

WATER AND ITS TREATMENT

Hardness and alkalinity of water: Units and determination

External and internal method of Softening of water

WATER:



- Most precious, wonderful and useful gift of nature
- Covers nearly 70% of the earth's surface
- Water on earth
 - Ocean seas (97%)
 - Polar ice and glaciers (2%)
 - Fresh water (1%) in rivers, lakes, streams, ground water, etc.

Common Impurities in water:

- Water is a very good solvent and hence dissolves many substances.
- **The common impurities in water:**
 - Dissolved impurities: salts, ions, dyes, gases-**change in taste/color/hardness**
 - Suspended impurities: like inorganic (clay, sand) organic (oil, plant, and animal matter)
Make water turbid
 - Colloidal impurities- finely divided silica and clay
 - Microorganisms – bacteria, fungi and algae
Foul smell/cause diseases

Water quality standards:

- Water is used for domestic as well as industrial uses
 - Potential application will determine the quality parameters
 - Environmental (ambient) water quality vary significantly according to the source: lakes, rivers, ocean etc.
-
- **Water quality parameters broadly fall in three categories**
 - Physical characteristics (Color, Taste, odor, temperature, etc.)
 - Chemical characteristics (pH, hardness, Total Dissolved Solids (TDS), dissolved oxygen (DO), Cl^- , F^- , NO_3^- , etc.)
 - Biological characteristics (E. coli, coliform, etc.)

Hardness of water:

It is defined as a characteristic property of water that prevents the lathering of soap.

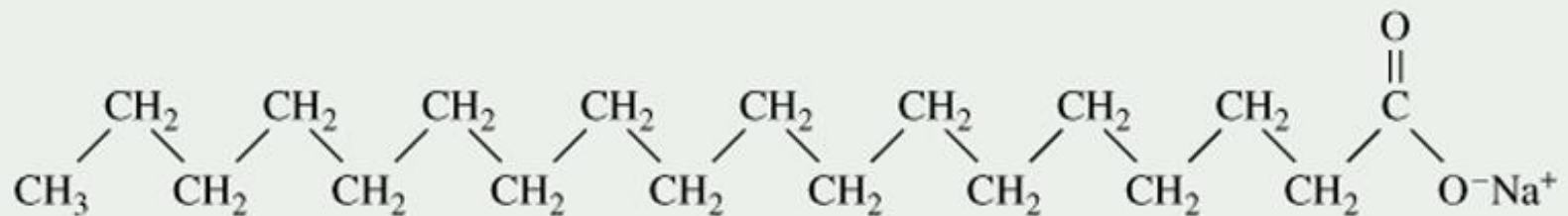
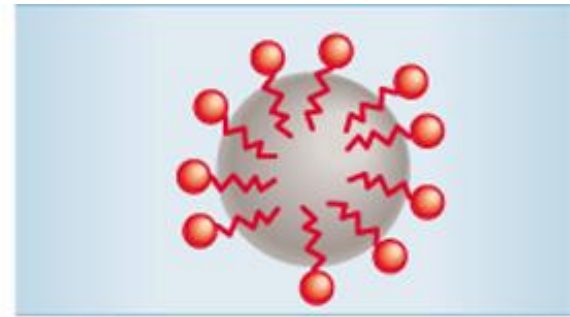
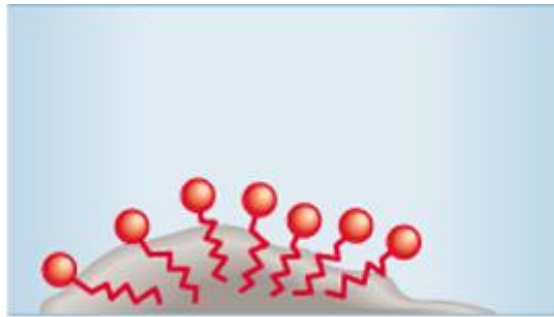
Hardness of water may also be defined as the soap-consuming capacity of water, or the capacity of precipitation of soap.

It is due to the presence of soluble salts of **Ca, Mg, Al, Fe, Mn**, etc. in water.

The Cleansing Action of Soap:



Grease



Sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$)

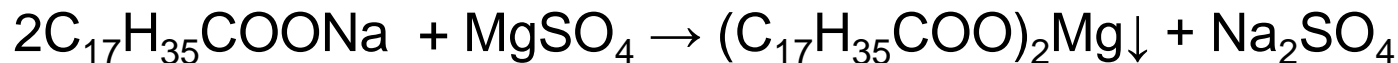
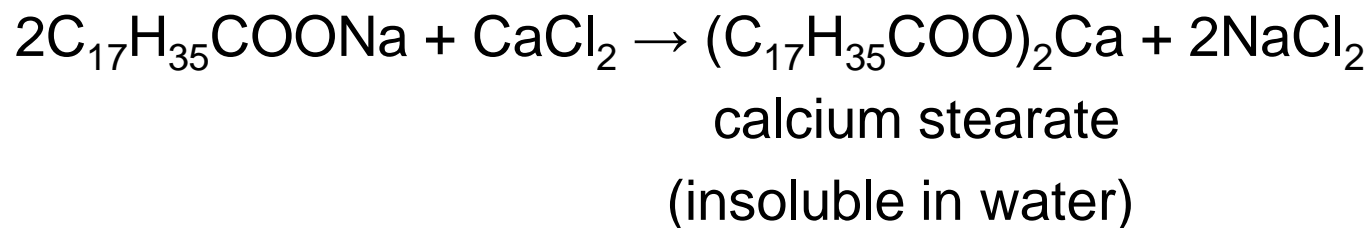
(a)



Soap ($\text{C}_{17}\text{H}_{35}\text{COONa}$) – Sodium or potassium salts of long chain fatty acids.

Hardness of Water: Reduce the cleansing action of soap

Hard water does not produce lather with soap solutions, but produces white precipitate (scum). For example, sodium stearate reacts with calcium or Mg present in hard water.

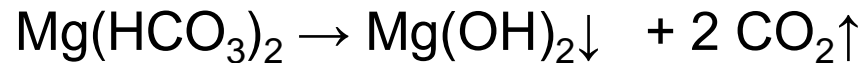


TYPES OF HARDNESS:

Temporary Hardness:

Caused by dissolved bicarbonates of Ca and Mg

Temporary hardness can be removed by boiling of water



Also, known as 'alkaline or carbonate hardness' determined by titration with HCl using methyl orange as indicator

Permanent Hardness: Non-carbonate/non-alkaline hardness

Due to sulphates or chlorides of Ca and Mg (e.g. CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , etc.,)

Cannot be destroyed on boiling the water

Also known as *non-carbonate* or *non alkaline* hardness

**Total hardness = Temporary + permanent hardness
= non alkaline + alkaline hardness**

Revision:

Q 1: What is the hardness of water?

Q 2: What is the chemical composition of soap and how does it work?

Q 3: Why the cleaning power of soap get reduce in hard water?

Q 4: How we classified the hardness?

Q 5: What are temporary and permanent hardness?

Q 6: How we can remove to the temporary hardness?

- Hard Water

Does not produce lather with soap

Contains Ca and Mg salts

Soap is wasted and cleaning quality is depressed

Boiling point elevated, more time and fuel for cooking

- Soft Water

Produces lather easily with soap

Does not contain dissolved Ca and Mg salts

Cleaning quality of soap not depressed.

Less fuel and time required for cooking

Degree Of Hardness Of Drinking Water

- Soft 0-60 mg/L
- Medium 60-120 mg/L
- Hard 120-180 mg/L
- Very hard >180 mg/L

EXPRESSION OF HARDNESS:

- Always calculated in terms of equivalent of CaCO_3
 - Calculation is easy as Mol. Wt. of $\text{CaCO}_3 = 100$
 - Insoluble CaCO_3 precipitated out from water:

$$\text{Hardness of water in equivalent of } \text{CaCO}_3 = \frac{W \times E}{\text{C.E.}} \quad \text{ppm or mg/l}$$

W = Mass of hardness producing substance

E = Equivalent weight of CaCO_3 (50)

C.E. = Equivalent weight of hardness producing substance

Examples:

- 1. A water sample contain 248 mg CaSO_4 /l. Calculate the hardness in terms of CaCO_3 equivalent.

Weight of hardness causing substance i.e. CaSO_4 =248 mg/l
Eq. wt of CaSO_4 =68

Eq. wt of CaCO_3 =50

Hardness of water in terms of CaCO_3 equivalent =

$$\frac{W \times E}{\text{C.E.}}$$

$$\frac{248 \times 50}{68}$$

182.35 CaCO_3 equivalent or ppm or mg/l

2. How many grams of FeSO_4 (mol. Wt. = 152) dissolved per liter gives 300 ppm of hardness.

Suppose **A** gram of FeSO_4 giving 300 ppm hardness

Equivalent weight of hardness producing substance = $152/2 = 76$

$$300 = A \times 50/76$$

$$A = 300 \times 76/50 = 456 \text{ ppm} = 456 \text{ mg/l} = 0.456 \text{ g/l}$$

UNITS OF HARDNESS:

Several different scales used to describe the hardness of water

1) ppm : Number of parts by weight of CaCO_3 equivalent hardness present in million (10^6) parts by weight of water.

2) mg/l : Usually defined as one milligram of calcium carbonate (CaCO_3) per liter of water.

$$1 \text{ mg/l} = 1 \text{ mg of } \text{CaCO}_3 \text{ in 1 liter of water}$$

3) Clark's Degree(°Cl): One degree Clark is defined as one grain (64.8 mg) of CaCO_3 per Imperial gallon (4.55 liters) of water

64.8 mg CaCO_3 present in 4.55 liter or Kg water

$$= 4.55 \times 10^6 \text{ mg water}$$

1 mg CaCO_3 will be in $= (4.55/64.8) \times 10^6$ mg water

$$= 70,000 \text{ mg water}$$

Thus 1 °Cl = parts of CaCO_3 equivalent hardness per 70,000 parts of water

$$1 \text{ ppm} = 1 \text{ mg/l} = 0.07 \text{ °Cl}$$

4) Degree French (°F): One degree French is defined as 10 milligrams of calcium carbonate per liter of water.

$$1 \text{ ppm} = 1 \text{ mg/l} = 0.07 \text{ °Clark} = 0.1 \text{ °F}$$

Q. Convert 50 ppm of CaCO_3 into mg/L, degree Clarke and degree French.

Ans. $1 \text{ ppm} = 1 \text{ mg/l} = 0.07^\circ \text{Clark} = 0.1^\circ \text{F}$

$50 \text{ ppm} = 50 \text{ mg/l} = 3.5^\circ \text{Cl} = 5^\circ \text{F}$

Q. Convert 70,000 $^\circ \text{Clarke}$ into ppm and $^\circ \text{French}$.

Ans: $70,000 \text{ Clark} = 10^6 \text{ ppm}$, $70,000 \text{ Clark} = 10^5^\circ \text{F}$

Q 1: A sample of water on analysis was found to $\text{Ca}(\text{HCO}_3)_2 = 4 \text{ mg/l}$, $\text{Mg}(\text{HCO}_3)_2 = 6 \text{ mg/l}$, $\text{MgSO}_4 = 10 \text{ mg/l}$, $\text{CaSO}_4 = 8 \text{ mg/l}$. Calculate the temporary, permanent and total hardness of water in ppm, $^\circ\text{Fr}$ and $^\circ\text{Cl}$.
Mol. Wt. of $\text{Ca}(\text{HCO}_3)_2 = 162$, $\text{Mg}(\text{HCO}_3)_2 = 146$, $\text{MgSO}_4 = 120$, $\text{CaSO}_4 = 136$

Constituent	Amount (mg/l)	Eq. of CaCO_3 (ppm = mg/l)
$\text{Ca}(\text{HCO}_3)_2$	4	$4 \times 50/81 = 2.469$
$\text{Mg}(\text{HCO}_3)_2$	6	$6 \times 50/73 = 4.11$
CaSO_4	8	$8 \times 50/68 = 5.88$
MgSO_4	10	$10 \times 50/60 = 8.33$

- **Temporary hardness = 6.579 ppm**
 - **Due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$**
- **Permanent hardness = 14.21 ppm**
 - **Due to MgSO_4 and CaSO_4**
- **Total hardness = 20.789 ppm = 20.789 mg/l**
- **1 ppm = 0.07 °Cl,**
- **$20.789 = 20.789 \times 0.07 = 1.455 \text{ °Cl}$**
- **1 ppm = 0.1 °Fr**
- **$20.789 = 20.789 \times 0.1 = 2.0789 \text{ ° Fr}$**

Q 2. Calculate the temporary and permanent hardness of a sample of water containing: $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$; $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$; $\text{MgCl}_2 = 9.5 \text{ mg/L}$; $\text{CaSO}_4 = 13.6 \text{ mg/L}$.

Ans: Temporary hardness = hardness due to $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$

$$[7.3 \times 100/146 + 16.2 \times 100/162] \text{ mg/l}$$

$$[5 + 10] = \mathbf{15 \text{ mg/l or 15 ppm.}}$$

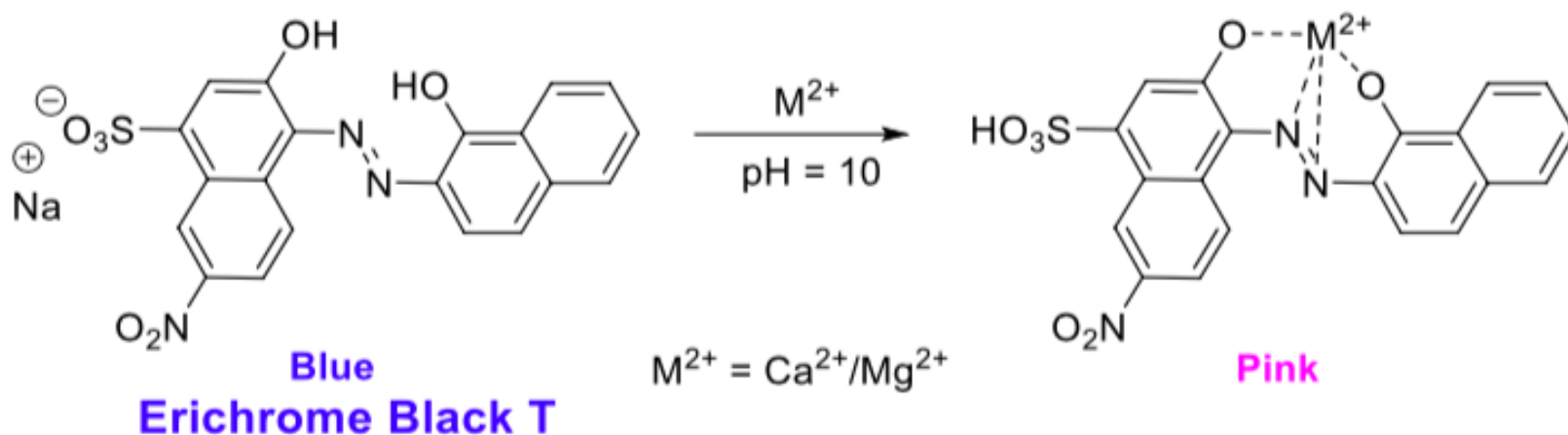
Permanent hardness = hardness due to MgCl_2 and CaSO_4

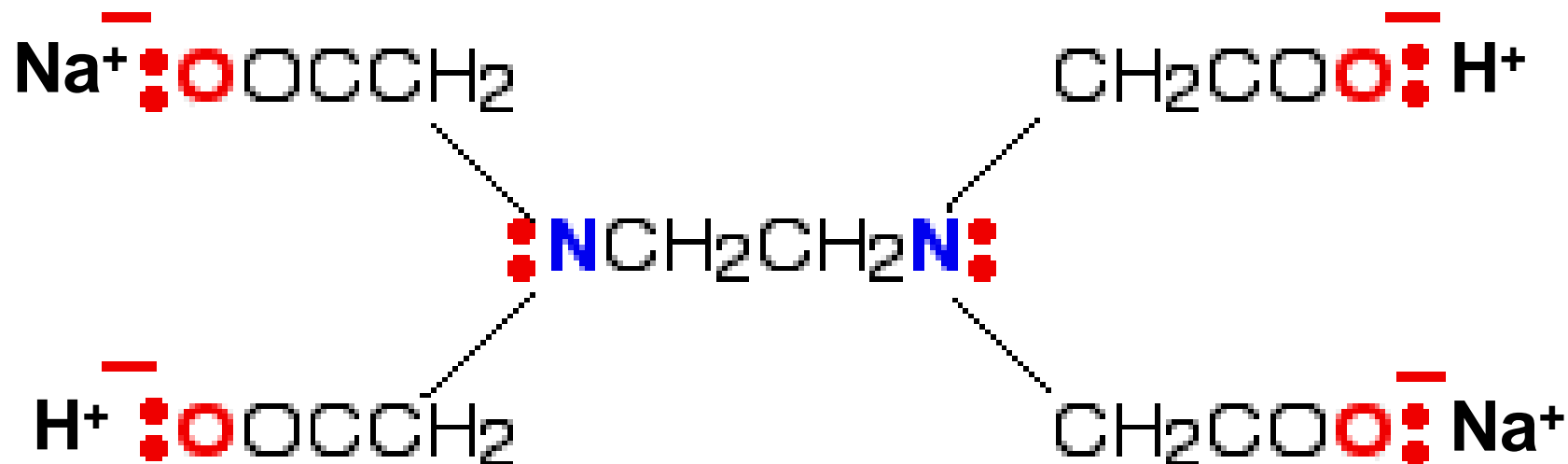
$$[9.5 \times 100/95 + 13.6 \times 100/136] = [10 + 10] = \mathbf{20 \text{ mg/l or 20 ppm.}}$$

Determination of hardness:

• Complexmetric titration:

- Hard water contain Ca, Mg ions
- EDTA is used as standard solution
- EBT (Eriochrome Black T) as indicator
- Titration was performed at pH ~9 ?





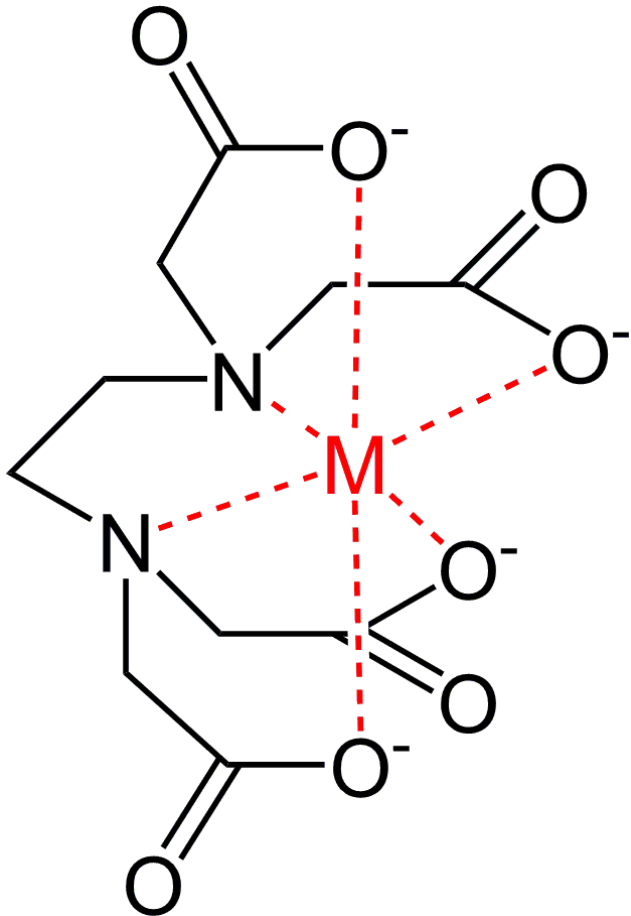
the EDTA⁴⁻ ion

EDTA is used as the disodium salt since it is more soluble in water than pure EDTA.

It is a strong chelating ligand, forms complex (1:1) with bivalent cations like Ca^{2+} & Mg^{2+}

The complexes formed are stable in alkaline medium i.e. pH= 8-10.

Metal- EDTA complex:



- EDTA being a chelating ligand (hexadentate) react with multivalent metal ions to form stable complex.
- In hard water, bivalent cations like Ca & Mg ions are present which form complex with EDTA.

Flow chart of Complexometric titration :

Take 10 mL of the water sample



Add 2-3 mL ammonium buffer solution to maintain pH~9-10



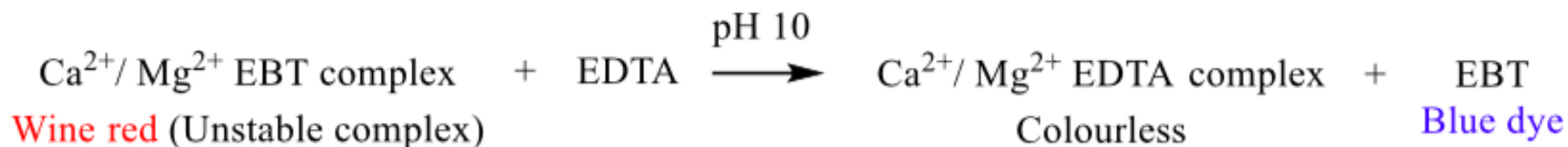
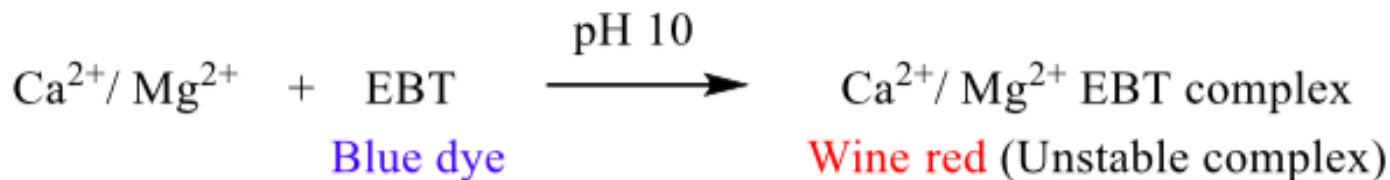
Add 2-3 drops of the EBT indicator (**solution becomes wine red**)



Titrate the hard water against the EDTA solution (**till the wine red color changes to blue**)



Note the EDTA volume used by burette reading



DETERMINATION OF HARDNESS: EDTA METHOD

FOR TOTAL HARDNESS:

$$\begin{array}{ccc} M_1 V_1 & = & M_2 V_2 \\ \text{(Hard Water)} & & \text{(Std. EDTA)} \\ M_1 & = & M_2 V_2 / V_1 \end{array}$$

$$\begin{aligned} \text{TOT. HARDNESS} &= M_1 \times 100 \text{ g/l} \\ &= M_1 \times 100 \times 1000 \text{ ppm} \end{aligned}$$

Note: Before boiling the water solution this method will give total hardness, after boiling the water sample this methods will give permanent hardness.

Temp. Hardness= Total hardness- permanent hardness

Important: If you use molarity then use molecular weight of CaCO_3 not the equivalent weight.

Example: A 100 ml sample of water required 13.5 ml of 0.02 M EDTA solution for titration using Eriochrome black –T as indicator. Another 100 ml of water from the same source was boiled and precipitate was removed by filtration. The filtrate required 6 ml of 0.02 M EDTA for titration. Calculate total, permanent and temporary hardness of water sample

Since molarity of EDTA is given then we will start with

$$M_1 V_1 = M_2 V_2$$

$$13.5 \times 0.02 = 100 \times M_2;$$

$$M_2 = 0.0027,$$

$$\begin{aligned} \text{Total Hardness in g/l} &= M_2 \times \text{Mol wt of CaCO}_3 \\ &= 0.0027 \times 100 = 0.27 \text{ g/l} = 270 \text{ mg/l (ppm)} \end{aligned}$$

$$\text{Permanent hardness} = 6 \times 0.02 = 100 \times M_3$$

$$M_3 = 0.0012$$

$$\begin{aligned} \text{Permanent hardness} &= 0.0012 \times 100 \text{ g/l} \\ &= 0.12 \text{ g/l} = 120 \text{ mg/l (ppm)} \end{aligned}$$

ALKALINITY OF WATER:

- The total amount of those substance present in water, which tend to increase the concentration of hydroxide ions on account of dissociation and hydrolysis.
- It is a measure of ability of water to neutralize acids.

CAUSE OF ALKALINITY:

Presence of HCO_3^- , HSiO_3^- , SiO_3^- , OH^-

Presence of salts of weak acids

Presence of buffer forming salts

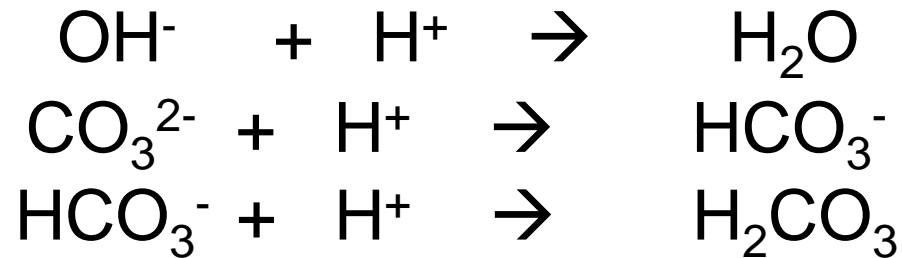
CLASSIFICATION OF ALKALINITY:

It is of three types:

- 1) OH^- (hydroxyl) *ALKALINITY*
- 2) CO_3^{2-} (carbonate) *ALKALINITY*
- 3) HCO_3^- (bicarbonate) *ALKALINITY*

Determination of Alkalinity:

The **type** and **extent** of alkalinity of water sample is determined by **TITRIMETRIC METHOD** using acid as standard solution.

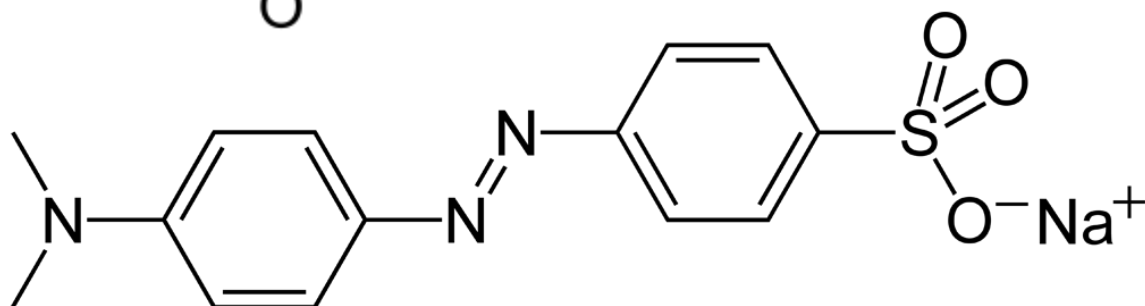
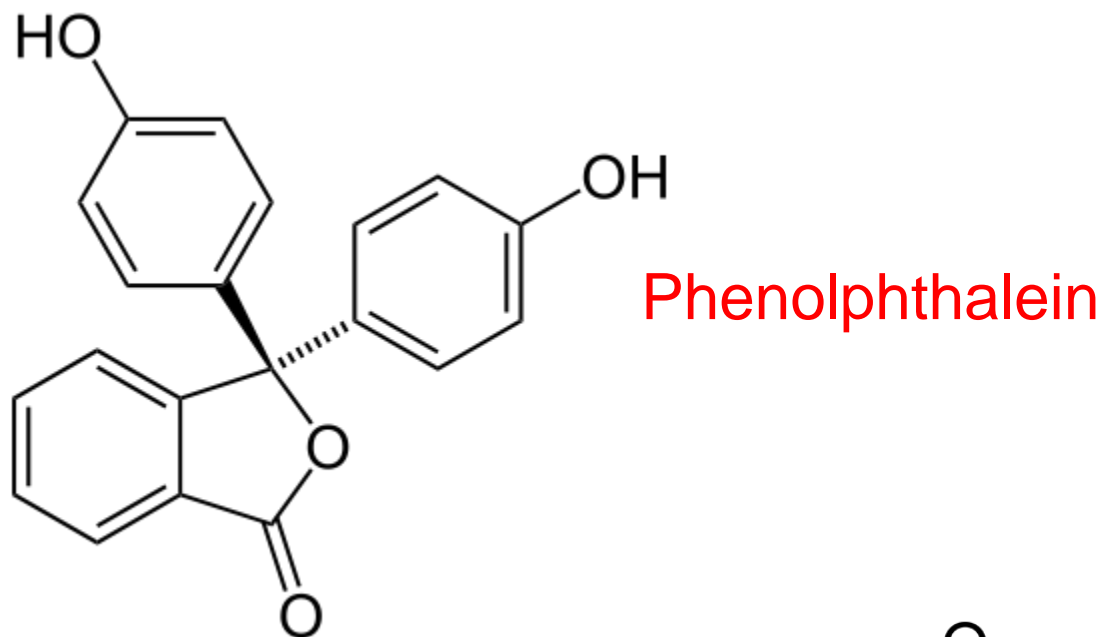


Indicator Used:

Phenolphthalein (pink above pH ~8, and colorless below pH ~8),

Methyl orange (yellow above pH ~4 and orange below pH~4)

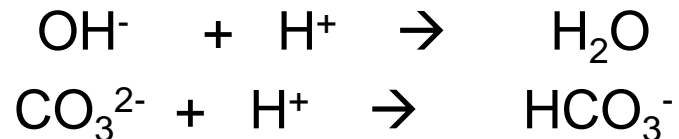
Structure of phenolphthalein and Methyl orange indicators:



Methyl orange

PROCEDURE:

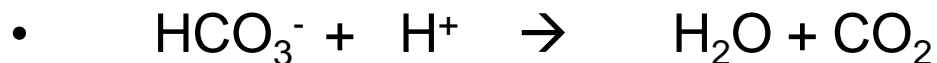
- Known volume of water sample + 1-2 drops of phenolphthalein.
- Pink color appeared.
- **Titration with std. Acid solution.**
- Initially hydroxide neutralizes followed by conversion of carbonate into bicarbonate



Color changes pink to colorless (pH ~8)

Phenolphthalein end point, volume of acid consumed is noted (V_1).

- Titration continued with same sample with same std. acid by adding 1-2 drops methyl orange Indicator, yellow color appeared.



- End point, yellow to orange at pH ~4

- methyl orange end point, total volume of acid consumed is noted (V_1).

CALCULATIONS:

For phenolphthalein alkalinity (P):

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ \text{(AWS)} &\quad \quad \quad \text{(Std. Acid)} \\ N_1 &= N_2 V_2 / V_1 \\ P &= N_1 \times 50 \times 1000 \text{ ppm} \end{aligned}$$

For methyl orange alkalinity (M):

$$\begin{aligned} N_1' V_1 &= N_2 V_2 \\ \text{(AWS)} &\quad \quad \quad \text{(Std. Acid)} \\ N_1 &= N_2 V_2 / 'V_1 \\ M &= N_1 \times 50 \times 1000 \text{ ppm} \end{aligned}$$

AWS= Alkaline water solution

Interpretation of alkalinity values:

Alkalinity	OH^-	CO_3^{2-}	HCO_3^-
$P = 0$	0	0	M
$P = \frac{1}{2} M$	0	2P	0
$P < \frac{1}{2} M$	0	2P	M-2P
$P > \frac{1}{2} M$	2P-M	2(M-P)	0
$P = M$	P	0	0

Example: A 100 ml water sample required 25 ml of 0.05N sulphuric acid for phenolphthalein end point and another 10 ml for methyl orange end point. Determine the nature and amount of alkalinity

$$\bullet N_1 V_1 = N_2 V_2$$

$$\bullet 100 \times N_1 = 25 \times 0.05$$

$$\bullet N_1 = 0.00125$$

$$\begin{aligned} \bullet \text{Phen alkalinity as CaCO}_3 \text{ eq.} &= 0.00125 \times 50 = 0.625 \text{ g/l} \\ &= 0.625 \times 1000 = 625 \text{ mg/l (ppm)} \end{aligned}$$

Methyl orange alkalinity: Total Vol of acid used

$$= 25 + 10 = 35 \text{ ml}$$

$$N_2 = 35 \times 0.05 / 100 = 0.0175$$

$$\begin{aligned} \text{MO alkalinity as CaCO}_3 \text{ eq.} &= 0.0175 \times 50 = 0.875 \text{ g/l} \\ &= 875 \text{ mg/l (ppm)} \end{aligned}$$

Since $P > M/2$, alkalinity is due to OH^- and carbonate ions.

2. 100 ml of water sample required 4 mL of N/50 H₂SO₄ for neutralization of phenolphthalein end point. Another 16 mL of the same was needed for further titration to the methyl orange end point. Determine the type of alkalinity and amount of alkalinity.

Solution Volume of water sample for titration = 100 mL
 Volume used to phenolphthalein end point (A) = 4 mL
 Volume used to methyl orange end point (B) = 16 mL
 Total volume used to methyl orange end point (A + B) = 20 mL
 Phenolphthalein alkalinity (in terms of CaCO₃ equivalent)

$$\begin{aligned}
 N_1 V_1 &= N_2 V_2 \\
 \text{(Water)} \quad \text{(Acid)} \\
 N_1 \times 100 &= \frac{N}{50} \times 4 \\
 N_1 &= \frac{4}{50 \times 100} \\
 \text{Strength} &= N_1 \times \text{Eq. wt of CaCO}_3 \\
 &= \frac{4}{50 \times 100} \times 50 \\
 \text{Phenolphthalein alkalinity (P)} &= \frac{4}{50 \times 100} \times 50 \times 1000 \text{ ppm} \\
 &= 40 \text{ ppm}
 \end{aligned}$$

Similarly, for methyl orange alkalinity,

$$\begin{aligned}
 N_3 V_3 &= N_4 V_4 \\
 \text{Water} \quad \text{Acid} \\
 N_3 \times 100 &= \frac{N}{50} \times 20 \\
 N_3 &= \frac{N}{50} \times \frac{20}{100}
 \end{aligned}$$

$$\text{Methyl orange alkalinity (M)} = \frac{1}{50} \times \frac{20}{100} \times 50 \times 1000 \text{ ppm}$$

$$M = 200 \text{ ppm}$$

Hence,
$$P < \frac{1}{2} M$$

$$P(40) < \frac{1}{2} M(100)$$

So CO₃²⁻ and HCO₃⁻ ions are present.

$$\text{Now, alkalinity due to CO}_3^{2-} \text{ ions} = 2P = 2 \times 40 \text{ ppm} = 80 \text{ ppm}$$

$$\text{alkalinity due to HCO}_3^- \text{ ions} = M - 2P = 200 - 80 = 120 \text{ ppm}$$

3. 100 ml of a sample of hard water neutralize exactly 12 ml of 0.12 N HCl using methyl orange as indicator. What kind of hardness is present? Express the same in terms of equivalent of CaCO_3 .

Q. A sample of water on analysis gave the following results: $\text{Ca}^{2+} = 30 \text{ mg/L}$; $\text{Mg}^{2+} = 18 \text{ mg/L}$; $\text{K}^+ = 19.5 \text{ mg/L}$; $\text{CO}_2 = 11 \text{ mg/L}$; $\text{HCO}_3^- = 122 \text{ mg/L}$; $\text{Cl}^- = 35.5 \text{ mg/L}$; $\text{SO}_4^{2-} = 48 \text{ mg/L}$. Calculate total hardness and alkalinity present in water sample.

Ans:

$$\text{Ca}^{2+} = 30 * 100/40 = 75 \text{ mg/L}$$

$$\text{Mg}^{2+} = 18 * 100/24 = 75 \text{ mg/L}$$

$$\text{CO}_2 = 11 * 100/44 = 25 \text{ mg/mL}$$

$$\text{HCO}_3^- = 122 * 100/122 = 100 \text{ mg/L}$$

Hardness causing substance are Ca^{2+} and Mg^{2+} only, Since K^+ , CO_2 , HCO_3^- , Cl^- and SO_4^{2-} do not cause any hardness

So Total hardness = (hardness due to Ca^{2+} + hardness due to Mg^{2+}) = $75 + 75 = 150 \text{ ppm}$

Alkalinity causing ions available here HCO_3^- , however there is CO_2 also available which cause acidity so total alkalinity will be = $\text{HCO}_3^- - \text{CO}_2 = 100 - 25 = 75 \text{ ppm}$.

Industrial Uses of water

1. Textile Industry
2. Sugar Industry
3. Dyeing Industry
4. Paper Industry
5. Pharmaceutical Industry
6. In Steam generation in Boilers

Boiler Feed Water:

- On heating, water absorbs large amount of heat and expand to form steam
- The steam is capable of carrying out large quantities of heat
- Thus, water is an ideal raw material for heating and power generation
- **A boiler is a closed vessel in which water under pressure is transformed into steam by application of heat.**
- **The water used in boilers is called boiler feed water.**

Characteristics of boiler feed water

- Dissolved and suspended matter and dissolved gases cause boiler problem.
- The amount of impurities permitted in boiler feed water are based on the pressure at which boiler works.
- **For pressure upto 100 bar, the boiler feed water should have the following characteristics**
 - Dissolved oxygen < 0.02 mg/l
 - Total hardness < 0.5 ppm
 - Total iron below < 0.03 ppm, Cu < 0.01 ppm and Si < 5 ppm
 - Caustic alkalinity (P-alkalinity) < 0.5 ppm and soda (M-alkalinity) < 1 ppm

Boiler: Troubles due to Hard Water

1. Scale and Sludge formation

2. Caustic embitterment

3. Priming and Foaming

4. Boiler corrosion

SLUDGE FORMATION IN BOILERS:

SLUDGE: Sludge is a soft, loose and slimy precipitate formed within the boiler.

It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.

Formed by substances which have greater solubility in hot water than in cold-water e.g. MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 .

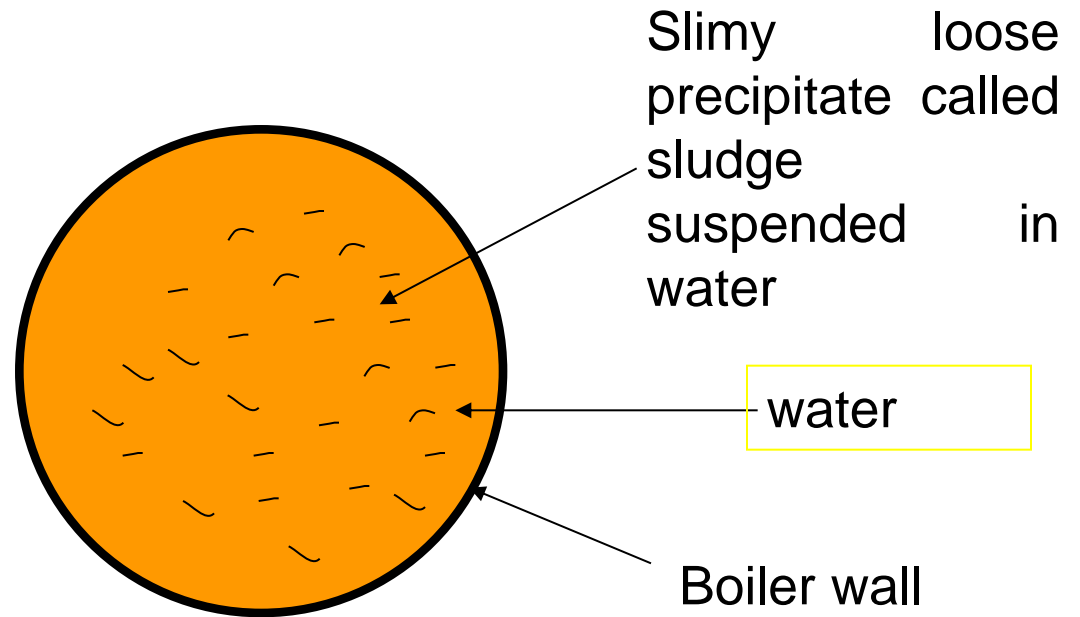
Remedy: Sludge can be removed using wire brush or mild acid.

SCALES are hard substances which sticks very firmly to the inner surfaces of the boiler wall.

Scales are difficult to remove even with the help of a hammer and chisel e.g. CaSO_4 , CaCO_3 , Mg(OH)_2

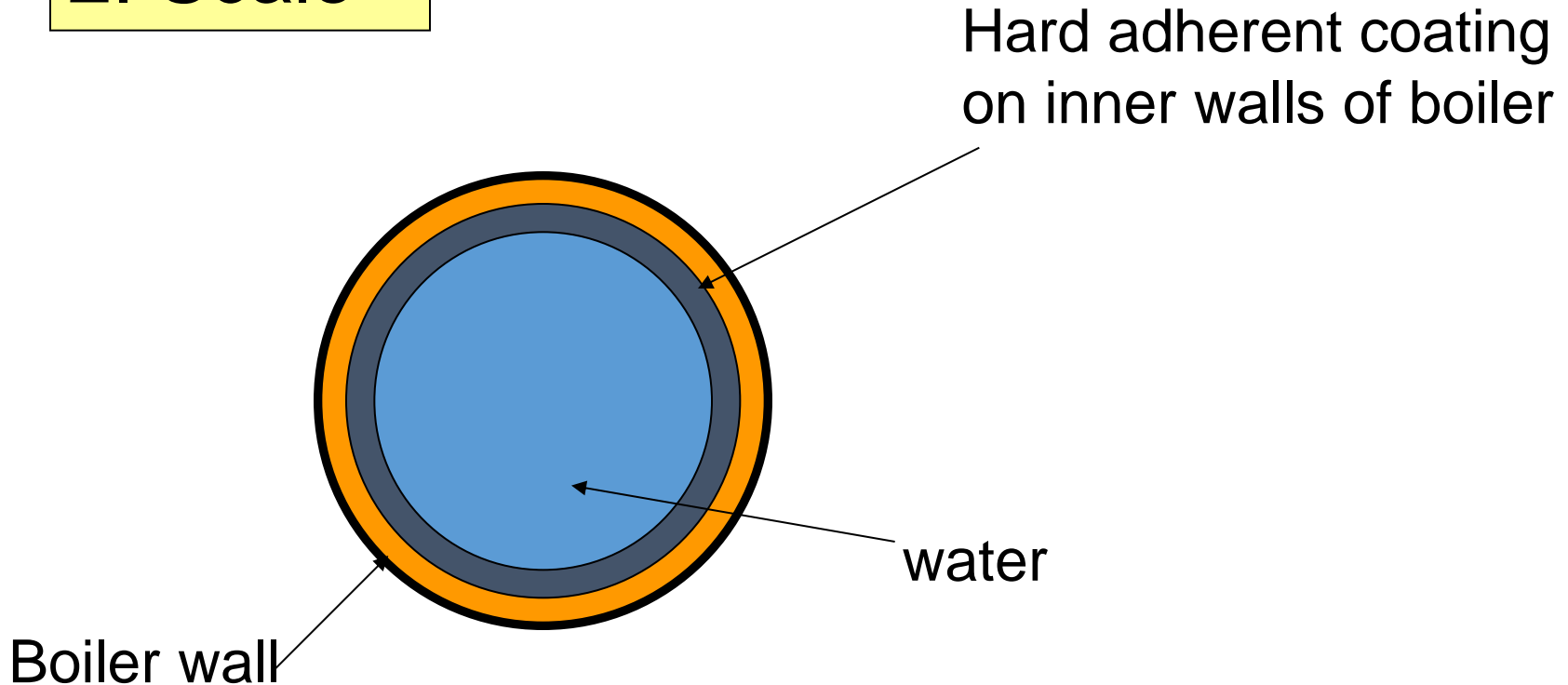
Remedy: Scales formation can be prevent by using various internal and external treatment.

1. Sludge



Remedy: Sludge can be removed using wire brush or mild acid

2. Scale



Scales are hard substances which sticks very firmly to the inner surfaces of the boiler wall.

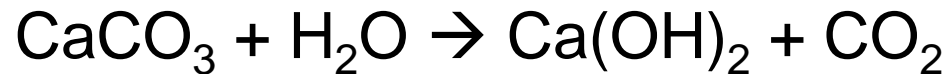
Scales are difficult to remove even with the help of a hammer and chisel e.g. CaSO_4 , CaCO_3 , Mg(OH)_2

Reasons for scale formation:

1. Presence of $\text{Ca}(\text{HCO}_3)_2$ in low pressure boilers



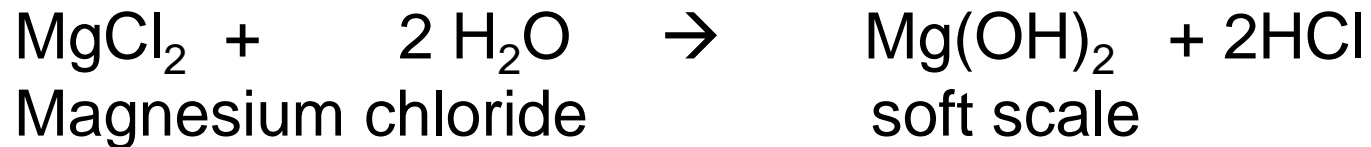
In high pressure boilers it is soluble by forming $\text{Ca}(\text{OH})_2$



2. Presence of SiO_2

It forms insoluble hard adherent CaSiO_3 and MgSiO_3 as scales

4. Presence of MgCl_2 in high temperature boilers



Mg(OH)_2 can also be generated by thermal decomposition of $\text{Mg(HCO}_3)_2$

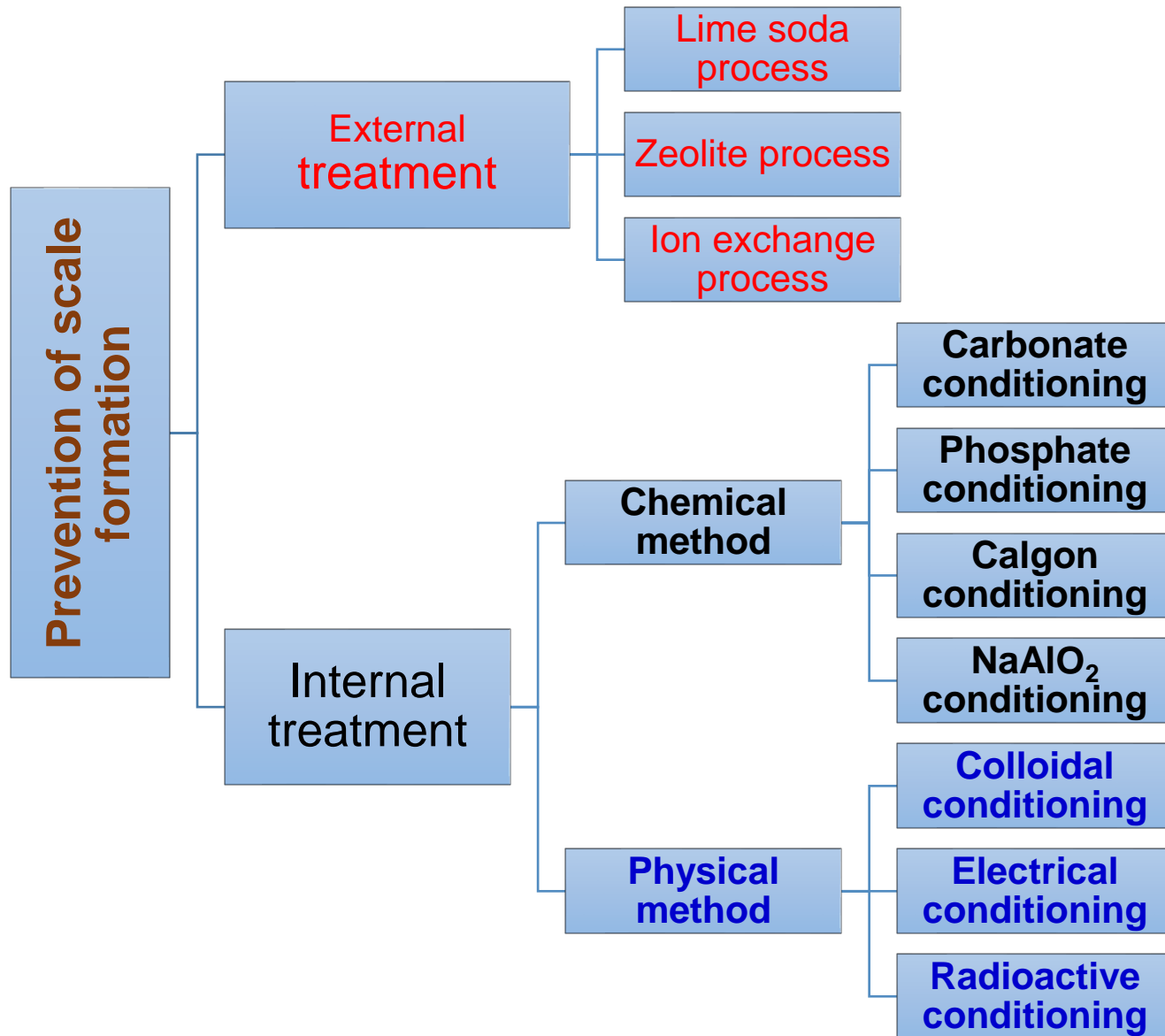
Disadvantages of scale formation

- **Fuel wastage:** Scales have poor thermal conductivity.
- **Lowering boiler safety:** Due to poor conductivity of scale, the boiler over heating is required which will make the boiler material softer and weaker. Thus boiler becomes unsafe at high pressure
- **Decrease in efficiency:** Scale deposition partially chokes the valves and condensers
- **Danger of explosion:** Due to cracking of scales, a gap between boiler wall and scale is formed. When water comes in contact with overheated boiler walls, it generate the excessive steam which may cause the boiler explosion

Removal of Scale

- Loosely adhering scale can be removed either by scraping or wire brush or by blow down operation.
- Brittle scales by thermal shock (i.e. heating the boiler followed by sudden cooling).
- Hard and adherent scales (CaCO_3) can be dissolved in 5-10% HCl, CaSO_4 can be removed by adding EDTA as Ca-EDTA complex is highly water soluble.

Prevention of scale formation:



External treatment:

- Carried out before water enter into the boiler

Internal treatment:

- Conditioning of water in the boiler itself by adding suitable chemicals
- Involves the treatment of boiler water inside the boiler by adding suitable chemicals which either
 - precipitate the scale forming substance or
 - convert them into compounds, which will remain water soluble.

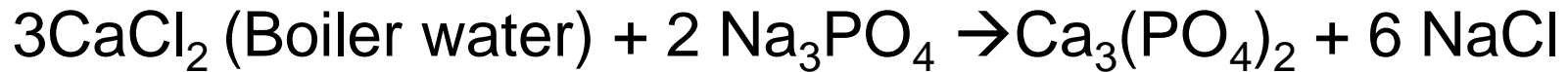
Internal conditioning of boiler water

- Phosphate conditioning – addition of phosphate compound
- Carbonate conditioning – addition of carbonate compound
- Calgon conditioning – addition of sodium hexametaphosphate
- Colloidal conditioning – spreading of organic compounds like tannin, agar gel
- Sodium Aluminate – removes oil and silica
- Complexometric method – using EDTA

Prevention of scale formation:

1. Phosphate conditioning

Sodium phosphate is added to the boiler water which reacts with the hardness producing ions and forms easily removable phosphate salts of respective ions



Calcium
chloride

Sodium
phosphate

calcium phosphate
(non adherent and can be
removed by blow down method)

Selection of Phosphate compound:

The choice of phosphate salt depends upon the alkalinity of the feed water

Calcium can be precipitated at a pH of 9.5 or more, hence the selection of phosphate has to be based on the pH of the boiler feed water.

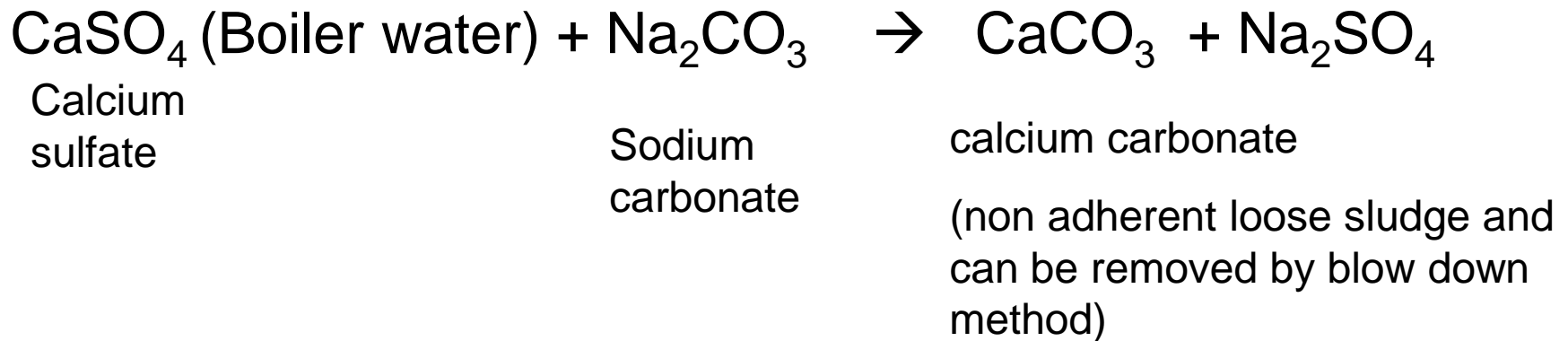
NaH_2PO_4 (acidic in nature) ,

Na_2HPO_4 (weakly alkaline in nature),

Na_3PO_4 (Alkaline in nature)

2. Carbonate conditioning

Sodium carbonate is added to the boiler water which reacts with the hardness producing ions and forms easily removable carbonate salts of respective ions



Caution: Excess Na_2CO_3 can result in caustic embrittlement

Caustic embrittlement:

Excess sodium carbonate used for removing hardness can also result in the formation of NaOH in high pressure boilers.



NaOH has better mobility and can penetrate into fine cracks present in boiler walls.

A tube damaged by caustic embrittlement.



Preventions:

- Addition of tannin or lignin block the minute cracks and prevent the accumulation of NaOH
 - Using phosphate salts instead of sodium carbonate
 - Using Na_2SO_4 to block the hair cracks
 - Avoiding excess use of Na_2CO_3 and adjusting the pH between 8-9
- ❖ **Note:** Tannins and lignins are organic compounds found in plants and trees, particularly in bark, leaves, and seeds

3. Calgon conditioning:

Sodiumhexametaphosphate is added to the boiler water which reacts with the hardness producing ions

Calgon –Sodiumhexametaphosphate



Sodiumhexametaphosphate



Calcium sulfate

Soluble complex ion of calcium - can be removed easily

Calgon tablets are used in the cleaning of washing machine drums

External treatment:
Softening of hard water

Softening of hard water can be done by the following methods

1. Zeolite methods
2. Ion exchange resin method
3. Mixed bed deionizer method

WATER AND ITS TREATMENT

External method of Softening of water

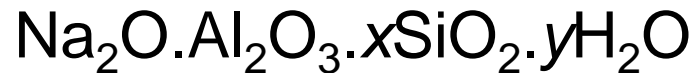
Softening of hard water can be done by the following methods

1. Zeolite methods
2. Ion exchange resin method
3. Mixed bed deionizer method

1. Zeolite (Permutit) method of Softening of water

Zeolite (Na_2Ze) is a Hydrated Sodium Alumino Silicate (HSAS), capable of exchanging reversibly its sodium ions for hardness producing ions in water.

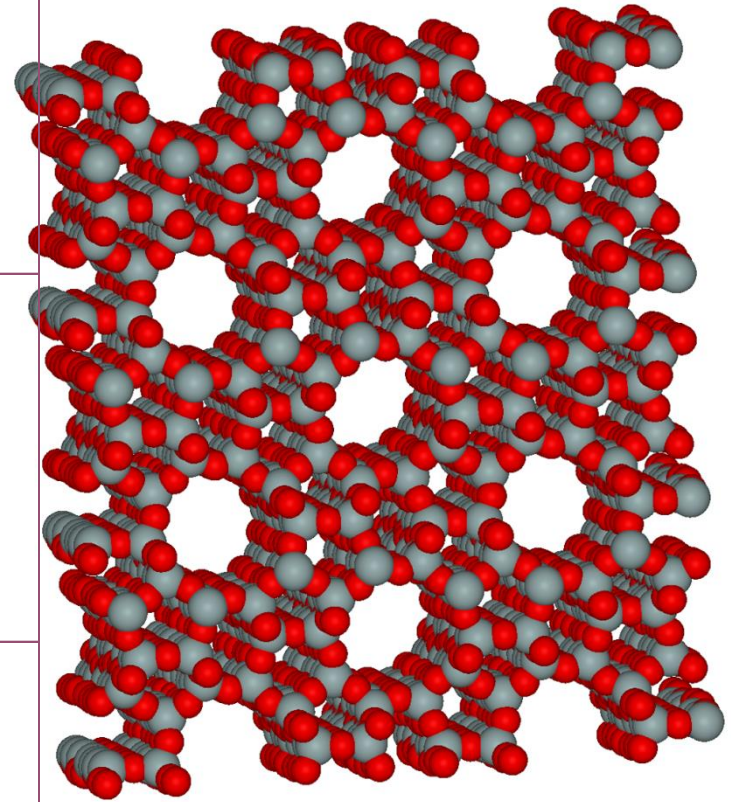
The general chemical structure of zeolite is given below



($x = 2-10$ and $y = 2-6$)

Why synthetic zeolite is better than natural zeolite for the softening of water?

Ans: Natural zeolites are non-porous



Porous Structure of zeolite

Zeolite (Permutit) method of Softening of water

- ❖ Zeolites are synthetic as well as natural
- ❖ Synthetic zeolites are used for the water purification due to their porous structure
- ❖ Porosity or cavity size of synthetic zeolite structures can be controlled by varying the Si/Al ratio
- ❖ Ion-exchange process of zeolite structure is associated with sodium ions

Process of softening by Zeolite method

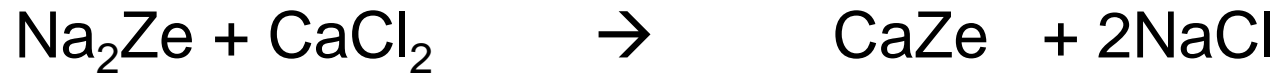
- The hardness causing ions such as Ca^{2+} , Mg^{2+} are retained by the zeolite bed as CaZe and MgZe respectively.
- The outgoing water contains sodium salts. The following reactions takes place during softening process

To remove temporary hardness



Process of softening by Zeolite method

To remove permanent hardness



Regeneration of Zeolite Bed



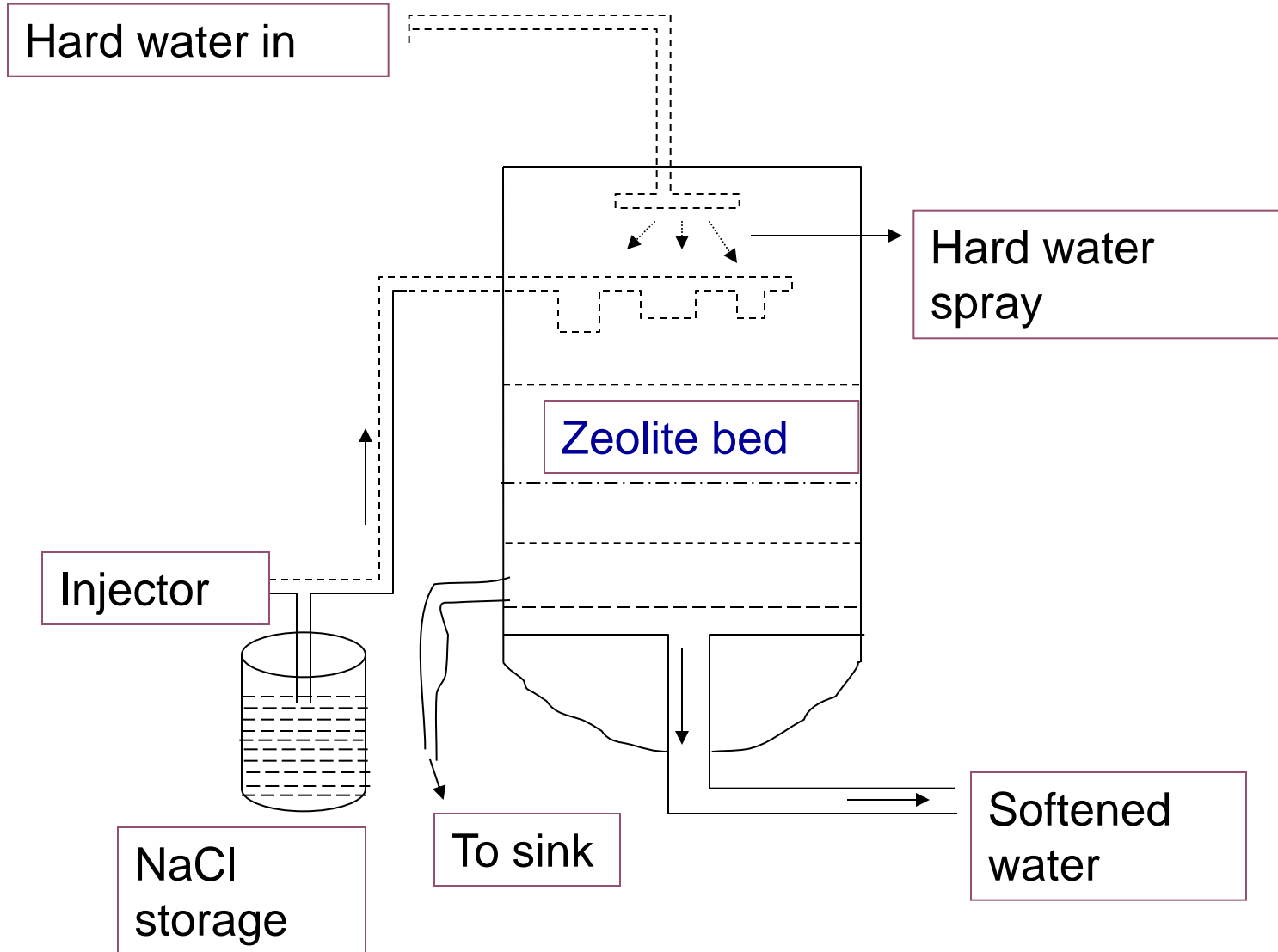
Used
Zeolite

10% brine
solution

Regenerated
Zeolite

Washings
drained

Zeolite water softener method:



Limitations of Zeolite process

1. If the water is turbid, the turbidity causing particles clogs the pores of the Zeolite and making it inactive
2. The ions such as Mn^{2+} and Fe^{2+} forms stable complex Zeolite, the strong and irreversible binding will make the zeolite regeneration extremely difficult.
3. Any acid impurity in water will hydrolyze SiO_2 into silicic acid , hence, acidic water should be neutralized with soda before zeolite treatment.

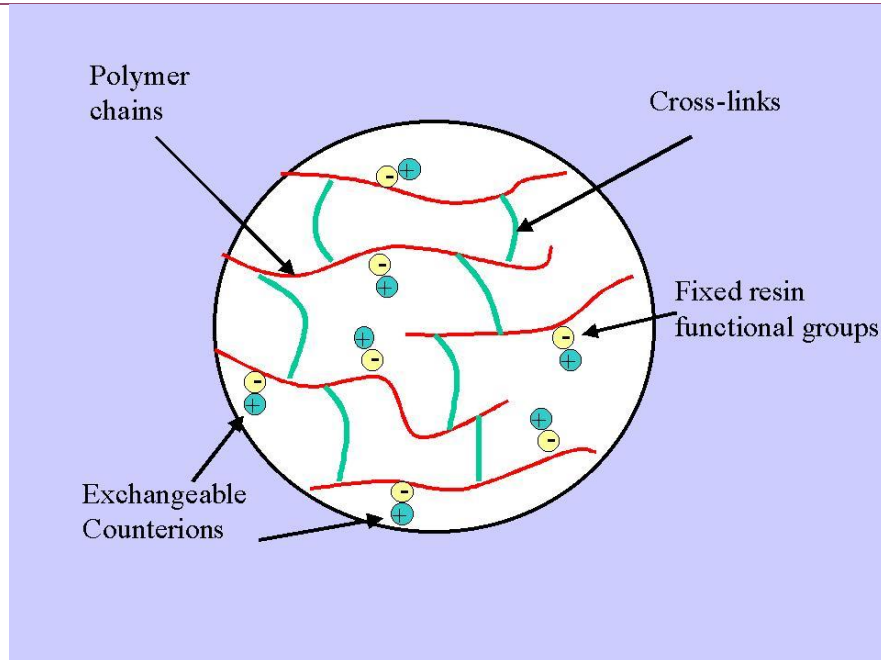
Advantages of Zeolite process

1. Soft water with $< 10\text{-}15$ ppm hardness can be produced by this method
2. The equipment occupies less space
3. No impurities are precipitated, hence no danger of sludge formation in the treated water
4. It does not require more time and more skill

Disadvantages of Zeolite process

1. Soft water contains more sodium salts than in lime soda process
2. It replaces only Ca^{2+} and Mg^{2+} with Na^+ but leaves all the other ions like HCO_3^- and CO_3^{2-} in the softened water (may form NaHCO_3 and Na_2CO_3 which on boiling releases CO_2 and causes corrosion)
3. It also causes caustic embitterment when sodium carbonate hydrolyses to give NaOH

2. Ion-Exchange resin (or) deionization (or) demineralization process



Ion exchange resin

- Ion exchange resins are insoluble, cross linked, long chain organic polymers with a microporous structure, and the functional groups attached to the chain is responsible for the “ion-exchange” properties.

Resins are classified into two types:

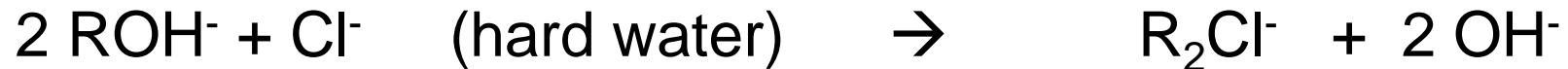
- 1. Cation exchange resin (RH^+)** – Acidic functional group
Strongly acidic (SO_3^-H^+) and weakly acidic (COO^-H^+) cation exchange resins
- 2. Anion Exchange resin (ROH^-)** – Basic functional group
Strongly basic ($\text{R}_4\text{N}^+\text{OH}^-$) and weakly basic ($\text{RNH}_2^+\text{OH}^-$) anion exchange resins

Process or Ion-exchange mechanism involved in water softening:

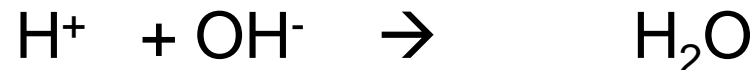
Reactions occurring at Cation exchange resin



Reactions occurring at Anion exchange resin

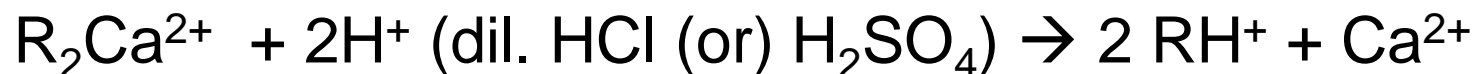


At the end of the process



Regeneration of ion exchange resins

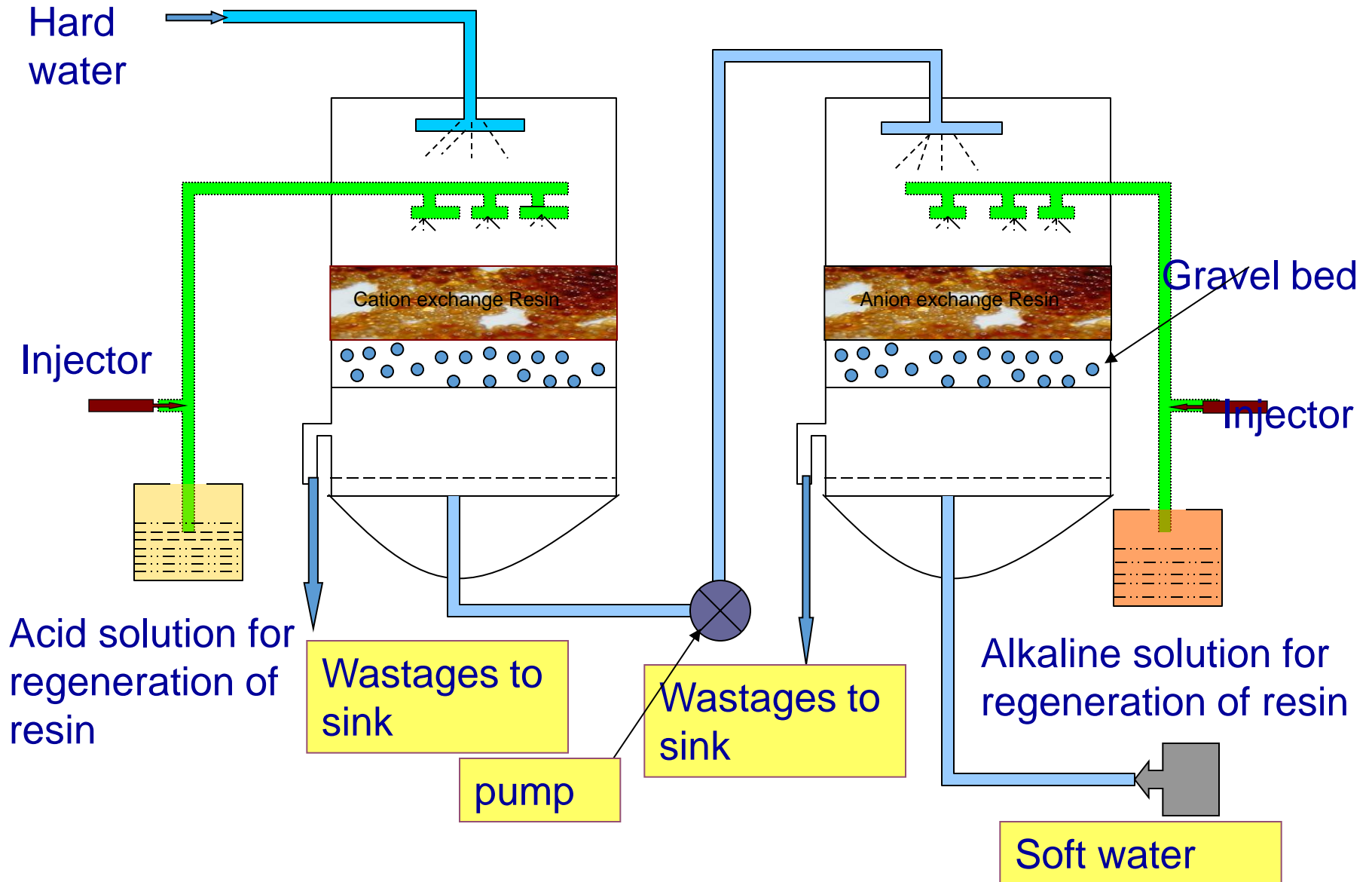
Regeneration of Cation exchange resin



Regeneration of Anion exchange resin



Ion exchange purifier or softener



Advantages

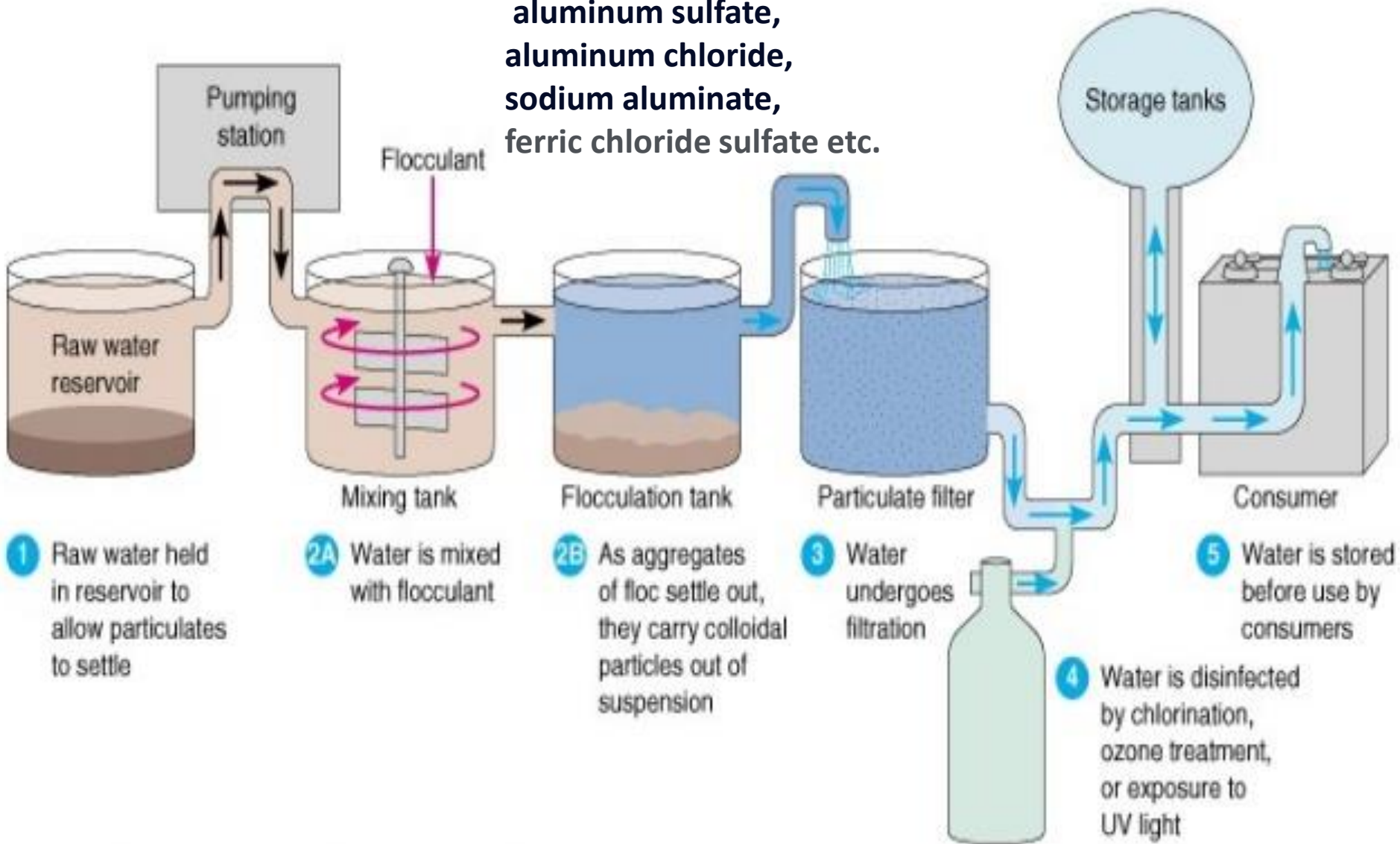
1. The process can be used to soften highly acidic or alkaline waters
2. It produces water of very low hardness of 1-2ppm. So the treated waters by this method can be used in high pressure boilers

Disadvantages

1. The setup is costly and it uses costly chemicals
2. The water should not be turbid

Municipal Water Purification Plant

aluminum sulfate,
aluminum chloride,
sodium aluminate,
ferric chloride sulfate etc.



Desalination of seawater

- **Desalination, refers to any process that removes some amount of salt and other minerals from water.**

Technologies for desalination process

- **Reverse Osmosis (Pressure membrane process)**
- **Electrodialysis membrane process**

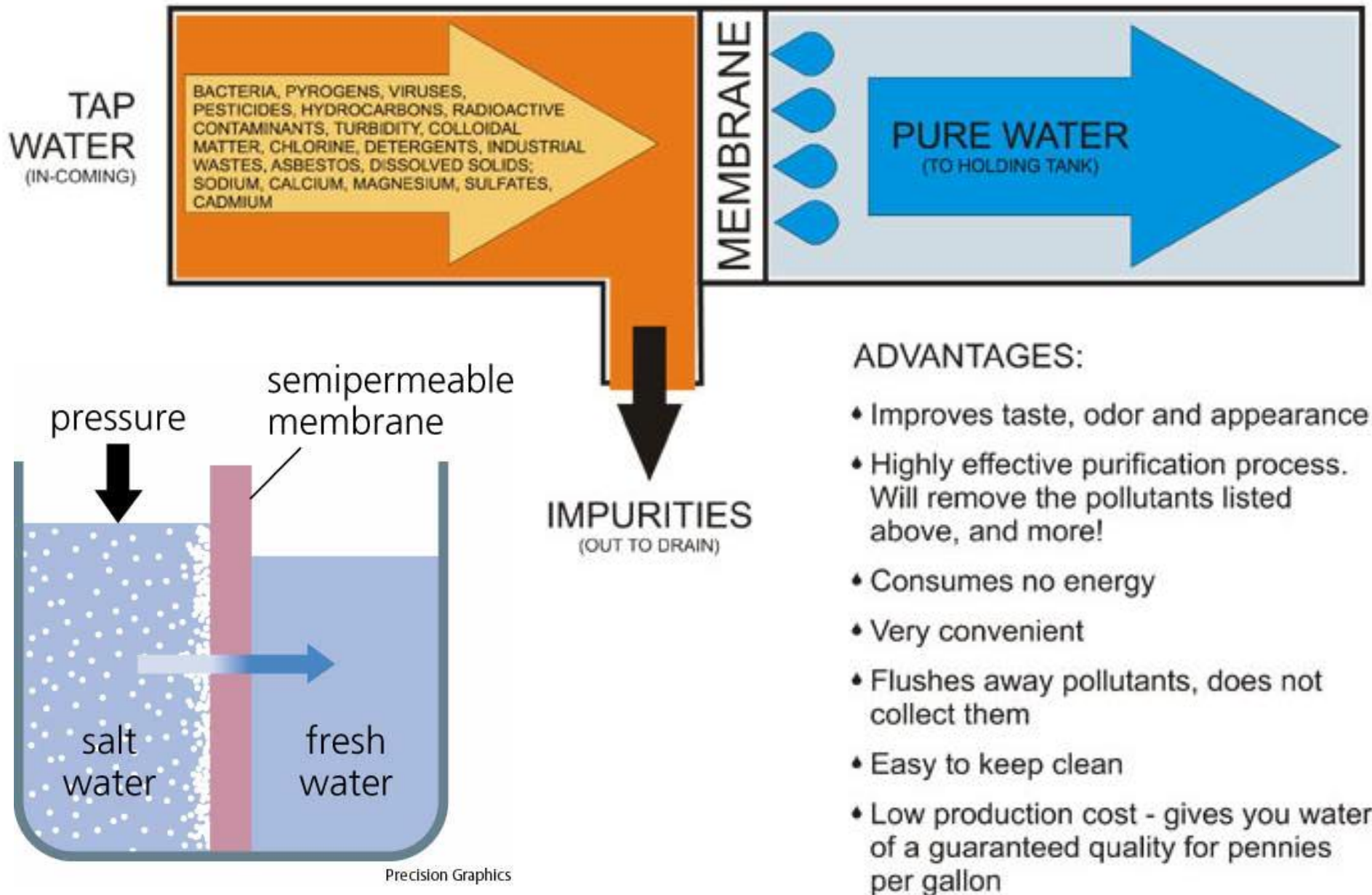
Reverse Osmosis (Pressure Membrane Processes)

- **Microfiltration (MF)**, which can remove particles ranging in size from 10-100 μm . It is operated in the pressure range of 10 psig.
- **Ultrafiltration (UF)**, which can remove particles ranging in size from 0.01 to 10 μm . It is operated in the pressure range of 15 psig.
- **Nanofiltration (NF)**, which can remove particles size from 0.001 μm to 0.01 μm . It is operated in the pressure range of 75-250 psig.
- **Reverse osmosis (RO)**, which can remove particles in the size range of 0.1-1.0 nm. It operates in the pressure range of 200-1200 psig.

Principle - Reverse osmosis

- ❖ When two solutions of unequal concentration are separated by a semi-permeable membrane, flow of solvent takes place from dilute to concentration side, due to increase in osmotic pressure, which is termed as osmosis.
- ❖ However, when a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow is reversed from concentrated side to dilute side, across the membrane. This principle is termed as reverse osmosis.
- ❖ The semi-permeable membrane (in reverse osmosis) is selective in not permitting the passage of dissolved solute particles such as molecules, ions, etc.) It permits only the flow of water molecules (solvent) from the concentrated to dilute side.
- ❖ Cellulose acetate, polyamide, etc., are used as membrane.
- ❖ Reverse osmosis process requires only mechanical force to generate the required hydrostatic pressure.
- ❖ Hydrostatic pressure generated is in the order of $15\text{-}40 \text{ Kg m}^{-2}$

Reverse Osmosis

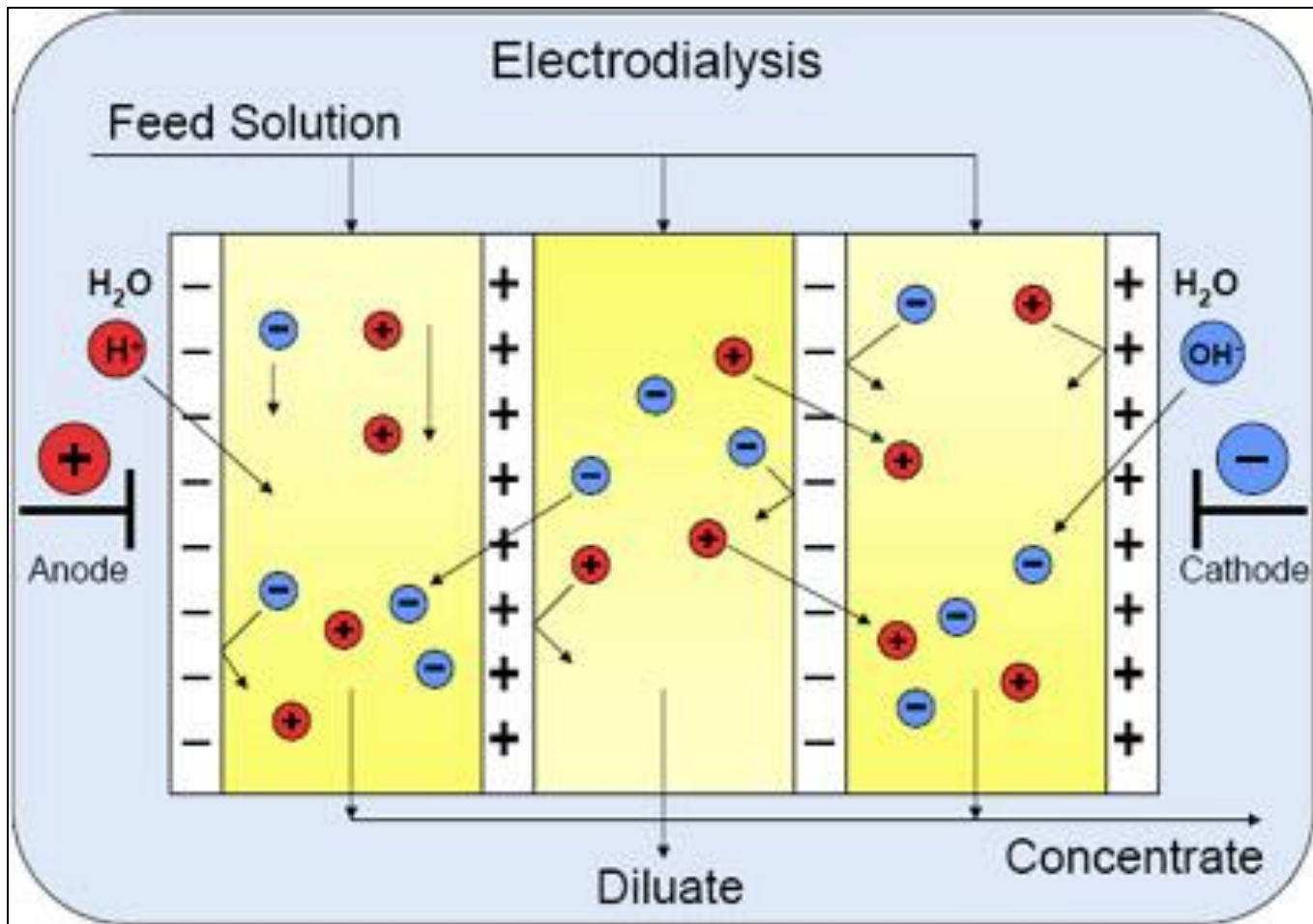


ADVANTAGES:

- Improves taste, odor and appearance
- Highly effective purification process. Will remove the pollutants listed above, and more!
- Consumes no energy
- Very convenient
- Flushes away pollutants, does not collect them
- Easy to keep clean
- Low production cost - gives you water of a guaranteed quality for pennies per gallon

Principle -Electrodialysis

- Electrodialysis is an electrochemical process whereby electrically charged particles, ions, are transported from a raw solution (retentate, diluate) into a more concentrated solution (permeate, concentrate) through ion-selective membranes by applying an electric field.



Theory of Electrodialysis

- **Electrodialysis chamber comprises of sheet like barriers made out of high-capacity, highly cross-linked ion exchange resins that allow passage of ions but not of water.**
- **There are two types : (a) Cation exchange and (b) Anion exchange membranes**
- **Cation exchange membranes consists of an insoluble matrix and mobile cation reside in the pore space that allows the pass through of only cations.**
- **Anion exchange membranes consists of an insoluble matrix and mobile anion reside in the pore space that allows the pass through of only anions.**
- **Cation- and Anion- exchange membranes are installed alternatively in the tank.**
- **By impressing electricity on the electrodes, the positive anode attracts negative ions in solution, while the negative cathode attracts positive ions in the solution.**

Q. The hardness of 25,000 litres of a sample of water was removed by passing it through a zeolite softener. The softener then required 100 litres of NaCl solution, containing 125 gm/L of NaCl for regeneration. Calculate the hardness of the sample of water.

Ans: 1 liter of NaCl solution contain 125 gm of NaCl

100 liters of NaCl solution contain= $100 \times 125 = 12500$ g NaCl

In the equivalent of $\text{CaCO}_3 = 12500 \times 50/58.5$ g of CaCO_3 eq.= 10683.76 g of CaCO_3 eq.

25000 L of sample water has hardness = 10683.76 g of CaCO_3

1 L of sample water has hardness = $10683.76 / 25000 = 0.427$ g/L= 427 mg/L or ppm

Q. A zeolite bed was exhausted after completely removing the total hardness of 10,000L of hard water. The zeolite bed was regenerated using 8 L of NaCl containing 150 gm/L of NaCl. Calculate the hardness of water.

Ans: 1 liter of NaCl solution contain 150 gm of NaCl

8 liters of NaCl solution contain= $8 \times 150 = 1200$ g NaCl

In the equivalent of $\text{CaCO}_3 = 1200 \times 50/58.5$ g of CaCO_3 eq.= 1025.64 g of CaCO_3 eq.

10, 000 L of sample water has hardness = 1025.64 g of CaCO_3

1 L of sample water has hardness = $1025.64 / 10,000 = 0.102$ g/L= 102 mg/L or ppm

Q. After treating 10,000 L of water by ion exchanger, the cationic resin required 200 L of 0.1 N HCl and anionic resin required 200 L of 0.1 N NaOH solutions. Find the hardness of the water sample.

Ans: Hardness of 10000 L of water = 200 L of 0.1 N HCl = 200 L of 0.1 N CaCO₃ eq. = 20 L of 1 N CaCO₃ eq. = 20×50 g of CaCO₃ eq. = 1000 g CaCO₃ eq.

Hardness in 1L in water = $1000 / 10,000$ g of CaCO₃ = 0.1 g/L of CaCO₃ eq.
= 100 mg/L or ppm