



Unit-4

Water Analysis

Hard & Soft Water

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Hard and Soft Water

Water, that does not give lather with soap,
Hard Water.

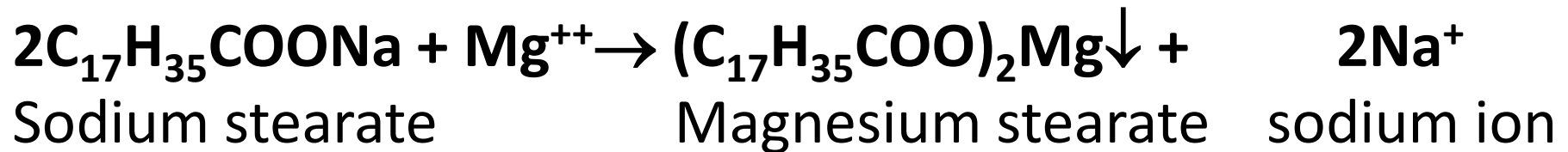
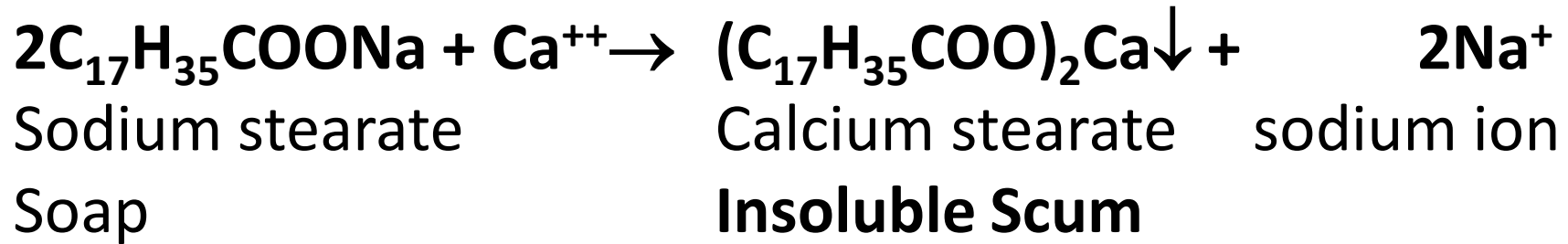
Water, that gives lather with soap easily, is called as
Soft Water.

Cause of Hardness of Water

Soap is a sodium or potassium salt of higher fatty acids ,
such as sodium stearate.

Water contains certain soluble salts of Calcium,
Magnesium and other Heavy metal ions. These ions react
with soap to form an insoluble compound called as Scum
which hinders the formation of lather.





Thus, the cause of hardness of water is presence of Ca^{++} , Mg^{++} and other heavy metal ions like Fe^{++} , Zn^{++} , Ni^{++} etc.



Types of Hardness of Water

There are two types of hardness

1. Temporary Hardness or Carbonate Hardness

The hardness of water which can be removed by boiling of water.

It is due to presence of soluble

Calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$ and Magnesium bicarbonate

$\text{Mg}(\text{HCO}_3)_2$

2. Permanent Hardness or Non-Carbonate Hardness

The hardness of water that can not be removed by simple boiling but some chemical treatment is required for its removal then it is called as Permanent Hardness.

It is due to the presence of sulphates, chlorides and nitrates of Ca^{++} and Mg^{++} .

For example

CaSO_4 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, MgSO_4 , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$,





Q. How can temporary hardness be removed by boiling of water?

A. Cause of temporary hardness is

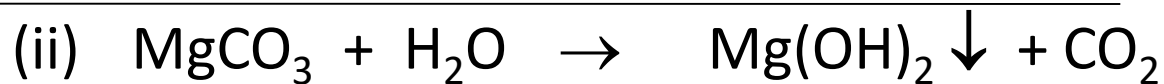
soluble Calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$ and Magnesium bicarbonate $\text{Mg}(\text{HCO}_3)_2$

When these compounds are heated, they get converted to insoluble compounds which can be removed by filtration.

Calcium removal



Magnesium removal





Units of Hardness

Hardness of water is expressed in following terms

1. **Parts per million (ppm) of CaCO_3**
2. **Degree French $^\circ\text{Fr}$**
3. **Degree Clarke $^\circ\text{Cl}$**

ppm of CaCO_3

1 ppm = 1part CaCO_3 equivalent hardness present in 10^6 parts (1 million parts) of water.
= 1 part CaCO_3 equivalent/ 10^6 parts water

Degree French $^\circ\text{Fr}$

1 $^\circ\text{Fr}$ = 1part CaCO_3 equivalent hardness present in 10^5 parts (1 Lakh parts) of water.
= 1 part CaCO_3 equivalent/ 10^5 parts water

Degree Clark $^\circ\text{Cl}$

1 $^\circ\text{Cl}$ = 1part CaCO_3 equivalent hardness present in 1 Gallon (70000 parts) of water.
= 1 part CaCO_3 equivalent/ 70000 parts water

Thus, 1ppm = 0.1 $^\circ\text{Fr}$ = 0.07 $^\circ\text{Cl}$



Q. Hardness of Water is expressed in terms of CaCO_3 equivalent. Why?

A. Because of

1. CaCO_3 is the most insoluble salt that can be precipitated in water.
2. The molecular weight of CaCO_3 is 100 and Equivalent weight is 50 that makes the calculation simple.



- Q.1** A water sample contains hardness of
- CaSO₄ = 20 ppm of CaCO₃
 - Ca(HCO₃)₂ = 30 „
 - MgCl₂ = 40 „
 - Mg(HCO₃)₂ = 20 „
 - Ca(NO₃)₂ = 10 „

Calculate Temporary and permanent and Total hardness and express in ppm, °Fr and °Cl.

Temporary Hardness		Ppm of CaCO ₃	°Fr × 0.1	°Cl × 0.07
1	Ca(HCO ₃) ₂	30	3.0	2.1
2	Mg(HCO ₃) ₂	20	2.0	1.4
Total Temporary Hardness		50	5.0	3.5
Permanent Hardness				
1	CaSO ₄	20	2.0	1.4
2	MgCl ₂	40	4.0	2.8
3	Ca(NO ₃) ₂	10	1.0	0.7
Total Permanent Hardness		70	7.0	4.9
Total Hardness = Temporary hardness + Permanent Hardness		50 + 70=120	5.0 +7.0 = 12.0	3.5 + 4.9 = 8.4



Equivalents of Calcium Carbonate CaCO_3

As we know that the hardness of water is expressed in terms of CaCO_3 equivalent, so how to convert the concentration in terms of CaCO_3

The equivalent of $\text{CaCO}_3 =$

(Mass of Hardness producing substance) \times (Chemical equivalent of CaCO_3) / Chemical equivalent of hardness producing substance

Equivalent Weight of CaCO_3	$= 100/2 = 50$	or
„ $\text{Ca}(\text{HCO}_3)_2$	$= 162/2 = 81$	
„ $\text{Mg}(\text{HCO}_3)_2$	$= 146/2 = 73$	
„ CaSO_4	$= 136/2 = 68$	

And so on.....

Thus, If a water sample contains CaSO_4 340 ppm or (mg/L)

The CaCO_3 equivalent $= \text{Mass of } \text{CaSO}_4 \times \text{Eq. Wt. of } \text{CaCO}_3 / \text{Eq. Wt. of } \text{CaSO}_4$
 $= 340 \times 50 / 68$

If we multiply by 2, Then, $= 340 \times 100 / 136$

The figure enclosed in circle is called as **Multiplication Factor** for conversion into CaCO_3 Equivalent



Dissolved Salt/Ion	Molecular Wt.	Equivalent. Wt.	Multiplication Factor
CaCO₃	100	50	100/100
Ca(HCO ₃) ₂	162	81	100/162
Mg(HCO ₃) ₂	146	73	100/146
CaSO ₄	136	68	100/136
CaCl ₂	111	55.5	100/111
MgSO ₄	120	60	100/120
MgCl ₂	95	47.5	100/95
MgCO ₃	84	42	100/84
CO ₂	44	22	100/44
Ca(NO ₃) ₂	164	82	100/164
Mg(NO ₃) ₂	148	74	100/148
HCO ₃ ⁻	61	61	100/122
OH ⁻	17	17	100/34
CO ₃ ⁻⁻	60	30	100/60
NaAlO ₂	82	82	100/164
Al ₂ (SO ₄) ₃	342	57	100/114
FeSO ₄ .7H ₂ O	278	139	100/278
H ⁺	1	1	100/2
HCl	36.5	36.5	100/73



Q. Show that, 1ppm = 1mg/L

A. Let's take

$$\begin{aligned}
 1\text{mg/L} &= 1\text{mg/kg} && (1\text{ L weighs } 1\text{ kg at } 4^\circ\text{C}) \\
 &= 1\text{ mg}/1000\text{ g} && (1\text{ kg} = 1000\text{g}) \\
 &= 1\text{ mg}/1000 \times 1000\text{ mg} && (1\text{ g} = 1000\text{ mg}) \\
 &= 1\text{ mg}/10^6\text{ mg} \\
 &= 1\text{ part substance}/10^6\text{ parts water} \\
 &= 1\text{ ppm}
 \end{aligned}$$

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

Solution: conversion into CaCO_3 equivalents:

A. Constituent	Multiplication factor	CaCO_3 equivalent	
$\text{Mg}(\text{HCO}_3)_2 = 7.3\text{mg/L}$	100/146	$7.3 \times 100 / 146$	= 5ppm
$\text{Ca}(\text{HCO}_3)_2 = 16.2\text{mg/L}$	100/162	$16.2 \times 100 / 162$	= 10ppm
$\text{MgCl}_2 = 9.5\text{mg/L}$	100/95	$9.5 \times 100 / 95$	= 10ppm
$\text{CaSO}_4 = 13.6\text{mg/L}$	100/136	$13.6 \times 100 / 136$	= 10ppm

Therefore,

Temporary hardness of water due to

$\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$ = 5+10 = 15ppm of CaCO_3 .

Permanent hardness due to

MgCl_2 and CaSO_4 = 10+10 = 20ppm of CaCO_3 .



Lime-Soda Process



Lime-Soda process:

In this process, lime $[(\text{Ca}(\text{OH})_2)]$ and soda $[\text{Na}_2\text{CO}_3]$ are the reagents used to precipitate the dissolved salts of Ca^{+2} and Mg^{+2} as CaCO_3 and $\text{Mg}(\text{OH})_2$ which are later on filtered off.

Types of L-S Process

1. Cold Lime Soda Process
2. Hot Lime Soda Process

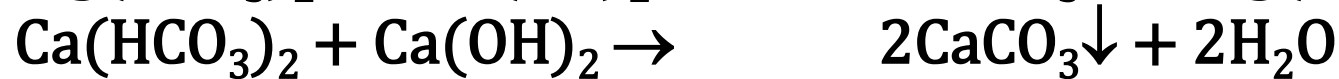
The process may be carried out in

- a. Batch Method
- b. Continuous Method

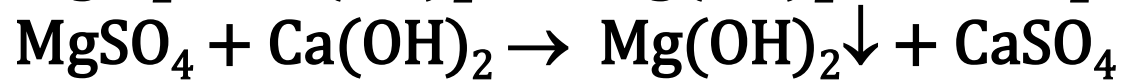
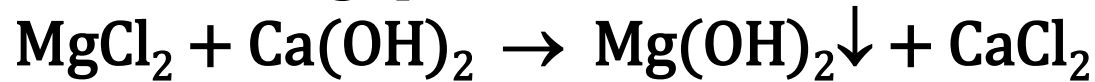


Role of Lime Ca(OH)_2

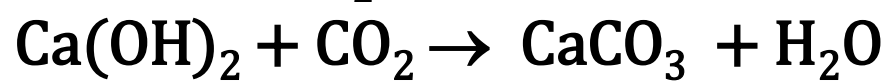
1. Lime removes all temporary hardness



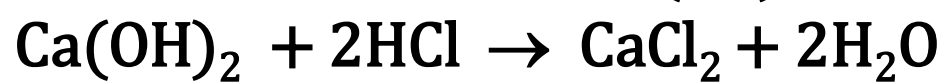
2. Removes Mg -permanent hardness



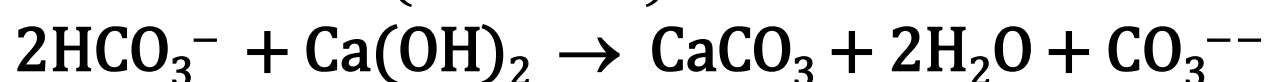
3. Removes CO_2



4. Removes mineral acids (H^+)

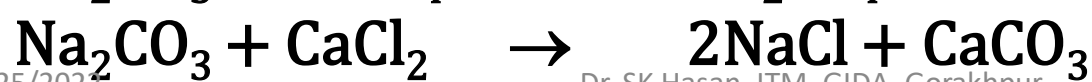
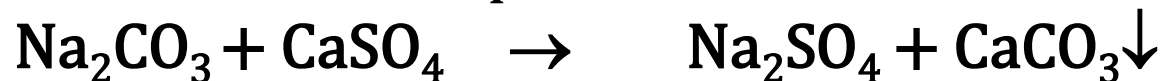


5. Bicarbonates (NaHCO_3)



Role of Soda Na_2CO_3

1. Soda removes all permanent hardness





Cold Lime -Soda Process:

Calculated amounts of lime and Soda are mixed with water at room temperature.

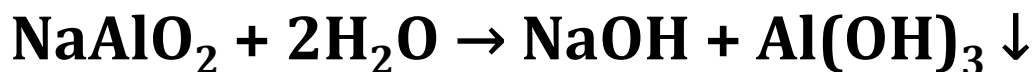
For rapid precipitation of fine particles, it is essential to add small amounts of coagulants.

(like Alum, Aluminium Sulphate, Sodium Aluminate etc.)

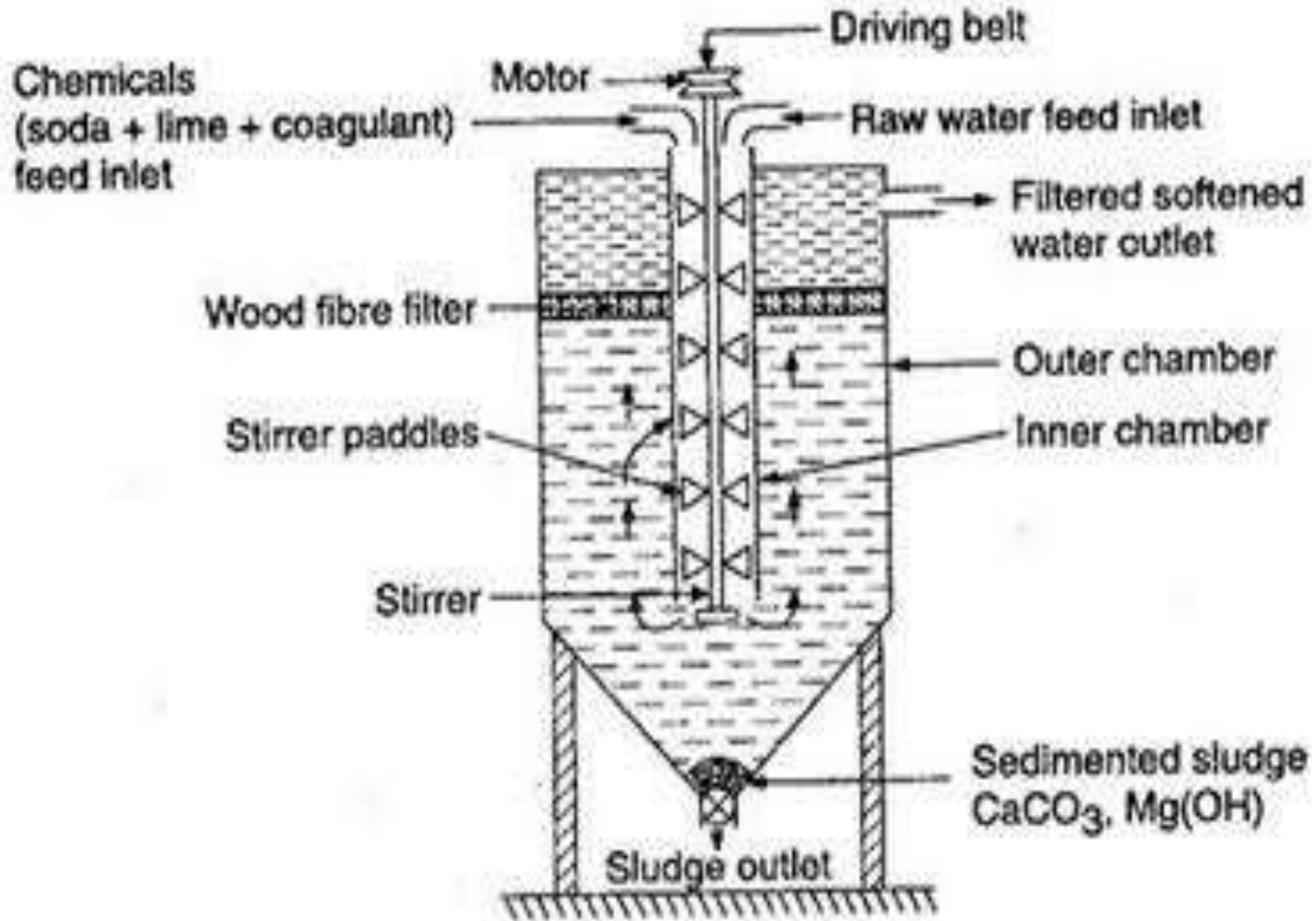
which hydrolyses to flocculent, gelatinous precipitate of $\text{Al}(\text{OH})_3$.

Use of sodium aluminate as **Coagulant also helps in the removal of silica as well as oil present in the water.**

Cold lime soda process provides water containing residual hardness of 50-60 ppm.



Cold Lime Soda Process





Hot Lime Soda Process:

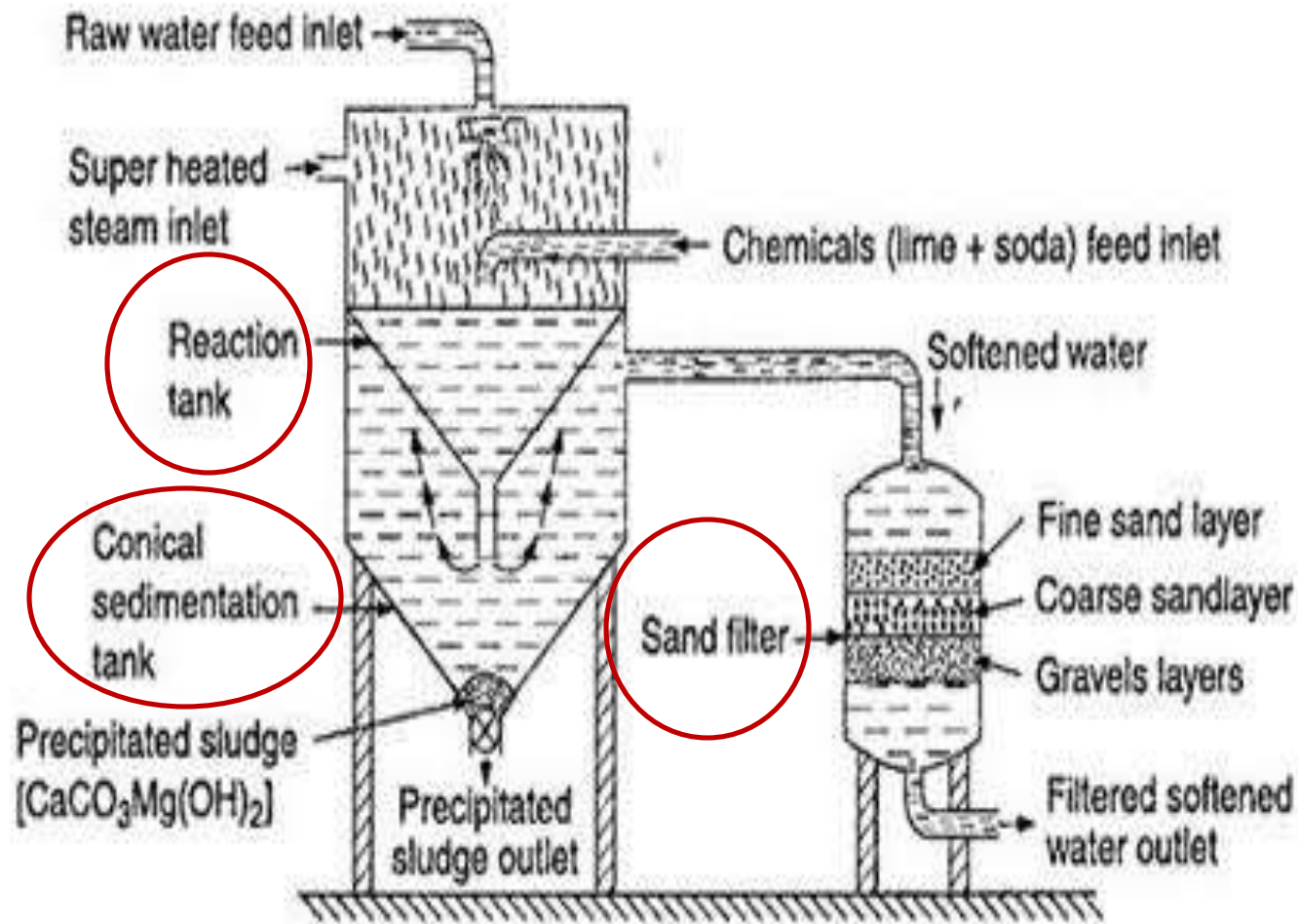
It involves treating water with softening chemicals (Lime+Soda) at a temperature of 80°C - 100°C . Since hot process is operated at a temperature close to the boiling point of the solution, so

- a) The reaction proceeds faster,
- b) Softening capacity of hot process is increased,
- c) The precipitate and sludge formed settle down rapidly and hence no coagulants are needed,
- d) Much of the dissolved gases (CO_2) are driven out,
- e) Viscosity of softened water is lower so filtration of water becomes much easier.

Process:

It contains essentially three parts

- 1) A reaction tank in which water, chemical and steam are thoroughly mixed.
- 2) A conical sedimentation vessel in which sludge settle down.
- 3) A sand filter which ensures complete removal of sludge from the softened water.





Advantages of Lime-Soda process:

- 1) It is very economical.
- 2) The process increases the pH value of treated water thereby corrosion of distribution pipes is reduced.
- 3) Besides removal of hardness causing salts, minerals, iron and manganese present in water is removed.
- 4) Due to alkaline nature, amount of pathogenic bacteria in water is considerably reduced.

Disadvantages of Lime-Soda Process:

- 1) Skilled supervision is required for efficient and economical softening.
- 2) Disposal of large amounts of sludge poses a problem.
- 3) This can remove hardness only up to 15ppm, which is not good for boilers.



Differences between cold and hot lime soda process:-

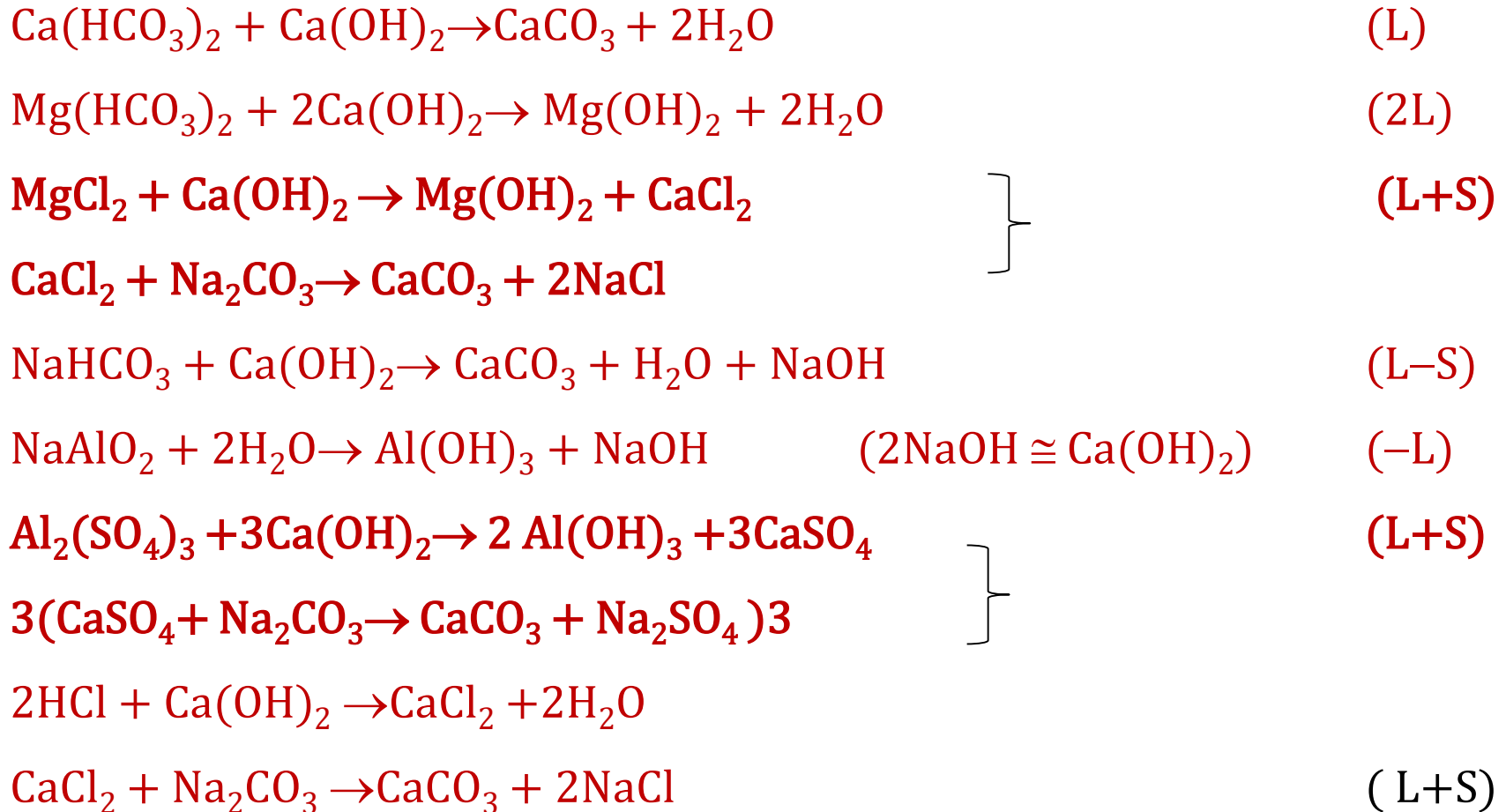
S.No	Cold Lime Soda Process	Hot Lime Soda Process
1.	It is done at room temperature.	It is done at elevated temperatures (84-100 °C).
2.	It is slow process.	It is rapid process.
3.	Use of coagulants is must.	Coagulants are not needed.
4.	Filtration is not easy.	Filtration is easy as viscosity of water becomes low at elevated temperatures.
5.	Softened water has residual hardness around 60 ppm.	Softened water has residual hardness around 15-30 ppm.
6.	Dissolved gases are not removed.	Dissolved gases such as CO ₂ are removed to some extent.
7.	It has low softening capacity.	It has high softening capacity.



Calculation on Requirement of Lime & Soda



Lime & Soda Requirement





Formula for Lime & Soda Requirement

∴ Lime requirement for softening =

$$74/100[\text{Mg}^{2+} + \text{Ca-Temp.} + 2 \times \text{Mg-Temp.} + \text{Perm}(\text{Mg}^{+2}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- + \text{Al}_2(\text{SO}_4)_3 + \text{FeSO}_4 - \text{NaAlO}_2] \times \text{Vol. of Water (L)} \times (100/\text{purity \%})$$

mg

all in terms of CaCO_3 equivalents (Mol. Wt. of Lime = 74).

∴ Soda requirement for softening =

$$106/100 [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Permanent} (\text{Ca}^{+2} + \text{Mg}^{+2}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- + \text{Al}_2(\text{SO}_4)_3 + \text{FeSO}_4 - \text{NaAlO}_2] \times \text{Volume of Water (in L)} \times (100/\text{purity \%})$$

mg

all in terms of CaCO_3 equivalents (Mol. Wt. of Soda = 106).



Q. 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).

$$\text{Ca}^{+2} = 160 \text{ ppm}$$

$$\text{Mg}^{+2} = 72 \text{ ppm}$$

$$\text{HCO}_3^- = 73.2 \text{ ppm}$$

$$\text{CO}_2 = 44 \text{ ppm}$$

$$\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ ppm}$$

$$\text{HCl} = 36.5 \text{ ppm}$$

Conversion into CaCO_3 equivalents.

Solution

Iron or salt	Amount present (ppm)	Conversion (MF)	CaCO_3 equivalent (ppm)
Ca^{+2}	160	100/40	$160 \times 100/40 = 400$
Mg^{+2}	72	100/24	$72 \times 100/24 = 300$
HCO_3^-	73.2	100/122	$73.2 \times 100/122 = 60$
CO_2	44	100/44	$44 \times 100/44 = 100$
NaAlO_2	16.4	100/164	$16.4 \times 100/164 = 10$
$\text{Al}_2(\text{SO}_4)_3$	34.2	100/114	$34.2 \times 100/114 = 30$
HCl	36.5	100/73	$36.5 \times 100/73 = 50$



∴ Lime requirement for softening

$$\begin{aligned} &= 74/100[\text{Mg}^{2+} + \text{Ca-Temp.} + 2x \text{ Mg-Temp.} + \text{Perm}(\text{Mg}^{+2}) + \\ &\text{CO}_2 + \text{H}^+(\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- + \text{FeSO}_4 - \text{NaAlO}_2 + \\ &\text{Al}_2(\text{SO}_4)_3] \times \text{Volume of Water (in L)} \times 100/\% \text{ purity} \\ &\text{all in terms of CaCO}_3 \text{ equivalents (Mol. Wt. of Lime = 74).} \\ &= 74 / 100 [300 + 0 + 0 + 0 + 100 + 50 + 60 + 0 - 10 + 30] \times 20000 \\ &= 74 / 100 [530] \times 20000 \\ &= 7844000 \text{ mg} = 7.844 \text{ kg} \end{aligned}$$



∴ Soda requirement for softening

$$\begin{aligned} &= 106/100 [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Permanent } (\text{Ca}^{+2} + \text{Mg}^{+2}) + \text{H}^+(\text{HCl} \\ &\text{or } \text{H}_2\text{SO}_4) + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \text{HCO}_3^- - \text{NaAlO}_2] \times \\ &\text{Volume of Water (in L)} \times (100/\text{purity } \%) \text{ mg} \\ &\text{all in terms of } \text{CaCO}_3 \text{ equivalents (Mol. Wt. of Soda} = 106). \\ &= 106/100[400 + 300 + 0 + 50 + 0 + 30 - 60 - 10] \times 20000 \text{ mg} \\ &= 106/100[710] \times 20000 \text{ mg} \\ &= 15052000 \text{ mg} \\ &= 15.052 \text{ kg} \end{aligned}$$

Therefore, Lime Required = 7.844 Kg
Soda Required = 15.052 Kg

Zeolite or Permutit Method





Zeolite Process of Softening of Water (Permutit Method)

Zeolites are naturally occurring (hydrated) sodium aluminium silicates, having different amounts of water of crystallization. They are represented as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \cdot \text{H}_2\text{O}$, where x varies from 2 to 10 and y from 2 to 6.

Zeolite is an inorganic compound with a property of exchanging Na^+ with hardness causing ions Ca^{++} and Mg^{++} .

The naturally occurring mineral though more durable, is non-porous and has lower exchange capacity. Synthetic zeolites, on the other hand, are porous and have more exchange capacity per unit weight.

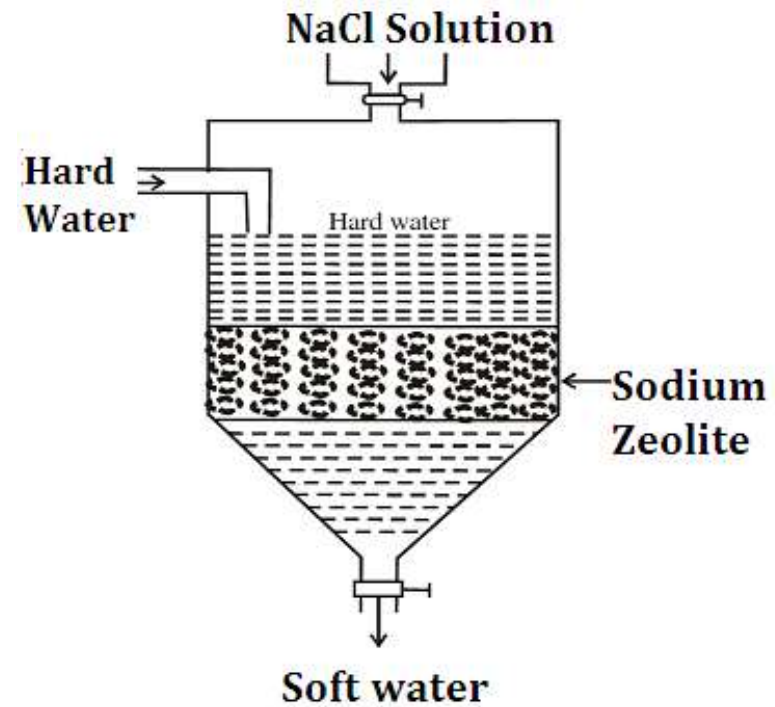
Whether natural or synthetic, zeolites have the property of exchanging their Na^+ ions for hardness causing ions like Ca^{++} and Mg^{++} .



Method

The reactions taking place during the process of softening are presented below:

For convenience sodium zeolite can be written as Na_2Ze , where Ze represents $(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O})$ zeolite.



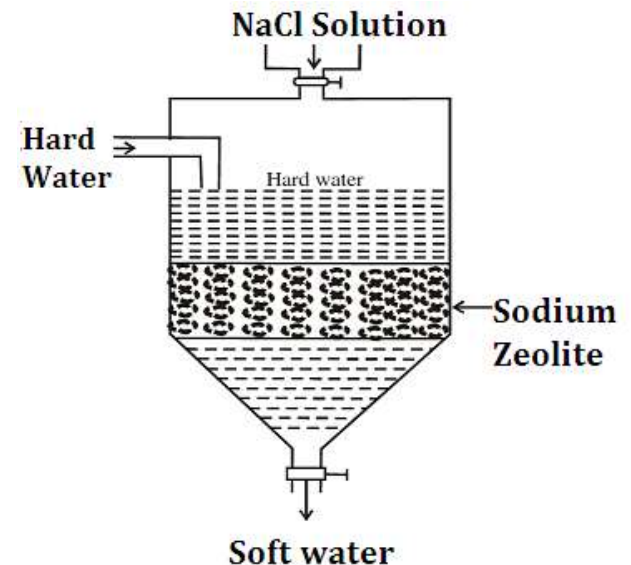
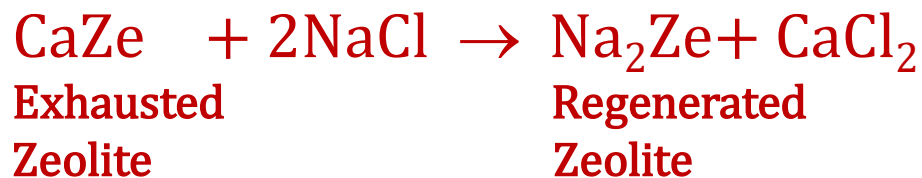


Regeneration of Exhausted Zeolite

The zeolite mineral gets exhausted when all the Na^+ ions are replaced by Ca^{++} and Mg^{++} ions.

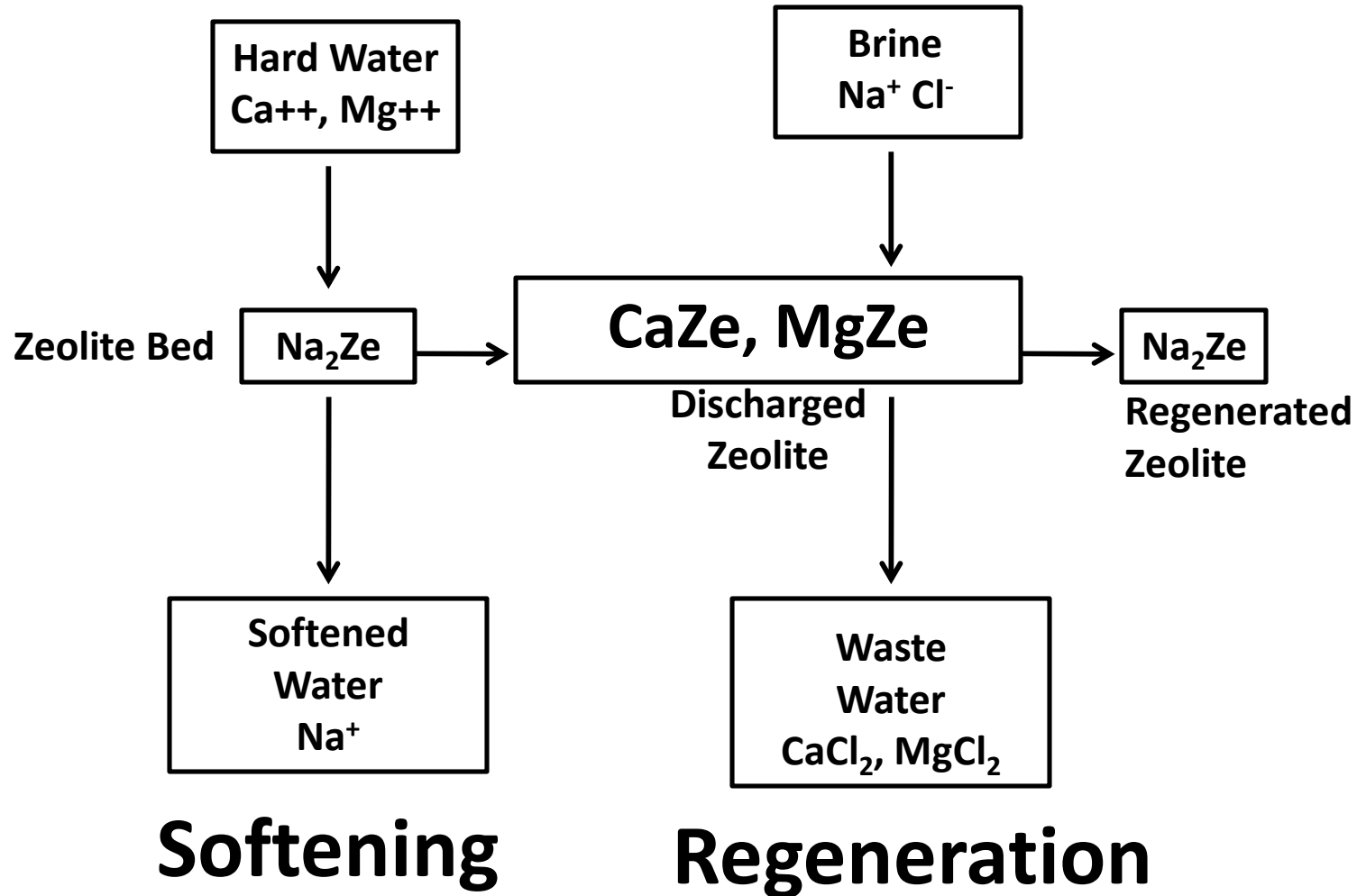
This indicates such an exhausted zeolite no longer has the capacity to exchange any more Ca^{++} and Mg^{++} ions. Under such situation, the hardness of incoming water will not be removed. The discharged Zeolite can be regenerated by passing NaCl solution (Brine).

Calcium and magnesium zeolite on treatment with a solution of NaCl can replace Ca^{++} and Mg^{++} ion with Na^+ ions, thereby regenerating the zeolite.





Zeolite Process





Advantages of Zeolite Process

1. Hardness is almost completely removed. Soft Water upto 5 ppm hardness can be obtained.
2. Equipment occupies less space.
3. It automatically adjust itself to waters of different hardness.
4. The equipment can be used as many as times needed.
3. The materials used are cheap and easily available.
4. The process can be operated under pressure also.
5. Since the reaction involves only replacement of Ca^{++} and Mg^{++} ions with Na^{+} ions, there is no chance of sludge formation after precipitation at later stage.



Limitations of Zeolite Process

1. Water should be free from suspended impurities and turbidity otherwise pores of the zeolite bed will be blocked.
2. Water should be treated at room temperature as zeolite is soluble in hot water.
3. Water should not contain acidic impurities as zeolite being basic can react with the acid.
4. Water should not contain heavy metal ions (Fe^{++} , Mn^{++} etc.) because regeneration of zeolite is not possible after being exhausted.
5. Soft water obtained by this process contain Na^+ which needs to be removed.

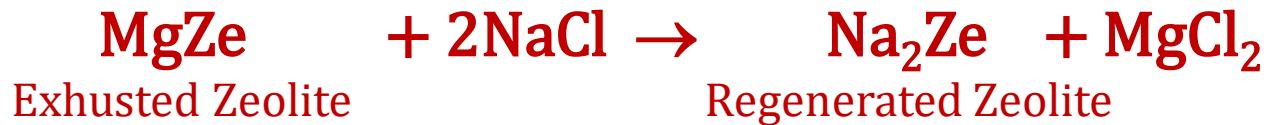
Calculations based on Zeolite method

For convenience sodium zeolite can be written as Na_2Ze , where Ze represents

$(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O})$ zeolite.



Regeneration of Exhausted Zeolite



Key Points:

1. **NaCl as CaCO₃ equivalent = Amount of NaCl × M. F.**
$$= W_{\text{NaCl}} \times \text{Eq. Wt. of CaCO}_3 / \text{Eq. Wt of NaCl}$$
$$= W_{\text{NaCl}} \times 50/58.5$$
$$= W_{\text{NaCl}} \times 100/117$$
2. **For Regeneration**
Amount of NaCl used as mg/L of CaCO₃ =
Hardness of water (ppm of CaCO₃)
3. **Calculation of volume of water softened:**
Amount of NaCl used as mg of CaCO₃ =
Hardness of Water × Volume of water
4. **Conc. of NaCl (mg/L as CaCO₃) × its Volume =**
Hardness × Vol. of hard water

Q.1 1000 litres of hard water is softened by zeolite process. The zeolite was regenerated by passing 20 litres of sodium chloride solution containing 1500 mg/lit. of NaCl. Calculate hardness of water.

Solution: **Key Point:** **Amount of NaCl used as mg/L of CaCO₃ for regeneration is equivalent to Hardness of water.**

1500 mg/L NaCl means,

1 Lit. NaCl solution contains 1500 mg of NaCl

20 litres of NaCl contain = $1500 \times 20 = 30000$ mg of NaCl

We have to convert it in terms of CaCO₃ equivalent.

Thus, 30000 mg of NaCl = $30000 \times MF = 30000 \times 100/117$ mg of CaCO₃

Since, 1000 litres of water required $30000 \times 100/117$ mg of NaCl as CaCO₃

\therefore 1 ltr. of water required $(30000 \times 100/117)/1000$ mg of NaCl as CaCO₃
= 25.641mg of NaCl as CaCO₃/L

Therefore,

Amount of NaCl in terms of CaCO₃ required for regeneration = 25.641 mg/L

Thus, **Hardness of water is 25.64 ppm of CaCO₃ (mg/L = ppm)**

Q.2 By passing 100 litres of NaCl solution containing 125 gm/litre of NaCl, a exhaust zeolite softener bed was regenerated. Calculate the volume of hard water sample (hardness equal to 100 ppm as CaCO₃) which can be softened by regenerated bed of zeolite softener.

Conversion of NaCl used for regeneration in terms of CaCO₃
 for the regeneration of zeolite 100 litres of NaCl

$$\begin{aligned}
 &= 100 \times 125 \text{ gm of NaCl} \\
 &= 12,500 \text{ gm of NaCl} \\
 &= 12500 \times \text{MF} = 12500 \times 100/117 \text{ gm as CaCO}_3 \\
 &= 10683.76 \text{ gm as CaCO}_3
 \end{aligned}$$

Suppose V Lit. of hard water needed NaCl = 10683.76 gm in terms of CaCO₃
 Therefore per liter NaCl required (as CaCO₃) = 10683.76/V gm/L
 = 10683760/V mg/L (or ppm)

Key Point:

Amount of NaCl used as mg/L of CaCO₃ for regeneration = Hardness of water.

Thus,

$$\begin{aligned}
 10683760/V &= 100 \text{ ppm} \\
 V &= 10683760/100 \\
 &= 106837.6 \text{ L } \text{Ans.}
 \end{aligned}$$



Thank You

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Institute of Technology & Management, GIDA, Gorakhpur