# Unit 1
# Water

## COMMON IMPURITIES IN WATER

Water is a great solvent and it dissolves and sustains numerous types of impurities. Water collects impurities from ground rocks or soil with which it comes in contact. The common impurities present in natural water may be classified as follows:

**(a) Suspended Impurities**

(i) Inorganic impurities e.g. sand & clay.
(ii) Organic impurities e.g. animal matter. vegetables, oil.
(iii) Colloidal impurities: e.g. organic wastes, colouring matter, finely divided silica, clay. aluminium hydroxide, ferric hydroxide.
(iv) Micro-Organism e.g. bacteria like B. coli, fungi, algae.

**(b) Dissolved Impurities**

(i) Inorganic impurities like carbonates, bicarbonates, nitrates, sulphates and chlorides of Ca Mg, Fe, Na. K. Al. and sometimes Cu & Zn.
(ii) Dissolved gases like $CO_2$, SO, $N_2$, NH, etc.

## HARDNESS OF WATER

Water should be free from pathogenic bacterium, and hardness. Water which does not produce lather with soap solution readily is called hardwater while which lathers easily on shaking with soap solution is called soft water. Hardness is termed as the soap consuming capacity of a water sample. i.e. hardness is that characteristic "which prevents the lathering of soap". Hardness to water is due to salts of calcium, magnesium and other heavy metals.

$2C_{17}H_{33}COONa + CaCl_2$ $(C_{17}H35COO)_2Ca\downarrow + 2NaCl$

*Sodium Stearate (Soap)* *Calcium Stearate (insoluble)*

$2C_{17}H_{33}COONa + MgSO_4$ $(C_{17}H_{35}COO)_2\,Mg\downarrow + Na_2SO_4$

*Sodium Stearate (Soap)* *Magnesium Stearate (insoluble)*

**Types of Hardness**

1. *Temporary hardness or carbonate hardness:* The temporary hardness is due to presence of bicarbonates of calcium and magnesium. It can be removed by boiling of water, when bicarbonate ions are decomposed to form insoluble carbonates or hydroxides. It is also referred to as alkaline hardness.

   $Ca\,(HCO_3)_2$ $CaCO_3\downarrow + H_2O + CO_2\uparrow$

   *Calcium Bicarbonate* *Calcium Carbonate*

   $Mg\,(HCO3)_2$ $Mg\,(OH)_2\downarrow + 2CO_2\uparrow$

   *Magnesium Bicarbonate* *Magnesium Hydroxide*

2. *Permanent or non-carbonate hardness:* Permanent hardness is due to presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. It cannot be removed by simple boiling. It is also referred to as nonalkaline hardness.

**Degree of Hardness**

The hardness of water depends upon the amount of calcium, magnesium and other heavy metal salts present in it. The degree of hardness of water is usually expressed as equivalent amount of CaCO. This is because of two reasons:

- Its molecular weight is 100 (easy for calculation).
- It is the most insoluble salt that can be precipitated in water treatment.

Thus, it can be expressed as

$$Equivalents\ of\ CaCO_3\ for\ a\ hardness\ producing\ substance = \frac{Weight\ of\ hardness\ producing\ substance \times Chemical\ equivalent\ of\ CaCO_3\ (50)}{Chemical\ equivalent\ of\ hardness\ producing\ substance}$$

| Hardness Causing Ion | Molar Mass | Chemical Equivalent | Multiplication Factor to Convert into Its $CaCO_3$ Equivalent |
|---|---|---|---|
| $CaCO_3$ | 100 | 50 | 100/100 |
| $Ca\ (HCO_3)_2$ | 162 | 81 | 100/162 |
| $CaSO_4$ | 136 | 68 | 100/136 |
| $CaCl_2$ | 111 | 55.5 | 100/111 |
| $MgCO_3$ | 84 | 42 | 100/84 |
| $Mg\ (HCO_3)_2$ | 146 | 73 | 100/146 |
| $MgSO_4$ | 120 | 60 | 100/120 |
| $MgCl_2$ | 95 | 47.5 | 100/95 |
| $Mg\ (NO_3)_2$ | 148 | 74 | 100/148 |
| $Al\ (SO_4)_3$ | 342 | 57 | 100/114 or 100*3/342 |
| $NaAlO_2$ | 82 | 82 | 100/82*2 |
| HCO3 | 61 | 61 | 100/62*2 |
| $FeSO_4.7H_2O$ | 278 | 139 | 100/278 |
| $CO_2$ | 44 | 22 | 100/44 |
| $Ca^{2+}$ | 40 | 20 | 100/40 |
| $Mg^{2+}$ | 24 | 12 | 100/24 |
| $H^+$ | 1 | 1 | 100/1*2 |
| HCl | 36.5 | 36.5 | 100/35.5*2 |
| $H_2SO_4$ | 98 | 49 | 100/98 |
| $OH^-$ | 17 | 17 | 100/17*2 |
| $CO_3^{2-}$ | 60 | 30 | 100/60 |

**Units of Hardness**

| Units | Definition |
|---|---|
| 1 ppm | 1 part of $CaCO_3$ equivalent hardness in $10^6$ parts of water |
| 1 mg/L | 1 part of $CaCO_3$ equivalent hardness in $10^6$ parts of water |
| 1 °Fr | 1 part of $CaCO_3$ equivalent hardness in $10^5$ parts of water |
| 1 °Cl | 1 part of $CaCO_3$ equivalent hardness in 70,000 parts of water |

Relationship between various units of hardness:

1ppm = 1mg/L = 0.1°Fr = 0.07°Cl

1°Cl = 1.433°Fr = 14.3ppm = 14.3 mg/L

1°Fr = 10ppm = 10mg/L = 0.7°Cl

## DETERMINATION OF HARDNESS BY EDTA METHOD

The EDTA method is a complexometric titration technique. EDTA, or Ethylenediaminetetraacetic acid, is a chelating agent that forms stable, water-soluble complexes with $Ca^{2+}$ and $Mg^{2+}$ ions present in hard water. The reaction between EDTA and metal ions is:

$$M^{2+} + EDTA^{4-} \rightarrow [M - EDTA]^{2-}$$

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

EDTA forms a 1:1 stable chelate complex with each metal ion. This reaction proceeds sharply at a certain pH (10), which is maintained using a buffer solution (typically ammonium chloride–ammonium hydroxide buffer).

**Indicator Used: Eriochrome Black T (EBT)**

- EBT is a metal ion indicator used in EDTA titration.
- At pH 10, EBT forms a weak wine red colored complex with $Ca^{2+}/Mg^{2+}$ ions.
- When titrated with EDTA, the metal ions form more stable complexes with EDTA and are released from the EBT complex.
- The color change from wine red to pure blue marks the endpoint of the titration.

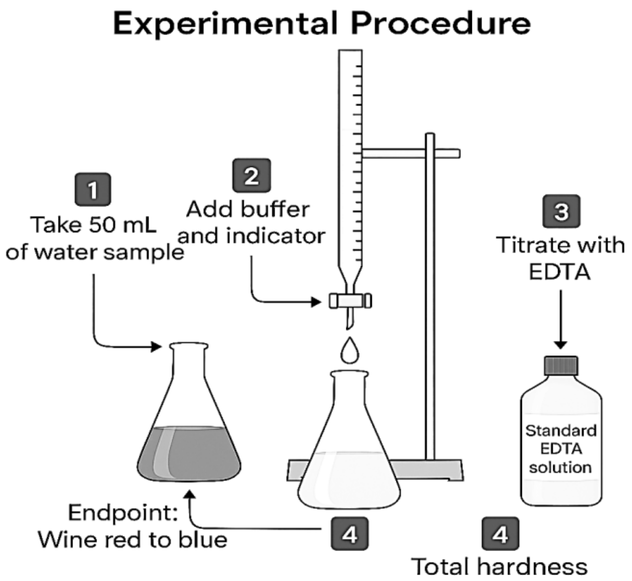
$$Ca^{2+}/Mg^{2+} + +EBT \rightarrow Wine\ Red\ Complex$$
$$Ca^{2+}/Mg^{2+} + +EDTA \rightarrow Colorless\ Complex$$
$$Free\ EBT\ (after\ titration) = Blue\ color$$

**Required Chemicals and Reagents**

- Standard hard water (with known $Ca^{2+}$ and $Mg^{2+}$ content)
- EDTA solution (0.01 M)
- Buffer solution $(NH_4Cl + NH_4OH, pH \approx 10)$
- Eriochrome Black T indicator (in alcohol)
- Water sample
- Distilled water

**Experimental Procedure**

1. Take 50 mL of the water sample into a clean conical flask.
2. Add 2–3 mL of buffer solution to maintain pH around 10.
3. Add 2–3 drops of Eriochrome Black T indicator.
    - The solution turns wine red.
4. Fill a burette with standard EDTA solution (0.01 M).
5. Titrate the solution slowly, with constant swirling.
6. As EDTA binds $Ca^{2+}$ and $Mg^{2+}$ ions, the wine-red color fades.
7. At the end point, the color changes from wine red to sky blue.
8. Note the volume of EDTA used ($V_1$ mL).




This gives the total hardness of water.

**Determination of Permanent Hardness**

To determine permanent hardness, boil another 50 mL of the same water sample for 15–20 minutes to remove bicarbonates (temporary hardness). Cool, filter, and titrate the clear filtrate using the same procedure.

- Note the volume of EDTA used as $V_2$ mL.

**Determination of Temporary Hardness**

Temporary hardness is simply:

$$Temporary\ Hardness = Total\ Hardness - Permanent\ Hardness$$

**Calculations**

Let:

- $V$ = volume of EDTA used for titration (mL)
- $M$ = molarity of EDTA
- $V_{Sample}$ = volume of water sample (usually 50 mL)

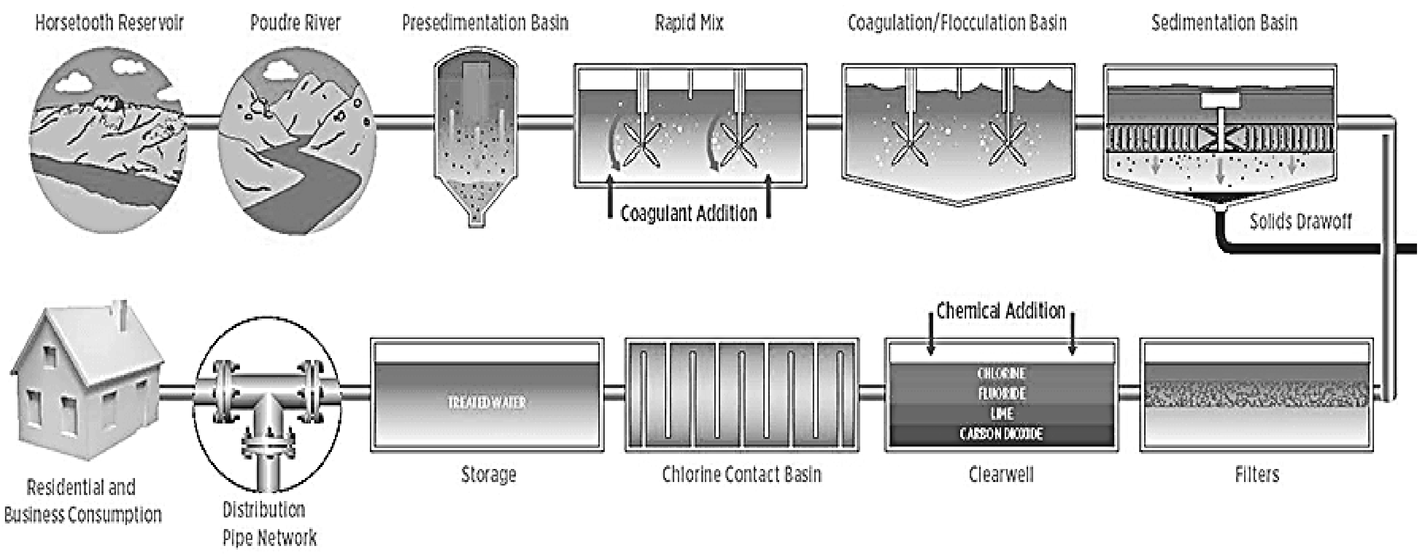
$$1\ mole\ of\ EDTA\ =\ 1\ mole\ of\ CaCO_3\ equivalent\ hardness\ =\ 100\ g\ CaCO_3$$

$$Hardness\ (mg/L) = \frac{V \times M \times 100{,}000}{\mathrm{V_{Sample}}}$$

## MUNICIPAL WATER SUPPLY PROCESS

Municipal water supply is the system responsible for delivering safe and potable water to the public for domestic, industrial, and commercial use. The process begins with the collection of water from natural sources such as rivers, lakes, reservoirs, or underground aquifers. The raw water undergoes treatment in a water treatment plant to remove physical, chemical, and biological contaminants. After proper purification, it is stored in overhead tanks and then distributed through a network of pipelines to households and industries.

The key objective of this process is to ensure that the water delivered is free from disease-causing organisms, color, Odor, turbidity, and toxic substances, thus meeting the health and aesthetic standards set by government and international bodies like WHO.




**Requirements of Drinking Water**

Drinking water must fulfil several essential requirements to be considered safe and suitable for human consumption. These requirements are categorized as follows:

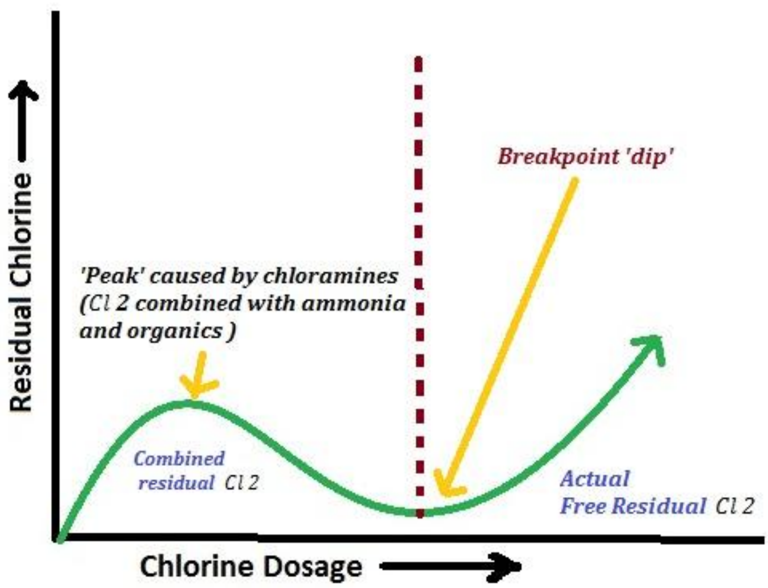
1. *Physical Requirements:*
   - Water should be colorless, tasteless, and odorless.
   - It should be free from suspended solids and turbidity.
   - Temperature should be moderate (not too hot or cold).
2. *Chemical Requirements:*
   - Should have a pH between 6.5 to 8.5.
   - Must be free from harmful chemicals such as lead, arsenic, mercury, and excessive fluoride or nitrates.
   - Total dissolved solids (TDS) should be below 500 mg/L.
3. *Biological Requirements:*
   - Must be free from pathogenic bacteria, viruses, and protozoa.
   - Coliform count should be zero in 100 mL of drinking water.

Meeting these parameters is critical for ensuring public health and preventing waterborne diseases.

**Water Purification Steps**

To meet drinking water standards, the raw water is subjected to the following treatment processes:

1. *Sedimentation*
   Sedimentation is a process of allowing suspended solids in water to settle under the influence of gravity. This step is typically carried out in sedimentation tanks, where water is held stationary, allowing heavier particles to settle at the bottom. The clarified water is then drawn off from the top.
2. *Filtration*
   The clarified water is passed through filters to remove fine suspended impurities and microorganisms. Filters are generally made up of layers of sand, gravel, and charcoal. This step further improves water clarity and removes residual turbidity.
3. *Disinfection*
   Disinfection is done to destroy pathogenic organisms. The most commonly used disinfectant is chlorine due to its effectiveness and residual action. Alternatives include ozone, UV light, and chloramines. Disinfection ensures the water is microbiologically safe for consumption.
4. *Breakpoint Chlorination*
   Breakpoint chlorination is a method of adding chlorine to water until the chlorine demand is satisfied, and a free residual chlorine remains. This point, known as the breakpoint, ensures that all ammonia and organic nitrogen compounds have been oxidized, leaving sufficient chlorine to disinfect any remaining pathogens. This is considered the most effective form of chlorination.



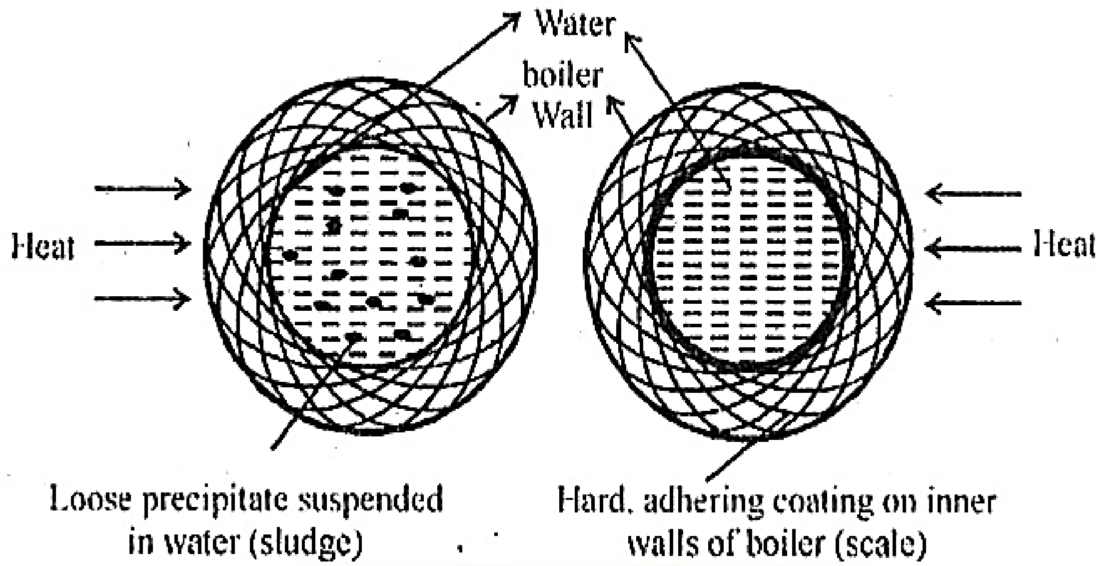
## BOILER PROBLEMS

When untreated or impure water is used in boilers, it gives rise to various problems, including:

**A. Scale and Sludge Formation**

- *Scale:* Hard, adherent deposits formed due to the precipitation of dissolved salts $(e.g., CaSO_4, CaCO_3)$ under high temperature and pressure.
- *Sludge:* Soft, loose, and non-adherent deposits formed from substances like $MgCl_2$ and $MgCO_3$.

*Consequences:* Reduced heat transfer, increased fuel consumption, and risk of boiler explosion.




**B. Priming and Foaming**

- *Priming:* Carryover of water droplets with steam due to high steam velocity or sudden boiling.
- *Foaming:* Formation of stable foam or bubbles on the water surface caused by oils, alkalies, or organic substances.

*Effects:* Impaired boiler efficiency, damage to turbine blades, and wet steam delivery.

**C. Boiler Corrosion**

Corrosion is the gradual destruction of boiler metal due to electrochemical or chemical attack. It may be caused by:



- Dissolved oxygen forming rust $(Fe_2O_3)$
- $CO_2$ forming carbonic acid
- Acids from decomposed salts

  *Result:* Thinning and weakening of boiler parts, leakage, or failure.

## WATER TREATMENT METHODS

Water treatment aims to prevent boiler problems and make water suitable for industrial or domestic use. It is classified into Internal and External Treatments.

**Internal Treatment Methods**

These are chemical treatments given inside the boiler to convert scale-forming salts into soft sludges that can be easily removed by blowdown. Some common methods include:

1. *Phosphate Conditioning:*
   - Addition of sodium phosphate $(Na_3PO_4)$ reacts with hardness salts to form soft sludges.
   - Example: $CaCl_2 + Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + NaCl$
2. *Carbonate Conditioning:*
   - Sodium carbonate $(Na_2CO_3)$ is added to convert calcium sulfate into calcium carbonate sludge.

3. *Colloidal Conditioning:*
    - Organic substances (e.g., tannin, starch) are added to keep precipitates in suspension.

**External Treatment Methods**

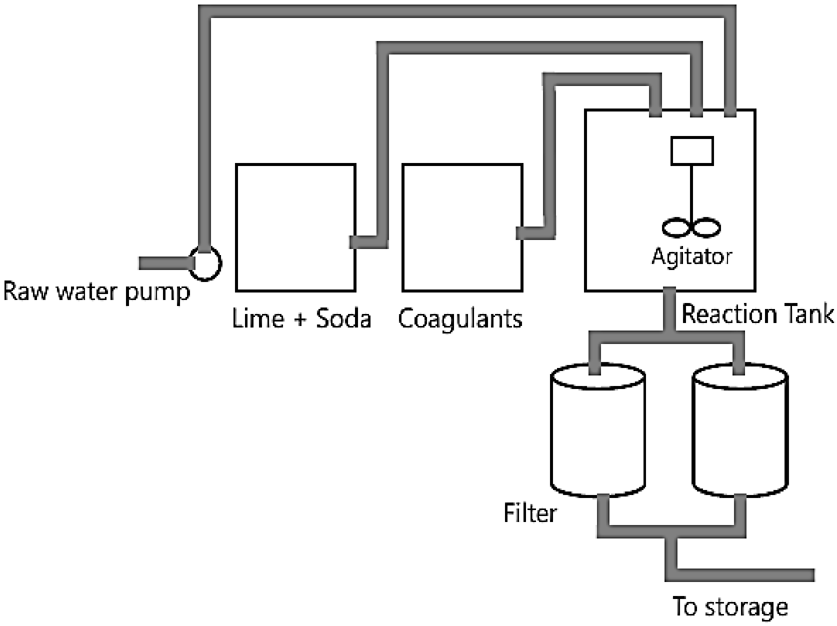
These are treatments applied before water enters the boiler. It includes:

1. *Lime-Soda Process*

   In this method, calculated amounts of lime ($Ca(OH)_2$) and soda ash ($Na_2CO_3$) are added to hard water. They precipitate calcium and magnesium ions as $CaCO_3$ and $Mg(OH)_2$ respectively.

   $$Ca^{2+} + CO_3{}^{2-} \rightarrow CaCO_3 \downarrow$$
   $$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow$$

   This process may be carried out in:
    - Cold Lime-Soda Process (at room temperature)
    - Hot Lime-Soda Process (at 80–90°C, more efficient)

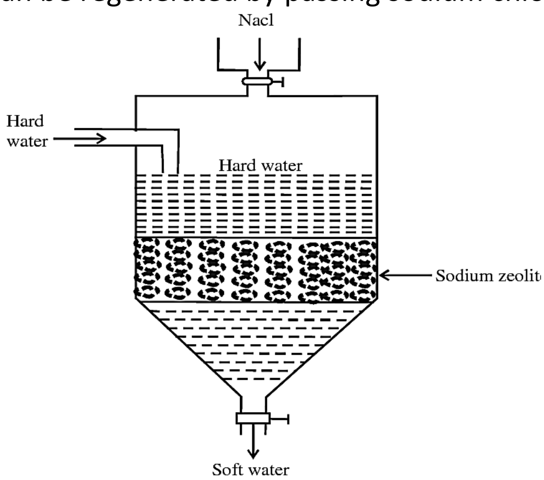



2. *Zeolite Process*

   Zeolite or permutit is a natural or synthetic sodium aluminosilicate which exchanges $Na^+$ ions with $Ca^{2+}$ and $Mg^{2+}$.

   $$Ca^{2+} + Na_2Ze \rightarrow CaZe + 2Na^+$$

   Once exhausted, zeolite can be regenerated by passing sodium chloride (NaCl) solution.




3. *Ion Exchange Process*

   In this method, both cation and anion exchangers are used:
    - Cation exchanger: Removes $Ca^{2+}$, $Mg^{2+}$ by replacing them with $H^+$.

- Anion exchanger: Removes $Cl^-$, $SO_4^{2-}$ by replacing them with $OH^-$.

$$H^+ + OH^- \text{ combine to form water} \rightarrow \text{pure demineralized water.}$$

This is one of the most effective and complete methods of water softening.

## DEMINERALIZATION PROCESSES

This refers to the complete removal of all ionic impurities from water. It is also called deionization.

**Mixed Bed Ion Exchangers**

In this system, cation and anion exchange resins are mixed in a single column. Water passes through, and all ions (both cations and anions) are removed in one step, producing ultrapure water. This is widely used in industries requiring high-purity water such as electronics and pharmaceuticals.

## REVERSE OSMOSIS (RO)

**Principle**

Reverse osmosis works on the principle of applying pressure greater than osmotic pressure on a concentrated solution, forcing water to move through a semi-permeable membrane from the concentrated side to the dilute side, thereby removing dissolved salts and impurities.

**Working of RO Plant**

- Raw water is passed through pre-filters to remove suspended solids and chlorine.
- Then it enters the RO membrane module, which blocks salts, bacteria, and large molecules while allowing pure water to pass.
- The purified water (permeate) is collected while the concentrated water (reject) is discarded or reused.

**Components of RO Plant**:

1. *Pre-treatment Unit* – sand filter, activated carbon filter
2. *High-Pressure Pump* – provides necessary pressure (~30–60 bar)
3. *Membrane Housing* – holds the RO membranes
4. *Storage Tank* – stores clean water

**Advantages**

- Removes 95–99% of dissolved salts
- Reduces TDS, hardness, and pathogens
- Suitable for both domestic and industrial use

**Applications**

- Drinking water purification
- Pharmaceutical and semiconductor industries
- Boiler feed water treatment