

UNIT I- Water

Q.1 What is hardness? Discuss its type.

Soap consuming capacity of water is called hardness.

Definition: Hardness is the property of water which prevents the formation of lather or foam and needs large quantities of soap. The water which does not produce lather with soap solution readily, but forms a white curd is called hard water. It forms scales in hot water pipes, heaters, boilers where the temperature of water is increased.

Hardness can be defined as "the soap consuming capacity of water simple" or it prevents the lathering of soap.



Causes: This is caused due to dissolve salts of calcium and magnesium and other heavy metal ions.

Types of hardness

There are two types of hardness temporary and permanent hardness

- 1. TEMPORARY HARDNESS :** Caused due to presence of carbonates and bicarbonates of calcium and magnesium this can be removed by boiling or by adding lime solution in water. Temporary hardness is also called carbonate hardness.
- 2. PERMENET HARDNESS :** Caused due to the presence of sulphates, chlorites and nitrates of calcium and magnesium. They cannot be removed by simple boiling and require special treatment of water softening it is also called as Non-carbonate hardness.

Difference between temporary and permanent hardness

Sr. No	Temporary hardness	Permanent hardness
1	Type of hardness which can be removed by simple techniques such as boiling is known as temporary hardness	Type of hardness which cannot be removed by simple techniques such as boiling is known as Permanent hardness
2	It is due to bicarbonates of <u>Ca, Mg</u> and carbonates of Mg hence known as carbonate hardness	It is due to other salts hence known as carbonate hardness
3	It is due to <u>Ca(HCO₃)₂</u> , Mg(HCO ₃) ₂ , MgCO ₃	It is due to CaCl ₂ , MgCl ₂ , CaSO ₄ , MgSO ₄ , Ca(NO ₃) ₂ , Mg(NO ₃) ₂ , FeCl ₂ ,

		&FeSO ₄
4	It is known as alkaline hardness	It is known as <u>non alkaline hardness</u>
5	It is removed by boiling not by chemicals	It is removed by chemicals lime and soda
6	<u>Ca(HCO₃)₂</u> → CaCO ₃ +CO ₂ +2H ₂ O Mg(HCO ₃) ₂ → Mg(OH) ₂ +2CO ₂	CaSO ₄ + Na ₂ CO ₃ → CaCO ₃ +Na ₂ SO ₄

Q.2 Write a note on degree of hardness. Why it is express in term of Calcium carbonate (CaCO₃) equivalent hardness?

The hardness of water is expressed in terms of calcium carbonate equivalent hardness known as degree of hardness.

Formula

CaCO₃ equivalent hardness =

$$\frac{(\text{Mass of Hardness producing substance}) * (\text{Chemical Equivalent of CaCO}_3)}{\text{Chemical Equivalent of Hardness producing substance}}$$

Reason for expressing hardness in term of CaCO₃ equivalent hardness

1. The molecular weight of calcium carbonate is 100gm/mol. It is easy to calculate.
2. Calcium carbonate is insoluble in water therefore it is easy to calculate its amount in water.

CALCULATION OF EQUIVALENTS OF CALCIUM CARBONATE

Example 1

Example 1. Sample contains 180 mg/L of $MgSO_4$

❖ *Molar mass of $MgSO_4 = 24 + 32 + (16 \times 4) = 120$*

❖ *Chemical equivalent of $MgSO_4 = 120/2 = 60$*

❖ *Chemical equivalent of $CaCO_3 = 50$*

$$\text{Equivalents of } CaCO_3 = \frac{\left(\text{Mass of hardness producing substance} \right) \times \left(\text{Chemical equivalent of } CaCO_3 \right)}{\left(\text{Chemical equivalent of hardness producing substance} \right)}$$

$$\text{Equivalents of } CaCO_3 = \frac{180 \times 50}{60} = 150 \text{ mg/L or ppm}$$

Hardness of the sample = 150 mg/L or ppm.

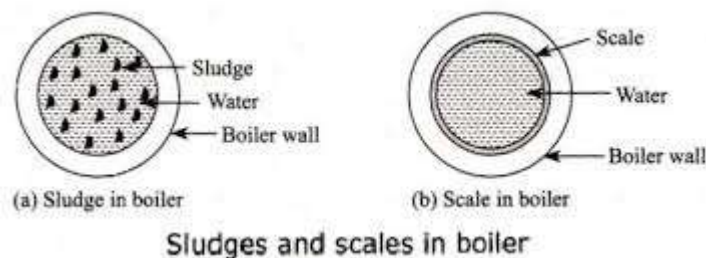
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Q.3 Discuss sludge and scale formation in boiler. Write disadvantages of sludge and scale formation.

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. It leads to formation of precipitates in boiler.

Scale: If the precipitated matter forms a **hard, adhering crust/coating** on the inner walls of the boiler, it is called scale.

Sludge: If the precipitation takes place in the form of **loose and 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, loosy and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.
Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$.

Disadvantages of sludges:

1. Sludges are bad conductors of heat and results in the wastage of heat and fuel.
2. Excessive sludge formation leads to the settling of sludge in slow circulation areas such as pipe connections, plug openings, gauge–glass connections leading to the choking of the pipes.

Prevention of sludge formation:

1. By using soft water which is free from dissolved salts like $MgCO_3$, $MgCl_2$, $CaCl_2$ and $MgSO_4$ can be prevented sludge formation.
2. By blow down operation

Scales: Scales are hard, adhering precipitates formed on the inner walls of the boilers. Scales are stick very firmly on to the inner walls of the boiler. It is removed with chisel and hammer.

Reasons for formation of scales:

1. **Decomposition of calcium bicarbonate:** The calcium bicarbonate at high temperature decomposes to calcium carbonate which is insoluble salt, forms scale in low pressure boilers.



2. **Hydrolysis of Magnesium salts:** Magnesium salts gets hydrolyzed at high temperature forming $Mg(OH)_2$ precipitation which forms salt type scale.



3. **Decomposition of calcium sulphate:** The solubility of $CaSO_4$ in water decreases with the increase in temperature and forms precipitation on the surface of the boiler further which forms hard scale. This type of scales is formed in high-pressure boilers.
4. **Presence of silica:** SiO_2 present even in small quantities, deposits as Calcium silicates ($CaSiO_3$) or Magnesium silicates ($MgSiO_3$). The deposits form hard scale and are very difficult to remove.
- 5.

Disadvantages of Scales:

1. Wastage of heat and fuels: Scales poor thermal conductivity so that rate of heat transformation is reduced.
2. Lowering of boiler safety is due to overheating of the boiler material becomes softer and weaker, which causes distortion of boiler.
3. Decrease in efficiency of the boiler due to scales deposited in the valves and condensers of the boiler cause choking.
4. Danger of explosion which happens the formation of the scales, If the scale formation is soft it can be removed by a scrapper, wire brush.

Prevention of scales:

1. By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing with wire brush.
2. If scale is very hard that is formed by CaCO_3 can be removed by washing with 5-10% HCl and CaSO_4 can be removed with EDTA solution.
- 3.

Q.4 Difference between sludge and scale

Sludge	Scale
Sludge are ooze and slimy precipitate	Scales are hard, adhering crust/coating
Easy to remove	Difficult to remove
Less dangerous	More dangerous
formed at comparatively colder portions of the boiler	formed at comparatively hotter portions of the boiler
Sludge are formed by salts like MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 .	Scales are formed by salts like CaSO_4 , MgOH_2

Q.5 What is Priming and foaming? Explain its cause effects and preventive measure.

Priming: When a boiler produces steam rapidly, some particles of the liquid water are carried along with the steam. This process of "Water-steam" formation is called priming. Priming is caused by the following reasons:

1. The presence of large amount of dissolved solids.
2. High steam velocities.
3. Sudden boiling.
4. Improper boiling design and
5. Sudden increase in steam production rate.

Foaming: The production foam or bubbles in boilers, which do not break easily. Foaming is due to presence of substances like oil and alkali in boiler feed water.

Prevention

1. By removing oil or sludge by addition of coagulants.e.g FeSO_4 , NaAlO_2
2. By addition of antifoaming chemicals e.g. Caster oil

Priming and foaming usually occur together. They are objectionable because

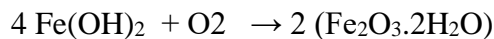
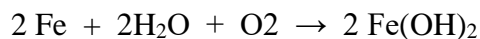
1. Dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This water reduces their efficiency.
2. Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery.

3. Actual height of the water column is judged properly; thereby making the maintenance of the boiler pressure becomes difficult.

Q.6 Write short notes on Boiler Corrosion

Boiler corrosion is decay of boiler material by a chemical or electro-chemical attack by its environment. Main reasons for boiler corrosion are:

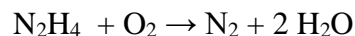
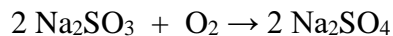
1. **Dissolved oxygen** : Water usually contains about 8 ml of dissolved oxygen per litre at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:



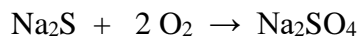
Ferrous hydroxide (Rust)

Removal of dissolved oxygen :

- A. **By adding calculated** quantity of sodium sulphite or hydrazine or sodium sulphide. Thus;



Hydrazine



- B. **By mechanical de-aeration**, i.e., water spraying in a perforated plate-fitted tower, heated from sides and connected to vacuum pump (see Fig. 2). High temperature, low pressure and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water

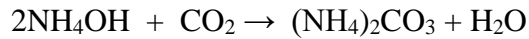
2. **Dissolved carbon dioxide** : CO_2 is carbonic acid,



Which has a slow corrosive effect on the boiler material? Carbon dioxide is also released inside the boiler, if water used for steam generation it contains bicarbonate, e.g.,

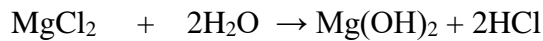
**Removal of CO₂ :**

By adding calculated quantity of ammonia. Thus,

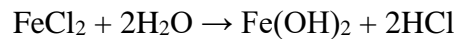
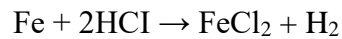


By mechanical-aeration process along with oxygen.

Acids from dissolved salts: Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,



The liberated acid reacts with iron (of the boiler) in chain like reactions producing HCl again and again. Thus



Consequently, presence of even a small amount of MgCl₂ will cause corrosion of iron to a large extent.

Disadvantages/effects

1. Decrease in life of boiler
2. Decrease efficiency
3. Increase repair and maintenance cost
4. Formation of holes and pit
5. Leakage of joints and rivets

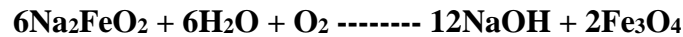
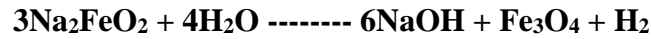
Q.7 Enumerate causes and preventive measures of Caustic embrittlement.**Caustic embrittlement:**

The material of the boiler is weakened and becomes brittle due to the accumulation of caustic substances. It is a form of stress corrosion takes place in boilers operating at high temperature and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.



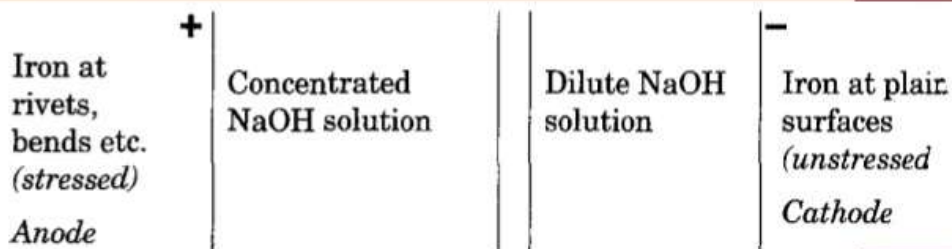
The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water. When concentrations of the NaOH reaches a value of 10% it attacks the metal at the stressed region dissolving it in the form of sodium ferroate (Na_2FeO_2). Sodium ferroate undergoes hydrolysis-depositing magnetite as follows



Mechanistically embrittlement arises due to setting up of concentration cell

CAUSTIC EMBRITTLEMENT

It can be explained by considering the following concentration cell.



Fe surrounded by dil NaOH becomes cathodic side and with conc NaOH becomes anodic side.

Preventive measure

1. Caustic embrittlement can be prevented by the addition of compounds like sodium sulphite, tannin, lignin, phosphates etc. which blocks the cracks thereby preventing the infiltration of alkali.
2. By phosphate conditioning of water

Q.8 Discuss Zeolite process of softening of hard water under following headings

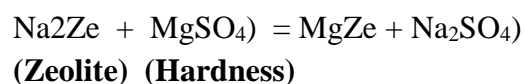
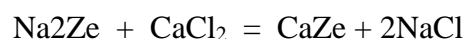
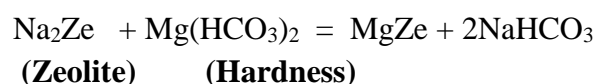
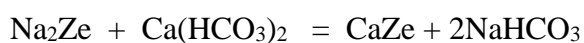
- a. Principle
- b. Process
- c. Softening and regeneration reactions
- d. Advantages

Principle: Zeolite is hydrated sodium alumino silicate. Zeolites are also known as permutits. Zeolite is capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Chemical Structure : $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where $X=2-10$ and $Y=2-6$.

Types of Zeolite Zeolites are of two types: Natural zeolite and Synthetic zeolite

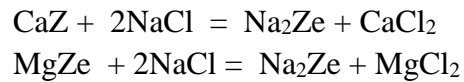
Process : For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions (Ca^{2+} , Mg^{2+} , etc.) are retained by the zeolite as CaZe and MgZe ; while the outgoing water contains sodium salts.

Reactions



Regeneration : After some time, the zeolite is completely is completely converted into calcium and magnesium zeolite and it ceases to soften water, i.e., it gets exhausted. At this stage, the supply

of hard water is stopped and the exhausted zeolite is regenerated by treating the bed with a concentrated (10%) brine (NaCl) solution.



(Exhausted zeolite) (Brine) (Reclaimed (Washings) zeolite) □

The washing (containing CaCl_2 and MgCl_2) are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.

Limitations of process:

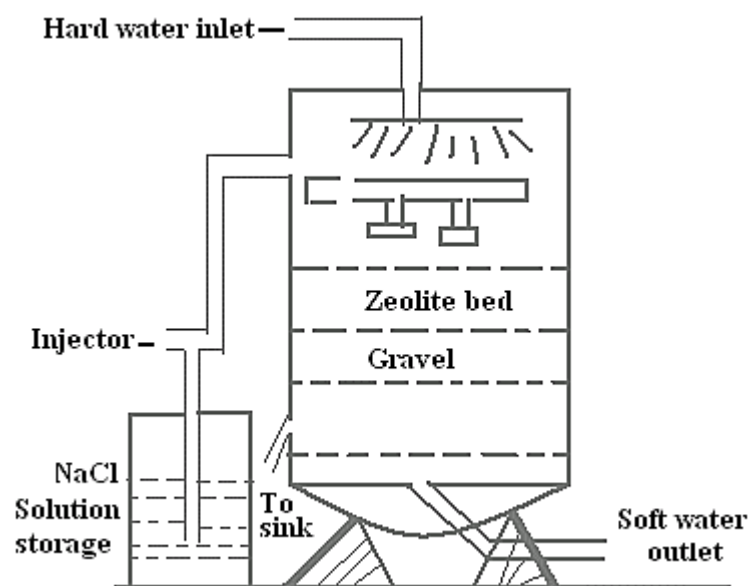
1. If the supply of water is turbid, it must be removed, otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.
2. If water contains large quantities of coloured ions such as Mn^{2+} and Fe^{2+} , they must be removed first, because these ions produce manganese and iron zeolite, which cannot be easily regenerated.
3. Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralised with soda, before admitting the water to the zeolite softening plant.

Advantages of process:

1. It removes the hardness almost completely and water of about 10 ppm hardness is produced.
2. The equipment used is compact, occupying a small space.
3. No impurities are precipitated, so there is no danger of sludge formation in the treated water at a later stage.
5. It is quite clean.
6. It requires less time for softening.
7. It requires less skill for maintenance as well as operation.

Disadvantages of process :

1. The treated-water contains more sodium more sodium salts than in lime-soda process.
2. The method only replaces Ca^{2+} and Mg^{2+} ions, but leaves all the acidic ions (like HCO_3^- and CO_3^{2-}) as such in the softened water.



Q.9 Discuss ion exchange process of softening of hard water under following headings
 a. Principle b. Process c. Softening and regeneration reactions
 d. Advantages

Ans. Ion-exchange or Deionization or Demineralization Process - Recently ion-exchange resins have been used to remove all minerals from water. It is a process by which ions held on a porous, essentially insoluble solid are exchanged for ions in water

Ion-exchange Resin – An ion-exchange resin is a crosslinked organic polymer network having some ionisable group. It may be of two types depending upon the nature of the ionizable group.

(i) Cation Exchange Resin or Cation Exchanger - Such resins have $-SO_3H$, $--COOH$ or $-OH$ (phenolic) group as the ionizable group. Since these resins exchange the cationic portion of minerals by their hydrogen atom, they are known as cation exchangers.

(ii) Anion Exchange Resin or Anion Exchanger – These resins have $-NH_2$, $-NHCH_3$, $-N(CH_3)_2$ or $-OH$ (alcoholic) group. They exchange the anionic portion of the minerals and they are known as anion exchanger.

Uses of Ion-exchange Resin – Water treatment by ion-exchange resin includes softening deionization and de-alkalization of water. Therefore, hard water can be converted into soft water by making use of ion-exchange resins.

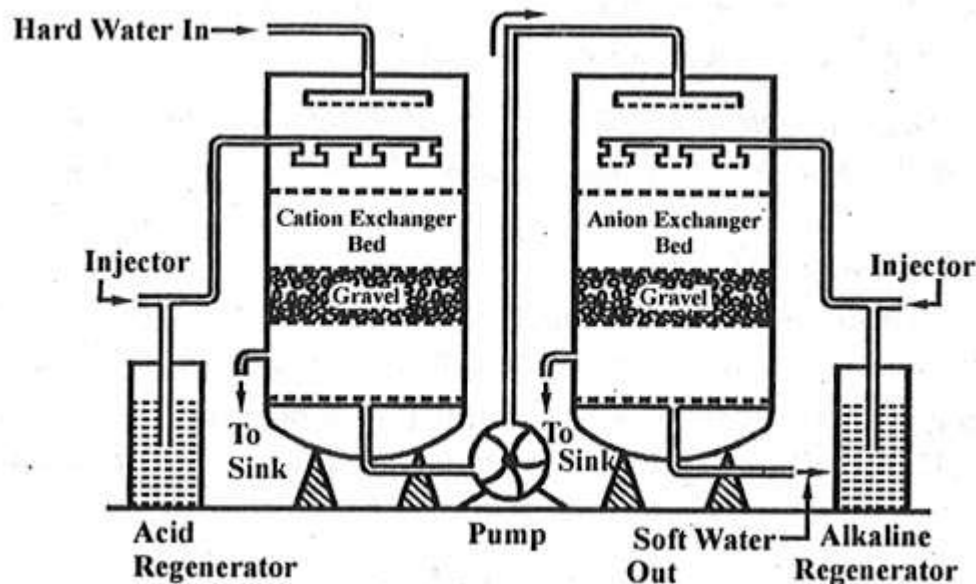
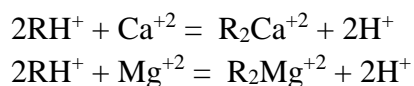


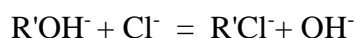
Fig. Demineralization of Water

Process – In this process first we passed hard water through cation exchange column, which removes all the cations (like Ca^{+2} , Mg^{+2} etc.) from it and equivalent amount of H^+ ions are released from this column to water.

Thus,



After this process, hard water is passed through anion exchange column, which removes all the anions (like SO_4^{2-} , Cl^- etc.) from it, and equivalent amount of OH^- ions are released from this column to water. Thus,



H^+ and OH^- ions get combined to produce water molecule



The water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as a deionized or demineralized water.

Advantages

1. It is very effective and efficient method of water softening.
2. The process can be used to soften highly acidic or alkaline waters.
3. It produces water of very low hardness (say 2 ppm).

Disadvantages

1. Expensive
2. Problem of disposal of waste

Q.10 A sample of water is found to contains following dissolving salts in milligrams per litre $Mg(HCO_3)_2 = 73$, $CaCl_2 = 111$, $Ca(HCO_3)_2 = 81$, $MgSO_4 = 40$ and $MgCl_2 = 95$. Calculate temporary and permanent hardness and total hardness.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/L)	Molecular weight of hardness causing salts	Multiplication factor	CaCO ₃ equivalent hardness (mg/L)
$Mg(HCO_3)_2$	73	146	100/146	$73 \times 100 / 146 = 50$
$CaCl_2$	111	111	100/111	$111 \times 100 / 111 = 100$
$Ca(HCO_3)_2$	81	162	100/162	$81 \times 100 / 162 = 50$
$MgSO_4$	40	120	100/120	$40 \times 100 / 120 = 33.3$
$MgCl_2$	95	95	100/95	$95 \times 100 / 95 = 100$
NaCl	5	NaCl does not impart hardness		

$$\begin{aligned}
 \text{Temporary hardness} &= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 \\
 &= 50 + 50 = 100\text{mg/L} \\
 &= 100 \times 0.07^\circ\text{Cl} = 7^\circ\text{Cl} \\
 &= 100 \times 0.1^\circ\text{Fr} = 10^\circ\text{Fr}
 \end{aligned}$$

$$\begin{aligned}
 \text{Permanent hardness} &= \text{CaCl}_2 + \text{MgSO}_4 + \text{MgCl}_2 \\
 &= 100 + 33.3 + 100 = 233.3\text{mg/L} \\
 &= 233.3 \times 0.07^\circ\text{Cl} = 16.33^\circ\text{Cl} \\
 &= 233.3 \times 0.1^\circ\text{Fr} = 23.33^\circ\text{Fr}
 \end{aligned}$$

$$\begin{aligned}
 \text{Total hardness} &= \text{Temporary hardness} + \text{Permanent hardness} \\
 &= 100 + 233.3 = 333.3\text{mg/L} \\
 &= 333.3 \times 0.07^\circ\text{Cl} = 23.33^\circ\text{Cl} \\
 &= 333.3 \times 0.1^\circ\text{Fr} = 33.33^\circ\text{Fr}
 \end{aligned}$$

Q.11 Water quality (fitness) Parameters

Physical- Color, Taste, odor, turbidity, temperature, etc.

Chemical- Hardness, pH, Acidity, Alkalinity, Chlorine, TDS, DO, BOD, COD, Tests for specific chemicals, etc.

Biological- Coliforms (E Coli), Tests for specific pathogens etc.