

SOFTENING METHODS

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. It should, therefore, be freed from hardness-producing salts before it is being put to use. The process of removing hardness-producing salts from water is known as softening of water. In industry three methods are mainly employed for softening of water.

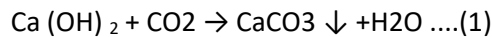
Lime soda process:

In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime $[\text{Ca}(\text{OH})_2]$ and soda $[\text{Na}_2\text{CO}_3]$. Calcium carbonate $[\text{CaCO}_3]$ and magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ are precipitated and removed.

Lime-Soda Softening Soda Softening

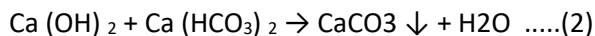
In this process Calcium and Magnesium ions are precipitated by the addition of lime $(\text{Ca}(\text{OH})_2)$ and soda ash (Na_2CO_3) . Following are the reactions that take place in this process:

- As slacked lime is added to a water, it will react with any carbon dioxide present as follows:



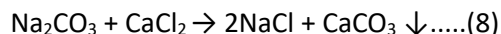
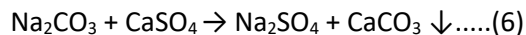
- The lime will react with bicarbonate hardness as follows:

- Removal of temporary hardness



The product magnesium carbonate in equation 3 is soluble. To remove it, more lime is added:

- Removal of permanent magnesium hardness



- Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:
- Lime addition removes only magnesium hardness and calcium carbonate hardness. In equation 5 and 7 magnesium hydroxide is precipitated, however, an equivalent amount of calcium is added. The water

now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5 and 7. Soda ash is added to remove calcium non-carbonate hardness. To precipitate CaCO_3 requires a pH of about 9.5; and to precipitate $\text{Mg}(\text{OH})_2$ requires a pH of about 10.8, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.

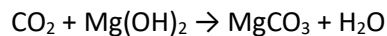
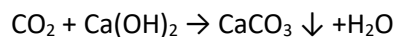
- **The amount of lime required:**

$$\text{lime (meq/l)} = \text{carbon dioxide (meq/l)} + \text{carbonate hardness (meq/l)} + \text{magnesium ion (meq/l)} + 1.25 \text{ (meq/l)}$$

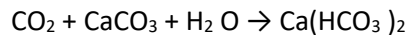
- **The amount of soda required:**

$$\text{soda ash (meq/l)} = \text{non-carbonate hardness (meq/l)}$$

After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate. Recarbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:



Further recarbonation, will bring the pH to about 8.5 and stabilize the calcium carbonate as the following:



It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

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- **Lime**

Lime is commercially available in the forms of:

- quicklime
- hydrated lime

- **Quicklime**

- available in granular form
- contains minimum of 90% CaO
- magnesium oxide is the primary impurity

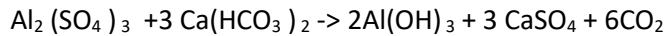
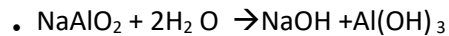
- **Hydrated Lime**

- contains about 68% CaO
- Slurry lime is written as $\text{Ca}(\text{OH})_2$.

A) COLD LIME-SODA PROCESS:

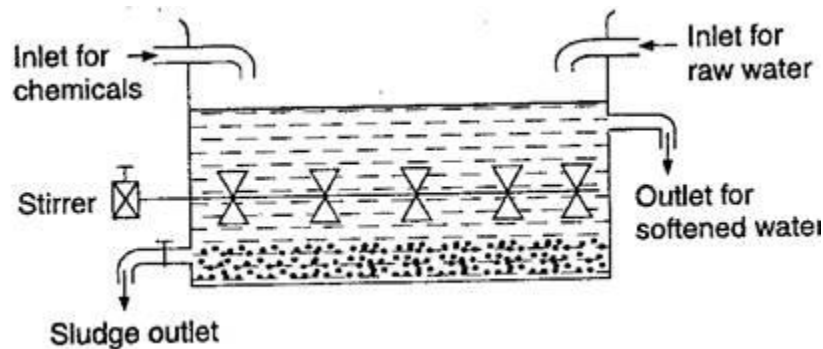
In this Method, Calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and

cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (Like Alum, aluminum sulphate, sodium aluminate, Etc.) Which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminate as coagulant, also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.



Method:

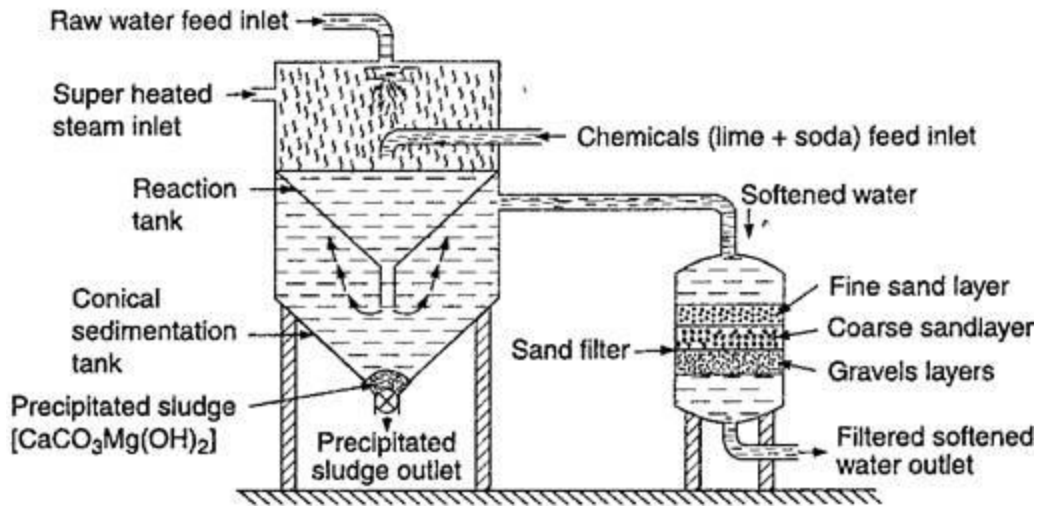
Raw water and calculated quantities of chemicals (Lime+soda+coagulant) are fed from the top into the inner vertical circular chambers, fitted with a vertical rotating shaft carrying a number of paddles , As the raw water and chemicals flow down there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer chamber of the lime the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn off occasionally.



HOT LIME-SODA PROCESS:

Involves in treating water with softening chemicals at a temperature of 80 to 150 C. Since hot process is operated at a temperature close to the boiling point of the solution, so (a) the reaction proceeds faster; (b) the softening capacity of hot process is increased to may fold; (c) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed;(d) much of the gases (Such as CO₂ and air) Driven out of the water;(e) Viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters, and (f) Hot Lime-Soda Produces water of comparatively lower residual hardness of 15 to 30ppm.

Hot lime-soda plant consists essentially of three parts (a) a 'reaction tank' in which raw water, chemicals 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 a very economical
- (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed
- (iii) The process increased the pH value of the treated water, thereby corrosion of the distribution pipes is reduced
- (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced
- (v) To certain extent, iron and manganese are also removed from the water.
- (vi) Due to alkaline nature of treated- water, amount of pathogenic bacteria's in water is considerably reduced

Disadvantages of Lime Soda Process:

For efficient and economical softening, careful operation and skilled supervision is required

- (i) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (ii) This can remove hardness only up to 15ppm, which is not good for boilers.

Limitation of Soda Lime Process:

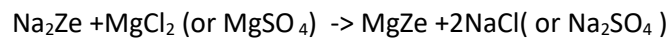
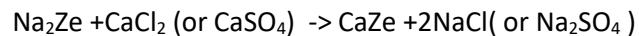
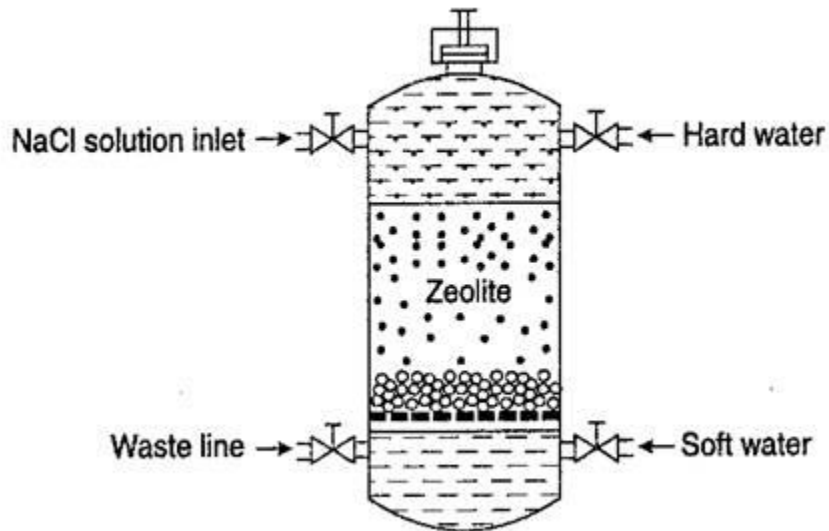
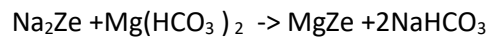
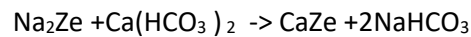
Lime soda softening cannot produce a water at completely free of hardness because of the solubility (little) of CaCO_3 and Mg(OH)_2 . Thus the minimum calcium hardness can be achieved is about 30 mg/L as CaCO_3 , and the magnesium hardness is about 10 mg/L as CaCO_3 . We normally tolerate a final total hardness on the order of 75 to 120 mg/L as CaCO_3 , but the magnesium content should not exceed 40 mg/L as CaCO_3 (because a greater hardness of magnesium forms scales on heat exchange elements).

2) ZEOLITE PROCESS:

Chemical structure of sodium zeolite may be represented as $\text{Na}_2\text{O}_3 \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x=2-10$ and $y=2-6$. Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness, producing ions in water. Zeolites are two types,

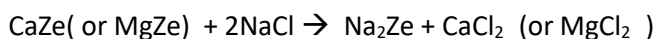
- (i) Natural zeolites are non porous for Ex; Natrolite $\text{Na}_2\text{Al}_3\text{O}_3 \cdot 4\text{SiO}_2 \cdot 22\text{H}_2\text{O}$
- (ii) Synthetic zeolites possess gel structure. Synthetic Zeolites possess higher exchange capacity than natural Zeolites

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 ($\text{Ca}^{+2}, \text{Mg}^{+2}$ etc.) are retained by the zeolite as CaZe and MgZe ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are



REGENERATION:

After Some time the zeolite is completely converted into calcium and magnesium Zeolites 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 reclaimed by treating the bed with a concentrated NaCl solution



The washings are led to drain and the regenerated zeolite bed thus obtained is used again for softening process

Limitations:

- (i) If the supply of water is turbid it will clog the pores of zeolite bed
- (ii) Water contains large quantities of colored ions such as Mn^{+2} and Fe^{+2} they may be removed first because these ions produce Mn and Fe Zeolites, which can't be easily regenerated
- (iii) Mineral acids destroy the zeolite bed

ADVANTAGES:

- (i) It removes the hardness almost completely
- (ii) Equipment occupying a small space
- (iii) Requires less time
- (iv) It is quite clean

DISADVANTAGES:

- (i) Treated water contains more sodium salts than in the soda process
- (ii) The method only replaces Ca^{+2} and Mg^{+2} ions by Na^{+} ions leaving all the acidic ions

Ion exchange or de-ionization or de-mineralization process:

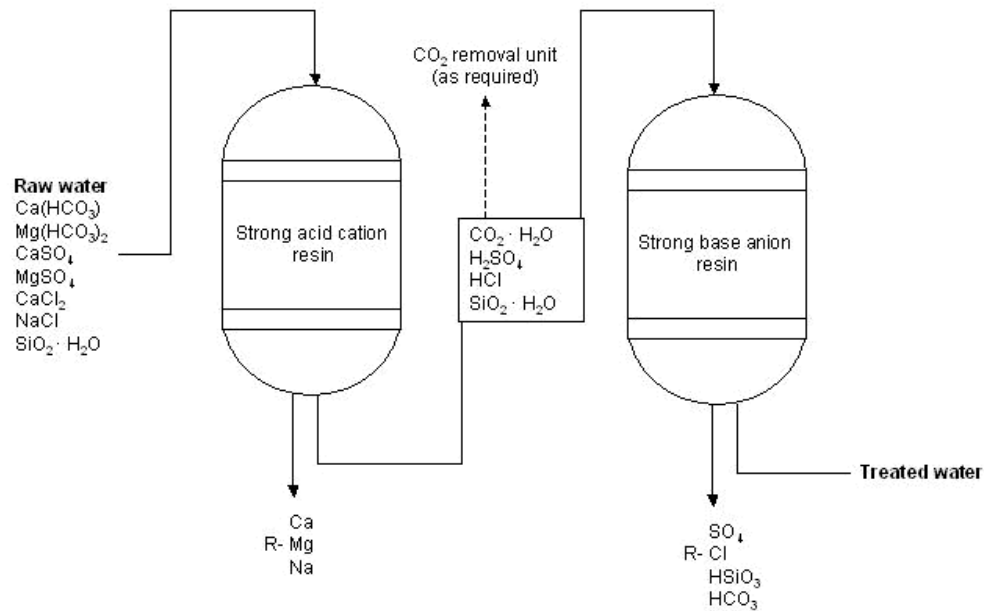
Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the "functional groups" attached to the chains are responsible for the ion-exchanging

properties. Resins containing acidic functional groups ($-COOH$, $-SO_3H$ etc.) are capable of exchanging their H^{+} ions with other cations, which come into their contact; whereas those containing basic functional groups ($-NH_2$ as hydrochloric acid) are capable of exchanging their anions with other anions, which come into their contact.

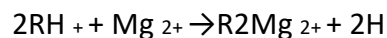
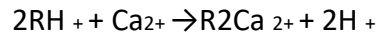
The ion-exchange resins may be classified as: (i) Cation exchange resins (RH^{+}) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation become capable to

exchange their hydrogen ions with the cations present in the raw water

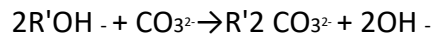
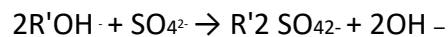
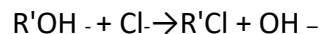
(ii) Anion exchange resins (ROH^{-}) are styrene-divinyl benzene amine-formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. $NaOH$ solution, become capable to exchange their OH^{-} anions with anions present in the raw water.



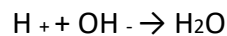
Process: The hard water is passed first through cation exchange column, which removes all the cations like Ca^{2+} , Mg^{2+} , etc., from it and an equivalent amount of H^+ ions are released from this column to water. Thus: 2



The water which is now free from cations, is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- , etc., present in the water and equivalent amount OH^- ions are released from this column to water. Thus:



H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) combine to produce water.



Thus the water coming out from the exchanger is free from all cations as well as anions. Ion-free

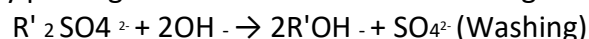
water is known as deionised or demineralised water.

Regeneration: When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or H_2SO_4 . The regeneration can be represented as:



The column is washed with deionized water and such washing (which containing Ca^{2+} , Mg^{2+} , etc. and cation SO_4^{2-}) is passed into sink or drain. The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH . The regeneration can be represented as:



The column is washed with deionized water and such washing (which contains Na⁺ and SO₄²⁻ or Clions) is passed into sink or drain.

Advantages

(1) The process can be used to soften highly acidic or alkaline waters. (2) It produces water of very low hardness (2 ppm) .

Disadvantages

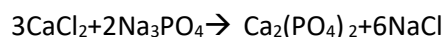
- (1) The equipment is costly and expensive chemicals are needed.
- (2) If water contains turbidity, then the output of the process is reduced.
- (3) The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation followed by filtration.

INTERNAL TREATMENT:

In this process; an ion is prohibited to exhibit its original character by 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 to precipitate the scale forming impurities in the form of sludge, which can be removed by blow down operations, or to convert them into compounds, which will stay in dissolved form in water and they do not cause any harm .

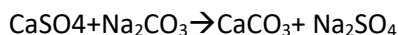
Important Internal treatment methods are:

- (i) **Colloidal conditioning:** In low pressure boilers, scale formation can be avoided by adding organic substances like Kerosene, tannin ,agar-Agar etc; which get coated over the scale firming precipitates, there by yielding coated non sticky and loose deposits
- (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

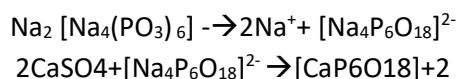


The main phosphates employed are (a) NaH₂PO₄ (b) Na₂HPO₄ (c) Na₃PO₄

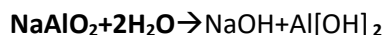
- (iii) **Carbonate Conditioning:** In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water, then CaSO₄ converted into CaCO₃ in equipment CaCO₃ forms loose sludge



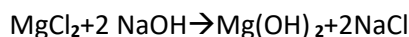
- (iv) **Calgon Conditioning:** Involves in adding calgon [(NaPO₃)₆] to boiler water then it forms soluble complex compound with CaSO₄



- (v) **Treatment with sodium aluminate (NaAlO₂).** Sodium aluminate gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminium hydroxide



The NaOH, so formed precipitates some of the magnesium as Mg(OH)₂ i.e.;



The precipitate of Mg(OH)₂ and Al(OH)₃ produced inside the boiler entraps finely suspended and colloidal impurities including oil drops and silica.

• Potable water

The water which is fit for human consumption is known as potable water. Municipalities have to supply potable water, i.e., water which is safe to human consumption should satisfy the following essential requirements

1. It should be sparkling clear and odourless.
2. It should be pleasant in taste
3. It should be perfectly cool
4. Its turbidity should not exceed 10 ppm
5. It should be free from objectionable dissolved gases like hydrogen sulphide.
6. It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
7. Its alkalinity should not be high. Its pH should not be above 8.0
8. It should be reasonably soft
9. Its total dissolved solids should be less than 500 ppm
10. It should be free from disease-producing micro-organisms.

Purification of domestic water for domestic use:

For removing various types of impurities in the natural water from various sources, the following

treatment process is employed;

Removal of suspended impurities :

The treatment water for municipal supply involves the following steps:

1.Screening :

It is a process of removing the floating materials like , leaves , wood pieces ,etc., from water. Here water is passed through a screen having a number of holes .

2.Aeration :

The process of mixing air with water is called aeration; here the gases like CO₂, H₂S and other volatile impurities responsible for the bad taste and odour, are removed; further

ferrous and manganese salts are converted into insoluble ferric and manganic salts .

3.Sedimentation :

In this process suspended impurities are removed by keeping the water undisturbed for 2 – 6 hours in a tank. This removes only 75 % of the suspended *impurities*.

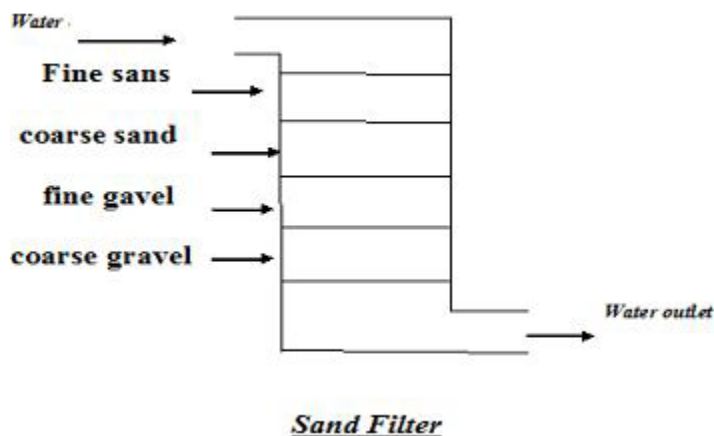
4.Coagulation :

In this method by adding coagulants like aluminium sulphate, the colloidal impurities like finely divided clay, silica, etc., are also removed. The aluminium sulphate hydrolysed to give gelatinous precipitate $\text{Al}(\text{OH})_3$; The suspended impurities adhere to the precipitate and settle down at the bottom.



5.Filtration :

The bacteria, colour, taste, odour and suspended impurities are removed by passing the water through the layers of fine sand, coarse sand and fine gravel and coarse gravel successively placed in a filter tank.



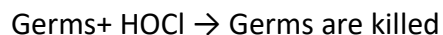
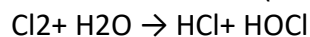
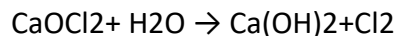
After a long time the rate of filtration is ceased as the holes in the filter are blocked by the impurities; so filtration is stopped and the top concentrated sand layer is scrapped off and replaced by fresh sand .

Removal of micro-organisms:

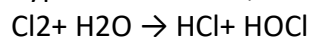
The process of destroying /killing the disease producing bacteria, micro-organisms, etc., from the water and making it safe for the use, is called disinfection.

a. Boiling: By boiling water for 10-15 minutes, all the disease producing bacteria is killed and the water becomes safe for use.

b. Adding bleaching powder: In small water works, about 1 kg of bleaching powder per 1000 kiloliter of water is mixed and allowed to standing undisturbed for several hours. The chemical action produces hypochlorous acid (a powerful germicide)



c. Chlorination: Chlorination (either gas or in concentrated solution form) produces hypochlorous acid, which is a powerful germicide.



Bacteria + HOCl → Bacteria are destroyed

Break point chlorination (or) or free residual chlorination :

It involves addition of sufficient amount of chlorine to oxidize: (a) organic matter (b) reducing substance and (c) free ammonia in raw water; leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing bacteria. The addition of chlorine at the dip or break is called “break point” chlorination. This indicates the point at which free residual chlorine begins to appear..

Advantages:

- (1) It oxidizes completely organic compounds, ammonia and other reducing compounds.
- (2) It removes color, odour and taste of water.
- (3) It removes completely all the disease causing bacteria/micro-organism
- (4) It prevents the growth of any weeds in water.

Using Chloramine (ClNH₂):

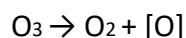
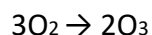
When chlorine and ammonia are mixed in the ratio of 2:1 by

volume, chloramine is formed. $\text{Cl}_2 + \text{NH}_3 \rightarrow \text{ClNH}_2 + \text{HCl}$

Chloramine is a better bactericidal than chlorine.

Disinfection by Ozone:

Ozone gas is an excellent disinfectant, which is produced by passing silent electric discharge through cold and dry oxygen.



Desalination of brackish water

The process of removing common salt (NaCl) from the water is known as desalination. Water containing high concentration of dissolved salts with a peculiar salty taste is called brackish water. Sea water is an example containing 3.5% of dissolved salts. The common methods for the

desalination of brackish water are;

Electrodialysis:

It is a method in which the ions are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair.

An Electrodialysis cell consists of a large number of paired sets of rigid plastic membranes.

Hard water is passed between the membrane pairs and an electric field is applied perpendicular to the direction of water flow. Positively charged membrane and negatively charged membrane repel positively charged ions and negatively charged ions respectively to pass through. So, in one

compartment of the cell, the salt concentration decreases while in the adjacent compartment it increases

Thus, we get alternative stream of pure water and concentrated brine. Advantages: 1. It is most compact unit

Reverse osmosis:

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrate sides, due to osmosis. If, however a

hydrostatic pressure in excess to osmotic pressure is applied on the concentrated side, the solvent

flow is reversed, i.e, solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis.(RO)

Thus in reverse osmosis method, pure solvent is separated from its contaminants, rather than removing contaminants from the water. The membrane filtration is sometimes also called superfiltration or hyper filtration.

METHOD:

In this process, pressure is applied to the sea water or impure water to force the pure water content of it out the semi-permeable membrane, leaving behind the dissolve solids. The principle

of reverse osmosis as applied for treating saline/sea water The membrane consists of very thin film of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

ADVANTAGES

1. Reverse osmosis possesses distinct advantages of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization.
3. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.
4. The life time of membrane is quite high, about 2 years,
5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
6. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining grounds at present for converting sea water into drinking water and for obtaining water for very high –pressure boilers.