

Sanjivani University

Applied Science

Unit-3

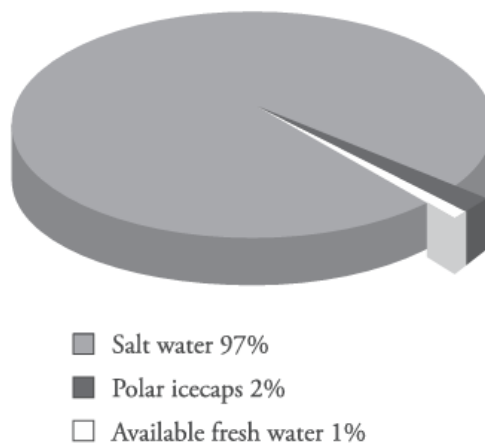
Water Technology

(24UETBS102)

Introduction:

Water is the most precious, wonderful and useful gift of nature. It is the most abundant and essential natural resource. It covers nearly 70% of the earth's surface. It is estimated that the hydrosphere contains about 1360 million cubic kilometer ($1.3 \times 10^{18} \text{ m}^3$) of water. Of this, about 97% is in the oceans and inland seas, which is not suitable for human consumption because of its high salt content. Of the remaining 3%, 2% is locked in the glaciers and polar ice caps and only 1% is available as fresh water in rivers, lakes, streams, reservoirs and ground water, which is suitable for human consumption.

Water on Earth



Sources of water:

The chief sources of water are

1. Surface water
2. Ground water
3. Rain water

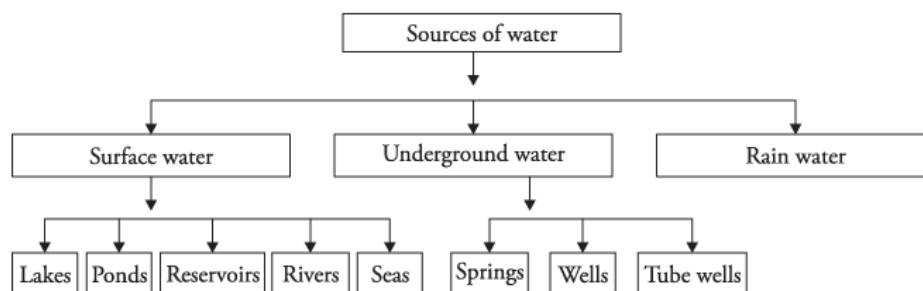
- (1) **Surface water sources** These include lakes, ponds, reservoirs, streams, rivers, seas and oceans.

River water It contains dissolved minerals of the soils such as chlorides, sulphates and bicarbonates of sodium, calcium, magnesium and iron. It also contains organic matter derived from dead and decayed plants and animals; besides this, it contains sand and soil in suspension.

Water of lakes, ponds and reservoirs They contain less of dissolved minerals but are rich in organic matter.

Sea water It is the most impure form of natural water. It contains on an average 3.5% of dissolved salts, of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

- (2) **Underground water sources** This is the water accumulated under the ground through seepage. It is obtained from wells, tube wells, springs, etc. Underground water is relatively free from suspended impurities because it is filtered as the water moves down through different layers of soil. The filtration also removes biological contamination. However, underground water is rich in dissolved salts.
- (3) **Rain water** It is considered to be the purest form of water. However, it dissolves large amount of gases and suspended solid particles from the atmosphere. Rain water is divided between the two sources, a part of it seeps down to underground water tables and a part of it goes to the surface sources like rivers, ponds, lakes and reservoirs.

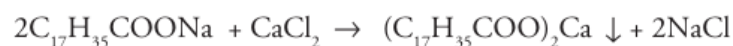


Hardness of water:

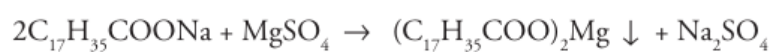
Definition It is defined as the characteristic of water that prevents lathering of soap. Originally, it was defined as the soap-consuming capacity of water.

Causes Hardness is due to the presence of certain soluble salts of calcium and magnesium in water. A sample of hard water, when treated with soap (sodium or potassium salts of higher fatty acids like oleic, palmitic or stearic acid), does not form lather or foam but forms a white precipitate or scum instead. This is because of the formation of insoluble salts of calcium and magnesium.

Chemical reactions involved are



Soap (Sodium stearate) (from hard water) Calcium stearate (Insoluble)



Soap (from hard water) Magnesium stearate (Insoluble)

Other salts of calcium and magnesium like CaSO_4 , $\text{Ca}(\text{NO}_3)_2$ and MgCl_2 also react in a similar way forming insoluble precipitates of calcium and magnesium salts of higher fatty acids.

Table 2.3 Difference between hard and soft water

S.No	Hard water	Soft water
1	Water that does not form lather with soap but forms white precipitate	Water that produces lather or foam easily with soap is called 'soft water'
2	It contains soluble salts of calcium magnesium and other heavy metal ions like Al^{3+} , Fe^{3+} , and Mn^{2+} dissolved in it	It does not contain dissolved salts of calcium and magnesium
3	In hard water, the cleaning properties of soap is depressed and lot of soap is wasted in bathing and washing	The cleaning quality of soap is not depressed hence it is good for washing and cleaning
4	Owing to dissolved hardness, boiling point of water is elevated, therefore more fuel and time is required for cooking	Less fuel and time is required for cooking

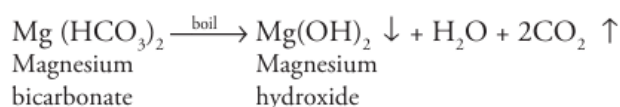
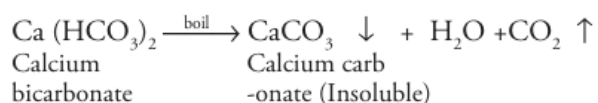
Types of hardness

Hardness is of two types:

1. Temporary hardness
2. Permanent hardness

(1) Temporary hardness

- (a) It is also called carbonate hardness or alkaline hardness. It is called alkaline hardness because it is due to the presence of bicarbonate, carbonate and hydroxide and can be determined by titration with HCl using methyl orange as an indicator.
- (b) It can be removed by boiling of water. During boiling, the bicarbonates are decomposed forming insoluble carbonates or hydroxides that are deposited at the bottom of the vessel.



(2) Permanent hardness

- (a) It is also called non-carbonate or non-alkaline hardness.
- (b) It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals.
- (c) Salts mainly responsible for permanent hardness are
CaCl₂, CaSO₄, MgCl₂, MgSO₄, Ca (NO₃)₂, etc.
- (d) It cannot be removed by simple boiling but can be removed by special chemical methods like lime–soda process, zeolite method, etc.

Table 2.4 Comparison between temporary and permanent hardness

S.No	Temporary hardness	Permanent hardness
1	Also called carbonate hardness or alkaline hardness	Also called non-carbonate or non-alkaline hardness
2	It is due to the presence of bicarbonates, carbonates of calcium and magnesium	It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals
3	It can be removed by boiling $\text{Ca(HCO}_3)_2 \xrightarrow{\text{boil}} \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ $\text{Mg (HCO}_3)_2 \xrightarrow{\text{boil}} \text{Mg(OH)}_2 \downarrow + \text{H}_2\text{O} + 2\text{CO}_2 \uparrow$	Cannot be removed by simple boiling but can be removed by specific chemical methods, like lime–soda process, zeolite method, etc.

Degree of hardness

Hardness is always calculated in terms of equivalent of CaCO_3 , although hardness is never present in the form of CaCO_3 . There are two basic reasons for choosing CaCO_3 as standard:

- (i) Calculations become easy as its molecular weight is exactly 100 (and equivalent weight is exactly 50).
- (ii) It is the most insoluble salt that can be precipitated in water treatment.

Calculation of equivalents of CaCO_3

To find out hardness in a given water sample, it is essential to convert hardness due to different salts (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4 , MgCl_2 , MgSO_4 , etc.) in terms of equivalent of CaCO_3 . This can be done by the formula:

$$\text{Equivalent of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

- Chemical equivalent of CaCO_3 is 50
- Chemical equivalent of salt = $\frac{\text{Molecular weight}}{\text{Valency}}$
- Chemical equivalent of acid = $\frac{\text{Molecular weight}}{\text{Basicity}}$

Basicity is the number of replaceable hydrogen ions in an acid.

- Chemical equivalent of base = $\frac{\text{Molecular weight}}{\text{Acidity}}$

Acidity is the number of replaceable hydroxyl ions in a base.

The ratio = $\frac{\text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$, is constant for a particular compound and is called multiplication factor.

Hence, equivalent of CaCO_3 = mass of hardness producing substance \times multiplication factor.

Solved Examples

1. A water sample contains 248 mg CaSO_4 per liter. Calculate the hardness in terms of CaCO_3 equivalent.

Solution

Weight of CaSO_4 per liter = 248 mg

Hardness in terms of CaCO_3 equivalent = ?

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

$$\frac{248 \times 100 / 2}{136 / 2} = 182.35 \text{ ppm.}$$

2. How many grams of FeSO_4 dissolved per liter gives 300 ppm of hardness?

(Fe = 56, S = 32, O = 16, Ca = 40, C = 12)

Solution

1 mole of FeSO_4 causes hardness equivalent to that caused by 1 mole of CaCO_3 because 1 mole of any two substances contain equal number of molecules, that is, Avogadro's number of molecules.

$$\therefore 1 \text{ mole } \text{FeSO}_4 = 1 \text{ mole of } \text{CaCO}_3$$

$$\text{or, } 56 + 32 + 64 = 152 \text{ g of } \text{FeSO}_4 = 40 + 12 + 48 = 100 \text{ g of } \text{CaCO}_3$$

$$\therefore 100 \text{ ppm of } \text{CaCO}_3 \text{ equivalent hardness is caused by } 152 \text{ ppm of } \text{FeSO}_4 \text{ or,}$$

$$300 \text{ ppm of hardness will be caused by } \frac{152}{100} \times 300 = 456 \text{ ppm of } \text{FeSO}_4 = 456 \text{ mg/L} = 0.456 \text{ g/L of } \text{FeSO}_4$$

[Ans = 0.456 g/L]

Alternative method

Calculation by direct application of formula

$$\text{Equivalents of CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

Let mass of hardness producing substance, that is, $\text{FeSO}_4 = x \text{ mg}$

$$\text{Then } 300 = \frac{x \times 100 / 2}{152 / 2}$$

$$\text{or } 300 = \frac{x \times 100}{152} = 456 \text{ ppm} = 456 \text{ mg/L} = 0.456 \text{ g/L}$$

Units of hardness and their interrelationship

(i) **Parts per million (ppm)** It is defined as the number of parts by weight of CaCO_3 equivalent hardness present in million (10^6) parts by weight of water.

1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

(ii) **Milligrams per liter (mg/L)** It is defined as the number of milligrams of CaCO_3 equivalent hardness present per liter of water.

1 mg/L = 1 mg of CaCO_3 equivalent hardness in one liter of water

Since weight of 1 liter of water = 1 kg

$$= 1000 \text{ g} = 1000 \times 1000 = 10^6 \text{ mg}$$

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

= 1 part of CaCO_3 per 10^6 parts of water.

= 1 ppm.

Thus mathematically, 1 ppm = 1 mg/L.

- (iii) **Degree Clarke ($^{\circ}\text{Cl}$)** It is defined as the number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water.

$1^{\circ}\text{Clarke} = 1 \text{ grain of } \text{CaCO}_3 \text{ equivalent hardness per gallon of water}$

$\therefore 1 \text{ grain} = 1/7000 \text{ lb (pounds)}$

And 1 gallon = 10 lb

$1 \text{ grain/gallon} = 1/7000 \text{ lb/10 lb}$

$= 1: 70,000$

1°Cl can also be defined as the number of parts of CaCO_3 equivalent hardness per 70,000 parts of water.

- (iv) **Degree French ($^{\circ}\text{Fr}$)** It is defined as the number of parts of CaCO_3 equivalent hardness per 10^5 parts of water. Thus,

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

Relationship between different units of hardness As,

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

$1 \text{ mg/L} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ parts of water.}$

$1^{\circ}\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 70000 \text{ parts of water.}$

$1^{\circ}\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^5 \text{ parts of water.}$

Hence,

$$10^6 \text{ ppm} = 10^6 \text{ mg/L} = 70,000^{\circ}\text{Cl} = 10^5^{\circ}\text{Fr}$$

Dividing by 10^6

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.07^{\circ}\text{Cl} = 0.1^{\circ}\text{Fr}$$

Similarly,

$$1^{\circ}\text{Cl} = 1.433^{\circ}\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/L}$$

$$1^{\circ}\text{Fr} = 10 \text{ ppm} = 10 \text{ mg/L} = 0.7^{\circ}\text{Cl}$$

Solved Examples

1. Three samples P, Q and R were analysed for their salt contents.
 - (i) Sample P was found to contain 155 mg of magnesium carbonate per liter.
 - (ii) Sample Q was found to contain 800 mg of calcium nitrate and 2.5 mg of silica and 5.1 mg of sodium chloride per liter.
 - (iii) Sample R was found to contain 15 g of potassium nitrate and 3 g of calcium carbonate per liter. Find the hardness of all the above three samples in ppm and in grains per gallon.

Solution

Sample	Constituent	Amount mg/L	Equivalents of CaCO_3
P	MgCO_3	155 mg/L	$\frac{155 \times 100 / 2}{84 / 2} = 184.52 \text{ mg/L}$
Q	$\text{Ca}(\text{NO}_3)_2$	800 mg/L	$\frac{800 \times 100 / 2}{164 / 2} = 487.80 \text{ mg/L}$
R	CaCO_3	3 g/L or 3000 mg/L	$\frac{3000 \times 100 / 2}{100 / 2} = 3000 \text{ mg/L}$

∴ Hardness of the three samples in ppm

Sample P = 184.52 ppm; Sample Q = 487.80 ppm; Sample R = 3000 ppm.

Hardness of the three samples in grains/gallon or degree Clarke

Since 1 ppm = 0.07 °Cl = 0.07 grains/gallon

Sample P = 184.52 ppm × 0.07 = 12.91 grains/gallon

Sample Q = 487.80 ppm × 0.07 = 34.146 grains/gallon

Sample R = 3000 ppm × 0.07 = 210 grains/gallon.

2. A sample of water on analysis was found to contain $\text{Ca}(\text{HCO}_3)_2 = 4 \text{ mg/L}$; $\text{Mg}(\text{HCO}_3)_2 = 6 \text{ mg/L}$; $\text{CaSO}_4 = 8 \text{ mg/L}$; $\text{MgSO}_4 = 10 \text{ mg/L}$. Calculate the temporary, permanent and total hardness of water in ppm, °Fr and °Cl [Mol wt of $\text{Ca}(\text{HCO}_3)_2 = 162$, $\text{Mg}(\text{HCO}_3)_2 = 146$; $\text{CaSO}_4 = 136$; $\text{MgSO}_4 = 120$].

Solution

Conversion into CaCO_3 equivalent

Constituent	Amount	Equivalent of CaCO_3
$\text{Ca}(\text{HCO}_3)_2$	4 mg/L	$\frac{4 \times 100 / 2}{162 / 2} = 2.469 \text{ mg/L}$
$\text{Mg}(\text{HCO}_3)_2$	6 mg/L	$\frac{6 \times 100 / 2}{146 / 2} = 4.110 \text{ mg/L}$
CaSO_4	8 mg/L	$\frac{8 \times 100 / 2}{136 / 2} = 5.882 \text{ mg/L}$
MgSO_4	10 mg/L	$\frac{10 \times 100 / 2}{120 / 2} = 8.333 \text{ mg/L}$

Temporary hardness is due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.

Hence, temporary hardness = 2.469 + 4.110
= 6.579 mg/L or 6.579 ppm

Since 1 mg/L = 1 ppm = 0.07 °Cl = 0.1 °Fr

= 6.579 × 0.1 °Fr = 0.6579 °Fr

= 6.579 × 0.07 °Cl = 0.4605 °Cl

Permanent hardness is due to salts of CaSO_4 and MgSO_4 , Hence

Permanent hardness = 5.882 + 8.333 = 14.215 mg/L = 14.215 ppm

= 14.215 × 0.1 = 1.42150 °Fr

= 14.215 × 0.07 = 0.995 °Cl

Total hardness = Temporary hardness + Permanent hardness

= 6.579 + 14.215 = 20.794 mg/L = 20.794 ppm

= 20.794 × 0.1 = 2.0794 °Fr

= 20.794 × 0.07 = 1.4555 °Cl

Practice Problems

1. A water sample contains $\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg/L}$, $\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ mg/L}$, $\text{CaSO}_4 = 13.5 \text{ mg/L}$. Calculate the temporary and permanent hardness of water.
[Ans Temporary hardness = $20 + 20 = 40 \text{ ppm}$; permanent hardness = 9.926 ppm]
2. A sample of water on analysis gives the following data:
 $\text{Ca}(\text{HCO}_3)_2 = 24.1^\circ\text{French}$; $\text{CaSO}_4 = 3.2^\circ\text{French}$; $\text{MgCl}_2 = 9.5^\circ\text{French}$
 $\text{SiO}_2 = 2.1^\circ\text{French}$; $\text{MgSO}_4 = 8.2^\circ\text{French}$
Calculate the temporary and permanent hardness on $^\circ\text{Clarke}$ and ppm scale.
[Ans Temporary hardness = $14.88^\circ\text{French} = 10.41^\circ\text{Clarke} = 148.88 \text{ ppm}$;
permanent hardness = $19.18^\circ\text{Fr} = 13.426^\circ\text{Cl} = 191.8 \text{ ppm}$]
3. A sample of water on analysis has been found to contain the following impurities
 $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg/L}$; $\text{Mg}(\text{NO}_3)_2 = 44.4 \text{ mg/L}$; $\text{MgSO}_4 = 36 \text{ mg/L}$;
 $\text{MgCl}_2 = 19.0 \text{ mg/L}$ and $\text{CaCO}_3 = 30 \text{ mg/L}$.
Calculate the temporary and permanent hardness in ppm and $^\circ\text{Clarke}$.
[Ans Temporary hardness = 40 ppm and 2.8°Clarke ;
permanent hardness = 80 ppm and 5.6°Clarke]

Disadvantage of using hard water for domestic use:

In domestic usage

- (a) *Drinking* Taste of soft water is better than hard water. The dissolved calcium in hard water can help to produce strong teeth and healthy bones in children. However, hard water can have bad affect on our appetite and digestive system; sometimes it produces calcium oxalate that causes different urinary problems.
- (b) *Cooking* The boiling point of hard water increases because of the presence of various salts; this causes wastage of time and fuel.
- (c) *Bathing and washing* As hard water does not form lather or foam with water, it adversely affects the cleaning properties of soap and a lot of it is wasted because of production of sticky precipitates of calcium and magnesium. The production of sticky precipitate continues till all the calcium and magnesium salts present in water are precipitated, after which the soap starts giving lather with water.

Moreover, the sticky precipitate adheres on the cloths giving stains, streaks and spots.

Disadvantage of using hard water for industrial use:

(1) *In Industries*

Large quantities of water is used for steam generation in industries like textile, paper, sugar, dyeing, pharmaceutical, etc.

- (a) *Steam generation in boilers* The use of hard water in boilers causes problems like scale and sludge formation, boiler corrosion, caustic embrittlement,

- (b) *Sugar industries* Salts dissolved in hard water cause problems in crystallisation of sugar.
- (c) *Paper industries* The cations (Ca^{2+} , Mg^{2+} , Fe^{2+} etc) present in hard water react with the chemicals involved in different steps of paper manufacturing. This produces various unwanted side products and undesirable effects like loss of gloss and smoothness, change in color of paper, etc.
- (d) *Textile industries* During washing of the fabric or yarn with hard water the calcium and magnesium salts stick to the surface causing undesirable changes in color or texture of fabric.
- (e) *Dyeing industries* The salts dissolved in hard water react with the functional groups present in the dyes causing precipitation or change in shade.
- (f) *Pharmaceutical industry* Use of hard water in the preparation of drugs can lead to the production of undesirable products that may be harmful or even poisonous.

Boiler problems with hard water:

Boiler feed water should correspond with the following composition

- (i) Its hardness should be below 0.2 ppm
- (ii) Its caustic alkalinity (due to OH^-) should lie in between 0.15 and 0.45 ppm
- (iii) Its soda alkalinity (due to Na_2CO_3) should be 0.45–1 ppm

Excess of impurities, if present, in boiler feed water generally cause the following problems

- (i) Scale and sludge formation
- (ii) Boiler corrosion
- (iii) Caustic embrittlement

Scale and sludge formation

Water evaporates continuously inside the boiler and the concentration of dissolved salts increases gradually. When the solution is saturated with respect to the salt concentration, the salts start precipitating out on the inner walls of the boiler. If the precipitate formed is soft, slimy and loose, it is called *sludge* and if the precipitate formed is hard and adhering on the inner walls of the boiler it is termed as *scale*.

SLUDGE

Definition It is soft, slimy and loose precipitate formed on the inner walls of the boiler.

Formation

- (a) Sludges are formed by substances which have greater solubility in hot water than in cold water like MgSO_4 , MgCl_2 , MgCO_3 , CaCl_2 etc.
- (b) They are formed at colder parts of the boiler and get collected at places where the flow rate is slow or at bends, plug opening, glass gauge connection, thereby causing even choking of the pipes.
- (c) They are poor conductors of heat.
- (d) They can be removed easily by scraping off with wire brush.

Prevention

- (i) By using softened water.
- (ii) By frequently 'blow-down operation', that is, drawing off a portion of the concentrated water from the boiler and replacing it with fresh water.

Disadvantages of sludge formation

- (i) Being poor conductors of heat they tend to waste a portion of heat generated and thus decreases the efficiency of the boiler.
- (ii) Excessive sludge formation disturbs working of the boiler.
- (iii) When formed along with scale, they get entrapped in scale and both get deposited as scales.
- (iv) It settles in regions of poor water circulation such as pipe connection, plug opening, and glass gauge connection thereby choking the pipes.

SCALE

Definition They are deposits firmly sticking to the inner surface of the boiler which cannot be removed mechanically even with the help of hammer and chisel.

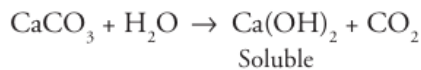
Formation of scale Scales are formed mainly due to four reasons:

(i) **Decomposition of calcium bicarbonate**



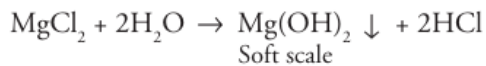
CaCO_3 scale is soft and it is the main cause of scale formation in low- pressure boilers

However in higher pressure boilers CaCO_3 is soluble due to the formation of Ca(OH)_2



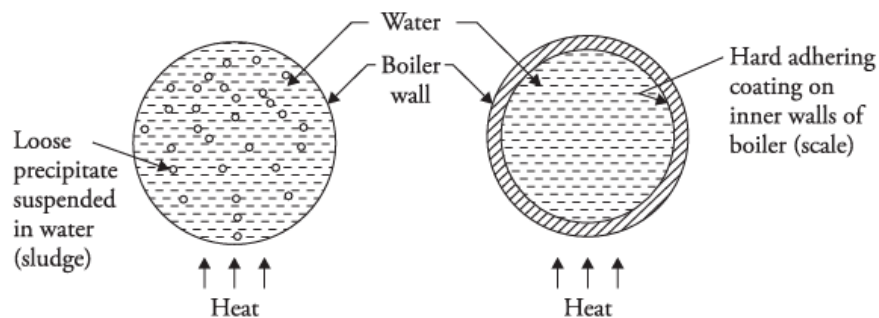
(ii) **Deposition of CaSO_4** The solubility of CaSO_4 decreases as temperature increases. CaSO_4 is soluble in cold water and is completely insoluble in superheated water. Therefore, CaSO_4 gets precipitated as hard scale on the hot portion of the boiler.

(iii) **Hydrolysis of magnesium salts** At high temperature, dissolved magnesium salts undergo hydrolysis forming a soft scale of magnesium hydroxide.



(iv) **Formation of calcium and magnesium silicates**

Very small quantities of SiO_2 present in hard water react with calcium and magnesium forming calcium silicate (CaSiO_3) and/or magnesium silicate (MgSiO_3). These are hard scales and are extremely difficult to remove.



S.No	Sludge	Scale
1	Sludges are soft, loose and slimy precipitates	Scale are hard deposits
2	Formed at comparatively colder portions of the boiler	Formed generally at heated portion of the boiler
3	Formed by carbonate, bicarbonates of calcium and magnesium along with $Mg(OH)_2$	Formed by substances like $CaSO_4$ and silicates of calcium and magnesium
4	They are non-adherent deposits and can be easily removed	They stick very firmly to the inner surface of the boiler and are very difficult to remove
5	Decrease efficiency of boiler but are less dangerous	Decreases the efficiency of boiler and can even lead to boiler explosion
6	Can be removed by blow-down operation	Cannot be removed by blow-down operation

Disadvantages of scale formation

1. **Wastage of fuel** Scales have poor thermal conductivity, therefore the rate of heat transfer from boiler to the water inside is greatly reduced. Hence extra heat is to be supplied to the boiler and this increases the fuel consumption.

Wastage of fuel depends upon the thickness of the scale. Greater the thickness of the scale larger is the wastage of fuel.

2. **Lowering boiler safety** Due to scale formation which is poor conductor of heat, the boiler is to be over heated to provide steady supply of heat. Overheating makes the boiler material softer and weaker. Therefore distortion of boiler tubes takes place and the boiler becomes unsafe to bear the pressure of the steam (in high-pressure boilers).
3. **Decrease in efficiency** Deposition of scale in the valves and condensers of the boiler, chokes them partially. This results in decrease in efficiency.
4. **Danger of explosion** Due to uneven expansion the thick scales crack, as a result water comes in contact with the overheated inner walls of the boiler resulting in excessive steam formation which can lead to boiler explosion.

Removal of scale

- (i) Loosely adhering scale can be removed either by scraper or wire brush or by blow-down operation.
- (ii) Brittle scales can be removed by thermal shocks (i.e heating the boiler and then suddenly cooling with cold water).
- (iii) Hard and adherent scales can be removed by dissolving in chemicals, for example, $CaCO_3$ scale can be dissolved by using 5–10% HCl. $CaSO_4$ scale can be removed by adding EDTA since the Ca-EDTA complex is highly soluble in water.

BOILER CORROSION

Definition It is defined as the decay or disintegration of boiler material by chemical or electrochemical attack by its environment. Boiler corrosion generally occurs due to three reasons.

1. Acid formation by dissolved salts
2. Dissolved carbon dioxide
3. Dissolved oxygen

(1) **Acid formation by dissolved salts** Magnesium chloride present in the boiler feed water undergoes hydrolysis producing hydrochloric acid

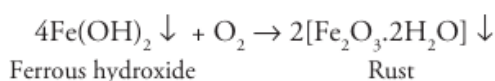


The acid thus liberated reacts with the boiler material (iron) to form ferrous hydroxide which is then converted to rust



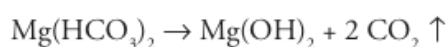
The HCl formed in step (2) again attacks boiler material. A chain reaction is set up which causes extensive corrosion.

The $\text{Fe}(\text{OH})_2$ formed further reacts with oxygen forming rust

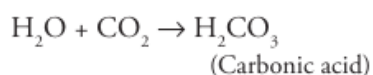


Prevention Boiler corrosion by acid formation can be prevented by adding calculated quantity of alkali which neutralises the acid thus formed.

(2) **Dissolved carbon dioxide** The main source of CO_2 in boilers is by the decomposition of bicarbonates of calcium and magnesium.

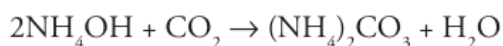


Carbon dioxide reacts with water forming carbonic acid

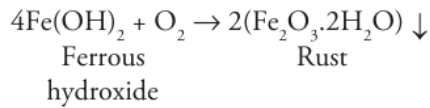
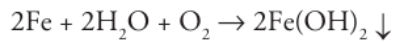


Carbonic acid has a slow corrosive effect on the boiler material.

Removal CO_2 can be removed either by adding ammonium hydroxide or by mechanical de aeration.

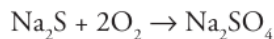
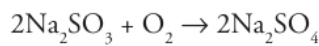
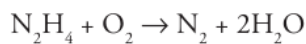


- (3) **Dissolved oxygen** Water normally contains 8 ppm of oxygen dissolved at room temperature. At high temperature, the dissolved oxygen reacts with iron of the boiler to form ferric oxide (rust):



Removal (i) By adding chemicals (ii) By mechanical de aeration

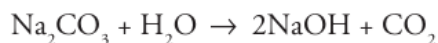
Addition of chemicals Dissolved oxygen can be removed by adding a reducing agent like hydrazine, sodium sulphite or sodium sulphide.



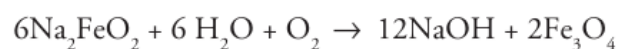
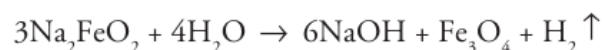
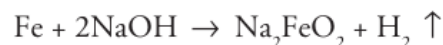
CAUSTIC EMBRITTLEMENT

It is the phenomenon in which the boiler material becomes brittle due to the accumulation of excess alkali in the boiler. Caustic embrittlement is a form of stress corrosion taking place in boilers operating at high temperature and pressure. It is caused by high alkalinity of water in the boiler, particularly at those places which are under stress such as rivets, joints and bends with the result that the metal plates become brittle.

When water is softened by lime – soda process, the excess sodium carbonate undergoes decomposition in high pressure boilers leading to the formation of NaOH.



This NaOH makes the water alkaline. The alkaline water penetrates into the minute cracks and crevices between the rivets and joints by capillary action. Inside the cracks, the water evaporates and the concentration of NaOH increases on these sites due to poor circulation of water. NaOH attacks the iron in boiler material converting it to sodium ferroate (Na_2FeO_2). A small quantity of sodium ferrite (NaFeO_2) is also formed.



It can be seen that NaOH is regenerated in the process and its concentration keeps on increasing maintaining the required environment.

The caustic embrittlement of the boiler may be explained by assuming the formation of a concentration cell as shown below:

Iron at bends, rivets, joints (stressed areas)	Concentrated NaOH solution	Dilute NaOH solution	Iron at plane surface (stress free)
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The iron in the anodic area undergoes corrosion and dissolves making the boiler material brittle.

Prevention

1. By adding tannin or lignin to the boiler water. These block the minute cracks and prevent the infiltration of NaOH.
2. Caustic embrittlement can be prevented if Na_2SO_4 is added to the boiler water, because it is useful in blocking the hair cracks. $\text{Na}_2\text{SO}_4/\text{NaOH}$ should be used in the ratio 1:1, 2:1 and 3:1 for boilers working at pressure 10, 20 and above 20 atm, respectively.
3. By using sodium phosphate instead of sodium carbonate for softening water.
4. By adjusting the pH of boiler water between 8–9.
5. Use of excess Na_2CO_3 should be avoided in the lime-soda process.