

## SOURCES OF WATER

\*Naturally available water can be classified as:

- Surface water : Flowing water - streams, rivers and Stillwater-ponds, lakes and reservoirs.
- Underground water from springs and wells and from coal mining cuttings.
- Sea water and
- Rain water

**Rainwater** : It is the purest form of natural water but contains dissolved toxic gases like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$  etc. and other solids. Also its supply is unpredictable.

**Sea water** : It is the most impure form of water containing about 3.5% dissolved salts of which about 6% is NaCl. Other salts present include sulphates, bicarbonates, bromides of sodium, potassium, magnesium etc.

It is therefore, necessary to depend on ground and surface water after removing different impurities that are present in them, as required.

Water has different physical, chemical and biological Impurities which can cause problems in both domestic and industrial applications.

### Impurities in water

#### **Physical**

- -Inorganic such as clay, sand
- Organic such as oil globules, vegetable/animal matter
- Colloidal such as  $\text{Fe}(\text{OH})_3$ , Complex proteins, amines

#### **Chemical**

- Anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  of Ca & Mg
- Cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$
- Dissolved gases such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$

#### **Biological**

- Microorganisms such as algae, fungi, bacteria  
(Pathogenic causing Malaria, diarrhoea, typhoid etc.)

### Hardness of water

Hardness of water is the characteristic of preventing lather formation of water with soap. Generally salts like chlorides, bicarbonates and sulfates of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  make water hard.

This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.



Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

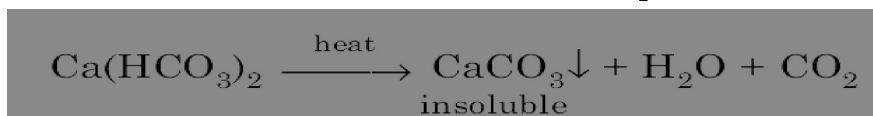
## Types Of hardness

Hardness of water is due to dissolved salts of mainly calcium and magnesium as well as iron and other heavy metals.

Hardness is two types:

a) Temporary :

- Due to dissolved bicarbonates of calcium and magnesium and carbonates of iron and other heavy metals. Hence it is also called as carbonate hardness.
- Can be easily removed by boiling where  $\text{CO}_2$  gas gets expelled removing the hardness.



b) Permanent:

- Due to dissolved chlorides and sulphates of calcium and magnesium. Also called as non-carbonate hardness.
- Can be removed through zeolite, Lime-soda, ion-exchange processes.

## Dissolved Oxygen

Dissolved oxygen (DO) is the amount of oxygen dissolved in a given quantity of water at a particular temperature and atmospheric pressure.

**DO depends on**

- Aeration,
- Photosynthetic activity of the water,
- Respiration of animals and plants
- Speed of water flow
- Roughness of surface over which water flows
- Temperature of the water body

**Oxygen Demanding Wastes**

- **Chemical Oxygen Demand (COD)**

Chemicals/Organic wastes present in water consume the DO

- **Biological Oxygen Demand (BOD)**

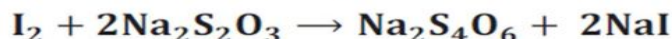
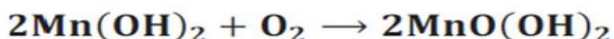
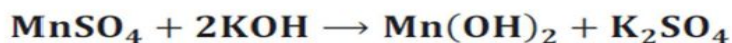
Organic wastes reaching water consume oxygen from water bodies for their decomposition by bacteria through biochemical oxidation

**These are useful measures to check water quality**

## Estimation of DO by Winkler's method

Theory of Winkler's Method:

- Oxygen in the water sample oxidizes iodide ion ( $\text{I}^-$ ) to iodine ( $\text{I}_2$ ) quantitatively.
- The amount of iodine generated is then determined by titration with a standard thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) solution.
- The endpoint is determined by using starch as a visual indicator.
- The amount of oxygen can then be computed from the titre values



### Total dissolved Solids(TDS)

Total dissolved solids (TDS) is the amount of particles dissolved in water

-They come from

- Organic sources (leaves)
- Silt
- Industrial wastage and sewage as well as runoff from urban sources, fertilizers and pesticides
- Inorganic materials such as rocks and air that may contain calcium bicarbonate, nitrogen, iron, sulphur and other minerals

-A constant level of minerals, eg. Phosphorous, nitrogen and sulphur, is necessary for aquatic life.

-Concentration of dissolved solids should not be too high or too low which can affect the growth and leads to death of many aquatic organisms.

-High concentration of dissolved solids reduces the clarity of water and can decrease the photosynthesis and raises the water temperature.

-It can be determined taking a known amount (say 100 mL) of water and by evaporating the contents carefully to dryness.

-The residue (W/g) left after evaporation of the filtered sample shows the total dissolved solids present in that particular water sample.

### Total Dissolved Solids

$$\text{TDS} = (\text{W}/100) \times 10^6 \text{ mg/L or ppm}$$

-Recommended TDS for drinking water is 25-250 mg/L

-At any cost drinking water TDS should not exceed 500 mg/L

-TDS for distilled water will be 0.5-1.5 mg/L

-TDS ranges from 100-20,000 mg/L in river water and will be generally higher in ground water

-Sea water will have 3500 mg/L of TDS

-Lakes and streams will have a TDS of 20-250 mg/L

### Measurement of Hardness of water

\*Hardness of water is measured in parts per millions (ppm.) as calcium carbonate equivalents.

\*Reasons for expressing hardness in  $\text{CaCO}_3$  equivalents:

- its molecular weight is 100 ; equivalent weight is 50.
- it is the most common insoluble impurity in water.

\*Units of hardness:

- parts per million in  $\text{CaCO}_3$  equivalents (1 mg/L is 1ppm.).
- if 146 mg/L of  $\text{MgSO}_4$  is present in water, the hardness of water is 146 ppm. as  $\text{MgSO}_4$ .

\*When expressed in  $\text{CaCO}_3$  equivalents, the formula for conversion is:

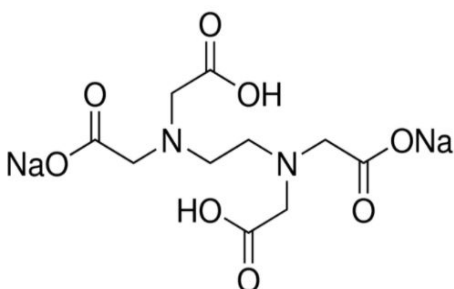
$$\frac{\text{mass of hardness causing substance}}{\text{Mol. wt of hardness causing substance}} \times 100$$

### Estimation of water hardness

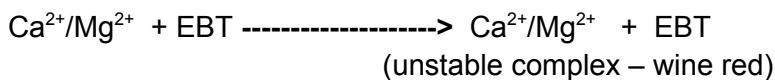
#### **EDTA method:**

-Ethylene diamine tetraacetic acid disodium salt (EDTA disodium salt) is used as a strong complexing agent with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in hard water.

The structure of EDTA disodium salt is:



-Initially,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are treated with Eriochrome Black T (EBT) indicator using ammonia buffer (to maintain pH between 9-10) to get an unstable complex of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  formed with EBT.

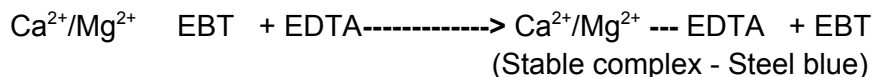


### Estimation of water hardness

On addition of EDTA, EBT gets replaced by EDTA since EDTA forms a stronger complex with the metal ions.

This is indicated by the formation of a steel blue coloured complex.

Ph 9-10



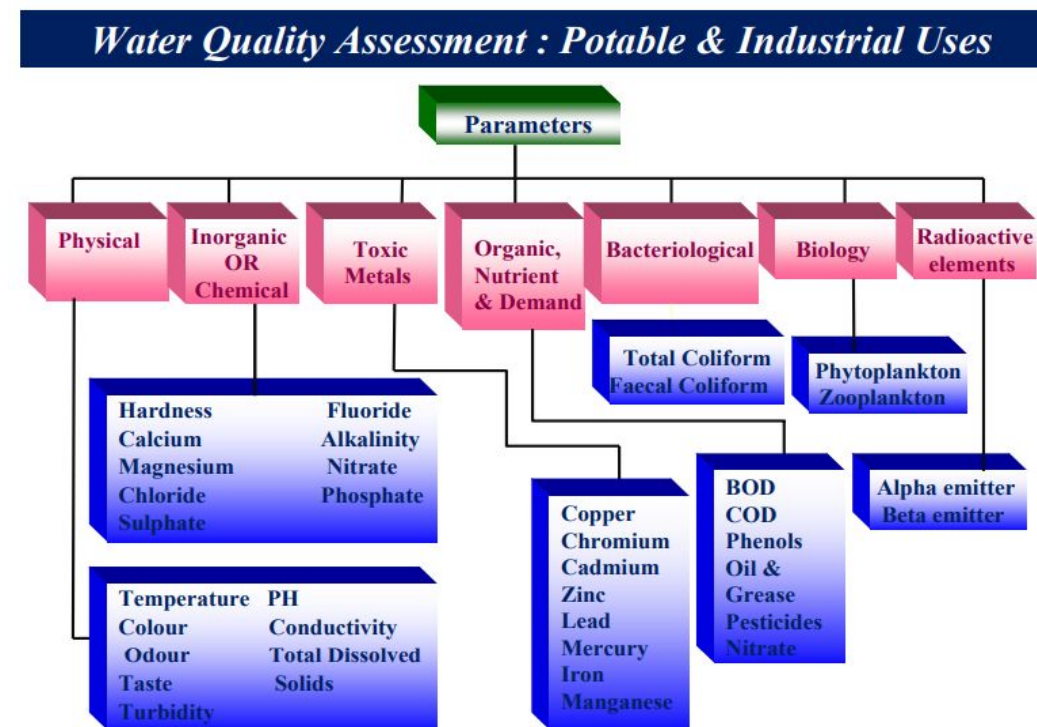
## Modern methods of water analysis

- **Importance of Water Analysis**

Water analysis is essential to ensure its quality or to detect pollutants that should be removed by water treatment. However, water quality does not mean making the water suitable for human consumption; it depends on its end use. For example, completely different quality standards are applied in case of industrial water compared to those applied to drink water, i.e., drinking water must be fit for human consumption, while industrial water should be free from any contaminants that may corrode or damage equipment.

- **Limitations of Traditional Methods of Water Analysis**

The traditional analysis includes chemical analysis, colorimetry, spectrometry, chromatography, and atomic absorption. Although these techniques differ in sensitivity and accuracy, most of them are highly accurate. Nevertheless, they require sampling, expensive devices, and manpower; besides, they are time-consuming and difficult to conduct onsite.



## Lab-on-a-chip

-A lab-on-a-chip (LOC) is a device that integrates one or several laboratory functions on a single integrated circuit (commonly called a "chip") of only millimeters to a few square centimeters to achieve automation and high-throughput screening

-Lab-on-a-chip devices are a subset of microelectromechanical systems (MEMS) devices and sometimes called "micro total analysis systems" ( $\mu$ TAS)

-LOCs may provide advantages, which are specific to their application. Typical advantages are:

- a) low fluid volumes consumption (less waste, lower reagents costs, and fewer sample volumes)
- b) faster analysis and response time due to short diffusion distance & high surface to volume ratio.
- c) better process control because of a faster response of the system compactness of the systems due to the integration of much functionality and small volumes
- d) lower fabrication costs, allowing cost-effective disposable chips, fabricated in mass production
- e) safer platform for chemical, radioactive or biological studies because of integration of functionality, smaller fluid volumes, and stored energies

## Lab-on-a-chip

### **Microfluidics and Lab-On-A-Chip for Water Analysis**

- Microfluidics and lab-on-a-chip systems are advanced technologies that may replace the traditional methods of water analysis in the near future.
- Lab-on-a-chip technology employs microfluidics, which deals with very minute amounts of fluids in microchannels, to perform the analysis.
- The lab-on-a-chip device is a chip that resembles electronic chips, but with micro-channels instead of electrical circuits.
- It shrinks the lab to the chip size and can perform complete analysis or even series of analysis.

#### **Advantages of using lab-on-a-chip for water analysis:**

- can reduce time and manpower in the sampling process because this technology can offer immediate, onsite results.
- In addition, this technique is much less expensive and offers higher accuracy, because of the small volumes analyzed and the possibility of eliminating the sampling process, which reduces the human error.

## Components of Lab-on-a-chip systems

The main components of a lab-on-a-chip system for water analysis are; a liquid delivery system (injector and fluidic transporter), mixer, reactor, separator, and power supply.

- **The Injector** is used to deliver precise volumes into the chip. The most common types of the injectors are syringe pumps and robotic pipets.
- **Transporters** control all aspects of the flow. They can be active, which need an energy source, or passive, which are achieved by manipulating the geometries of the channels and do not require any energy source. The choice between the active and passive types is based on the application. There are multiple types of active transporters, but the most preferred is electrochemical pumping systems, such as microsyringe pumps, because they eliminate the design complexity.
- **Mixers** are used to mix different fluids into the channels. Similar to the transporters, the types of mixers are divided into passive, which are achieved by design manipulation, and active, which require power.

- **The Reactor** is where the reaction takes place. There are three types of reactors used in lab-on-a-chip systems: gas phase, liquid phase, and packed-bed reactors.
- **Controllers** are used for controlling all types of activities in the chip as well as data acquisition and signal processing.
- **Power supplies**, such as batteries, are essential to run the lab-on-a-chip systems. Many research studies focus on finding more advanced power supplies because some types of lab-on-a-chip systems require high voltage.

### Current Applications in Water Analysis

- Lab-on-a-chip technology is rapidly developing and being used in different industrial and research fields.
- Most biological lab-on-a-chip devices are commercialized, while those for water analysis are still developing.
- However, some lab-on-a-chip applications in water analysis are already established, such as pH testing and detection of various chemicals (e.g., nitrates and nitrites, manganese, phosphates, and silicates).
- For example, the microfluidic pH analysis uses sulfonaphthalein as the main indicator.
- It includes the absorption cell, a static mixer, as well as a syringe pump and four valves attached to the chip to regulate the flow.

### Problems of hard water for domestic use

#### **A) Washing:**

- Hard water, when used for washing purposes, does not lather freely with soap.
- It produces sticky precipitates of calcium and magnesium soaps.
- Similar problem exists in bathing.

#### **B) Cooking**

- Due to the presence of dissolved hardness producing salts the boiling point of water is elevated.
- Consequently more fuel is and time are required for cooking.

#### **C) Drinking:**

- Hard water causes bad effect on our digestive system.
- The possibility of forming calcium oxalate crystals in urinary tracks is increased (Kidney stones).

### Disadvantages of hard water in industries

#### **Paper Industry:**

The presence of calcium and magnesium has impact on the properties and quality of paper and their products

#### **Textile industry :**

Hard water cause much of the soap to go as waste.

During dyeing process, calcium and magnesium salts present in water make the quality of the shades very poor.

**Sugar industry :**

If nitrates, sulphates of calcium and magnesium are present, they cause hindrance to crystallization of sugar

**Concrete making :**

Water containing chlorides and sulphates, if used for concrete making, affects the hydration of the cement and the final strength of the hardened concrete.

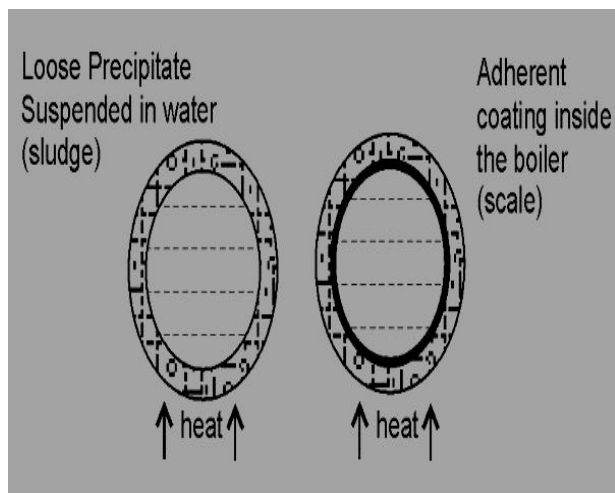
**In steam generation in boilers:**

If the hard water is fed directly to the boilers, which led to the many problems such as Formation of scales which corrodes the boiler, wastage of fuel etc.

### Disadvantages of hard water

**1) Scale and Sludge formation:****a) Sludges:**

- Soft, loose, slimy precipitates are sludge
- Can be easily scraped off with a wire brush
- Forms in comparatively colder portions of the boiler such as bends etc.
- Formed because of  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Mg(OH)}_2$  (more soluble in hot water)

**b) Scales:**

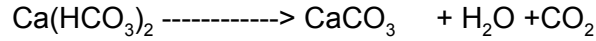
- Dissolved salts deposit because of continuous evaporation of water concentration of salts increases
- These are hard and stick strongly to the walls
- Difficult to be removed even with a hammer and chisel.
- Formed because of  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaSiO}_3$ ,  $\text{MgSiO}_3$



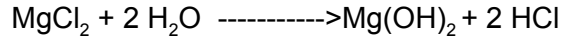
## Scales

-Scales are the main source of boiler troubles.

Scale are mainly formed by decomposition of calcium bicarbonate



-Dissolved magnesium salts undergo hydrolysis forming magnesium hydroxide precipitate which forms a soft type of scale



-Presence of silica in small quantities deposits as calcium silicate ( $\text{CaSiO}_3$ ) or magnesium silicate ( $\text{MgSiO}_3$ ).

These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove.

-Scales reduce the thermal conductivity and if there is a crack on the **scale**, it may lead to **differential heating and increases the possibility of boiler explosion**.

## Disadvantages of hard water

### **2. Priming and Foaming:**

#### **a) Foaming:**

-Foaming is the production of persistent foam or bubbles in boilers which do not break easily.

-This is because of presence of oils which reduce the surface tension of water.

-Can be avoided by adding anti-foaming agents like castor oil or removing oil from the boiler feed water by adding sodium aluminate.

#### **b) Priming:**

-Along with steam, some particles of water are carried (wet steam) which is called priming.

-This is because of large amounts of dissolved salts, high steam velocities, sudden boiling, improper boiler design, sudden increase in steam production rate.

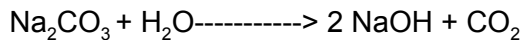
-Priming can be avoided by maintaining low water level in boilers, avoiding rapid steam generation, efficient softening, installing mechanical steam purifiers.

### **3. Caustic embrittlement:**

-Caused by using highly alkaline water in boiler

-When water is softened by lime-soda process, free  $\text{Na}_2\text{CO}_3$  is present in softened water.

-In high pressure boilers, this  $\text{Na}_2\text{CO}_3$  decomposes to  $\text{NaOH}$  and  $\text{CO}_2$



-This  $\text{NaOH}$  makes the water caustic.

-This  $\text{NaOH}$  flows through minute cracks present in the boiler by capillary action.

-As water is boiling it evaporates and the conc. of  $\text{NaOH}$  increases.

-This caustic soda attacks the boiler and forms sodium ferroate.

-This makes the boiler parts brittle (embrittlement).

### **Concentration cell representation of caustic embrittlement**

Caustic attack on boiler parts can be represented as:



## Additional Information on Boiler troubles

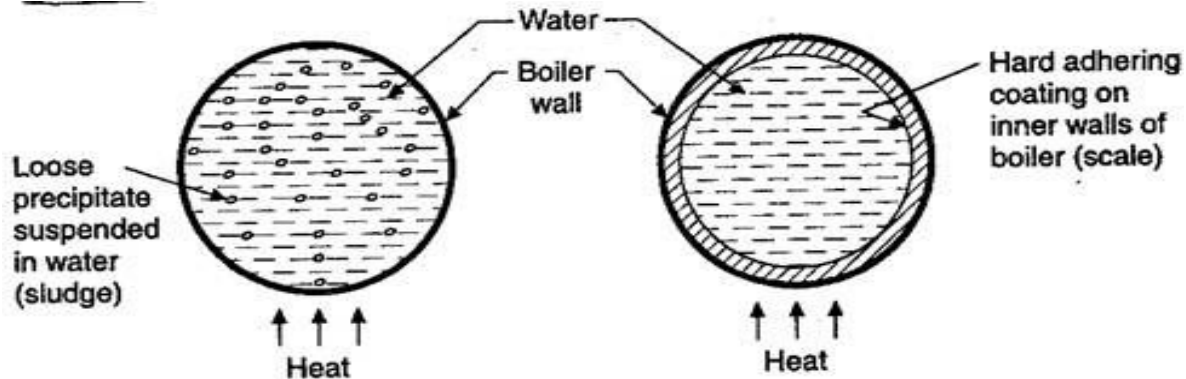
### **Scale & Sludge Formation in Boilers**

#### **In boilers**

– Concentration of the dissolved salts increases progressively when water evaporates during continuous steam generation. When their concentration reaches saturation point, the salts get precipitated probably on the inner walls of the boiler.

#### **If the precipitate is**

- Soft, Loose, slimy precipitate - **Sludge**
- Hard, adhering crust/coating on the inner walls of the boiler- **Scale**



#### **Scales**

- Hard deposits, stick very firmly to the inner surfaces of the boiler
- Difficult to remove even with the help of hammer
- Main source for the boiler corrosion

#### **Sludge - Soft, Loose, slimy precipitate**

- Can be washed easily using brush
- Formed at comparatively colder places of the boiler
- Collects in a system where the flow rate is slow like bends
- Which are formed by the substances which have greater solubilities in hot than cold water (Example –  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ )

#### **Disadvantages**

- Poor conductor of heat – wastage of energy
- If sludge formed along with the scale, sludge get entrapped within scale and both gets deposited as scale
- Excessive sludge formation disturbs the working condition of the boiler

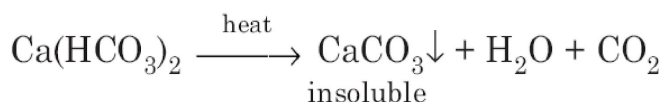
#### **Prevention**

- By using soft water
- Frequent blow-down operation

## Formation of Scales

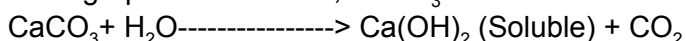
### Decomposition of calcium bicarbonate

-Scales are the main source of boiler troubles. Scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in **low-pressure boilers**.



### **Scale**

-But in high-pressure boilers,  $\text{CaCO}_3$  is soluble.



### Decomposition of calcium sulphate

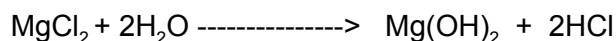
-The solubility of calcium sulphate in water decreases with increase of temperature

-The solubility of  $\text{CaSO}_4$  is 3,200 ppm at  $15^\circ\text{C}$  and it reduces to 55 ppm at  $230^\circ\text{C}$  and 27 ppm at  $320^\circ\text{C}$

- $\text{CaSO}_4$  gets precipitated as hard scale on the heated portion of the boiler. This is the main cause of scales in high-pressure boilers.

### Hydrolysis of magnesium salts

Dissolved magnesium salts undergo hydrolysis forming magnesium hydroxide precipitate which forms a soft type of scale



### **Presence of Silica**

presence of **silica in small quantities** deposits as **calcium silicate ( $\text{CaSiO}_3$ )** or **magnesium silicate ( $\text{MgSiO}_3$ )**. These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove

## Disadvantage of scale formation

-Low thermal conductivity

Thickness of scale in (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

-Lowering boiler safety

-Decrease in efficiency

-Danger of explosion

## Removal of Scales

-By giving thermal Shock if they are brittle (heating the boiler and then suddenly cooling with cold water)

-If they are adherent and hard dissolving them with help of chemicals.

- Calcium carbonate scales can dissolved by using 5-10% HCl.
- Calcium Sulphate scales can be dissolved by adding EDTA (**ethylene diamine tetra acetic acid**) with which they form soluble complex.

-Frequent blow down operation

## Prevention of scale formation

### **Internal Treatment**

- Colloidal Conditioning
- Phosphate conditioning
- Carbonate conditioning
- Calgon conditioning
- Treatment with sodium aluminate

### **External Treatment**

- The treatment includes efficient 'softening of water'
- Removing hardness-producing constituents of water

## Prevention of scale formation

### • **Internal Treatment**

In this process, an ion is prohibited to exhibit its original character by '**Complexing**' or **converting into other more stable salt by adding appropriate reagent.**

### **Colloidal Conditioning:**

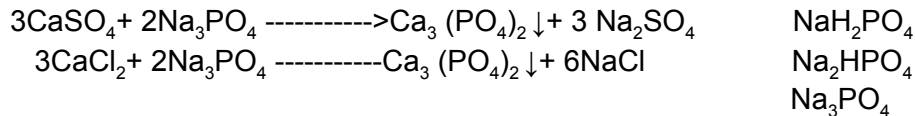
In low-pressure boilers, scale formation can be avoided by adding substances:

Kerosene, tannin, agar-agar : non-sticky and loose deposit

Blow-down operations - removal

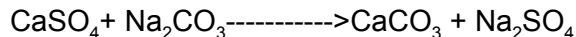
### **Phosphate Conditioning:** High-Pressure boilers

Sodium phosphate **Optimum pH – 9.5 to 10.5**



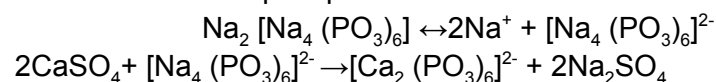
### **Carbonate Conditioning: Low-Pressure boilers**

Sodium carbonate

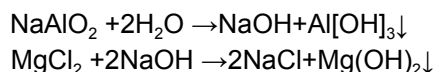


### **Calgon Conditioning:**

Sodium hexa meta phosphate



### **Treatment with sodium meta aluminate:**



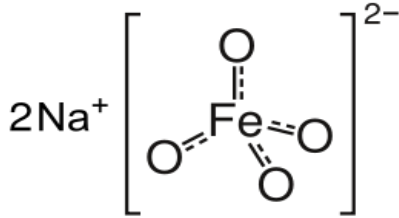
## Caustic Embrittlement

- Its a kind of boiler corrosion, caused by using highly alkaline water in the boiler



### **Minutes cracks – present in boilers**

Water evaporates – dissolved caustic soda concentration increases progressively



Sodium Ferrate

This causes embrittlement of boiler parts particularly stressed parts (bends, joints, rivets, etc.)

## Caustic embrittlement can be avoided

- By using sodium phosphate as softening reagent instead of sodium carbonate
- By adding tannin or lignin to the boiler water which block the hair cracks and pits
- By adding sodium sulphate to boiler water, which also blocks the hair cracks and pits



1:1

2:1

3:1

10 atm

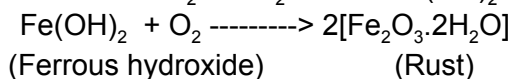
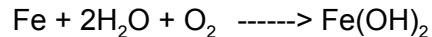
20 atm

>20 atm

## Boiler Corrosion

- It's a decay of boiler material by chemical or electro-chemical attack by its environment

(1) **Dissolved oxygen** in water at high temperature attack boiler material.

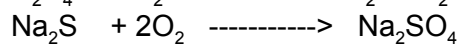
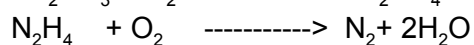
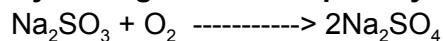


(Ferrous hydroxide)

(Rust)

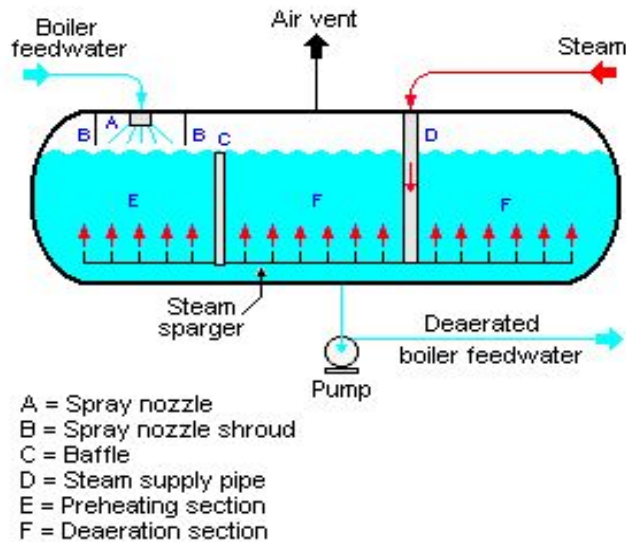
## Removal of dissolved oxygen

**By adding calculated quantity of** sodium sulphite or hydrazine or sodium sulphide



### Removal of dissolved oxygen by de-aeration

Water spraying in a perforated plate-fitted tower, heated from sides and connected to Vacuum pump. High temperature, low pressure and large exposed surface reduces dissolved oxygen in water

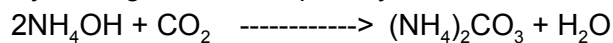


### Dissolved Carbon dioxide

$\text{H}_2\text{CO}_3$  is carbonic acid which has corrosive effect on the boiler material

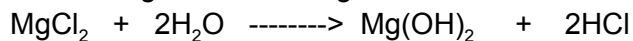
#### **Removal of $\text{CO}_2$**

By adding calculated quantity of ammonia

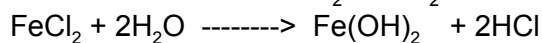
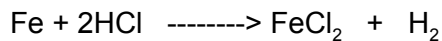


### Acids from Dissolved Salts

Water containing dissolved magnesium salts liberate acids on hydrolysis



The liberated acid reacts with iron of the boiler in **chain-like reactions producing HCl again and again**. As a result presence of even a small amount of  $\text{MgCl}_2$  will cause corrosion of iron to a large extent.



#### **Priming**

- When a boiler is steaming rapidly some particles of the liquid water are carried along with the steam. Its called priming.
- Presence of large amount of dissolved solids
- Sudden boiling

- Improper boiler design

### **Foaming**

- It is the **production of persistent foam or bubbles** in boilers, which do not break easily. It is due to the presence of oil.
- Priming and foaming occur together

### ***Priming can be avoided by***

Fitting mechanical steam purifier  
avoid rapid change in steaming rate

### ***Foaming can be avoided by***

adding anti-foaming agent like **castor oil**  
Removing oil from boiler water by adding compounds like **sodium aluminate**.





