METHODS OF WATER TREATMENT

1.7 METHODS OF BOILER WATER TREATMENT

EXTERNAL CONDITIONING

Demineralization (Or) Ion-Exchange Process

Zeolite (Or) Permutit Process

Differences between Zeolite and Demineralization process

INTERNAL CONDITIONING OR INTERNAL TREARMENT

1.8 DESALINATION OF BRACKISH WATER

Reverse Osmosis

1.7 METHODS OF BOILER WATER TREATMENT – SOFTENING METHODS

The objective of boiler feed water treatment is firstly to avoid trouble in the boiler plant and secondly to obtain steam of sufficient purity for the steam turbine. If the steam is not of sufficient purity, there is fouling of the blades of the steam turbine which reduces the capacity of the turbines.

The actual treatment to be given to boiler feed water depends to a great extenton the working pressure of the boiler. As the boiler pressure goes up, the specifications for feed water become more rigid. Water used for steam generation should be free from dissolved gases and salts, hardness producing substances, suspended impurities, etc. Accordingly, a treatment method has to be carefully chosen. The methods of removing hardness producing salts from water are known as **water softening** or **conditioning**.

The common treatments are described below:

(i) External treatments (or) External conditioning

(ii) Internal treatments (or) Internal conditioning

EXTERNAL CONDITIONING

External conditioning method involves the removal of hardness causing salts from the water before feeding into the boiler.

External treatment can be done by:

- Demineralization or ion-exchange process
- Zeolite or Permutit process
- Lime soda process

DEMINERALISATION (OR) ION-EXCHANGE PROCESS

This process removes both cations and anions present in the water. The soft water produced by lime-soda and zeolite process, does not contain hardness causing ions Ca^{2+} and Mg^{2+}, but it may contain other ions like Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, etc. On the other hand, demineralized water (D.M. water) does not contain both cations and anions. Thus, a soft water is not demineralized water whereas a demineralized water is soft water.

This process involves the use of ion-exchange resins for softening water. Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with micro-porous structure. The functional groups attached to the chains are responsible for the ion-exchanging properties.

There are two types of ion-exchange resins namely:

Cation exchange resins and

Anion exchange resins.

- **Cation Exchange Resins:**
  - Resins capable of **exchanging the cations** from hard water are called cation exchange resins.
  - It contains **acidic functional groups** like – COOH,-SO_3H or H^+ , which can replacetheir H^+ ions with the cations of hard water.
  - It can be represented as **RH^+** (or) **RH_2**.

Examples:

- Sulphonated coals
- Sulphonated polystyrene
- Phenol formaldehyde resin
- Commercial cation exchangers such as Amberlite and Dowex-50

- **Anion Exchange Resins:**
  - Resins capable of **exchanging the anions** from hard water are called anion exchangeresins.
  - It contains **basic functional groups** like -NH_2,-NR_3 or OH^- , which can replacetheir OH^- ions with the cations of hard water.
  - It can be represented as **R'' OH^-** (or) **R'' $(OH)_2$**.

Examples:

- Methyl ammonium hydroxy styrene
- Cross-linked quaternary ammonium salts.
- Urea formaldehyde resin
- Commercial cation exchangers such as Amberlite - 400 and Dowex-3

PROCESS OF DEMINERALISATION

The hard water is passed first through cation exchange column (containing cation exchange resins, RH^+). All the cations such Ca^{2+}, Mg^{2+}, Na^+, K^+, etc. present in hard water are exchanged with H^+ ions of the cation exchange resin. That is, it removes all the cations from hard water and equivalent amount of H^+ ions are released from this column to water.

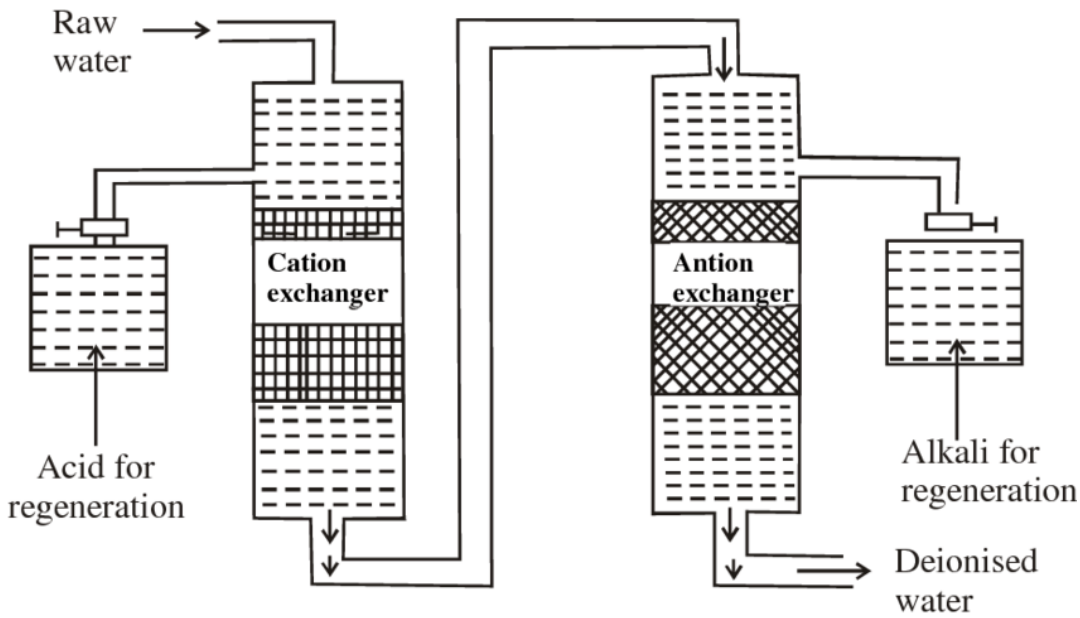

Figure 1.7.1 Demineralization process
[Source: "Engineering Chemistry II" by Dr.Syed Shabudeen.P.S., Page1.69]

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$

$$RH^+ + Na^+ \longrightarrow RNa^+ + H^+$$

$$RH^+ + K^+ \longrightarrow RK^+ + H^+$$

The water leaving the cation exchange column is now passed through anion exchange column (containing anion exchange resins, $R'OH^-$). All the anions such as Cl^-, SO_4^{2-}, HCO^{3-}, etc. present inthe water are exchanged with OH^- ions of anion exchange resins. So that all the anions are removed from water and equivalent amount of OH^- ions are released from this column to water.

$$R'OH + Cl^- \longrightarrow R'Cl + OH^-$$

$$R'OH + CO_3^{2-} \longrightarrow R'_2CO_3^{2-} + 2\,OH^-$$

$$R'OH^- + SO_4^{2-} \longrightarrow R_2'SO_4^{2-} + 2\,OH^-$$

H^+ and OH^- ions released from cation and anion exchange columns, combine to produce water.

$$H^+ + OH^- \longrightarrow H_2O$$

Thus, the water coming out of the anion exchange column is completely free from hardness causing cations and anions. This ion free water is known as **demineralized water or**

deionized water.

REGENERATION

When all the H^+ and OH^- ions of the ion exchange columns are exhausted, the ion exchange resins have to be regenerated.

The exhausted cation exchange column is regenerated by passing dilute HCl or dilutes H_2SO_4 through the column. The washing containing Ca^{2+}, Mg^{2+}, etc. is passed to sink.

$$R_2Ca^{2+} + 2\,H^+ \longrightarrow 2\,RH^+ + Ca^{2+}$$

Similarly, the anion exchange column is regenerated by passing dilute NaOH through the column. Then washing containing SO_4^{2-}, Cl^-, etc. is passed to sink.

$$R_2'SO_4^{2-} + 2\,OH^- \longrightarrow 2R'OH^- + SO_4{}^{2-}{}_4$$

The regenerated ion exchange resins are then used again.

ADVANTAGES OF ION-EXCHANGE PROCESS

- This method produces soft water of very low residual hardness
- Highly acidic and alkaline water can be treated by this process.
- Regeneration of ion-exchange resin is possible.
- Maintenance cost is less.
- No sludge disposal problem arises.

DISADVANTAGES OF ION-EXCHANGE PROCESS

- Cost of the equipment is high.
- Highly turbid waters cannot be treated. Turbidity should be less than 10 ppm.
- Expensive chemicals are required.
- Water containing turbidity, Fe and Mn cannot be treated, because turbidity reduces the output as it blocks the pores and Fe and Mn form stable compound with the resin which cannot be regenerated.

ZEOLITE (OR) PERMUTIT PROCESS

- Zeolites are naturally occurring hydrated sodium aluminosilicate. It general formula **is** $\mathbf{Na_2.Al_2O_3.xSiO_2.\ yH_2O}$

  Where, (x =2-10, y=2-6).

- Natural zeolite is green sand and non-porous in nature. The synthetic form of zeolite is known as Permutit, which is porous and possess gel like structure, hence it is generally used for water softening.

- Synthetic zeolite is represented by Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water.

PROCESS

When hard water is passed through a bed of sodium zeolite (Na_2Ze), kept in a cylinder, it exchanges its sodium ion with Ca^{2+} and Mg^{2+} ions present in the hard water to form Ca^{2+} and Mg^{2+} zeolites.

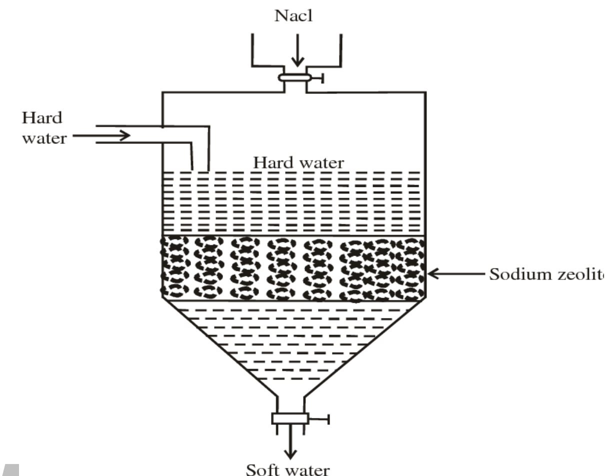

Figure.1.7.2 Zeolite process

[Source: "Engineering Chemistry II" by Dr.Syed Shabudeen.P.S., Page1.66]

The various reactions taking place during softening process are,

$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$

$$MgCl_2 + Na_2Ze \longrightarrow MgZe + 2NaCl$$

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$$

$$CaSO_4 + Na_2Ze \longrightarrow CaZe + NaSO_4$$

$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

The softened water is enriched with large amount of sodium salts, which do not cause any hardness,but cannot be used in boilers.

REGENERATION

After sometime zeolite gets exhausted. The exhausted zeolite is again regenerated by treated with10% solution of NaCl.

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

ADVANTAGES OF ZEOLITE PROCESS

- Water obtained by this process will have only hardness of 1-2 ppm.
- This method is cheap, because the regenerated zeolite can be used again.
- No sludge is formed during this process.
- The equipment used is compact and occupies a small space.
- It operation is easy.

DISADVANTAGES OF ZEOLITE PROCESS

- Turbidity water cannot be treated, because it blocks the porous of zeolite bed.
- Acidic water cannot be treated, because it decomposes the structure of zeolite.
- The softened water contains more dissolved sodium salts like $NaHCO_3$, Na_2CO_3, etc.
- When such water is boiled in boiler, CO_2 and NaOH is produced resulting in boiler corrosion and caustic embrittlement.
- Water containing Fe, Mn cannot be treated, because regeneration is very difficult.
- This process cannot be used for softening brackish water, because brackish water contains Na+ ions. The ion exchange reaction will not occur.

DIFFERENCES BETWEEN ZEOLITE AND DEMINERALIZATION PROCESS

S.No.	ZEOLITE PROCESS	DEMINERALISATION PROCESS
1.	It exchanges only cations.	It exchanges cations as well as anions.
2.	Acidic water cannot be treated because acid decomposes the zeolite.	Acidic water can be treated.
3.	The treated water contains relatively largeamount of dissolved salts, which leads to priming, foaming and caustic embrittlement in boilers.	The treated water does not contain any dissolved salts. Hence there is no priming and foaming.
4.	Water containing turbidity, Fe, Mn cannot be treated	Here also water containing turbidity, Fe, Mn cannot be treated.

Table 1.7.1 Differences between Zeolite and Demineralization process

INTERNAL CONDITIONING OR INTERNAL TREARMENT

This method involves the removal of scale forming substances and corrosive chemicals in water, which were not completely removed in the external treatment, by adding suitable chemicals directlyinside the boiler. These chemicals are called **boiler compounds**.

i. PHOSPHATE CONDITIONING

Scale formation in high pressure boilers can be avoided by adding sodium phosphate. The added phosphate reacts with calcium and magnesium salts to produce soft sludges of calcium and magnesium phosphates.

$$3\,CaSO_4 + 2\,Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 3\,Na_2SO_4$$

$$3\,CaCl_2 + 2\,Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6\,NaCl$$

$$3\,MgCl_2 + 2\,Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 6\,NaCl$$

$$3\,MgSO_4 + 2\,Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 3\,Na_2SO_4$$

Three types of phosphates are employed in phosphate conditioning. They are:

- ✓ Trisodium phosphate (Na_3PO_4)
- ✓ Disodium hydrogen phosphate (Na_2HPO_4)

- ✓ Sodium dihydrogen phosphate (NaH_2PO_4)

The optimum pH for the precipitation of $Ca_3(PO_4)_2$ is 9.5 to 10.5. The exact choice of the phosphatesalt depends upon the alkalinity of boiler feed water.

- ✓ **Trisodium phosphate (Na_3PO_4)**

When the alkalinity of boiler feed water is low, it has to be raised to 9.5-10.5 for this highly alkaline phosphate is preferred. Na_3PO_4 is highly alkaline, used for strong acidic water.

- ✓ **Disodium hydrogen phosphate (Na_2HPO_4)**

When the alkalinity of boiler feed water is already sufficient for precipitation, Na_2HPO_4 is preferred. Na_2HPO_4 is weakly alkaline, used for weakly acidic water.

- ✓ **Sodium dihydrogen phosphate (NaH_2PO_4)**

When the alkalinity of boiler feed water is too high, acidic phosphate is preferred. It reduces the pHto the optimum range. NaH_2PO_4 is acidic, used for alkaline water.

ii. CALGON CONDITIONING

When calgon (Sodium hexa meta phosphate $Na_2[Na_4(PO_3)_6]$) is added to boiler water, it interacts with calcium ions forming a highly soluble complex and thus prevents the precipitation of sludge and scale forming salts.

$$2\,CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2\,Na_2SO_4$$

The complex$Na_2[Ca_2(PO_3)_6]$ is soluble in water and there is no problem of sludge disposal.

iii. COLLOIDAL CONDITIONING

Scale formation can be avoided by adding colloidal containing agents like kerosene, agar – agar, gelatin, etc., It is used in low pressure boilers. These colloidal substances get coated over the sale forming particles and converted them into non-adherent, loose precipitate called sludge, which can be removed by blow down operation.

iv. SODIUM ALUMINATE CONDITIONING

Sodium Aluminate ($NaAl_2O_3$) undergoes hydrolysis in boiler water to give gelatinous white precipitate of aluminium hydroxide and sodium hydroxide.

$$NaAl_2O_3 + 2H_2O \longrightarrow Al(OH)_3\downarrow + NaOH$$

1.8 DESALINATION OF BRACKISH WATER

Water containing high concentration of dissolved salts or solids of peculiar salty or brackish taste is called **brackish water**. The sea water contains about 3.5% of dissolved salts. Before the removal of these salts, it is unfit for most of the domestic and industrial applications.

The process of removing common salt (sodium chloride) from the brackish or saline water is known as **Desalination** or **Desalting**.

Salinity of water is expressed in ppm or mg/L.

Based on the quantity of dissolved salts present, water is graded as,

- ✓ **FRESH WATER**

  It contains less than 1000 ppm of dissolved salts.

- ✓ **BRACKISH WATER**

  It contains above 1000 and below 35,000 ppm of dissolved salts.

- ✓ **SEA WATER**

  It contains above 35,000 ppm of dissolved salts.

The different methods of desalination are,

- ✓ **Distillation** – it involves separation of water from salts by evaporation followed by condensation.
- ✓ **Freezing** – it is based on the separation of pure water in the form of ice leaving the salt in the mother liquor when the saline water is cooled.
- ✓ **Electro dialysis** – It is the method of separation of ions from the salt water by passing electric current using a pair of electrodes and a pair of thin rigid plastic semipermeable membranes.
- ✓ **Reverse Osmosis**

The commonly used method of desalination are Electro dialysis and Reverse Osmosis.

REVERSE OSMOSIS

When two solutions of different concentrations are separated by a semi-permeable membrane, solvent molecules flow from a region of lower concentration (dilute) to higher concentration side. This process is called **Osmosis**. The driving force in this phenomenon is called **Osmotic pressure**.

If a pressure higher than that of osmotic pressure is applied on the concentrated side, solvent flow reverses. That is the solvent molecules pass from concentrated side to dilute side through the membrane. This phenomenon is called **Reverse Osmosis**.

Using reverse osmosis, pure solvent (water) is separated from salt water. This membrane filtration is also called **Super Filtration** or **Hyper Filtration**.

The membranes consist of very thin film of cellulose acetate and cellulose butyrate.

Polymers like polymethacrylate and polyamide of superior quality are also being used.

METHOD

In this process, pressure of about 15 to 40 kgcm^{-2} higher than that of osmotic pressure is applied to sea water so that pure water is forced to move through semi permeable membrane to pure water side. The membrane consists of very thin films of cellulose acetate.

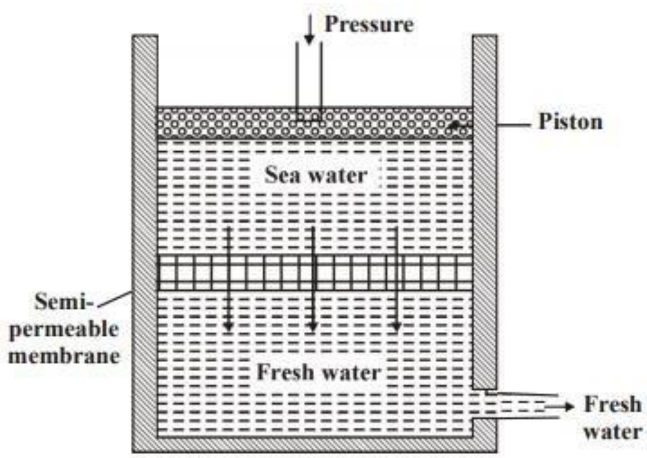

Figure.1.8.1 Reverse Osmosis process

[Source: "Engineering Chemistry II" by Dr.Syed Shabudeen.P.S., Page1.79]

ADVANTAGES:

- ✓ It removes ionic as well as non-ionic and colloidal impurities.
- ✓ Life time of the membrane is high (2 - 3 years) and it can be replaced within few minutes.
- ✓ Maintenance cost is less.
- ✓ Capital cost is low and operation is simple.