Applied Chemistry

Hard Water Problems, Softening, and Water Treatment

1. Cause of Poor Lathering of Soap in Hard Water

Soap is chemically a sodium (or potassium) salt of long-chain fatty acids, such as sodium stearate. When soap is dissolved in soft water, it dissolves freely and produces an abundant, stable lather on shaking, since soft water contains little or no dissolved calcium or magnesium salts to interfere with this process.

However, when soap is added to hard water, the dissolved calcium and magnesium ions present in the water react with the soluble sodium (or potassium) soap to form insoluble calcium and magnesium salts of the fatty acids, commonly seen as a curdy, white precipitate known as scum. This reaction can be represented in general terms as:

- 2 $C_{17}H_{35}COONa$ (soap) + $CaCl_2$ (hardness salt) → $(C_{17}H_{35}COO)_2Ca$ (insoluble scum) + 2 NaCl

Since this reaction consumes the soap in forming an insoluble, useless precipitate rather than producing lather, a considerable quantity of soap must first be used up in reacting with all the dissolved calcium and magnesium ions present in the hard water before any of the soap becomes available to dissolve freely and produce actual lather. This is the fundamental reason why hard water lathers poorly with soap and results in the wastage of a significant amount of soap during washing.

2. Problems Caused by the Use of Hard Water in Boilers

The use of untreated hard water as boiler feed water leads to several serious operational problems, since the dissolved calcium and magnesium salts undergo various changes when the water is repeatedly heated, evaporated, and concentrated within the boiler. The major problems encountered are summarised below:

Problem	Cause	Effect
Scale Formation	Deposition of a hard, adherent layer of calcium and magnesium salts (mainly CaCO3 and CaSO4) on the inner walls of the boiler, formed when hard water is repeatedly heated and salts precipitate out gradually	Reduces the rate of heat transfer through the boiler walls, leading to overheating, wastage of fuel, and a risk of boiler wall failure or bursting due to localised overheating

Sludge Formation	Deposition of soft, loose, slimy precipitates (such as magnesium bicarbonate and magnesium chloride sediments) that settle at the comparatively cooler parts of the boiler, such as bends and joints	Reduces boiler efficiency, obstructs the free flow of water, and can settle along with scale, making the scale layer more difficult to remove
Foaming	Presence of dissolved impurities such as oils, greases, and finely suspended matter in the boiler water, which produce a persistent layer of small bubbles on the surface of the boiling water	Causes water to be carried along with the steam in the form of foam, reducing the efficiency of the boiler and disturbing the normal working of the steam space
Priming	Rapid and violent boiling caused by excessive salt concentration, sudden increase in steam production rate, or high water level in the boiler, causing tiny droplets of water to be carried along with the steam	Impure, wet steam is produced (carrying dissolved salts), which can damage turbine blades and reduce the efficiency of the steam system
Boiler Corrosion	Chemical attack on the inner metal surface of the boiler, caused mainly by dissolved oxygen, dissolved carbon dioxide, and acids (or acid-forming salts such as magnesium chloride, which hydrolyses to give hydrochloric acid) present in the boiler feed water	Gradual wearing away (corrosion) of the boiler material, weakening its structure, shortening the working life of the boiler, and creating leakage points

Because of these problems, it is essential to treat hard water and reduce its hardness to an acceptable level before it is used as feed water in boilers, in order to maintain boiler efficiency, prevent damage, and extend the working life of the boiler.

3. Quantitative Measurement of Water Hardness by the EDTA Method

The EDTA method is a widely used complexometric titration technique for the accurate quantitative estimation of the total hardness of a water sample. EDTA (ethylenediaminetetraacetic acid) is a chelating agent capable of forming stable, soluble complexes with metal ions, particularly calcium and magnesium ions, in a fixed one-to-one molar ratio.

In this method, a measured volume of the water sample is buffered to a specific pH (usually around pH 10), and a small amount of an indicator, commonly Eriochrome Black T, is added, which forms a wine-red coloured complex with any free calcium and magnesium ions present in the water. The water sample is then titrated with a standard solution of EDTA, added slowly from a burette.

As EDTA is added, it progressively forms more stable complexes with the free calcium and magnesium ions in the solution, gradually displacing them from their loosely bound complex with the indicator. At the endpoint of the titration, essentially all the free calcium and magnesium ions have been complexed by the EDTA, and the indicator, now uncomplexed, reverts to its original colour (typically a distinct blue), signalling that the titration is complete.

From the volume of standard EDTA solution used to reach this endpoint, and knowing the concentration of the EDTA solution, the total concentration of calcium and magnesium ions in the water sample can be calculated and conveniently expressed as an equivalent hardness in terms of calcium carbonate ($CaCO_3$), typically reported in ppm or mg/L.

4. Total Dissolved Solids (TDS) and Alkalinity Estimation

4.1 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) refers to the total concentration of all dissolved inorganic and organic substances present in a water sample, including dissolved salts, minerals, and other soluble matter, but excluding suspended (undissolved) particles. TDS is generally determined by evaporating a known volume of filtered water sample to dryness and weighing the residue left behind, then expressing this mass per unit volume of the original sample, usually in mg/L.

TDS is an important indicator of the overall mineral content and general quality of water, and high TDS values are often associated with hard water, brackish water, or water contaminated by industrial or agricultural runoff, affecting its taste, suitability for drinking, and suitability for use in boilers and industrial processes.

4.2 Alkalinity Estimation

Alkalinity of water refers to its capacity to neutralise acids, and is a measure of the total concentration of bases present in the water, mainly bicarbonates, carbonates, and, occasionally, hydroxides of calcium, magnesium, sodium, and potassium. Alkalinity is generally determined by titrating a known volume of the water sample against a standard acid solution (such as dilute sulphuric acid or hydrochloric acid), using suitable indicators, phenolphthalein (to detect the endpoint corresponding to the neutralisation of hydroxide and carbonate alkalinity) and methyl orange (to detect the endpoint corresponding to the neutralisation of the remaining carbonate and bicarbonate alkalinity).

The results of this titration allow the different forms of alkalinity (hydroxide, carbonate, and bicarbonate) present in the water sample to be estimated separately, which is important information for water treatment processes, since alkalinity affects the tendency of water to form scale, its corrosiveness, and the effectiveness of various treatment and softening methods.

5. Water Softening Techniques

Water softening refers to the process of removing, or substantially reducing, the dissolved calcium and magnesium salts responsible for hardness in water, making it more suitable for domestic use, washing, and industrial applications such as boiler feed water. Several established methods are used for softening hard water, described below.

Method	Basic Principle
Soda-Lime Process	Hard water is treated with a calculated mixture of soda ash (sodium carbonate, Na_2CO_3) and lime [calcium hydroxide, $Ca(OH)_2$], which react with the dissolved calcium and magnesium salts present in the hard water, converting them into insoluble calcium carbonate and magnesium hydroxide, which are then removed by sedimentation and filtration.
Zeolite (Permutit) Process	Hard water is passed through a bed of zeolite (a hydrated sodium aluminium silicate, also called permutit), which exchanges its sodium ions for the calcium and magnesium ions present in the hard water, effectively removing the ions responsible for hardness and replacing them with sodium ions, which do not cause hardness.
Ion Exchange Process	Hard water is passed successively through a cation exchange resin (which exchanges hydrogen ions for calcium and magnesium ions) and an anion exchange resin (which exchanges hydroxide ions for the negatively charged anions present, such as chloride, sulphate, and bicarbonate), producing water essentially free from all dissolved ionic impurities, called demineralised (or deionised) water.

Among these methods, the ion exchange process is generally regarded as the most effective and versatile, since it can produce water of very high purity (demineralised water), essentially free from all dissolved ionic impurities, making it particularly suitable for use in high-pressure boilers and sensitive industrial processes where even very low levels of dissolved salts cannot be tolerated.

6. Municipal Water Treatment (In Brief)

Municipal water treatment refers to the series of processes carried out at a water treatment plant to convert raw water obtained from natural sources (such as rivers, lakes, or reservoirs) into water that is safe, clear, and suitable for public drinking water supply. The process typically involves the following main stages, carried out in sequence:

Stage	Purpose
Sedimentation	Raw water is allowed to stand undisturbed in large settling tanks so that heavier suspended particles settle down under gravity to the bottom of the tank, reducing the load of suspended matter carried forward to later stages.
Coagulation	A coagulant (such as alum, i.e. aluminium sulphate) is added to the water, which causes very fine, colloidal suspended particles (too small to settle by sedimentation alone) to clump together into larger particles called flocs, which then settle more readily.
Filtration	Water is passed through beds of fine sand and gravel (a sand filter), which physically trap and remove any remaining fine suspended particles, as well as a significant portion of microorganisms, producing clear, filtered water.
Sterilization (Disinfection)	The filtered water is treated with a disinfecting agent (commonly chlorine, or occasionally ozone or ultraviolet radiation) to kill any remaining disease-causing microorganisms (pathogens), making the water microbiologically safe for drinking.

These four stages, carried out together in a properly designed water treatment plant, ensure that the water finally supplied to the public is free from suspended impurities, clear in appearance, and microbiologically safe for drinking, meeting the required standards of water quality.

7. Multiple Choice Questions (MCQs)

Answer the following questions by selecting the most appropriate option.

1. Hard water lathers poorly with soap mainly because:

A) Hard water has a higher density than soft water

B) Calcium and magnesium ions in hard water react with soap to form an insoluble scum

C) Hard water contains no dissolved salts

D) Soap does not dissolve in water at all

2. Scale formation in a boiler is caused by:

A) Deposition of loose, slimy precipitates

B) Deposition of a hard, adherent layer of calcium and magnesium salts on the boiler walls

C) Excessive foaming of the boiler water

D) Corrosion of the boiler metal

3. Sludge in a boiler differs from scale mainly in that sludge is:

A) Hard and firmly adherent to the boiler walls

B) Soft, loose, and deposited mainly at cooler parts of the boiler

C) Never formed in hard water

D) Formed only from dissolved gases

4. Priming in a boiler refers to:

A) The gradual corrosion of the boiler shell

B) Carrying over of tiny water droplets along with steam due to violent boiling

C) The formation of a hard scale layer

D) The addition of chemicals to soften water

5. Foaming in a boiler is generally caused by the presence of:

A) Dissolved oxygen only

B) Oils, greases, and finely suspended impurities in the boiler water

C) Excess steam pressure only

D) Very pure, mineral-free water

6. Boiler corrosion is mainly caused by the presence of:

A) Dissolved oxygen, carbon dioxide, and acid-forming salts in the feed water

B) Excess sodium chloride only

C) Complete absence of dissolved gases

D) Presence of zeolite in the water

7. The EDTA method of measuring water hardness is an example of:

A) Gravimetric analysis

B) Complexometric titration

C) Acid-base titration

D) Redox titration

8. In the EDTA method, the indicator commonly used to detect the endpoint is:

A) Phenolphthalein

B) Methyl orange

C) Eriochrome Black T

D) Litmus

9. Total dissolved solids (TDS) in water refers to:

A) The total amount of suspended matter only
B) The total concentration of all dissolved inorganic and organic substances in water
C) Only the hardness-causing salts in water
D) Only the dissolved gases in water

10. Alkalinity of water is a measure of its capacity to:

A) Neutralise acids
B) Neutralise bases
C) Form scale in a boiler
D) Conduct electricity

11. In the soda-lime process of water softening, hardness-causing salts are converted into:

A) Soluble sodium salts
B) Insoluble calcium carbonate and magnesium hydroxide
C) Dissolved carbon dioxide
D) Sodium bicarbonate only

12. In the zeolite process, hardness-causing calcium and magnesium ions are exchanged for:

A) Hydrogen ions
B) Sodium ions
C) Chloride ions
D) Hydroxide ions

13. Water obtained after passing through both cation and anion exchange resins in the ion exchange process is called:

A) Hard water
B) Chlorinated water
C) Demineralised (deionised) water
D) Saline water

14. In municipal water treatment, the addition of alum to remove fine colloidal impurities is called:

A) Sedimentation
B) Coagulation
C) Filtration
D) Sterilization

15. Chlorination of water in municipal water treatment is carried out mainly to:

A) Remove suspended particles
B) Kill disease-causing microorganisms
C) Remove dissolved salts
D) Reduce the hardness of water

Answer Key

1. B) Calcium and magnesium ions in hard water react with soap to form an insoluble scum | 2. B) Deposition of a hard, adherent layer of calcium and magnesium salts on the boiler walls | 3. B) Soft, loose, and deposited mainly at cooler parts of the boiler | 4. B) Carrying over of tiny water droplets along with steam due to violent boiling | 5. B) Oils, greases, and finely suspended impurities in the boiler water | 6. A) Dissolved oxygen, carbon dioxide, and acid-forming salts in the feed water | 7. B) Complexometric titration | 8. C) Eriochrome Black T | 9. B) The total concentration of all dissolved inorganic and organic substances in water | 10. A) Neutralise acids | 11. B) Insoluble calcium carbonate and magnesium hydroxide | 12. B) Sodium ions | 13. C) Demineralised (deionised) water | 14. B) Coagulation | 15. B) Kill disease-causing microorganisms

8. Broad / Long Answer Questions

1. Explain why hard water lathers poorly with soap, referring to the chemical reaction that takes place.

2. Explain the problems of scale and sludge formation in a boiler, distinguishing clearly between the two.

3. Explain the problems of foaming and priming in a boiler, and state their effects on the working of the boiler.

4. Explain the causes and effects of boiler corrosion when hard or untreated water is used as boiler feed water.

5. Describe the principle of the EDTA method for the quantitative estimation of water hardness.

6. Explain the terms total dissolved solids (TDS) and alkalinity of water, and state their significance in water quality assessment.

7. Describe the soda-lime process of water softening, explaining the chemical basis of the method.

8. Describe the zeolite (permutit) process of water softening, explaining how hardness-causing ions are removed.

9. Describe the ion exchange process of water softening, and explain how it differs from the zeolite process in the quality of water produced.

10. Describe, in brief, the four main stages of municipal water treatment — sedimentation, coagulation, filtration, and sterilization — explaining the purpose of each stage.