

## Section -B

### Water and its treatment part -1 &2

#### **Water & its treatment : Part – I**

**Sources of water, impurities in water, hardness of water and its determination ,(EDTA method )units of hardness, alkalinity of water and its determination, Related numerical problems, scale and sludge formation ( composition properties and methods of prevention ) Boiler corrosion & caustic embrittlement.**

#### **Water and its treatment : Part – II**

**Treatment of water for domestic use, coagulation, sedimentation, filtration and disinfection. water softening : Lime-Soda treatment, Zeolite, Ion – exchange process, mixed bed demineralization, Desalination ( Reverse Osmosis , electro dialysis) & related numericals.**



# WATER AND ITS TREATMENT

## PART - I



# Water: most essential creation of nature

One cannot survive without water”.

**Drinking**

**Industrial**

**Water**  
Essential for  
survival of life

**Household**



# Sources of Water

## Surface water

- Flowing water (eg. Streams and rivers)
- Still water (eg. Lake, ponds, reservoirs)
- Sea water

## Underground water

- Springs and well
- Tubewell

## Rain water



# Impurities of Water

## Dissolved impurities

- Inorganic salts (sulphates, chlorides, nitrates of Mg, K, Ca, Al, Zn, Cu )
- Gases(eg. CO<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub>, ammonia)
- Organic matter (domestic and industrial waste)

## Suspended and colloidal impurities

- Soil minerals, silt etc

## Bacteriological

- Bacteria, virus, fungi, algae

# Hardness of water

**Hardness in Water is characteristic that prevents the 'lathering of soap' thus water which does not produce lather with soap solution readily, but forms a white curd is called hard water.**

## **Soft water**

**Produces lather  
with soap**

## **Hard water**

**Does not readily  
produce lather with  
soap**

# Type of Hardness

## Temporary hardness

- Due to presence of bicarbonates of Ca & Mg
- Removable by boiling

## Permanent hardness

- Due to presence of chlorides and sulphates of Ca & Mg
- Can not be removed by boiling

## Alkaline hardness

- Due to presence of bicarbonate, carbonates & hydroxides of Ca & Mg

## Non-alkaline hardness

- Total hardness-alkaline hardness

# Cause of Hardness

## Temporary hardness



– Calcium/Magnesium Carbonates thus formed being almost insoluble, are deposited as a scale at the bottom of vessel, while carbon dioxide escapes out.

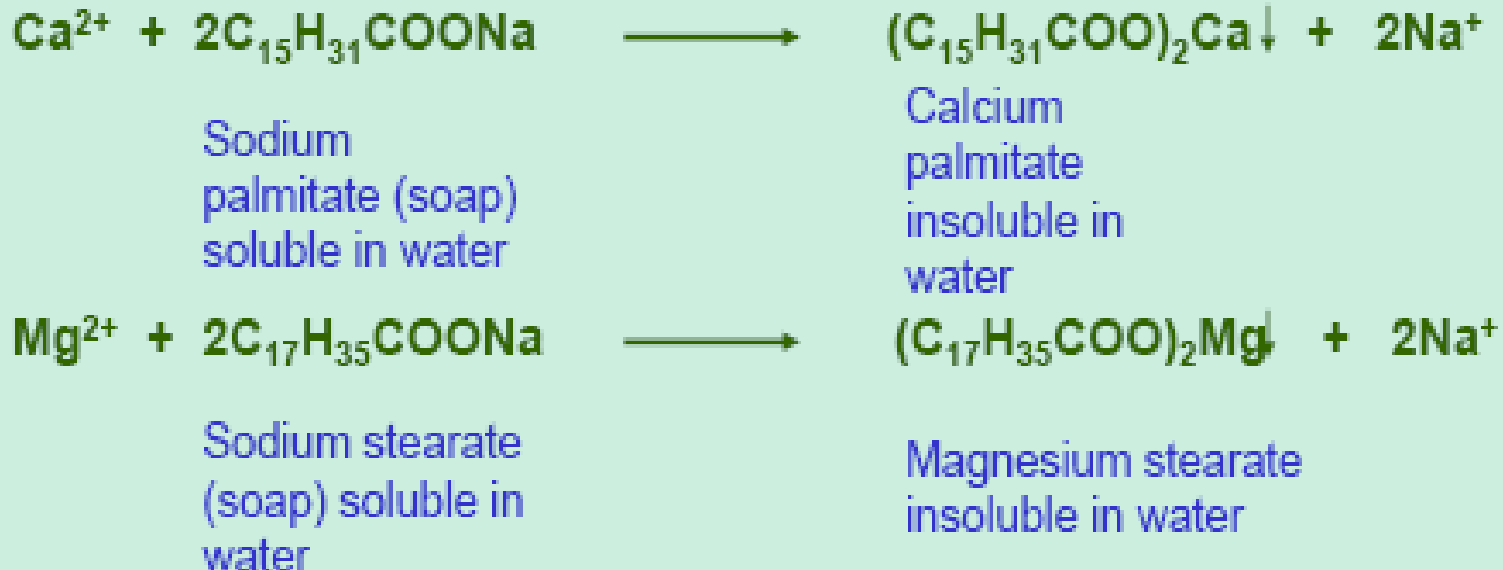


# Cause of Hardness

## Permanent hardness

- Presence of bicarbonates, chlorides and sulphates of Ca and Mg.
- Precipitation of insoluble Ca and Mg salts with soap (sodium palmitate;  $C_{15}H_{31}COONa$ , sodium stearate;  $C_{17}H_{35}COONa$ )

### *Action of Soap with hard water*



# Expression of Hardness

Hardness  $\approx$  Equivalents of  $\text{CaCO}_3$

Why  $\text{CaCO}_3$ ?

- Molecular mass is 100, equivalent mass =50
- Most insoluble salt

$$\text{Calcium carbonate equivalent} = \frac{\text{Mass of hardness producing substance} \times \text{Molecular weight of } \text{CaCO}_3}{\text{Molecular weight of hardness producing substances}}$$

$$\text{Equivalent of } \text{CaCO}_3 = \frac{w \times 50}{E}$$

Where,  $w$  = mass of hardness producing substance

$E$  = equivalent mass of hardness producing substance

## Problem

Calculate the calcium carbonate equivalent hardness of a water sample containing 204mg of  $\text{CaSO}_4$  per litre

## Solution :

$$\text{Calcium carbonate equivalent hardness} = \frac{204 \times 100}{136} = 150 \text{ mg of CaCO}_3/\text{L} \\ = 150 \text{ ppm}$$

Mol. wt of  $\text{CaCO}_3 = 100$

Mol. Wt of  $\text{CaSO}_4 = 136$

Hardness producing salt	Mol. Mass	Equiv. Mass
$\text{Ca}(\text{HCO}_3)_2$	162	
$\text{Mg}(\text{HCO}_3)_2$	146	
$\text{CaSO}_4$	136	
$\text{MgCl}_2$	95	
$\text{MgCO}_3$	84	
$\text{NaAlO}_2$	82	
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	
$\text{Al}_2(\text{SO}_4)_3$	342	

### Units of Hardness:

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

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

1 °Cl = 1 part of  $\text{CaCO}_3$  hardness per 70,000 parts of water

1 °Fr = 1 part of  $\text{CaCO}_3$  hardness per  $10^5$  parts of water

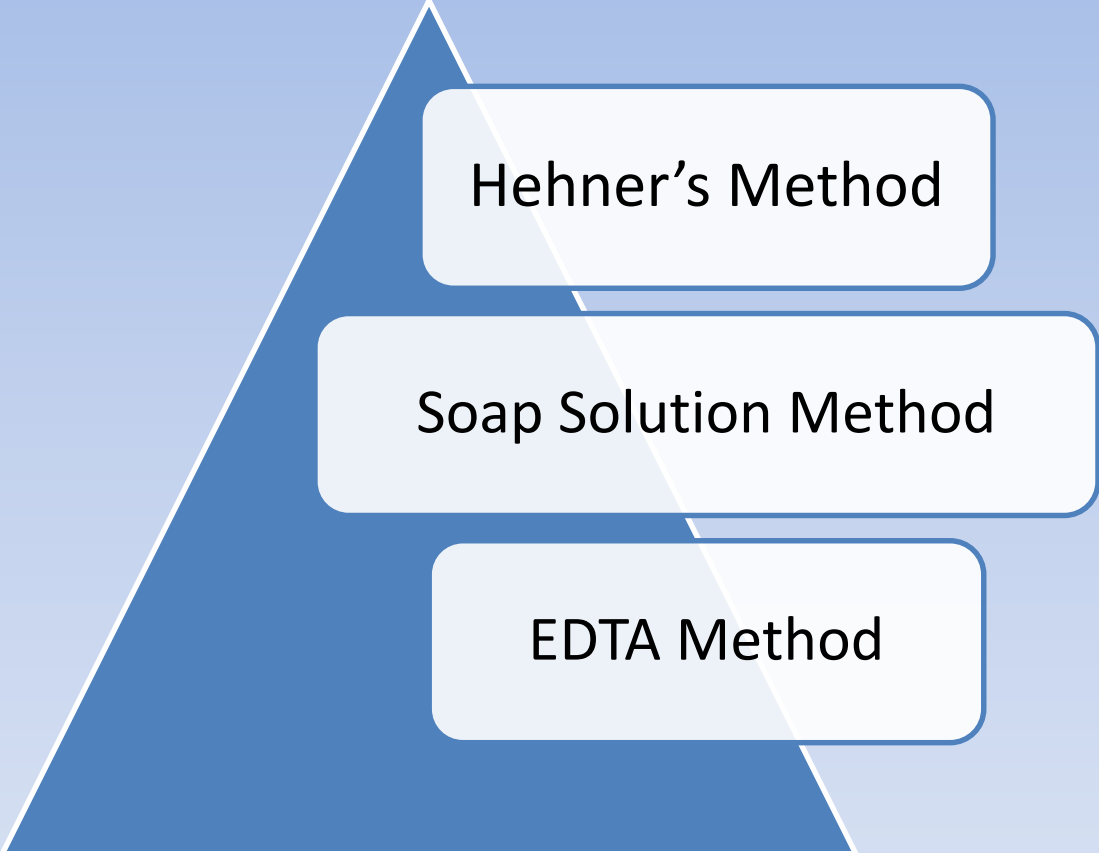
# Relationship between different units

- $1\text{ ppm} = 1\text{ mg/L} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl}$
- $1^\circ\text{Fr} = 10\text{ ppm} = 10\text{ mg/L} = 0.7^\circ\text{Cl}$
- $1^\circ\text{Cl} = 14.3\text{ ppm} = 1.43^\circ\text{Fr} = 14.3\text{ mg/L}$

## Assignment

- What is permanent hardness? What is the cause of permanent hardness?
- What are the units of hardness?
- What is  $\text{CaCO}_3$  equivalent?

# Determination of Hardness



Hehner's Method

Soap Solution Method

EDTA Method

## Hehner's Method

### Principle:

**Hard water sample is titrated against standard acid using suitable indicator.**

## Soap Solution Method

### Principle:

**Certain quantity of the soap required for lather formation**

### Procedure:

**Hard water sample is titrated against standard soap solution, persistent lather formation for more than 30 seconds indicates the end point.**





## EDTA Method

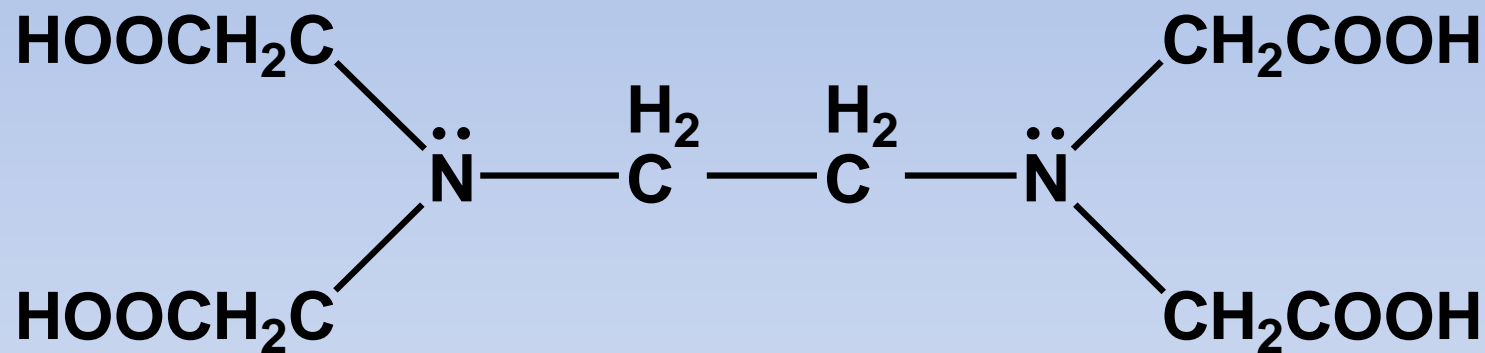
### Principle:

**The Ca and Mg ions present in hard water forms stable complexes with both EBT and EDTA but more stable with EDTA.**

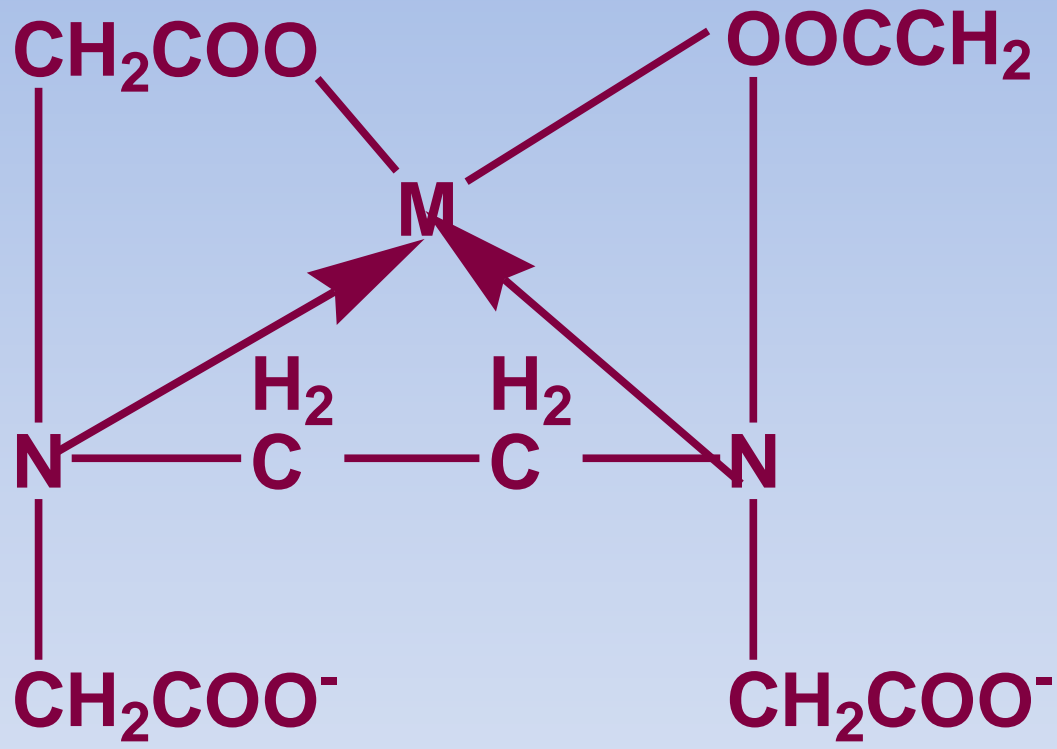
### Procedure:

**The total hardness in water is determined by titrating the water sample against standard EDTA solution in Ammonia buffer having pH~9-10 using EBT as an indicator.**

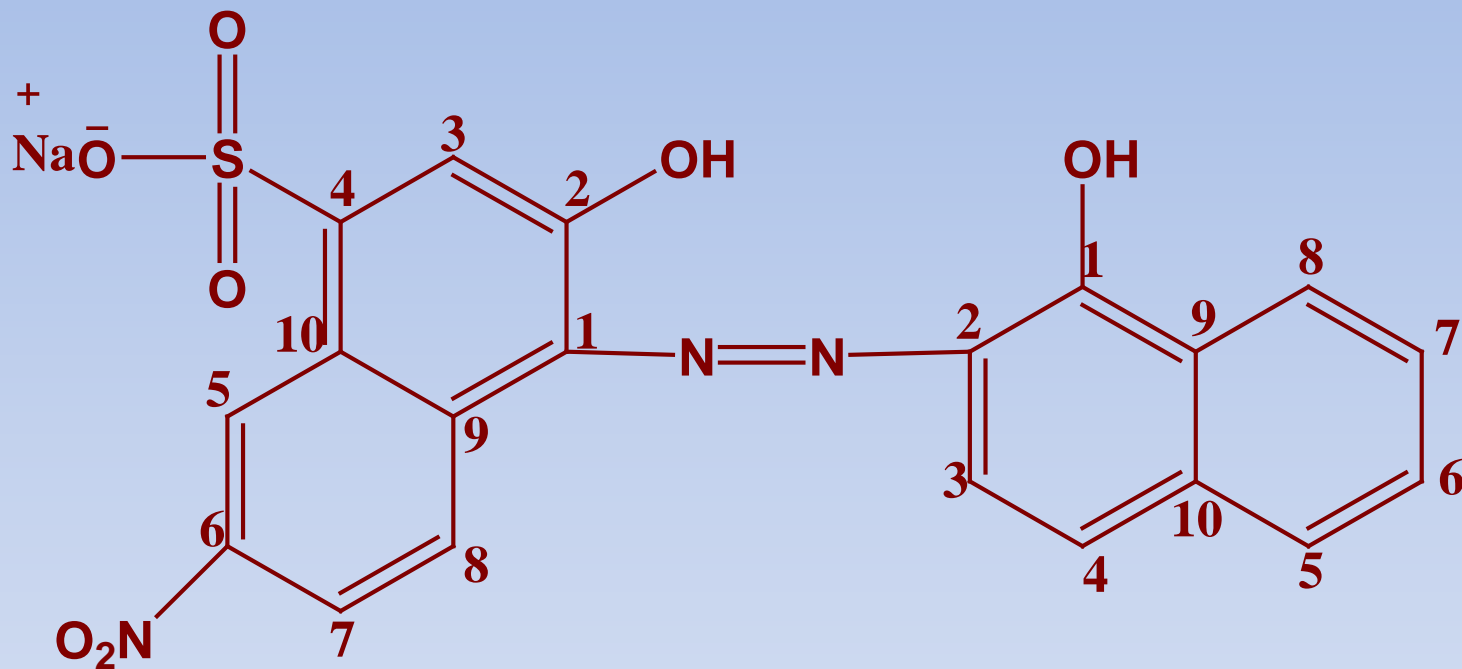
# Structure of EDTA



EDTA

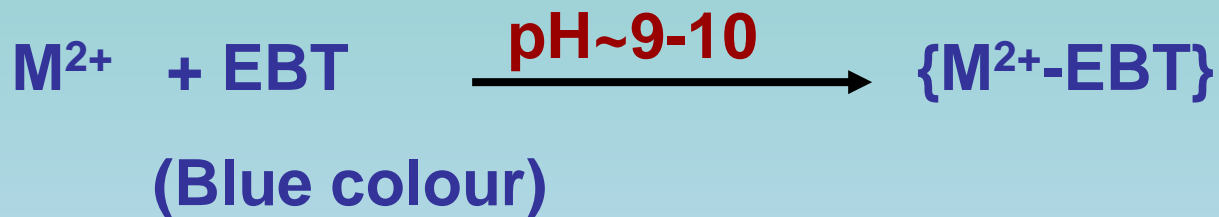


# Structure of EBT



**EBT (Eriochrome Black-T)**

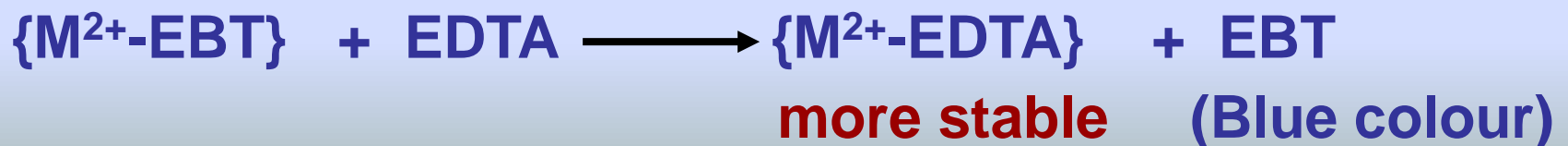
*[Sodium 4-(1-hydroxy-2-naphthylazo)-3-hydroxy-7-nitronaphthalene-1-Sulphonate*



When EDTA is added. The free  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  forms Stable complex



When all  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  get complexed with EDTA. Then further addition of EDTA sets free the metal ions from metal indicator complex and form more stable complex with metal ions



# Assignment

- What is the principle and procedure of different methods used for determination of hardness.
- What is the structure of EDTA and EBT molecule.

# Alkalinity Of Water

**The amount of substances tent to increase the concentration of OH<sup>-</sup> ions either by hydrolysis or by dissociation of water**

## *Factors*

- 1. Presence HCO<sub>3</sub><sup>-</sup>, HSiO<sub>3</sub><sup>-</sup> and SiO<sub>3</sub><sup>-2</sup> ions**
- 2. Presence of salts of weak organic acids**
- 3. Presence of buffer forming salts**

# Determination Of Alkalinity

## **Titrimetric method**

**A Known volume of hard water sample is titrated against standard acid using methyl orange and phenolphthalein as indicator**

**Color Change at end point**

**Methyl orange: Pale yellow to red**

**Phenolphthalein: Pink to colourless**



# Procedure

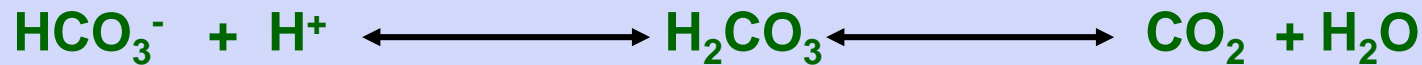
## Calculation

*Conclusion: Result of titration i.e. P and M end point*

		$\text{OH}^-$	$\text{CO}_3^{-2}$	$\text{HCO}_3^-$
(i)	$P=0$	0	0	M
(ii)	$P=M$	P or M	0	0
(iii)	$P=1/2M$	0	2P	0
(iv)	$P>1/2M$	$M-2(M-P)$ $=2P-M$	$2(M-P)$	0
(v)	$P<1/2M$	0	2P	$M-2P$

EXPRESSION OF ALKALINITY IN TERMS OF  $\text{CaCO}_3$  EQUIVALENTS

*Determination is based on following reactions*



### ***Causes of alkalinity***

1.  $\text{OH}^-$  only
2.  $\text{CO}_3^{2-}$  only
3.  $\text{HCO}_3^-$  only
4.  $\text{OH}^-$  and  $\text{CO}_3^{2-}$
5.  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$

Combination of  $\text{OH}^-$  and  $\text{HCO}_3^-$  is not possible because they combine instantaneously to form carbonate ions



# Assignment

- Explain alkalinity of water and the ions responsible for causing alkalinity?
- What is the method of determination of alkalinity?

# Applications

## Domestic Use

1. Washing
2. Bathing
3. Drinking
4. Cooking

The sticky precipitate adheres on the fabric/cloth and gives spots and streaks. Fe salts stain the cloths.

Produces sticky scum on the bath tub and the body

Bad to the digestive system and calcium oxalate formation is possible in urinary tracts

Requires more fuel and time. Certain food don't cook soft and also gives unpleasant taste

## Industrial Use

1. Textile Industry
2. Sugar Industry
3. Dyeing Industry
4. Paper Industry
5. Pharmaceutical Industry
6. In Steam generation in Boilers

## Boiler troubles due to Hard Water

1. Scale and Sludge

2. Boiler corrosion

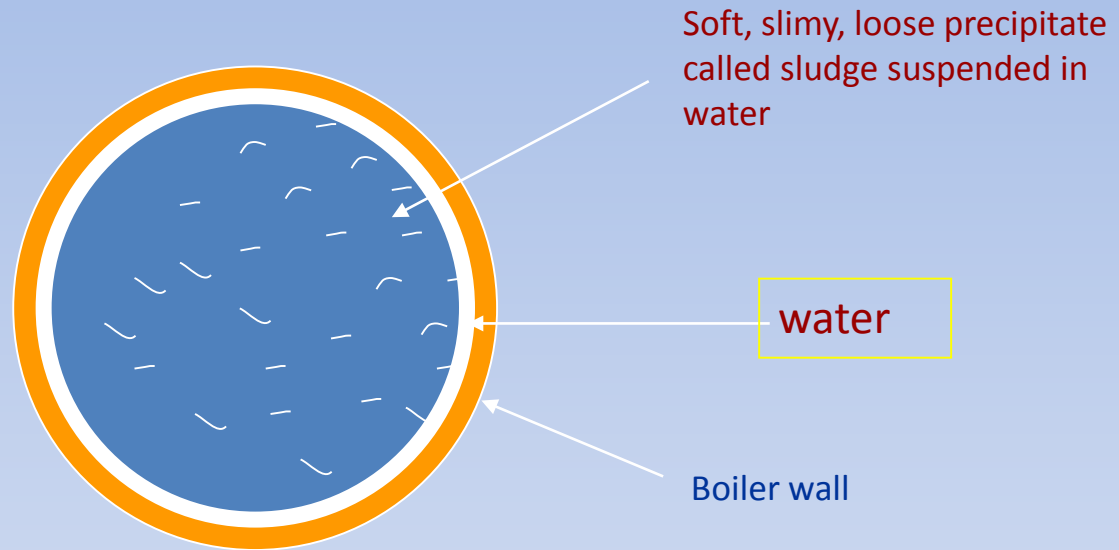
3. Priming and Foaming

4. Caustic embitterment

# Boiler troubles due to Hard Water

## 1. Sludge Formation

It is formed  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  etc.,



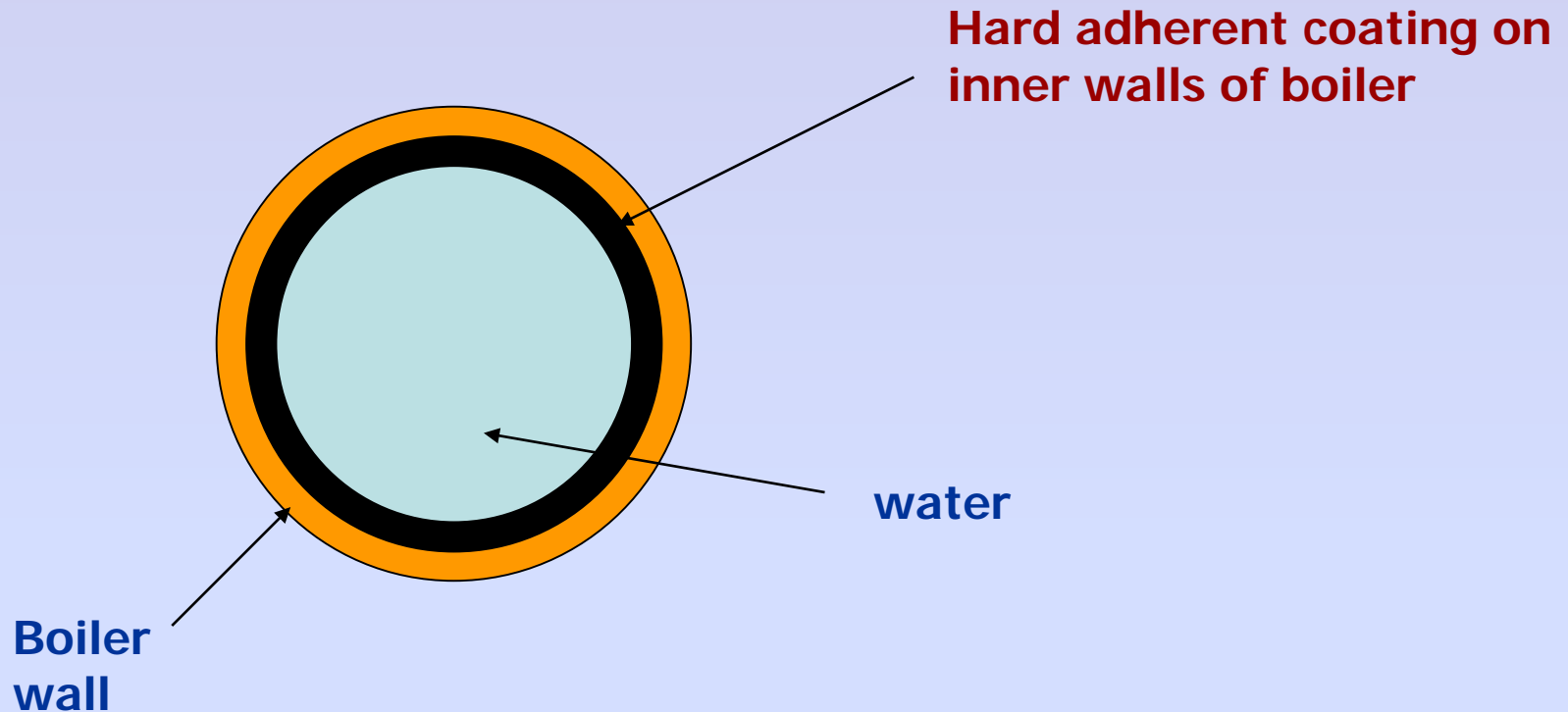
### Disadvantages:

- (i) Sludge is poor conductor of heat, so they tend to waste the portion of heat generated
- (ii) Its excess, decrease the efficiency of boiler

### Prevention

- (i) Boiler feed water should be well softened
- (ii) Blow-down operation should be carried out

## 2. Scale



**Scale:** This is hard and adherent, coating formed on inner wall of boilers, during steam generation

Low pressure boilers

$\text{Ca}(\text{HCO}_3)_2$ ,  $\text{MgCl}_2$

High pressure boilers

$\text{CaSO}_4$ , Silica

## **Disadvantages of scale formation**

- (i) It is poor conductor of heat so reduce the rate of heat transfer.**
- (ii) Due to scale formation on heating surfaces, overheating occurs, so metal becomes soft and weak, and this make boiler unsafe**
- (iii) Boiler tubes may clog due to scale formation**
- (iv) Scale formation leads to uneven expansion of boiler metal, thick scale cracks and when water comes suddenly in contact with overheated iron plate. This result in the formation of large amount of heat suddenly, which in turn develops a sudden high pressure that may lead to explosion of boiler**



# *Prevention of scales*



## ***a. Internal treatment (Sequestration)***

**Addition of chemicals to remove impurities in the boiler: Conditioning methods**

## ***b. External treatment***

**Removing before feeding to the boiler: lime soda process, zeolite or ion exchange process.**

# Prevention of scale formation

Scale formation can be prevented by two methods

1. Internal conditioning or Internal Treatment
2. External conditioning or External treatment- will be discussed later

## 1. Internal conditioning methods - of boiler water to prevent scale formation

1. Phosphate conditioning – addition of phosphate compound
2. Carbonate conditioning – addition of carbonate compound
3. Calgon conditioning – addition of sodium hexa meta phosphate
4. Colloidal conditioning – spreading of organic compounds like tannin, agar gel
5. Sodium Aluminate – removes oil and silica
6. Complexometric method – using EDTA (refer expt. 1 chemistry lab manual)

## 1. Phosphate conditioning

Scale formation can be prevented by adding sodium phosphate to the boiler water which reacts with the hardness producing ions and forms easily removable phosphate salts of respective ions



Calcium  
chloride

Sodium  
phosphate

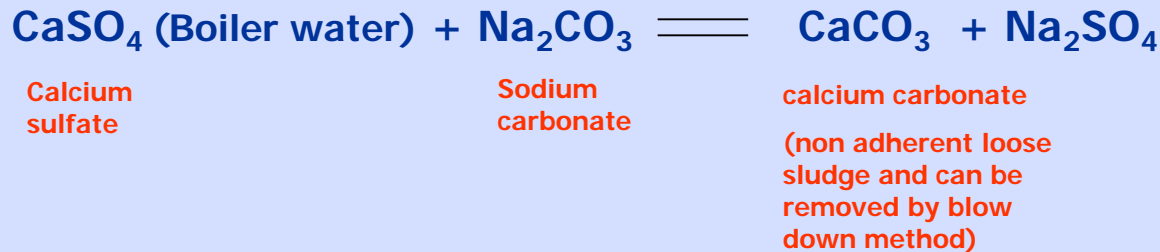
calcium phosphate  
(non adherent and can be  
removed by blow down  
method)

## Selection of Phosphate compound

Calcium can not be precipitated below a pH = 9.5, hence the selection of phosphate has to be based on the pH of the boiler feed water.

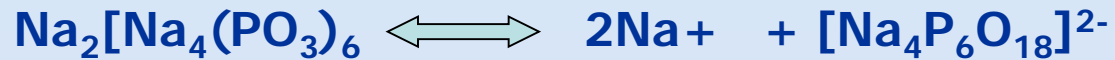
$\text{NaH}_2\text{PO}_4$  (acidic in nature) ,  
 $\text{Na}_2\text{HPO}_4$  (weakly alkaline in nature),  
 $\text{Na}_3\text{PO}_4$  (Alkaline in nature)

## 2. Carbonate conditioning



**Caution: Excess  $\text{Na}_2\text{CO}_3$  can result in caustic embrittlement**

### 3. Calgon conditioning



Calgon – sodium hexa  
meta phosphate



Calcium  
sulfate

Soluble complex ion of  
calcium - can be  
removed easily

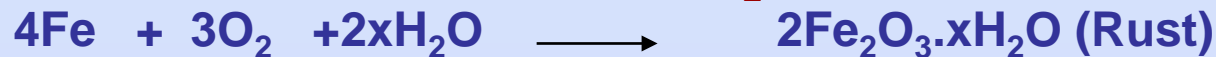
Calgon tablets are used in the cleaning of washing machine drums

## 2. Boiler corrosion

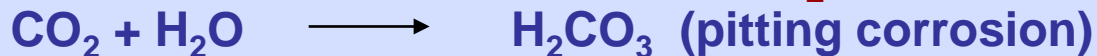
Degradation or destruction of boiler materials (Fe) due to the chemical or electrochemical attack of dissolved gases or salts is called boiler corrosion

**Factors causing:**

1. Corrosion due to dissolved  $O_2$



2. Corrosion due to dissolved  $CO_2$



3. Corrosion due to acid forming salts

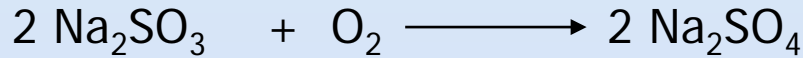


Here HCl is formed again and again in a chain like process and silicic acid catalyse the reaction, if silica is present in water rate of the reaction increases

# Prevention of boiler corrosion

## 1. By the addition of chemicals

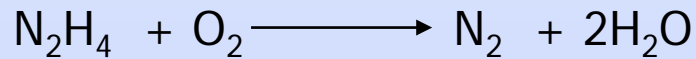
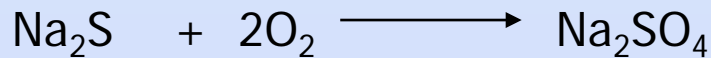
The dissolved oxygen present in the boiler feed water can be removed by the addition of sodium sulphite or hydrazine



Sodium sulphite

DO

Sodium sulphate



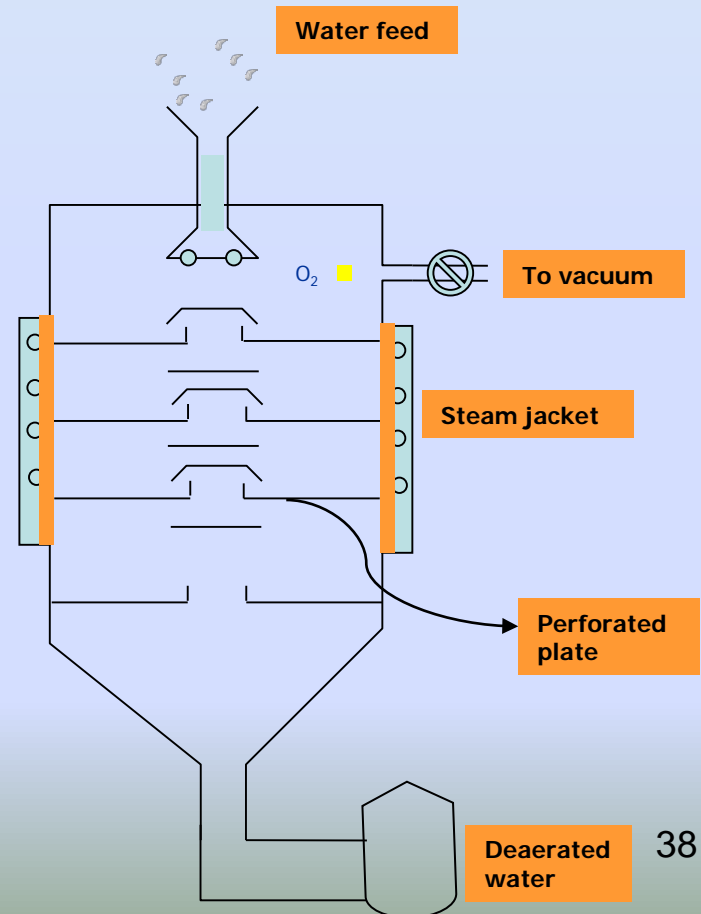
Hydrazine

Nitrogen

## 2. By mechanical deaeration

Principle: High tempt and low pressure favors lower solubility of gases in water (Henry's law)

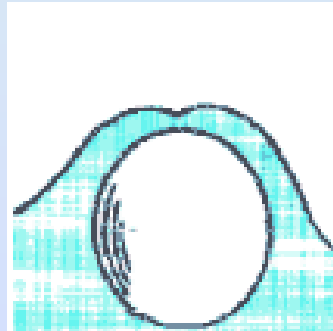
## 3. By addition of alkali



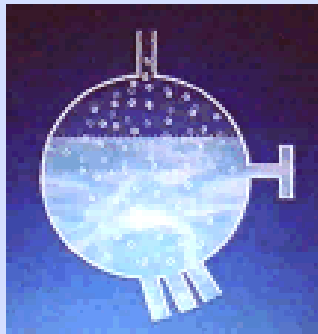
### 3. Priming and foaming



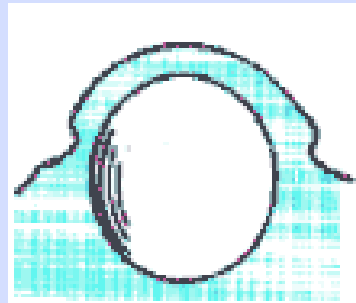
Foaming



Normal bubble



Priming



Carry over bubble

Disadvantages of Priming and foaming –  
refer Jain and Jain Text book

#### Foaming

Formation of continuous foam or hard bubblers in boilers.

**Cause:** Due to the presence of substance like oil & grease in boiling water., presence of sludge particles

**Prevention:** 1.Addition of coagulants; 2. Addition of antifoaming chemicals

#### Priming

Process in which some particles in water are carried along with the steam. The resulting process is called as wet steam or carry over. The process of formation of wet steam in boilers is called as priming.

##### Causes:

1. Presence of dissolved salts
2. High velocity steam due to sudden boiling
3. Improper boiler design

Prevention: Mechanical Steam purifier, low water level, controlling steam rate, boiler design

## 4. Caustic embitterment

The formation of irregular intergranular cracks on boiler metal particularly at the point of high local stress by the use of highly alkaline water in the boiler

❖ NaOH has better mobility and can percolate into fine cracks present in boiler walls.



❖ NaOH gets concentrated in the fine cracks present in the boiler walls.

❖ A concentration cell corrosion is established between the conc. NaOH and dilute NaOH solution in contact with boiler walls.

❖ **STRESS CORROSION:** Concentrated NaOH region behaves as anode thus resulting in corrosion of boiler leading to the formation of sodium ferroate.





## *Prevention:*

1. By phosphate conditioning of water
2. By addition of certain chemicals like lignin, tannin etc. These prevent the infiltration of NaOH through air cracks and thus help in preventing it
3. By addition of  $\text{Na}_2\text{SO}_4$  to boiler water  
Ratio of  $\text{Na}_2\text{SO}_4$  : NaOH(present in boiler water should be
  - 1:1 For up to 10 atm boiler pressure
  - 2:1 For up to 20 atm boiler pressure
  - 3:1 For more than 20 atm boiler pressure
4. Neutralization of excess alkali by suitable technique