the boiler water.

  These block the minute cracks and prevent the infiltration of NaOH

- By using sodium phosphate instead of sodium carbonate for softening water.

- By adjusting the pH of boiler water between 8–9.

- Use of excess Na_2CO_3 should be avoided in the lime-soda process.

- Caustic embrittlement can be prevented if Na_2SO_4 is added to the boiler water, because it is useful in blocking the hair cracks.

- Na_2SO_4/NaOH should be used in the ratio 1:1, 2:1 and 3:1 for boilers working at pressure 10, 20 and above 20 atm, respectively.

Priming & Foaming

When boiler produces steam rapidly, droplets of water are carried out along with the steam

Priming is the process of wet steam formation.

Foaming is the formation of continuous, persistent foam or bubbles on the surface of boiler water.

Priming & foaming generally occurs together

Causes of Priming:

• Very high level of boiler feed water

• High steam velocity (speed of steam generation)

• Presence of excessive foam on the surface

• Faulty design of boiler

• Sudden drop in steam pressure owing to a high demand for steam

Priming & Foaming

Priming and Foaming:

Causes of Foaming:

- High concentration of dissolved salts in boiler feed water

- Presence of oil droplets and alkali in boiler feed water

- Presence of finely dispersed suspended materials

- Violent agitation of boiler feed water

Disadvantages Priming and Foaming :

- Priming decreases the efficiency & life of machinery as dissolved salts present in the droplets enter in the parts of machinery

- Actual height of boiler water cannot be judged because of foaming

- Foaming causes wet steam formation

Priming & Foaming

Prevention of Priming and Foaming:

- Priming can be prevented using Softened and filtered water

- Maintaining low water levels, priming can be prevented

- Avoiding rapid changes in the water level, priming can be minimised

- Using steam purifiers, if priming happens

- Foaming can be prevented by adding antifoaming agents like castor oil, alcohol

- By adding chemicals like sodium aluminate , oil from water can be removed

- Blow down operations at appropriate time

Scale and Sludge Formation

Water evaporates continuously inside the boiler and the concentration of dissolved salts increases gradually. When the solution is saturated with respect to the salt concentration, the salts start precipitating out on the inner walls of the boiler. If the precipitate formed is soft, slimy and loose, it is called *sludge* and

if the precipitate formed is hard and adhering on the inner walls of the boiler it is termed as *scale*.

SLUDGE: It is soft, slimy and loose precipitate formed on the inner walls of the boiler.

Scale and Sludge Formation

Sludge formation:

(a) Sludges are formed by substances which have greater solubility in hot water than in cold water like $MgSO_4$, $MgCl_2$, $MgCO_3$, $CaCl_2$ etc.

(b) They are formed at colder parts of the boiler and get collected at places where the flow rate is slow or at bends, plug opening, glass gauge connection, thereby causing even choking of the pipes.

(c) They are poor conductors of heat.

Prevention :

(i) By using softened water.

(ii) By frequently 'blow-down operation' (drawing off a portion of the concentrated water from the boiler and replacing it with fresh water)

Scale and Sludge Formation

Disadvantages of sludge formation:

(i) Being poor conductors of heat, they tend to waste a portion of heat generated and thus decreases the efficiency of the boiler.

(ii) Excessive sludge formation disturbs working of the boiler.

(iii) When formed along with scale, they get entrapped in scale and both get deposited as scales.

(iv) It settles in regions of poor water circulation such as pipe connection, plug opening, and glass gauge connection thereby choking the pipes.

Scale and Sludge Formation

Scales: Hard adherent coating or deposits produced when dissolved salts are precipitated out of boiler feed water after saturation point is reached during boiler operation.

Scales gets adhered firmly to the inner surface or walls of boiler which cannot be removed mechanically even with the help of hammer and chisel

Causes of Scale formation:

- **Decomposition of Bicarbonates:** At high temperature, bicarbonates undergo decomposition to form precipitate as scale

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

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

Scale and Sludge Formation

$CaCO_3$ scale is soft and it is the main cause of scale formation in low- pressure boilers. However in higher pressure boilers $CaCO_3$ is soluble due to the formation of soluble $Ca(OH)_2$

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2$$
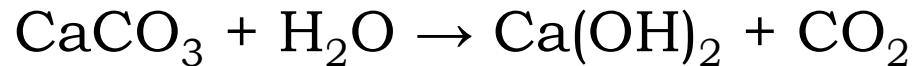
- ***Deposition of $CaSO_4$:*** The solubility of $CaSO_4$ decreases as temperature increases. $CaSO_4$ is soluble in cold water and is completely insoluble in superheated water. Therefore, $CaSO_4$ gets precipitated as hard scale on the hot portion of the boiler.

- ***Hydrolysis of magnesium salts*** At high temperature, dissolved magnesium salts undergo hydrolysis forming a soft scale of magnesium hydroxide.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$
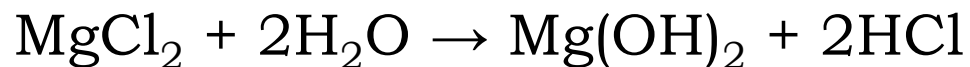
Scale and Sludge Formation

- *Formation of calcium and magnesium silicates*

Very small quantities of SiO_2 present in hard water react with calcium and magnesium forming calcium silicate ($CaSiO_3$) and/or magnesium silicate ($MgSiO_3$). These are hard scales and are extremely difficult to remove.

Removal of scale:

(i) Loosely adhering scale can be removed either by scraper or wire brush or by blow-down operation.

(ii) Brittle scales can be removed by thermal shocks (i.e heating the boiler and then suddenly cooling with cold water).

(iii) Hard and adherent scales can be removed by dissolving in chemicals, for example, $CaCO_3$ scale can be dissolved by using 5–10% HCl. $CaSO_4$ scale can be removed by adding EDTA since the Ca-EDTA complex is highly soluble in water.

(iv) By external and internal treatment

Scale and Sludge Formation

Disadvantages of scale formation:

- ***Wastage of fuel*** Scales have poor thermal conductivity, therefore the rate of heat transfer from boiler to the water inside is greatly reduced. Hence extra heat is to be supplied to the boiler and this increases the fuel consumption.

- Wastage of fuel depends upon the thickness of the scale. Greater the thickness of the scale larger is the wastage of fuel.

- ***Lowering boiler safety*** Due to scale formation which is poor conductor of heat, the boiler is to be over heated to provide steady supply of heat. Overheating makes the boiler material softer and weaker. Therefore distortion of boiler tubes takes place and the boiler becomes unsafe to bear the pressure of the steam (in high-pressure boilers).

Scale and Sludge Formation

Disadvantages of scale formation:

- ***Decrease in efficiency*** Deposition of scale in the valves and condensers of the boiler, chokes them partially. This results in decrease in efficiency.

- ***Danger of explosion*** Due to uneven expansion the thick scales crack, as a result water comes in contact with the overheated inner walls of the boiler resulting in excessive steam formation which can lead to boiler explosion.

Unit 1: Water Softening Techniques

Water Softening:

Process of converting hard water into soft water. Softening methods are of 2 types:

1) **Internal Treatment**

2) **External Treatment Process:** Based on following Principle

1) Precipitation   2) **Ion-exchange**

        a) Zeolite Method or Permutit Process

        b) Demineralization or Deionization Method

        c) Lime Soda Method (Hot/Cold)

Zeolite Method

- Zeolites are also known as permutit and in Greek it means 'boiling stone'. They occur naturally as hydrated alumino silicate minerals like

  $Na_2O.Al_2O_3.\ x\ SiO_2.\ y\ H_2O$

- where x = 2–10 and y is 2–6. They are capable of exchanging reversibly sodium ions for hardness producing ions in water.

- 1. *Natural Zeolites* Non porous, amorphous and durable, for example, Natrolite **$Na_2O.Al_2O_3.\ 4SiO_2.\ 2H_2O$**

- 2. *Synthetic Zeolites* Porous with gel-like structure. They are prepared by heating sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2).

Zeolite Softener

Hard water inlet —

Injector —
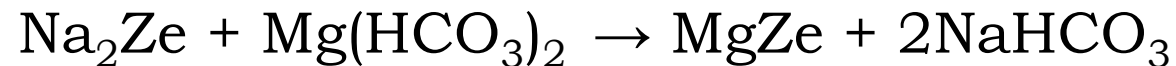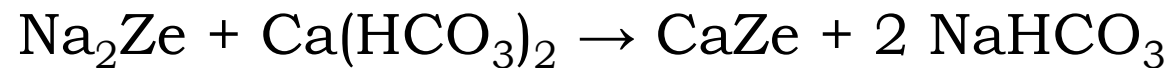
Zeolite bed

Gravel

NaCl Solution storage

To sink

Soft water outlet
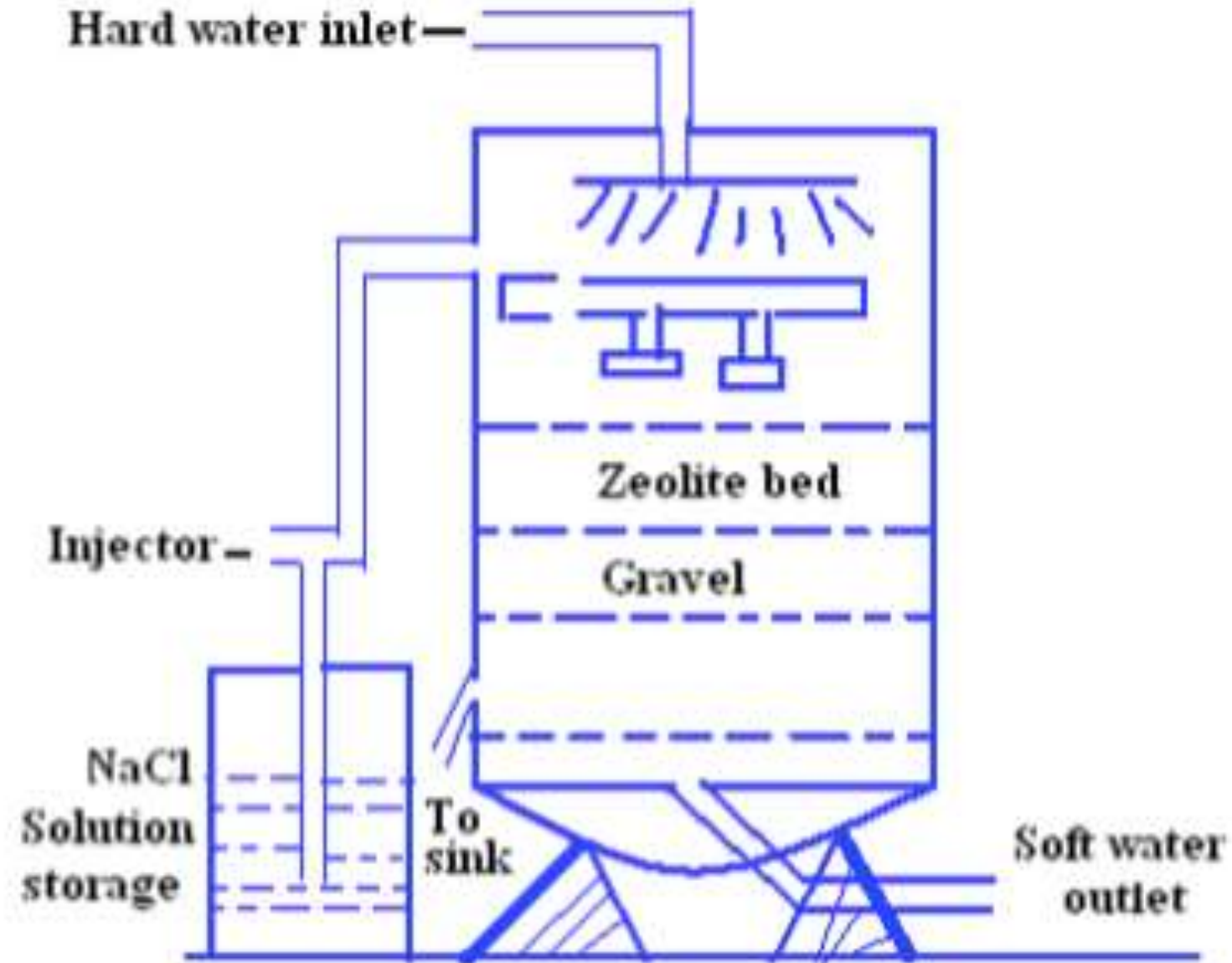
Zeolite Method

- **Process** Hard water is percolated at a specified rate through a bed of zeolite stacked in a cylindrical unit. The hardness causing elements (Ca^{2+}, Mg^{2+} etc) are retained by zeolite as CaZe and MgZe, while the outgoing water contains sodium salts.

- The chemical reactions involved are

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2\ NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$$

$$Na_2Ze + CaCl_2\ (or\ CaSO_4) \rightarrow CaZe + 2NaCl\ (or\ Na_2SO_4)$$

$$Na_2Ze + MgCl_2\ (or\ MgSO_4) \rightarrow MgZe + 2NaCl\ (or\ Na_2SO_4)$$
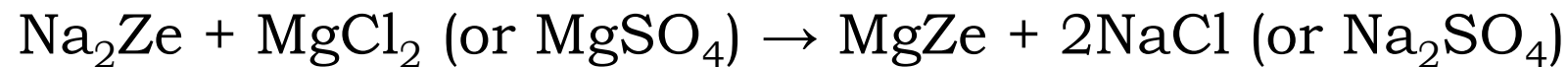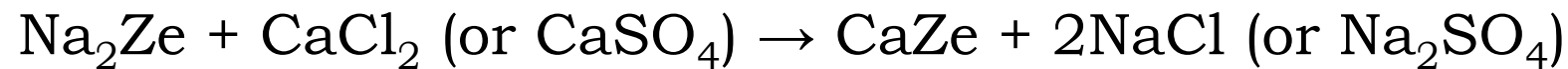
Zeolite Method

- After some time, all the sodium ions in zeolite are replaced by Ca and Mg ions giving CaZe/ MgZe. Such a zeolite bed is unable to soften water further and is said to be exhausted. It has to be regenerated to enable it to soften water again. It may be noted that the water obtained by zeolite process is used mostly for laundry purpose; it cannot be used in boilers.

- **Regeneration**

- When the zeolite bed is exhausted the supply of hard water is stopped and it is regenerated by treating with a concentrated brine (10% NaCl) solution.

- CaZe (or MgZe) + 2NaCl → **Na_2Ze** + $CaCl_2$ (or $MgCl_2$)
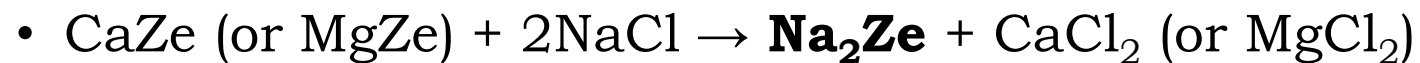
  (exhausted zeolite) (Brine) **Reclaimed** (Washings)

Zeolite Method

- The washings (containing $CaCl_2$, $MgCl_2$, etc.) are led to drain and the regenerated zeolite bed is used again for softening. ($NaNO_3$, KCl, KNO_3, etc. can also be used for regeneration instead of NaCl, but NaCl is mostly used because of its low cost and the products of regeneration process ($CaCl_2$ or $MgCl_2$,) are highly soluble and can be easily rinsed out of the zeolite bed).

- By knowing the amount of NaCl used for regeneration of the exhausted zeolite bed, the hardness of the water sample can be calculated by using the formula.

Hardness (H) = 50 × m× V_1 ×10^3 /58.5×V

V = Total Volume of water softened in litres;

V_1 = Total volume of NaCl used for regeneration and

M = amount of NaCL in g/L present in V_1

Zeolite Method

- **Advantages of Zeolite Process**

- Hardness is removed almost completely, and the residual hardness is about 10 ppm.

- The equipment is compact and occupies less space.

- It is a clean and rapid process. Sludge is not formed as the impurities are not precipitated.

- It requires less skill for maintenance as well as operation.

Zeolite Method

Limitations and Disadvantages of Zeolite Process

- Turbid water cannot be used as turbidity clogs the pores of zeolite bed making it inactive.

- Mn^{2+} and Fe^{2+} present must be removed first because these ions react with zeolite bed to give manganese and iron zeolites which cannot be easily regenerated.

- Mineral acids, if present in water, destroy the zeolite bed and hence they must be neutralised with soda in advance.

- This method does not remove anions. The bicarbonates present in hard water get converted into $NaHCO_3$ which goes into soft water effluent. If this water is used in boiler, $NaHCO_3$ dissociates as $NaOH$ and CO_2. $NaOH$ leads to caustic embrittlement and CO_2 makes the water acidic and corrosive.

- The treated water contains more sodium salts.

- Moreover, high cost of the plant and material also acts as limiting factor.

Numericals on Zeolite Method

- A zeolite softener was used to remove the hardness of 95,000 liters of hard water completely. The softener required 475 liters of NaCl solution containing 18 g/liter of NaCl for regeneration. Calculate the hardness of hard water in ppm.

    (Hardness (H) = 76.92 ppm)

- An exhausted zeolite softener was regenerated by 325 liters of NaCl solution containing 60 g/liter of NaCl. How many liters of hard water of hardness 250 mg/L can be softened by the zeolite softener.

    (Total volume of hard water softened = 66666.67 liters)

1) Quantity of $NaCl$ =

2) in terms of $CaCO_3$ eqvt. =

3) Quantity of water =

$$V_{Water} (l) \times Hardness \left(\frac{mg}{l}\right) = V_{NaCl} (l) \times C_{NaCl} \left(\frac{mg}{l}\right) \times \frac{50}{58.5}$$

$$(\because 2\, NaCl \equiv 1\, CaCO_3)$$

Numericals on Zeolite Method

1. A zeolite softener was completely exhausted and was regenerated by passing 100 liters of NaCl solution containing 120 g/liter of NaCl. How many liters of sample of water of hardness 500 ppm can be softened by this softener.

[Ans 20512.8 liters]

2. A zeolite softener was completely exhausted after softening 145,000 liters of hard water. To regenerate the zeolite softener 540 liters of NaCl solution containing 110 g/liter of NaCl is required. Calculate the hardness of one liter water sample in ppm.

[Ans 350.13 ppm]

3. 200 liters of NaCl solution containing 85 g/liter of NaCl was required to regenerate a completely exhausted zeolite softener. How many liters of hard water of hardness 600 ppm can be softened by the softener.

[Ans 24216.5 liters]

4. When a zeolite softener was completely exhausted it was regenerated by passing 200 liters of NaCl solution containing 120 g/liter of NaCl. How many liters of a sample of water of hardness 550 mg/liter can be softened by the zeolite softener before regenerating it again.

[Ans 37296.037 liters]

Water Softening Techniques

Demineralization or Deionization Method:

Principle: Ion Exchange

Ion Exchange Process: Ion exchange process is defined as the reversible exchange of ions in the structure of an ion exchanger to ions in solution that is brought in contact with it.

- The resins used for the purpose are called ion exchange resins.

- Resins are porous, insoluble, cross linked, long chain organic polymers capable of exchanging ions.

- **Two types of resins** are employed for the softening of water.

(i) ***Cation exchange resin:*** They are materials capable of exchanging a cation in their structure to the cation in solution. For softening of water, the resins used should be capable of exchanging H+ ions in their structure to other cations in solution.

Commonly used resins are **styrene divinyl benzene copolymers, which on sulphonation or carboxylation** become capable of exchanging hydrogen ions with the cations in water. They are represented as R–H$^+$ (R represents insoluble polymer matrix and H is the exchangeable ion).

(ii) ***Anion exchange resin :*** They are materials capable of exchanging an anion in their structure (for water softening the exchangeable anion should be OH$^-$ ion) to anion in solution.

Anion exchangers employed for water softening are **styrene divinyl benzene copolymers, which contain basic functional group such as amino or quaternary ammonium groups** as an integral part of the resin matrix. These after treatment with dilute NaOH solution become capable of exchanging OH$^-$ ions with the anions in water. They are represented as R$^+$OH$^-$ (where, R$^+$ is the insoluble polymer matrix and OH$^-$ is the exchangeable ion).

Process : The hard water is first passed through a column containing cation exchange resin. All cations are removed and equivalent amount of H^+ ions are released from this column to water. The water coming out of this chamber has low pH.

The exchange reactions :

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

$$2RH^+ + Mg^{2+} \rightarrow R_2Mg + 2H^+$$
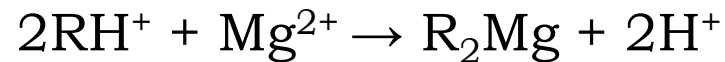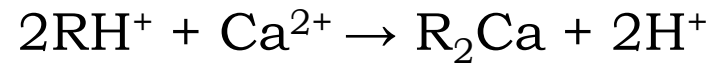
- After this the water is passed into second column containing anion exchange resin. All the anions are removed and an equivalent amount of OH^- ions are released.

$$ROH + Cl^- \rightarrow RCl + OH^-$$

$$ROH + SO_4^{2-} \rightarrow R_2SO_4 + 2OH^-$$

$$ROH + CO_3^{2-} \rightarrow R_2CO_3 + 2OH^-$$
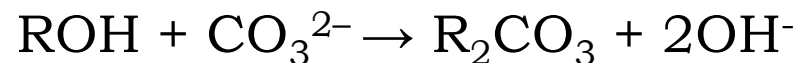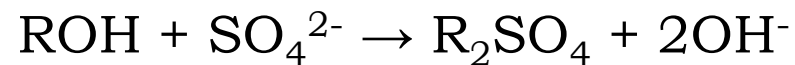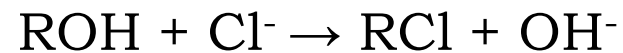
Water Softening Techniques

Process :

The H^+ ions released from cation exchange column and OH^- ions released from anion exchange column combine to produce water molecule.

$$H^{\pm} + OH^- \rightarrow H_2O$$
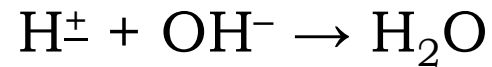
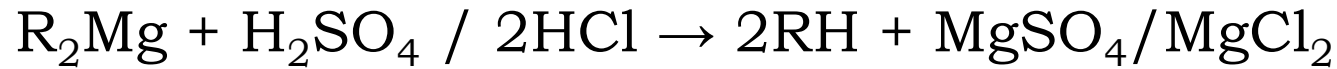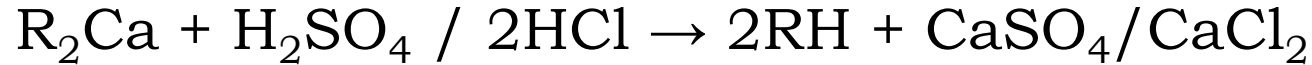The water coming out of the exchanger is free from all cations (except H^+) and anions (other than OH^-).

This ion free water is known as **deionised water or demineralised water** and has a neutral pH.

Regeneration: After some time, the resin loses all its H^+ and OH^- ions and then its capacity to exchange ions is lost. In such a condition they are said to be exhausted.
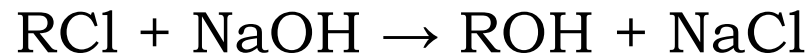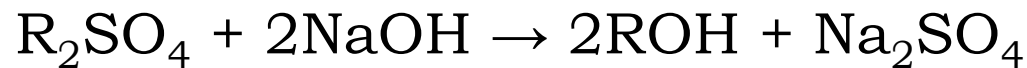
Water Softening Techniques

- The exhausted cation exchange resin is regenerated by passing a solution of HCl or H_2SO_4.

$$R_2Ca + H_2SO_4 \ / \ 2HCl \rightarrow 2RH + CaSO_4/CaCl_2$$

$$R_2Mg + H_2SO_4 \ / \ 2HCl \rightarrow 2RH + MgSO_4/MgCl_2$$

The column is then rinsed with distilled water to remove the salts formed. Ideally, HCl is used for regeneration as $CaCl_2$ and $MgCl_2$ are more soluble.

- The anion exchange resin is regenerated by passing a dilute solution of NaOH and then washing with distilled water

$$R_2SO_4 + 2NaOH \rightarrow 2ROH + Na_2SO_4$$

$$RCl + NaOH \rightarrow ROH + NaCl$$

NaCl, Na_2SO_4 are removed by washing with distilled water.

Water Softening Techniques

Advantages

- The process can be used to soften highly acidic or alkaline water.

- Unlike zeolite process the soft water does not contain sodium ions.

- It removes all cations and anions other than H+ and OH– ions.

- All ionisable impurities are removed.

- It produces water of very low residual hardness (about 2 ppm).

Disadvantages

1. The process is expensive, both the equipment and resins are costly.

2. Turbid water decreases the efficiency of the process.