

Water

As an engineering material water is used for producing steam, in boilers to generate hydro-electric power, furnishing steam for engines, for construction of concrete structures for manufacturing purposes & as a solvent in chemical processes

Types of impurities in water

Dissolved Impurities

- **Inorganic dissolved impurities:** the carbonates, bicarbonates, sulphates, chlorides of calcium, magnesium, iron, potassium, and aluminium.
- **Organic dissolved impurities:** Organic water products, amino acids, proteins, etc. Gases: O₂, CO₂, Oxides of nitrogen and sulphur, H₂S etc.

Suspended impurities

- Inorganic- sand & clay;
- Organic- vegetable and animal matter.

Biological Impurities

- Micro-organisms like pathogenic bacteria, fungi, algae, etc.

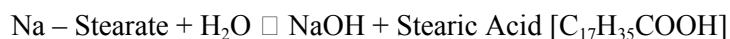
Disadvantages of Hard Water / Cause of Hardness in Water

1. Hard water does not form lather easily with **soap**, so soap is wasted
2. Hard water causes bad effects on our **digestive system**. Sometimes, stone formation takes place in kidneys.
3. The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking. **Food and beverages industry**.
4. Hard water causes wastage of soap. Precipitates of calcium and magnesium soap adhere to the **fabrics and cause problems**: difference in colour shades, dull shades, patches, etc.
5. Calcium and Magnesium salts in water may affect the quality of **paper**.
6. Water containing sulphates, carbonates, nitrates affects the **crystallisation of sugar**.
7. Hard water may form some undesirable by-products while preparation of **pharmaceutical** products.
8. **Steam generation in boilers: For steam generation, boilers are employed. If hard water is used in boilers, It may lead to the following troubles-**
 - **Boiler corrosion**
 - **Scale and sludge formation**
 - **Priming and foaming**
 - **Caustic embrittlement**

Hardness of Water

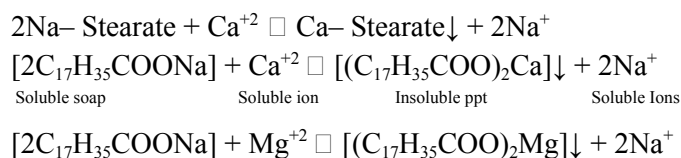
- Soft water readily produces a lot of lather when mixed with little soap.
- Hard Water: The water which does not produce lather (or) very little lather with soap is called Hard Water. The Hardness of water is caused by the presence of dissolved salts such as Bicarbonates, Sulphates, Chlorides and Nitrates of bivalent metal ions like Ca^{+2} & Mg^{+2} .

Soap is sodium/ potassium salt of higher fatty acids like stearic, oleic, and palmitic acids. When soap is mixed with **soft water**, lather is produced due to stearic acid and sodium stearate.



Stearic Acid + Na-Stearate \rightleftharpoons Formation of lather.

When soap comes in contact with **hard water**, Sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is a white precipitate.



Types of Hardness:

1. **Permanent hardness/Non-Carbonate hardness:** Permanent hardness of water is due to the dissolved chlorides, sulphates, and nitrates of calcium and magnesium. These salts are CaCl_2 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, MgCl_2 , MgSO_4 , $\text{Mg}(\text{NO}_3)_2$. These hardness cannot be removed easily by boiling. Hence it is called “Permanent Hardness”. Only chemical treatment can remove this hardness.
2. **Temporary hardness/Carbonate hardness:** Temporary hardness is caused by two dissolved bicarbonate salts $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. The hardness is called “Temporary Hardness” because it can be removed easily by boiling.

$$\text{Ca}(\text{HCO}_3)_2 + \Delta \rightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O} + \text{CO}_2\uparrow$$

$$\text{Mg}(\text{HCO}_3)_2 + \Delta \rightarrow \text{Mg}(\text{OH})_2\downarrow + 2\text{CO}_2\uparrow$$

Degree of Hardness

- The concentration of hardness as well as non-hardness constituting ions is usually expressed in the term of “Equivalent amount of CaCO_3 ”
- Since this mode permits the multiplication and division concentration, when required.
- The choice of CaCO_3 in particular is because its molecular weight (m.wt.) is “100” (Equivalent wt. = 50)
- Moreover, it is insoluble salt that can be precipitated in water treatment.
- Hardness causing salt in terms of equivalent of $\text{CaCO}_3 = \frac{\text{Mass of hardness causing salt} * 100}{\text{Molecular weight of hardness causing salt}}$

Units of hardness

- Parts per million (PPM): PPM is the number of parts of CaCO₃ equivalent hardness per 10⁶ (a million) parts of water. i.e., 1 PPM = 1 part of CaCO₃ equivalent hardness in 10⁶ parts of water.
- Milligrams Per Litre (mg/litre): mg/L is the number of milligrams of CaCO₃ equivalent hardness present per litre of water. **1 mg/L = 1 ppm**
- It is defined as the number of parts of CaCO₃ equivalent hardness per 70,000 parts of water. **1 ppm = 0.07°Cl**
- It is the number of parts of CaCO₃ equivalent hardness per 10⁵ parts of water. **0.1 °Fr = 1 ppm**
- Milliequivalent per litre (meq/L): It is the number of milliequivalent of hardness present per litre of water. **1 meq/L = 50 ppm**

How many grams of FeSO₄ dissolved per litre gives 210.5ppm of hardness?

Solution: M. wt. of FeSO₄= 152; M. wt. of CaCO₃= 100

FeSO₄ >>> CaCO₃

152 >>>>> 100

100ppm hardness >>>> 152 ppm of FeSO₄

So, 210.5 ppm hardness= 152 x 210.5 ÷ 100= 319.96ppm of FeSO₄

Thus, 0.319g of FeSO₄ dissolved per litre gives 210.5ppm of hardness

Determination of hardness using the EDTA method

- This is a complexometric titration method where Ethylenediamine tetraacetic acid (EDTA) is used.
- EDTA forms complexes with different metal ions at different pH.
- Calcium & magnesium ions form complexes with EDTA at pH 9- 10.
- To maintain the pH 9- 10 NH₄Cl, NH₄OH buffer solution is used.
- The disodium salt of EDTA is used for complexation.
- An alcoholic solution of Eriochrome Black-T (EBT) is used as an indicator.
- When hard water comes in contact with EDTA at pH 9- 10, the Ca⁺² & Mg⁺² form a stable, colourless complex with EDTA.
 $\text{Ca}^{+2} + \text{EDTA} + \text{pH}_{9-10} \rightarrow \text{Ca-EDTA}$
 $\text{Mg}^{+2} + \text{EDTA} + \text{pH}_{9-10} \rightarrow \text{Mg-EDTA}$
- To the hard water sample, the alcoholic blue coloured EBT indicator is added along with the NH₄Cl + NH₄OH buffer (pH 9- 10) solution. EBT forms an unstable wine-red complex with Ca⁺² & Mg⁺².

$(\text{Ca}^{+2} + \text{Mg}^{+2}) + \text{EBT} + \text{Buffer (pH 9-10)} \rightleftharpoons (\text{Ca-EBT} + \text{Mg-EBT}) \text{ complex}$
(Hard water) (Indicator) (Unstable **wine-red** complex)

- This wine-red coloured [Ca-EBT & Mg-EBT] complex is then titrated against EDTA; when EDTA replaces EBT from Ca-EBT & Mg-EBT complex and forms stable colourless [Ca-EDTA] & [Mg-EDTA] complex releasing the blue coloured indicator EBT into H₂O.



Steps:

1. **Preparation of SHW:** Dissolve 1 gm of pure, dry CaCO₃ in a minimum quantity of dilute HCl and evaporate the solution to dryness on a water-bath. Dissolve the residue in distilled water to make 1 litre in a standard flask and shake well.
Molarity of SHW = $\frac{\text{wt of CaCO}_3}{\text{Mol. Wt of CaCO}_3} = \frac{1\text{gm}}{100\text{gm}} = .01M$
2. **Preparation of EDTA solution:** Dissolve 4 gms of pure EDTA-disodium salt crystals along with 0.1 gm of MgCl₂ in one litre of distilled water.
3. **Preparation of EBT:** Dissolve 0.5 gms of Erichrome Black-T in 100 ml of alcohol.
4. **Prep of Buffer Soln:** Add 67.5 g of NH₄Cl to 570 ml of concentrated ammonia solution and dilute with distilled water to one litre.
5. **Standardization of EDTA Soln:** Pipette out 20 ml of standard hard water solution into a conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured complex with EDTA taken in a burette after rinsing it with EDTA solution till the wine red colour changes to clear blue. Note the burette reading and let the volume be “x”ml. Repeat the titration to get concurrent values.
6. **Titration of SHW:** Pipette out 20 ml of the water sample into a 250ml conical flask, add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured solution with EDTA taken in the burette till a clear blue coloured end point is obtained. Let the volume of EDTA be “y” ml. Repeat the titration to get concurrent values
7. **Titration for Permanent Hardness:** Pipette out 100 ml of hard water sample in a beaker and boil till the volume reduces to 20 ml. All the bicarbonates of Ca⁺⁺ and Mg⁺⁺ decomposes to CaCO₃ and Mg(OH)₂. Cool the solution and filter the water into a flask, wash the beaker and precipitate with distilled water and add the washing to conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator and titrate with EDTA solution taken in the burette till a clear blue colour end point is obtained. Note the burette reading. Let the volume be “z” ml.

Boiler Troubles

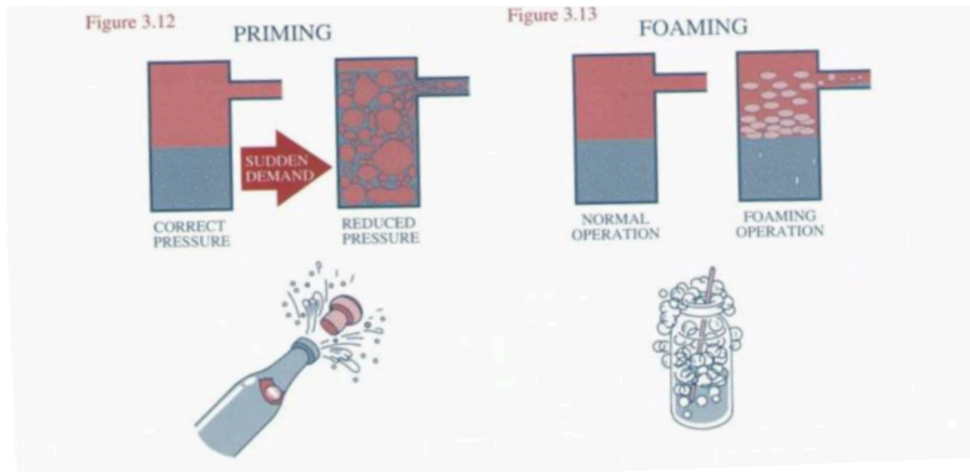
Water is greatly useful for generation of steam in boilers. Hard water causes harm to these boilers.

1. Priming and foaming

The bubbles which form when foam of champagne etc is flown into the air is priming. Droplets of liquid and water throughout the boiler get spread out. When you blow in air, the bubbles that arise are foaming. Foam in boilers accumulates on the top. In boilers, along with steam, these water droplets and foam get transported to the outlet. This reduces boiler efficiency.

Priming: When the boiler is steaming quickly, the particles of liquid are carried along with the steam.

Foaming: Formation of bubbles and foam on the surface. Caused due to large quantities of suspended impurities and oils.



Can be avoided by:

- Maintaining low water level
- Using soft water
- Fitting mechanical steam purifiers
- Using a good designed boiler
- Avoiding a sudden change in the speed of steam rate
- Blow down of boiler
- Adding anti foaming element

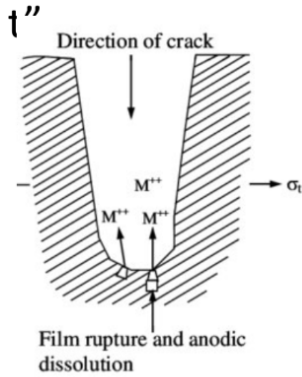
Disadvantage of priming and foaming:

- Actual water level is invisible.
- Wastage of heat with the result that it becomes difficult to keep up steam pressure: low efficiency.

2. Caustic embrittlement

Appearance of cracks inside the boiler. Especially at places which are under stress, for example, riveted joints. Steam accumulates in these cracks and becomes water. This water solvates sodium salt and becomes impure. When this water is heated again, the steam transported is not pure, it leaves behind NaOH. The NaOH in turn accumulates slowly in these cracks and joints. The NaOH will start eating away the material of the boiler, and decompose into different compounds eventually forming rust. Thus, the hairline crack turns into wider and longer cracks, forming holes. The water leaks and pressure drops, the boiler collapses and becomes useless.

During the softening of water, free sodium carbonate is usually present in small amounts in the water. Under high pressure and temperature, this releases NaOH and CO₂.



Can be avoided by:

- Adding sodium sulphate and tannin. Prevents infiltration of caustic soda.
- Using sodium phosphate instead of sodium carbonate.

Disadvantages:

- Failure and breakdown of boiler.

3. Boiler Corrosion

The decay of boiler material by chemical/electrochemical attack by its environment is called Boiler Corrosion.

Reasons:

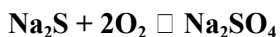
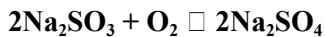
(a) Dissolved oxygen

Water usually contains about 8 mg/L of dissolved oxygen at room temperature.

Disadvantage: Dissolved O_2 at high temperature attacks boiler material.



Removal: By adding a calculated quantity of sodium sulphate (or) hydrazine (or) sodium sulphide.



(b) Dissolved CO_2

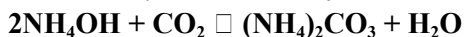
Dissolved CO_2 has a slow corrosive effect on the materials of boilerplate. The boiler feed has bicarbonates, which adds CO_2 into the water. Under the high temperature and pressure, the bicarbonates decompose to produce CO_2 .



Disadvantage: CO_2 causes a slow corrosion on the boiler plate by producing carbonic acid.



Removal: By the addition of a calculated quantity of ammonia.



(c) Acids from dissolved salts

Water containing dissolved Mg-salts liberate acids on hydrolysis:



Disadvantage: The acid reacts with iron on the boiler plate to produce decay of the material of the boiler. Even a small amount of MgCl_2 can cause a lot of damage to the boiler.



Removal/Prevention:

- Softening the water to remove MgCl_2
- Adding corrosion inhibitors like sodium silicates, sodium phosphate & sodium chromate.
- **Blow-down operation:** Replacing the salt-concentrated water with fresh soft water in the boiler.

4. Scale and sludge formation

In a boiler, water evaporates continuously and the concentration soon reaches saturation point.

This forms precipitates (scale or sludge) on the inner wall of the boiler.

Sludge: Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludge are formed by substances which have greater solubility in hot water than in cold water. Salts like MgCO_3 , MgSO_4 , MgCl_2 , CaCl_2 etc., are responsible for sludge formation in boilers.

Prevention: Use of soft water and frequent blow-down operations.

Scales: Scales are the hard, adhering ppt formed on the inner wall of the boiler. Very difficult to remove once they are deposited on the inner wall of the boiler. They formed due to decomposition of Calcium bicarbonate, Calcium sulphate etc. $\text{Ca(HCO}_3)_2 \rightleftharpoons \text{CaCO}_3\downarrow + \text{H}_2\text{O} + \text{CO}_2\uparrow$

Removal: Thermal shocks, washing with 5-10% HCl, frequent blow-down for loose scales.

Prevention: Use of soft water.

Softening of Water

The removal of hardness causing salts from water is called softening of water.

There are three industrial processes for this:

1. Lime-Soda Process
2. Zeolite (or) Permutit Process
3. Ion-Exchange (or) Demineralization process

Lime-Soda Process

When we add lime (Calcium hydroxide) and soda (Sodium Carbonate) to the water, soluble salts of calcium and magnesium are turned into insoluble precipitates of calcium carbonate and magnesium hydroxide. The precipitate is easily removed by filtration.

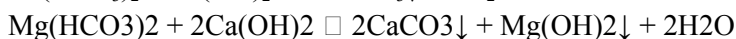
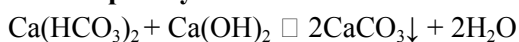
Formulae:

$$\text{Lime} = \frac{74}{100} \times \text{Hardness equivalents (L + L... etc)} \times \frac{\text{Volume of water in ml}}{1000} \times \frac{100}{\text{Percentage purity of lime}}$$

$$\text{Soda} = \frac{106}{100} \times \text{Hardness equivalents (S + 2S... etc)} \times \frac{\text{Volume of water in ml}}{1000} \times \frac{100}{\text{Percentage purity of soda}}$$

Any free dissolved CO₂ and acids are also removed by this process.

a. For temporary hardness <bicarbonates>: ONLY LIME



b. For MgSO₄ or MgCl₂: SODA AND LIME



c. For CaSO₄ and CaCl₂: ONLY SODA



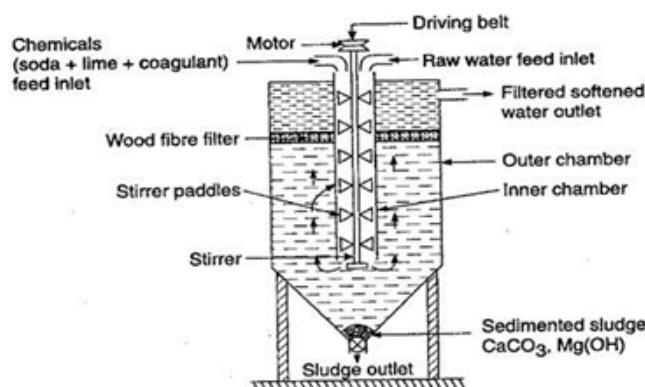
Free acids, CO₂, and H₂S dissolved iron and aluminium salts etc are also removed in this process.

- $2\text{HCl} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2\uparrow$
- $\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2\uparrow$
- $\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$
- $\text{H}_2\text{S} + \text{Ca(OH)}_2 \rightarrow \text{CaS}\downarrow + 2\text{H}_2\text{O}$
- $\text{FeSO}_4 + \text{Ca(OH)}_2 \rightarrow \text{Fe(OH)}_2\downarrow + \text{CaSO}_4$
- $\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3\downarrow + 3\text{CaSO}_4 + \text{H}_2\text{O}$

Constituent	Reaction	Requirement
Ca ⁺² (Permanent)	(i) $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3\downarrow + \text{Na}_2\text{SO}_4$ (ii) $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3\downarrow + 2\text{NaCl}$	S
Mg ⁺² (Permanent)	(iii) $\text{MgSO}_4 + \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2\downarrow + \text{CaCO}_3\downarrow + \text{Na}_2\text{SO}_4$ (iv) $\text{MgCl}_2 + \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2\downarrow + \text{CaCO}_3 + 2\text{NaCl}$	L + S
HCO ₃ ⁻	(v) $2\text{NaHCO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	L - S
Ca(HCO ₃) ₂ (Temporary)	(vi) $\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3\downarrow + 2\text{H}_2\text{O}$	L
Mg(HCO ₃) ₂ (Temporary)	(vii) $\text{Mg(HCO}_3)_2 + 2\text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3\downarrow + \text{Mg(OH)}_2\downarrow + 2\text{H}_2\text{O}$	2L

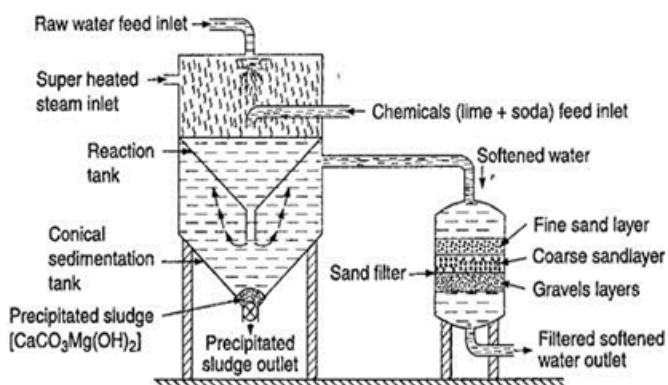
CO_2	(viii) $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$	L
H^+	(ix) $2\text{HCl} + \text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl} + \text{H}_2\text{O}$	L + S
Coagulants FeSO_4 <CHAIN RXN>	(x) $\text{FeSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 + \text{CaSO}_4$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe}(\text{OH})_3$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	L + S
$\text{Al}_2(\text{SO}_4)_3$	(xi) $\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3\downarrow + 3\text{CaSO}_4 + \text{H}_2\text{O}$ $3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 3\text{Na}_2\text{SO}_4$	L + S
NaAlO_2	(xii) $\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$	-L

Cold Lime Soda Process



- In this method the lime & soda are mixed with hard water at room temperature with constant stirring via the triangular paddles.
- Generally the precipitates formed by this process are finely divided. To ensure that the precipitates settle, coagulants like alum, ferrous sulphate, etc. are added.
- The chemical reactions take place and the hardness producing salts get converted into insoluble precipitates.
- The softened water passes through a wood fibre filter to ensure the complete removal of any residual, very fine sludge particles. The clear softened water is withdrawn from the top of the outer chamber.
- The sludge is removed from the bottom of the outer chamber.
- The softened water from this process contains a residual hardness of 50-60 ppm. This is still unfit to send to the boiler.

Hot Lime Soda Process



- This process is similar to the cold lime-soda process, but *no coagulant is needed*.
- Here the process is carried at a temperature of 80° to 150°C.
- a) The reaction takes place faster.
- b) The sludge settles rapidly.
- c) Viscosity of soft water is lower, hence filtered

easily. d) The dissolved gases such as CO_2 , air, etc. are driven out of the water. e) The residual hardness is low.

- Hot lime soda process consists of three parts:
 1. Reaction Tank: The complete mixing of water, chemicals and steam takes place and water gets softened.
 2. Conical Sedimentation Vessel: The majority part of sludge settles down here.
 3. Sand filter: Where sludge is completely removed by passing through three levels of sand.
 The softened water from this process contains a residual hardness of 15-30 ppm. This is still not soft enough.

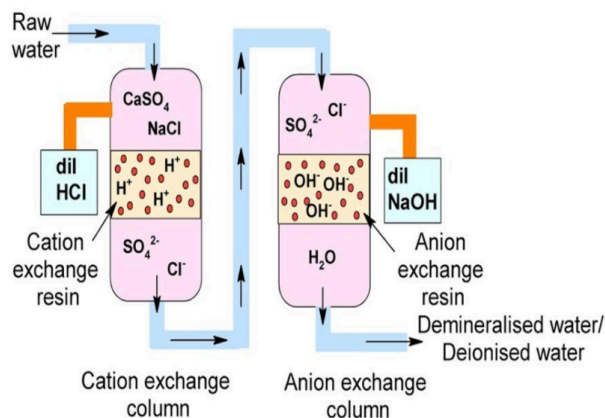
<u>Disadvantages of Lime Soda Process</u>	<u>Advantages of Lime Soda Process</u>
Due to still residual hardness, water is unfit for boilers.	Economical
	Low mineral content in resultant water
	Increases pH, reduces pathogenic bacteria
Large amounts of sludge are difficult to dispose of.	Mg and Fe salts are also removed
	Improves corrosion resistance

Ion Exchange / Demineralisation Process

Resins used in this process are insoluble, cross-linked, and long chained organic polymers. The functional groups of these resin chains exchange the hardness-causing ions in the water.

1. The first chamber is packed with cation exchange resin RH^+ . The hard water passed through the bed exchanges calcium magnesium ions in the water with H^+ ions.
2. The second chamber is packed with anion exchange resin. In this exchange, OH^- is sent into the water and negative ions of Cl^- , SO_4^- , etc are embedded in the bed.

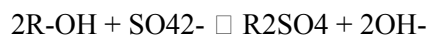
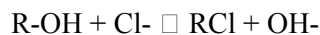
DEMINERALISATION PROCESS/ ION-EXCHANGE PROCESS



Cation:



Anion:



Net:



Regeneration of Resins

The exhausted cation exchange resin is regenerated by adding dil HCl

For anion exchange resin, we add NaOH (dil.) which regenerates the OH^- lost to softening.

Advantage:

- Works for boilers since the water is very soft. 2ppm or less

Disadvantage:

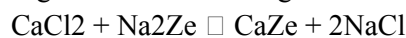
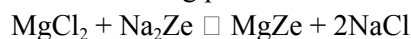
- Cost
- Lacks nutritional value

Numerical 1: In ion exchange process, the cation exchanger required 150 litres of 1N HCl and the anion exchanger required 150 litres of 1N NaOH. If the hardness of water is 250 ppm, find the volume of water softened.

Zeolite or Permutit Process

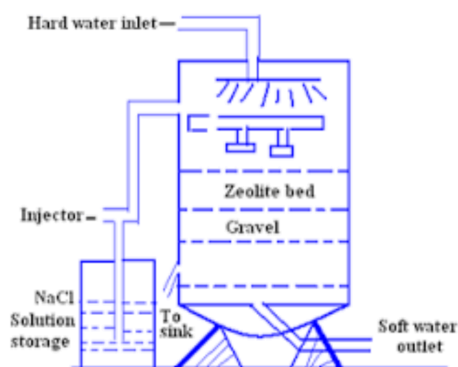
Zeolite is “Hydrated sodium alumino silicate”. Its general formula is: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$; $x = 2-10$ $y = 2-6$. Eg: Natrolite: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Natural zeolites are generally non-porous. The artificial zeolite is called Permutit. These are prepared by heating together with chain clay, feldspar and soda ash. These are porous and have greater softening capacity than natural zeolite. They exchange Na^+ ions with the hardness producing ions (Ca^{2+} , Mg^{2+} , etc.) in water. Sodium Zeolite is denoted as Na_2Ze .

PROCESS: In this process hard water is passed through a bed of zeolite at ordinary temperature. The hard water percolates (filter) Ca^{+2} , Mg^{2+} present in hard water are exchanged with Na^+ ions. The following reactions taking place:



Regeneration Of Zeolite: On continuous passing of hard water through sodium zeolite bed it is converted to calcium and magnesium zeolite which is known as ‘Exhausted Bed’. Hence, it must be regenerated. This can be done by washing zeolite beds with 10% sodium chloride solution.





ADVANTAGES:

- The equipment is **small and easy to handle**.
- It requires **less time for softening**.
- Water obtained from this process contains a residual hardness **upto 10 ppm**.
- Easy to regenerate.
- **No sludge is formed in this process**.

DISADVANTAGES:

- Highly turbid water cannot be treated by this process.
- The process exchanges only Ca^{+2} & Mg^{2+} ions by sodium ions and hence the softened water contains more sodium salts.
- All the acidic ions like HCO_3^- , CO_3^{2-} , etc. are not removed by this process. Sodium bicarbonate decomposes in the boiler releasing CO_2 which leads to corrosion. While Na_2CO_3 is hydrolysed to NaOH which creates caustic embrittlement of boiler.

Methods to Determine Extent of Water Pollution

Biological Oxygen Demand: (BOD)

Biological oxygen demand (BOD) is the **amount of free oxygen** needed for the **biological oxidation** of **organic material** under **aerobic conditions** in a given water sample at a certain temperature over a **specific time period** (most common 5 days of incubation at 20°C .). The BOD value is most commonly expressed in mg/L or ppm.

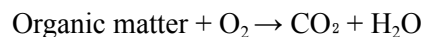
Determination of BOD:

1. Specialized 300 mL BOD bottles designed to allow full filling with no air space and provide an airtight seal are used. The bottles are filled with the sample to be tested or dilution (distilled or deionized) water and various amounts of the wastewater sample are added to reflect different dilutions. At least one bottle is filled only with dilution water as a control or "blank."

2. A D.O. meter is used to measure the initial dissolved oxygen concentration (mg/L) in each bottle, which should be at least 8.0 mg/L. Each bottle is then placed into a dark incubator at 20°C for five days.
3. After five days (± 3 hours) the DO meter is used again to measure a final dissolved oxygen concentration (mg/L), which ideally will be a reduction of at least 4.0 mg/L.
4. The final DO reading is then subtracted from the initial DO reading and the result is the BOD concentration (mg/L). If the wastewater sample required dilution, the BOD concentration reading is multiplied by the dilution factor.

$$\begin{aligned}
 &= \text{BOD} = (\text{Dob} - \text{DOI}) \times \text{dilution factor} \\
 &= (\text{DOB} - \text{DOI}) \times \frac{\text{volume of diluted sample}}{\text{volume of sample before dilution}}
 \end{aligned}$$

BOD is influenced by type of microorganisms, presence of toxins, pH, reduced minerals, etc.



BOD is proportional to the amount of organic material to be degraded. An average sewage has BOD 100-150 ppm. Above this, the sewage should be treated before disposing in the ocean. Drinking water should have BOD less than 1 ppm.

Significance of BOD:

1. Indicates the amount of decomposable organic matter in sewage.
2. Higher BOD means a higher amount of decomposable matter in the sample, thus higher pollution.
3. From BOD, the self purifying capacity of streams is determined. Thus, BOD is used to find the degree of pollution at any time in the sewage stream.

Biochemical oxygen demand / biological oxygen demand is an important water quality parameter because it provides an index to assess the effect discharged wastewater will have on the receiving environment. The BOD is important in sewage treatment because it indicates the amount of decomposable organic matter in sewage water.

Chemical Oxygen Demand (COD)

COD is the amount of oxygen needed to oxidise chemically degradable organic matter in hot conditions using oxidants like acidified $\text{K}_2\text{Cr}_2\text{O}_7$ in 2 to 3 hours. The unit is the same: mg/L and ppm.

The chemical oxygen demand (COD) is a measure of water and wastewater quality. The COD test is often used to monitor water treatment plant efficiency. The COD is the amount of oxygen consumed to chemically oxidise organic water contaminants to inorganic end products. The COD is often measured using a strong oxidant (e.g. potassium dichromate) under acidic conditions.

- A known volume of waste water sample (say 250 ml) is refluxed with a known excess of

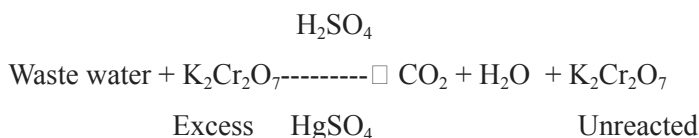
standard potassium dichromate (1 N) and dilute sulfuric acid mixture in the presence of silver sulphate catalyst for about 3 hours.

- This oxidises organic matter to CO_2 , NH_3 and H_2O .
- The unreacted potassium dichromate is titrated against ferrous ammonium sulphate (Mohr's salt) $((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$ with ferroin indicator till blue colour changes to wine red, or pink to green: the reading is (**Vt**).
- This gives the amount of potassium dichromate consumed (in terms of equivalent oxygen) required for degradation of organic pollutants.

Blank Titration:

Distilled water + $\text{K}_2\text{Cr}_2\text{O}_7$ (excess) + (HgSO_4 and H_2SO_4 as catalyst) \square Distilled water + $\text{K}_2\text{Cr}_2\text{O}_7$

Sample Titration:



Formula:

$$\text{COD} = \frac{(V_b - V_s) \times NFAS \times 8000}{\text{Volume of sample}}$$

Where,

$V_b - V_s$ = initial oxygen - final oxygen (amount of oxygen consumed by the waste for oxidation)

8000 = 8×1000 , millimoles to moles. 8 because oxygen's equivalent weight = 8

NFAS = number of moles in mohr's salt.

V_b : Volume of FAS for blank titration

V_s : Volume of FAS for sample titration

Significance of COD:

- COD remains unaffected by the presence of toxins and unfavourable conditions for the microbial growth.
- The COD test only takes a few hours to complete, giving it a major advantage over the 5-day BOD test. Wastewater treatment system personnel can use COD as an almost real-time operational adjustment parameter.
- COD can test wastewater that is too toxic for the BOD test.
- The COD test should be considered an independent measure of the organic matter in a wastewater sample rather than a substitute for the BOD test.
- The COD test uses a chemical (potassium dichromate in a 50% sulfuric acid solution) that "oxidizes" both organic (predominate) and inorganic substances in a wastewater sample, which

results in a higher COD concentration than BOD concentration for the same wastewater sample since only organic compounds are consumed during BOD testing.

- Taken as a basis for calculation of efficiency of treatment plant.
- It helps in designing the water treatment plant.

BOD	COD
It measures oxygen demand of bio-degradable organic pollutants only	It measures oxygen demand of bio-degradable and non biodegradable organic pollutants
Less stable measurement technique as micro-organisms are susceptible to variables such as pH and temperature	More stable measurement technique as no micro-organisms are used and potassium dichromate oxidizes any type of organic pollutants in water
Slow process, takes 5 days	Fast process , takes 3 hours
BOD values are generally less than COD values	COD values are generally greater than BOD values

Treatment of Sewage / Industrial waste:

In activated sludge process, wastewater containing organic matter is sprinkled using a sprinkler for higher dissolution of oxygen in an aeration basin in which micro-organisms metabolise the suspended and soluble organic matter. The microorganisms digest this waste and make this a sludge. The remains are called activated sludge. Half is sent for manure and the rest is sent for the next set of processing of water.

Step 1: Screening and Pumping

The incoming wastewater passes through screening equipment where objects such as rags, wood fragments, plastics, and grease are removed. The material removed is washed and pressed and disposed of in a landfill. The screened wastewater is then pumped to the next step: grit removal.

Step 2: Grit Removal

In this step, heavy but fine material such as sand and gravel is removed from the wastewater. This material is also disposed of in a landfill.

Step 3: Primary Settling

The material, which will settle, but at a slower rate than step two, is taken out using large circular tanks called clarifiers. The settled material, called **primary sludge**, is pumped off the bottom and the wastewater exits the tank from the top. Floating debris such as grease is skimmed off the top and sent with the settled material to digesters. In this step, chemicals are also added to remove phosphorus.

Step 4: Aeration / Activated Sludge

In this step, the wastewater receives most of its treatment. Through biological degradation, the pollutants are consumed by microorganisms and transformed into cell tissue, water, and nitrogen.

The biological activity occurring in this step is very similar to what occurs at the bottom of lakes and rivers, but in the bottom, the degradation takes years to accomplish.

Step 5: Secondary Settling

Large circular tanks called secondary clarifiers allow the treated wastewater to separate from the activated sludge from the aeration tanks at this step, yielding liquid waste (effluent), which is now over 90% treated. The biology (activated sludge) is continuously pumped from the bottom of the clarifiers and returned to the aeration tanks in step four.

Step 6: Disinfection

To assure the treated wastewater is virtually free of bacteria, ultraviolet disinfection is used after the filtration step. The ultraviolet treatment process kills remaining bacteria to levels within our discharge permit.

Water standard for domestic use

The following are the specification of water drinking purpose:

- This water should be clear, colourless and odourless.
- The water must be free from pathogenic bacteria and dissolved gases like H_2S .
- The optimum hardness of water must be 125 ppm and pH must be 7.0 to 8.5
- The turbidity in drinking water should not exceed 25ppm
- The recommended maximum concentration of total dissolved solids in potable water must not exceed 500ppm