Module 2

Water softening methods: - Lime-soda, Zeolite and ion exchange processes and their applications.

Specifications of water for domestic use (ICMR and WHO);

Unit processes involved in water treatment for municipal supply - Sedimentation with coagulant- Sand Filtration - chlorination;

Domestic water purification – Candle filtration- activated carbon filtration; Disinfection methods- Ultrafiltration, UV treatment, Ozonolysis, Reverse Osmosis; Electro dialysis

Water Softening methods

- The process of removing the hardness producing substance from the water is called softening of water
- In Industry three main methods are employed for softening of water
  - Lime soda process
  - Zeolite (permutit) process
  - Ion-exchange and Mixed bed ion-exchange process

Lime-Soda process

Soluble calcium and magnesium salts in water are chemically converted into insoluble compounds by adding calculated amount of lime [$Ca(OH)_2$] and Soda [Na_2CO_3]. Calcium carbonate [$CaCO_3$] and Magnesium hydroxide [$Mg(OH)_2$] so precipitated, are filtered off.

1. Lime soda

a) Batch process
b) continuous process

- Cold lime-soda
- Hot lime-soda

Lime Soda Process - Reactions of Lime and Soda

Reaction of Perm. Ca^{2+}

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^{+}$$

Reaction of Perm. Mg^{2+}

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Ca^{2+} + Mg(OH)_2$$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^{+}$$

Reaction of HCO_3^- (ex. NaH CO_3)

$$2(HCO_3^-) + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + CO_3^{2-}$$

Reaction of $Ca(HCO_3)_2$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

Reaction of $Mg(HCO_3)_2$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O + Mg(OH)_2$$

Reaction of CO_2

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

Reaction of H^+

$$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$

Reactions of Coagulants

Reaction of $FeSo_4$

$$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2 + Ca^{2+}$$

$$Fe(OH)_2 + H_2O + \mathbf{O}_2 \longrightarrow 2Fe(OH)_3$$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$

Reactions of $Al_2(So_4)_3$

$$2Al^{3+} + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3Ca^{2+}$$

$$3\ Ca^{2+} + 3Na_2CO_3 \longrightarrow 3\ CaCO_3 + 6Na^{+}$$

Reactions of $NaAlO_2$

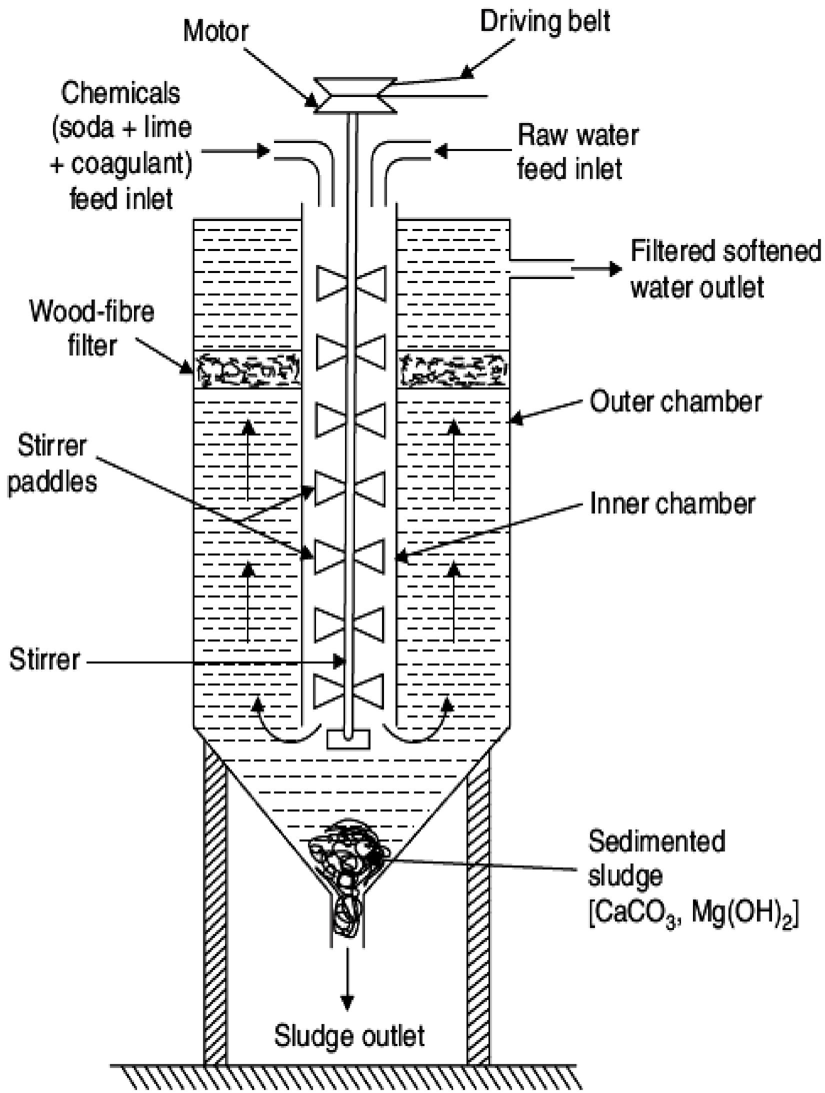
$$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$$

Lime requirement for softening

$$= \frac{74}{100}\left\{ \begin{array}{l} \text{Temp } Ca^{2+} + 2 \text{ X Temp } Mg^{2+} + \text{Perm.}(Mg^{2+} + Fe^{2+} + Al^{3+}) + CO_2 + H^{+} \\ +\ HCO_3^{-} - NaAlO_2 \end{array} \right\}$$

Soda requirement for softening

$$= \frac{106}{100}\left\{ \text{Perm. } (Ca^{2+} + Mg^{2+} + Fe^{2+} + Al^{3+}) + H^{+} - HCO_3^{-} \right\}$$



Continuous cold lime-soda softener.

- Occurring at room temperature
- precipitate formed are finely divided hence do not settle down easily
- It is essential to add small amount of coagulant (alum, sodium aluminate)
- Coagulant hydrolyse to form gelatinous ppt. and entraps the fine ppt.
- $NaAlO_2 + H_2O \rightarrow NaOH + Al(OH)_3$
- It provides water with a residual hardness of 50 to 60 ppm

Hot lime-soda process

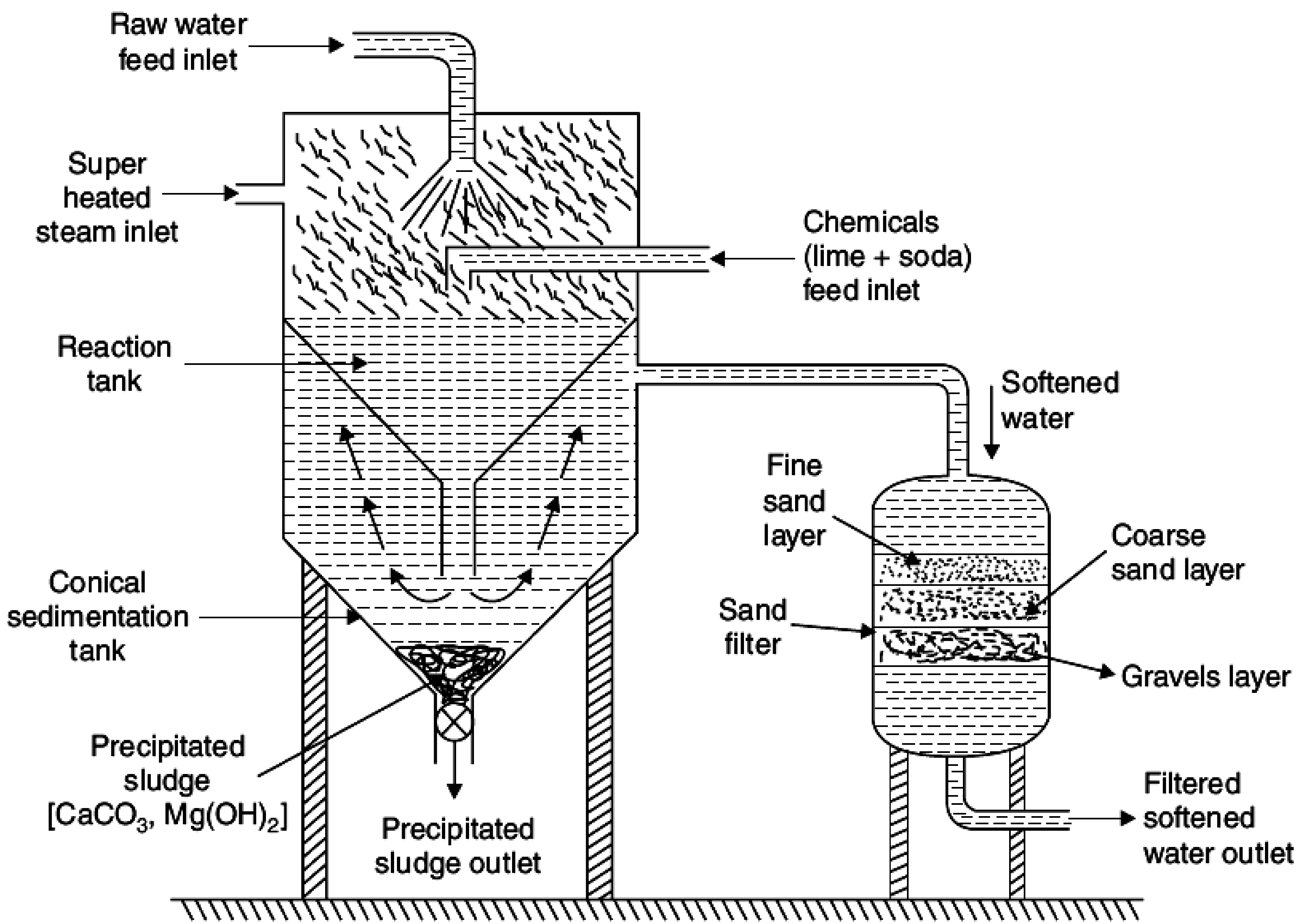
Hot lime-soda process consists of three parts:

a) Reaction tank to mix all ingredients

b) Conical sedimentation vessel where the sludge settles down

c) Sand filter where sludge is completely removed

- **Occurring at 80 to 150 °C close to the boiling point of the solution**
- **Reaction proceed faster**
- **The precipitate and sludge formed settle down rapidly so no coagulant needed**
- **Viscosity of the softened water is lower, so filtration of water becomes much easier**
- **Produce water contain the residual hardness of 15 to 30 ppm**



Continuous hot lime-soda softener.

Hot Lime-Soda Process

Advantages

(*i*) the precipitation reaction becomes almost complete.
(*ii*) the reaction takes place faster.
(*iii*) the sludge settles rapidly.
(*iv*) no coagulant is needed.
(*v*) dissolved gases (which may cause corrosion) are removed.
(*vi*) viscosity of soft water is lower, hence filtered easily.
(*vii*) Residual hardness is low compared to the cold process.

Hot lime-soda process consists of three parts:

(*a*) 'Reaction tank' in which complete mixing of the ingredients takes place.
(*b*) 'Ionical sedimentation vessel' where the sludge settles down and
(*c*) 'Sand filter' where sludge is completely removed.

The soft water from this process is used for feeding the boilers

Hot Lime-Soda Process

Advantages Include:

(*i*) Lime soda process is economical.
(*ii*) The process improves the corrosion resistance of the water.
(*iii*) Mineral content of the water is reduced.
(*iv*) pH of the water rises, which reduces the content of pathogenic bacteria.

Disadvantages Include:

(*i*) Huge amount of sludge is formed and disposal is difficult.
(*ii*) Due to residual hardness, water is not suitable for high pressure boiler.

Advantages & disadvantages of lime-soda process:

Advantages of Lime – soda process:

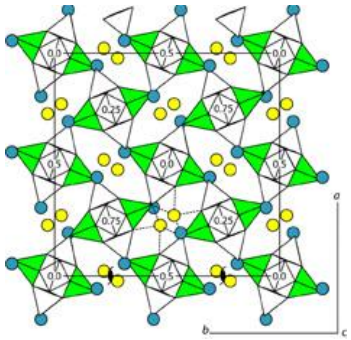
- Economical
- Process improves the corrosion resistance of water
- Mineral content of water is reduced
- pH of water raises thus reducing content of pathogenic bacteria
- No skilled labour is required

Disadvantages of Lime – soda process:

- Huge amount of sludge is formed and its disposal is difficult
- Due to residual hardness, water is not suitable for high pressure boilers

Zeolite or Permutit Process

- Zeolite is hydrated sodium aluminium silicate having a general formula, $Na_2OAl_2O_3.xSiO_2.yH_2O$.
- **It exchanges Na^+ ions for Ca^{2+} and Mg^{2+} ions**.
- **Common Zeolite is $Na_2OAl_2O_3.3SiO_2.2H_2O$ known as natrolith.**
- Other gluconites, green sand (iron potassium phyllosilicate with characteristic green colour, a mineral containing Glauconite)etc. are used for water softening.
- **Artificial zeolite used for water softening is Permutit.**
- These are porous, glassy particles having higher softening capacity compared to green sand.
- They are prepared by heating china clay (hydrated aluminium silicate), feldspar ($KAlSi_3O_8$-$NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) are a group of rock-forming tectosilicate minerals which make up as much as 60% of the earth’s crust) and soda ash (Na_2CO_3)

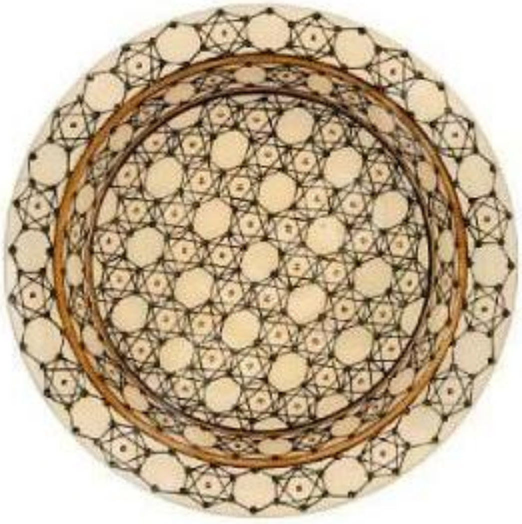


Natural Zeolite

Natrolite

Artificial Zeolite

Artificial zeolite used for softening purpose is permutit. These are porous and glassy and have greater softening capacity than green sand. They are prepared by heating together with china clay, feldspar and soda ash.



China clay $Al_2Si_2O_5(OH)_4$

Feldspars ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$)

Zeolite process

- **Method of softening:**

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow 2\ NaHCO_3 + CaZe$$

$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow 2\ NaHCO_3 + MgZe$$

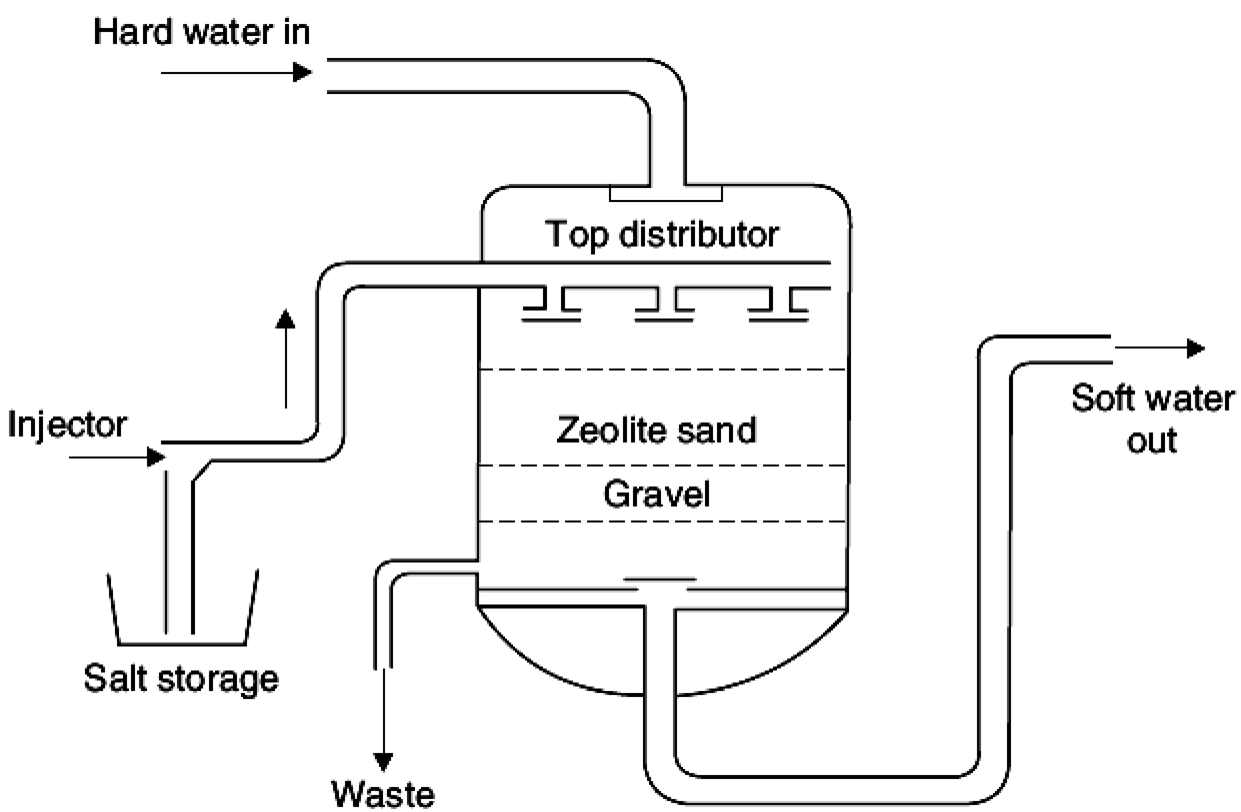
$$Na_2Ze + CaSO_4 \longrightarrow Na_2SO_4 + CaZe$$

$$Na_2Ze + CaCl_2 \longrightarrow 2\ NaCl + CaZe$$

- **Regeneration of Zeolite:**

$$CaZe\ (or)\ MgZe + \underset{\substack{\downarrow \\ \text{Brine solution}}}{2\ NaCl} \longrightarrow Na_2Ze + CaCl_2\ or\ MgCl_2$$

Zeolite process equipment diagram



Softening of hard water by permutit process.

Zeolite Process

Advantages:

- Residual hardness of water is about 10 ppm only
- Equipment is small and easy to handle
- Time required for softening of water is small
- No sludge formation and the process is clean
- Zeolite can be regenerated easily using brine solution
- Any type of hardness can be removed without any modifications to the process

Disadvantages:

- Coloured water or water containing suspended impurities cannot be used without filtration
- Water containing acidic pH cannot be used for softening since acid will destroy zeolite.

Ion-Exchange Process

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

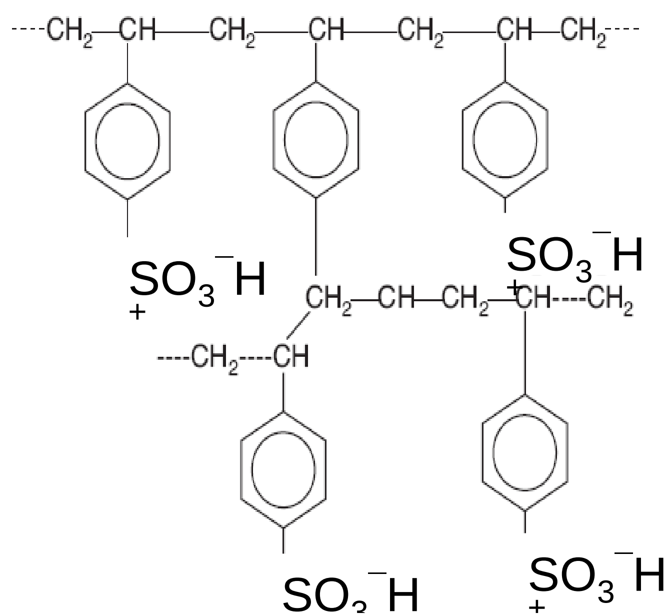
- o Cation exchange resins will exchange cations with H^+.
- o Anion exchange resins will exchange anions with OH^-.
- o Functional groups present are responsible for ion-exchange properties.
- o Acidic functional groups (-COOH, -SO_3H etc.) exchange H^+ for cations &
- o Basic functional groups (-NH_2, =NH etc.) exchange OH^- for anions.

Ion-Exchange Process

A. Cation-exchange Resins(RH^+):

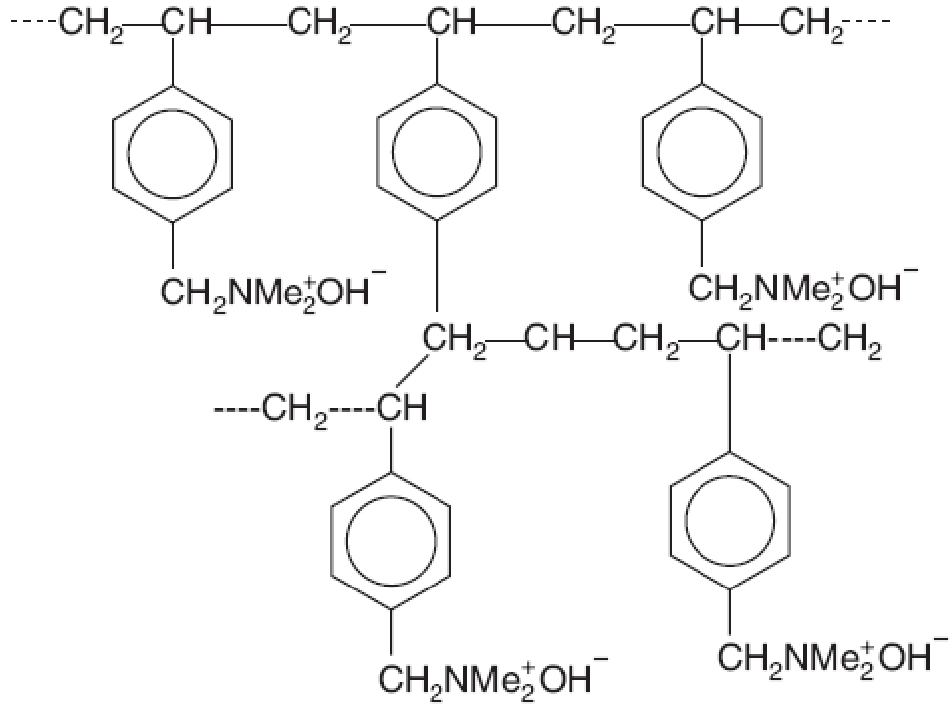
- Styrene divinyl benzene copolymers

- which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water



cation exchange resin

Ion Exchange Process



Anion exchange resin

Styrene-divinyl benzene or amine-formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phophonium or tertiary sulphonium groups as an integral part of the resin matrix. These after treatment with dil. NaOH solution capable to exchange their OH^- ions with the anions in the water

Ion Exchange Process

The Process of Ion-exchange is:

$$2\,RH^{+} + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2\,H^{+} \text{ (Cation exchange)}$$

$$R'OH^{-} + Cl^{-} \longrightarrow R'^{+}Cl^{-} + OH^{-} \text{ (anion exchange)}$$

$$2\,R'OH- + SO_4^{2-} \longrightarrow R'_2\,SO_4^{2-} + 2\,OH^{-} \text{ (anion exchange)}$$

$$2\,R'OH- + CO_3^{2-} \longrightarrow R'2\,CO_3^{2-} + 2\,OH^{-} \text{ (anion exchange)}$$

Finally,

$$H^{+} + OH^{-} \longrightarrow H_2O$$

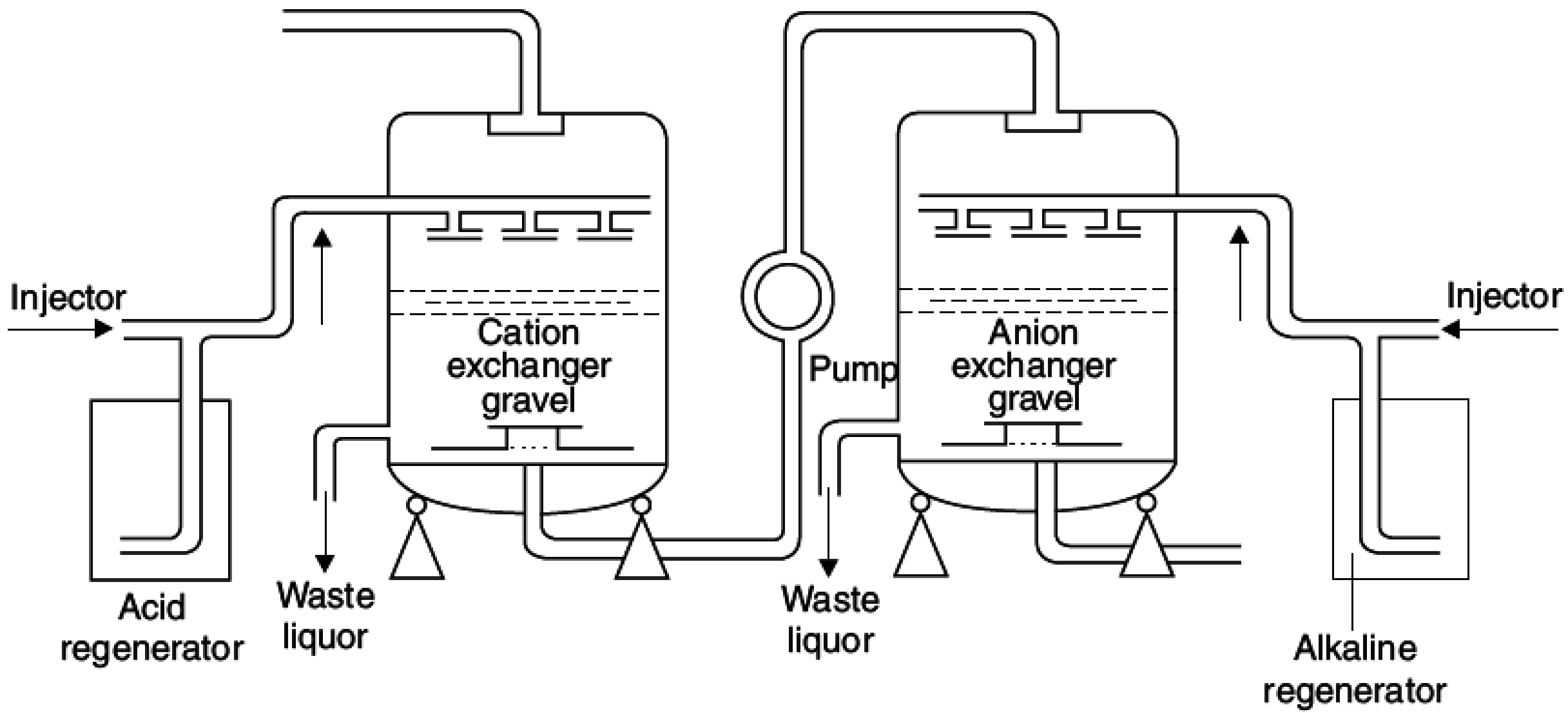
Regeneration of exhausted resins:

Saturated resins are regenerated by treating with strong mineral acid or alkali respectively

$$R_2Ca^{2+}/R_2Mg^{2+} + 2H^{+} \longrightarrow 2\,RH^{+} + \underset{\text{(washings)}}{Ca^{2+}/Mg^{2+}} \text{ (Strong acid)}$$

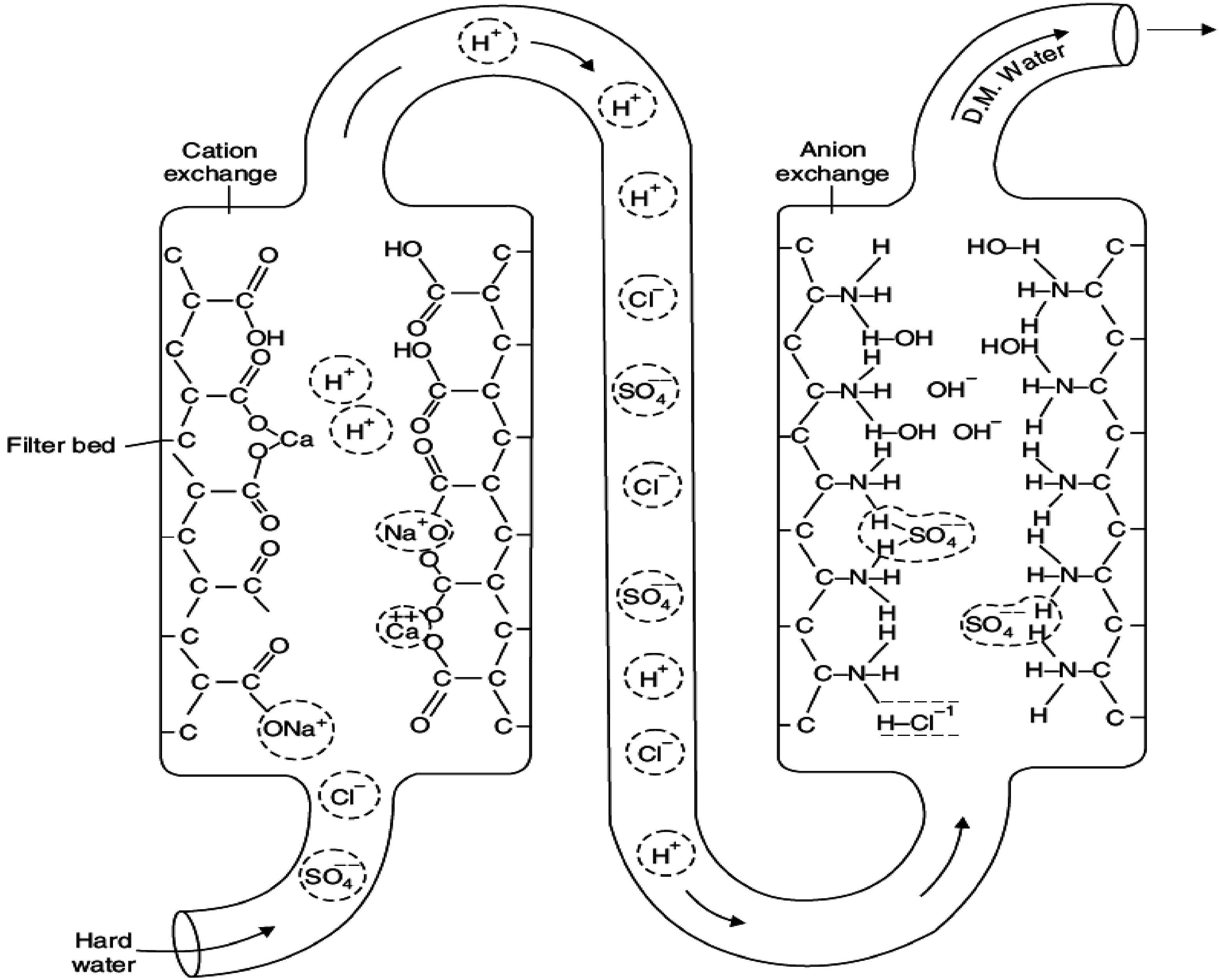
$$R'_2\,SO_4^{2-} + 2\,OH^{-} \longrightarrow 2\,R'OH^{-} + \underset{\text{(washings)}}{SO_4^{2-}} \text{ (Strong base)}$$

Ion-exchange process



Demineralisation of water.

Note: Hard water should be first passed through the cation exchanger and then Anion exchanger to avoid hydroxides of Ca^{2+} and Mg^{2+} getting formed



Cation exchange reaction:

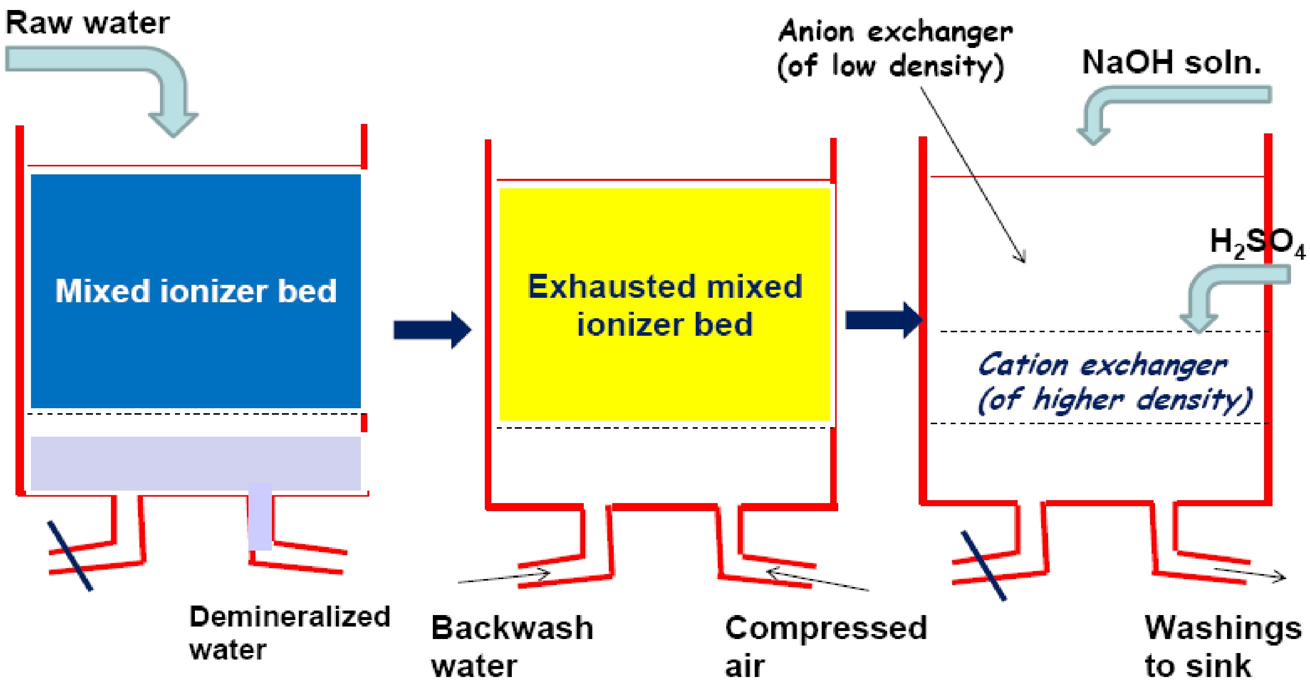
$$2R^-H^+ + Ca^{+2} \rightleftharpoons CaR_2 + 2H^+$$

Anion exchange reaction:

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3OH^-$$

$$R\overset{+}{N}H_3OH^- + Cl^- \rightleftharpoons R\overset{+}{N}H_3Cl^- + OH^-$$

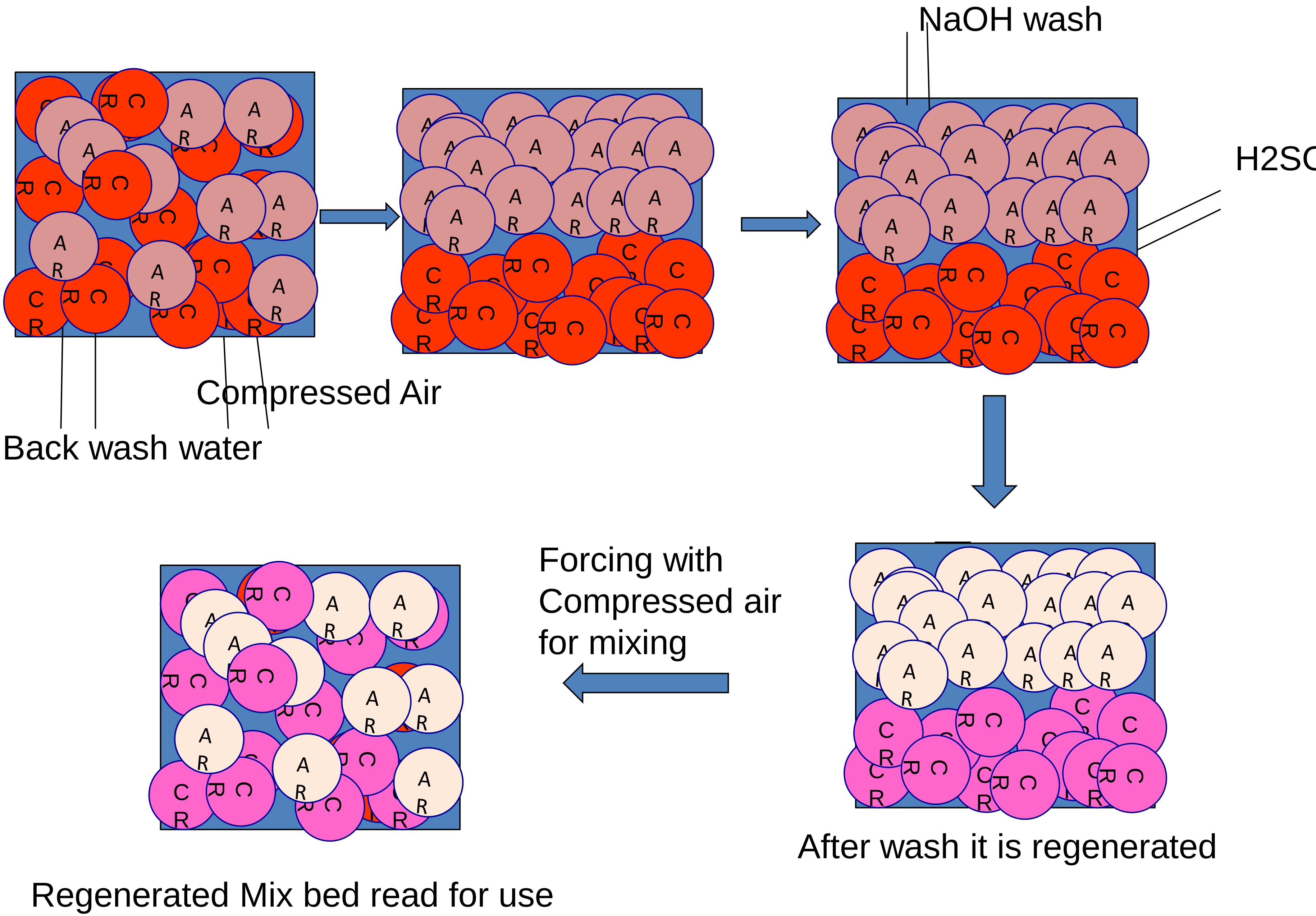
Mixed Bed Deionizer



Containing an intimate mixture of hydrogen exchanger and strongly basic anion exchanger

The outgoing water from the mixed-bed contains even less than 1 ppm of dissolved salts

Mix bed to be regenerated



The mixed bed deionizer consist of cation and anion exchange resins mixed together in a single pressure vessel.
When water is passed through mixed bed it comes in contact, a number of times, with the two kinds of exchanges alternatively. As a result the net effect of mixed bed exchanger is equivalent to passing water through a series of several cation and anion exchangers.
The quality of water obtained from mixed bed is appreciably higher than the water produced from two bed plants.
Mixed bed exchange produce water with hardness less than 1 ppm

Regeneration:

The mixed bed is back washed by forcing water in the upward direction. This separate the cation and anion exchanges from the mixed bed. Being lighter the cation resin occupes upper part and the denser on at the bottom. Now they layers will be washed with NaOH and H2SO4 respectively to regenerate anion and cation exchange resins. After regeneration again they are mixed by forcing compressed air.

Generally soften water (eg RO, etc) will be further purified by this method

Advantages & Disadvantages of ion-exchange process

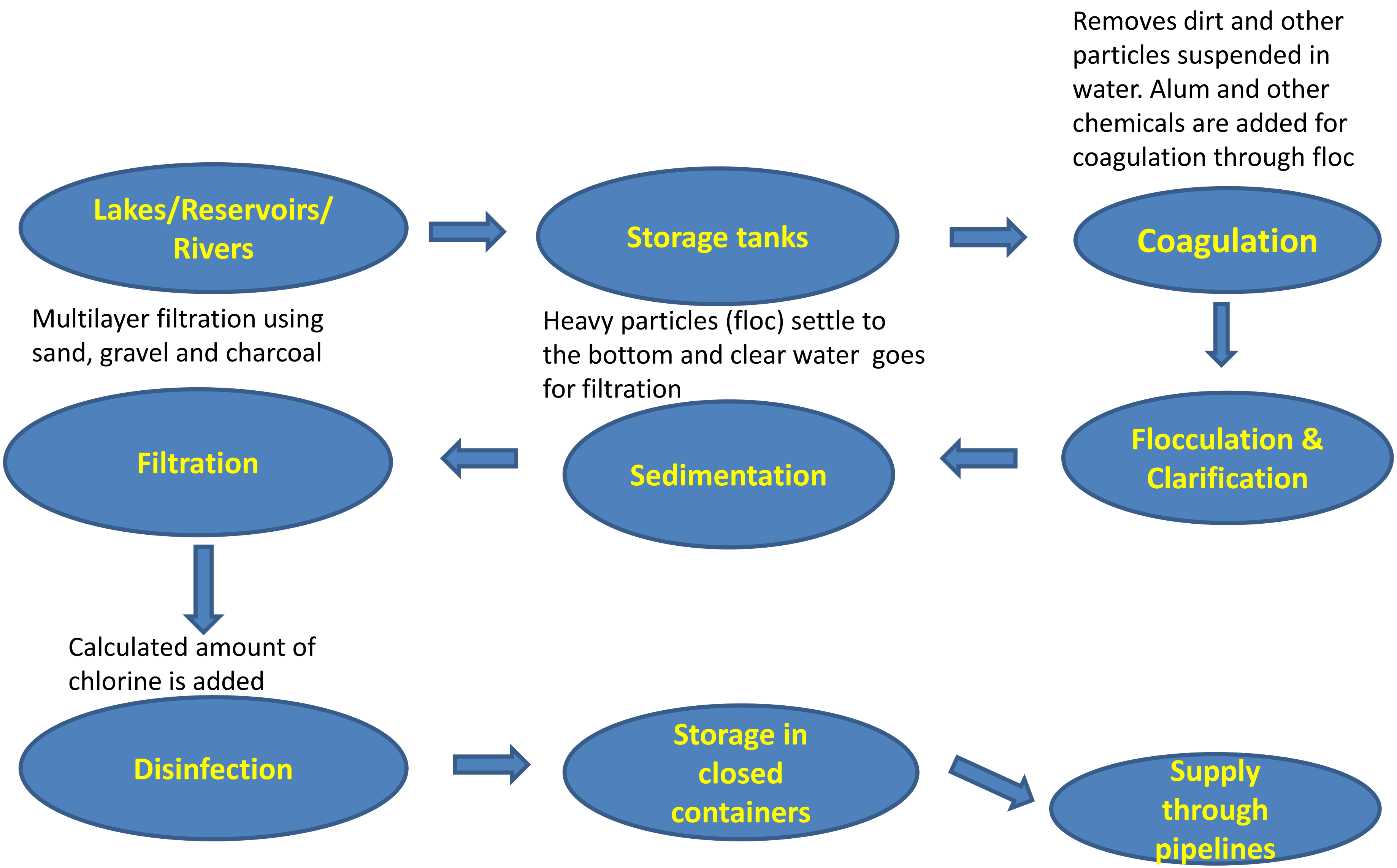
- **Advantages:**
  - Can be used for highly acid and highly alkaline water
  - Residual hardness of water is as low as 2 ppm.
  - Very good for treating water for high pressure boilers

- **Disadvantages:**
  - Expensive equipment and chemicals
  - Turbidity of water should be < 10 ppm. Otherwise output will reduce; turbidity needs to be coagulated before treatment.
  - Needs skilled labour

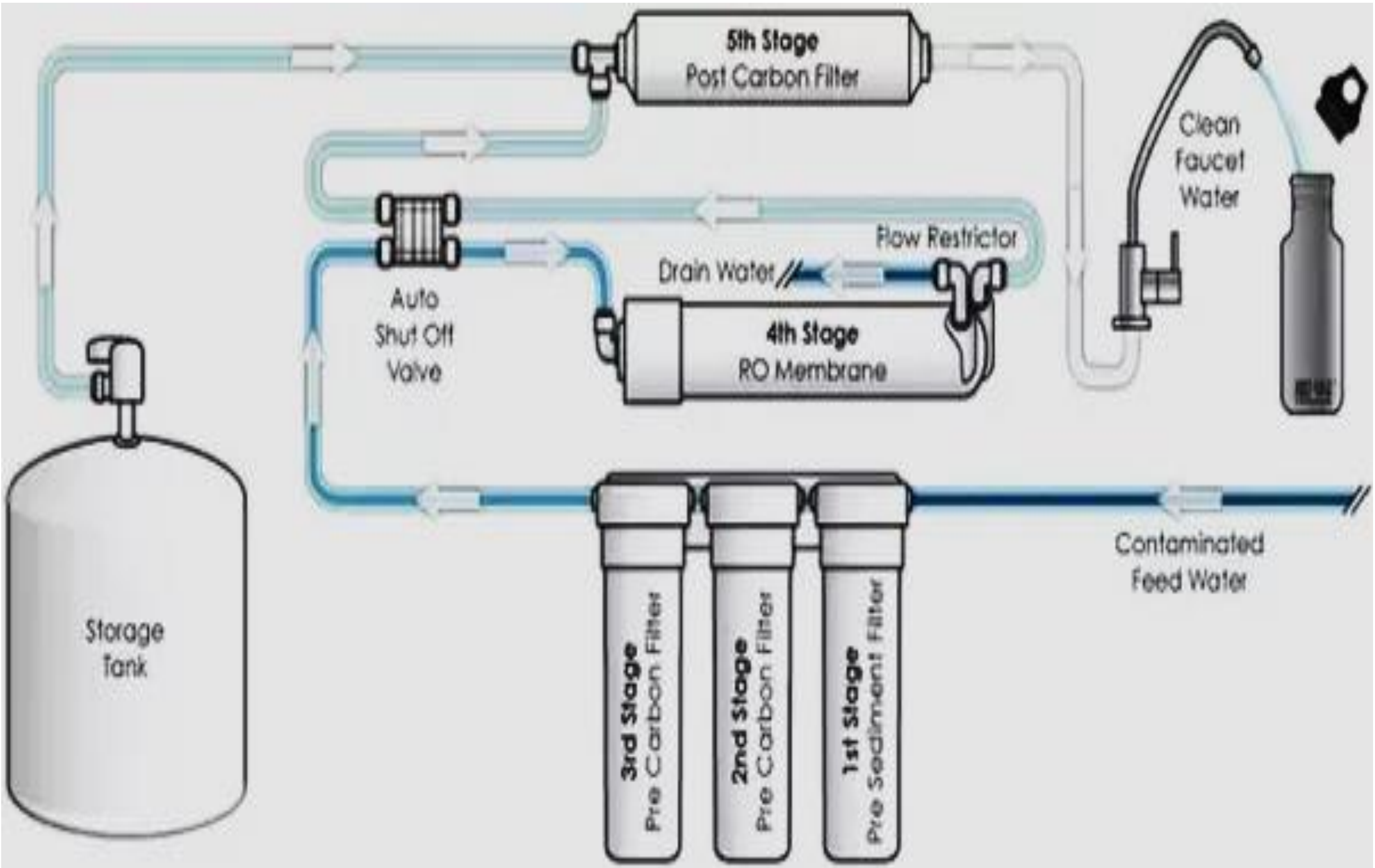
Specifications of different materials in drinking water (ICMR and WHO)

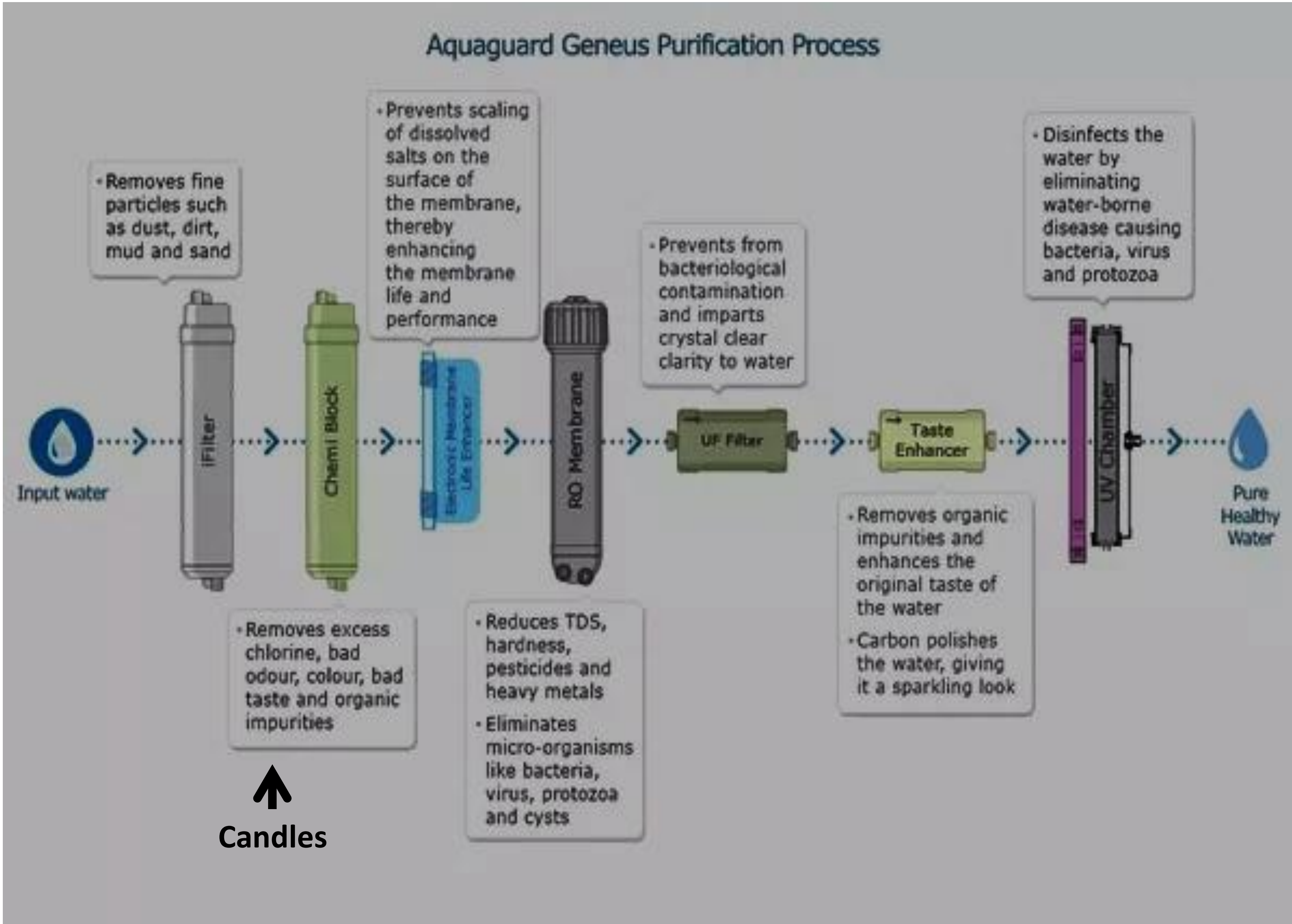
S.No.	Parameter/Material	WHO Standards/ppm	ICMR/BIS Standards/ppm
1	Colour	Clear	Clear
2	Odour	Pleasant	Pleasant
3	Turbidity	2.5	2.5
4	pH	6.0 – 8.5	6.0 – 8.5
5	TDS	300	500
6	Total Hardness as $CaCO_3$	200	300
7	Calcium	75	75
8	Chlorides	200	200
9	Sulphates	200	200
10	Fluoride	0.5	1.0
11	Mercury	0.006	0.001
12	Cadmium	0.003	0.01
13	Arsenic	0.01	0.02
14	Chromium as hexavalent	0.01	0.1
15	Lead	0.01	0.01
16	E.Coli	No colony Should be present in 100 mL water	No colony Should be present in 100 mL water

Water treatment for municipal supply



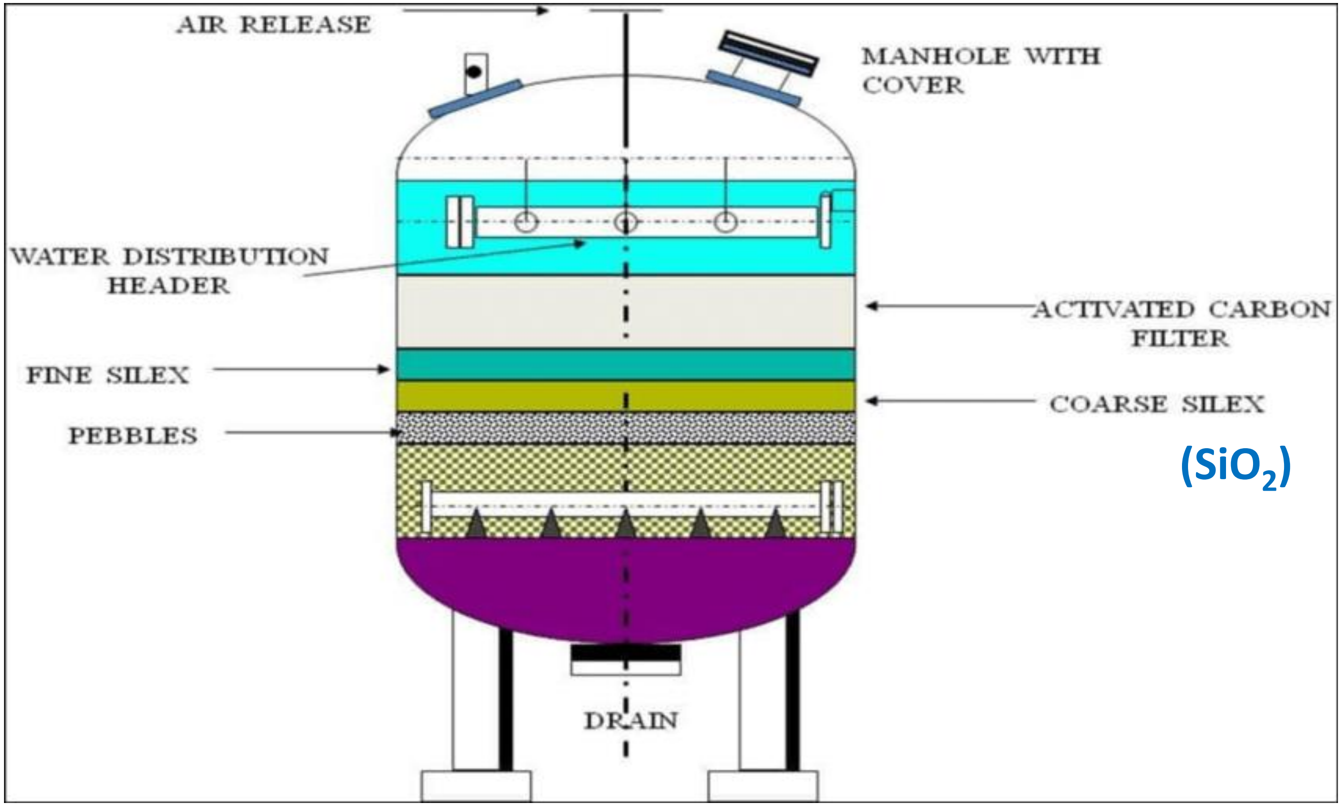
Domestic water purification system




Aquaguard Geneus Purification Process
Input water
iFilter
• Removes fine particles such as dust, dirt, mud and sand
Chemi Block
• Removes excess chlorine, bad odour, colour, bad taste and organic impurities
• Prevents scaling of dissolved salts on the surface of the membrane, thereby enhancing the membrane life and performance
Electronic Membrane Life Enhancer
RO Membrane
• Reduces TDS, hardness, pesticides and heavy metals
• Eliminates micro-organisms like bacteria, virus, protozoa and cysts
UF Filter
• Prevents from bacteriological contamination and imparts crystal clear clarity to water
Taste Enhancer
• Removes organic impurities and enhances the original taste of the water
• Carbon polishes the water, giving it a sparkling look
UV Chamber
• Disinfects the water by eliminating water-borne disease causing bacteria, virus and protozoa
Pure Healthy Water
Candles

Activated Carbon Filtration

- **Activated carbon filters** are generally used in the process of removing organic compounds and/or extracting free chlorine from water.
- Coconut shells and coal (anthracite or bituminous) are both organic sources of activated carbon.



Working Mechanism in the fabrication of Activated Carbon

- **Carbon forms when an organic source is burned in an environment without oxygen. This process leaves only about 30% of the organic mass intact, driving off heavy organic molecules.**

- **Prior to being used for water treatment, the organic mass must then be "activated by either Steam Activation (800°C-1000°C) or Chemical Activation (a powerful dehydrating agent like phosphoric acid (P_2O_5) or zinc chloride ($ZnCl_2$)."**

- **The process of activation opens up the carbon's massive number of pores and further drives off unwanted molecules. The open pores are what allow the carbon to capture contaminants, through adsorption.**

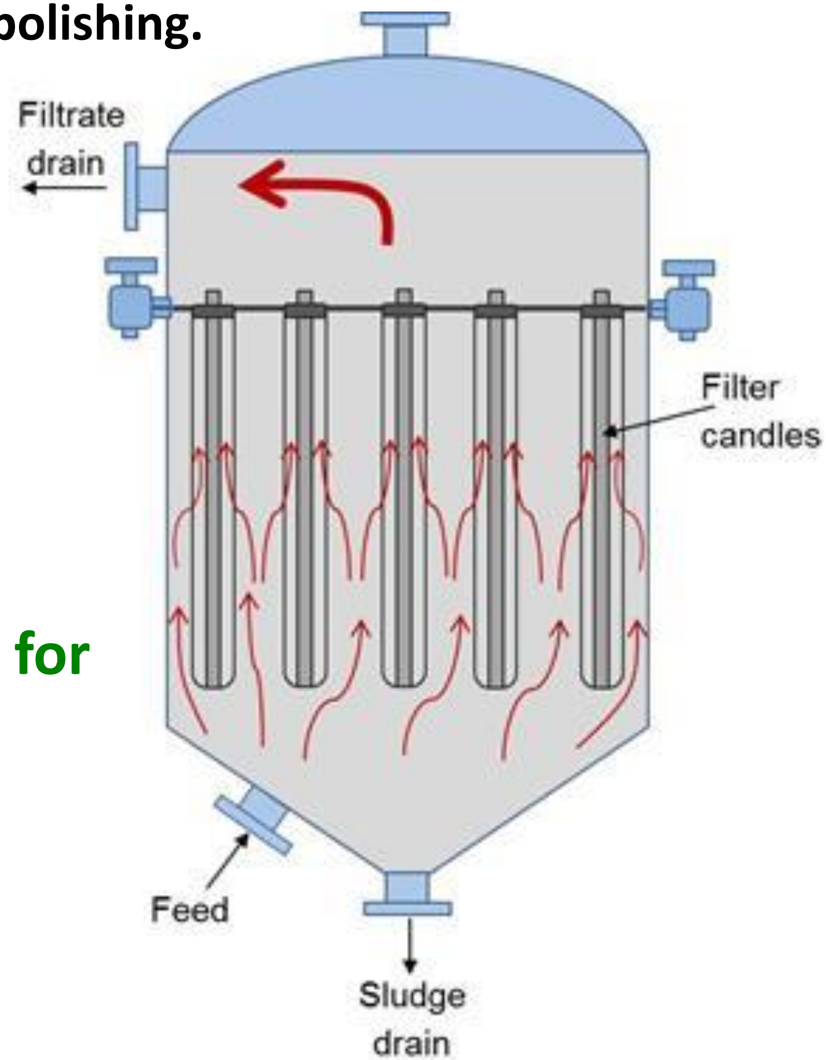
- **The rate of adsorption for a surface area of a just one pound (0.45 kg) of Activated Carbon is equal to 60-150 acres!**

Candle Filtration

The Candle Filters are, like all pressure filters, operating on a batch cycle and may be seen in process lines handling titanium dioxide, flue gas, brine clarification, red mud, china clay, fine chemicals and many other applications that require efficient low moisture cake filtration or high degree of polishing.

The Candle Filter consists of three major components:

- **The vessel**
- **The filtering elements**
- **The cake discharge mechanism**



- **Candle Filters are very well suited for handling flammable, toxic and corrosive materials.**

Candle Filtration

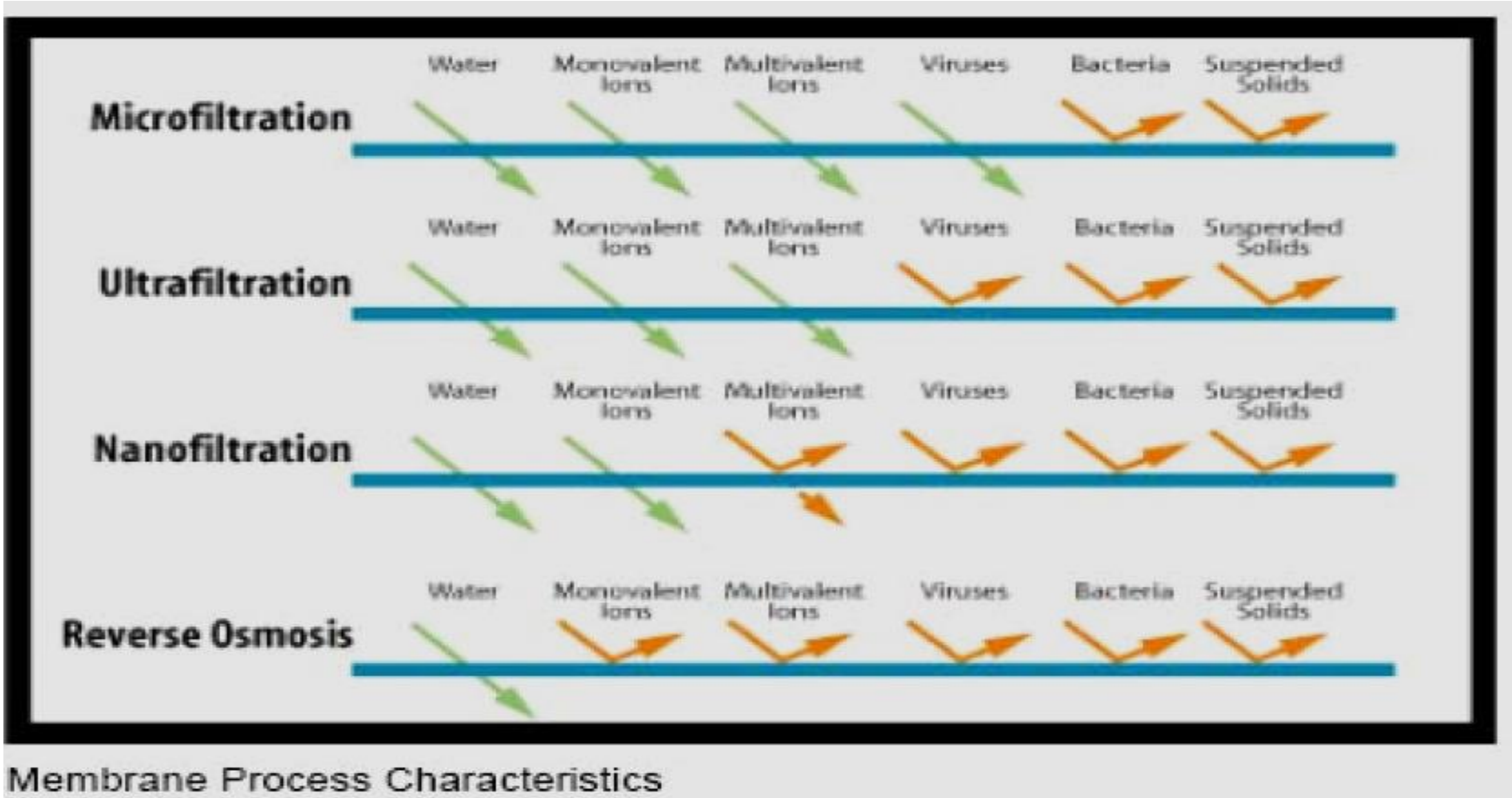
- **Advantages**
- Excellent cake discharge.
- Adapts readily to slurry thickening.
- Minimum floor space.
- Mechanically simple since there are no complex sealing glands or bearings.
- **Disadvantages**
- High headroom is required for dismantling the filtering elements.
- The emptying of the vessel in between cake filtration, washing and drying requires close monitoring of the pressure inside the vessel to ensure that the cake holds on to the candles.

Disinfection Methods

Disinfection methods used for disinfecting water for drinking purpose are

- Ultrafiltration
- UV treatment
- Ozonolysis
- Reverse Osmosis

Water purification by Filtration process



Substances Removed From Water By Membrane Filtration Processes

The green arrow indicates that the particle is small enough to pass through the filter, whereas the deflected orange arrow indicates that the filter blocks the particle from passing through the filter.

Different filtration processes

A. Ultrafiltration:

- An ultrafiltration filter has a pore size around 0.01 micron.
- A microfiltration filter has a pore size around 0.1 micron, so when water undergoes microfiltration, many microorganisms are removed, but viruses remain in the water. Ultrafiltration would remove these larger particles, and may remove some viruses.
- Neither microfiltration nor ultrafiltration can remove dissolved substances unless they are first adsorbed (with activated carbon) or coagulated (with alum or iron salts).

B. Nanofiltration

- A nanofiltration filter has a pore size around 0.001 micron.
- Nanofiltration removes most organic molecules, nearly all viruses, most of the natural organic matter and a range of salts.
- Nanofiltration removes divalent ions, which make water hard, so nanofiltration is often used to soften hard water.

C. Reverse osmosis

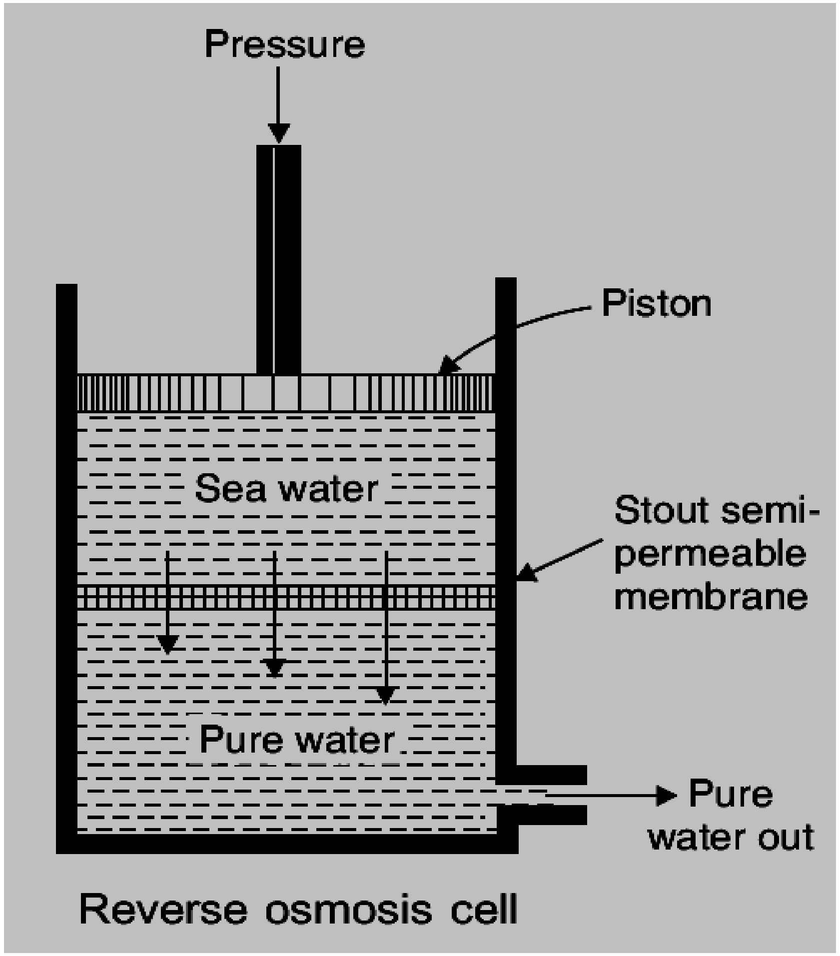
- Reverse osmosis filters have a pore size around 0.0001 micron.
- After water passes through a reverse osmosis filter, it is essentially pure water. In addition to removing all organic molecules and viruses, reverse osmosis also removes most minerals that are present in the water.
- Reverse osmosis removes monovalent ions, which means that it desalinates the water.

REVERSE OSMOSIS

- RO membranes give 96%-99% NaCl rejection. Greater than 95-99% of inorganic salts and charged organics will also be rejected by the membrane due to charge repulsion established at the membrane surface.
- RO membranes are made of polymers, cellulosic acetate and aromatic polyamide types.
- Applications:

1. Potable water from sea or brackish water
2. Ultra pure water for food processing and electronic industries
3. Pharmaceutical grade water
4. Water for chemical, pulp & paper industry
5. Waste treatment etc.
6. Municipal and industrial waste treatment

Reverse Osmosis



- When two solutions of unequal concentrations are separated by a Semipermeable membrane, solvent will flow from lower conc. to higher conc. due to osmotic pressure

- This phenomenon can be reversed by making the solvent to flow in the opposite direction by applying hydrostatic pressure on the concentrated side (Reverse Osmosis)

- In reverse osmosis, pressure of 15-40 kg/cm^2 is applied on the contaminated water compartment.

- The water gets forced through the semipermeable membrane leaving behind the dissolved solids.

- Thus water is separated from the contaminants rather than removing contaminants from water.

- Both ionic and non-ionic impurities as well as colloidal impurities are left behind.

- This process is also called as ***"Super-filtration"*** or ***"Hyper-filtration"***

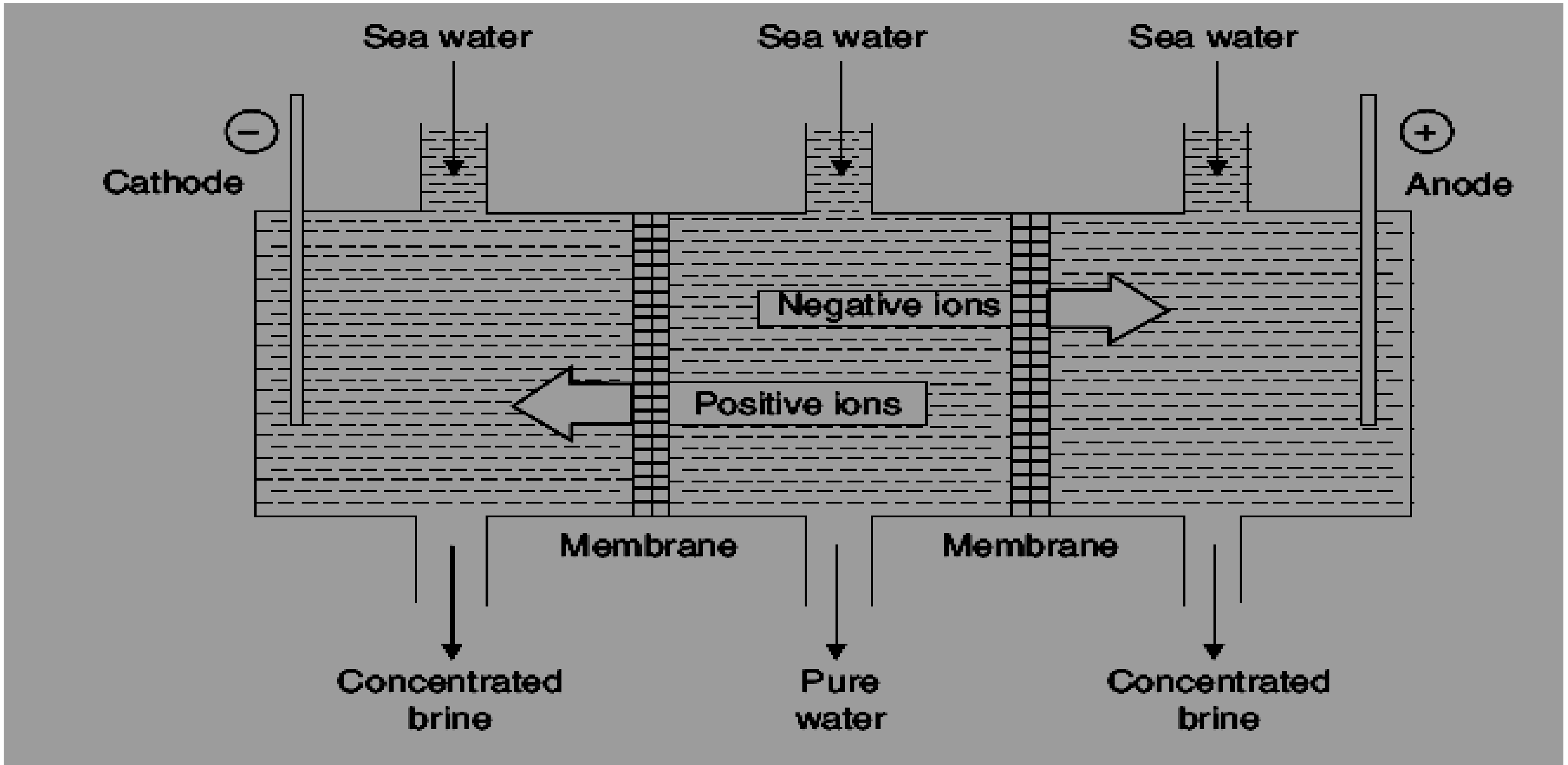
Advantages of Reverse Osmosis

- Advantage is in removing ionic, non-ionic, colloidal and high molecular wt. organic matter.
- It removes colloidal silica (which is not removed during demineralisation)
- Cost is only the replacement cost of membranes (life is 2 years)
- Membrane replacement is fast and hence uninterrupted water supply can be ensured
- Because of the above reasons this process is being adopted for converting sea water into potable water and for high pressure boilers.
- It can be used as desalination process for removing salt from sea water.

Desalination of brackish water

- Water containing dissolved salts with a peculiar salty (brackish) taste is brackish water
- The process of removing common salt from water is desalination
- Electrodialysis consists of a large container with two membrane separators, one permeable to positive ions and the other permeable to negative ions.
- In the outer compartments anode and cathode are arranged to pass DC Voltage.
- When DC voltage/current is passed through the cell, Na^+ will move towards cathode and Cl^- will move towards anode through the membrane.
- Hence, the concentration of salt decreases in the middle compartment and increases in the side compartments.
- Water from the middle compartment is collected and this water is desalinated water.

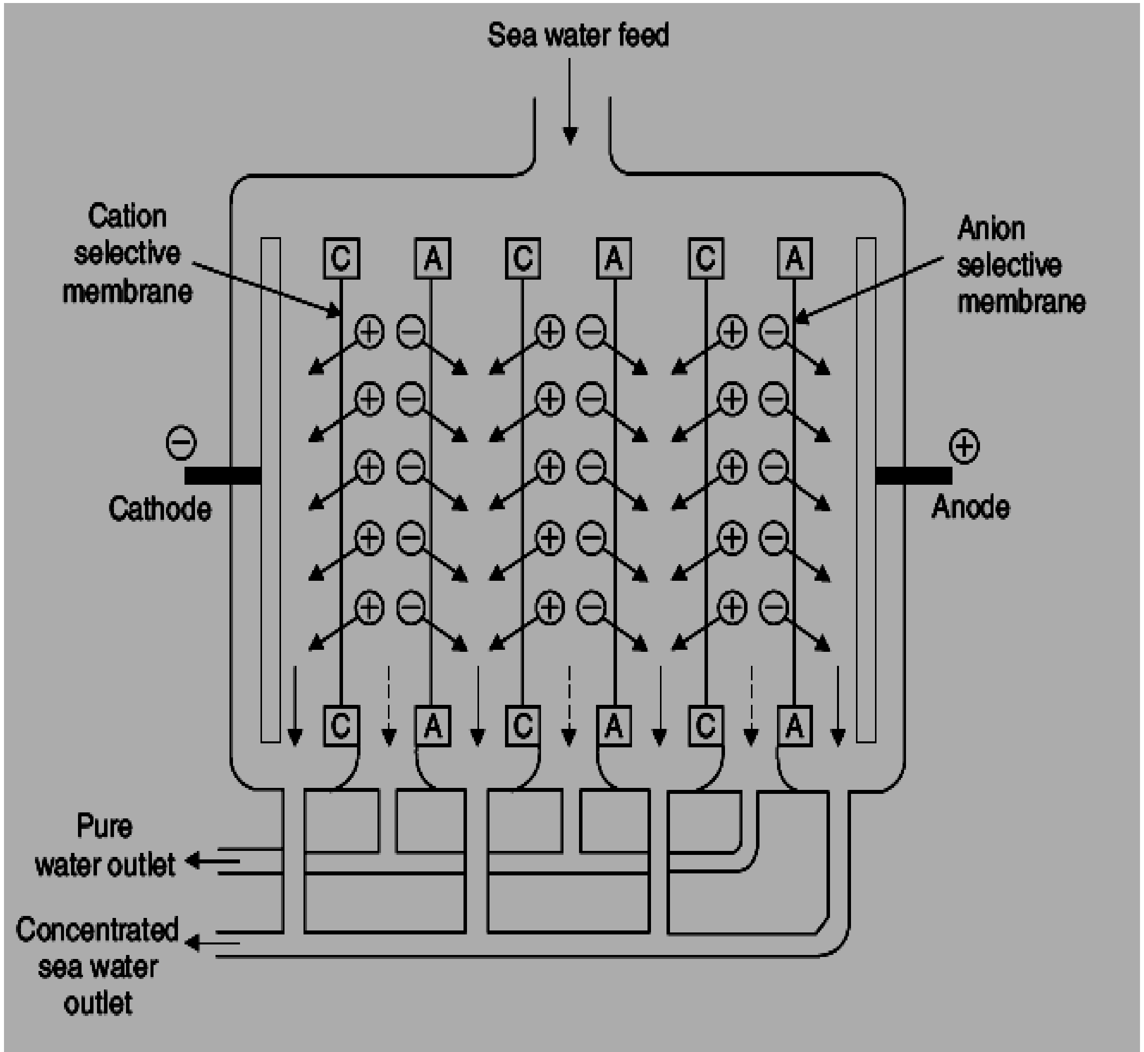
Electrodialysis diagram



Line diagram of electrodialysis.

For efficient separation, ion-selective membranes are used which selectively allow cations or anions to pass through them.

Electrodialysis cell



Electrodialysis cell.

- Electrodialysis cell consists of Large number of pairs of rigid Plastic membranes.
- Saline water at a pressure of 5-6 kg/cm^2 is passed through the membrane pairs.
- DC current is applied perpendicular to the direction of water flow.

Advantages are:

1. Unit is compact and installation is economical
2. Best suited if electricity is available.