

Water technology

Introduction :

Water is a ubiquitous chemical substance that is composed of hydrogen and oxygen and is vital for all known forms of life. In typical usage, *water* refers only to its liquid form or state, but the substance also has a solid state, ice, and a gaseous state, water vapor or steam . Water covers 71% of the Earth's surface. On Earth, it is found mostly in oceans and other large water bodies, with 1.6% of water below ground in aquifers and 0.001% in the air as vapor, clouds (formed of solid and liquid water particles suspended in air), and precipitation. Oceans hold 97% of surface water, glaciers and polar ice caps 2.4%, and other land surface water such as rivers, lakes and ponds 0.6%. A very small amount of the Earth's water is contained within biological bodies and manufactured products.

Clean, fresh drinking water is essential to human and other life forms. Access to safe drinking water has improved steadily and substantially over the last decades in almost every part of the world. There is a clear correlation between access to safe water and GDP per capital. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability. A recent report (November 2009) suggests that by 2030, in some developing regions of the world, water demand will exceed supply by 50%. Water plays an important role in the world economy as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70% of freshwater is consumed by agriculture.

Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. Probably its most important use as an engineering material is in the steam generation. Water is also used as coolant in power and chemical plants. In addition to it water is widely used in other fields such as production of steel, rayon, paper, atomic energy, textiles etc.

CHARACTERISTICS IMPARTED BY IMPURITIES IN WATER

The natural water is usually contaminated by different types of impurities. The characteristic and consequent effects of impurities on the quality of water are disclosed under the following three heads:

Physical impurities: (a) Color in water is caused by metallic substance like salts of iron ,manganese, human materials, tannins, industrial effluents etc. Actually color in water is due to dissolved substances and substances present in fine colloids. The change in color of water is not harmful, unless it is associated with toxic nature. Usually yellowish tinge indicates the presence of chromium and appreciable amount of organic matter. Yellowish red color indicates the presence of iron; while red brown indicates the presence of peaty matter.

(b) Turbidity:

Turbidity is due to the colloidal, extremely fine suspension such as clay, slit, finely divided matters (organic and inorganic) micro organisms like plankton, etc. Turbidity expresses the optical properties of water containing insoluble substances, which scatter light rather than to transmit I straight lie. The turbidity depends not only on the quantity of the insoluble substances, but also on the size shape, and refractive index. Turbidity in water can be eliminated by sedimentation, followed b coagulation, filtration etc.

(c) Taste:

Taste is usually interlinked directly with odour. However in some waste water, taste is not accompanied by odour. Thus the presence of dissolved mineral I water produces taste, but not odour. For example

- i) Bitter taste can be due to the presence of iron, aluminum, manganese, sulphur or excess lime.
- ii) Sopyy taste can be due to the presence of large amount of sodium bicarbonate.
- iii) Brackish taste is due to the presence of unusual amount of salts.
- iv) Palatable taste is due to the presence of dissolves gases and minerals in water.

(d) Odour:

Odour in water is undesirable for the domestic as well as industrial purposes. Disagreeable odour in water may be caused by the presence of living organisms, decaying vegetation including algae, fungi and weeds. The receiving water may be offensive where heavy pollution is caused by sewage/industrial effluents. The most common disagreeable odour in water is due to the presence of small quantity of sulphides. The cause of odour in polluted water are :

- i) Presence of inorganic and organic compounds of N, S and P and the putrefaction of proteins and other organic mistrials present in sewage.
- ii) Industrial effluents containing organic substances such as alcohol, aldehyde, phenols, ethers, ketones, etc. flowing into the water bodies.

Besides these (i) presence of alga in water bodies impart a strong grassy odour, due to the liberation of traces of essential oils from their bodies, (ii) growth of iron and sulphur bacteria may produce offensive odour, (iii) presence of colloidal vegetable matter in surface water evolves a faint flavour called peaty odour (iv) clay and sand in finely divided state impart a faint earthy odour,(v) improper bituminous coating on cast iron main pipes may give off a tarry odour to water which passes through it, (vi) a faint odour is imparted to water. This ordour is due to the impure hydrogen.

Chemical impurities in water

- i) Inorganic and organic chemicals released from dyes, paints, drugs, pesticides, textiles, tanneries etc .All these pollute water bodies .
- ii) Acid discharge in water by DDT, high explosives, battery, industries etc. The use of this water causes harmful effect on health of human beings.

- a) Acidity is not any specific pollutant and it simply determines the power to neutralize hydroxyl ions and is usually expressed in terms of ppm of calcium carbonate equivalent. Surface water and ground waters attain acidity from industrial wastage like acid, mine, drainage, etc. Usually acidity is caused by the presence of free CO₂, mineral acid and weakly dissociated acids. Mineral acid are released when iron and aluminum salts hydrolyzed.
- b) Gases: All the natural water contains dissolved atmosphere CO₂. Its solubility depends upon temperature, pressure and dissolved mineral content of water. Also polluted waters acquire CO₂ from the biological oxidation of organic matter. Its presence in water is of no significance.
- c) Concentration of dissolved atmospheric O₂ in water depends on temperature, pressure and salt content in water. Dissolved O₂ in industrial waters is nuisance since it induces corrosion reaction. On the other hand dissolved oxygen in water is essential to the life of aquatic organisms such as fish.
- d) Dissolved NH₃ in water arises from the decomposition of nitrogenous organic matter. Polluted waters and sewages contain nitrogen in the form of nitrogenous organic compounds and urea which are partially converted to NH₃.
- e) Mineral matters have origin from rocks and industrial effluents. These include mineral acids Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe²⁺, Cl⁻, NO₃⁻, F⁻, SiO₂ etc.
- f) Biological impurities are algae, pathogenic bacteria, fungi, viruses, pathogens, parasites worms etc. The source of this contamination is discharge of domestic and sewage wastes, excreta etc.
- g) Micro organisms are usually abundant in surface waters, but their count is often quite low or even nil in deep well waters. The commonest type of micro organism form the point of treatment are algae, fungi and bacteria, which often form slime thereby causing fouling as well as corrosion. The slime of formed logs the spray nozzles and screens of the circulating pumps in air conditioning and other industrial plants.
- h) Sediment or suspended matter: Insoluble particles of soil and other inorganic and organic materials that become suspended in water and that in terms of total mass are the largest sources of water pollution. Suspended particulate matter clouds the water reduces the ability of some organisms to find food, reduces the photosynthesis by aquatic plants, disrupts aquatic food webs, and carries pesticides bacteria and other harmful substances.
- i) Radioactive substances: radioisotopes that are water soluble or capable of being biologically amplified to higher concentrations as they pass through food chains and webs. Ionizing radiation from such isotopes can cause birth defects, cancer and genetic damage.

Contaminant	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Antimony	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Arsenic	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass & electronicsproduction wastes

Asbestos (fiber >10 micrometers)	Increased risk of developing benign intestinal polyps	Decay of asbestos cement in water mains; erosion of natural deposits
Barium	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits
Beryllium	Intestinal lesions	Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries
Cadmium	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (total)	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Copper	<p>Short term exposure: Gastrointestinal distress</p> <p>Long term exposure: Liver or kidney damage</p> <p>People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level</p>	Corrosion of household plumbing systems; erosion of natural deposits
Cyanide (as free cyanide)	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories
Fluoride	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Lead	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities	Corrosion of household plumbing systems; erosion of natural deposits

	Adults: Kidney problems; high blood pressure	
Mercury (inorganic)	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Nitrate (measured as Nitrogen)	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue- baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Nitrite (measured as Nitrogen)	Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue- baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Selenium	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines
Thallium	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories

Radionuclides

Contaminant	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Alpha particles	Increased risk of cancer	Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation
Beta particles and photon emitters	Increased risk of cancer	Decay of natural and man- made deposits of certain minerals that are radioactive and may emit forms of radiation known as photons and beta radiation

Radium 226 and Radium 228 (combined)	Increased risk of cancer	Erosion of natural deposits
Uranium	Increased risk of cancer, kidney toxicity	Erosion of natural deposits

Drinking water standards comparative table

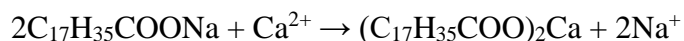
Parameters	Units	WHO standard	ISI Standard
pH		6.5-9.2	6.5-8.5
TDS (Total dissolved salts)	mg/l	500	500
Sulphate	mg/l	200	200
Chloride	mg/l	250	200
Cyanides	mg/l	0.05	0.05
Fluride	mg/l	1.5	0.6-1.2
Aluminium	mg/l	0.2	
Arsenic	mg/l	0.01	0.01
Antimony	mg/l	0.005	
Barium	mg/l	0.3	
Boron	mg/l	0.3	
Cadmium	mg/l	0.003	0.01
Lead	mg/l	0.01	0.05
Mercury	mg/l	0.001	0.001
Sodium	mg/l	200	
Zinc	mg/l	3	5

Hard water:

Hard water is water that has high mineral content (in contrast with *soft water*). Hard water minerals primarily consist of calcium (Ca^{2+}), and magnesium (Mg^{2+}) metal cations, and sometimes other dissolved compounds such as bicarbonates and sulfates. Calcium usually enters the water as either calcium carbonate (CaCO_3), in the form of limestone and chalk, or calcium sulfate (CaSO_4), in the form of other mineral deposits. The predominant source of magnesium is dolomite ($\text{CaMg}(\text{CO}_3)_2$). Hard water is generally not harmful to one's health.

The simplest way to determine the hardness of water is the lather/froth test: soap or toothpaste, when agitated, lathers easily in soft water but not in hard water. More exact measurements of hardness can be obtained through a wet titration. The total water 'hardness' (including both Ca^{2+} and Mg^{2+} ions) is read as parts per million (ppm) or weight/volume (mg/L) of calcium carbonate (CaCO_3) in the water. Although water hardness usually measures only the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminium, and manganese may also be present at elevated levels in some geographical locations. Iron in this case is important for, if present, it will be in its trivalent form, causing the calcification to be brownish (the color of rust) instead of white (the color of most of the other compounds).

Hardness in water is defined as the presence of multivalent cations. Hardness in water can cause water to form scales and a resistance to soap. It can also be defined as water that does not produce lather with soap solutions, but produces white precipitate (scum). For example, sodium stearate reacts with calcium:

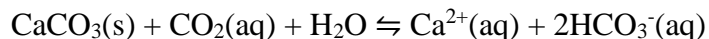


Hardness of water may also be defined as the soap-consuming capacity of water, or the capacity of precipitation of soap as a characteristic property of water that prevents the lathering of soap.

Temporary hardness

Temporary hardness is caused by a combination of calcium ions and bicarbonate ions in the water. It can be removed by boiling the water or by the addition of lime (calcium hydroxide). Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

The following is the equilibrium reaction when calcium carbonate (CaCO_3) is dissolved in water:



Upon heating, less CO_2 is able to dissolve into the water. Since there is not enough CO_2 around, the reaction cannot proceed from left to right, and therefore the CaCO_3 will not dissolve as rapidly. Instead, the reaction is forced to the left (i.e., products to reactants) to re-establish equilibrium, and solid CaCO_3 is formed. Boiling the water will remove hardness as long as the solid CaCO_3 that precipitates out is removed. After cooling, if enough time passes, the water will pick up CO_2 from the air and the reaction will again proceed from left to right, allowing the CaCO_3 to "re-dissolve" into the water.

Permanent hardness

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence in the water of calcium and magnesium sulfates and/or chlorides which become more soluble as the temperature rises. Despite the name, permanent hardness can be removed using a water softener or ion exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column.

Hard water causes scaling, which is the left-over mineral deposits that are formed after the hard water had evaporated. This is also known as lime scale. The scale can clog pipes, ruin water heaters, coat the insides of tea and coffee pots, and decrease the life of toilet flushing units.

Similarly, insoluble salt residues that remain in hair after shampooing with hard water tend to leave hair rougher and harder to untangle.

In industrial settings, water hardness must be constantly monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment that comes in contact with water. Hardness is controlled by the addition of chemicals and by large-scale softening with zeolite ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$) and ion exchange resins.

Unit of hardness:

Hardness is expressed in terms of equivalent of calcium carbonate. The reason for choosing calcium carbonate as standard is that it is the most insoluble salt that can be precipitated in water treatment.

Hence whatever dissolved salts are present in water they are first converted into calcium carbonate equivalents. In general calcium carbonate equivalent of hardness is given by

$$\text{Hardness} = \frac{\text{Wt. of the substance producing hardness} \times \text{Eq.wt. of CaCO}_3}{\text{Eq.wt. of substance}}$$

Various units used to express hardness of water are as under

1. Parts per million (ppm)
2. Milligrams per liter (mg/L)
3. Degree French ($^{\circ}\text{Fr}$)

Parts per million (ppm)

It is defined as parts of calcium carbonate equivalent hardness present in 10^6 parts of water. This is the most common unit for expressing the hardness of water.

Milligrams per liter (mg/L)

It is defined as the number of milligram of CaCO_3 equivalent hardness present per liter of water.

Degree French

It is defined as parts of calcium carbonate equivalent hardness present in 10^5 parts of water.

Very Soft water	0-70 ppm of CaCO_3
Soft water	70-140 ppm of CaCO_3
Slightly hard water	140-210 ppm of CaCO_3
Moderately hard	210-320 ppm of CaCO_3
Hard water	320-530 ppm of CaCO_3
Very hard water	> 530 ppm of CaCO_3

Determination of total hardness of water:

Total hardness includes both permanent and temporary hardness.

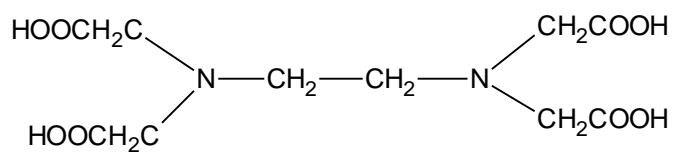
EDTA method:

It is the most important and more accurate method to determine the hardness of water.

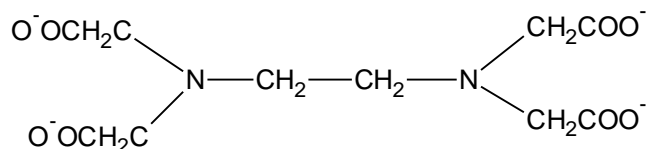
The total hardness (permanent as well as temporary) in water is determined by titrating the known volume of the water sample against standard ethylenediaminetetraacetic acid (EDTA) solution in ammonia buffer solution having pH = 10 using erichrome black-T (Erio T) as an indicator. The calcium and magnesium ions present in water form stable compound with EDTA and less stable complex with erichrome black-T solution. The end point of the titration is clear blue without any reddish tinge from wine red.

Principle

EDTA is a weak acid and has a structure as shown below.



1.a



1.b

a- The structure of EDTA

b- The structure of tetracarboxylate $[\text{EDTA}]^{4-}$ ion formed by the dissociation of EDTA

In aqueous solution buffered at pH 10 EDTA dissociate to form tetracarboxylate ion as shown in figure 1.b. This ion is electron rich having six bonding sites. The four carboxylate groups and the two nitrogen atoms. Each site has an electron pair available for bonding. The $[\text{EDTA}]^{4-}$ anion wraps itself around a Ca^{2+} or Mg^{2+} ion so that all six electrons pairs are shared with the metal ion as shown in the figure. In this manner $[\text{EDTA}]^{4-}$ forms strong 1:1 complexes known as chelates with metal ions like Ca^{2+} and Mg^{2+} .

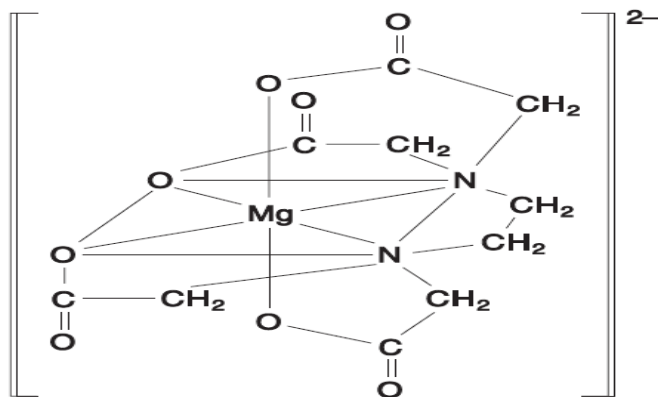
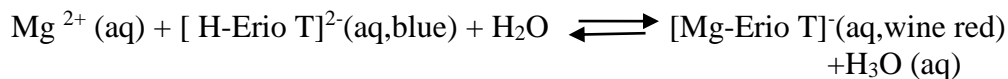
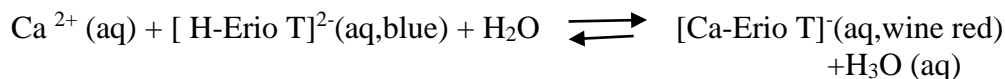
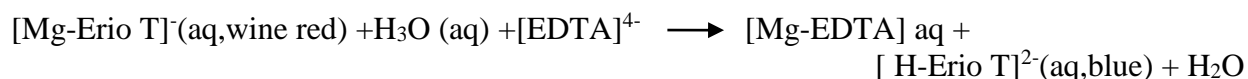
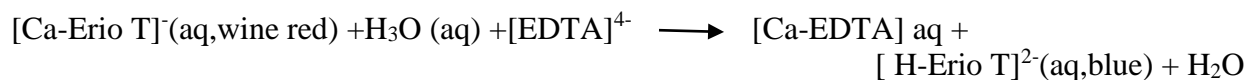


Figure 2 Structure of $[\text{Mg-EDTA}]^{2-}$ chelate

In an aqueous solution buffered at pH 10, Erio T also dissociate forming $[\text{H-Erio T}]^{2-}$ ion a blue ion that bonds with either Mg^{2+} or Ca^{2+} ion to form a wine red complex. The reaction of $[\text{H-Erio T}]^{2-}$ ion with Ca^{2+} and Mg^{2+} ions are reversible.



Complexes of Ca^{2+} and Mg^{2+} ions with $[\text{EDTA}]^{4-}$ and $[\text{H-Erio T}]^{2-}$ ions have different stability. When the indicator is added to properly buffered hard water Ca^{2+} and Mg^{2+} ions form unstable complexes with the indicator and turns the solution to wine red. The color persists until the end point is reached during the titration with EDTA. When the end point is reached $[\text{EDTA}]^{4-}$ anion breaks up the wine red $[\text{Mg-Erio T}]^{-}$ and $[\text{Ca-Erio T}]^{-}$ complexes releasing the $[\text{H-Erio T}]^{2-}$ ion and hence the solution changes from wine red to permanent blue color.



To determine the temporary hardness another sample of the same volume of water is boiled to convert the bicarbonate to carbonate and the precipitated calcium carbonate is filtered off. The filtrate after cooling is titrated against EDTA in the same way as above. This gives the permanent hardness. The difference between the total and hardness and the permanent hardness gives the temporary hardness.

Procedure:

Total hardness: Pipette out 50 ml of the sample of water into a clean titration flask, add 1 ml of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution and 3-4 drops of indicator. Titrate against 0.01 M EDTA till the color changes from wine red to clear blue without any reddish tinge. Let the volume of EDTA required be V_1 ml.

Permanent hardness:

Transfer 50 ml of the sample of water into a clean 500 ml beaker and boiled gently for 20-30 minutes. Cool and filtered it directly into a 250 ml conical flask. Add 1 ml of buffer solution followed by 3-4 drops of indicator. Titrate against standard 0.01 M EDTA as described above. Let the volume of EDTA required be V_2 ml.

Calculation :

1000ml of 1 M EDTA = 100g CaCO_3 (Mol.weight of CaCO_3 =100g)

1ml of 1 M EDTA = 100/ 1000 g of CaCO_3

$$V_1 \text{ ml of 0.01 M EDTA} = \frac{V_1 \times 0.01 \times 100}{1000} \text{ g of CaCO}_3$$

$$50 \text{ ml of water sample contains} = \frac{V_1 \times 0.01 \times 100}{1000} \text{ g of CaCO}_3$$

$$10^6 \text{ (1 million) ml of water sample contains} = \frac{V_1 \times 0.01 \times 100 \times 10^6}{1000 \times 50} \text{ g of CaCO}_3$$

Similarly

$$\text{Permanent hardness} = \frac{V_2 \times 0.01 \times 100 \times 10^6}{1000 \times 50} \text{ g of CaCO}_3$$

Softening of water:

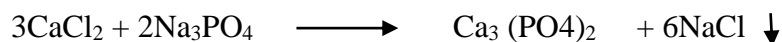
Internal treatment:

In this process (also called sequestration) an ion is prohibited to exhibit its original character by complexing or converted into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to the boiler water either

- a) To precipitate the scale forming impurities in the form of sludges
- b) To convert them into compounds which will stay in dissolved form in water

Phosphate conditioning:

In high pressure boilers scale formation can be avoided by adding sodium phosphate which reacts with hardness of water forming non-adherent and easily removable soft sludge of calcium and magnesium phosphate which can be removed by blow down operation

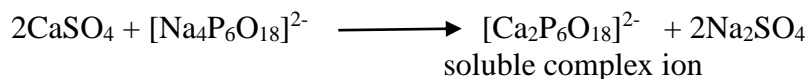
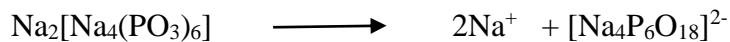


The main phosphate used are NaH_2PO_4 , sodium dihydrogen phosphate (acidic), Na_2HPO_4 , disodium hydrogen phosphate (weakly alkaline) Na_3PO_4 , trisodium phosphate (alkaline).

The choice of salt depends upon the alkalinity of the boiled water. Calcium cannot be precipitated below a pH 9.5. Trisodium phosphate is most suitable for treatment when alkalinity is low and disodium phosphate is used when the water alkalinity is sufficient. Monosodium phosphate is used when the alkalinity of boiler water is too high.

Calgon conditioning:

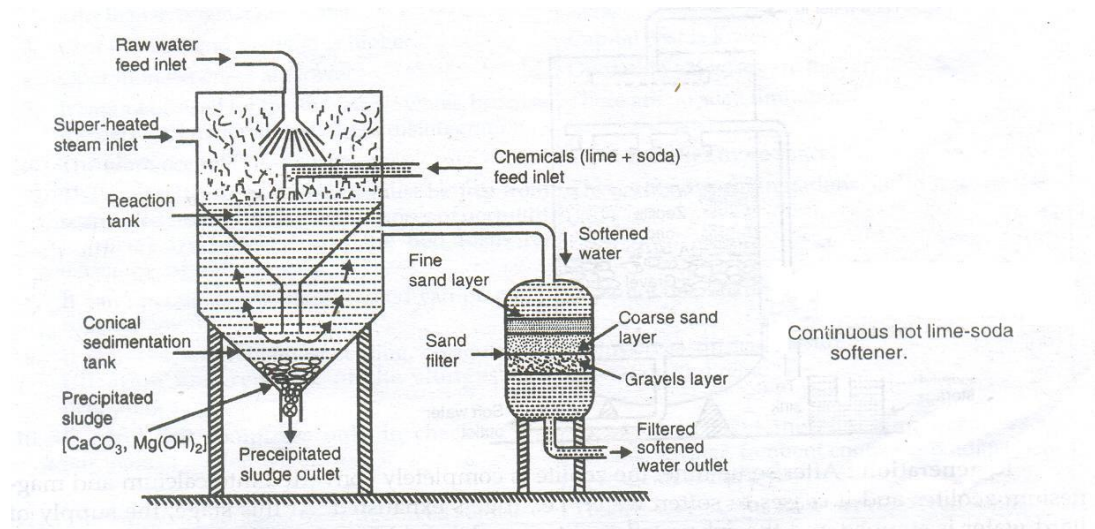
It involves in adding calogen (Sodium hexa meta phosphate $(\text{NaPO}_3)_6$ to boiler water. It prevents the scale and sludge formation soluble complex compound with CaSO_4 .



Lime soda process:

In this method the soluble calcium and magnesium salts in water are chemically converted into soluble compound by adding calculated amount of lime $\text{Ca}(\text{OH})_2$ and soda Na_2CO_3 . Calcium carbonate and magnesium hydroxide so precipitated are filtered off.

Hot lime soda process:



This process involves in treating water with softening chemicals at a temperature of 80 to 150⁰C. Since hot process is operated at a temperature close to the boiling point of the solution i) the reaction proceeds faster ii) softening capacity is increased to many fold iii) the precipitate and sludge formed settle down rapidly and hence no coagulant are needed iv) much of the dissolved gases driven out o water v) viscosity of soften water is lower so filtration of water becomes easier. Vi) this process produces water of comparatively low residual hardness 15 to 30 ppm.

Hot lime soda plant consists essentially of three parts (a) a reaction tank in which raw water, chemical and steam are thoroughly mixed (b) a conical sedimentation vessel in which sludge settles down and (c) a sand filter which ensures complete removal of sludge from the softened water.

Advantages of lime soda process:

- i) It is very economical
- ii) If the process is combined with sedimentation with coagulation lesser amounts of coagulants shall be needed.
- iii) The process increases the pH of the treated water thereby corrosion reduced.
- iv) In addition to the removal of hardness, the quantities of minerals in the water are reduced.
- v) Due to alkaline nature of treated water amount of pathogenic bacterias in water is considerably reduced.

Disadvantages of lime soda process:

- i) For efficient and economical softening careful operation and skilled supervision is required.
- ii) Disposal of large amount of sludge poses a problem.
- iii) This can remove hardness upto 15 ppm which is not good for boilers.

Boiler feed Water: Scales and Sludges

In boilers, water evaporates continuously and the concentrations of the dissolved salts increase progressively. When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose slimy precipitate, it is called **sludge**. On the other hand, if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called **Scale**.

Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludge can easily be scrapped off with a wire brush. It is formed at comparatively colder portion of the boiler and collects in areas of the system, where the flow rate is slow or at a bends. Sludge's are formed by substances which have greater solubility's in hot water than in cold water, e.g., MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 , etc.

Disadvantages of sludge formation 1) Sludge's are poor conductor of heat, so they tend to waste a portion of heat generated. (2) If sludge's are formed along-with scales, then former gets entrapped in the latter and both get deposited as scales. (3) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

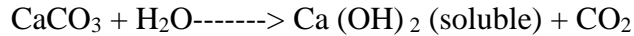
Prevention of sludge formation: (1) By using well softened water (2) By frequently 'blow-down operation', i.e., drawing off a portion of the concentrated water.

Scales are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer and chisel. Scales are the main source of boiler troubles. Formation of scales may be due to:

(1) Decomposition of calcium bicarbonate:



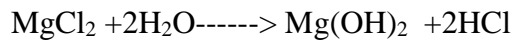
However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, CaCO_3 is soluble.



(2) Deposition of Calcium Sulphate: The solubility of calcium sulphate in water decrease with rise of temperature. Thus, 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 . In other words, CaSO_4 is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, CaSO_4 gets precipitated as hard scale on the heated portions of the boiler. This is the main cause of scales in high pressure boilers.

Note: Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(3) Hydrolysis of magnesium salts: Dissolved magnesium salts undergo hydrolysis (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a soft type of scale, e.g. ..



(Scale)

(4) Presence of silica: (SiO_2), even present in small quantities, deposits as calcium silicate (CaSiO_3) and / or magnesium silicate (MgSiO_3). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

Disadvantages of scale formation:

(1) Wastage of fuel: Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, excessive or over-heating is done and this causes increase in fuel consumption. The wastage of fuel depends upon the thickness and the nature of scale:

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

(2) Lowering of boiler safety: Due to scale formation, over heating of boiler is to be done in order to maintain a constant supply of steam. The over -heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam, especially in high -pressure boilers.

(3) Decrease in efficiency: Scales may sometimes deposit in the valve and condensers of the boiler and choke them partially. This results in decrease in efficiency of the boiler.

(4) Danger of explosion: When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes in formation of a large amount of steam suddenly. So sudden high- pressure is developed, which may even cause explosion of the boiler.

Removal of scales: (i) With the help of scraper or piece of wood or wire brush, if they are loosely adhering. (ii) By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water), if they are brittle. (iii) By dissolving them by adding them chemicals, if they are adherent and hard. Thus calcium carbonate scales can be 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 complexes. (iv) By frequent blow -down operation, if the scales are loosely adhering.

Prevention of scales formation : (1) **External Treatment** includes efficient ‘softening of water’ (i.e., removing hardness-producing constituents of water). These will be discussed separately.

(2) Internal Treatment: In this process (also called sequestration), an ion is prohibited to exhibit its original character by ‘complexing’ or converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to the boiler water either: (a) to precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down operation, or (b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

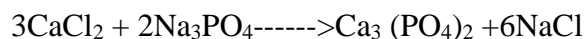
Notes: (i) Blow down operation is partial removal of hard water through top at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.

(ii) ‘Make up’ water is addition of fresh softened water to boiler after blow down operation.

Internal Treatments methods are, generally, followed by ‘blow-down operation’, so that accumulated sludge is removed. Important internal conditioning/ treatment methods are:

(i) **Colloidal conditioning:** In low-pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar (a gel), etc., which get coated over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.

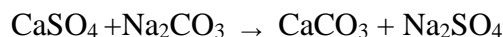
(ii) **Phosphate Conditioning:** In high- pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphates, which can be removed by blow down operation, e.g.,



The main phosphates employed are: (a) NaH_2PO_4 , sodium dihydrogen phosphate (acidic); (b) Na_2HPO_4 , disodium hydrogen phosphate (weakly alkaline); (c) Na_3PO_4 , trisodium phosphate (alkaline).

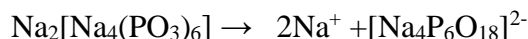
Note: The choice of salt depends upon the alkalinity of the boiler –feed water. Calcium cannot be precipitated properly below a pH 9.5, so select a phosphate that adjusts pH to optimum value (9.5-10.5). Trisodium phosphate is most suitable for treatment, when the alkalinity of boiler water is low, as it is most alkaline in nature. If boiler water's alkalinity is sufficient, then disodium phosphate is more preferred. But if the alkalinity of boiler is too high and requires to be reduced, then monosodium phosphate, being acidic in nature, is preferred.

(iii)**Carbonate Conditioning:** In low pressure boilers, scale- formation can be avoided by adding sodium carbonate to boiler water, when CaSO_4 is converted into calcium carbonate in equilibrium.

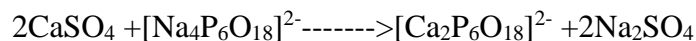


Consequently, deposition of CaSO_4 as scale does not take place and calcium is precipitated as loose sludge of CaCO_3 , which can be removed by blow-down operation.

(iv)**Calgon Conditioning:** involves in adding calgon [sodium hexa meta phosphate $(\text{NaPO}_3)_6$ to boiler water. It prevents scale and sludge formation by forming soluble complex compound with CaSO_4 .

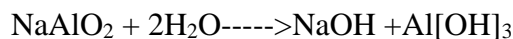


Calgon



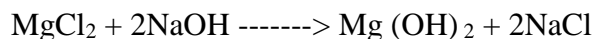
Soluble complex ion

(v)**Treatment with sodium aluminate (NaAlO_2):** Sodium aluminate gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminium hydroxide. Thus:



Sod.meta-aluminate (Gelatinous ppt.)

The sodium hydroxide, so-formed, precipitates some of the magnesium as $\text{Mg}(\text{OH})_2$, i.e.



The flocculent precipitate of $\text{Mg}(\text{OH})_2$ and $\text{Al}[\text{OH}]_3$ produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitate can be removed by pre-determined blow-down operation.

Note: sodium aluminate in thick solution form is available in plenty and at a cheap rate from bauxite refining units and this can be used as such for boiler-water treatment.

(vi) **Electrical conditioning:** sealed glass bulbs, containing mercury connected to a battery, are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, which prevents scale forming particles to adhere/stick together to form scale.

(vii) **Radioactive conditioning:** Tablets containing radioactive salts are placed inside the boiler water at a few points. The energy radiations emitted by these salts prevent scale formation.

(viii) **Complexometric method:** involves adding 1.5% alkaline ($\text{pH}=8.5$) solution of EDTA to feed water. The EDTA binds the scale-forming cations to form stable and soluble complex. As a result, the sludge and scale formation in boiler is prevented. Moreover this treatment:

(i) Prevents the deposition of iron oxides in the boiler

(ii) Reduces the carry over oxides with steam, and

(iii) Protects the boiler units from corrosion by wet steam (steam containing liquid water).

Priming and Foaming

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with steam. This process of 'wet steam' formation is called Priming. Priming is caused by: (i) the presence of large amount of dissolved solids (ii) high steam velocities; (iii) Sudden boiling (iv) Improper boiler design and (v) Sudden increase in steam-production rate

Foaming is the production of persistent foam or bubbles in boilers, which do not break easily. Foaming is due to presence of substances like oils (which greatly reduce the surface tension of water).

Priming and foaming usually occur together. They are objectionable because (i) Dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency (ii) Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery (iii) Actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

Priming can be avoided by (i) fitting mechanical steam purifiers; (ii) avoiding rapid change in steaming rate; (iii) Maintaining low water levels in boilers and; (iv) efficient softening and filtration of the boiler-feed water.

Foaming can be avoided by (i) Adding anti-foaming chemicals like castor oil

(ii) Removing oil from boiler water by adding compounds like sodium aluminate.

WASTE WATER TREATMENT

Desalination of brackish water by reverse osmosis and electrodialysis

There are many countries in the world where the demand for fresh water far exceeds the availability of natural water. There are some countries like Kuwait, which have no fresh water, and have to look inevitably to the ocean for their fresh water demand. But high salt content of sea water prohibits its use for human consumption and other uses of water. There are three grades of water based on the level of dissolved salts, as given below.

(a) Fresh water with dissolved salts less than 1000mg/L.

(b) Brackish water with dissolved salt between 1000-35,000mg/L.

(c) Sea water with dissolved salts greater than 35,000mg/L.

Definition

The process of removal of dissolved salts from sea water (or brackish water) to the extent, that water becomes usable is described as '**Desalination ' or desalting'**. **OR** The process of removing common salt (sodium chloride) from the water is known as desalination.

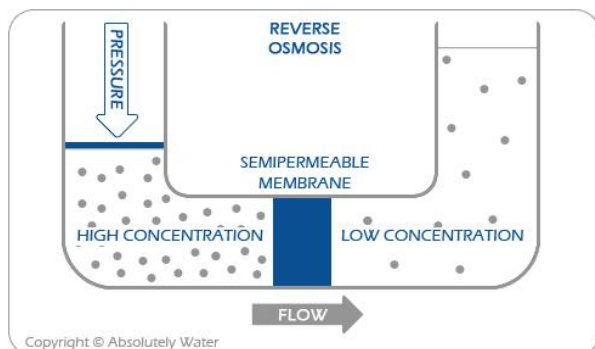
Desalination is a very expensive process and is used in places experiencing an acute shortage of fresh water. The water containing dissolved salts with the peculiar salty (or brackish) taste is called brackish water. Sea water containing on an average about 3.5% salts, comes under this category. Brackish water is totally unfit for drinking purpose. Commonly used methods for the desalination of brackish water are:

(a) Reverse Osmosis

(b) Electro dialysis

(a) Reverse osmosis: When two solutions of unequal concentrations are separated by a semi permeable membrane (which selectively does not permit the passage of dissolved solute particles, i.e., molecules, ions etc), flow of solvent takes place from dilute to concentrated sides, due to osmosis. If however a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses, i.e., solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. Thus, in reverse

osmosis methods, pure solvent (water) is separated from its contaminants, rather than removing contaminants from the water. This membrane filtration is sometimes also called “super - filtration” or “hyper filtration”.



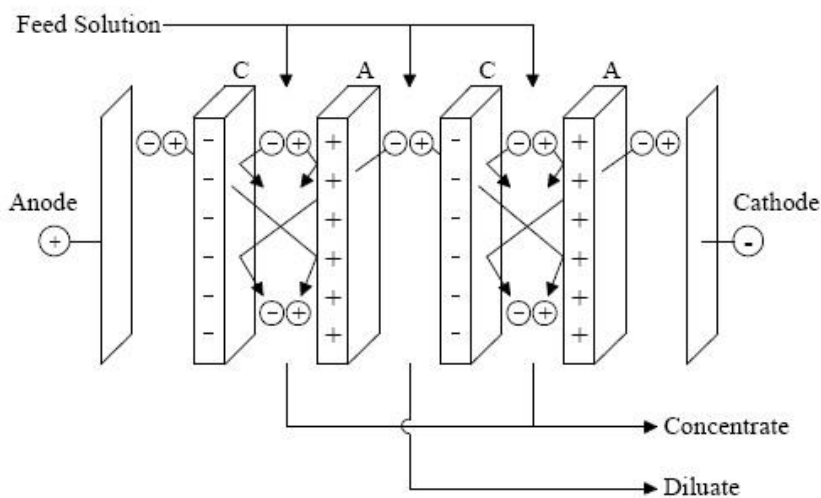
Method: In this process, pressure (of the order $15 \text{ to } 40 \text{ kg cm}^{-2}$) is applied to the sea water /impure water (to be treated) to force its pure water out through the semi permeable membrane; leaving behind the dissolved solids (both ionic as well as non-ionic). The principle of reverse osmosis, as applied for treating saline/ sea water, is illustrated in figure. The membrane consists of very thin films of cellulose acetate, affixed to either side of perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

Advantages(i)Reverse osmosis possesses a distinct advantage of removing ionic as well as non –ionic , colloidal and high molecular weight organic matter (ii)It removes colloidal silica which is not removed by demineralization.(iii) The maintenance cost is almost entirely on the replacement of the semi permeable membrane(iv) The life time of membrane is quite high, about two years(v) The membrane can be replaced within a few minutes there by providing nearly uninterrupted water supply.(vi) Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high-pressure boilers.

(b)**Electro dialysis** is method in which the ions (of the salts present) are **pulled out** of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair (natural or synthetic) Fig. illustrates the method of desalination by electrodialysis. When direct electric current is passed through saline water, the sodium ions (Na^+) start moving towards negative pole (Cathode); while the chloride ions start moving towards the positive pole (anode), through the membrane. As a result, the concentration of brine decreases in the central compartment; while it increases in two side compartments. Desalinated brine (or pure water) is removed from the central compartment from time to time; while concentrated brine (in the side compartments) is replaced by fresh brine or sea water.

For more efficient separation, usually, **ions-selective membranes** are employed. An ion-selective membrane has permeability for only one kind of ions with specific charge. For example a cation-selective membrane is permeable to cations only, because of the presence of charged fixed (inside the membrane) functional groups (such as RSO_3^- , RCOO^-) reject anions (having the same charge as that of fixed functional groups). Similarly anion-selective membrane has positively charged fixed functional groups such as $\text{R}_4\text{N}^+\text{Cl}^-$.

An electro dialysis cell (in fig) consists of a large number of paired sets of rigid plastic membranes. Saline water is passed under a pressure (of about $5\text{--}6 \text{ kg m}^{-2}$) between membrane pairs and an electric field is applied perpendicular to the direction of water flow. Just as magnets of like charges repel each other, the fixed positive charges inside the membrane repel positively charged ions (Na^+), yet permit negatively charge ions (Cl^-) to pass through. Similarly, the fixed negative charges inside the other type of membrane repel negatively charge ions (Cl^-), yet permit positively charged ions (Na^+) to pass through. Therefore water is one compartment of the cell is deprived of its salts: While the salt concentration in adjacent compartments is increased. Thus, we get alternate streams of pure water and concentrated brine.



Advantages (1) It is most compact unit

(2) The cost of installation of the plant and its operation is economical.

(3) If electricity is easily available, it is best suited.