

**Swami Keshvanand Institute of Technology,  
Management and Gramothan, Jaipur**

**Engineering Chemistry**

**For B. Tech I Year**

**Students**

# **The Water Lecture - 1**

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(Rajasthan Technical University)**

**Contents:**

**Sources of water**

**Impurities in water**

**Hardness**

**Units of Hardness**

**Numerical**

# Sources of water

## **Surface Water:**

(i) Flowing water e.g. rivers and streams (Moorland surface drainage)

In general river water contains dissolved minerals from soil such as chlorides, sulphates, bicarbonates of sodium, calcium or magnesium, iron and organics matters derived from decomposition of plants, small particles of sand and rocks in suspensions.

(ii) Still waters e.g. lakes, ponds and reservoirs ( Lowland surface drainage)

Lake water has more constant chemical composition.

**Underground Water:** water from shallow and deep spring and wells

**Rain water:** It is probably the purest form of natural water

**Sea Water:** It is probably the most impure form of natural water

# Impurities Present in water

## **Dissolved impurities:**

- (a) Inorganic salts e.g.
  - (i) Cations:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$
  - (ii) Anions:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{F}^-$ ,  $\text{NO}_2^-$
- (b) Gases:  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$
- (c) Organics salts

## **Suspended impurities:**

- (a) Inorganic e.g. clay and sand
- (b) Organics e.g. oil globules, vegetable and animal matters

## **Colloidal impurities:**

Clay and finely divided silica colloidal partials of  $10^{-4} - 10^{-6}$  mm size

## **Micro-organisms:**

Bacteria, Fungi, algae and other forms of animal and vegetable life

## Effects of Impurities in natural water

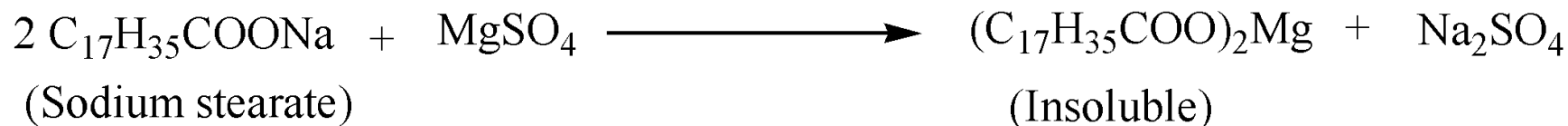
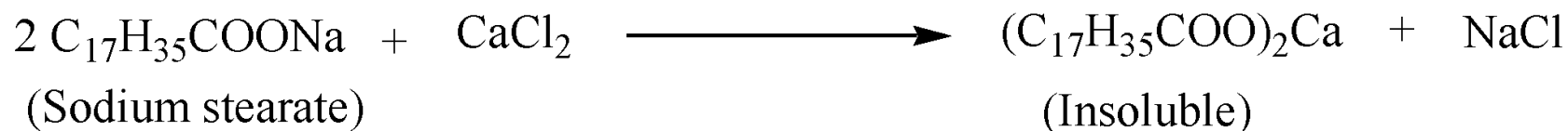
- **Colour**
- **Taste and odour**
- **Turbidity and sediments**
- **Micro-organisms**
- **Dissolved minerals matters**
  - (a) hardness*
  - (b) Alkalinity*
  - (c) Total solids*
  - (d) corrosion*
- **Dissolved gases**
- **Silica contents**

# Hardness of water

**Hardness of water is defined as the soap consuming capacity of a water sample. It is caused due to the salts of Ca/ Mg and other heavy metals dissolved in it.**

**Hardness is the characteristic of water which prevents leathering of soap.**

The soap is generally consists of sodium salts of fatty acids such as Oleic acid, palmitic acid and stearic acid. Calcium and magnesium react with the sodium salts of long chain fatty acid present in the soap to form insoluble scums of calcium and magnesium soaps.

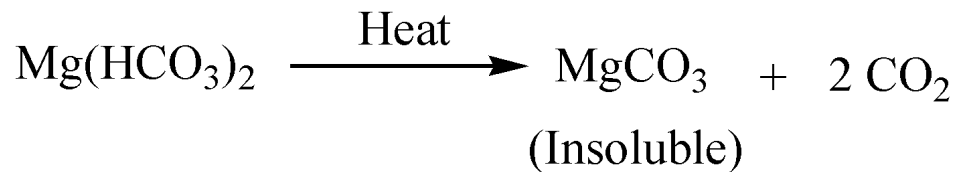
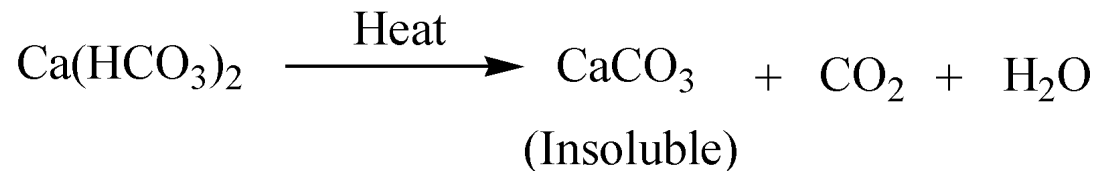


***Other metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$  also contributing to hardness, but they are present in water only in traces***

## Temporary hardness (carbonate hardness)

Temporary hardness is caused by the presence of dissolved bicarbonate of calcium and magnesium and other heavy metal ions .

Temporary hardness is mostly destroyed by boiling of water. During boiling bicarbonate are decomposed in the insoluble carbonate and hydroxide, which are deposited at the bottom of the vessel.



## Permanent hardness (non-carbonate hardness)

This is due the presences of chlorides and sulphates and nitrates of calcium, magnesium, iron and other heavy metal ions.

# Units of Hardness

Hardness is expressed in terms of equivalent of calcium carbonate.

CaCO<sub>3</sub> is taken as a reference because

- (i) it is the most insoluble salt that can be precipitated in water treatment.
- (ii) Its molar mass is 100 which gives ease in calculation.

$$\text{Equivalent of CaCO}_3 = \frac{\text{Mass of hardness producing substances} \times 50}{\text{Chemical equivalent of hardness producing substances}}$$

Dissolved salt	Molar Mass	Eq Wt.	Multiplication factor
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	81	100/162
Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	73	100/146
CaSO <sub>4</sub>	136	68	100/136
CaCl <sub>2</sub>	111	55.5	100/111
MgSO <sub>4</sub>	120	60	100/120
MgCl <sub>2</sub>	95	47.5	100/95
MgCO <sub>3</sub>	84	42	100/84

## Multiplication Factor and Equivalents of CaCO<sub>3</sub>

$$\text{CaCO}_3 = 100/2 = 50 \text{ mg}$$

$$\text{Ca(HCO}_3)_2 = 162/2 = 81 \text{ mg}$$

$$81 \text{ mg Ca(HCO}_3)_2 = 50 \text{ mg CaCO}_3$$

$$1 \text{ mg} \text{----} = 50/81$$

$$x \text{ mg} \text{----} = 50/81 * x$$

or

$$100/162 \text{----} \square \text{ Multiplication Factor}$$

$$\text{Equivalent of CaCO}_3 = \frac{\text{Mass of hardness producing substances} \times 50}{\text{Chemical equivalent of hardness producing substances}}$$

## Numericals

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

EQ. weights:

$\text{Ca}(\text{HCO}_3)_2$  -  $16.2 \text{ mg/L} = 162/2 = 81$ ;  $50/81 * 16.2 = 10 \text{ mg/l} - \text{T}$

$\text{Mg}(\text{HCO}_3)_2$   $7.3 \text{ mg/L} = 146/2 = 73$ ;  $50/73 * 7.3 = 5 \text{ mg/l} - \text{T}$

$\text{CaSO}_4 = 136/2 = 68$ ;  $13.6 \text{ mg/l} = 10 - \text{P}$

$\text{MgCl}_2$   $9.5 \text{ mg/l} = 10 \text{ mg/l} - \text{P}$

Temp Hard =  $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2$   
 $5 + 10 = 15 \text{ mg/l}$

Perm Hard =  $\text{MgCl}_2 + \text{CaSO}_4$   
 $10 + 10 = 20 \text{ mg/l}$

**Calculate the temporary hardness and total hardness of a sample of water containing:  $\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/L}$ ;  $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg/L}$ ;  $\text{MgCl}_2 = 95 \text{ mg/L}$ ;  $\text{CaSO}_4 = 136 \text{ mg/L}$**

Molecular weights:

$\text{Ca}(\text{HCO}_3)_2 = 162$ ;  $\text{Mg}(\text{HCO}_3)_2 = 146$ ;  $\text{CaSO}_4 = 136$ ;  $\text{MgSO}_4 = 120$ ; ;  $\text{MgCl}_2 = 95$ ;  
 $\text{Al}_2(\text{SO}_4)_3 = 114$

$$\begin{array}{rcl}
 \text{Mg}(\text{HCO}_3)_2 & = & \text{CaCO}_3 \\
 146 & & 100 \\
 146/2 & & 100/2 \\
 1 \text{-----} & = & 100/2 \\
 & & \text{-----} = 100/146 \\
 & & 146/2 \\
 73 \text{-----} & = & 100/146 \times 73 = 50
 \end{array}$$

**Three samples A, B and C were analyzed for their salts contents:  
Sample A was found to contain 168 mg of magnesium carbonate  
per L Sample B was found to contain 820 mg of calcium nitrate  
and 2 mg of silica per L Sample C was found to contain 2 g  
calcium carbonate per 500 ml  
Determine the hardness in all above three sample in ppm**

Molecular weights:

$\text{Ca}(\text{NO}_3)_2 = 164$ ;  $\text{MgCO}_3 = 84$ ;  $\text{CaCO}_3 = 100$

Queries are welcome at  
[archanasaxena@skit.ac.in](mailto:archanasaxena@skit.ac.in)

**Swami Keshvanand Institute of Technology,  
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**Engineering Chemistry  
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**The Water  
Lecture – 2**

**Content:**

**Determination of  
Hardness by EDTA  
Method**

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# Estimation of Hardness

## **EDTA Titration Method**

## **or Complexometric Titration Method**

In this method water sample is titrated against EDTA in the presence of Eriochrome Black T Indicator and buffer solution.

EDTA is a hexadentate ligand which forms stable complex with hardness causing cations.

**End Point – Wine red to Blue**

## EDTA Method:

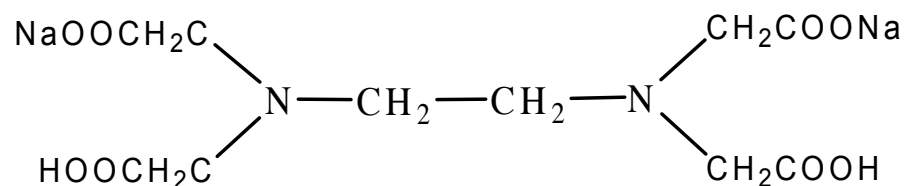
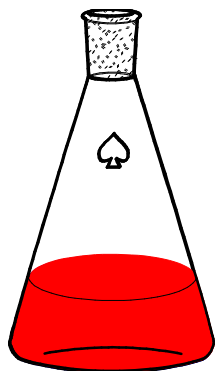
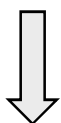
Hard water (10ml)

+

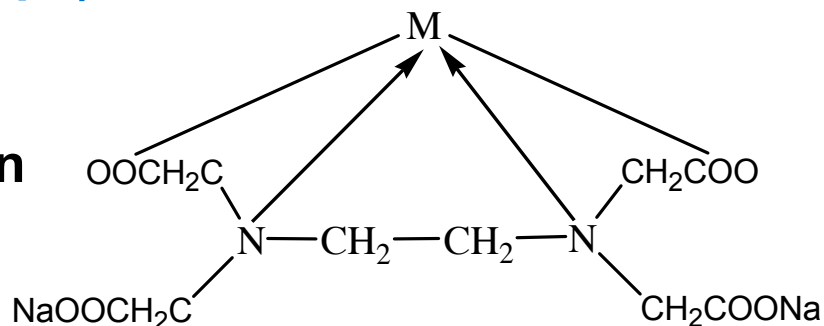
EBT Indicator (2-3 drops)

+

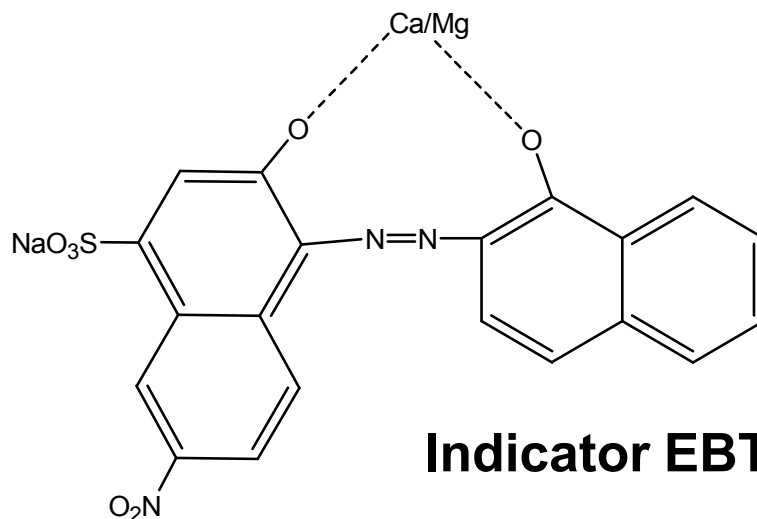
10 PH buffer solution  
(2-3 ml)



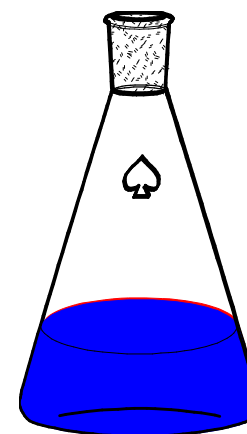
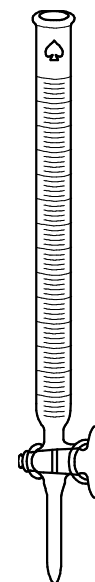
**EDTA**



**Metal EDTA Complex**

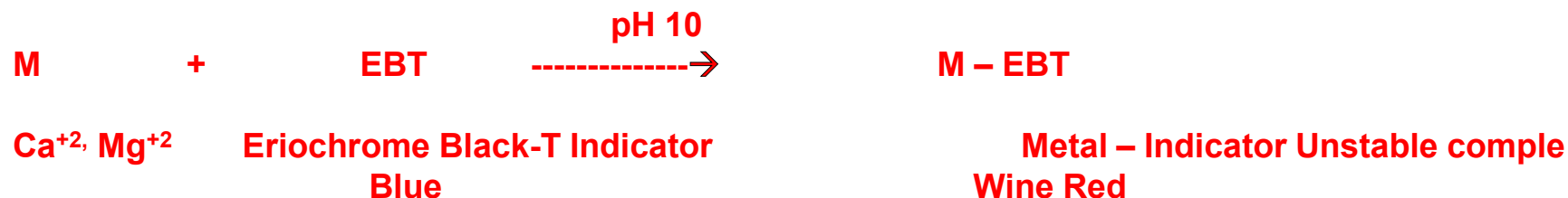


**Indicator EBT**

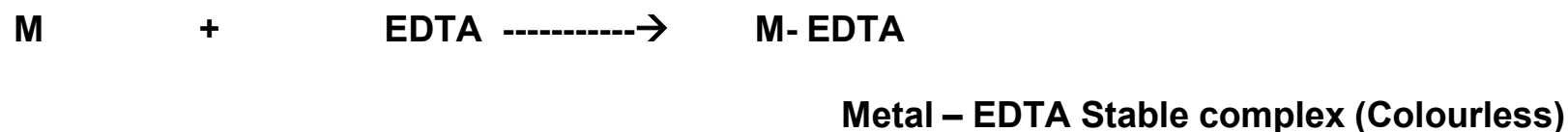


## Theory:

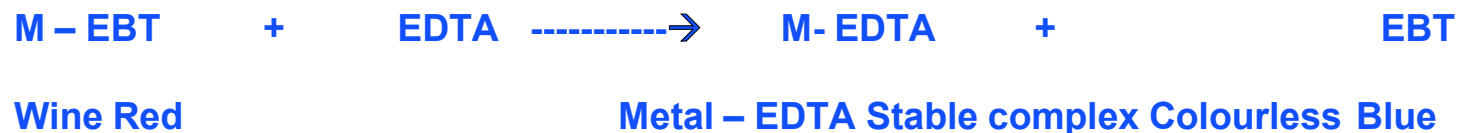
1. There are hardness causing metal ions in present in the water . When Indicator EBT is added to water, it combines with  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  and forms unstable metal – EBT complex of wine red colour.



2. Ethylene diammine tetra acetic acid (EDTA) is a well known powerful complexing agent. EDTA forms complex with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions as well as with many other metal cations. When hard water is titrated against EDTA solution then EDTA or its sodium salt forms complex with  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  ions in water.



3. When more EDTA is run from burette it starts taking metal ions from M-EBT. The moment all the metal ions leave EBT and join EDTA, the EBT turns in to its own blue colour and the end point is observed that is wine red to blue



## **Preparation of solutions**

### **1. Preparation of Standard hardwater**

Dissolve 1 gm of  $\text{CaCO}_3$  in minimum quantity of dil.  $\text{HCl}$ . Boil the solution to expel  $\text{CO}_2$ . Cool and dissolve the residue in distilled water and make up to 1 litre. This gives a standard hard water sample of strength 1 mg/ml. or 1000 ppm.

### **2. Standard EDTA Solution -**

Take 5 gm. disodium salt of EDTA and dry it in an oven at  $80^\circ\text{C}$  for about 2 hrs. Cool the salt and weigh 3.7224 gm. from it, and dissolve it in distilled water to make 1 litre of solution.

### **3. Eriochrome Black-T indicator solution :**

0.5 gm of pure EBT is dissolved in 100 ml. alcohol.

### **4. Buffer Solution :**

675 gm. of  $\text{NH}_4\text{Cl}$  and 570 ml. of ammonia solution is mixed and made up to 1 litre with distilled water. Rinse and fill the burette with EDTA solution.

# Titration Procedure

## **Standardization of EDTA:**

Pipette out 10 ml of standard hard water sample in a conical flask. Add 2 ml of buffer solution and 2 drops of Eriochrome Black – T as an indicator. Titrate it against EDTA solution from burette till the colour changes from wine red to blue. Repeat it to get concordant reading – **V1 mL**

## **Determination of Total hardness of water sample:**

Pipette out 10 ml of sample hard water in a conical flask. Add 2 ml of buffer solution and 2 drops of EBT as an indicator. Titrate it against EDTA solution from burette till the colour changes from wine red to blue. Repeat it to get concordant reading – **V2 mL**

## **Determination of Permanent hardness of water sample:**

Take 250 ml of hard water in 500 ml beaker and boil gently for half an hour. Filter the solution in 250 ml volumetric flask and make up to the mark with distilled water thoroughly. Pipette out 10 ml of boiled water sample in a conical flask. Add 2 ml of buffer solution and 2 drops of Eriochrome Black – T as an indicator. Titrate it against EDTA solution from burette till the colour changes from wine red to blue. Repeat it to get concordant reading – **V3 mL**

# Calculation

## Standardization of EDTA

1 mL of standard hard water contains = 1 mg of  $\text{CaCO}_3$

10 mL of standard hard water = 10 mg of  $\text{CaCO}_3$

$V_1$  mL of EDTA = 10 mL of standard hard water

= 10 mg of  $\text{CaCO}_3$  eq. hardness

1 mL of EDTA =  $10/V_1$  mg of  $\text{CaCO}_3$  eq. hardness

## Determination of Total hardness of water sample

10 mL of water sample =  $V_2$  mL of EDTA solution

=  $10/V_1 \times V_2$  mg of  $\text{CaCO}_3$  eq.

10 mL of water sample =  $10/V_1 \times V_2$  mg of  $\text{CaCO}_3$  eq.

1 mL of water sample =  $10/V_1 \times V_2/10$  mg of  $\text{CaCO}_3$  eq.

**1000 mL of water sample =  $V_2/V_1 \times 1000$  mg of  $\text{CaCO}_3$  eq. / l or ppm-----Total Hardness**

## Determination of Permanent hardness of water sample

10 mL of boiled water sample =  $V_3$  mL of EDTA solution

=  $10/V_1 \times V_3$  mg of  $\text{CaCO}_3$  eq.

10 mL of boiled water sample =  $10/V_1 \times V_3$  mg of  $\text{CaCO}_3$  eq.

1 mL of boiled water sample =  $10/V_1 \times V_3/10$  mg of  $\text{CaCO}_3$  eq.

**1000 mL of boiled water sample =  $V_3/V_1 \times 1000$  mg of  $\text{CaCO}_3$  eq./ l or ppm----- Perm. Hardness**

**Temporary Hardness of water sample = Total hardness – Permanent hardness**

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**The Water  
Lecture - 3**

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**Contents:**

**Boiler Troubles:**

**Scale & Sludge  
Formation**

**Caustic  
Embrittlement**

# **BOILER TROUBLES**

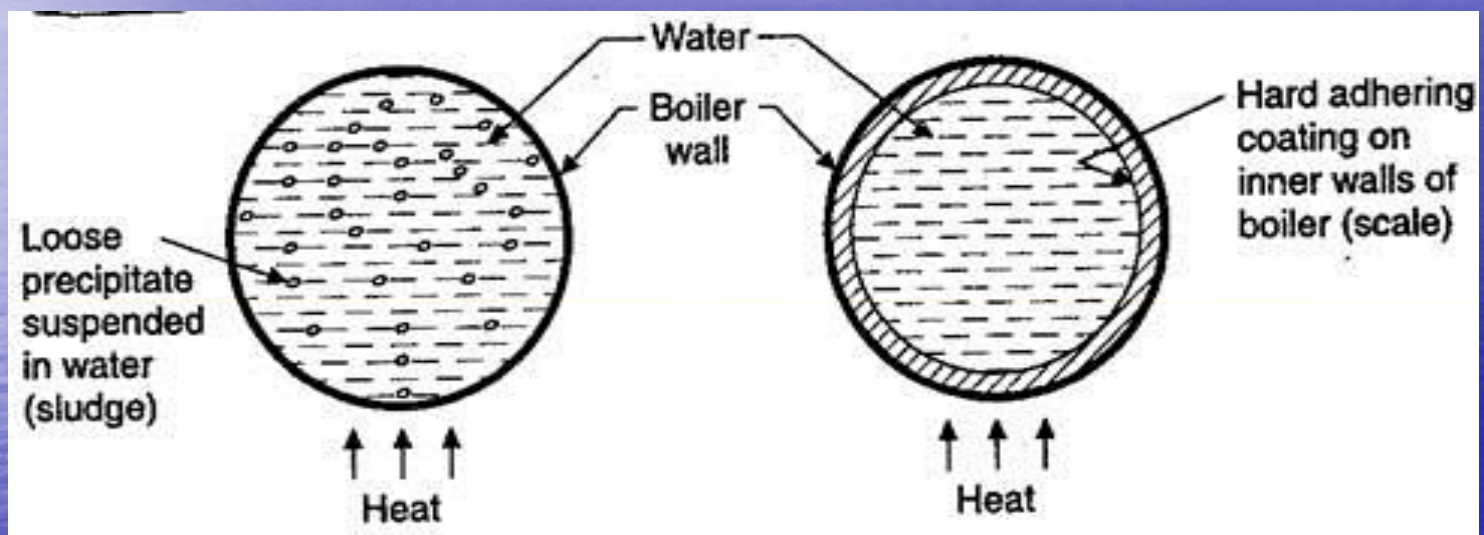
1. Scale and Sludge Formation
2. Caustic Embrittlement
3. Priming and Foaming
4. Boiler Corrosion

## Scale and Sludge Formation In Boilers

In boilers, water evaporates continuously and the concentrations of the dissolved salts increases progressively.

when concentrations of dissolved salts reach saturation point, they form loose and slimy precipitates it is called **sludge**.

On the other hand, if the precipitate matter form a hard adhering crust/coating on the inner walls of the boiler, it is called **scale**.



# Causes

## Sludges

$\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$

## Scales

$\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{Mg(OH)}_2$ ,  $\text{CaSiO}_3$ ,  
 $\text{MgSiO}_3$



## **Disadvantages of sludge formation**

- Sludge's are poor conductor of heat, so they tend to waste a portion of heat generated.
- Sludge's get entrapped in the scale and both get deposited as scales.
- Excessive sludge formation, disturbs the working of the boiler. It settle in the regions of poor water circulation such as pipe connection etc.

## **Prevention of sludge formation:**

- By using well softened water
- By frequently 'blow-down operation', i.e., drawing off a portion of the concentrated water.

## Disadvantages of scale formation

- **Wastage of fuel:** Scales have a low thermal conductivity, so that rate of heat transfer from boiler to inside water is greatly decreased
- **Lowering of boiler safety:** Due to scale formation, over heating of boiler is done, which causes distortion of boiler tube.
- **Decrease in efficiency:** Scales may deposit in the valve and condensers of the boiler and choke them partially.
- **Danger of explosion:** When thick scales crack, the water comes suddenly in contact with over heated iron plates.

## Removal of scales

- With the help of scraper or piece of wood or wire brush.
- By giving thermal shocks, if they are brittle.
- By dissolving them by adding chemicals, (5-10% HCl, EDTA) if they are adherent and hard.
- By frequent blow-down operation, if the scales are loosely adhering.

## **Prevention of scales formation**

**(1) External Treatment:** Includes efficient softening of water by following methods (i.e., removing hardness-producing constituents of water)

Lime – Soda Method

Zeolite Method

Ion Exchange Method

**(2) Internal Treatment:** Accomplished by adding a proper chemical to the boiler water either:

## Caustic Embrittlement

It is the phenomenon in which the material of a boiler becomes brittle due to the accumulation of caustic substances. Sodium carbonate is used in softening of water by lime soda process, due to this some sodium carbonate maybe left behind in the water



As Conc. of NaOH increases, water flows into minute hair cracks. Water get evaporated and NaOH increases further and react with iron of boiler, hence cause Embrittlement.

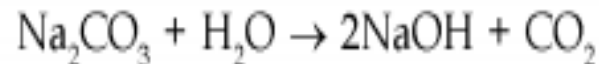
### Prevention

Addition of sodium sulphate or sodium phosphate. Which will block hair-cracks.

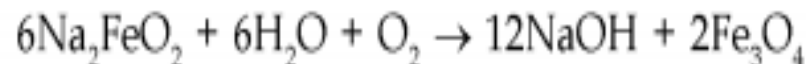
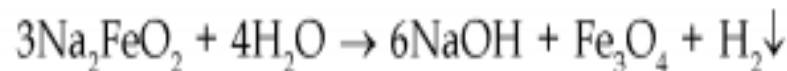
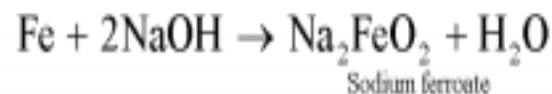
Addition of tannin and lignin- blocks the cracks.

Excess of  $\text{Na}_2\text{SO}_4$  is avoided else it will form  $\text{CaSO}_4$

**Process :**



- The formation of NaOH makes the boiler water caustic.
- This caustic water penetrates into the minute hair cracks present in the inner side of boiler by capillary action.
- When the water evaporates and the concentration of dissolved NaOH increases, it dissolves the iron of boiler as sodium ferroate.



- This causes the formation of inter granular cracks on the boiler metal particularly at place of high local stress like riveted joints, bend etc.
- Caustic embitterment is the type of stress corrosion and is a localized electrochemical phenomenon.

- The concentration cell set up can be explained as shown.

Iron at the point of the local stress e.g. rivets, bends, joints	Concentration NaOH (aq) solution	Dilute NaOH (aq) solution	Iron at plain surface
--	----------------------------------	---------------------------	-----------------------

Iron at plain surface remain in contact of dilute NaOH acting as the cathode, while the iron remain in contact of Conc. NaOH work as anode and always anodic part under goes corrosion.

#### **Prevention of Caustic Embrittlement :**

- (i) Sodium phosphate can be used for softening of water instead of  $\text{Na}_2\text{CO}_3$ .
- (ii) The tannin or lignin should be added to the boiler water which blocks the minute hair cracks and thus preventing the infiltration of NaOH.
- (iii) The excess of alkali in boiler feed water should be neutralized.
- (iv) Sodium sulphate also used for block of hair cracks, generally the concentration of  $\text{Na}_2\text{SO}_4$ , NaOH are maintained 1 : 1, 2 : 1 or 3 : 1 for operating pressure of 10, 20 and greater than 20 atmosphere respectively.

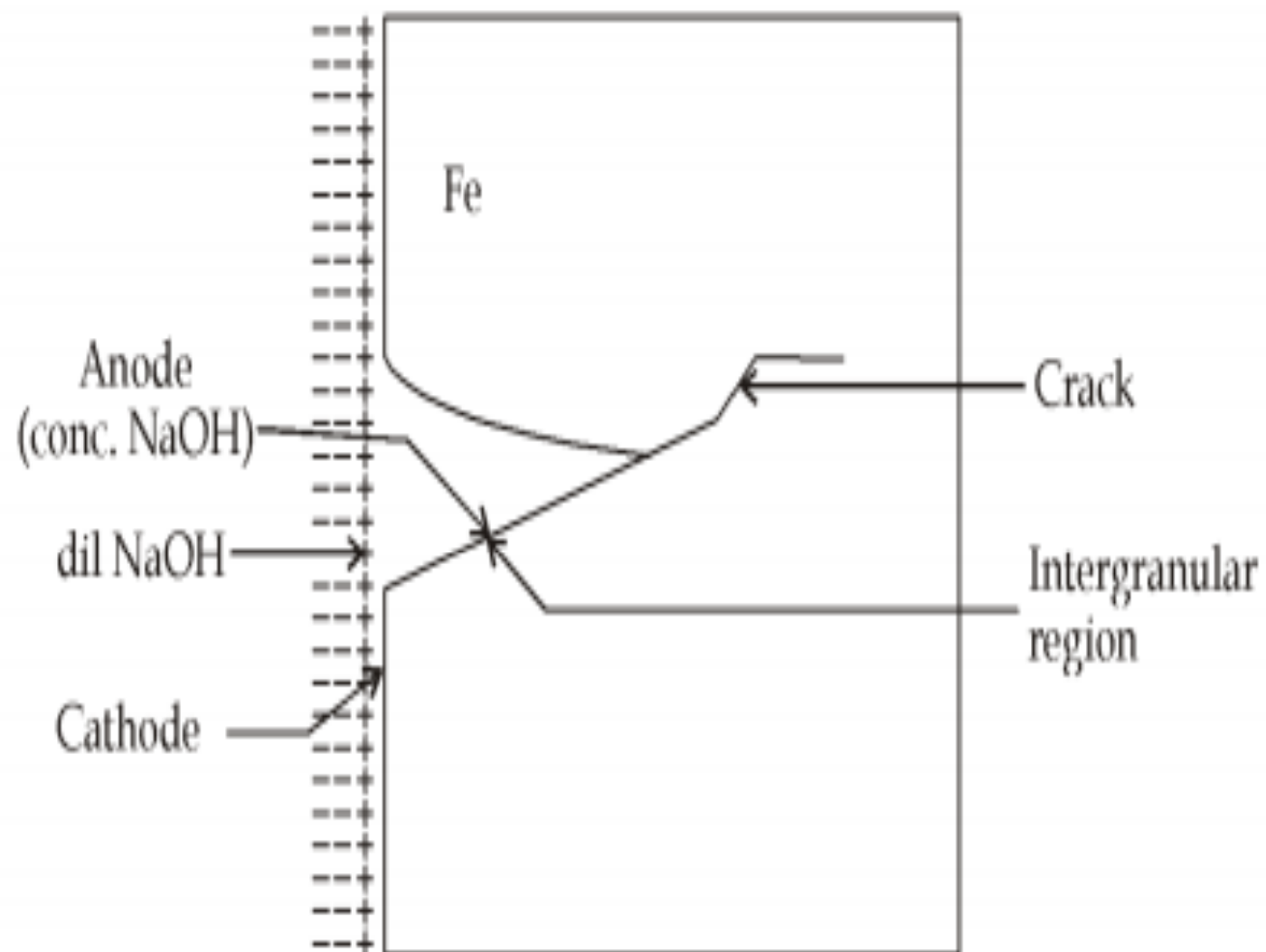


Figure 2.9: Caustic embrittlement at cracks.



Drink luckworm water  
Stay Safe

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**The Water  
Lecture - 4**

**Contents:**

**Boiler Troubles:**

**Priming & Foaming**

**Boiler Corrosion**

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# **BOILER TROUBLES**

1. Scale and Sludge Formation
2. Priming and Foaming
3. Boiler Corrosion
4. Caustic Embrittlement

# **BOILER TROUBLES**

1. Scale and Sludge Formation
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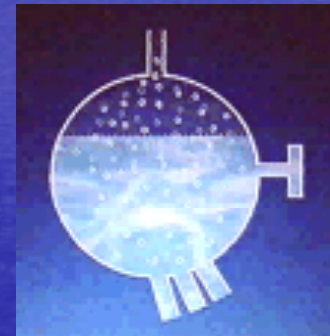
# Priming and Foaming

## Priming

When a boiler is steaming rapidly, some particles of the liquid water are carried along-with steam. this process of wet steam is called Priming.

### Reasons for Priming:

- The presence of large amount of dissolved solids
- High steam velocities
- Sudden boiling
- Improper boiler design
- Sudden increase in steam- production rate.



### Priming can be avoided by

- Fitting mechanical steam purifiers.
- Avoiding rapid change in steaming rate.
- Maintaining low water levels in boilers.
- Efficient softening and filtration of the boiler-feed water.

Priming



Foaming



**Foaming:** Production of persistent foam or bubbles in boilers. This is due to presence of substances (oils) which reduce the surface tension of water.

**Priming and foaming usually occur together.**

They are *objectionable* because

- Efficiency reduces as dissolved salts in boiler water get deposited on super-heater and turbine blades, as water evaporates.
- Life of the machinery may decrease as dissolved salts may enter the parts of other machinery.
- Maintenance of the boiler pressure becomes difficult, as actual height of the water column cannot be judged properly.

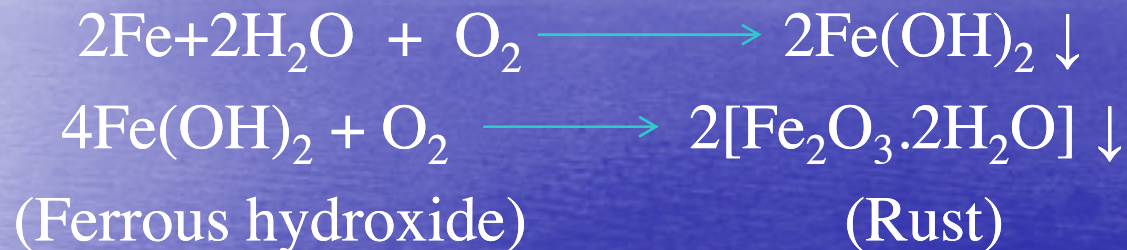
**Foaming can be avoided by**

- Adding anti-foaming chemicals like castor oil.
- Removing oil from boiler water by adding compounds like sodium aluminate

# BOILER CORROSION

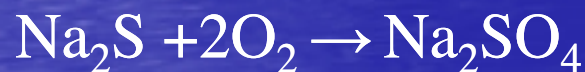
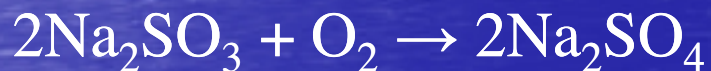
Decay of boiler material due to chemical or electro-chemical attack by its environment. Main reasons for boiler corrosion are:

(i) **Dissolved oxygen:** Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material



**Removal of dissolved oxygen:**

(i) Adding calculated quantity of sodium sulphite, sulphide or hydrazine

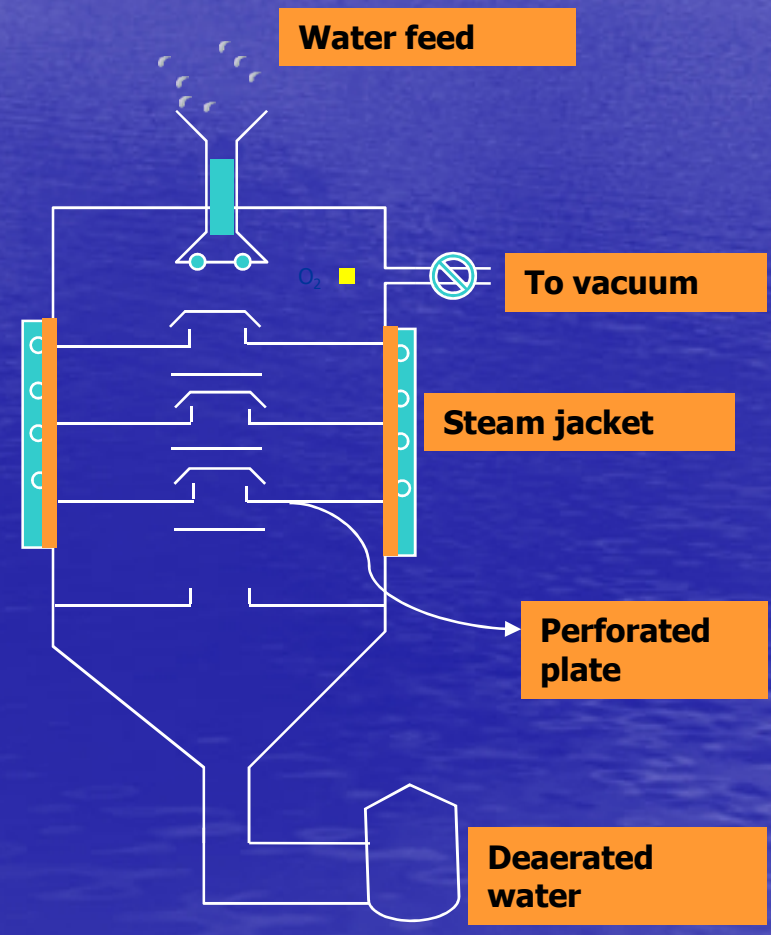


## Mechanical Deaeration

**It comprises of a tall stainless tower with different layers capped with baffles to facilitate multiple equilibration.**

**The entire chamber is vacuumized and also maintained at high tempt using perforated heating plates on the walls.**

**Principle: High tempt and low pressure favors lower solubility of gases in water (Henry's law)**

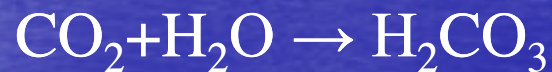


## **(ii) Dissolved carbon dioxide (carbonic acid)**

CO<sub>2</sub> has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler.



Carbon dioxide reacts with water and forms carbonic acid which corrodes boiler material



### **Removal of CO<sub>2</sub>**

- By adding calculated quantity of ammonia.



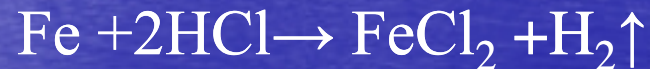
- By mechanical-aeration process along with oxygen.

### **(iii) Acids from dissolved salts**

Water containing dissolved magnesium salts liberate acids on hydrolysis.



acid reacts with iron (of the boiler) in chain-like reactions producing HCl again and again



Consequently, presence of even a small amount of  $\text{MgCl}_2$  will cause corrosion of iron to a large extent.

### **Removal**

Using softened water for steam generation

Do Pranayam  
Stay Safe

**Swami Keshvanand Institute of Technology,  
Management and Gramothan, Jaipur**

**Engineering Chemistry  
For B. Tech I Year  
Students**

**The Water  
Lecture – 5**

**Prof. Archana Saxena  
Swami Keshvanand Institute of Technology  
Management and Gramothan, Jaipur  
(Rajasthan Technical University)**

**Content:**

**Lime Soda Method  
of Softening of hard  
water**

**Cold Lime Soda Method**

**Hot Lime Soda Method**

# WATER SOFTENING

- removal of hardness
- Hardness is?...

primarily cations like Ca, Mg, plus Fe, Mn, Al

- How is Softening done?...

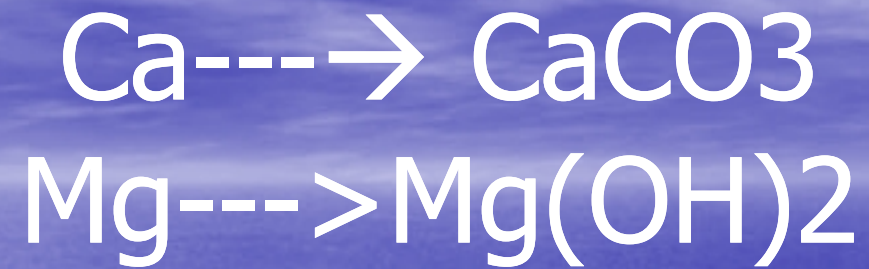
Precipitation of Ca and Mg, or  
Ion exchange of Ca / Mg with ion such as Na

- Hardness in 300-500 mg/l as  $\text{CaCO}_3$  range considered excessive



high soap consumption  
scaling in heating vessels and pipes

- Even  $> 150$  mg/l may result in consumer objection
- 60-120 mg/l as  $\text{CaCO}_3$  is considered a moderate amount



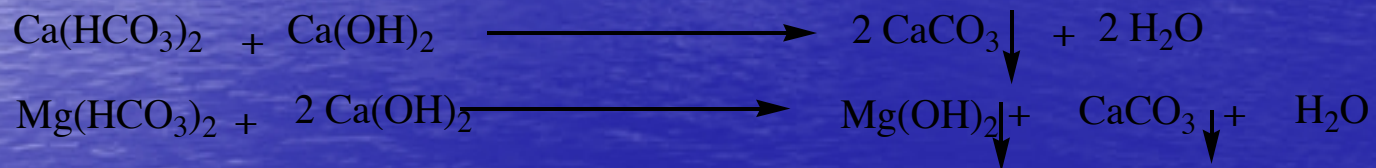
Ca (OH)<sub>2</sub>... SLAKED LIME  
Na<sub>2</sub> CO<sub>3</sub>...SODA

# Lime-Soda process

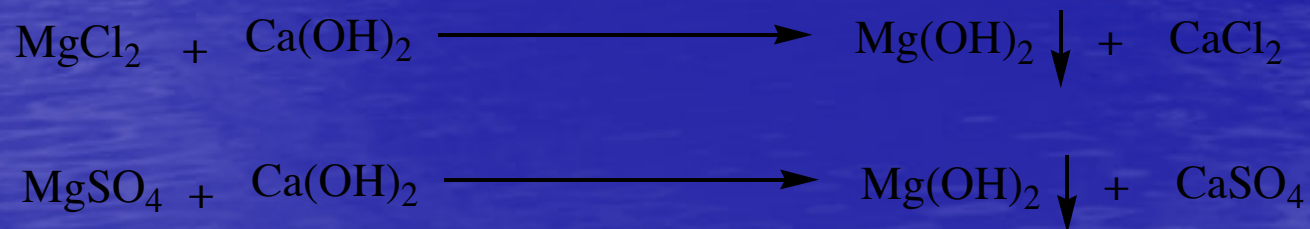
**In this process, all the soluble hardness-causing impurities are converted into insoluble precipitates which may be removed by settling and filtration .**

In the lime soda process, a calculated quantity of lime  $\text{Ca(OH)}_2$  and soda  $\text{Na}_2\text{CO}_3$  is added in the hard water. The soluble calcium and magnesium salts in water are converted into insoluble compounds such as calcium carbonate and magnesium hydroxide which may be removed by settling and filtration.

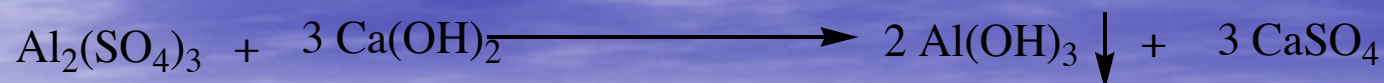
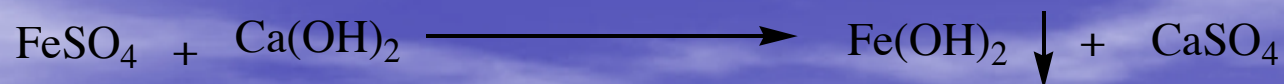
## **(i) Lime removes the temporary hardness: (L, 2L)**



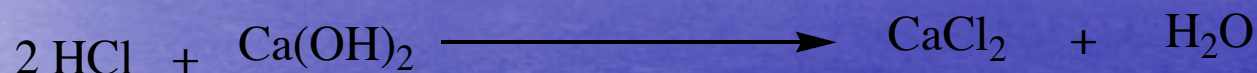
## **(ii) Lime removes the permanent magnesium hardness: (L+S)**



**(iii) Lime removes the dissolved iron and aluminum salts: (L+S)**



**(iv) Lime removes free mineral acids: (L+S)**



**(v) Lime removes dissolved CO<sub>2</sub> and H<sub>2</sub>S: L**



**(vi) Soda removes all calcium permanent hardness: S**



Now the 100 parts by mass of  $\text{CaCO}_3$  are equivalent to :

- (i) 74 part of  $\text{Ca(OH)}_2$  and
- (ii) 106 parts of  $\text{Na}_2\text{CO}_3$

**Lime required for softening:**

$$= \frac{74}{100} [ \text{Temp. Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- ]$$

**Soda required for softening:**

$$= \frac{106}{100} [ \text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- ]$$

# **Types Lime Soda Process**

## **1.Cold Lime Soda Process :**

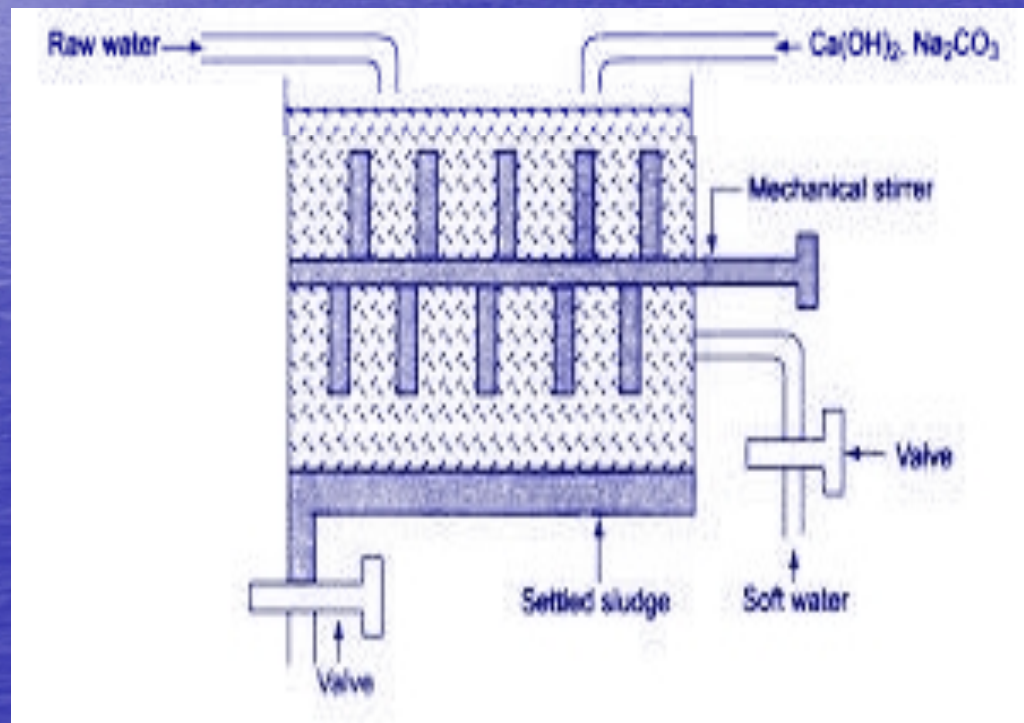
(a) Batch Process (Intermittent type Softener)

(b) Continuous Softener

## **2. Hot Lime Soda Process**

## Batch Process (Intermittent Softener)

- Two inlets
- Two outlets
- Mechanical Stirrer
- Small amounts of coagulants like  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{NaAlO}_2$  etc. used



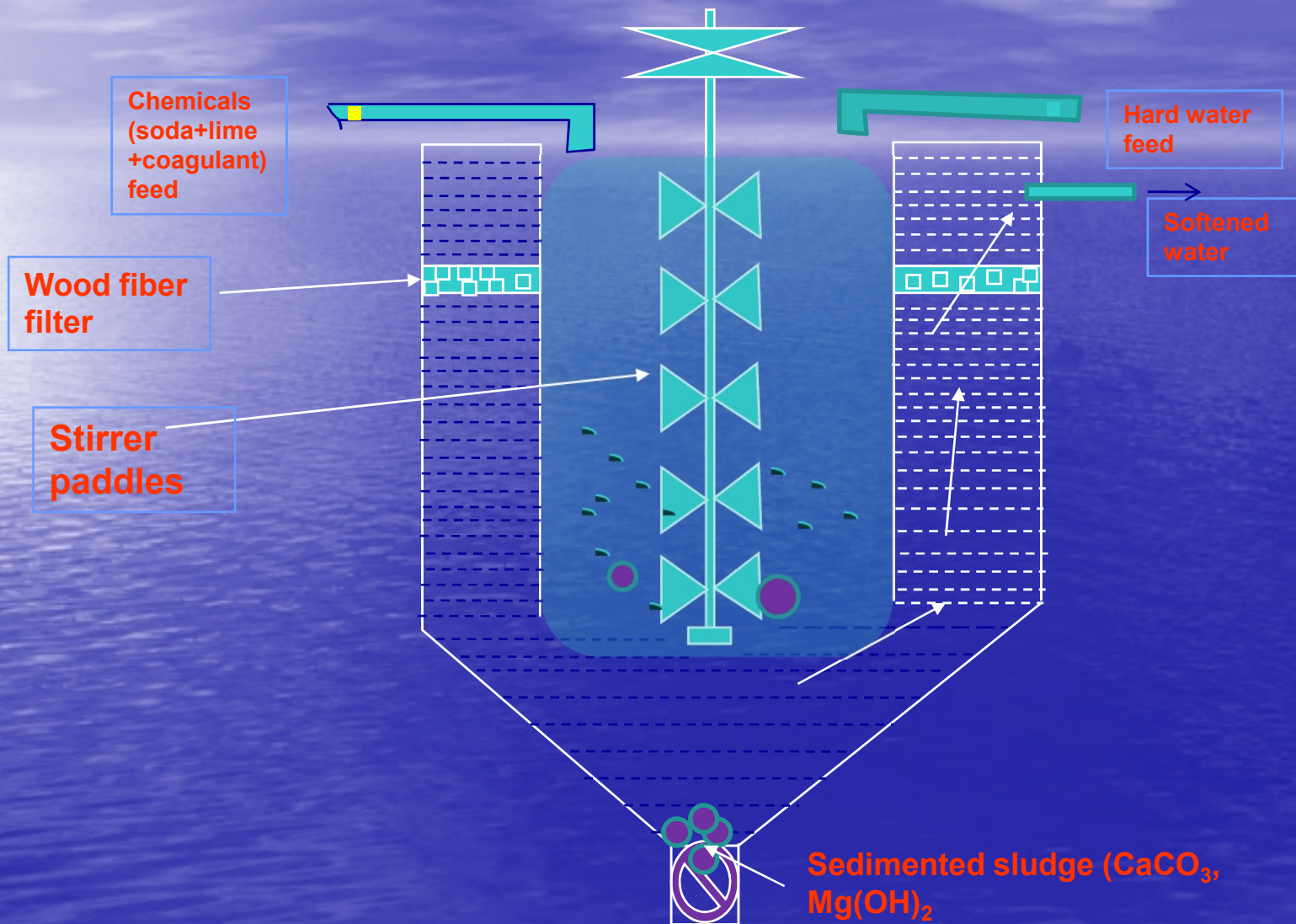
## Continuous Cold lime soda process

Calculated quantity of lime and soda are mixed with water at room temperature the precipitates formed are finely divided, so they do not settle down easily. Therefore, It is essential to add small amounts of coagulants (like alum, aluminum sulphate, sodium aluminates *etc*).

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



# Continuous cold lime soda softener



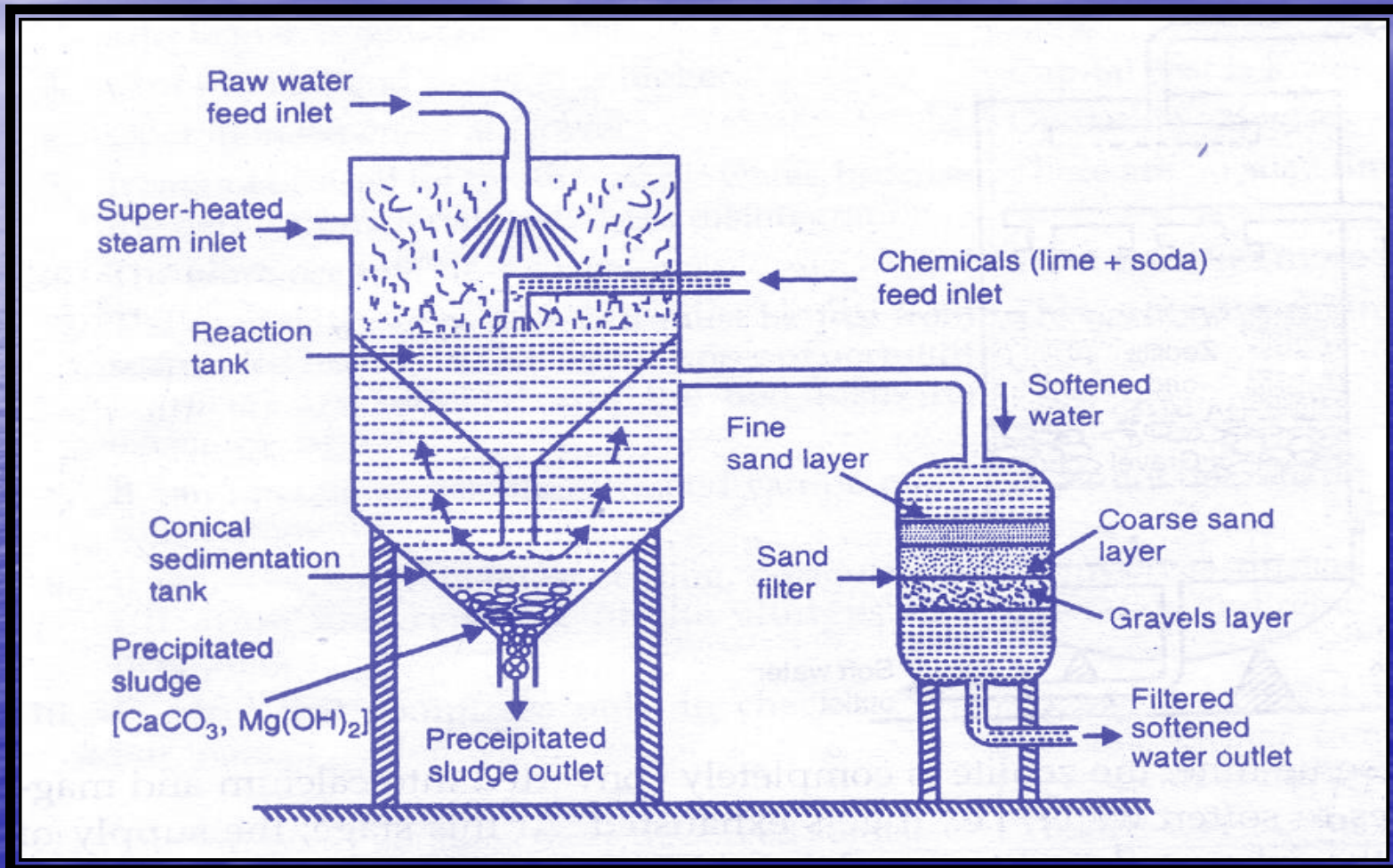
## Hot lime soda process

Calculated quantity of lime and soda is mixed with water at 80 to 150°C.

### Advantages of high temperature

- The reaction proceeds faster.
- Softening capacity is increased.
- No coagulant needed as the precipitate and sludge formed settle down rapidly.
- Much of the dissolved gases are driven out of water.
- Viscosity of softend water is lower, so filtration of water becomes easier.
- This process produces water of comparatively low residual hardness 15 to 30 ppm.

## Continuous Hot Lime Soda Softener



## **Advantages of lime soda process:**

- It is very economical.
- If the process is combined with sedimentation/coagulation lesser amounts of coagulants shall be needed.
- The process increases the pH of the treated water thereby corrosion reduced.
- In addition to the removal of hardness, the quantities of minerals in the water are reduced.
- Due to alkaline nature of treated water amount of pathogenic bacteria in water is considerably reduced.

## **Disadvantages of lime soda process:**

- For efficient and economical softening, careful operation and skilled supervision is required.
- Disposal of large amount of sludge poses a problem.
- This can remove hardness up to 15 ppm which is not good for boilers.

Queries are welcome at  
[archanasaxena@skit.ac.in](mailto:archanasaxena@skit.ac.in)

Do not delay testing if any symptom of  
corona appears, Stay Safe

**Swami Keshvanand Institute of Technology,  
Management and Gramothan, Jaipur**

**Engineering Chemistry  
For B. Tech I Year  
Students**

**The Water  
Lecture – 6**

**Contents:**

**Water Softening method**

**Reactions of Lime Soda  
Method**

**Calculation on Lime Soda  
Requirement**

**Prof. Archana Saxena  
Swami Keshvanand Institute of Technology  
Management and Gramothan, Jaipur  
(Rajasthan Technical University)**

# WATER SOFTENING

- removal of hardness
- Hardness is?...

primarily cations like Ca, Mg, plus Fe, Mn, Al

- How is Softening done?...

Precipitation of Ca and Mg, or  
Ion exchange of Ca / Mg with ion such as Na

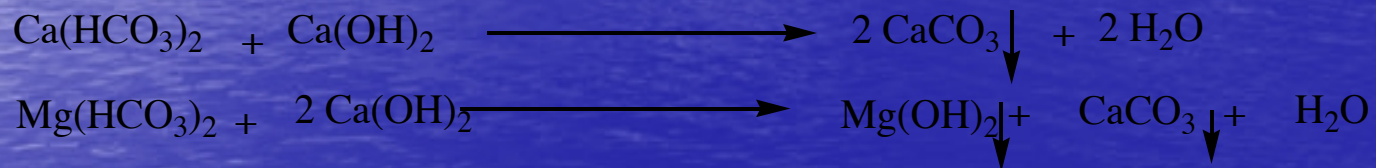
- Hardness in 300-500 mg/l as  $\text{CaCO}_3$  range considered excessive
- high soap consumption  
scaling in heating vessels and pipes
- Even  $> 150$  mg/l may result in consumer objection
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# Lime-Soda process

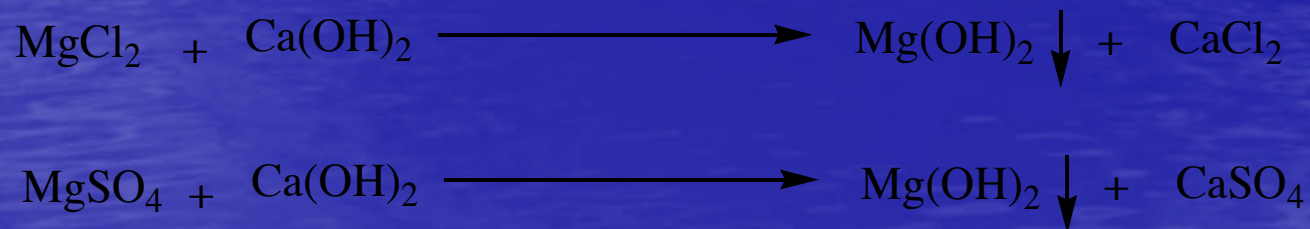
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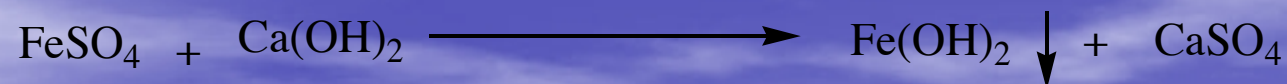
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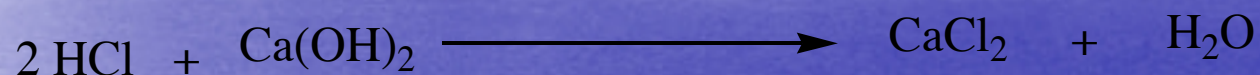
**(ii) Lime removes the permanent magnesium hardness:**



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**Soda required for softening:**

$$= \frac{106}{100} [ \text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- ]$$

Explain with chemical equation and calculate the amount of lime  
 And soda needed for softening 1,00,000 litres of water containing  
 $\text{HCl} = 7.3 \text{ mg/L}$ ;  $\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ mg/L}$ ;  $\text{MgCl}_2 = 9.5 \text{ mg/L}$ ;  
 $\text{NaCl} = 29.25 \text{ mg/L}$ , Purity of lime is 90% and that of the soda is 98%.

Molecular weights:

$\text{Ca}(\text{HCO}_3)_2 = 162$ ;  $\text{Mg}(\text{HCO}_3)_2 = 146$ ;  $\text{CaSO}_4 = 136$ ;  $\text{MgSO}_4 = 120$ ; ;  $\text{MgCl}_2 = 95$ ;  
 $\text{Al}_2(\text{SO}_4)_3 = 114$

**Lime required for softening:**

$$= \frac{74}{100} [\text{Temp. Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^-]$$

**Soda required for softening:**

$$= \frac{106}{100} [\text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^-]$$



# Solved Numerical Problems

## Calculations of Lime Soda Requirements

**Formula for lime and soda requirement :**

As 100 parts by mass of  $\text{CaCO}_3$  are equivalent to (i) 74 parts of  $\text{Ca(OH)}_2$  and (ii) 106 parts of  $\text{Na}_2\text{CO}_3$ . (As molecular weight of  $\text{Ca(OH)}_2 = 74$  and  $\text{Mg(OH)}_2 = 106$  )

**$\therefore$  Lime requirement**

$$= \frac{74}{100} \left[ \text{Tem. Ca}^{+2} + 2 \times \text{Tem. Mg}^{+2} + \text{Per. (Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3}) \right]$$

$\text{H}^+ + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2$  ] all in terms of  $\text{CaCO}_3$  eq.  $\times$  volume of water.

**$\therefore$  Soda requirement :**

$$= \frac{106}{100} \left[ \text{Per. (Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2}) + \text{H}^+ - \text{HCO}_3^- \right]$$

All in terms of  $\text{CaCO}_3$  equivalent  $\times$  volume of water.

*Table 2.1 : Calculation of soda-lime requirement*

Constituents	Chemical reactions	Requirement lime/soda	Explanations
Ca(HCO <sub>3</sub> ) <sub>2</sub> , (CaCO <sub>3</sub> ) (Temporary Ca hardness)	Ca(HCO <sub>3</sub> ) <sub>2</sub> + Ca(OH) <sub>2</sub> → 2CaCO <sub>3</sub> ↓ + 2H <sub>2</sub> O	L	It is completely removed, by lime only when reported as CaCO <sub>3</sub> consider it as temporary Ca hardness.
Mg(HCO <sub>3</sub> ) <sub>2</sub> , (MgCO <sub>3</sub> ) (Temporary Mg hardness)	Mg(HCO <sub>3</sub> ) <sub>2</sub> + Ca(OH) <sub>2</sub> → MgCO <sub>3</sub> + CaCO <sub>3</sub> ↓ + 2H <sub>2</sub> O MgCO <sub>3</sub> + Ca(OH) <sub>2</sub> → Mg(OH) <sub>2</sub> ↓ + CaCO <sub>3</sub> ↓	L	It is completely removed by lime When reported as MgCO <sub>3</sub> , consider it as temporary Mg hardness. Since 1 mole requires 2 mole of Ca(OH) <sub>2</sub> , M.F. (multiplication factors) is $2 \times \frac{100}{146}$
Ca <sup>2+</sup> (CaCl <sub>2</sub> , CaSO <sub>4</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> ) (Permanent Ca hardness)	Ca <sup>2+</sup> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> + 2Na <sup>+</sup>	S	Ca <sup>2+</sup> reacts with soda only

$\text{Mg}^{2+}$ ( $\text{MgCl}_2$ , $\text{MgSO}_4$ , $\text{Mg}(\text{NO}_3)_2$ (permanent Mg hardness)	$\begin{array}{l} \text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \\ \text{Ca}^{2+} + \text{Mg}(\text{OH})_2 \\ \xrightarrow{\text{Soda } (\text{Na}_2\text{CO}_3)} \\ \text{CaCO}_3 + 2\text{Na}^+ \end{array}$	L + S	$\text{Mg}^{2+}$ (Permanent hardness) is removed but soluble $\text{Ca}^{2+}$ species produced which is removed by soda, therefore, soda and lime bath required.
$\text{HCO}_3^-$	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \rightarrow \\ \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{CO}_3^{2-}$	Only lime but (-) soda	$\text{CO}_3^{2-}$ is evolved, for every 1 equivalent of $\text{HCO}_3^-$ considered to be 1 equivalent $\text{Na}_2\text{CO}_3$ , production and hence $\text{HCO}_3^-$ to be subtracted from the total requirement of data.
$\text{CO}_2$	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \\ \text{CaCO}_3 + \text{H}_2\text{O}$	L	It is completely removed by lime

Constituents	Chemical reactions	Requirement lime/soda	Explanations
H <sub>2</sub> S	$\text{H}_2\text{S} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaS} + 2\text{H}_2\text{O}$	L	Does not produce hardness but reacts with lime only.
H <sup>+</sup> (free acids like HCl, H <sub>2</sub> SO <sub>4</sub> , etc)	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S	It reacts with lime to give hardness causing soluble Ca <sup>2+</sup> species which consume soda. 2 mole of HCl combine with 1 mole of Ca(OH) <sub>2</sub> , hence M.F. is 100/73
FeSO <sub>4</sub> (Coagulant)	$\text{Fe}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + \text{Fe}(\text{OH})_2$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{Fe}(\text{OH})_3 \downarrow$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S	Fe <sup>2+</sup> reacts with lime and produce Ca <sup>2+</sup> hardness (permanent) which require soda

$\text{Al}_2(\text{SO}_4)_3$ (coagulant)	$\text{Al}_2(\text{SO}_4)_3 + 3 \text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3\downarrow + 3\text{CaSO}_4$ $3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{Na}_2\text{SO}_4 + 3\text{CaCO}_3$	L + S	1 mole of $\text{Al}_2(\text{SO}_4)_3$ reacts with 3 mole of $\text{Ca}(\text{OH})_2$ and gives 3 mole $\text{CaSO}_4$ , M.F. is $3 \times \frac{100}{342} \text{ or } \frac{100}{114} \text{ or } \frac{50}{57}$
$\text{NaAlO}_2$	$\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{OH}^- + \text{Al}(\text{OH})_3\downarrow$	(-) amount subtracted from lime (-L)	On hydrolysis give $\text{OH}^-$ , which is considered 1 equivalent of $\text{Ca}(\text{OH})_2$ . Hence lime requirement is diminished by an amount equivalent of $\text{OH}^-$ formed.
$\text{OH}^-$ (excess of lime in treated water)	$\text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S	Hence, equivalent amount of $\text{OH}^-$ ion is added to the total requirement of $\text{Ca}(\text{OH})_2$ and $\text{Na}_2\text{CO}_3$
$\text{CO}_3^{2-}$	$\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-}$	L	Hence equivalent amount of $\text{CO}_3^{2-}$ is added to the total requirement of $\text{Na}_2\text{CO}_3$ .

**Example 1 : A water sample has the analytical report as under.**

$$\text{MgCO}_3 = 84 \text{ mg/L}$$

$$\text{CaCl}_2 = 55.5 \text{ mg/L}$$

$$\text{KCl} = 20 \text{ mg/L}$$

$$\text{CaCO}_3 = 40 \text{ mg/L}$$

$$\text{Mg}(\text{NO}_3)_2 = 37 \text{ mg/L}$$

Calculate the amount of lime (86% pure) and soda (83% pure) needed for the treatment of 80,000 liters of water. [RTU, ISem Feb, 2010]

**Solution :** Conversion into  $\text{CaCO}_3$  equivalent of hardness producing substance.

S.No.	Substance	Amount of Substance (mg/L)	M.F.	$\text{CaCO}_3$ equivalent
1.	$\text{MgCO}_3$	84	100/84	$84 \times \frac{100}{84} = 100$
2.	$\text{CaCO}_3$	40	100/100	$40 \times \frac{100}{100} = 40$
3.	$\text{CaCl}_2$	55.5	100/111	$55.5 \times \frac{100}{111} = 50$
4.	$\text{Mg}(\text{NO}_3)_2$	37	100/148	$37 \times \frac{100}{148} = 25$
5.	KCl20	20	Does not impart any hardness	

**Lime required :**

$$= \frac{74}{100} \left[ \text{CaCO}_3 + 2 \times \text{Mg}(\text{NO}_3)_2 \right] \text{ as } \text{CaCO}_3 \text{ equivalent} \times \text{volume of water}$$

$$= \frac{74}{100} [40 + 2 \times 100 + 25] \text{ mg/lit} \times 80,000 \text{ lit}$$

$$= \frac{74}{100} [265] \text{ mg/lit} \times 80,000 \text{ lit}$$

$$= 196.1 \text{ mg/lit} \times 80,000$$

$$= 15688000$$

$$\text{or lime required of given quality (i.e. 86\% of purty)} = 15688000 \frac{100}{86}$$

$$= 18241860.47 \text{ mg/lit} = 18.241 \text{ kg}$$

**Soda required :**

$$= \frac{106}{100} [\text{CaCl}_2 + \text{Mg}(\text{NO}_3)_2] \text{ as CaCO}_3 \text{ equivalent} \times \text{volume of water} \times \% \text{ purity}$$

$$= \frac{106}{100} [50 + 25] \text{ mg / lit} \times 80,000 \text{ lit} \times \frac{100}{83} \times \frac{1\text{kg}}{10^6 \text{mg}}$$

$$= \frac{106}{100} [75] \text{ mg / lit} \times 80,000 \text{ lit} \times \frac{100}{83} \times \frac{1\text{kg}}{10^6 \text{mg}}$$

$$= 7662.650.6 \text{ mg/lit}$$

$$= 7.662 \text{ kg}$$

**Example 2 : A water sample on analysis given the following data**

$$\text{Ca}^{+2} = 20 \text{ ppm}$$

$$\text{Mg}^{+2} = 25 \text{ ppm}$$

$$\text{CO}_2 = 30 \text{ ppm}$$

$$\text{HCO}_3 = 150 \text{ ppm}$$

$$\text{K}^+ = 10 \text{ ppm}$$

**Calculate the lime (87% pure) and soda (91% pure) required to soften 1 million litres of water sample**

**Solution :** Calculation of  $\text{CaCO}_3$  equivalent of given impurities

S.No.	Substance	Amount of Substance	M.F.	$\text{CaCO}_3$ equivalent (mg/L)
1.	$\text{Ca}^{+2}$	20 ppm	100/40	$20 \times \frac{100}{40} = 50$
2.	$\text{Mg}^{+2}$	25 ppm	100/24	$25 \times \frac{100}{24} = 104.1$
3.	$\text{CO}_3$	30 ppm	100/44	$30 \times \frac{100}{44} = 68.18$
4.	$\text{HCO}_3$	150 ppm	100/122	$150 \times \frac{100}{122} = 122.9$
5.	$\text{K}^+$	10 ppm	Does not impart any hardness	

**Lime required :**

$$= \frac{74}{100} [\text{Mg}^{+2} + \text{CO}_2 + \text{HCO}_3^- \text{ as CaCO}_3 \text{ equivalent}] \times \text{volume of water}$$

$$= \frac{74}{100} [104.1 + 68.18 + 122.9] \text{mg / lit} \times 10^6 \text{ lit} \times \frac{\text{1kg}}{10^6 \text{mg}}$$

$$= \frac{74}{100} [295.18] \text{mg / lit} \times 10^6 \text{ lit} \times \frac{\text{1kg}}{10^6 \text{mg}}$$

$$= 218.43 \text{mg / lit} \times 10^6 \text{ lit} \times \frac{\text{1kg}}{10^6 \text{mg}}$$

$$= 218.43 \text{kg} \frac{100}{87}$$

$$= 251.06 \text{ kg}$$

$$= \frac{106}{100} [\text{Ca}^{+2} + \text{Mg}^{+2} - \text{HCO}_3^- \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{106}{100} [50 + 104.1 \times 122.9] \text{mg / lit} \times 10^6 \text{ lit}$$

$$= \frac{106}{100} [31.2] \text{mg / lit} \times 10^6 \text{ lit} \times \frac{100}{91} (\% \text{purity}) \times \frac{\text{1kg}}{10^6 \text{mg}}$$

$$= 33.07 \text{mg / lit} \times 10^6 \text{ lit} \times \frac{100}{91} (\% \text{purity}) \times \frac{\text{1kg}}{10^6 \text{mg}}$$

$$= 33.07 \frac{100}{91} \text{kg} = 36.34 \text{kg}$$

**Example 3 :** A sample of water contains following

- (i)  $\text{CO}_2 = 22 \text{ mg/L}$                       (iv)  $\text{MgCl}_2 = 47.5 \text{ mg/L}$   
(ii)  $\text{Ca}(\text{HCO}_3)_2 = 20 \text{ mg/L}$             (v)  $\text{CaSO}_4 = 34 \text{ mg/L}$   
(v)  $\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ mg/L}$     (vi)  $\text{Al}_2(\text{SO}_4)_3 = 57 \text{ mg/L}$

Calculate the amount of lime and soda required for softening of 60,000 litre of water. [RTU Aug, II sem, 2009]

**Solution :** Calculation of  $\text{CaCO}_3$  equivalent hardness producing substance.

Constituent	Amount (mg/lit)	Multiplication factor	$\text{CaCO}_3$ eq. in (mg/lit)
$\text{CO}_2$	22	100/44	$22 \times \frac{100}{44} = 50$
$\text{Ca}(\text{HCO}_3)_2$	20	100/162	$20 \times \frac{100}{162} = 12.34$
$\text{Mg}(\text{HCO}_3)_2$	29.2	100/146	$29.2 \times \frac{100}{146} = 20$
$\text{MgCl}_2$	47.5	100/95	$47.5 \times \frac{100}{95} = 50$
$\text{CaSO}_4$	34	100/136	$34 \times \frac{100}{136} = 25$
$\text{Al}_2(\text{SO}_4)_3$	57	100/114	$57 \times \frac{100}{114} = 50$

### Lime required

$$= \frac{74}{100} \left[ \text{Ca}(\text{HCO}_3)_2 \right] + 2 \times \text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{Al}_2(\text{SO}_4)_3 + \text{CO}_2 \Big] \\ \times \text{volume of water}$$

$$= \frac{74}{100} [12.34 + 2 \times 20 + 50 + 50 + 50] \text{mg / lit} \times 60,000 \text{ lit}$$

$$= \frac{74}{100} [202.34] \times 60,000 = 8983896 \text{mg} = 8.9838 \text{kg}$$

### Soda required

$$= \frac{106}{100} \left[ \text{MgCl}_2 + \text{Al}_2(\text{SO}_4)_3 + \text{CaSO}_4 \right] \times 60,000 \text{ lit}$$

$$= \frac{106}{100} [50 + 50 + 25] \text{mg / lit} \times 60,000 \text{ lit}$$

$$= \frac{106}{100} [125] \times 60,000 = 79,50,000 \text{mg} = 7.950 \text{kg}$$

Example 4 : A sample of water was analysed and found to contain temporary magnesium hardness 25 mg/lit, permanent  $\text{MgCl}_2$  hardness 15 mg/lit and permanent calcium sulphate hardness 20 mg/lit,  $\text{SiO}_2 = 300$  mg/lit. Calculate the lime and soda required for softening 30,000 litre hard water. [RTU, I-sem, 2009]

Solution : Conversion into  $\text{CaCO}_3$  equivalents

Constituent	Amount (mg/lit)	Multiplication factor	$\text{CaCO}_3$ eq. in (mg/lit)
$\text{Mg}(\text{HCO}_3)_2$	25	100/146	$25 \times \frac{100}{146} = 17.12$
$\text{MgCl}_2$	15	100/95	$15 \times \frac{100}{95} = 15.79$
$\text{CaSO}_4$	20	100/136	$20 \times \frac{100}{136} = 14.71$

$\text{SiO}_2$  neither causes hardness, nor is considered for lime-soda requirement.

$\therefore$  Lime required

$$= \frac{74}{100} [2 \times \text{Temporary Mg} + \text{MgCl}_2] \times \text{Volume of water}$$

$$= \frac{74}{100} [2 \times 17.12 + 15.79] \text{mg / lit} \times 30,000 \text{ lit}$$

$$= \frac{74}{100} [50.03] \times 30,000 = 11,10,666 \text{mg} = 1.1107 \text{kg}$$

Soda requirement :

$$= \frac{106}{100} [\text{MgCl}_2 + \text{CaSO}_4] \times \text{Volume of water}$$

$$= \frac{106}{100} [15.79 + 14.71] \text{mg / lit} \times 30,000 \text{ lit}$$

$$= \frac{106}{100} [30.5] \times 30,000 = 9,69,900 \text{mg.} = 0.9699 \text{kg}$$



Solve the Numerical Problems

Calculate the amount of lime required for softening 50,000 litre of hard water containing  $\text{CaCO}_3=25\text{ppm}$ ;  $\text{MgCO}_3=144\text{ppm}$ ;  $\text{CaCl}_2=111\text{ppm}$   $\text{MgCl}_2=95\text{ ppm}$ ;  $\text{Na}_2\text{SO}_4= 15\text{ ppm}$ ;  $\text{Fe}_2\text{O}_3 = 25\text{ ppm}$ .

**Molecular weights:**

$\text{Ca}(\text{HCO}_3)_2 = 162$ ;  $\text{Mg}(\text{HCO}_3)_2=146$ ;  $\text{CaSO}_4= 136$ ;  $\text{MgSO}_4 = 120$ ; ;  $\text{MgCl}_2 = 95$ ;  
 $\text{MgCO}_3 = 84$ ;  $\text{CaCl}_2 = 111$

**Lime required for softening:**

$$= \frac{74}{100} [ \text{Temp. Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- ]$$

**Soda required for softening:**

$$= \frac{106}{100} [ \text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- ]$$

Calculate the amount of lime and soda required for softening 50,000 litre of hard water containing  $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg}$ ;  $\text{Mg}(\text{HCO}_3)_2 = 7.5 \text{ mg}$ ;  $\text{CaSO}_4 = 13.6 \text{ mg}$ ;  $\text{MgSO}_4 = 12.0 \text{ mg}$ ;  $\text{MgCl}_2 = 2.0 \text{ mg}$ ;  $\text{NaCl} = 4.7 \text{ mg}$ .

Molecular weights:

$\text{Ca}(\text{HCO}_3)_2 = 162$ ;  $\text{Mg}(\text{HCO}_3)_2 = 146$ ;  $\text{CaSO}_4 = 136$ ;  $\text{MgSO}_4 = 120$ ;  
 $\text{MgCl}_2 = 95$

### **Lime required for softening:**

$$= \frac{74}{100} [ \text{Temp. Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- ]$$

### **Soda required for softening:**

$$= \frac{106}{100} [ \text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- ]$$

A water sample on analysis gave the following data:

$\text{Ca}^{2+} = 30 \text{ mg/L}$ ;  $\text{Mg}^{2+} = 24 \text{ mg/L}$ ;  $\text{CO}_2 = 24 \text{ mg/L}$ ;  $\text{K}^+ = 10 \text{ mg/L}$

Calculate the quantities of lime (90%) and soda (94%) required to soften one million litres of water sample.

**Lime required for softening:**

$$= \frac{74}{100} [ \text{Temp. } \text{Ca}^{2+} + 2 \times \text{Temp. } \text{Mg}^{2+} + \text{Perm. } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- ]$$

**Soda required for softening:**

$$= \frac{106}{100} [ \text{Perm. } (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- ]$$

A water sample have the following impurities :  $\text{Ca}^{2+} = 20\text{ppm}$ ;  $\text{Mg}^{2+} = 18 \text{ ppm}$ ;  $\text{HCO}_3^- = 183 \text{ ppm}$ ;  $\text{SO}_4^{2-} = 24 \text{ ppm}$ . Calculate the amount of lime and soda needed for softening.

**Lime required for softening:**

$$= \frac{74}{100} [ \text{Temp. } \text{Ca}^{2+} + 2 \times \text{Temp. } \text{Mg}^{2+} + \text{Perm. } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- ]$$

**Soda required for softening:**

$$= \frac{106}{100} [ \text{Perm. } (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- ]$$

Queries are welcome at  
[archanasaxena@skit.ac.in](mailto:archanasaxena@skit.ac.in)

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Management and Gramothan, Jaipur**

**Engineering Chemistry  
For B. Tech I Year  
Students**

**The Water  
Lecture - 7**

**Content:**

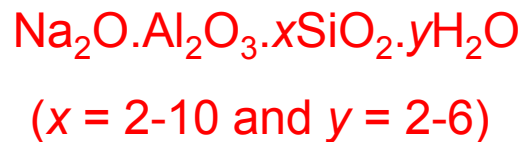
**Zeolite Method of  
Softening of Hard Water**

**Prof. Archana Saxena  
Department of Chemistry  
Swami Keshvanand Institute of Technology  
Management and Gramothan, Jaipur  
(Rajasthan Technical University)**

# Zeolite (Permutit) method of Softening of Hard Water

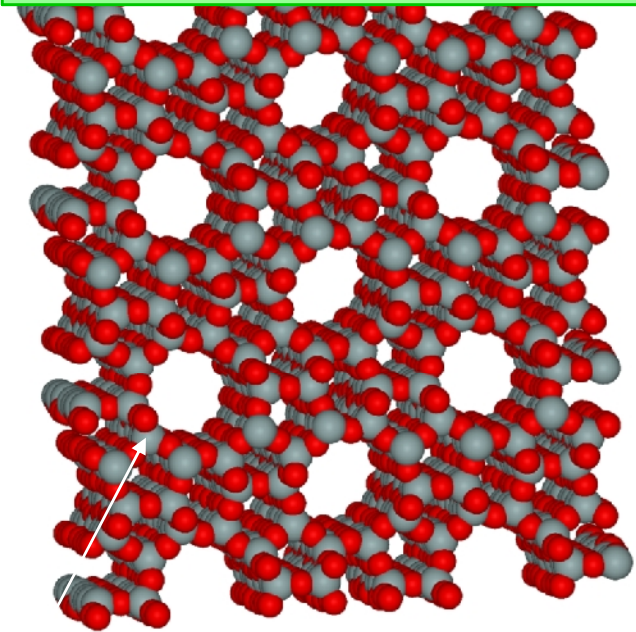
Zeolite is a Hydrated Sodium Alumino Silicate mineral capable of exchanging reversibly its sodium ions with hardness producing ions in water.

The general chemical formula

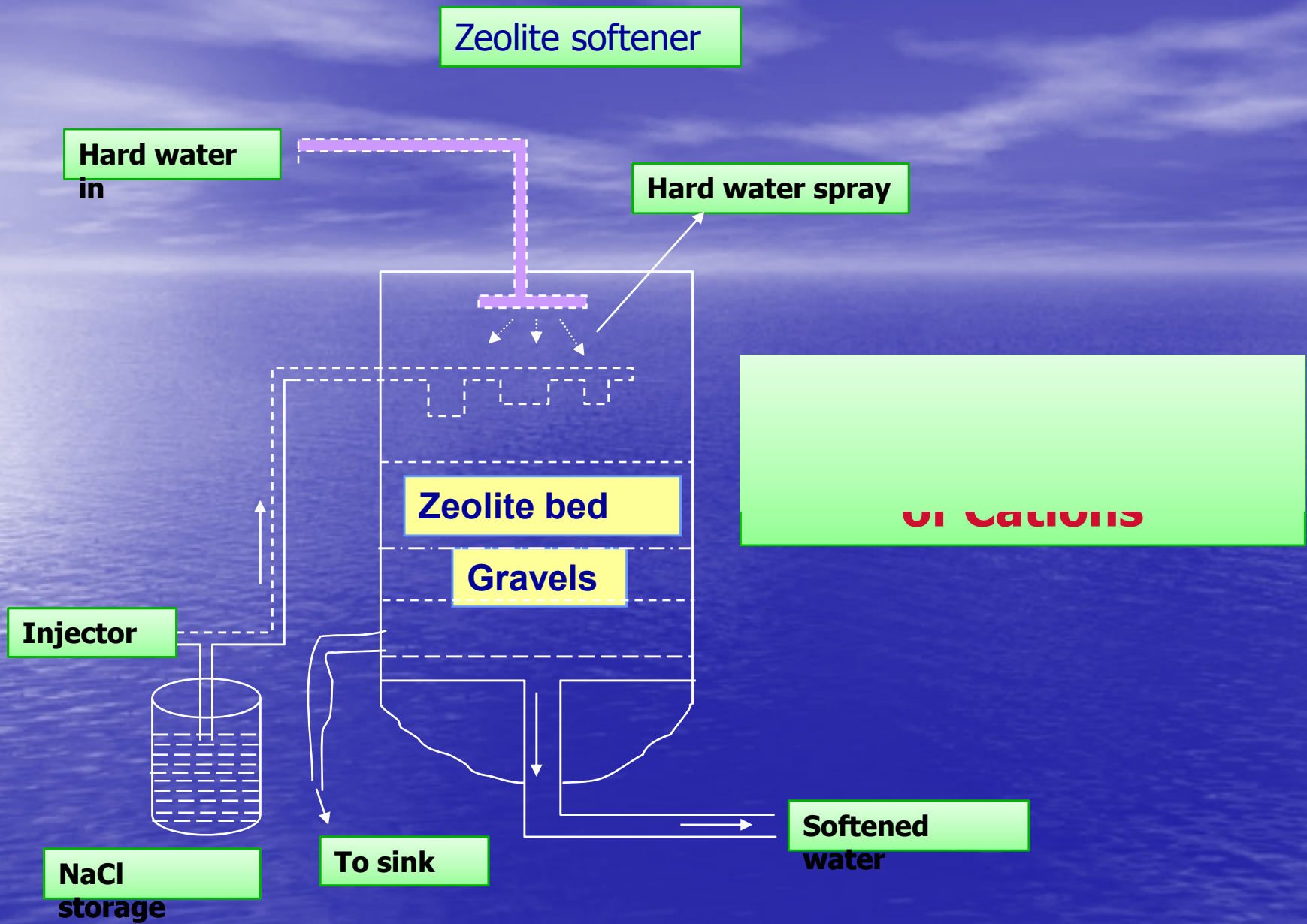


Porosity or cavity size of synthetic zeolite structures can be controlled by varying the Si/Al ratio  
Ion-exchange process of zeolite structure is associated with sodium ions

Porous Structure of zeolite



Micro pores of Zeolite



## Process of softening by Zeolite Method

In this Method hard water is passed through the zeolite bed at a specified rate. The hardness causing ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  are retained by the zeolite bed as  $\text{CaZ}$  and  $\text{MgZ}$  respectively; while the outgoing water contains sodium salts. The following reactions takes place during softening process

### Removal of Temporary Hardness



### Removal of Permanent Hardness



## Regeneration of Zeolite Bed

After some time when all the pores of zeolite bed are clogged it is said to be exhausted and needs regeneration. The process of softening is stopped and zeolite bed is treated with 10% brine. All the CaZ/ MgZ is again revived by reversibly exchanging Ca/Mg with Na ions of brine

### Reactions of Regeneration



**Used  
Zeolite**

**10% brine  
solution**

**Regenerate  
d Zeolite**

**Washings  
drained**

## Limitations of Zeolite process

1. Turbid or oily water can not be used as it clogs the pore.
2. The ions such as  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  forms stable complex with Zeolite which can not be regenerated
3. Acidic water can not be treated with this method since acid will hydrolyze  $\text{SiO}_2$  forming silicic acid.

## Advantages of Zeolite process

## Disadvantages of Zeolite process

1. Soft water contains more sodium salts than in lime soda process.
2. It replaces only  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{Na}^{+}$  but leaves all the other ions like  $\text{HCO}_3^{-}$  and  $\text{CO}_3^{2-}$  in the softened water (then it may form  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  which releases  $\text{CO}_2$  when the water is boiled and causes corrosion).
3. It also causes caustic embitterment when sodium carbonate hydrolyses to give  $\text{NaOH}$

The background is a deep blue gradient, transitioning from a lighter blue at the top to a darker blue at the bottom. A thin, white, wavy line representing a horizon or clouds is visible near the top. In the center, there is a white rectangular box with a slight 3D effect, containing the text.

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**Engineering Chemistry  
For B. Tech I Year Students  
The Water  
Lecture - 8**

**Contents:**

**Ion Exchange Method of  
Softening of Hard Water**

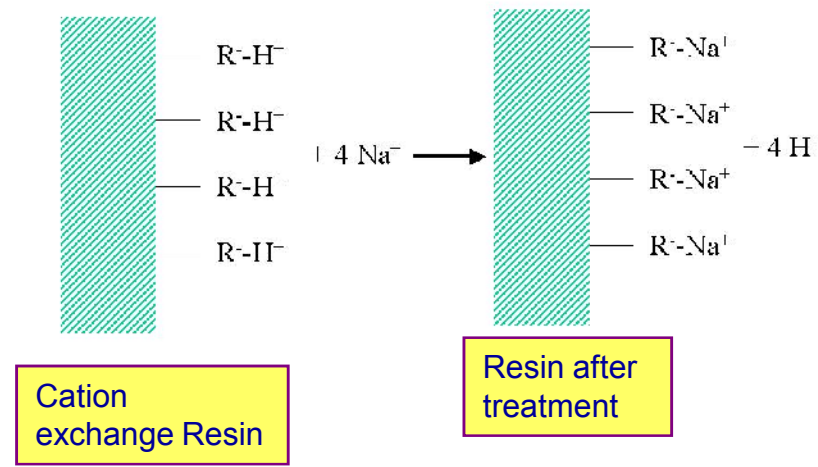
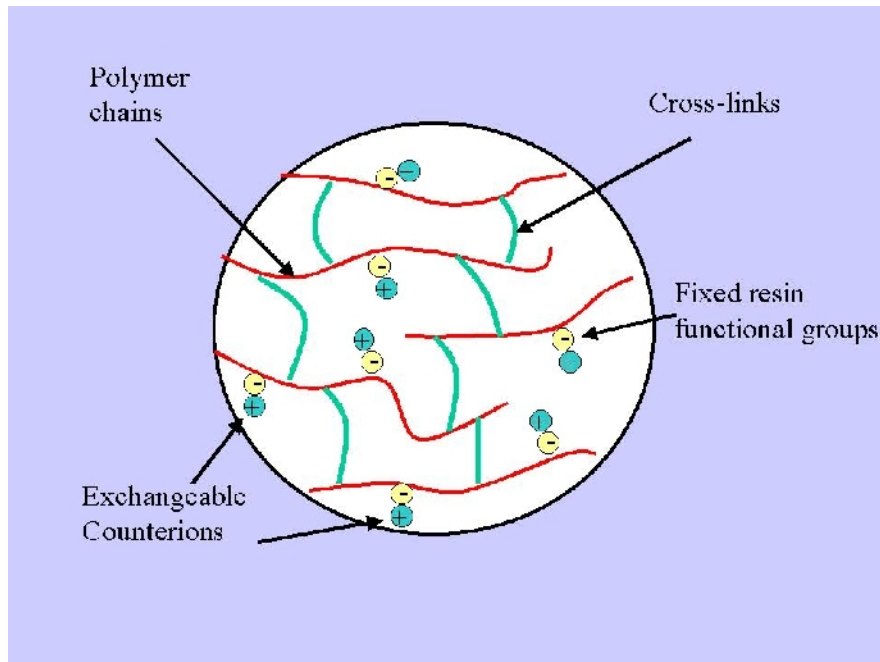
**Prof. Archana Saxena  
Swami Keshvanand Institute of Technology  
Management and Gramothan, Jaipur  
(Rajasthan Technical University)**

# WATER SOFTENING

## Ion exchange or deionization or demineralization

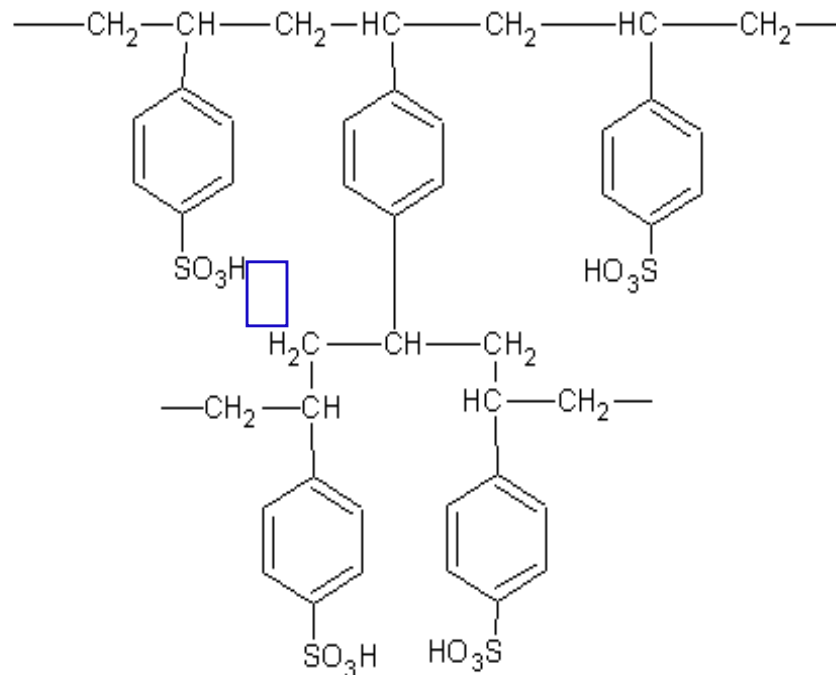
**process:** Ion-exchange resins are widely used in different separation, purification, and decontamination processes. The most common examples are water softening and water purification.

*Ion-exchange resins are insoluble, cross linked, long chain organic polymer with micro porous structure and the functional groups attached to the chains are responsible for the ion exchange properties.*



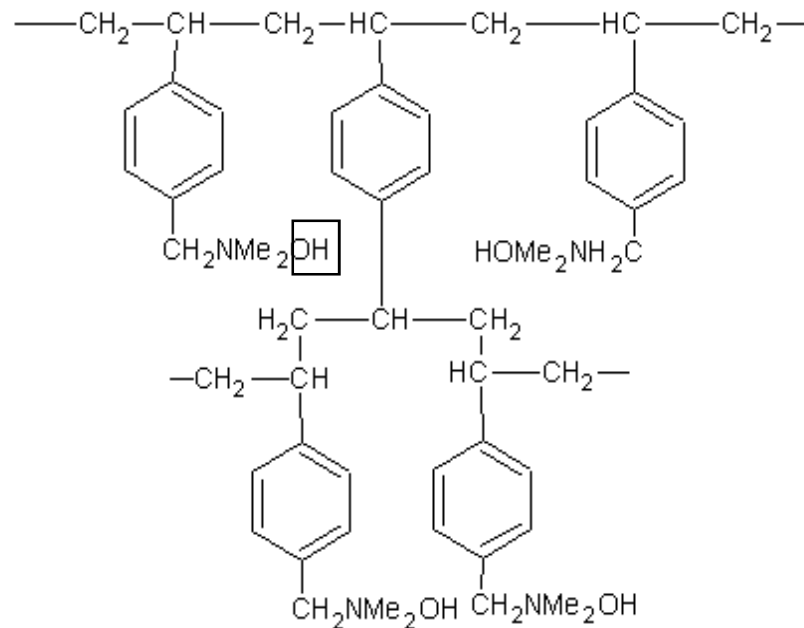
Resins containing acidic functional groups ( $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ) are capable of exchanging their  $\text{H}^+$  ions with other cations which comes in their contacts, known as a **cation exchange resins** ( $\text{RH}^+$ ).

e.g. *styrene-divinyl benzene copolymer*, which on sulphonation and carboxylation, become capable to exchange their hydrogen ions with the cations in the water.

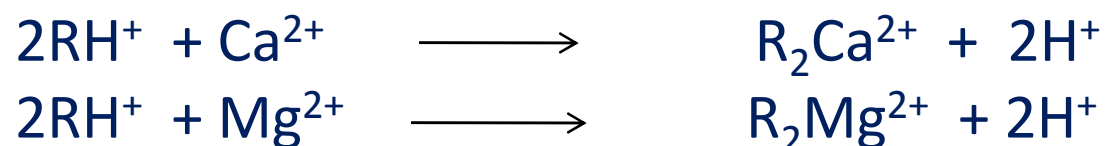


Resins containing basic functional groups ( $-\text{NR}_2^+\text{OH}^-$ ) are capable of exchanging their anions with other anions which comes in their contacts, known as a **Anion exchange resins ( $\text{ROH}^-$ )**.

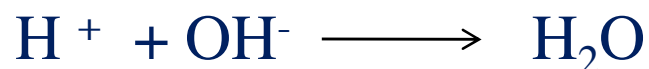
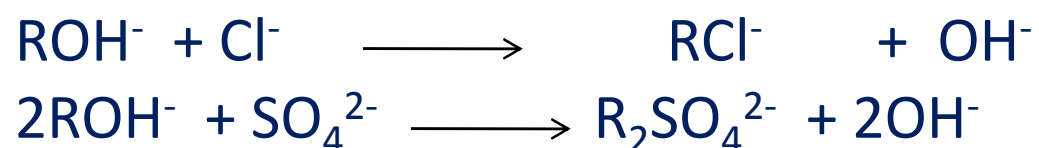
They are styrene divinyl benzene or amine-formaldehyde copolymerization which contains quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These after treated with dil  $\text{NaOH}$  becomes



**Process:-** The hard water is passed first through cation exchange column, which removes all the cations from it and equivalent amount of hydrogen ions are released from this column to water:



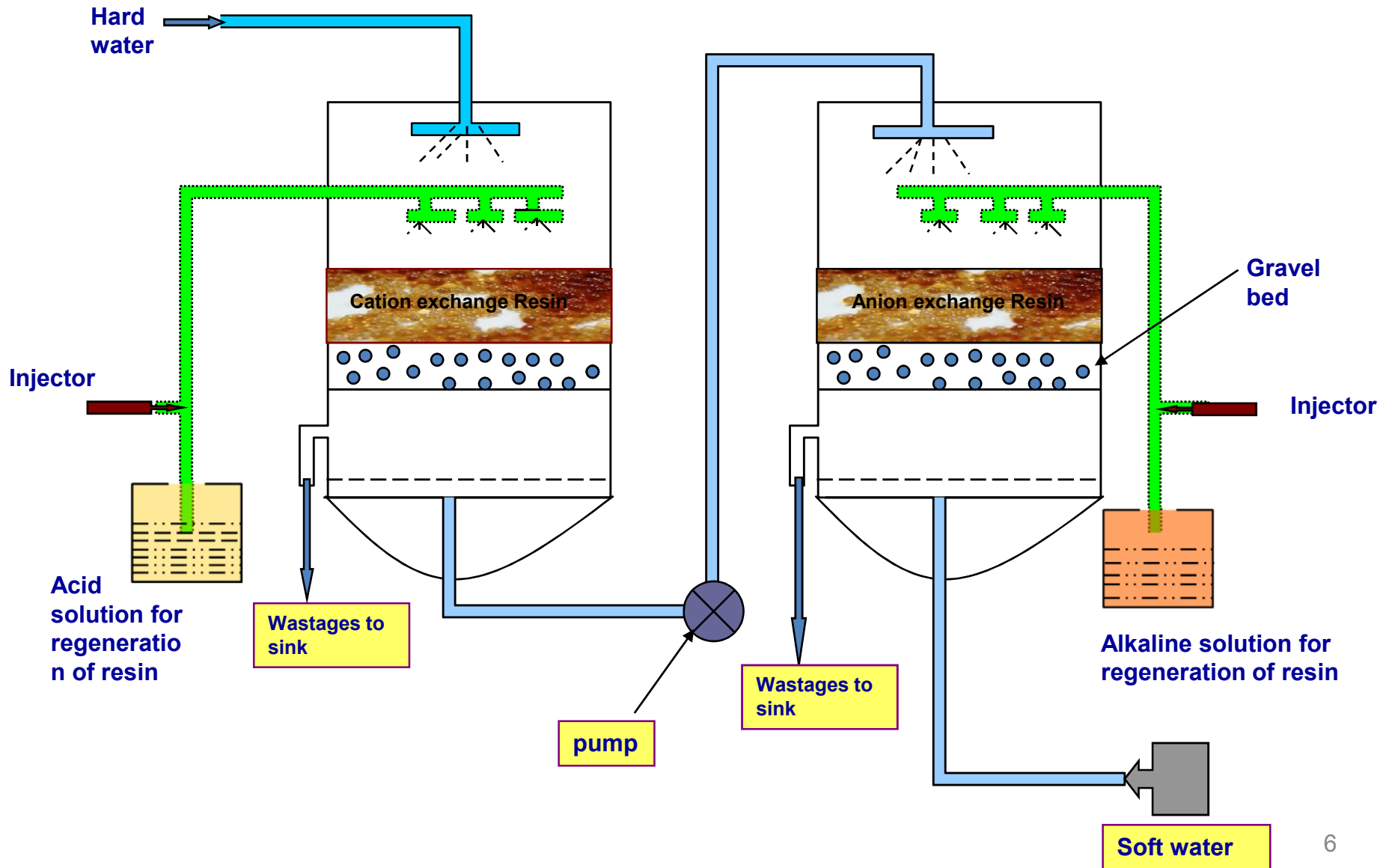
After cation exchange column the hard water is passed through anion exchange resin column, which remove all the anions from it and equivalent amount of hydroxide ions are released from this column to water :



Thus water coming out from the exchange is free from cations as well as anions.

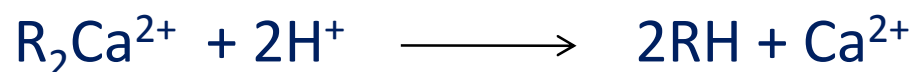
**Ion free water is known as deionized or demineralised water.**

## Ion exchange purifier or softener

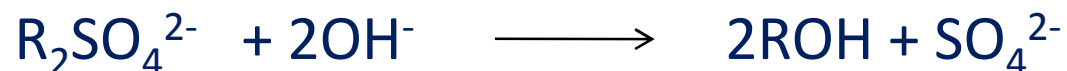


# Regeneration:

Cation exchange column is regenerated by passing a solution of dil HCl or dil H<sub>2</sub>SO<sub>4</sub>. The regeneration can be represented as



Exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as



## **Advantages:**

- Can be used to soften highly acidic or alkaline waters.
- It produces water of very low hardness.

## **Disadvantages:**

- The equipment is costly
- Expensive chemicals are needed
- Output of the process is reduced if water contains turbidity.(turbidity must be below 10 ppm)