

# **UNIT- I**

## **WATER TECHNOLOGY**

# INTRODUCTION

Water is essential for the existence of human beings, animals and plants. Though 80% of the earth's surface is occupied by water, less than 1% of the water is available for ready use.

The main sources of water are

1. Rain
2. rivers and lakes (surface water)
3. wells and springs (ground water)
4. sea water

Among the above sources of water, rain water is the purest form of water but it is very difficult to collect whereas sea water is the most impure form. Thus, surface and ground water are normally used for industrial and domestic purposes. Such water must be free from undesirable impurities.

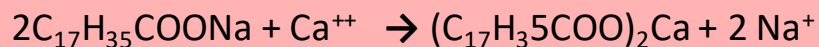
## WATER TECHNOLOGY

“The process of removing all types of impurities from water and making it fit for domestic or industrial purposes are called water treatment.” Before treating water one must know the nature as well as the amount of impurities.

## HARD WATER AND SOFT WATER

### Hard Water

“Water which does not produce lather with soap solution, but produces white precipitate is called hard water”. This is due to the presence of dissolved Ca and Mg salts.



### Soft Water

“Water which produces lather readily with soap solution is called soft water.”

This is due to the absence of Ca and Mg salts.

## ESTIMATION OF HARDNESS BY EDTA METHOD

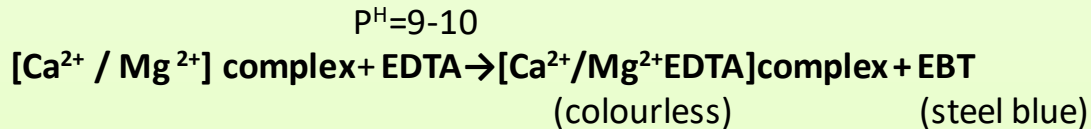
## PRINCIPLE

When EDTA is added to hard water, it reacts with calcium and magnesium ions present in hard water to form stable EDTA metal complexes. From the volume of EDTA consumed the hardness can be calculated. Eriochrome Black – T is used as a indicator. The indicator forms a weak complex with the metal ions present in the hard water and gives wine red colour.

$\text{pH}=9-10$



When EDTA is added into the hard water. The metal ions form a stable metal complex with EDTA by leaving the indicator. When all the metal ions are taken by EDTA from the indicator metal ion complex, the wine red colour changes into steel blue, which denotes the end point. The metal EDTA complex is stable at PH 8-10. This PH range can be maintained by adding ammoniacal buffer ( $\text{NH}_4\text{Cl}+\text{NH}_4\text{OH}$



## PROCEDURE

## Titration – I

## Estimation of Total hardness

The burette is washed & rinsed with EDTA solution. Then the burette is filled with EDTA solution up to zero mark. 20 ml of given water sample solution is pipetted out into a clean conical flask. To this 5 ml of ammonia buffer & 2 drops of Eriochrome Black – T ( EBT ) indicator is added and titrated against EDTA solution taken in the burette. The end point is the colour changes from wine red to steel blue . The titration is repeated to get concordant value.

## Titration – II

## Estimation of Temporary hardness

The burette is washed & rinsed with EDTA solution. Then the burette is filled with EDTA solution up to zero mark. 20 ml of boiled water solution is pipetted out into a clean conical flask. To this 5 ml of ammonia buffer & 2 drops of Eriochrome Black – T ( EBT ) indicator is added and titrated against EDTA solution taken in the burette. The end point is the colour changes from wine red to steel blue . The titration is repeated to get concordant value.

# calculation

## Estimations of total hardness of water sample

50 ml of the given hard water sample consumes =  $V_2$  ml of EDTA  
=  $V_2 \times 50 / V_1$  mgs of  $\text{CaCO}_3$  equivalent hardness

1000 ml of the given sample water =  $V_2 \times 50 / V_1 \times 1000 / 50$   
=  $1000 \times V_2 / V_1$  mgs of  $\text{CaCO}_3$  equivalent hardness

## Estimations of permanent hardness of water sample

50 ml of the hot hard water sample consumes =  $V_3$  ml of EDTA  
=  $V_3 \times 50 / V_1$  mgs of  $\text{CaCO}_3$  equivalent hardness

1000 ml of the given sample water =  $V_3 \times 50 / V_1 \times 1000 / 50$   
=  $1000 \times V_3 / V_1$  mgs of  $\text{CaCO}_3$  equivalent Hardness

## Temporary Hardness

Temporary Hardness = Total – Permanent  
=  $1000 (V_2 - V_3)$  ppm.

# BOILER FEED WATER

In Industry, one of the chief uses of water is generation of steam by boilers. The water fed into the boiler for the production of steam is called boiler feed water.

## **Requirements of boiler feed water**

- It should have zero hardness.

- It must be free from dissolved gases like  $O_2$ ,  $CO_2$ , etc.

- It should be free from suspended impurities.

- It should be free from dissolved salts and alkalinity

- It should be free from turbidity and oil.

- It should be free from hardness causing and scale forming constituents like Ca and Mg salts.

# Formation of deposits (Scales and Sludges) in boilers and heat exchangers

In a boiler, water is continuously converted into steam. Due to this continuous evaporation of water, the concentration of soluble matters increases progressively. Then the salts separating out from the solution in the order of their solubility, the least soluble ones separating out first.

- (i) Sludge :** If the precipitate is loose and slimy it is called sludges. Sludges are formed by substances like  $\text{MgCl}_2$ ,  $\text{MgCO}_3$ ,  $\text{MgSO}_4$  and  $\text{CaCl}_2$ . They have greater solubilities in hot water than cold water.
- (ii) Scale :** If the precipitate forms hard and adherent coating on the inner walls of the boiler, it is called scale. Scales are formed by substances like  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{CaSO}_4$  and  $\text{Mg}(\text{OH})_2$ .

## Disadvantages of Scale Formation

### (i) Wastage of fuels

Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a supply of heat to water, excessive or over-heating is done. This causes increase in fuel consumption. The wastage of fuel depends upon the thickness and the nature of scale

### (ii) Decrease in efficiency

Scales sometimes deposit in the valves and condensers of the boiler and choke them partially. This results in decrease in efficiency of the boiler.

### (iii) Boiler explosion

When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes in formation of a large amount of steam suddenly. So sudden high-pressure is developed, which may even cause explosion of the boiler.

## Prevention of scale formation

At the initial stage, scales can be removed using scraper, wire brush etc.

If scales are brittle, they can be removed by thermal shocks.

If the scales are loosely adhering, they can be removed by frequent blow down operation.

## PREVENTION OF SCALE FORMATION (OR) SOFTENING OF HARD WATER

The process of removing hardness – producing salts from water is known as softening or conditioning of water. Since water is a source for industrial purpose. It is mandatory to soften water to make it free from hardness producing substances, suspended impurities and dissolved gases, etc.

Softening of water can be done by two methods.

**i) External treatment ii) Internal treatment.**

# External Treatment or Conditioning

It involves the removal of hardness producing salts from the water before feeding into the boiler. The external treatment can be done by the following method

## Zeolite (or) Permutit proces

Zeolites are naturally occuring hydrated sodium aluminosilicate minerals. The chemical formula is  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ . The synthetic form zeolite is called permutit and is represented by  $\text{Na}_2\text{Ze}$ . In this process the hard water is allowed to percolate through sodium zeolite. The sodium ions which are loosely held in this compound are replaced by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.

When zeolite comes in contact with hard water, it exchanges its sodium ions with calcium and magnesium ions of hard water to form calcium and magnesium zeolites. As sodium ions do not give any hardness to water, the effluent will be soft. The exhausted zeolite is again regenerated by treated with 5 to 10 percent of sodium chloride solution

## Advantages

No sludge is formed during this process.

Water of nearly zero hardness is obtained.

This method is very cheap because the generated permutit can be used again.

The equipment used is compact and occupies a small space.

Its operation is also easy.

The process can be made automatic and continuous.

## Disadvantages

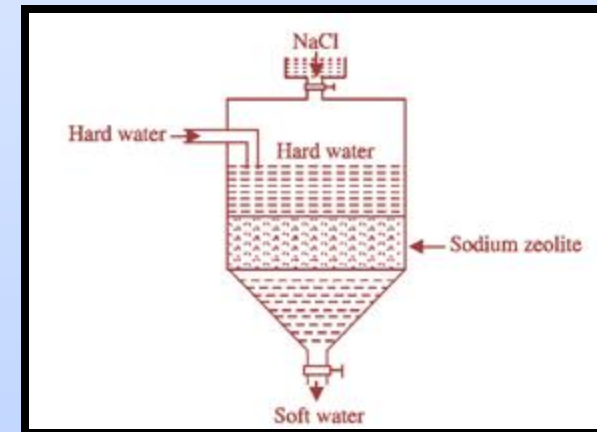
This process cannot be used for turbid and acidic water as they will destroy the zeolite bed.

This treatment replaces only the cations, leaving all the anions like  $(\text{HCO}_3)^-$  and  $(\text{CO}_3)^{2-}$  in the soft water.

When such water is boiled in boilers,  $\text{CO}_2$  is liberated. Free  $\text{CO}_2$  is weakly acidic in nature and extremely corrosive to boiler metal.  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$

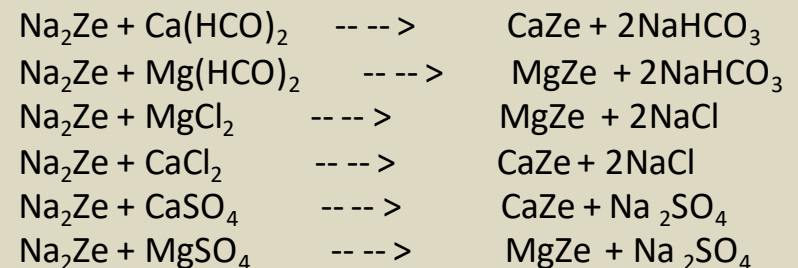
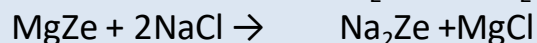
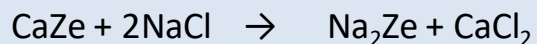
Due to the formation of sodium hydroxide, the water becomes alkaline and can cause caustic embrittlement. Water containing Fe, Mn cannot be treated, because regeneration is very difficult.

This process cannot be used for softening brackish water. Because, brackish water also contains  $\text{Na}^+$  ions. So, the ions exchange reaction will not take place.



## Regeneration

After some time zeolite gets exhausted. The exhausted zeolite is again regenerated by treating with 10% solution of NaCl.





# Ion exchange or Demineralisation process

Ion exchange or demineralisation process removes almost all the ions (both anions and cations) present in the hard water. The soft water, produced by lime-soda and zeolite processes, does not contain hardness producing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, but it will contain other ions like  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  etc.,

On the other hand demineralised (DM) water does not contain both anions and cations. Thus a soft water is not demineralised water whereas demineralised water is soft water. This process is carried out by using ion exchange resins, which are long chain, cross linked, insoluble organic polymers with a micro process structure. The functional groups attached to the chains are responsible for the ion exchanging properties.

## (i) Cation exchanger

Resins containing acidic functional groups ( $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ) are capable of exchanging their  $\text{H}^+$  ions with other cations of hard water. Cation exchange resin is represented as  $\text{RH}_2$ .

Examples: Sulphonated coals

Sulphonated polystyrene

$\text{R}-\text{SO}_3\text{H}$ ;  $\text{R}-\text{COOH} \equiv \text{RH}_2$

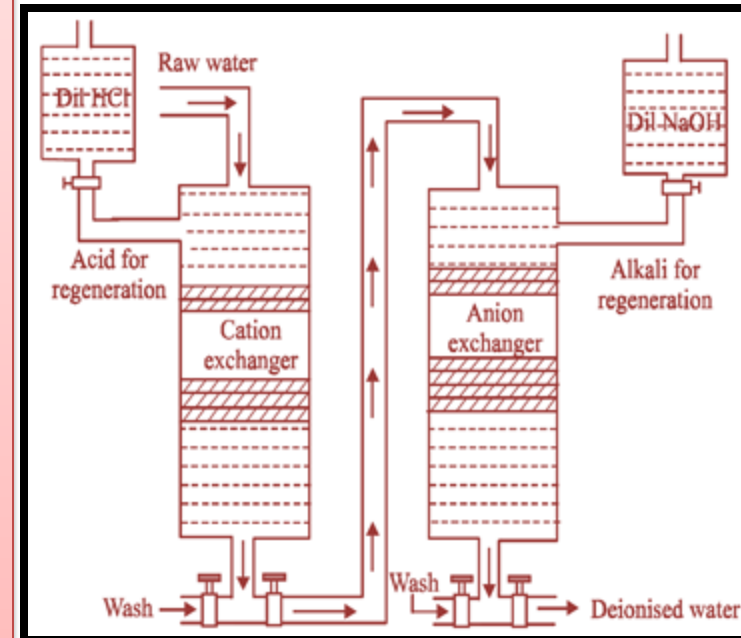
## (ii) Anion Exchanger

Resins containing basic functional groups ( $-\text{NH}_2$ ,  $-\text{OH}$ ) are capable of exchanging their anions with other anions of hard water. Anion exchange resin is represented as  $\text{R}(\text{OH})_2$ .

Examples • Cross-linked quaternary ammonium salts.

Urea-formaldehyde resin.

$\text{R}-\text{NR}_3\text{OH}$ ;  $\text{R}-\text{OH}$ ;  $\text{R}-\text{NH}_2 \equiv \text{R}(\text{OH})_2$



**Process**

The hard water first passed through a cation exchange which absorbs all the cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ , etc. present in the hard water.

$\text{RH}_2 + \text{CaCl}_2 \rightarrow \text{RCa} + 2\text{HCl}$

$\text{RH}_2 + \text{MgSO}_4 \rightarrow \text{RMg} + \text{H}_2\text{SO}_4$

$\text{RH} + \text{NaCl} \rightarrow \text{RNa} + \text{HCl}$

The cation free water is then passed through a anion exchange column, which absorbs all the anions like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , etc., present in the water.

$\text{R}'(\text{OH})_2 + 2\text{HCl} \rightarrow \text{R}'\text{Cl}_2 + 2\text{H}_2\text{O}$

$\text{R}'(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{R}'\text{SO}_4 + 2\text{H}_2\text{O}$

The water coming out of the anion exchanger completely free from cations and anions. This water is known as demineralised water or deionised water.

**Regeneration**

When the cation exchange resin is exhausted, it can be regenerated by passing a solution of dil.HCl or dil. $\text{H}_2\text{SO}_4$ .

$\text{RCa} + 2\text{HCl} \rightarrow \text{RH}_2 + \text{CaCl}_2$

$\text{RNa} + \text{HCl} \rightarrow \text{RH} + \text{NaCl}$

Similarly, when the anion exchange resin is exhausted, it can be regenerated by passing a solution of dil.NaOH.

$\text{R}'\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{R}'(\text{OH})_2 + 2\text{NaCl}$

**Advantages**

The water is obtained by this process will have very low hardness.

Highly acidic or alkaline water can be treated by this process.

**Disadvantages**

The equipment is costly.

More explosive chemicals are needed for this process.

Water containing turbidity, Fe and Mn cannot be treated, because turbidity reduces the the output and Fe, Mn form stable compound with the resin.

## INTERNAL TREATMENT

Internal treatment involves adding chemicals directly to the water in the boilers for removing dangerous scale– forming salts which were not completely removed by the external treatment for water softening. This method is used to convert scale to sludge which can be removed by blow-down operation.

1. Calgon conditioning, 2. Carbonate conditioning , 3. Phosphate conditioning, 4. Colloidal conditioning and 5. Sodium aluminate conditioning

### 1. Calgon conditioning

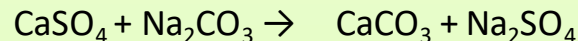
Calgon is sodium hexa meta phosphate with a Composition  $\text{Na}_2(\text{Na}_4(\text{PO}_3)_6)$ . A highly soluble complex containing Ca is formed by replacing the sodium ions and thus prevents their formation of scale forming salts like  $\text{CaSO}_4$ . The reaction is as follows:



Since the complex is highly soluble there is no problem of sludge disposal.

### 2. Carbonate conditioning

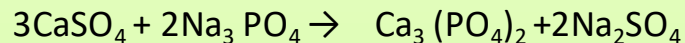
Scale formation due to  $\text{CaSO}_4$  in low pressure boilers can be avoided by adding  $\text{Na}_2\text{CO}_3$  to the boilers.



The forward reaction is favored by increasing the concentration of  $\text{CO}_3^{2-}$  &  $\text{CaCO}_3$  formed can be removed easily.

### 3. Phosphate conditioning

In high pressure boilers,  $\text{CaSO}_4$  scale whose solubility decrease with increase of temperature. Such scale can be converted into soft sludge by adding excess of soluble phosphates.



There are three types of phosphates employed for this purpose.

Tri-sodium phosphate –  $\text{Na}_3\text{PO}_4$  (too alkaline): used for too acidic water.

Di-sodium hydrogen phosphate –  $\text{Na}_2\text{HPO}_4$  (weakly alkaline): Used for weakly acidic water.

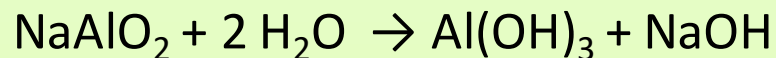
Sodium dihydrogen phosphate  $\text{NaH}_2\text{PO}_4$  (acidic) used for alkaline acidic water.

#### **4. Colloidal conditioning**

The colloidal conditioning agents are kerosene, agar-agar, gelatin, glue, etc. They are Used in low pressure boilers. The colloidal substances convert scale forming substance like  $\text{CaCO}_3$ ,  $\text{CaSO}_4$  into a Non-adherent, loose precipitate called sludge, which can be removed by blow-down Operation.

#### **5. Sodium aluminate conditioning**

Sodium aluminate ( $\text{NaAlO}_2$ ) under goes hydrolysis in boiler water to give gelatinous white precipitate of aluminium hydroxide and sodium hydroxide.



The sodium hydroxide, thus formed, precipitates magnesium as magnesium hydroxide. The gelatinous precipitates of aluminium hydroxide and magnesium hydroxide entrap the colloidal silica and finely divided solids and settled easily. This can be removed easily by blow down operations.

# DESALINATION OF BRACKISH WATER

Depending upon the quantity of dissolved solids, water is graded as

Fresh water has  $< 1000$  ppm of dissolved solids.

Brackish water has  $> 1000$  but  $< 35,000$  ppm of Dissolved solids.

Sea water has  $> 35,000$  ppm of dissolved solids

Water containing dissolved salts with a peculiar salty or brackish taste is called brackish water. It is totally unfit for drinking purpose. Sea water and brackish water can be made available as drinking water through desalination process.

The removal of dissolved solids (NaCl) from water is known as desalination process. The need for such a method arises due to the non-availability of fresh water. Desalination is carried out either by electro dialysis or by reverse osmosis.

# Reverse Osmosis

When two solutions of different concentrations are separated by a semi-permeable membrane, flow of solvent takes place from a region of low concentration to high concentration until the concentration is equal on both the sides. This process is called osmosis.

The driving forces in this phenomenon are called osmotic pressure. If a hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration side, the solvent flow reverses, i.e., solvent is forced to move from higher concentration to lower concentration .

This is the principle of reverse osmosis. Thus, in reverse osmosis method pure water is separated from its dissolved solids. In this method pure water is separated from sea water. This process is also known as super-titration. The membranes used are cellulose acetate, cellulose butyrate, etc.

## Advantages

The life time of the membrane is high.

It can be replaced within few minutes.

It removes ionic as well as non-ionic, colloidal impurities

Due to simplicity low capital cost, low operating, this process is used for converting sea water into drinking water

