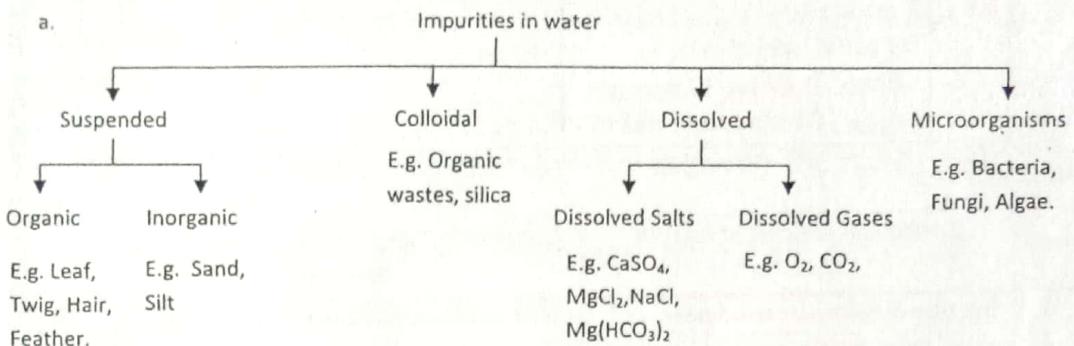


WATER

1. Introduction, Impurities In Water:-

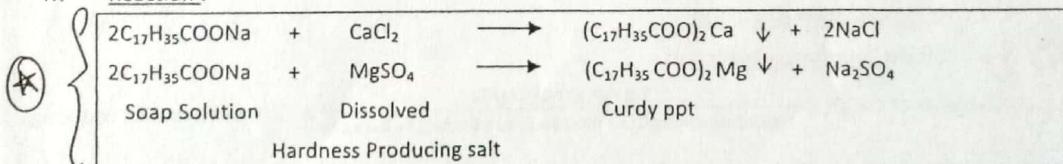


- b. Suspended impurities can be easily removed by physical methods like filtration, sedimentation etc.
- c. The colloidal impurities can also be removed by first breaking the colloid and converting them into precipitates.
- d. It is the dissolved impurities which are the most difficult to remove.
- e. Out of the dissolved impurities, the source of the organic dissolved impurities is manmade (decomposition of suspended organic matters like twigs, hair etc.) and can be controlled, it is the inorganic dissolved impurities which is the most difficult to remove as its source is natural (salts get dissolved as rainwater flows).
- f. Dissolved gases like O_2, CO_2 , etc. Also come under dissolved impurities.
- g. However, from industrial point of view, Alkalinity and Hardness are important.

2. Hardness Of Water:-

- i. "It is that characteristic, which prevents water from lathering when it is treated with soap solution and instead forms a white curdy precipitate (Scum)".
- ii. It is caused due to the presence of dissolved salts of calcium, magnesium, iron and other heavy metals.
- iii. The white precipitate is formed due to the reaction of soap with these dissolved salts to form insoluble soaps of calcium, magnesium, iron and other heavy metals.

iv. Reaction :-



3. HARD WATER & SOFT WATER:-

NO.	HARD WATER	SOFT WATER
1.	Water that does not produce lather on treatment with soap solution.	Water that produces lather on treatment with soap solution.
2.	Hard water contains dissolved salts of Ca, Mg, Fe & other heavy metals.	Soft water is free of dissolved salts of Ca, Mg, Fe & other heavy metals.

elevated. Conseq.
and time are required for cooking.

(5). Soap gets wasted. (5). Soap does not get
wasted.

Degrees of Hardness:-

NO.	Temporary/ Carbonate/ Alkaline Hardness	Permanent/ Non-Carbonate/ Non-Alkaline Hardness
1.	This type of hardness can be easily destroyed on boiling. Hence the name 'Temporary Hardness'.	This type of hardness can't be destroyed on boiling and can be removed only by chemical treatment. Hence 'permanent Hardness'.
2.	It is caused due to the presence of bicarbonate salts of Ca, Mg, Fe & other heavy metals.	It is caused due to the presence of other than bicarbonate salts such as nitrates, phosphate, chlorides etc. of Ca, Mg, Fe & other heavy metals.
3.	Bicarbonate salts on boiling are decomposed into precipitates of carbonate & hydroxides. $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ $\text{Mg}(\text{HCO}_3)_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + 2\text{CO}_2 \uparrow$	These salts are not destroyed on boiling.
4.	It is also called as carbonate hardness or alkaline hardness.	It is also called as non-carbonate hardness or non-alkaline hardness.
5.	It can be removed by use of Lime only.	It can be removed by use lime and soda.

5. DEGREE OF HARDNESS:-

- a. "It is the net amount of hardness producing substance in a finite volume of water".
- b. It is expressed in the terms of calcium carbonate equivalents. All the hardness causing impurities are first converted in terms of their respective weight equal to CaCO_3 .
- c. The choice of CaCO_3 is made as,

-  i. Its molecular weight is 100.
ii. It is the most insoluble salt.

d. Equivalents of $\text{CaCO}_3 = \frac{\text{Eq. weight of } \text{CaCO}_3}{\text{Equivalent weight of hardness producing substance}} \times \frac{\text{Wt. of Hardness Producing Substance}}{\text{Substance}}$

$$= \frac{50}{\text{equivalent weight of hardness producing substance}} \times \frac{\text{Wt. of Hardness Producing Substance}}{\text{Substance}}$$

6. UNITS OF HARDNESS:-

- a. Parts per million (ppm):- It is the number of parts of calcium carbonate equivalent hardness per 10^6 parts of water.

$$1\text{ ppm} = 1 \text{ parts of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ parts of water}$$

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Water

b. Milligrams per liter (mg/L) - It is the number of milligrams of calcium carbonate equivalent hardness present per liter of water.

$1\text{mg/L} = 1\text{ mg of CaCO}_3$ equivalent hardness present in per liter of water

c. Degree Clarke ($^{\circ}\text{Cl}$) - It is the number of parts of calcium carbonate equivalent hardness present per in 70,000 parts of water.

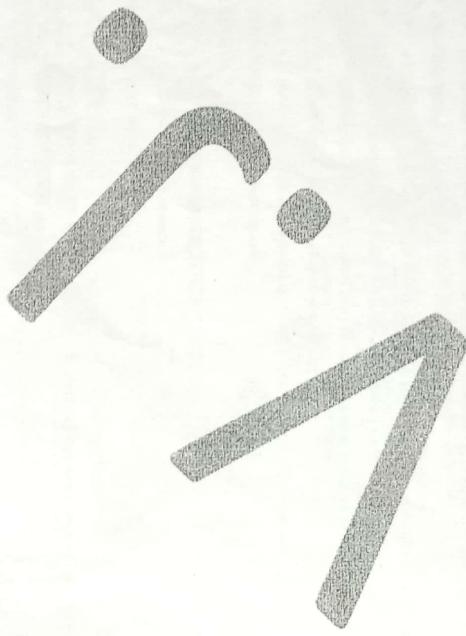
$1\text{ Cl} = 1$ parts of CaCO_3 equivalent hardness in 70,000 parts of water

d. Degree French ($^{\circ}\text{Fr}$): - It is the number of parts of calcium carbonate equivalent hardness present per 10^5 parts of water.

$1^{\circ}\text{Fr} = 1$ parts of CaCO_3 equivalent hardness in 10^5 parts of water

7. RELATIONSHIP BETWEEN VARIOUS UNITS OF HARDNESS:-

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



a. Domestic use:-

- i. Washing: - Hard water used for washing, does not produce lather easily with soap but instead forms a white sticky precipitates of Ca, Mg soaps. This continues till all the hardness causing salts present in water are precipitated. Thereafter the soap produces lather. This cause -
 -  A lot of wastage of soap.
 -  Formation of spots and streaks on the cloth.
 -  Staining due to the adherence of precipitates on the cloth.

- ii. Bathing: - Hard water does not lather freely with soap solution and instead forms a sticky precipitates on the body causing irritation to the skin.

iii. Cooking: - Presence of dissolved salts in water causes-

- Boiling point of water to rise, as a result the food takes a longer time to cook, fuel is wasted.

 iv. Unpleasant taste to the food.

- The dissolved salts are deposited as bicarbonates on the inner walls of the heating utensils.

v. Drinking: - Hard water gives-

 vi. Increase the possibility of causing kidney stones.

b. Industrial use:-

i. Textile industry: - Hard water causes-

- Wastage of soap as the water does not lather easily. The fabric is washed thoroughly prior to dyeing & printing.
- Precipitates of calcium, magnesium soap adheres to the fabrics and cause weakening of the fabric and also improper shade is produced when such a fabric is dyed.
- Iron and manganese salts containing water produce coloured spots on the fabrics.

 vii. Sugar industry:-

- Water containing Sulphates, nitrates, carbonate etc. if used in sugar refining, cause difficulties in the crystallization of sugar.

 viii. Paper industry:-

- Calcium and magnesium salts tend to react with chemicals used to provide a smooth and glossy finish to the paper.

 ix. Laundry: - Hard water causes

- Wastage of soap
- Iron and manganese salts cause colouration of the clothes.

x. Concrete making:-

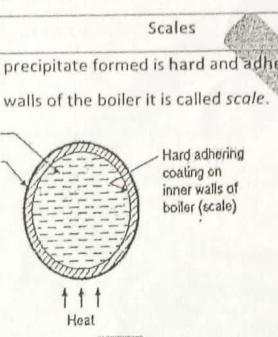
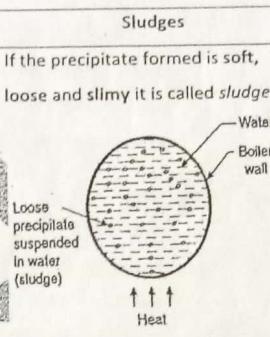
- Water containing chlorides and sulphates if used in concrete making, affects the hydration of cement and the final strength of the hardened concrete.



vi. Food industry: - Salts present in the hard water give unpleasant taste to the food.

- c. Boilers: - Boilers are employed in industry for steam generation. If hard water is directly fed to boilers there arises many problems such as:
- 1) Scale and sludge formation
 - 2) Boiler corrosion
 - 3) Caustic embrittlement
 - 4) Priming and foaming

1) SCALE and SLUDGE Formation:

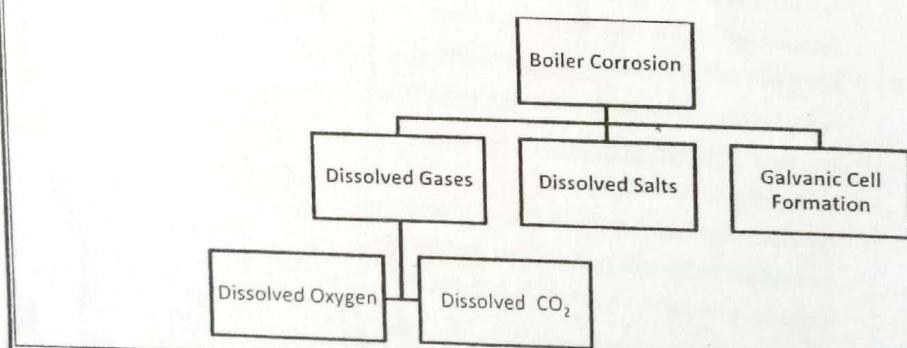
	As water evaporates continuously in boilers the concentration of the dissolved salts increases. When their saturation point is reached the salts are precipitated on the inner walls of the boilers.	
Concept	<p>Scales</p> 	<p>Sludges</p> 
Causes	<p>1. <u>Decomposition of calcium bicarbonates</u>:</p> $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$ <p>CaCO_3 forms comparatively <u>softer scale</u> and is the main cause of scale formation in <u>low pressure boilers</u>, as in high pressure boilers CaCO_3 dissolves to form $\text{Ca}(\text{OH})_2$ & CO_2.</p> <p>2. <u>Deposition of calcium sulphate</u>:</p> <p>the solubility of calcium sulphate in water decreases with rise in temperature. As a result CaSO_4 gets precipitated as a <u>hard scale</u> on the heated portions of the boiler. This is the main cause of scales in <u>high pressure boilers</u>.</p> <p>3. <u>Hydrolysis of magnesium salts</u>:</p> <p>Dissolved magnesium salts like MgCl_2, undergoes hydrolysis at high temperature forming magnesium hydroxide precipitate, which forms a soft type of scale.</p> $\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{HCl}$	<p>1. Sludges are formed by those substances which have greater solubility in hot water than cold water. E.g. CaCl_2, MgCl_2, MgSO_4, MgCO_3 etc.</p> <p>2. They are formed at comparatively cooler portion of the boiler and they collect in such areas of the system where the flow rate is slow or at bends in the lines.</p>

*Soft / Hard
Scale*

	<p>4. Presence of silica: SiO_2 reacts with Ca & Mg salts to form calcium silicate & magnesium silicate which deposit very firmly on inner side of boiler surface and are very difficult to remove.</p>	
Problems (Disadvantages)	<ol style="list-style-type: none"> 1. Wastage of fuel: Poor conductor of heat so they tend to waste a portion of heat generated. 2. Lowering of boiler safety: Due to overheating of the boiler material the boiler becomes soft and weak making the boiler unsafe to beat the pressure of the steam. 3. Danger of explosion: sometimes scales crack due to uneven expansion and the comparatively cooler water suddenly comes in contact with the overheated boiler material. This causes formation of large quantity of steam suddenly. A sudden high pressure is developed which can even lead to explosion of the boiler. 	<ol style="list-style-type: none"> 1. Poor conductor of heat so they tend to waste a portion of heat generated. 2. They tend to <u>chock pipe connection, plug opening, valve sets</u> where they tend to deposit.
Removal	<ol style="list-style-type: none"> 1. They stick firmly and cannot be easily removed even with the help of a hammer and chisel. 2. Scales can be dissolved in suitable chemicals e.g. CaCO_3 scale can be dissolved by using 5-10% HCl. CaSO_4 can be dissolved by adding EDTA. 	They can be easily scrapped off with a wire brush.
Prevention	<ol style="list-style-type: none"> 1. Frequent Blow down operation: A portion of highly concentrated water is replaced by fresh water containing smaller quantities of dissolved salts. 2. Using soft water. 	<ol style="list-style-type: none"> 1. By frequent blow down operation. 2. By using good quality (soft) water.

2) BOILER CORROSION:

- a) Boiler corrosion is decay of the boiler material by chemical or electrochemical attack by its environment.
- b) Boiler corrosion is caused due to



I. Corrosion due to Dissolved Gases:

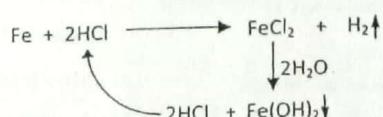
	Corrosion due to Dissolved Gases	
	Dissolved Oxygen	Dissolved CO ₂
Concept	<p>1. Water contains about 8 ppm of dissolved oxygen at room temp.</p> <p>2. This dissolved oxygen at high temperature, attacks the boiler.</p> $2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Fe(OH)}_2$ $\downarrow \text{O}_2$ $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ <p>Rust</p>	<p>1. Beside small amount of dissolved CO₂, CO₂ is formed inside boiler due to decomposition of bicarbonates.</p> <p>2. CO₂ forms carbonic acid (H₂CO₃) with water which has a slow corrosive effect on the boiler iron.</p>
Prevention	<p>O₂ can be removed by:</p> <ol style="list-style-type: none"> 1. Mechanical deaeration: Feed water is injected into a hot vacuum chamber where high temperature, low pressure and large exposed surface reduce dissolved O₂. 2. Preheating feed water. 3. Chemical treatment: by adding calculated quantity of sodium sulphide (Na₂S), sodium sulphite (Na₂SO₃) or hydrazine (H₂N-NH₂). $2\text{Na}_2\text{SO}_3 + \text{O}_2 \longrightarrow 2\text{Na}_2\text{SO}_4$ $\text{Na}_2\text{S} + 2\text{O}_2 \longrightarrow \text{Na}_2\text{SO}_4$ $\text{N}_2\text{H}_4 + \text{O}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ <p>4. Sodium sulphite is suitable only for <u>low pressure boilers</u> because in high pressure boilers it leads to SO₂ formation which causes corrosion of metal.</p> <p>5. Hydrazine is most suitable because it reacts with O₂ to form harmless N₂ and water.</p>	<p>CO₂ can be removed by:</p> <ol style="list-style-type: none"> 1. Mechanical deaeration. 2. Adding calculated amounts of NH₄OH $2\text{NH}_4\text{OH} + \text{CO}_2 \longrightarrow (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$

II. Corrosion due to Dissolved Salts:

i. Boiler feed water if contain dissolved salts like MgCl₂, it undergoes hydrolysis liberating HCl acid.



ii. Liberated HCl reacts with iron material of boiler in a chain like reaction producing HCl again and again.

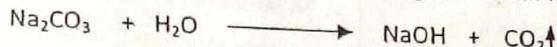


iii. Hence presence of even a small amount of MgCl₂ will cause corrosion of iron to a large extent.

boiler & connecting the rods to boiler.

3) CAUSTIC EMBRITTLEMENT:

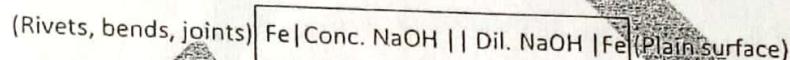
- Caustic embrittlement is the decay of stressed boiler material (brittlement) caused by using highly alkaline (caustic) water.
- During lime soda process of softening of water a small amount of Na_2CO_3 usually remains in the softened water.
- In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide.



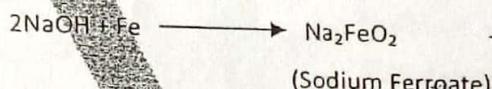
This makes the water caustic.

- The NaOH containing water flows into minor hair cracks, always present in the inner side of boilers, by capillary action.

- Here the water evaporates and concentration of NaOH progressively rises. This leads to the formation of concentration cell.



- Iron in cracks in contact with the concentrated NaOH becomes anodic and consequently corrodes as follows,



- This causes embrittlement of boiler parts, particularly stressed parts like bends, joints, rivets etc. where there are more hair cracks.

h) Prevention:

- The pH of feed water should be adjusted to 8-9.
- Sodium phosphate can be used as a softening agent in place of Na_2CO_3 .
- Tannin or Lignin can be added to water which blocks hairline cracks in the boiler walls thus preventing the infiltration of NaOH in these areas.

4) PRIMING and FOAMING:

	PRIMING	FOAMING
Concept	<ol style="list-style-type: none">When a boiler produces steam rapidly, some particles of water are carried along with the steam.<i>This phenomenon of 'wet steam' formation is known as Priming.</i>	<ol style="list-style-type: none">Foaming is the formation of persistent bubbles in the boiler which does not break easily.Priming and Foaming usually occur together.
Causes	<ol style="list-style-type: none">High steam velocity.Sudden increase in steam production rate.Improper boiler design.	Presence of substances like oils, clay, fine particles etc. which greatly reduce surface tension of water.

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Water

	4. Presence of large amount of dissolved and suspended solids.	
Problems (Disadvantages)	<p>1. The dissolved salts in the boiler are carried along with the wet steam to <u>super heaters and turbine blades</u> (called <u>Carry Over</u>), where they get deposited as the water evaporates. This deposit causes corrosion of these parts & reduces efficiency.</p> <p>2. Steam carries along with it suspended solids which impinge on the boiler parts like <u>tubes, pipes etc.</u> and causes physical damage to them.</p>	Foaming make it difficult to note exact level of water inside the boiler.
Prevention	<p>1. Good boiler design for proper evaporation of water.</p> <p>2. Maintaining low water levels.</p> <p>3. Avoiding sudden change in rate of steam production.</p> <p>4. Softening and filtration of boiler feed water.</p> <p>5. Fitting mechanical steam purifier.</p>	<p>1. Removing oil from water by adding compounds like sodium aluminate.</p> <p>2. Adding antifoaming agents like castor oil, polyamide antifoamer etc.</p>

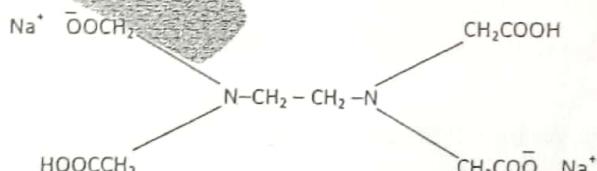
NaAlO_2

9. DETERMINATION OF HARDNESS BY EDTA METHOD:-

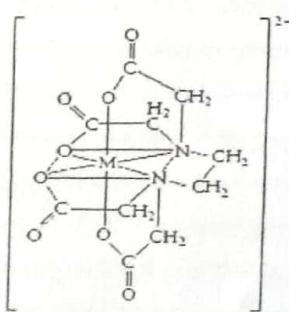
a. This is complexometric method of titration.

b. Principle:-

i. Ethylenediaminetetraacetic acid (EDTA) in the form of its sodium salts yield the anion:



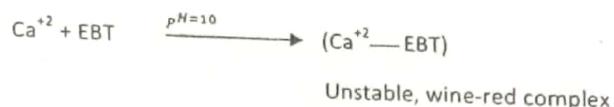
ii. It forms stable and colourless complexes with metal ions like Ca^{+2} , Mg^{+2}



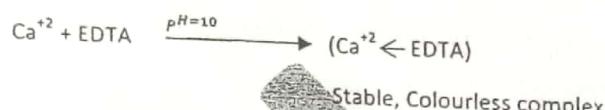
The coordination of EDTA with a $2+$ metal ion.

Where $\text{M} = \text{Ca}^{+2}, \text{Mg}^{+2}$

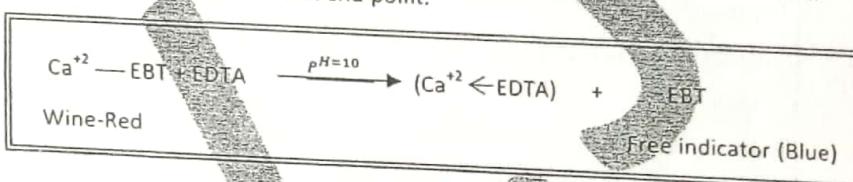
- iii. The indicator used is **Eriochrome Black T** or **EBT** which forms an unstable wine-red coloured complex with metal ions like Ca^{+2} , Mg^{+2} at the P^{H} of titration, i.e. $\text{P}^{\text{H}} = 10$.
 - iv. So, when hard water is added to a solution of indicator buffered at $\text{p}^{\text{H}}=10$, in a conical flask, a few of the metal ions react with the indicator to form an unstable wine-red coloured complex and the solution turns wine-red.



- v. To this solution, EDTA is added from the burette, EDTA reacts with the remaining free metal ions to form a stable colourless complex.



- vi. When all the free metal ions in the solution have been complexed with EDTA, further addition of EDTA cause it to break the unstable metal ion-indicator complex and itself complexes with metal ion leaving the indicator free. The free indicator is blue coloured at this pH° . Hence the wine-red coloured solution turns blue at end-point.



C. Method:

i. Preparation

- 1) Standard Hard Water: - prepared by dissolving 1g of pure, dry CaCO_3 in minimum quantity of dil. HCl and then making up the volume up to 1 L with distilled water.
 - 2) EDTA Solution: - 4g of pure EDTA crystals and 0.1g MgCl_2 is dissolved in 1L of distilled water.
 - 3) Erichrome Black T Indicator: - 0.5g of EBT indicator is dissolved in 100mL of alcohol.
 - 4) Buffer Solution: - 67.5g of NH_4Cl is added to 570 ml of concentrated ammonia solution and then diluted with distilled water to 1L.

ii. Standardisation of EDTA Solution: - 50 mL of standard hard water solution is taken in a conical flask. 10-15 mL of buffer solution and 4-5 drops of the indicator solution is added to it. The titration is carried out.

iii. Determination of Total Hardness: $\text{EDTA} \rightarrow \text{Ca}^{2+}$

Total Hardness: - SoML of unknown hard water solution is taken in the conical flask and titrated in a similar manner. Let the volume be V_2 mL.

iv. Determination of Permanent Hardness: - 250ml of the hard water sample is boiled till its volume is reduced to about $1/5^{\text{th}}$. The solution is filtered to remove the precipitates (of bicarbonate salts). The filtrate and washing given to the precipitates are collected and the volume made back to

250mL with distilled water. 50mL of this solution is taken in a conical flask and titrated. Let volume V_3 mL.

d. CALCULATIONS:-

- 1 mL of Standard Hard Water = 1 mg of CaCO_3 equ.
- 50mL of Standard Hard Water = V_1 mL of EDTA.
 $\therefore 50 \times 1 \text{ mg CaCO}_3 = V_1 \text{ mL EDTA}$
 $\therefore 1 \text{ ml of EDTA} = 50/V_1 \text{ mg of CaCO}_3 \text{ equivalents}$
- 50mL of unknown hard water sample = V_2 mL of EDTA
 $= V_2 \times 50/V_1 \text{ mg of CaCO}_3 \text{ equivalent.}$
 1000mL of unknown hard water = $1000 \times V_2/V_1 \text{ mg of CaCO}_3 \text{ eq.}$
- $\therefore \text{Total hardness} = 1000 \times V_2/V_1 \text{ ppm.}$

- 50 mL of boiled water = V_3 mL of EDTA
 $= V_3 \times 50/V_1 \text{ mg of CaCO}_3 \text{ eq.}$
 $\therefore 1000 \text{ mL of boiled water} = 1000 \times V_3/V_1 \text{ mg of CaCO}_3 \text{ eq.}$
- $\therefore \text{Permanent hardness} = 1000 \times V_3/V_1 \text{ ppm.}$
- $\text{Temporary hardness} = \text{Total} - \text{Permanent hardness}$
 $= 1000 (V_2/V_1 - V_3/V_1) \text{ ppm.}$

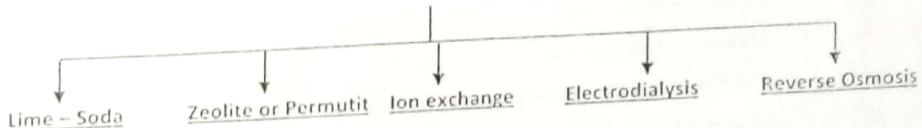
e. Advantages of EDTA method:-

- Highly accurate.
- Highly convenient.
- Highly rapid.
- Colour change at end point is sharp.

10. SOFTENING OF WATER:-

- Water used for industrial purpose should be free from salts especially hardness producing salts, before putting it to use.
- "This process of removing salts from water is known as softening of water".
- c.

Softening methods

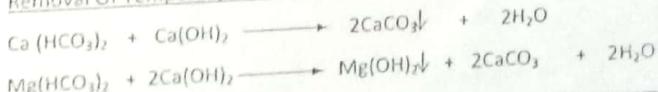


i. Lime - Soda Method:-

- Principal: - In this method, the soluble salts present in water is chemically converted into insoluble precipitates, on adding calculated quantities of lime, Ca(OH)_2 , and soda, Na_2CO_3 . The precipitates are filtered off.

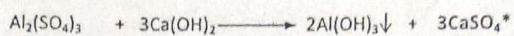
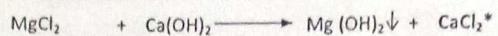
2) Reaction Of Lime:-

a. Removal Of Temporary Hardness:-

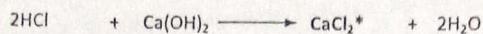
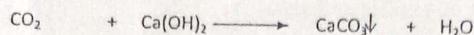
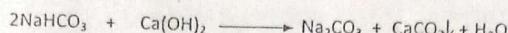


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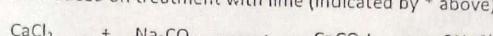
b. Removal Of Permanent Hardness:-



c. Removal Of Acids :-

d. Removal Of CO_2 :-e. Reaction With NaHCO_3 :-

- 3) Reaction of Soda: - Soda reacts with all permanent calcium hardness including those introduced on treatment with lime (indicated by * above).



- 4) Now 100 parts by mass of CaCO_3 are equivalent to 74 parts of $\text{Ca}(\text{OH})_2$ and 106 parts of Na_2CO_3

$$\therefore \text{Lime required} = \frac{74}{100} (\text{Temp } \text{Ca}^{+2} + 2 \times \text{Temp } \text{Mg}^{+2} + \text{perm } (\text{Mg}^{+2}, \text{Fe}^{+2}, \text{Al}^{+3}, \text{etc.}) + \text{H}^+(\text{HCl, H}_2\text{SO}_4, \text{etc.}) + \text{CO}_2 + \text{NaHCO}_3 - \text{NaAlO}_2)$$

All in terms of CaCO_3 equivalents.

$$\therefore \text{Soda required} = \frac{106}{100} (\text{Perm } \text{Ca}^{+2}, \text{Mg}^{+2}, \text{Fe}^{+2}, \text{Al}^{+3}, \text{etc.} + \text{H}^+(\text{HCl, H}_2\text{SO}_4, \text{etc.}) - \text{NaHCO}_3)$$

All in terms of CaCO_3 equivalents.

Notes:

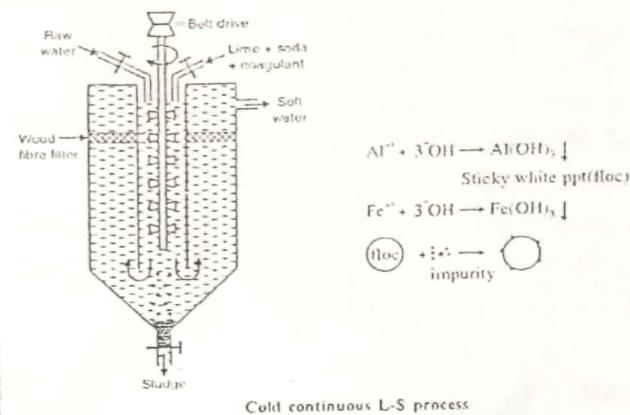
- ✓ $\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al(OH)}_3$ i.e. $\frac{1}{2}\text{NaOH}$ is equivalent to $\text{Ca}(\text{OH})_2$.
- ✓ Equivalent weight of NaAlO_2 is equal to its molar mass.
- ✓ When impurities are given as CaCO_3 , these should be considered due to bicarbonates of calcium and / or magnesium resp.
- ✓ Substances like NaCl , KCl , Na_2SO_4 , SiO_2 , Fe_2O_3 , etc., do not import any hardness and, therefore, these do not consume any lime or soda. These should not be taken into consideration for calculating the lime and soda requirement.

- 3) Lime soda process can be classified on the basis of Temperature as

- Cold Lime Soda process.
- Hot Lime Soda process.

a. Cold - lime soda process:-

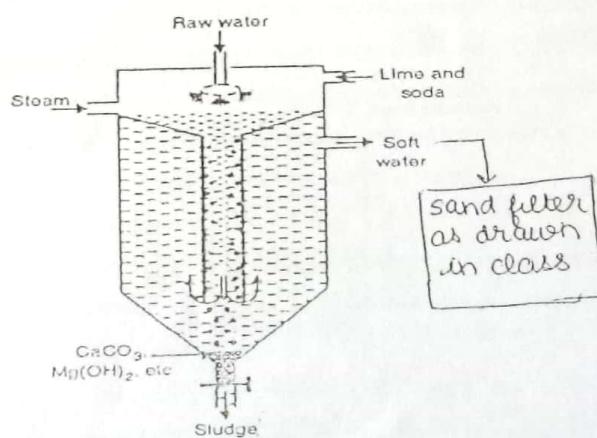
- i. In this method, calculated quantity of chemicals, lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$ are mixed with water at room temp.
- ii. At room temperature the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily. Also the viscosity of solution is high so filtration is slow.
- iii. Consequently, it is essential to add small amount of coagulants (like alum, aluminum sulphate, sodium aluminate, etc)
- iv. As the reactions are slow, the process takes a longer time, a few hours.
- v. The residual hardness is 50 to 60 ppm.



Cold continuous L-S process

Hot - lime soda process:-

- i. The calculated amount of chemicals lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$ are added to water maintained at 80 to 150°C.
- ii. The reactions proceed faster.
- iii. The precipitates formed are larger in size and the viscosity of solution is also low at higher temp. So filtration is faster.
- iv. As a result, it is not necessary to add coagulants.
- v. Much of the dissolved gases are also driven out.



: Hot continuous soda-lime process

- vi. The reactions are faster at the higher temp. & process taken much lesser time.
- vii. The residual hardness is comparatively lower, 15 to 30 ppm.

Advantages of Lime -Soda Process	Disadvantages of Lime-Soda Process
<ol style="list-style-type: none"> 1. Economical. 2. Process increases the pH value of the treated water; thereby corrosion of the distribution pipes are reduced. 3. Along with hardness, acids as well as CO_2 are eliminated. 4. Due to alkaline nature of water, pathogenic bacteria are reduced. 	<ol style="list-style-type: none"> 1. Skilled personnel are required for supervising the process. 2. Disposal of large amounts of sludge is an environment problem. 3. Residual hardness is very high, even 15 ppm. Hardness is not good for boilers. 4. Softened water cannot be used for specific industrial application such as high pressure boiler.

ii. Zeolite or Permutit Process:-

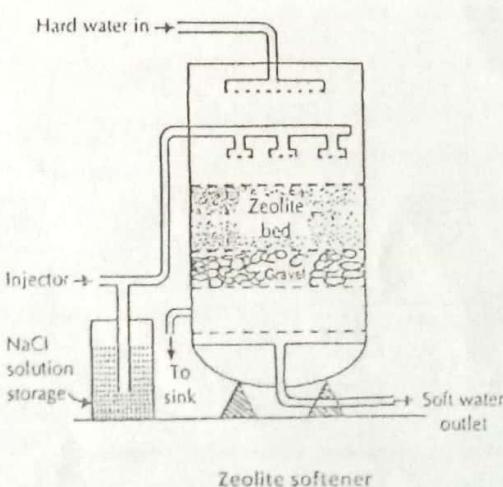
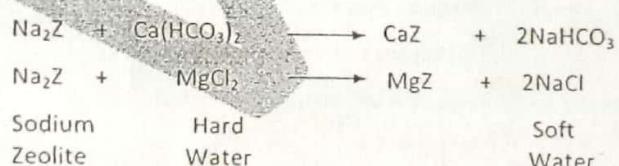
1) Principal:-

Zeolite or permutit is hydrated sodium aluminosilicate and have the general molecular formula – $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ Where $x=2-10$ and $y=2-6$ & generally represented as Na_2Z . Zeolites are capable of exchanging reversibly its sodium ions for hardness producing ions in water.

2) Process:-

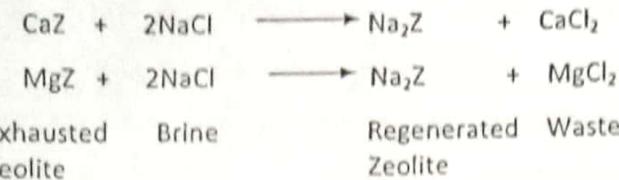
a) Softening: – Hard water is passed through a Zeolite bed at a specified rate. The hardness causing ions present in water like Ca^{+2} , Mg^{+2} , etc. are retained by the Zeolite bed, and sodium ions discharged by the bed enter the water. Thus all the hardness causing salts present in water are converted into the corresponding sodium salts. In other words, the hard water becomes soft.

Reaction:-



Zeolite softener

- b) Regeneration:- After sometimes the Zeolite bed loses its capability to exchange Na^+ ions as all the sodium ions get replaced by other metal ions. Such a Zeolite bed is said to be exhausted. The bed can be regenerated by treating the bed with concentrated brine solution (10% NaCl solⁿ.)



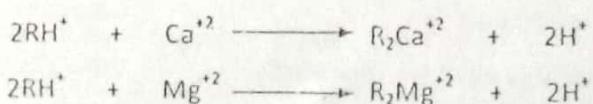
Advantages	Disadvantages
<ol style="list-style-type: none"> Residual hardness is 2 to 10 ppm. Sludge is not produced. Skilled personnel are not required. The equipment used is compact. Time required for softening is very less. 	<ol style="list-style-type: none"> Turbid water cannot be used as it clogs the pores of the Zeolite bed. If the water contains large amount of coloured ions like Mn^{+2}, Fe^{+2}, they must be removed first, because these ions produce manganese and iron Zeolite which are difficult to regenerate. Acidic as well as alkaline water tend to destroy the Zeolite bed, hence the water has to be neutralized first before pouring down the bed. The treated water contains more sodium salts as compared to the lime soda process. Softened water contains sodium salts of bicarbonate and carbonate ions which decompose in the boiler to form NaOH that may cause caustic embrittlement.

III. Ion -Exchange Or Demineralization Or Deionization Process:-

- 1) Ion-exchange resins are cross-linked, long chain polymers with a micro porous structure.
- 2) Ion-exchange resins are of 2 types.
 - a) Cation Exchange Resins (RH^+):- These resins are mainly styrene- divinyl benzene copolymers and contain acidic functional group like – COOH , – SO_3H , etc. that are capable of exchanging their H^+ ions for the cations present in water.
 - b) Anion Exchange Resins (ROH):- These resins are styrene – divinyl benzene or amine – formaldehyde copolymers containing Amino or quarter nary ammonium or quarter nary phosphonium or tertiary sulphonium Hydroxyl functional groups that are capable of exchanging their OH^- anions with the anions in water.

3) PRINCIPAL AND PROCESS:-

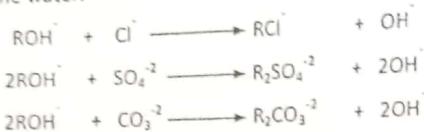
- a. Hard water is first passed through Cation exchange column. All the cations like Ca^{+2} , Mg^{+2} , etc. present in water are removed and an equivalent amount of H^+ are discharged from the column into water.



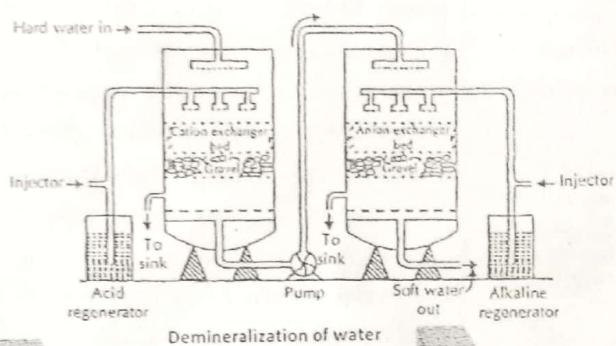
Thus, all the salts are converted in to the corresponding Acids in the Cation exchange column.

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b. The water is next pumped into the anion exchange column. All the anions present in the column get adsorbed into the bed and an equivalent amount of OH^- ions discharged from the bed enters the water.

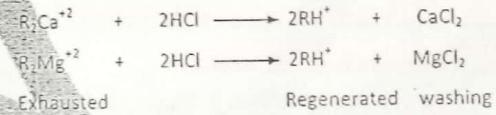


- c. H⁺ and OH⁻, released from cation and Anion exchange columns respectively get combined to form water molecule.
 - d. Thus the water coming out of the exchange is free from cations as well as Anions.
 - e. This ion free water is known as deionised or demineralised water.

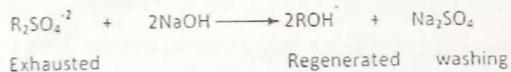


4) REGENERATION:-

- a) After sometimes both the cation and anion exchanger lose their capacity to exchange H^+ and OH^- respectively, they are then said to be exhausted.
 - b) The exhausted cation exchanger can be regenerated by passing a solution of dilute acid like HCl .



- c) The anion exchange column is regenerated using dil NaOH.



- d) The columns are then washed with deionised water and the washing is passed into the drain.

Advantages	Disadvantages
<ol style="list-style-type: none"> 1. The residual hardness is only around 0-2 ppm. 2. The process can be used to treat both acidic as well as alkaline water. 3. The equipment is compact. 4. The process is suitable even for removing coloured metal ions like Mn^{+2} and Fe^{+2}. 5. No sludge is produced. 	<ol style="list-style-type: none"> 1. Turbid water blocks the pores of the exchanger. Hence turbidity has to be removed before pouring the water in the exchanger. Turbidity must be less than 10 ppm. 2. The equipment is costly.

5) Application:-

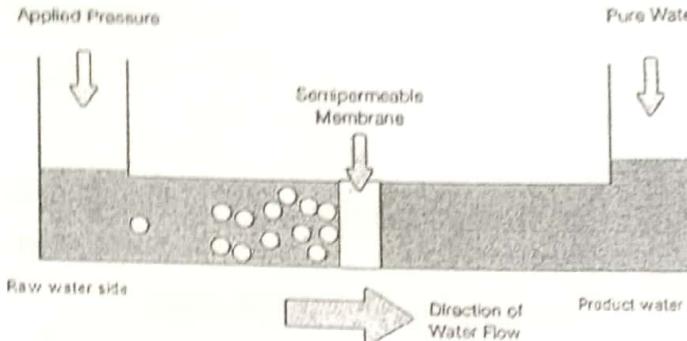
- In manufacturing of photographic materials.
- In pharmaceuticals.
- In power plants.
- In cosmetics.

No.	Lime-Soda process	Permutit (Zeolite) process	Ions exchange (de-ionization) process
1.	Through study of water wrt amount of various salts, necessary.	Self-adjust with different hardness waters.	Self-adjusts with different hardness waters.
2.	Lower initial investment but running cost higher.	High initial investment but lower running cost.	Higher initial investment but lower running cost.
3.	Treated water contains lesser quantity of total dissolved solids than original water.	Treated water contains amount similar total dissolved solids as in original water.	Treated water contains almost zero total dissolved solids.
4.	Residual hardness 15-60 ppm CaCO ₃ equivalent.	Almost zero residual hardness.	Almost zero residual hardness.
5.	Water containing suspended, colloidal impurities, can be softened. (pretreatment not necessary)	Water containing suspended, colloidal impurities, cannot be softened. (Pretreatment necessary).	Water containing suspended, colloidal impurities, cannot be used (Pretreatment necessary).
6.	Large scale treatment possible with batch process.	Method applicable for small scale treatment of water.	Method applicable for small scale treatment of water.
7.	Involves problem of setting, filtration and disposal of precipitates formed.	Involves no precipitates.	Involves no precipitates.
8.	Acidic water can be treated.	Acidic water cannot be treated.	Acidic water can be treated.

iv. REVERSE OSMOSIS:-1) Principal:-

- Osmosis: - When two solutions of unequal concentration are separated by a semi-permeable membrane, the solvent flows from the dilute solution side to the concentrated solution side till the concentration is equal on both the sides.
- Reverse Osmosis: - When a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated solution side, the solvent flow is reversed; i.e. the solvent is forced to move from the concentrated solution to the dilute solution.
- Thus in reverse osmosis pure solvent is separated from its salts and other impurities, rather than removing the impurities from water.

Reverse Osmosis



2) Process:-

- A pressure of the order of 15 to 40 kg/cm² is applied to the sea water or impure water to be treated.
- The pure water is forced out through the semi-permeable membrane, leaving behind the dissolved salts and other impurities.
- The membranes usually consist of very thin films of cellulose acetate, affixed on either side of a perforated tube.
- Now a day, membrane made of Polymethylmethacrylate (PMMA) and polyamide polymers are being used.
- This method is being used for desalination of sea - water.
- This method is also called super filtration or hyper filtration.

Advantages	Disadvantages
<ol style="list-style-type: none"> Simple system, easy to operate and install. Maintenance cost is low and requires only the replacement of the membrane once every two years. The replacement can be done in few minutes. Thus providing an uninterrupted water supply. Low capital cost, low operating cost and high reliability. Impact on environment is low. 	<ol style="list-style-type: none"> Reverse osmosis removes salts along with healthy, natural minerals in water. Reverse osmosis, although it is less waste full than distillation is still an incredibly inefficient process. On an average the reverse osmosis wastes three gallons of water for every one gallon of purified water it produces. Reverse osmosis is also an incredibly slow process when compared to other water treatment alternatives.

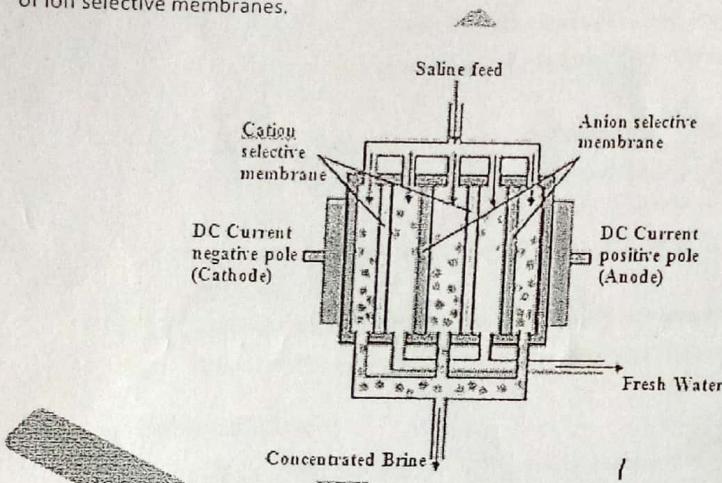
3) Application:-

- Desalination of sea water as small pores of semi-permeable membranes are restrictive to salts, minerals, bacteria, disease causing pathogens.
- An excellent choice for drinking water purification processes as it provides pathogen-free water.
- Waste water recovery in the food and beverage processing industries.
- Industrial process water, i.e. boiler feed water softening.

- e. Production of ultra-pure water for use in the semiconductor industry, power industry and medical applications.
- f. Minerals free water for use in photo shops.

4. Electrodialysis (ED):

- i. Principle: Electrodialysis is a method in which the ions (of salts) present in saline water are pulled out by passing direct current so that they migrate towards oppositely charged electrodes, through ion-selective membrane.
- ii. Construction: The unit consists of electrodes and thin, rigid ion-selective membranes which are permeable to either cations or anions. The anode is placed near the anion-selective membrane while the cathode is placed near the cation-selective membrane. (in a membrane presence of particular type of functional group (e.g. RSO_3^- , RCOO^- , R_4N^+ etc) keeps away similarly charged ions & hence make them selective). For practical purposes an electrodialysis cell is used which consists of a large no. of paired sets of ion selective membranes.



iii. Working: Saline water is passed under a pressure of about $5-6 \text{ kg/cm}^2$ between membrane pairs and an electric field is applied perpendicular to direction of flow of water. Under the influence of an applied emf across the electrodes the cations move towards the cathodes through cation selective membrane and anions move towards the anode through anion selective membrane the net result is the depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is periodically drawn out from the central compartment while the concentrated brackish water is replaced by fresh sample.

iv. Advantages:

1. It is the most compact unit.
2. The cost of installation and its operation is economical.
3. If electricity is easily available, the method is best suited.

