

Module -1

Water Technology

Dr. M. Akhila Maheswari

Contents

- Characteristics of hard water
- Hardness, DO, TDS in water and their determination
- Numerical problems in hardness determination by EDTA
- Modern techniques of water analysis for industrial use - Disadvantages of hard water in industries.

Sources of Water

Naturally available water can be classified as:

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

Rainwater : It is the purest form of natural water but contains dissolved toxic gases like CO_2 , SO_2 , 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.

Impurities in water

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

○ **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**

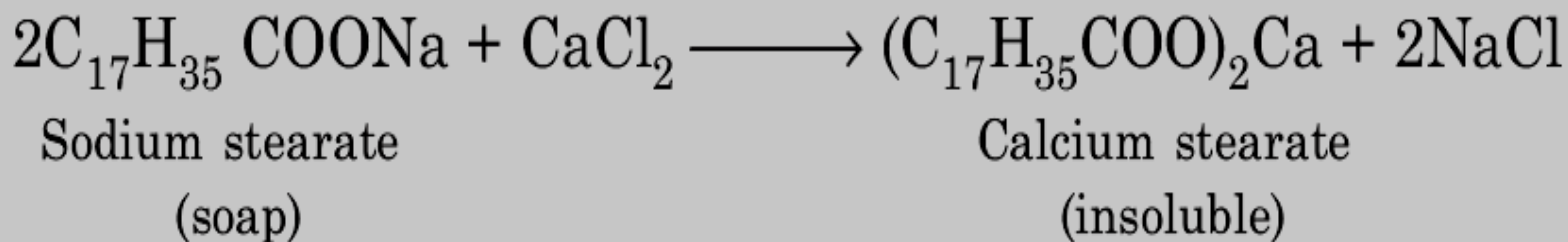
- Anions such as Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , NO_3^- of Ca & Mg
- Cations such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Al^{3+}
- Dissolved gases such as O_2 , N_2 , CO_2 , H_2S , NH_3

○ **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 Ca^{2+} , Mg^{2+} and 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.



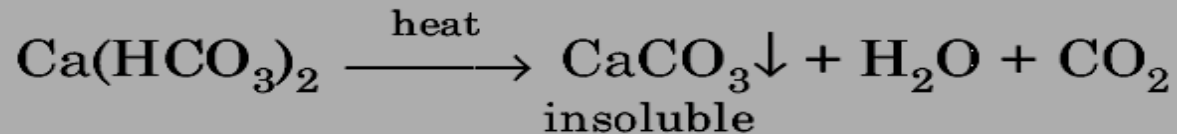
- Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

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 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)**

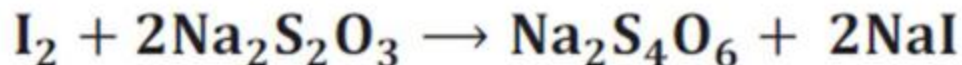
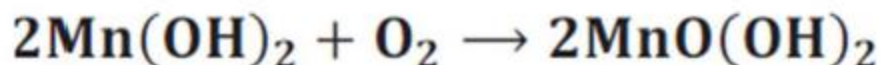
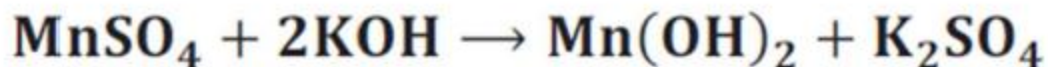
Organic wastes reaching water consume oxygen from water bodies for their decomposition by bacteria through biochemical oxidation

- **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 (I-) to iodine (I₂) quantitatively.
- The amount of iodine generated is then determined by titration with a standard thiosulfate (S₂O₃⁻²) 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
 - a) Organic sources (leaves)
 - b) Silt
 - c) Industrial wastage and sewage as well as runoff from urban sources, fertilizers and pesticides
 - d) 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 articular water sample.

Total Dissolved Solids

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

- 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 100-2000 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 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 CaCO_3 equivalents (1 mg/L is 1ppm.).
 - if 146 mg/L of MgSO_4 is present in water, the hardness of water is 146 ppm. as MgSO_4 .
- When expressed in CaCO_3 equivalents, the formula for conversion is:
$$\frac{\text{mass of hardness causing substance}}{\text{Mol. wt of hardness causing substance}} \times 100$$

Units of Hardness

Most Commonly used

- **Parts per million (ppm)**

1ppm=1 part of CaCO_3 equivalence hardness causing substance present in 10^6 parts of water

- **Milligrams per liter (mg/litre)**

1mg/L=1mg of CaCO_3 equivalence hardness causing substance present in one liter of water

1mg/L=1ppm

Relationship; 1L water = 1Kg = 1000 g = 1000 X 1000 mg = 10^6 mg

1mg/L = 1mg of CaCO_3 eq per 10^6 mg of water

= 1 part of CaCO_3 eq per 10^6 parts of water = 1ppm

- **Clare's Degree($^{\circ}\text{Cl}$)**

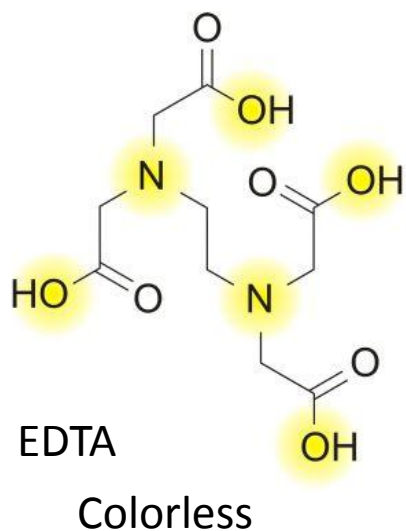
1 $^{\circ}$ Clarke= 1part of CaCO_3 equivalent hardness in 70000 parts of water

- **Degrees French ($^{\circ}\text{Fr}$)**

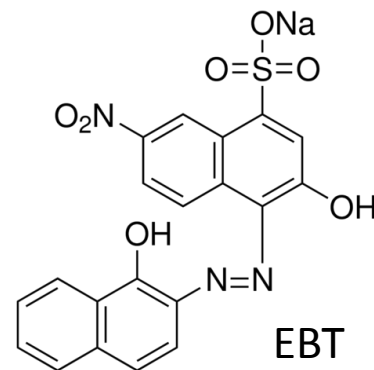
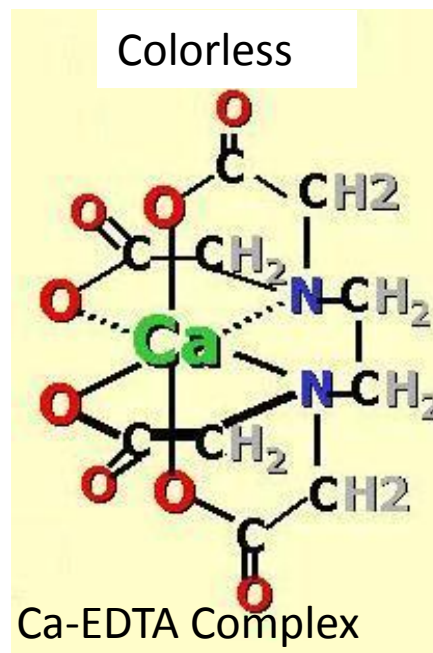
1 $^{\circ}$ Fr = 1 part of CaCO_3 eq per 10^5 parts of water

EDTA method: Estimation of Hardness

- Complexometric titration.
- Pipette solution: water sample
- Titrant: **EDTA** (Strong complexing agent)
- Condition for titration: **pH-9-10** – Ammonia-ammonium chloride buffer added.
- **Indicator: Eriochrome Black – T (EBT)**
- End point: **wine red to steel blue**



Ca^{2+}

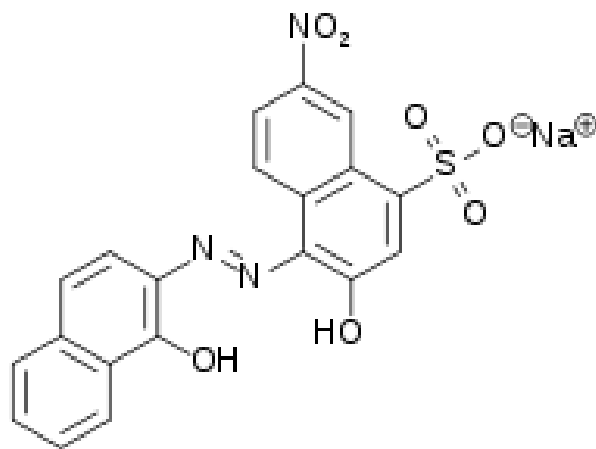


Color of Ca-EBT

Color of free EBT

EDTA forms permanent complex with Ca^{2+} and Mg^{2+} present in the hard water

EDTA: Colorless solution

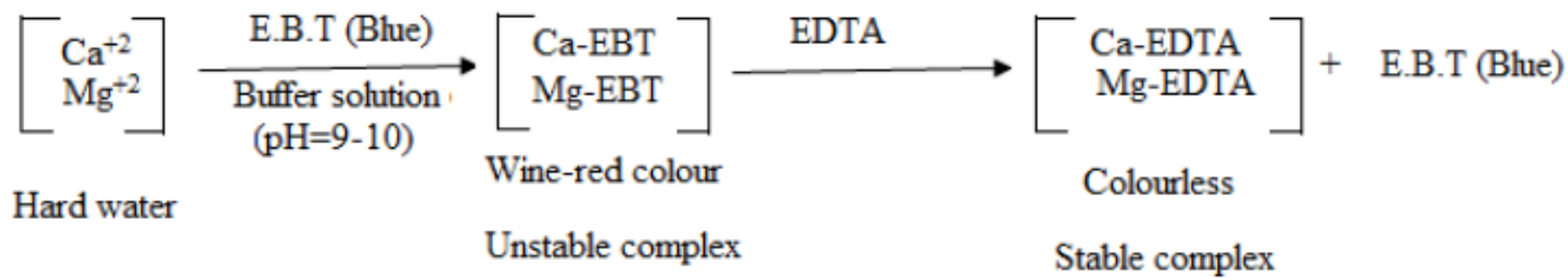


Eriochrome Black T



EBT is blue in a buffered solution at pH 10, it turns red when Ca^{2+} ions were added

The characteristic blue end-point is reached when sufficient EDTA is added and metal ions is chelated by EDTA, leaving the free indicator molecule



Procedure

- First EDTA Solution is standardized using standard hard water (1 mg/mL of CaCO_3 equivalents is prepared as standard hard water).
- For this, first known aliquot of Standard hard water is taken and 10-15 mL of ammonia buffer is added to bring the pH between 9-10.
- Then a few drops of EBT solution is added to form the unstable complex giving wine red colour.
- This solution is titrated with the EDTA solution till the solution turns to steel blue indicating the formation of stable EDTA-Metal ion complex.
- This volume of EDTA is noted as V_1 .
- The above procedure is repeated with sample hard water of unknown hardness.
- Volume of EDTA is noted as V_2 .
- Then sample hard water of 250 mL is taken and evaporated to a volume of 50mL when the temporary hard salts settle down.
- The solution is filtered and washed thoroughly and made up again to 250mL.
- From this solution, 50 mL is pipetted out and titrated in similar manner as done with standard hard water.
- Volume of EDTA is noted as V_3 .

Calculations

a) Total hardness:

V_1 mL of EDTA is consumed by 50 mL of std. hard water

$$V_1 \text{ mL of EDTA} = 50 \text{ mg of CaCO}_3$$

$$1 \text{ mL of EDTA} = 50/V_1 \text{ mg of CaCO}_3$$

EDTA consumed by sample hard water = V_2 mL

$$\text{So, } V_2 \text{ mL of EDTA} = 50/V_1 \times V_2 \text{ mg of CaCO}_3$$

Hence, 50 mL of sample hard water contains $50/V_1 \times V_2$ mg of CaCO_3

Therefore, 1000 mL of sample hard water = $50/V_1 \times V_2/50 \times 1000$ mg/L

i.e. Total hardness of sample hard water = $V_2/V_1 \times 1000$ mg of CaCO_3
(ppm.)

Calculations

Permanent hardness:

50 mL of sample hard water after removing temporary hardness consumed V_3 mL of EDTA.

$$1 \text{ mL of EDTA} = 50/V_1 \text{ mg of CaCO}_3 \text{ equiv.}$$

Therefore, $V_3 \text{ mL of EDTA} = 50/V_1 \times V_3 \text{ mg of CaCO}_3 \text{ equiv.}$

50 mL of sample hard water after boiling contained $50/V_1 \times V_3 \text{ mg of CaCO}_3 \text{ equiv.}$

Therefore, 1000 mL of sample hard water contains

$$= 50/V_1 \times V_3/50 \times 1000 \text{ mg/L CaCO}_3 \text{ equiv.}$$

Permanent hardness $= V_3/V_1 \times 1000 \text{ mg/L CaCO}_3 \text{ equiv.}$

Temporary hardness:

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

Temporary hardness calculation

Temporary hardness:

Temporary hardness = Total hardness – permanent hardness

$$\frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000$$

$$= 1000 \times \frac{V_2 - V_3}{V_1}$$

Examples of hardness calculations

A sample hard water contains,

8.1 mg/L $\text{Ca}(\text{HCO}_3)_2$; 7.5 mg/L $\text{Mg}(\text{HCO}_3)_2$; 13.6 mg/L CaSO_4 ;
12.0 mg/L MgSO_4 and 2.0 mg/L MgCl_2 .

To calculate the hardness and express in CaCO_3 equivalents:

Constituent	Multiplication factor	CaCO_3 equivalents
$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/L}$	100/162	$8.1 \times 100/162 = 5.0 \text{ mg/L}$
$\text{Mg}(\text{HCO}_3)_2 = 7.5 \text{ mg/L}$	100/146	$7.5 \times 100/146 = 5.14 \text{ mg/L}$
$\text{CaSO}_4 = 13.6 \text{ mg/L}$	100/136	$13.6 \times 100/136 = 10.0 \text{ mg/L}$
$\text{MgSO}_4 = 12.0 \text{ mg/L}$	100/120	$12.0 \times 100/120 = 10.0 \text{ mg/L}$
$\text{MgCl}_2 = 2.0 \text{ mg/L}$	100/95	$2.0 \times 100/95 = 2.11 \text{ mg/L}$

Modern methods of water analysis

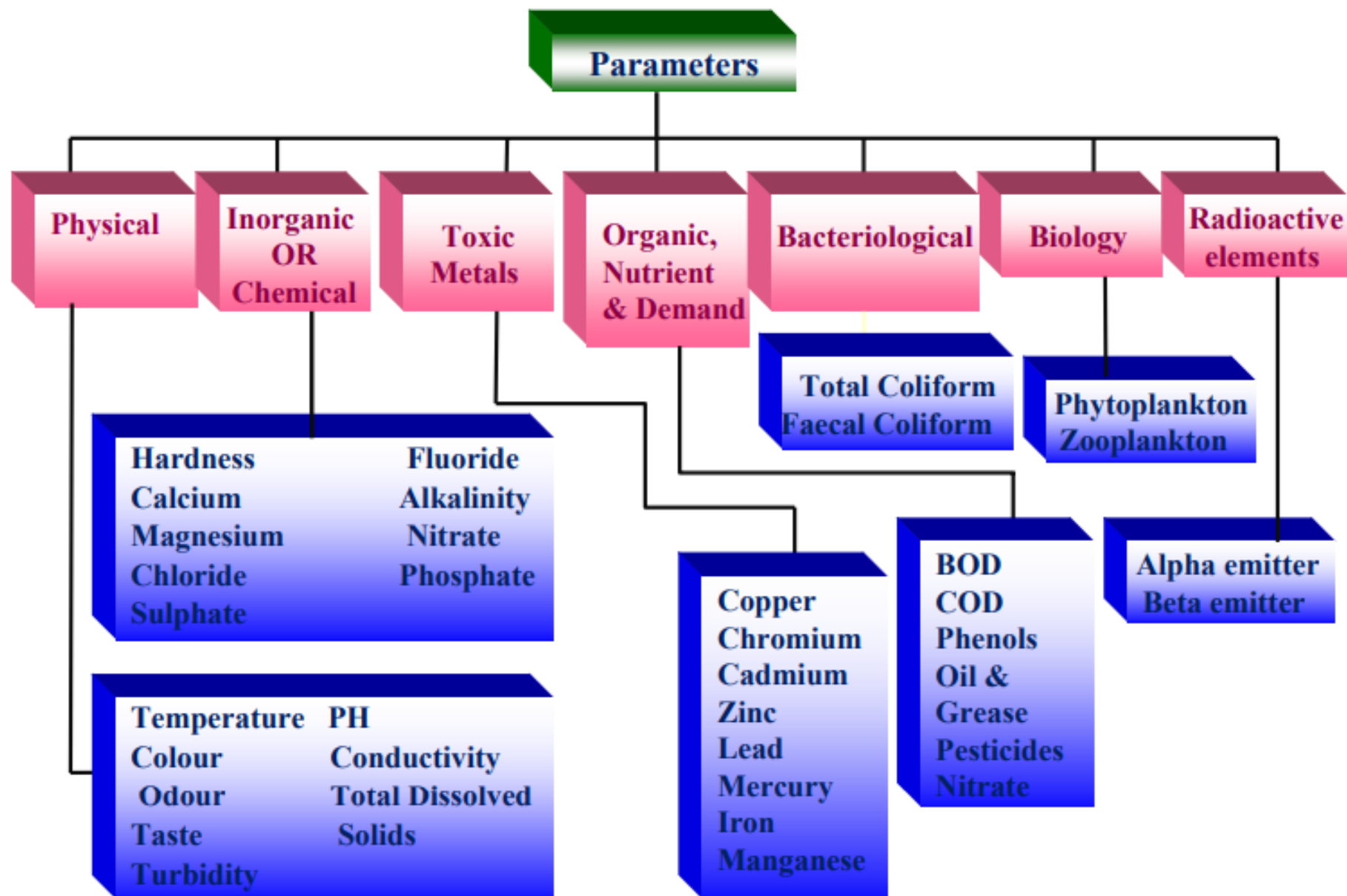
○ Importance of Water Analysis

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.

Water Quality Assessment : Potable & Industrial Uses



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" (μ 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

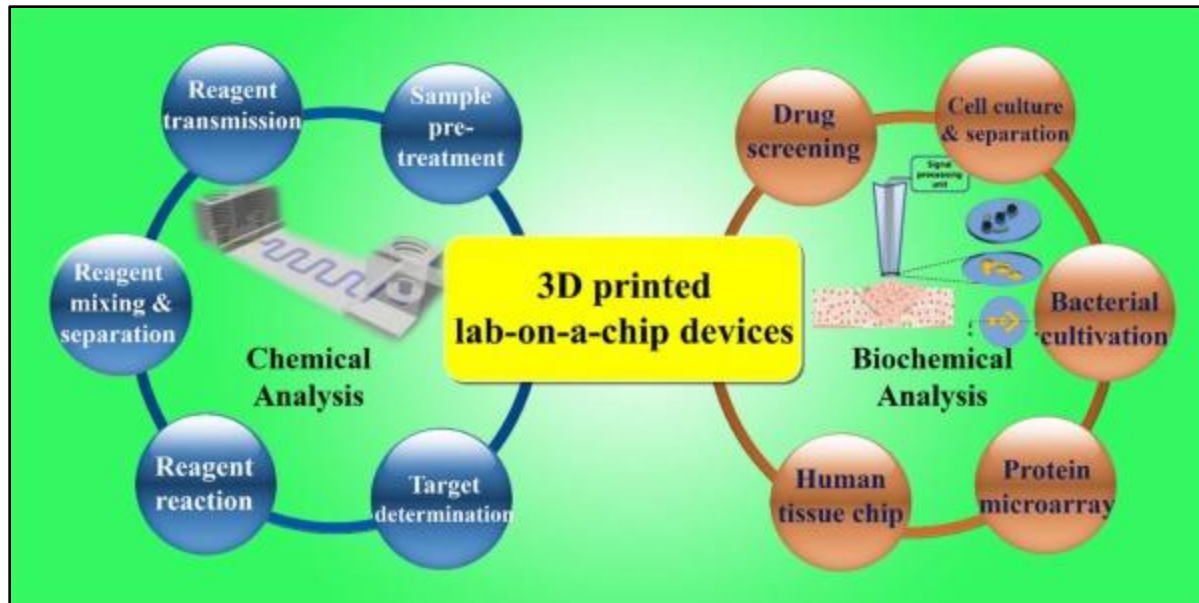
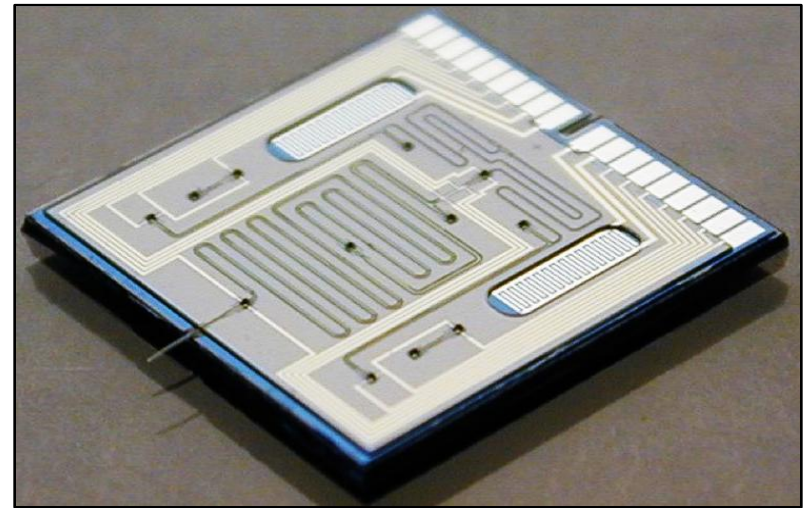
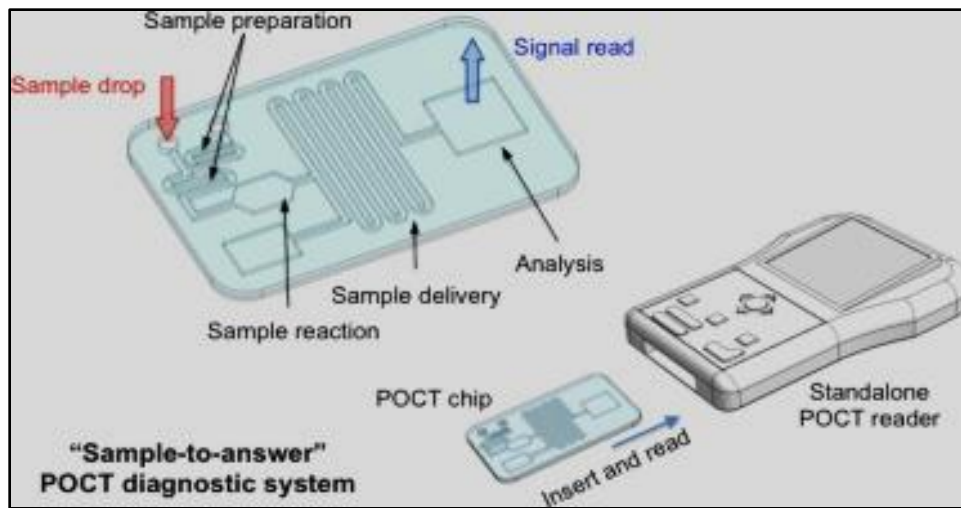
Components of Lab-on-a-chip systems

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 sulfonephthalein 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.



References:

1. J. Cleary, C. Slater, D. Diamond, Analysis of phosphate in wastewater using an autonomous microfluidics-based analyser, World Acad. Sci. Eng. Technol. 52 (2009) 196–199.
2. R. Paul Payel, "Lab on a Chip" Systems for Environmental Analysis, University of Stavanger, 2014.

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.

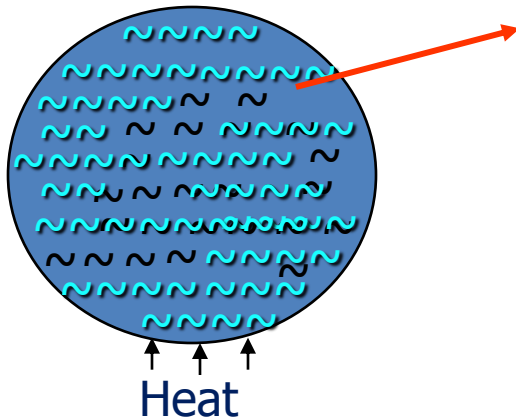
Boiler troubles due to Hard Water

1. Scales and sludges
2. Caustic embrittlement
3. Priming and foaming
4. Boiler corrosion

Disadvantages of hard water

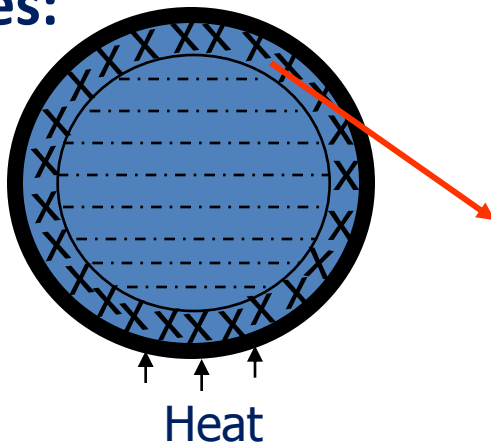
1. Scale and Sludge formation:

a) Sludges:



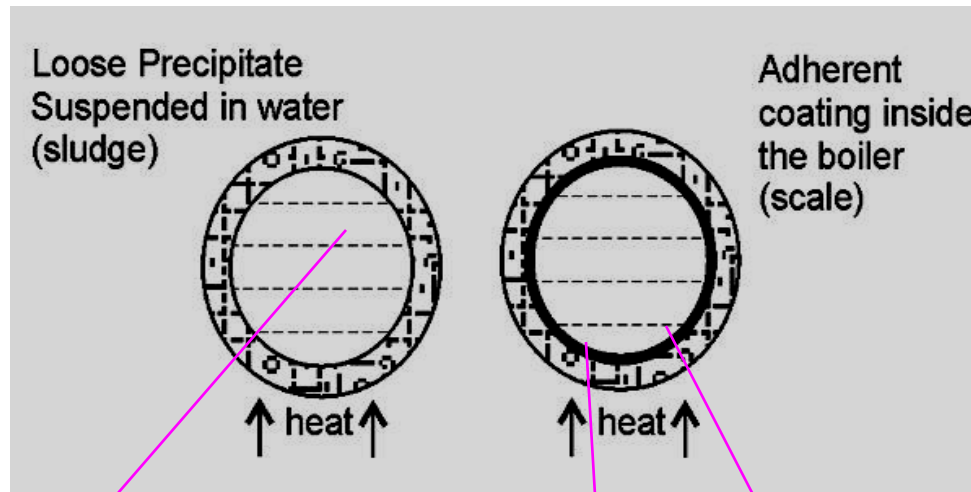
- Soft, loose, slimy precipitates are sludge
- Can be easily scrapped off with a wire brush
- Forms in comparatively colder portions of the boiler such as bends etc.
- Formed because of MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 , Mg(OH)_2 , (more soluble in hot water)

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 CaCO_3 , CaSO_4 , CaSiO_3 , MgSiO_3

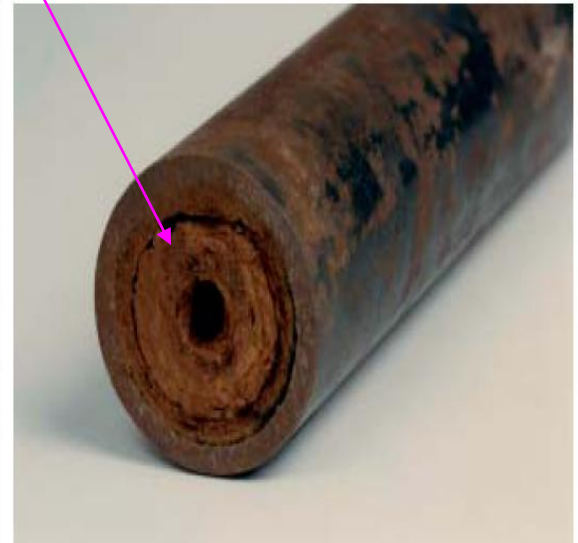
Examples of Sludge and Scale



**Could this sludge be inside
your central heating system?**



Boiler scale on water side



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 (CaSiO_3) or magnesium silicate (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.

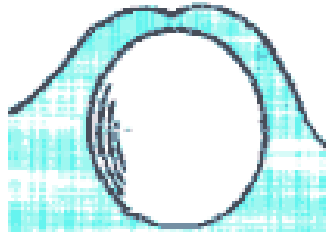
b) Priming:

- 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.

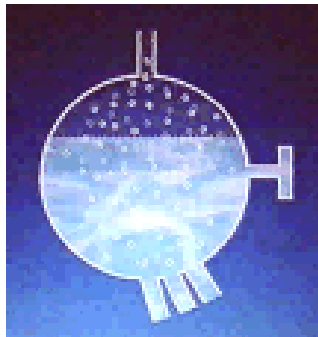
Priming and foaming



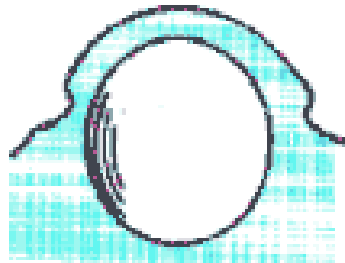
Foaming



Normal bubble



Priming



Carry over bubble

Priming can be avoided by

Fitting mechanical steam purifier
avoid rapid change in steaming rate

Foaming can be avoided by

Removing oil from boiler water by
adding compounds like sodium aluminate

Foaming

It is the production of continuous foam or hard bubblers in boilers. Foaming is due to the presence of substance like oil in boiling water.

Priming

It is the 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 of Priming

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

3. Caustic embrittlement:

- Caused by using highly alkaline water in boiler
- When water is softened by lime-soda process, free Na_2CO_3 is present in softened water.
- In high pressure boilers, this Na_2CO_3 decomposes to NaOH and CO_2



- This NaOH makes the water caustic.
- This NaOH flows through minute cracks present in the boiler by capillary action.
- As water is boiling it evaporates and the conc. of 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:



- The iron in contact with dil. NaOH becomes cathode and the iron in contact with conc. NaOH becomes anode.
- The anodic part slowly dissolves and corrodes.
- Caustic embrittlement can be avoided by adding:
 - a) sodium phosphate (Softening agent)
 - b) tannin or lignin (Blocks hair line cracks)
 - c) sodium sulphate (Blocks hair line cracks)

4. Boiler corrosion:

- Decay of boiler material by chemical or electrochemical attack by surrounding environment.
- Reasons for boiler corrosion are:
 - a) Dissolved oxygen
 - b) Dissolved carbon dioxide
 - c) Acids from dissolved salts

a) Dissolved oxygen (DO):



- DO can be removed by adding calculated qty. of sodium sulphite or hydrazine or sodium sulphide:



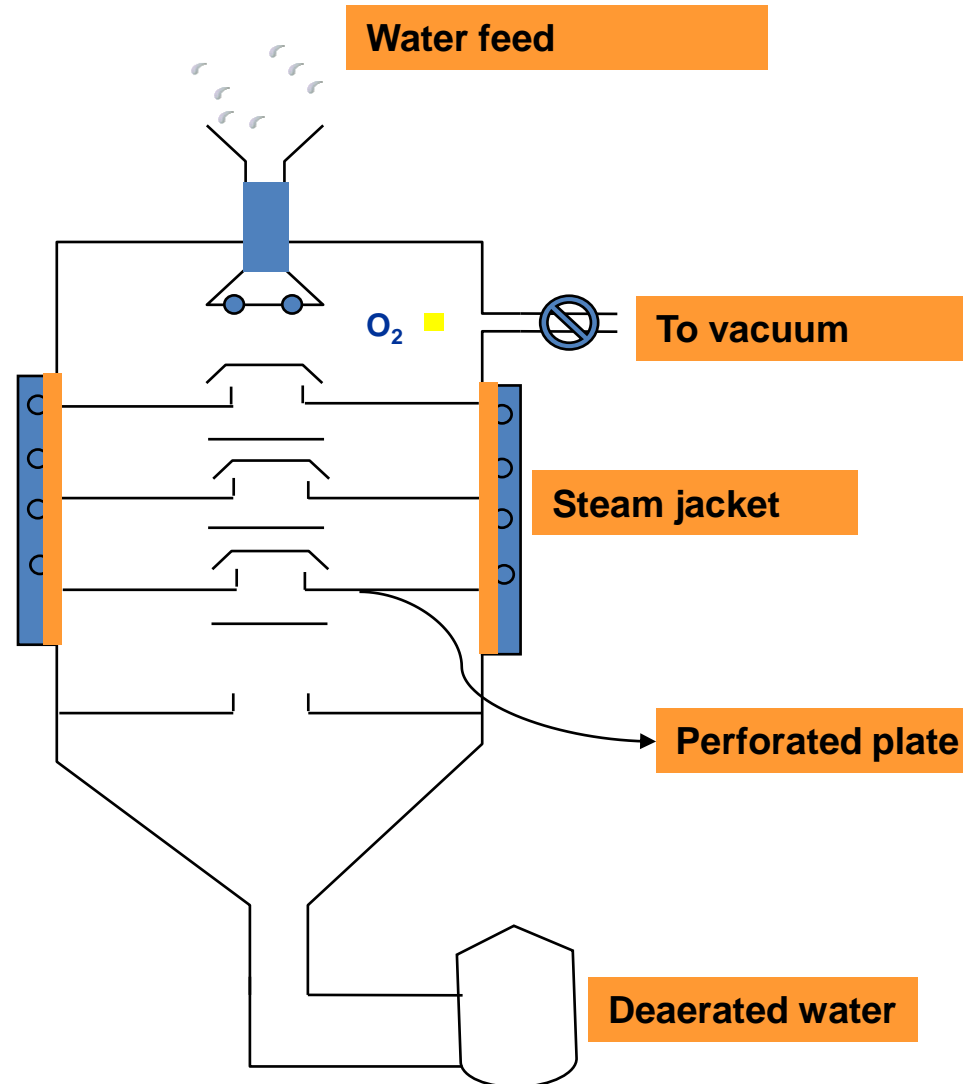
- DO can be removed by mechanical de-aeration also

Removal of DO – By mechanical deaeration

It comprises of a tall stainless tower with different layers capped with baffles to facilitate multiple equilibration.

The entire chamber is vacuumized and also maintained at high tempt using perforated heating plates on the walls.

Principle: High T and low P favors lower solubility of gases in water (Henry's and dalton's law)



4. Boiler corrosion:

b) Dissolved CO₂:

- Dissolved CO₂ forms carbonic acid which corrodes the boiler slowly.



- CO₂ is removed by adding calculated quantity of ammonia:



- It is also removed by mechanical de-aeration along with oxygen.

c) Acids from dissolved salts:

- Dissolved magnesium salts hydrolyse to form acids:



- This acid reacts with boiler and corrodes:



- Small quantity of magnesium salts will lead to large amount of boiler corrosion

Additional Information on Boiler troubles

Scale & Sludge Formation in Boilers

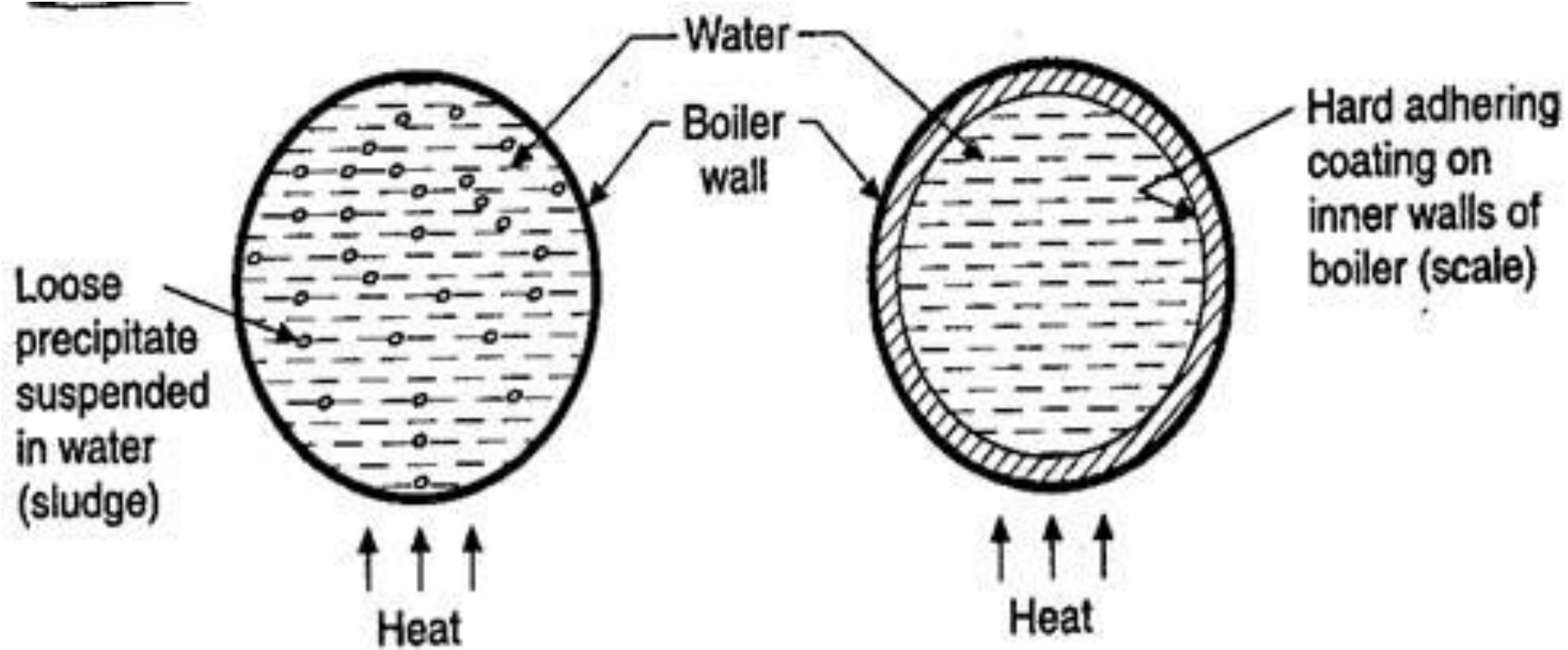
In boilers

– Concentration of the dissolved salts increases progressively when water evaporates during continuous steam generation. When their concentration reaches saturation point, the salts gets 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**



Sludge

Scale

Loose precipitate
suspended in water

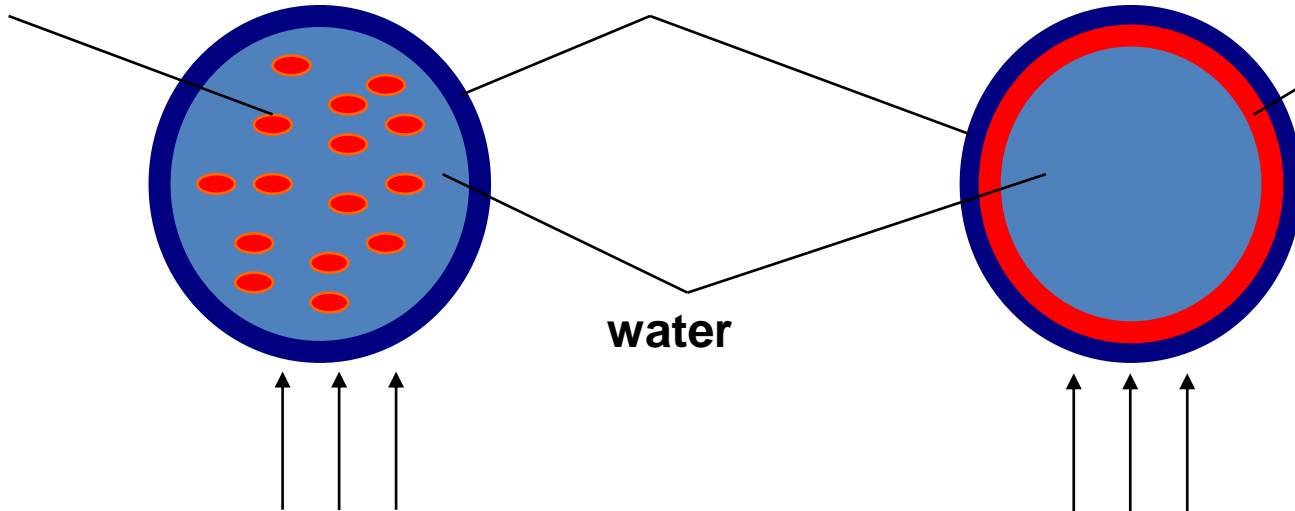
Boiler wall

scale

water

Heat

Heat



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 – MgCO_3 , MgCl_2 , CaCl_2 , 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**

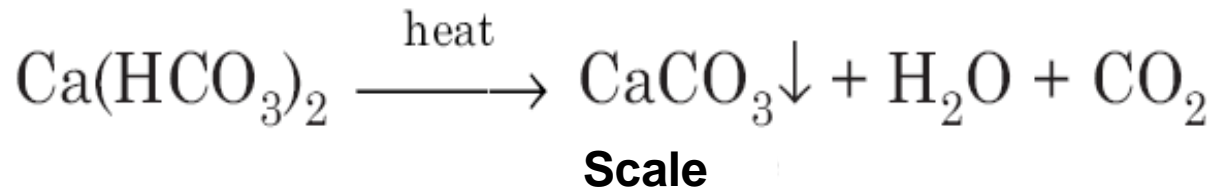
Prevention

- **By using soft water**
- **Frequent blow-down operation**

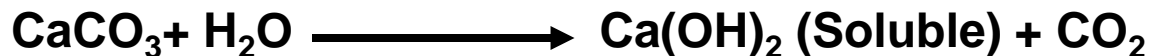
Formation of Scales

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**.



- But in **high-pressure boilers**, CaCO_3 is soluble.



Decomposition of calcium sulphate

- The solubility of calcium sulphate in water decreases with increase of temperature
- The solubility of CaSO_4 is 3,200 ppm at 15°C and it reduces to 55 ppm at 230°C and 27 ppm at 320°C
- 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 (CaSiO_3)** or **magnesium silicate (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:

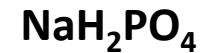
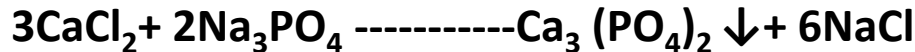
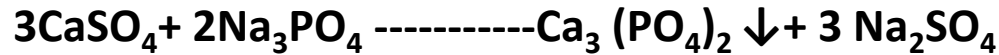
In low-pressure boilers, scale formation can be avoided by adding substances

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



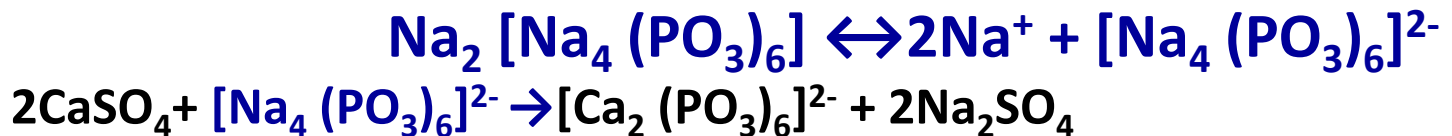
Carbonate Conditioning: Low-Pressure boilers

Sodium carbonate

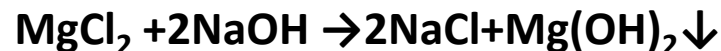
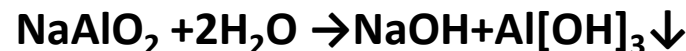


Calgon Conditioning:

Sodium hexa meta phosphate

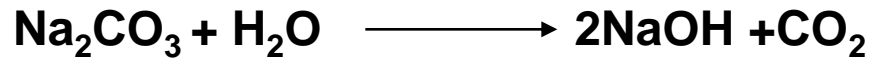


Treatment with sodium meta aluminate:



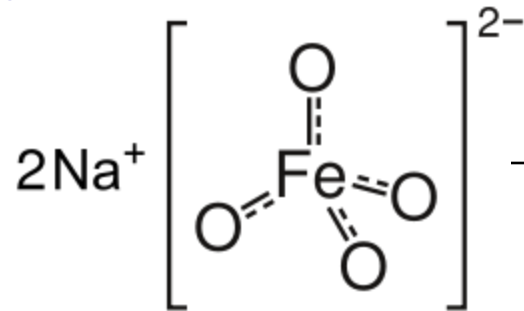
Caustic Embrittlement

- 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.)

+			
Iron at stressed parts	Conc. NaOH solution	Dil. NaOH solution	Iron at plane surfaces

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

$[\text{Na}_2\text{SO}_4]$	1:1	2:1	3:1
<hr/>			
$[\text{NaOH}]$	10 atm	20 atm	>20 atm

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**

Numerical Problems

Sample problems

1. 0.5 g of CaCO_3 was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample req. 15 ml EDTA and after boiling and filtering req. 10 ml of EDTA solution calculate the hardness.

1 ml of hard water contain 1 mg of CaCO_3

50 ml of hard water contain 50 mg of CaCO_3

50 ml of hard water consumes 48 ml of EDTA (V_1)

48 ml of EDTA	= 50 mg of CaCO_3 equivalent hardness
1 ml of EDTA	= 50 mg of CaCO_3 equivalent hardness
	= $\frac{50}{48}$ mg of CaCO_3 equivalent hardness

Calculation of total hardness:

50 ml of water sample consumes 15 ml of EDTA (V_2)

$$\text{Total Hardness} = (15/48) \times 1000 \times 1 \text{ mg of CaCO}_3$$

$$= 312.5 \text{ ppm}$$

Permanent hardness: (non – carbonate hardness)

50ml of water sample = 10 ml of EDTA (V_3)

$$\text{Permanent Hardness} = (10/48) \times 1000 \times 1 \text{ mg of CaCO}_3$$

$$= 208.4 \text{ ppm}$$

Temporary Hardness (1L) = Total hardness – Permanent hardness

$$= 312.5 - 208.4 = 104.1 \text{ ppm}$$

2. In an EDTA titration, 50 ml of standard hard (1mg CaCO_3 in 1ml) water sample consumed 25 ml of EDTA, 50 ml of hard water sample consumed 35 ml of EDTA and the 50ml sample hard water (after boiling, cooling and filtering) required 10ml EDTA . Calculate the permanent and temporary hardness of the given water sample.

1 mL std. hardwater = 1mg CaCO_3

50 mL std. hardwater = 25 mL EDTA (V_1)

Therefore, 1 mL EDTA = $(50/25) \times 1\text{mg } \text{CaCO}_3$

50 ml of hard water = 35 ml of EDTA (V_2)

1000 mL of hardwater contains = $(35/25) \times 1000 \times 1\text{mg } \text{CaCO}_3$

Total hardness = 1400 ppm

After boiling, EDTA consumed = 10 mL

50 mL of sample hardwater = 10 mL of EDTA (V_3)

1000 mL of hardwater after boiling contains = $(10/25) \times 1000 \times 1\text{mg } \text{CaCO}_3$

Permanent hardness = 400 ppm

Therefore, temp. hardness = $1400 - 400 = 1000$ ppm

3. Calculate Total, Temporary and Permanent hardness of the given hard water sample with following analysis report:-

[i] 50 mL of standard hard water sample consume 42 mL of EDTA solution.

[ii] 50 mL of hard water sample consume 19.9 mL of EDTA solution before boiling.

[iii] 50 mL of hard water sample consume 8.9 mL of EDTA solution after boiling.

Standard hard water is prepared by dissolving 1.5 gram of CaCO_3 per Litre.

Solution:

1mL of SHW contains 1.5mg of CaCO_3

[i] total hardness: 710.7 ppm

[ii] permanent hardness: 317.8 ppm

[iii] Temporary hardness: 392.9