

**Hardness:** Water which does not produce lather with soap solution readily, but forms a white scum (mass) is called hard water. The soap consuming capacity of water is called hard water.

**Hard water consumes a lot of soap:** This is due to the presence of salts of metal ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  dissolved in water. Such metal salts react with soap (sodium or potassium salt of higher fatty acid like oleic acid, palmitic acid, stearic acid) to form insoluble white scum.



**Difference between hard water and soft water:**

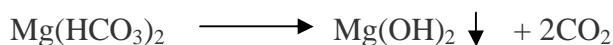
S.No	Hard Water	Soft water
1	Water which does not produce lather with soap solution readily but forms a white scum is called hard water	Water which easily lathers with soap solution is called soft water
2	The presence of calcium and magnesium salts in water forms hard water	The absence of calcium and magnesium salts in water leads to soft water
3	Hard water causes wastage of soap due to depressed cleansing and detergent action Presence of calcium and magnesium salts results in elevated boiling point of water; thus more fuel and time are required for cooking	Soft water lathers easily and does not result in wastage of soap. It also does not result in wastage of fuel and time during cooking due to absence of calcium and magnesium salts.

**Classification of hard water:**

Hardness is of two types:

**1. Temporary hardness:** This type of hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium and other heavy metals and the carbonate of iron.

Thus the salts responsible for temporary hardness are  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ . It is also known as carbonate hardness or alkaline hardness. Alkaline hardness is due to presence of bicarbonate, carbonate and hydroxides of the hardness producing metal ions. Temporary hardness can be removed by boiling of water when bicarbonates are decomposed yielding insoluble carbonates or hydroxides which are deposited as a crust at the bottom of the vessel.



**2. Permanent hardness:** It is due to the presence of dissolved chlorides and sulphates of calcium and magnesium, iron and other heavy metals. Hence the salts responsible for permanent hardness of water are  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc. Permanent hardness cannot be removed by boiling. It is also known as non-carbonate or non-alkaline hardness. It can be removed by following processes:

- (i) **Lime-soda process:**
- (ii) **Zeolite process:**
- (iii) **Ion-exchange process**
- (iv) **Reverse Osmosis**

**3. Total hardness:** Temporary hardness + Permanent hardness

**Advantages and disadvantages of hard water:**

S.No	Advantages of hard water	Disadvantages of hard water
1	Hard water tastes better. The dissolved calcium in water is beneficial for stronger bones and teeth in children.	Hard water produces scum with soap. Washing and detergent efficiency of soap decreases and the economy decreases. Cooking with Hard water results in more fuel consumption and more time consumption due to elevated boiling point of hard water.

**Degree of hardness**

Hardness of water is expressed in equivalents amounts of  $\text{CaCO}_3$  because it forms the insoluble precipitate which can be removed easily in water treatment and also because its molecular mass is 100 (which makes calculations easier).

Equivalent of  $\text{CaCO}_3$  (mg/L) or (ppm) =

(Strength of hardness producing substance mg/L) x (Molecular weight of  $\text{CaCO}_3/2$ )

Molecular weight of substance / Valency of Substance

**Units of Hardness:**

- i. **Part per million (ppm)** It is defines as the number of parts by weight of calcium carbonate ( $\text{CaCO}_3$ ) present per million ( $10^6$ ) parts by weight of water.  
1 ppm = 1 part of  $\text{CaCO}_3$  equivalents hardness in ( $10^6$ ) parts of water
- ii. **Milligrams per litre (mg/L).** It is defines as the number of milligrams of  $\text{CaCO}_3$  present in one litre of water.  
1 ppm = 1mg/L
- iii. **Degree Clarke ( $^\circ\text{Cl}$ ).** It is defines as the parts of  $\text{CaCO}_3$ equivalen hardness per 70,000 parts of water.  
 $^\circ\text{Cl} = 1$  part of  $\text{CaCO}_3$  per 70000 parts of water
- iv. **Degree French ( $^\circ\text{Fr}$ ).** It is defines as the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.  
 $^\circ\text{Fr} = 1$  part of  $\text{CaCO}_3$  per  $10^5$  parts of water

**Relationship between various units of hardness:**

$$1\text{ppm} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl} = 1\text{mg/L}$$

### Water Softening

Processes involved in removal of temporary and permanent hardness is called as “softening of water”. It is very essential process since hard water is unsuitable for domestic and industrial use. Use of hard water for generating steam in boilers so as to generate electricity results in problems like sludge formation, priming, foaming, boiler corrosion and caustic embrittlement.

**Boiler Hard water** can be removed by two ways:

1. **External Treatment:** Treatment of hard water is done before its entry into the boiler. This involves lime-soda, zeolite and ion exchange process. All are preventive methods.
2. **Internal treatment:** Treatment of raw water is done inside the boiler by two processes.
  - a. Appropriate chemicals are added to the boiler water to precipitate the scale forming impurities in the form of sludges which can be later removed.
  - b. Cations causing hardness are converted into compounds which will stay in dissolved form in water and thus do not cause any harm.

The processes involved are Colloidal conditioning, carbonate conditioning, phosphate conditioning and calgon conditioning.

Difference b/w Internal and Colloidal conditioning

S.No	Internal Treatment	External Treatment
1.	These are corrective methods	These are preventive methods
2.	It is carried out inside the boiler	It is carried out outside the boiler, before the entry of water into the boiler.
3.	Includes Colloidal conditioning, carbonate conditioning, phosphate conditioning and calgon conditioning	Includes lime-soda, zeolite and ion exchange process

### Lime soda process:

- The basic principle of this process is to chemically convert all the soluble hardness causing salts of calcium and magnesium into insoluble precipitates which can then be removed by settling and filtration.
- Lime  $[\text{Ca}(\text{OH})_2]$  and soda ash  $(\text{Na}_2\text{CO}_3)$  is added to facilitate precipitation. The precipitates thus formed are  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{Al}(\text{OH})_3$ . These are then filtered off.
- But the precipitates formed at room temperature are not coarse and hence do not settle down and thereby cause difficulty in filtration.
- To facilitate precipitation, addition of lime is done at high temperature. This is followed by addition of Coagulants like Alum  $[\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$ , Aluminum sulphate  $[\text{Al}_2(\text{SO}_4)_3]$  or Sodium aluminate  $[\text{NaAlO}_2]$ . By this process coarse precipitate are formed which can then be filtered off.
- Thus there are two methods of Lime soda: Cold Lime process and Hot Lime process. Both operate under the same principle but their difference is as follows:

**Difference**

<b>Cold lime process</b>	<b>Hot lime process</b>
(i) It operates at room temperature (25°C to 30°C)	(i) It operates at 90°–100°C.
(ii) It is a slow process.	(ii) It is a fast process.
(iii) Coagulants are required like $\text{Al}_2(\text{SO}_4)_3$ .	(iii) No coagulant is required.
(iv) Dissolved gases are not removed.	(iv) Dissolved gases are removed due to high temperature.
(v) Softened water contains hardness of about 60 ppm.	(v) Softened water contains hardness of about 15-30 ppm.
(vi) Filtration of ppts is a difficult task.	(vi) Filtration at raised temperature is easy because viscosity of liquid to be filtered becomes low.

- Following are the reactions that takes place in this process when the following substituent is present in hard water:

Constituent	Reactions	Lime/Soda required
$\text{Ca}(\text{HCO}_3)_2$	$\text{Ca}(\text{OH})_2 + \text{Ca}(\text{HCO}_3)_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	1Lime
$\text{Mg}(\text{HCO}_3)_2$	$2\text{Ca}(\text{OH})_2 + \text{Mg}(\text{HCO}_3)_2 \rightarrow \text{Mg}(\text{OH})_2 + 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	2Lime
$\text{Mg}^{2+}$	$\text{Ca}(\text{OH})_2 + \text{Mg}^{2+} \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L S
$\text{MgCl}_2$	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCl}_2$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$	
$\text{MgSO}_4$	$\text{MgSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaSO}_4$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	1lime+1Soda
$\text{Ca}^{2+}$ $\text{CaSO}_4$	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	1Soda
$\text{CaCl}_2$	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{NaCl}$	1Soda
$\text{HCO}_3^-$ [ $\text{NaHCO}_3$ ]	$\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	L-S

**Advantage of L-S Process:**

- It is very economical
- Treated water is alkaline and has less corrosion tendencies
- It removes not only hardness causing salts but also minerals.
- Iron and magnesium are also removed from water to some extent

**Disadvantage of L-S Process:**

- The process results in sludge formation
- The process cannot be used for high pressure boilers

**Calculation for Lime/ Soda Requirement:**

$$\text{Lime requirement} = \frac{\text{MW of lime}}{\text{MW of CaCO}_3} [\text{Hardness in ppm}] \times \text{Volume of water (L)}$$

$$\text{Soda requirement} = \frac{\text{MW of soda}}{\text{MW of CaCO}_3} [\text{Hardness in ppm}] \times \text{Volume of water (L)}$$

MW of lime= 74, MW of soda= 106

**NUMERICALS on L-S Process:**

**Q1. Calculate the amount of lime required for softening of 5000L of hard water containing 72ppm of  $\text{MgSO}_4$ .**

Ans: 72 ppm of  $\text{MgSO}_4 = 72 \times 100/120 = 60\text{ppm}$  of  $\text{CaCO}_3$  equivalent.

Lime requirement =  $74/100 \times 60 \times 5000 \text{ mg} = 222\text{g}$ .

**Q2. Calculate the amount of lime required for softening 50,000L of hard water containing  $\text{Mg}(\text{HCO}_3)_2 = 144\text{ppm}$ ,  $\text{Ca}(\text{HCO}_3)_2 = 25\text{ppm}$ ,  $\text{MgCl}_2 = 95 \text{ ppm}$ ,  $\text{CaCl}_2 = 111\text{ppm}$ ,  $\text{Fe}_2\text{O}_3 = 25 \text{ ppm}$ ,  $\text{Na}_2\text{SO}_4 = 15 \text{ ppm}$**

Ans:

Constituent	Reactions	Lime/Soda required
$\text{Ca}(\text{HCO}_3)_2$	$\text{Ca}(\text{OH})_2 + \text{Ca}(\text{HCO}_3)_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	1Lime
$\text{Mg}(\text{HCO}_3)_2$	$2\text{Ca}(\text{OH})_2 + \text{Mg}(\text{HCO}_3)_2 \rightarrow \text{Mg}(\text{OH})_2 + 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	2Lime
$\text{CaCl}_2$	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{NaCl}$	1Soda
$\text{MgCl}_2$	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCl}_2$	1Lime

$\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  do not cause hardness and hence do not require L or S

Hardness causing salt	Amount (ppm)	Multiplication factor	$\text{CaCO}_3$ equivalent
$\text{Mg}(\text{HCO}_3)_2$	144	100/146	$144 \times 100/146 = 98.6\text{ppm}$
$\text{Ca}(\text{HCO}_3)_2$	25	100/162	$25 \times 100/162 = 15.4 \text{ ppm}$
$\text{MgCl}_2$	95	100/95	$95 \times 100/95 = 100 \text{ ppm}$

Lime requirement =  $74/100 (2 \times 98.6 + 15.4 + 100) \text{ mg/L} \times 50,000\text{L} = 1156200\text{mg} = 11.57\text{kg}$

**Q3. A water sample on analysis gave the following results:**

$\text{Ca}^{2+} = 30\text{mg/L}$ ;  $\text{Mg}^{2+} = 18\text{mg/L}$ ,  $\text{K}^+ = 19.5\text{mg/L}$ ,  $\text{HCO}_3^- = 122\text{mg/L}$ ,  $\text{Cl}^- = 35.5\text{mg/L}$ ,  $\text{SO}_4^{2-} = 48\text{mg/L}$

**Calculate the total hardness and alkalinity present in water sample.**

**Also, calculate the lime soda required for softening 1L sample of the hard water.**

Ans: Total hardness =  $[\text{Ca}^{2+} + \text{Mg}^{2+} + \text{HCO}_3^-] = 30 \times 100/40 + 18 \times 100/24 + 122 \times 100/122 = 250\text{ ppm}$

Alkalinity =  $[\text{HCO}_3^-] = 122 \times 100/122 = 100\text{ppm}$

Lime required =  $74/100[\text{Mg}^{2+} + \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} \times V \text{ (L)} = 74/100[18 \times 100/24 + 122 \times 100/122] \times 1\text{ L} = 129.5\text{mg}$

Soda required =  $106/100[[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} \times V \text{ (L)} = 106/100[30 \times 100/40 + 18 \times 100/24 - 122 \times 100/122] \times 1\text{ L} = 53\text{mg}$

**Q4. Calculate the amount of lime and soda needed for softening a water sample containing 36ppm  $\text{Mg}^{2+}$ , 20ppm  $\text{Ca}^{2+}$  and 183ppm  $\text{HCO}_3^-$**

Ans:

Lime required =  $74/100[\text{Mg}^{2+} + \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 74/100[36 \times 100/24 + 183 \times 100/122] \text{ mg/L} = 222\text{ppm}$

Soda required =  $106/100[[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 106/100[36 \times 100/40 + 20 \times 100/24 - 183 \times 100/122] \text{ mg/L} = 53\text{ppm}$

**Q5. A water sample contains 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 lime and soda required for softening**

Ans:

Lime required =  $74/100[\text{Mg}^{2+} + \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 74/100[18 \times 100/24 + 183 \times 100/122] \text{ mg/L} = 166.5\text{ppm}$

Soda required =  $106/100[[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ in CaCO}_3 \text{ equiv.}] \text{ mg/L} = 106/100[20 \times 100/40 + 18 \times 100/24 - 183 \times 100/122] = -26.5\text{ppm}$

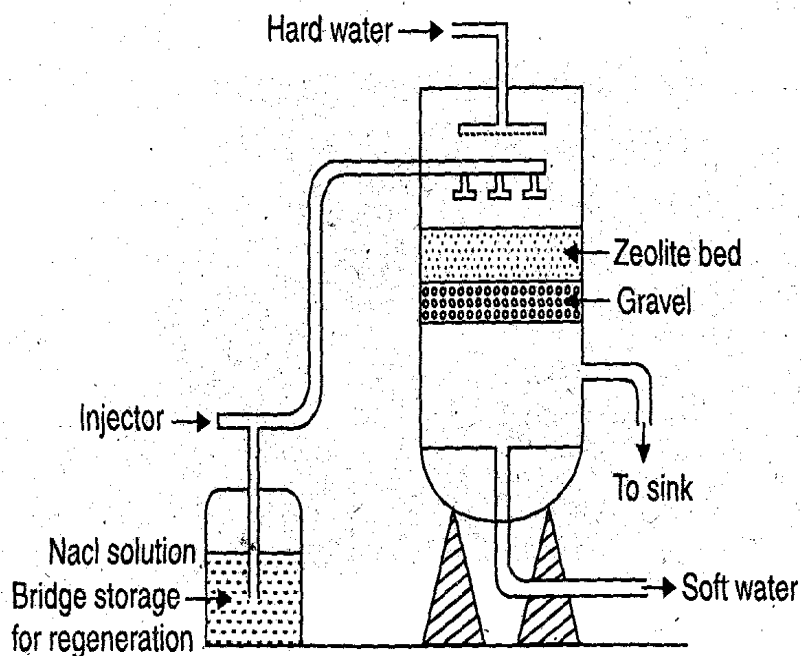
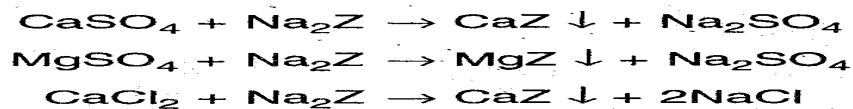
Soda is hence not required

**Zeolite or permutite process:**

- Zeolites are naturally occurring hydrated sodium aluminosilicate minerals capable of exchanging reversibly its sodium ions for the ions present and responsible of formation of hard water.
- Permutite-is the trade name given to sodium zeolites.
- Chemical formula of zeolite is  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot x\text{H}_2\text{O}$ .  $y=2-10$ ,  $x=2-6$   
When  $y = 2$ , we get  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ .
- For simplicity, we can write zeolites as  $\text{Na}_2\text{Z}$  Where  $\text{Z} = \text{OAl}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$
- Zeolites are of two types: Natural zeolites and synthetic zeolites.

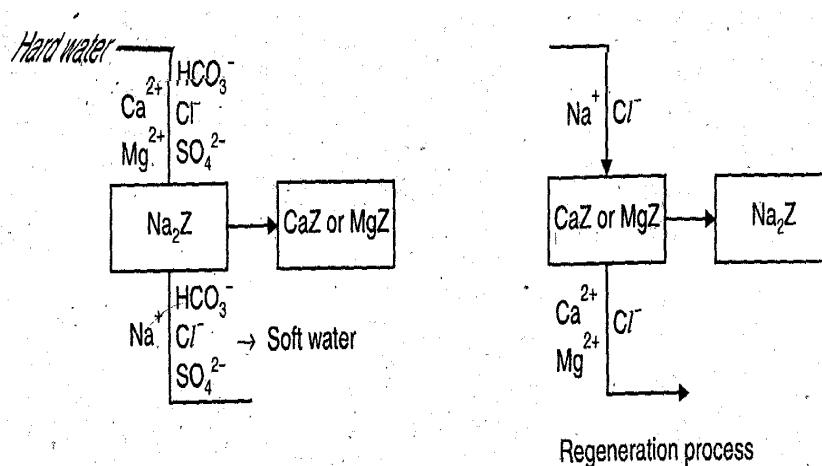
**Process involved:**

In this method, hard water is passed through a bed of permutite contained in a cylindrical vessel. The water percolates at a specified rate through the bed. The loose sodium ions of the zeolite are exchanged for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions of hard water. Thus calcium and magnesium salts get removed in the form of the insoluble zeolites and soft water is collected.

**Zeolite softener**

This process removes both temporary and permanent hardness. After long use, the zeolite bed gets exhausted. It can be regenerated by using chemicals, such as brine solution, NaCl or sodium nitrate or sodium sulphate. However, NaCl is preferred on account of its

cheapness, easy availability and low molecular weight. The products 'calcium chloride and magnesium chloride are highly soluble in water and can be easily washed out. The softening and regeneration process can be represented as follows:



### Merits of Zeolite Process

1. The equipment used is compact. So time saving process.
2. No impurities are precipitated. So no sludge formation occurs.
3. Requires less time for softening
4. Requires less skill for maintenance.

### Demerits

- a. Treated water contains more number of Na ions
- b. This method leaves acidic ions ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions) in soft water which if enters a boiler, generates  $\text{CO}_2$  which leads to corrosion.
- c. Turbid water can't be made soft by this process because it leads to clogging of the holes of zeolite bed.

### Numericals on Zeolite process

**Q1. The hardness of 1000L of a sample of water was removed by passing it through a zeolite softener. The zeolite softener required 30L of NaCl containing 1.5g/L of NaCl for regeneration. Find the hardness of water sample.**

Ans:

Quantity of NaCl in 30L of NaCl solution =  $1.5\text{g/L} \times 30\text{L} = 45\text{g}$

$\text{CaCO}_3$  equivalent of NaCl =  $45 \times [(100/2)/(58.5/1)] = 45 \times 50/58.5 = 38.46\text{gm equiv.}$

1000L of water sample is contains 38.46gm equiv of  $\text{CaCO}_3$  equiv.

1L of water sample contains  $38.46 \times 1000\text{mg}/1000\text{L} = 38.46\text{ ppm}$

Hardness of water sample = 38.46ppm

**Q2. An exhausted zeolite softener was regenerated by passing 150L of NaCl solution having strength of 1.5g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 600 ppm.**

Ans:

Quantity of NaCl in 150L of NaCl solution =  $1.5\text{g/L} \times 150\text{L} = 225\text{g}$



$\text{CaCO}_3$  equivalent of NaCl =  $225 \times [(100/2)/(58.5/1)] = 225 \times 50/58.5 = 192.308 \text{g equiv.}$

Hardness of water = 600ppm

i.e 600mg of  $\text{CaCO}_3$  equiv is present in 1L of water

$192.308 \times 1000 \text{ mg of CaCO}_3 \text{ is present in } 192308/600 = 320.5 \text{ L}$

**Q3. A zeolite softener was 90% exhausted by removing the hardness completely when 10,000L of hard water sample was passed through it. The exhausted zeolite bed required 200L of 3% NaCl solution for its complete regeneration. Calculate the hardness of water solution.**

Ans:

Quantity of NaCl in 200L of 3% NaCl solution =  $3/100 \times 1000 \times 200 \text{L} = 6000 \text{g}$

$\text{CaCO}_3$  equivalent of NaCl =  $6000 \times [(100/2)/(58.5/1)] = 6000 \times 50/58.5 = 5128 \text{g equiv.}$

90% of 10000 L of water = 5128g equiv =  $5128 \times 1000 \text{mg equiv}$

1L of water =  $[5128 \times 1000]/[90/100 \times 10000] = 569.8 \text{ mg/L} = 569.8 \text{ ppm}$

Hardness = 569.8 ppm

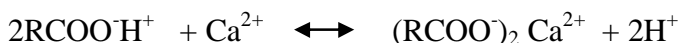
**Ion –exchange method**

Ion exchange is a process by which ions held on a porous, essentially insoluble solid (resin) are exchanged for ions in solution that is brought in contact with it.

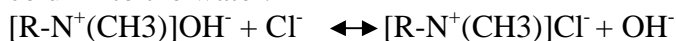
Ion exchange resins are insoluble, cross linked, high molecular weight organic polymers having a porous structure. The functional groups attached to the chains are responsible for the ion exchange properties.

**Process:**

The hard water is passed through a cation exchange column. All cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  etc are removed by the resin and equivalent amount of  $\text{H}^+$  ions are released from the column to the water.



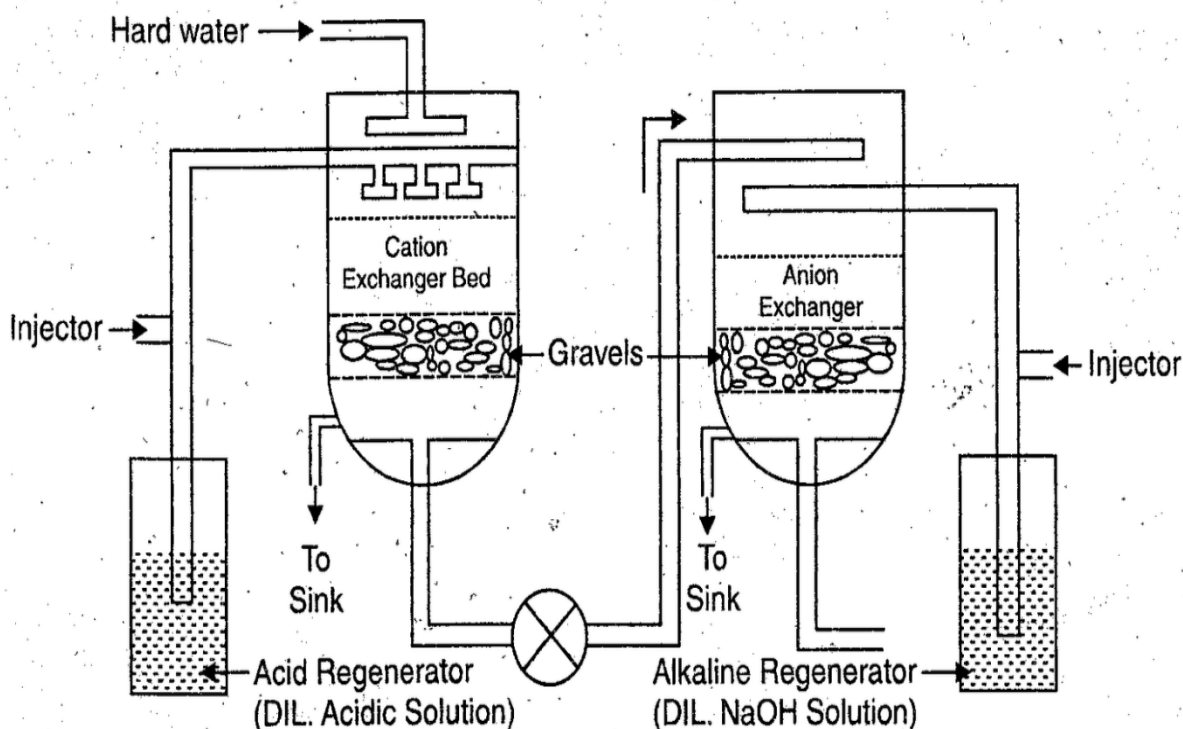
After passing through the cation exchange column, the hard water is passed through anion exchange column, when all the anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  etc present in hard water are removed and taken up by the resin. An equivalent amount of  $\text{OH}^-$  is released from this column to the water.



The  $\text{H}^+$  and  $\text{OH}^-$  ions released from the cation exchange resin and the anion exchange resin respectively combine to give water molecule.



Such water produced is free from any ions; hence is known as demineralised water. Since it is free from any ions, acidity or alkalinity, it is pure like distilled water.



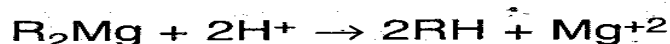
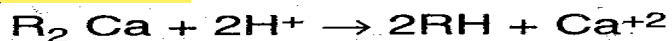
**Demineralization of water by ion exchange process**

**Regeneration**

During process, both cation and anion exchange the resins get exhausted i.e capacity to exchange  $H^+$  and  $OH^-$  ions is lost.

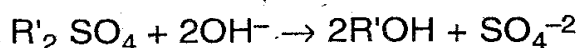
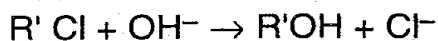
The cationic resins can be generated by passing solution of dil. HCl or  $H_2SO_4$  through first the 1<sup>st</sup> column.

The regeneration reactions are:



Washing the column with deionized water releases the  $Ca^{2+}$ ,  $Mg^{2+}$  ions or  $Cl^-$ ,  $SO_4^{2-}$  ions into the sink.

Similarly the anion exchange resins can be regenerated by passing solution of dil. NaOH through the second column and regeneration is represented as:



The column is washed with deionized water and ions like  $Na^+$ ,  $Cl^-$ ,  $SO_4^{2-}$  are released into the sink.

Advantages and disadvantages of ion exchange process are:

Advantages	Disadvantages
The ion exchange process can be used to soften highly acidic or alkaline waters	Very costly process as equipment and chemicals are costly
The process produces water of very low hardness (<2ppm). Very good for use in high pressure boilers	Presence of turbidity reduces the efficiency of the process

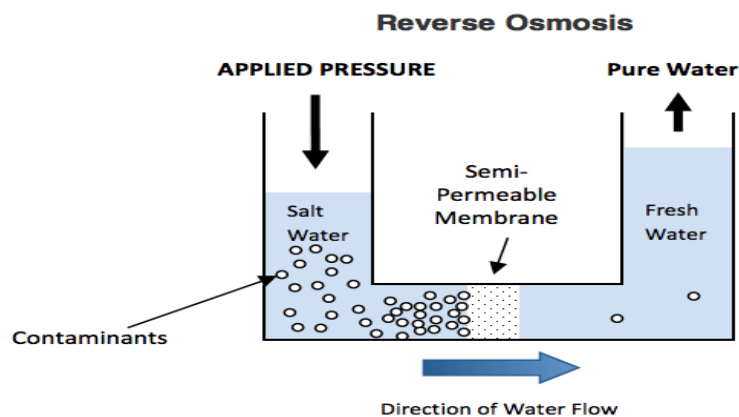
For water to be used for domestic purpose, water softening by ion exchange process will include only cation exchange resin. This is because, only cations responsible for hardness like  $Ca^{2+}$ ,  $Mg^{2+}$  etc need to be removed. Regeneration is carried out by using inexpensive brine or NaCl solution.

**Reverse Osmosis (RO):**

Reverse Osmosis is a process where water is demineralized using a semi permeable membrane at high pressure. Reverse osmosis is osmosis in reverse.

A semi permeable membrane is a selective membrane which does not permit the passage of dissolved solute particles.

Osmosis is the phenomenon by which water or any solvent starts to flow from a region of low concentration to high concentration when the two solutions are separated by a semi permeable membrane. The flow continues till the concentration is equal on both sides of the membrane. This is most commonly observed in plants. If you don't water your plants they wilt. A plant cell is a semi permeable (water flows through the membrane but salts don't) membrane with the living stuff on the inside in a salt solution. Water is drawn into the cell from the outside because pure water will move across a semi permeable membrane to dilute the higher concentration of salt on the inside. This is how water is drawn in from the ground when you water your plants. If you salt your plants (over fertilize or spill some salt on the grass), the plant will wilt because the salt concentration on the outside of the cell is higher than the inside and water then moves across the membrane from the inside to the outside. To reverse this process, you must overcome the osmotic pressure equilibrium across the membrane because the flow is naturally from dilute to concentrate. We want more pure water so we must increase the salt content in the cell (concentrate side of the membrane). To do this we increase the pressure on the salty side of the membrane and force the water across. The amount of pressure is determined by the salt concentration. As we force water out, the salt concentration increases requiring even greater pressure to get more pure water.



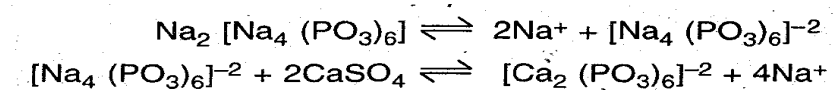
**Diagrammatic representation of Reverse Osmosis**

**Advantage:**

1. It is simple and reliable process of water softening.
2. It is not expensive.
3. It is energy efficient
4. It operates at low temperature.
5. The life of semi permeable membrane is 2 years and can be replaced within minutes.

**What is calgon conditioning of a boiler feed water?**

**Ans:** It is addition of calgon i.e.: sodium hexa metaphosphate in boiler water to prevent the formation of scale and sludge. Calgon removes scale forming  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ .



**Q 7. Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20000 litres of water whose analysis is as follows :**

$\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ ppm}$  ;  $\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$

$\text{MgSO}_4 = 30 \text{ ppm}$  ;  $\text{CaSO}_4 = 34 \text{ ppm}$

$\text{CaCl}_2 = 27.75 \text{ ppm}$  ;  $\text{NaCl} = 10 \text{ ppm}$

Also calculate temporary and permanent hardness of water sample [Given atomic masses  $\text{H} = 1$ ,  $\text{Na} = 23$ ,  $\text{Ca} = 40$ ,  $\text{Mg} = 24$ ,  $\text{O} = 16$ ,  $\text{C} = 12$ ,  $\text{S} = 32$ ,  $\text{Cl} = 35.5$ ].

(PTU, May 2007 ; Dec. 2006 ; 2005)

**Ans.** Hardness due to  $\text{Ca}(\text{HCO}_3)_2 = 40.5 \times \frac{100}{162}$   
 $= 25 \text{ ppm}$

Hardness due to  $\text{Mg}(\text{HCO}_3)_2 = 36.5 \times \frac{100}{146} = 25 \text{ ppm}$

Hardness due to  $\text{MgSO}_4 = 30 \times \frac{100}{120} = 25 \text{ ppm}$

Hardness due to  $\text{CaSO}_4 = 34 \times \frac{100}{136} = 25 \text{ ppm}$

Hardness due to  $\text{CaCl}_2 = 27.75 \times \frac{100}{111} = 25 \text{ ppm}$

Amount of lime required  $= \frac{74}{100} (25 + 2 \times 25 + 25) \times \frac{100}{84} \times 20000$   
 $= \frac{74}{100} (100) \times \frac{100}{84} \times 20000$   
 $= 1.76 \text{ Kg}$

Amount of soda required  $= \frac{106}{100} \times [25 + 25 + 25] \times \frac{100}{92} \times 20000$   
 $= \frac{106}{100} (75) \times \frac{100}{92} \times 20000 = 1.752 \text{ Kg}$

Temporary hardness = [i.e. due to  $\text{Ca}(\text{HCO}_3)_2$  and  $(\text{HCO}_3)_2$ ]  
 $= 25 + 25 = 50 \text{ ppm}$

Permanent hardness = (due to  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ )  
 $= 25 + 25 + 25 = 75 \text{ ppm}$

**Q 4. Calculate amount of lime (91% pure) and soda (97.2%) required to soften one million litres of water containing :**

$\text{H}^+$  (Free acidity) = 1.5 ppm,  $\text{HCO}_3^- = 396.5 \text{ ppm}$ .

$\text{Mg}^{+2} = 42 \text{ ppm}$   $\text{Ca}^{+2} = 90 \text{ ppm}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 14 \text{ ppm}$ .

(PTU, Dec. 2007)

**Ans.** Hardness due to  $\text{H}_1^+ = 1.5 \times \frac{100}{2} = 75 \text{ ppm}$

Hardness due to  $\text{HCO}_3^- = 396.5 \times \frac{100}{122} = 325 \text{ ppm}$

Hardness due to  $\text{Mg}^{+2} = 42 \times \frac{100}{24} = 175 \text{ ppm}$

Hardness due to  $\text{Ca}^{+2} = 90 \times \frac{100}{40} = 225 \text{ ppm}$

Hardness due to  $\text{FeSO}_4 = 14 \times \frac{100}{278} = 5 \text{ ppm}$

Amount of lime required  $= \frac{74}{100} [175 + 75 + 325 + 5] \times \frac{100}{91} \times 10^6$   
 $= 487.9 \text{ kg}$

Amount of soda required  $= \frac{106}{100} [225 + 75 + 175 - 325 + 5] \times \frac{100}{97.2} \times 10^6$   
 $= 169 \text{ kg}$

Q. A sample of water has the following impurities in mg/liter. Find the temporary and permanent hardness in ppm.

Ca (HCO<sub>3</sub>)<sub>2</sub> = 10.0 pm Mg (HCO<sub>3</sub>)<sub>2</sub> = 8 ppm

CaSO<sub>4</sub> = 12.00 ppm.

$$\begin{aligned}\text{Ans. Hardness due Ca(HCO}_3)_2 &= 10 \times \frac{100}{162} \\ &= 6.2 \text{ ppm}\end{aligned}$$

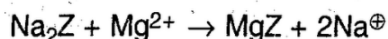
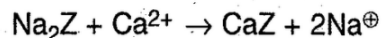
$$\begin{aligned}\text{Hardness due to Mg (HCO}_3)_2 &= 8 \times \frac{100}{146} \\ &= 5.5 \text{ ppm.}\end{aligned}$$

$$\text{Hardness due to CaSO}_4 = 12 \times \frac{100}{136} = 8.8 \text{ ppm}$$

$$\text{Temporary hardness} = \text{Hardness due to Ca (HCO}_3)_2 + \text{Mg (HCO}_3)_2$$

Q. What are zeolites? Why is water softened by zeolite process unfit for use in Boilers?

**Ans.** Zeolites are hydrated sodium aluminosilicates Na<sub>2</sub>OAl<sub>2</sub>O<sub>3</sub>xSiO<sub>2</sub>yH<sub>2</sub>O (Na<sub>2</sub>Z) or we can say sodium zeolite. Where Z = Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>yH<sub>2</sub>O. Na<sup>⊕</sup> ions present in it, can exchange the Ca<sup>2+</sup> and Mg<sup>2+</sup> ions of hard water and thus soften it.



In this process although Ca<sup>2+</sup> and Mg<sup>2+</sup> ions are removed, but yet water contains a number of Na<sup>⊕</sup> ions and anions like HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>. So these ions will lead to formation of scale and sludges in the boilers, so water is still unfit for use in boilers.

Q. Give specifications of boiler feed water.

Ans The specifications of boiler feed water are as follows

- Water for boilers: Boiler feed water should be free from soluble salts of Mg<sup>2+</sup> and Ca<sup>2+</sup>. It should not contain any organic matter.
- Boiler feed water should be free from suspended impurities.
- Boiler feed water should not be acidic or alkaline.