WATER SOFTENING

Environmental Engineering –I

Semester-VI

WATER SOFTENING

- **Removal of hardness**
  - **Hardness is?...**
  - **Hardness is due to presence of polyvalent metal ions in water like C_a^{++} ,M_g^{++} ,F_e^{++} , M_n^{++} ,S_r^{++}**
- **How is Softening done?...**
- **Precipitation of Ca and Mg, or**
- **Ion exchange of Ca / Mg with ion such as Na**

Water softening is the removal of calcium, magnesium, and certain other metal cations in hard water. The resulting soft water is more compatible with soap and extends the lifetime of plumbing. Water softening is usually achieved using lime softening or ion-exchange resins.

Usually done for ground water (lime stone dissolved)

Advantages & Disadvantages of Hard water

Adv. **1.Supplies Ca for growth,**

2. Less lead poisoning as soft water dissolves lead.

Disadv.

1. **More soap consumed,**
2. **Scale formation in boilers—more fuel wasted, metals over heated**
3. **Incrustation in pipes—pipes get clogged due to precipitation of salts.**
4. **Serious troubles in manufacturing process like textiles, paper making, dyeing, ice-making.**
5. **Makes food tasteless.**

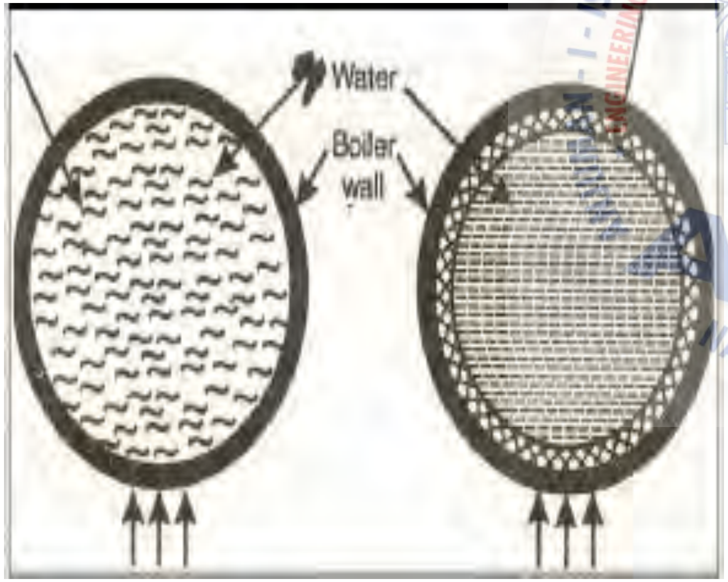
Calcium Sulphate

Forms a hard scale on the heating surfaces

Calcium Bi-carbonate

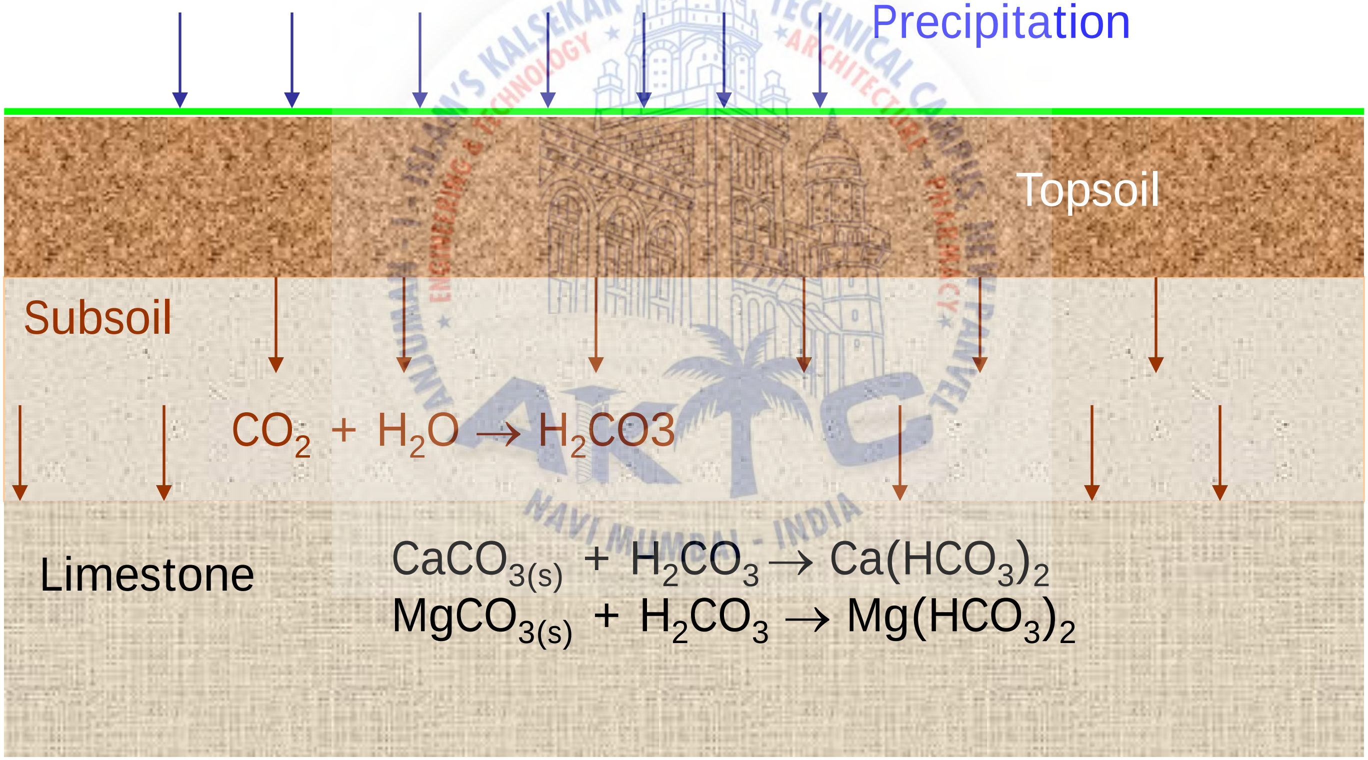
Decomposes at a low temperature when CO_2 is liberated. Remaining Calcium carbonate deposits on the heating surface as a soft scale.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$



- **Temporary hardness -also called Carbonate hardness (CH) –caused by Calcium and Magnesium carbonates and bicrbonates, removed by-**
- **1.Boiling and**
- **2.Addition of lime.**
- **Permanent hardness (NCH) -Due to Sulphates, Chlorides and Nitrates of Calcium & Magnesium. Removed by-**
- **1. Lime –Soda process,**
- **2. Base exchange, Zeolite or Ion exchange process,**
- **3. Demineralisation or Deionisation process,**
- **4. Revese Osmosis**
- **Lime & Soda help in removing entire hardness, both CH and NCH**

Formation of Hardness



Precipitation

Topsoil

Subsoil

$CO_2 + H_2O \rightarrow H_2CO3$

Limestone

$CaCO_{3(s)} + H_2CO_3 \rightarrow Ca(HCO_3)_2$

$MgCO_{3(s)} + H_2CO_3 \rightarrow Mg(HCO_3)_2$

Hardness Table

Water Classification	Hardness, mg/L	Hardness. Grains/Gal	Sodium Added mg/L
Soft	0 to 49	0 to 2.9	0 to 22.5
Medium Hard	50 to 149	2.9 to 8.7	23 to 68.5
Hard	150 to 249	8.7 to 14.6	69 to 115
Very Hard	250 to 299	14.6 to 173	115 to 138
Extremely Hard	300 and up	17.5 and up	138 and up
mg/L = milligrams/Liter			

Water softening

- **Temporary hardness of water [carbonate hardness]→ Due to the presence of carbonate and bicarbonate of calcium and magnesium**
- **$CaCO_3$, dissolves in water containing CO_2 and exists in the form of bicarbonates in natural water**

Removal → By boiling

Calcium bicarbonate Calcium carbonate

$$Ca(HCO_3)_2 + Heat \text{------------}\rightarrow CaCO_3 \downarrow + CO_2 + H_2O$$

The magnesium carbonate ($MgCO_3$) is fairly dissolved in water and cannot be removed by boiling, but can be removed by adding lime →

Soluble Hydrated lime Insoluble Insoluble

↑ ↑ ↑ ↑

$MgCO_3$ +Ca $(OH)_2$ ---------→ Mg $(OH)_2$ $\downarrow$ ------+-------- $CaCO_3$ $\downarrow$

Similarly Magnesium bicarbonate →

Calcium bicarbonate Magnesium hydroxide↓

↑ ↑

Mg $(HCO_3)_2$+Ca $(OH)_2$ ---→ Ca $(HCO_3)_2$-------- +--------Mg $(OH)_2$

Ca $(HCO_3)_2$+Ca $(OH)_2$ ---→ $2CaCO_3$ $\downarrow$ + $2H_2O$

Permanent hardness [Noncarbonate hardness] → due to presence of sulphate, chlorides, and nitrates of calcium and magnesium.Ca^{++}, Mg^{++}, Fe^{++}, Mn^{++} etc. also contribute hardness to the water

Methods of removal of hardness →

- Lime soda process
- Base-exchange process/zeolite process
- Demineralization

Lime soda process

Lime ($Ca(OH)_2$ and soda ash (Na_2CO_3)are added to the water which reacts with the Ca. and Mg. salts so as to form insoluble precipitate of $CaCO_3$ and $Mg(OH)_2$

The chemical reactions are →

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

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow Ca(HCO_3)_3 + Mg(OH)_2\downarrow$$

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

$$MgCO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + Mg(OH)_2\downarrow$$

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$

Noncarbonate hardness of calcium

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + \underset{\downarrow}{CaSO_4}$$

Noncarbonated hardness

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

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

- **Lime helps in removing the entire carbonate hardness and it reacts with non-carbonate hardness of Mg to convert it to non carbonate hardness of Ca.**

- **Soda then removes the non-carbonate hardness of Ca also**
- **Similarly the lime removes the CO_2, from the water**

Note: normally CO_2, is applied as pressurized liquid

Most of the hardness is due to carbonates

Alum, lime, soda→ Are added together as a single process

Re carbonation process →

When CO_2 pass through the water containing finely divided particles of $CaCO_3$, it combines with $CaCO_3$ to form soluble bicarbonate

$CaCO_3 + CO_2 + H_2O \text{---------}\rightarrow Ca\,(HCO_3)_2$

↓ ↓

Insoluble Cal. carbonates soluble cal. Bicarbonate

$Mg\,(OH)_2 + CO_2 \text{------------}\rightarrow MgCO_3 + H_2O$

$Mg\,CO_3 + CO_2 + H_2O \text{----}\rightarrow Mg\,(HCO_3)_2$

Advantages of lime soda process

- Economical
- Easily combined with treatment without trouble
- When used along with coagulant, quantity of coagulants can be reduced
- Increased pH reduce corrosion of distribution pipes.

Increased causticity cause killing of pathogenic bacteria, especially when Calcium and magnesium hydroxide alkalinity is between 20-50mg/lit.

- Helps to reduce the total mineral content
- Remove Iron and manganese, to some extant

Disadvantages

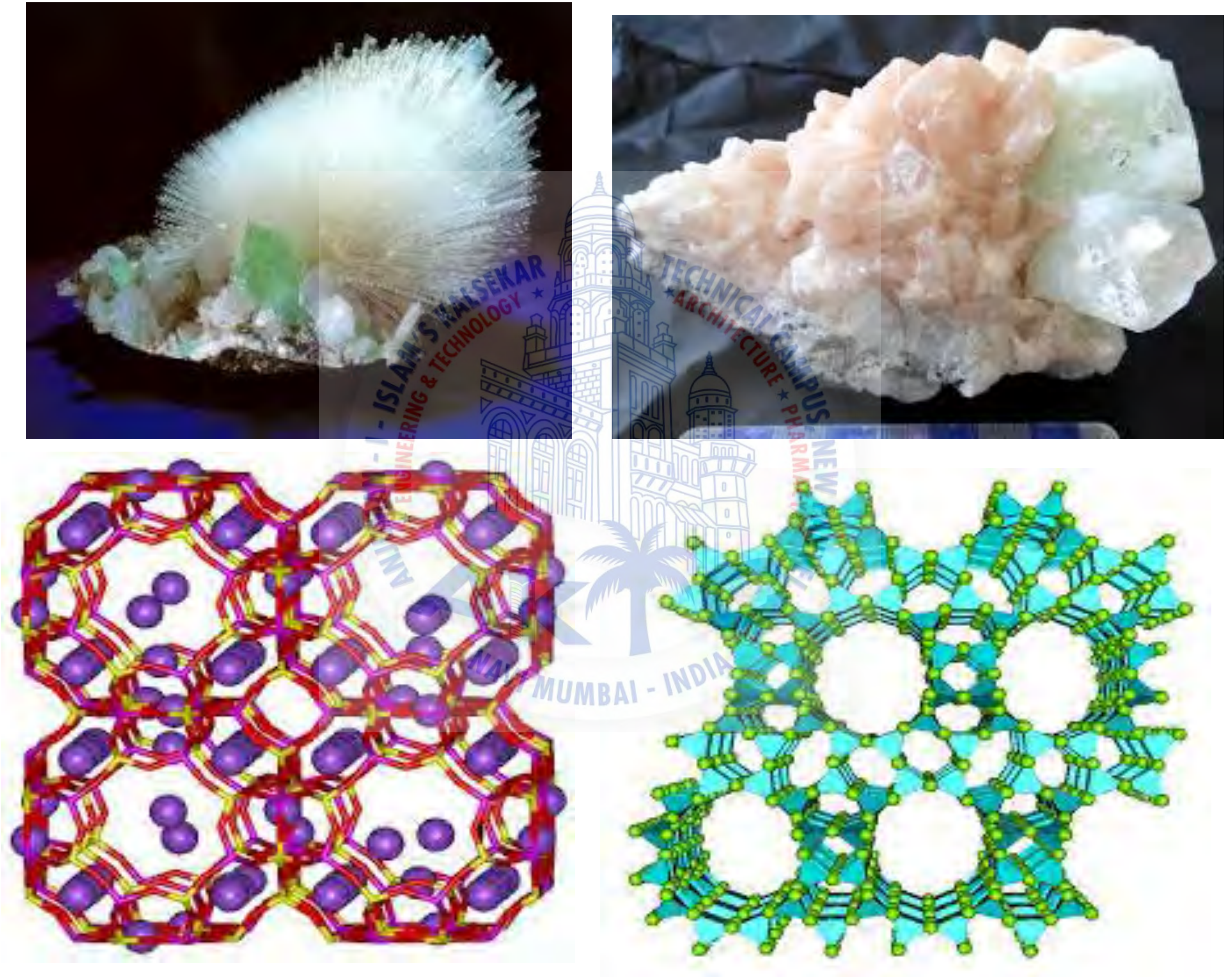
- A large quantity of sludge
- Careful operation and skilled supervision
- Incrustation of pipes and trouble in filter bed, if recarbonation is not done properly
- No zero hardness as $CaCO_3$ is slightly soluble in water, hence remain hardness up to about 50mg/lit

Zeolite/ Base exchange/ Cation exchange process

- **Zeolite are the natural salts or clay which are hydrated silicates of sodium and aluminium, having the general formula as-**
- **$Na_2OAl_2O_3x.SiO_2y.H_2O$ (green sand-green coloured)**

- **Synthetic Zeolite → Resins (a white coloured-manufactured from feldspar, kaolin, clay and soda)**
- **Zeolites and Resins have the excellent property of exchanging their cations and hence during softening operations the sodium ions of the zeolite get replaced by the calcium and magnesium ions of hard waters.**

Zeolites and their atomic structure



Sodium Ions of the Zeolite gets replaced by the Ca & Mg ions present in water

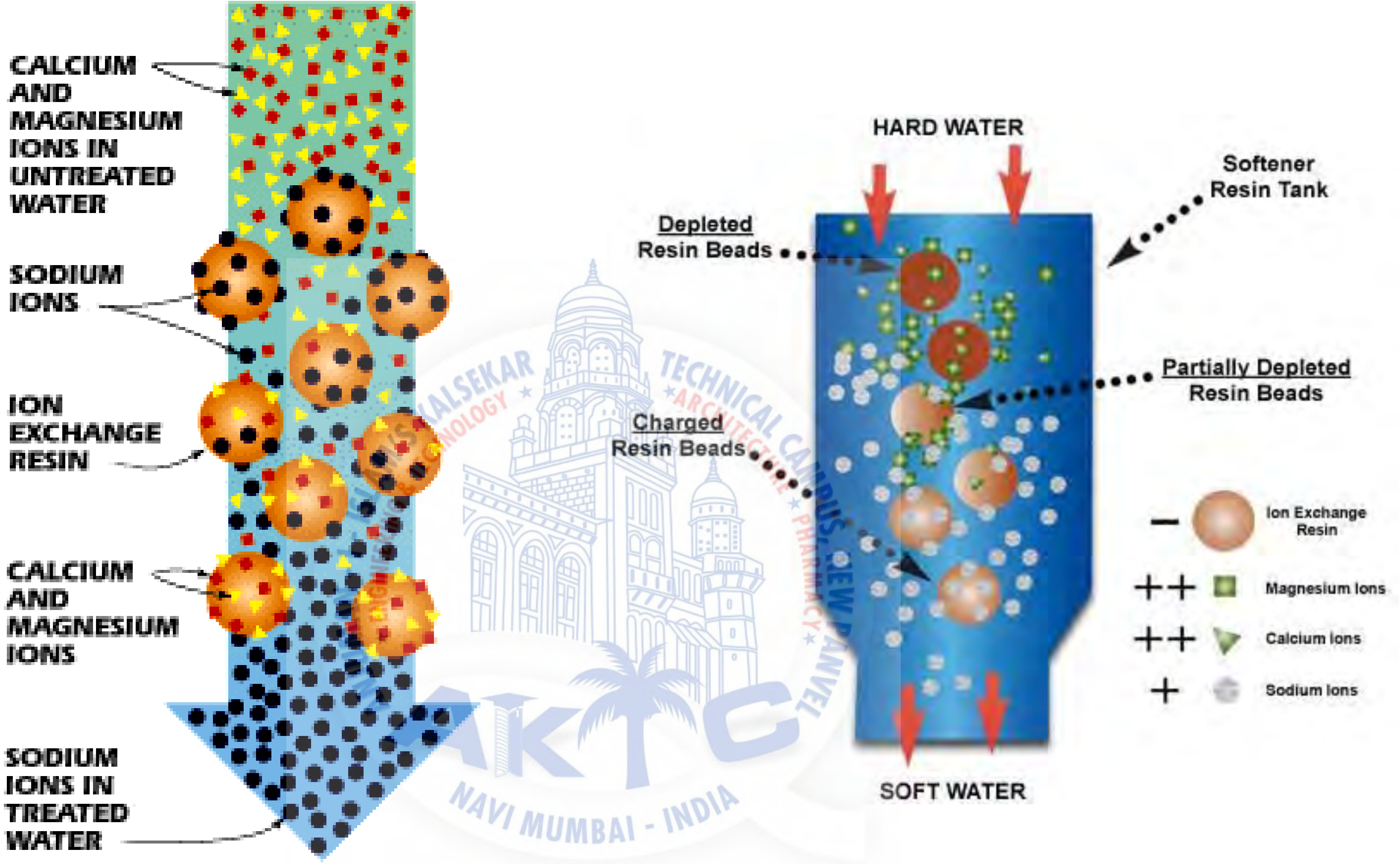
$$Na_2Z\text{----}\ +\text{---------}\quad Ca/\,Mg \left\{\begin{matrix}(HCO_3)_2\\ SO_4\\ Cl_2\end{matrix}\right. \rightarrow Na_2\left\{\begin{matrix}(HCO_3)_2\\ SO_4\\ Cl_2\end{matrix}\right. + \left.\begin{matrix}\\ Ca/Mg\\ \\ \end{matrix}\right\} Z$$

↓ Sodium/active Zeolite

↓ Ca/Mg salts

↓ Na, salts (Which do not cause hardness)

↓ Used Zeolite



The water softening process: highly positive Mg and Ca ions are exchanged for less-positively charged Na ions.

The calcium and magnesium Zeolite can be regenerated into active sodium zeolite by treating it with 5-10% solution of NaCl. The Zeolite softener resembles as filter bed with Zeolite as media, washing is reversed with brine solution (10%) for regeneration of Zeolite. The excess brine is removed by washing with fresh water

The exchange reaction that take place during regeneration can be represented as-

Z =Complex zeolite radicals.

Ca./Mg. Z----- +-------- 2NaCl--------------→ Na_2Z ----+---- Ca/Mg Cl_2

↓ ↓ ↓

Used Zeolite **NaCl solution(5-10%)** **Regenerated Zeolite**

- **Advantages→**

- **Zero hardness→ can be used for specific purpose/ in industries like textile, dyeing etc.**
- **Plant is automatic, no skilled supervision, compact unit.**
- **No sludge is formed, hence no disposal problem.**
- **Process is quite economical where salt is cheaply available.**
- **Remove ferrous iron and manganese.**
- **No difficulty to treat water of varying quality.**
- **No incrustation.**
- **Any degree of hardness can be treated.**

Disadvantages→

- Not suitable for highly turbid water (suspended particles get deposited around zeolite particles). Trouble in filter bed functioning.

- Form sodium bicarbonate in water which causes priming and foaming in boiler feed water.

- Unsuitable for water containing iron and manganese, the iron and manganese zeolite cannot be regenerated in to Na. zeolite

Zeolite process	Lime soda process
1. This process produces water of very low hardness.	1. This process produces water of hardness of 15-60 ppm depending on whether it is a hot or cold process.
2. The cost of the plant and zeolite is higher. Hence, capital cost is higher.	2. The capital cost is lower.
3. The exhausted zeolite bed can be regenerated with brine which is very cheap. Hence, operating cost is less.	3. The chemicals required are consumed in this process thus operating cost is higher.
4. The plant is compact and occupies less space. The size of plant depends on the hardness of water being treated.	4. The plant occupies more space. The size of the plant depends on the amount of water being handled.
5. Cannot be used for hot water, acidic water and water having turbidity and suspended impurities.	5. The process is free from such limitation

	Zeolite process		Lime soda process
6.	This process can operate under pressure and can be designed for fully automatic operations.	6.	This process cannot be operated under pressure.
7.	This process does not involve cumbersome operations like settling, coagulation and filtration.	7.	This process involves all the problems associated with settling, coagulation and filtration.
8.	The water contains larger amounts of sodium salts and greater percentage of dissolved salts.	8.	Treated water contains lesser percentage of dissolved solids and lesser quantities of sodium salts.
9.	This process adjusts itself to water of different hardness.	9.	Reagent doses must be adjusted for waters of different hardness.
10.	Salts causing temporary hardness are converted into $NaHCO_3$ which will be present in the softened water. The insoluble $CaCO_3$ and $Mg(OH)_2$ in water creates problems when used as feed water in boilers.	10.	Temporary hardness is completely removed. The process is free from such limitation
11.	No problems of after precipitation.	11.	There may be problems of after precipitation.

Demineralization Process or (Deionization) →

- The process involves first cation exchange as in zeolite process (H$_2$ is exchanged instead of Na$_2$)
- Then again subjected to anion exchange process
- The cation exchange resins are produced by sulphonation of phenol aldehyde condensation products.

The reactions are cation exchange resin.

↑

$Ca(HCO_3)_2$+---- $H_2R \rightarrow CaR + 2H_2O + 2CO_2$

$Ca\,Cl_2$-------+---- $H_2R \rightarrow CaR + 2HCl$

$Mg\,So_4$------+-----$H_2R \rightarrow$-$MgR + H_2SO_4$

$2NaCl$-------+----- $H_2R \rightarrow Na_2R + 2HCl$

The water coming out of the cation exchange process will contain diluted HCl, H_2SO_4, Carbonic acid etc. and can be removed by passing through the anion exchange bed

Anion exchange resins are produced by condensation of amine with formaldehyde

Replace Cl^-, SO_4^- Ions

Anion exc.resin exhausted resin water
↑ ↑ ↑
ROH----- +------HCl -------→RCl---------- +---------H_2O

2ROH----+------H_2SO_4----→R_2SO_4 ------+ -------$2H_2O$

Resultant water will be fresh ionized water

Regeneration

Ca. Ca.
Mg.{----- R+2HCl-----→H_2R----+---- Mg.}----Cl_2
Na_2 ↓ Na_2
↓ **Regenerated cation exc. resin**
Exhausted cation exc. resin

$$\begin{array}{lll} \text{Ca.} & & \text{Ca.} \\ \text{Mg.}\{\text{-----}\ R+\text{----}H_2SO_4\text{-----}\rightarrow & H_2R\text{----}+\text{-} & \text{Mg.}\}\text{----}SO_4 \\ \text{Na}_2 & \downarrow & \text{Na}_2 \end{array}$$

↓ Regenerated cation exc. resin

Exhausted cation exc. resin

Similarly Exhausted anion exchange resin can be regenerated by treating them with sodium carbonate solution

$$RCl + Na_2CO_3 + 2H_2O \text{-----------}\rightarrow 2ROH + 2NaCl + CO_2\uparrow + H_2O$$

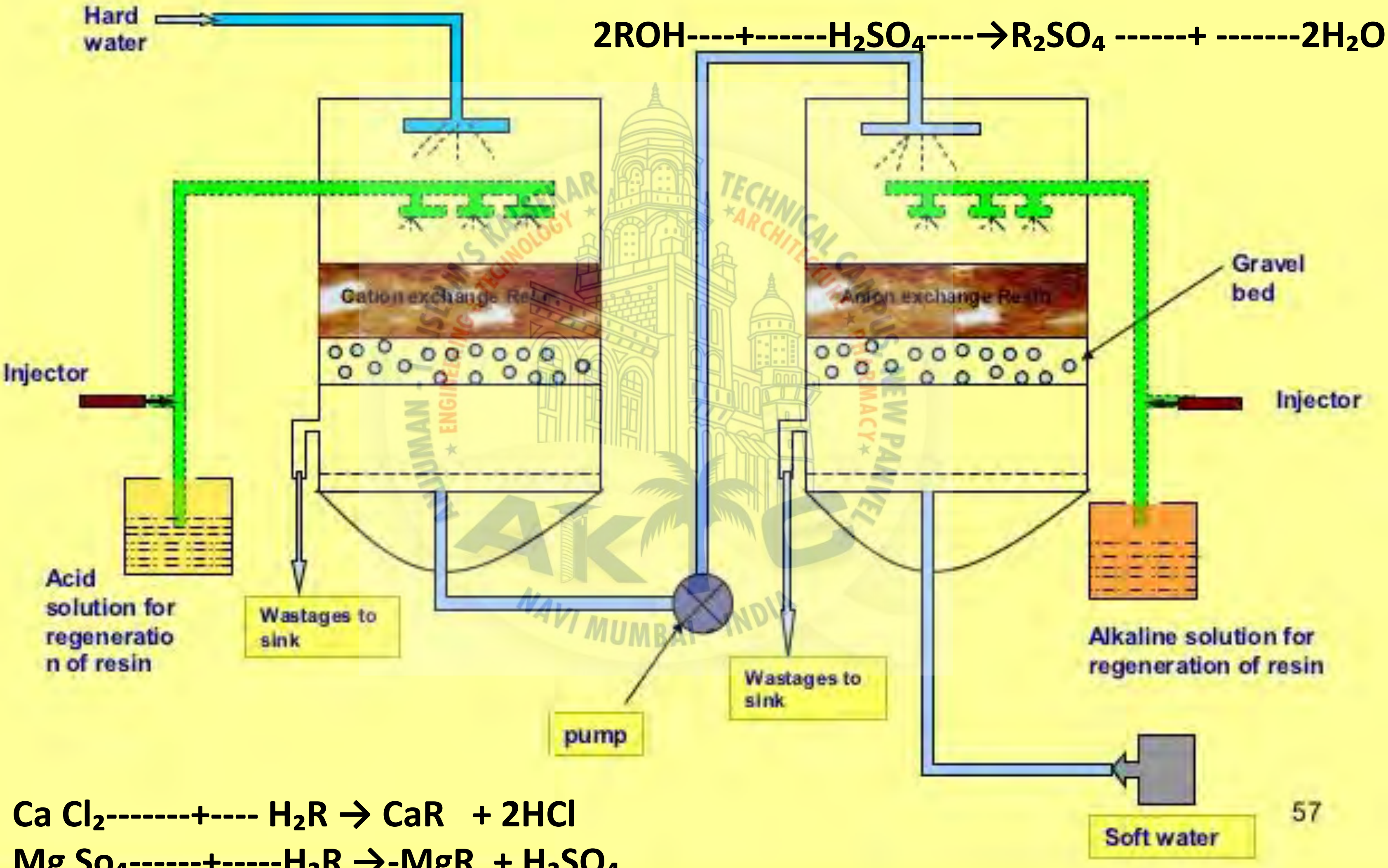
↓ ↓

Exhausted anion exc. resin Regenerated anion exc. resin

Ion exchange purifier or softener

ROH----- +------HCl -------→RCl---------- +---------H_2O

$2ROH$----+------H_2SO_4----→R_2SO_4 ------+ -------$2H_2O$



$Ca\ Cl_2$-------+---- H_2R → CaR + $2HCl$

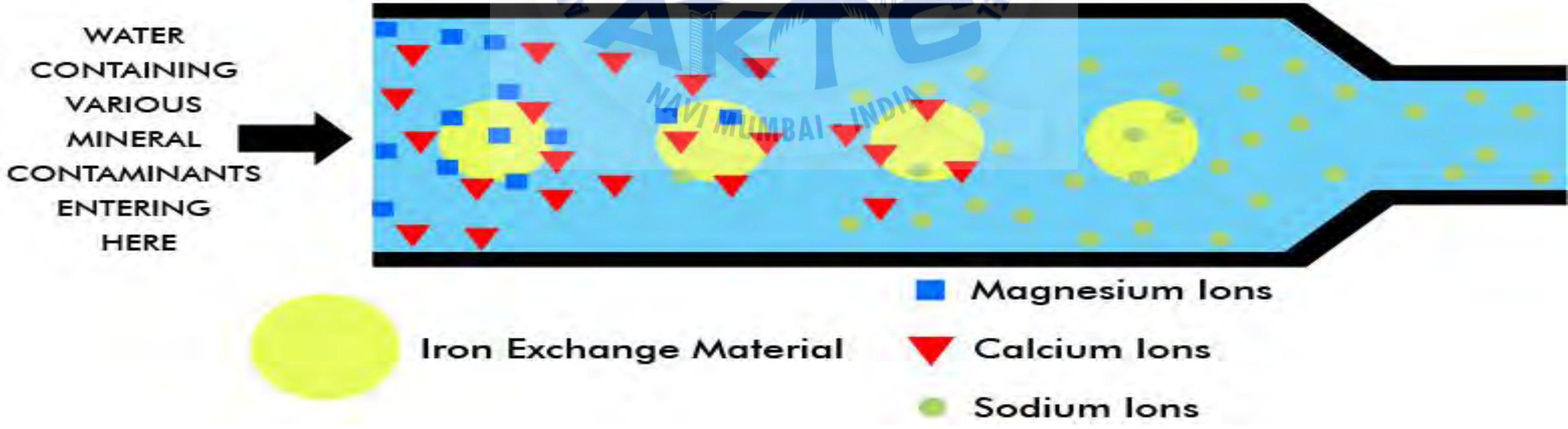
$Mg\ So_4$------+-----H_2R →-MgR + H_2SO_4

Advantage:

1. Produces soft water
2. Can treat highly acidic or alkaline water
3. Regeneration of ion resins are possible
4. Maintenance cost is low

Disadvantage:

1. Cost of equipment is high
2. Highly turbid water can not be treated
3. Expensive chemicals are required.



Flouride effects

Level in water	Effects
0.8–1.2 mg/l	Prevention of tooth decay, strengthening of skeleton
Above 1.5 mg/l	Fluorosis: pitting of tooth enamel and deposits in bones
Above about 10 mg/l	Crippling skeletal fluorosis

Adverse effects due to the excessive exposure to fluoride in drinking-water

Chronic kidney disease (CKD)

Mild dental fluorosis to crippling skeletal fluorosis

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Fluoridation: Water **fluoridation** is the controlled addition of **fluoride** to a public water supply to reduce tooth decay. **Fluoridated** water has **fluoride** at a level that is effective for preventing cavities; this can occur naturally or by adding **fluoride**.

Defluoridation: is a treatment used to remove excess fluoride from drinking water. The process of this technique is to remove fluoride, which is a highly toxic chemical, to prevent health issues and dental issues that contains in humans.

- Excessive dosage of fluoride result in bone fluorisis > 5 mg/L

- Removal of fluoride → passing water through defluoridation media such as tricalcium phosphate, bone char, bone meal, activated alumina.

Nalgonda technique

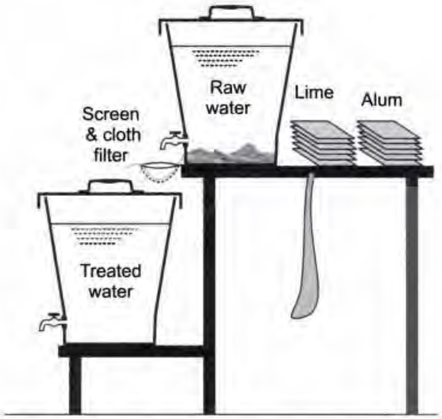
- The Nalogonda technique (named after the village in India where the method was pioneered) employs flocculation principle.
- Nalgonda technique is a combination of several unit operations and the process involves rapid mixing, chemical interaction, flocculation, sedimentation, filtration, disinfection and sludge concentration to recover waters and aluminium salts.
- Alum (hydrated aluminium salts) - a coagulant commonly used for water treatment is used to flocculate fluoride ions in the water. Since the process is best carried out under alkaline conditions, lime is added.

For the disinfection purpose bleaching powder is added. After thorough stirring, the chemical elements coagulate into flocs and settle down in the bottom. The reaction occurs through the following equations-

- $3\ Al_2\ (SO4)_3\ .\ 18H_2\ O + NaF + 9Na_2CO_3 \rightarrow [5Al(OH)_3.Al(OH)_2F] + 9Na_2SO_4 + NaHCO_3 + 8\ CO_2 + 9\ H_2O$

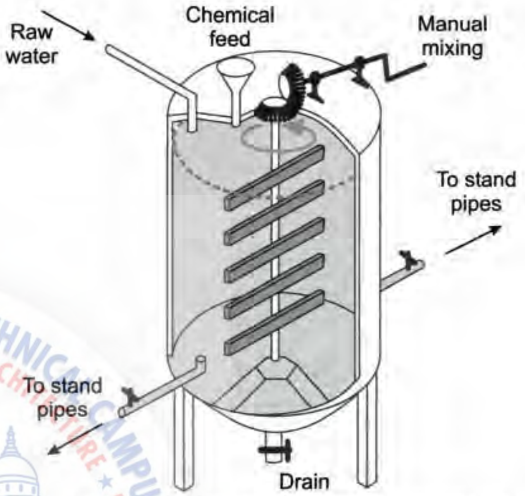
- $3\ Al_2\ (SO4)_3\ .\ 18H_2\ O + NaF + 17NaHCO_3 \rightarrow [5Al(OH)_3.Al(OH)_2F] + 9Na_2SO_4 + 17\ CO_2 + 18\ H_2O$

Removal of Excessive Fluoride

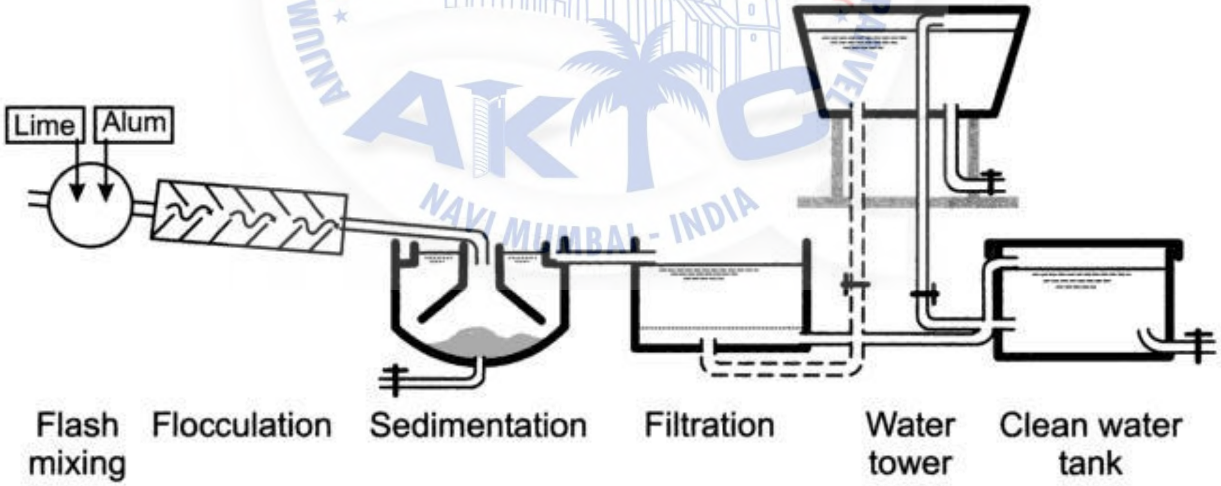


The Nalgonda defluoridation as adopted for domestic use in the United Republic of Tanzania. After Dahi *et al.*, 1996.

Fluoride in Drinking-water



The fill and draw type Nalgonda technique for domestic and



The Nalgonda process as installed in the United Republic of Tanzania.

Salient features of Nalgonda technique

- No regeneration of media
- No handling of caustic acids and alkalis
- Readily available chemicals used in conventional municipal water treatment are only required
- Adaptable to domestic use, Flexible up to several thousands m3 / day
- Applicable in batch as well as in continuous operation to suit needs, simplicity of design, construction, operation and maintenance
- Highly efficient removal of fluorides from 1.5 to 20 mg/L to desirable levels

- **Simultaneous removal of color, odor, turbidity, bacteria and organic contaminants**
- **Normally associated alkalinity ensures fluoride removal efficiency**
- **Sludge generated is convertible to alum for use elsewhere, little wastage of water and least disposal problem**
- **Needs minimum of mechanical and electrical equipment, No energy except muscle power for domestic equipment**
- **Economical - annual cost of defluoridation (1991 basis) of water at 40 lpcd works out to Rs.20/- for domestic treatment and Rs.85/- for community treatment using fill and draw system based on 5000 population for water with 5 mg/L and 400 mg/L alkalinity which requires 600 mg/L alum dose.**
- **Provides defluoridated water of uniform acceptable quality**

Special processes (taste, odor, color, dissolved solids):

- Contaminants like algae, hydrogen sulfide, methane, inorganic salts or metal ions can cause taste and odor problems.
- Oxidizing agents like chlorine, ozone, and potassium permanganate can reduce taste, odor, color, and dissolved solids.

Special treatment processes:

- Aeration is used to remove volatile compounds, and oxidize some metal ions.
- Activated carbon adsorption in powdered (PAC) or granulated (GAC) forms can be used prior to (or during) filtration to improve taste, odor, and color.
- UV radiation can also be used to improve taste and odor problems.

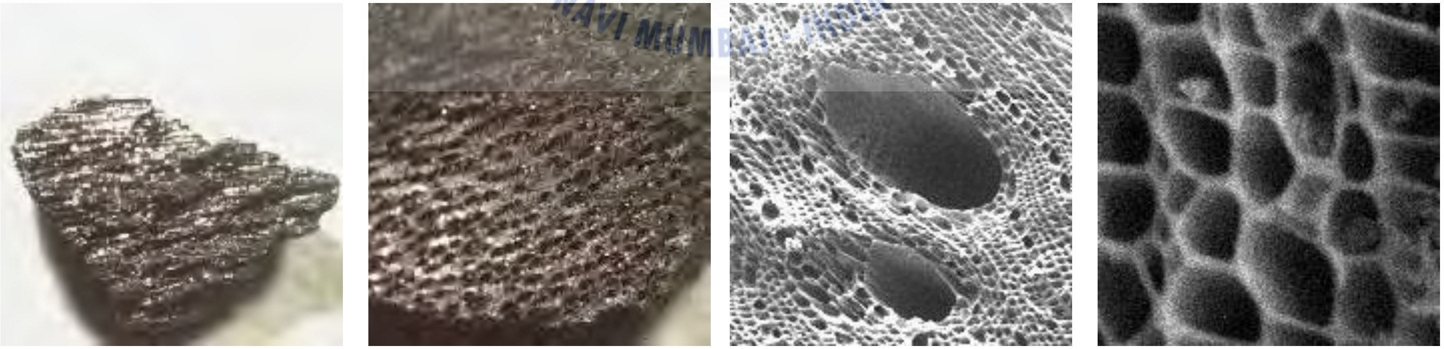
Adsorption: Odour and Colour Removal

- Adsorption can be defined as the accumulation of substances at the interface between two phases. In water treatment plant, the interface is between liquid and solid surface that are artificially provided.

- The material removed from the liquid phase is called the absorbate and the material providing the solid surface is called the absorbant.

What is Activated Carbon?

- It acts as an adsorbent having very large surface area/ mass ratio ranging from 500-1500 m^2/gm
- Activated carbon is a material derived mostly from charcoal that has been treated with oxygen creating many tiny pores between the carbon atoms.
- Production of activated carbon comes from different carbonaceous materials like coal, wood, coconut shells, etc.
- Two types of activated carbon production are physical reactivation and chemical activation.



Contaminants Removed by Activate Carbon from Water

Primary Drinking Water Standards

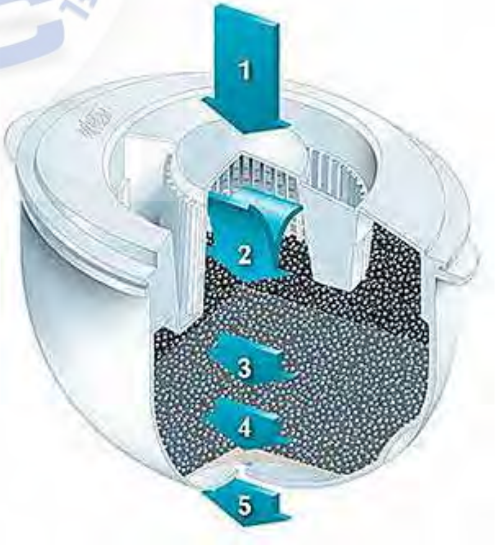
Contaminant	*MCL, mg/L
Inorganic Contaminants	
Organic Arsenic Complexes	0.05
Organic Chromium Complexes	0.05
Mercury (Hg+2) Inorganic	0.05
Organic Mercury Complexes	0.002
Organic Contaminants	
Benzene	0.005
Endrin	0.0002
Lindane	0.004
Methoxychlor	0.1
1,2-dichloroethane	0.005
1,1-dichloroethylene	0.007
1,1,1-trichloroethane	0.200
Total Trihalomethanes (TTHMs)	0.10
Toxaphene	0.005
Trichloroethylene	0.005
2,4-D	0.1
2,4,5-TP (Silvex)	0.01
Para-dichlorobenzene	0.075

Secondary Drinking Water Standards

Contaminant	**SMCL
Color	15 color units
Foaming Agents (MBAS)	0.5 mg/L
Odor	3 threshold odor number

*Maximum Contaminant Level

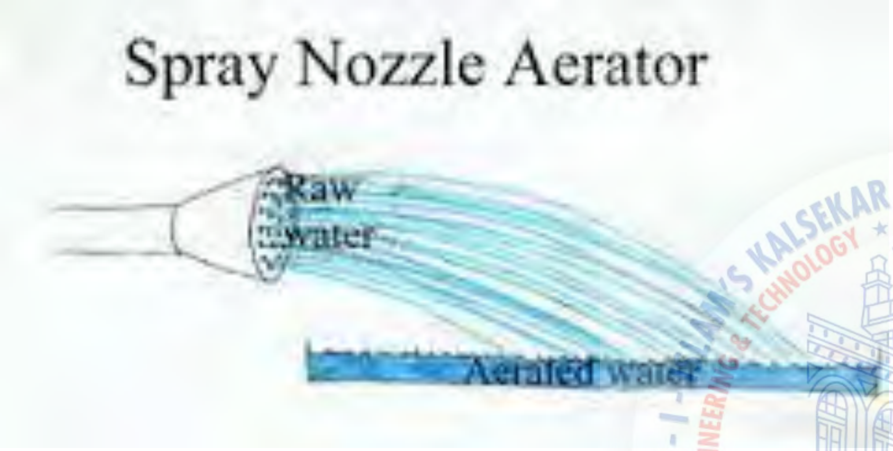
**Secondary Maximum Contaminant Level



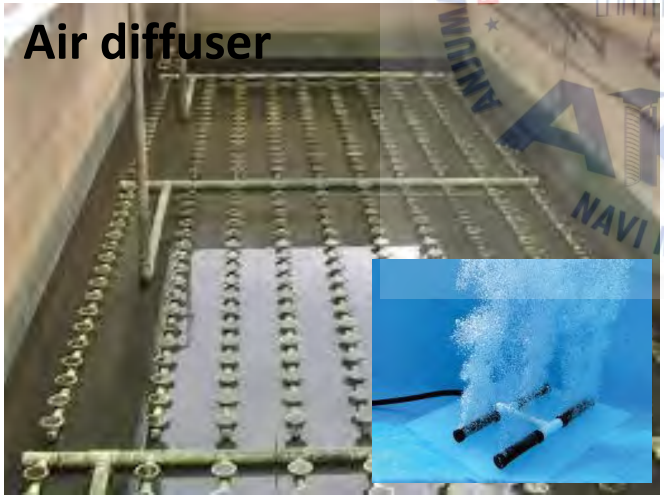
- **Aeration:** is an important unit operation in which the principle of gas transfer used. The process is exposing large surface of water to atmospheric air is called aeration. Its main purpose is to absorb more oxygen and let out unpleasant odours and gases and oxidize Fe and Mn in water.
- Objectives-
- To increase oxygen content in water for imparting freshness
- To expel volatile substances and gases like H_2S, CO_2 causing bad taste and odour.
- To oxidize iron and mangnese so that these can be precipitated and removed.
- To destroy bacteria to some extent, by agitation of water during aeration.

- **Limitation of Aeration-**
- **It is insufficient to remove or reduce tastes and odours caused by-**
- **Non-voaltile substances like oils of algae**
- **Chemical discharged in industrial waste.**
- **Due to over oxygenation, water becomes corrosive and de-aeration may be required.**
- **Aeration is economical only in warmer climate months**
- **Possibility of airborne contamination of water. Iron and Manganese can be precipitated by aeration only when organic matter is absent.**

Techniques of Aeration



Cascade Aerator



Air diffuser

Air diffuser

Desalination

- Processes that remove some amount of salt and other minerals from Water.
- Brackish Water: contain 3.5 % salts & salty taste. Unfit for drinking.
- Separation of salts from water by evaporation followed by condensation.
- Freezing method can also be employed
- **Commonly used methods:**

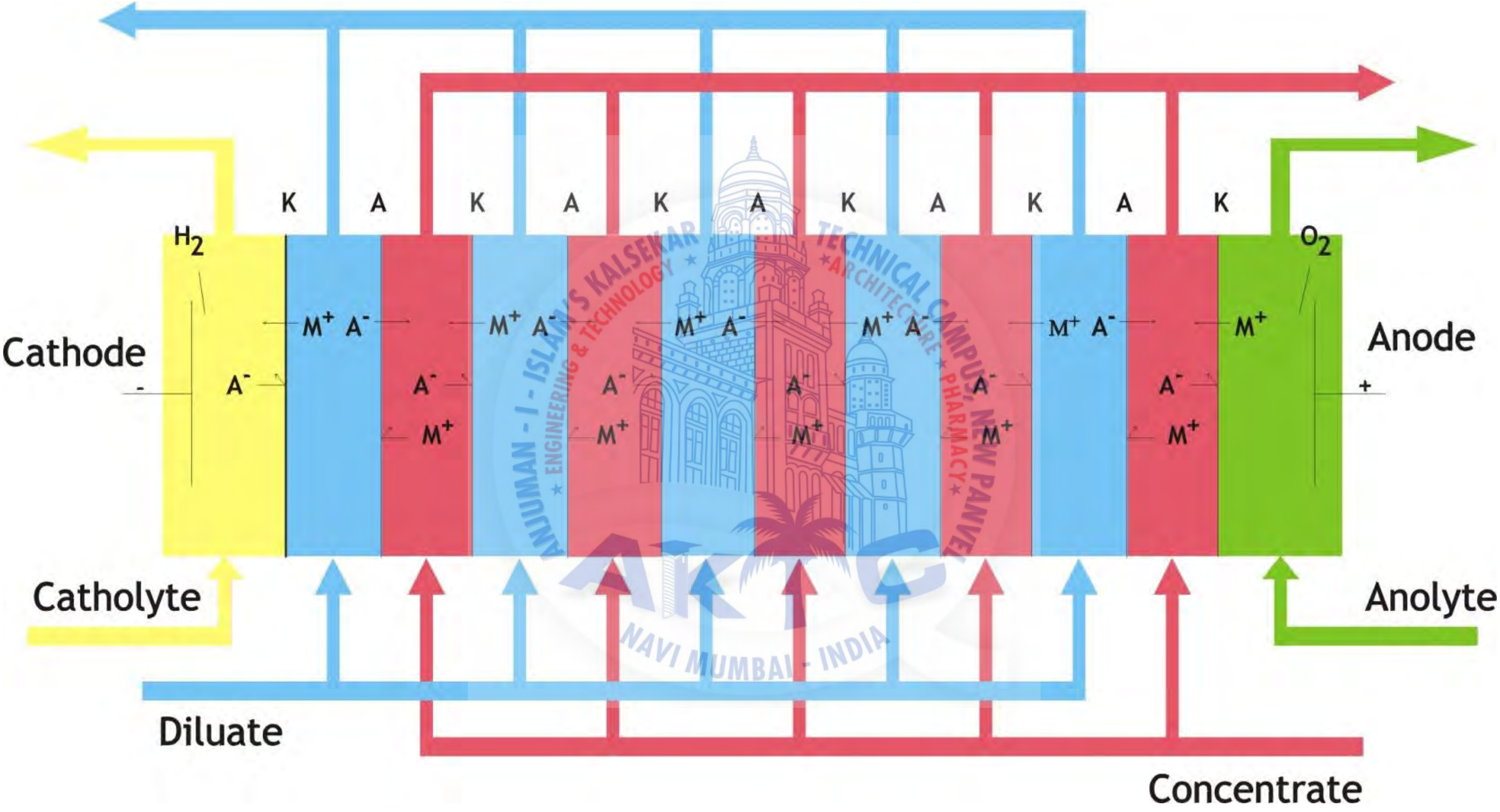
1. Electrodialysis
2. Reverse Osmosis

Electrodialysis

- Inside an electrodialysis unit, the solutions are separated by alternately arranged anion exchange membranes, permeable only for anions and cation exchange membranes, permeable only for cations. By this, the two kinds of compartments are formed, distinguishing in the membrane type facing the cathode's direction. Applying a current, cations within the diluate (blue compartment set) move toward the cathode passing the cation exchange membrane facing this side and anions move towards the anode passing the anion exchange membrane. A further transport of these ions, now being in a chamber of the concentrate (red compartments), is stopped by the respective next membrane.

A. **Electrodialysis:**

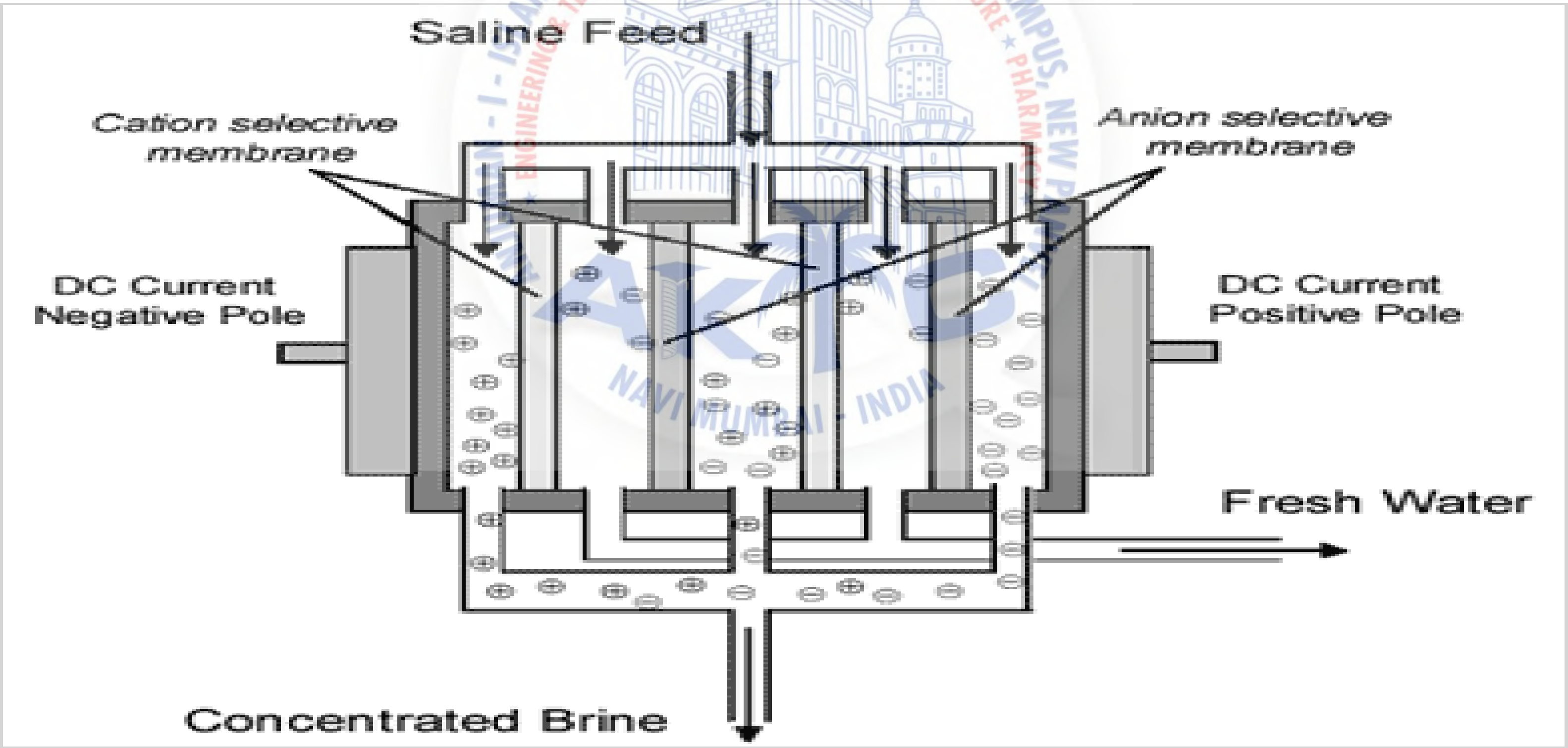
- Method of separation of ions from salt water by passing electric current. Semi permeable membranes are placed



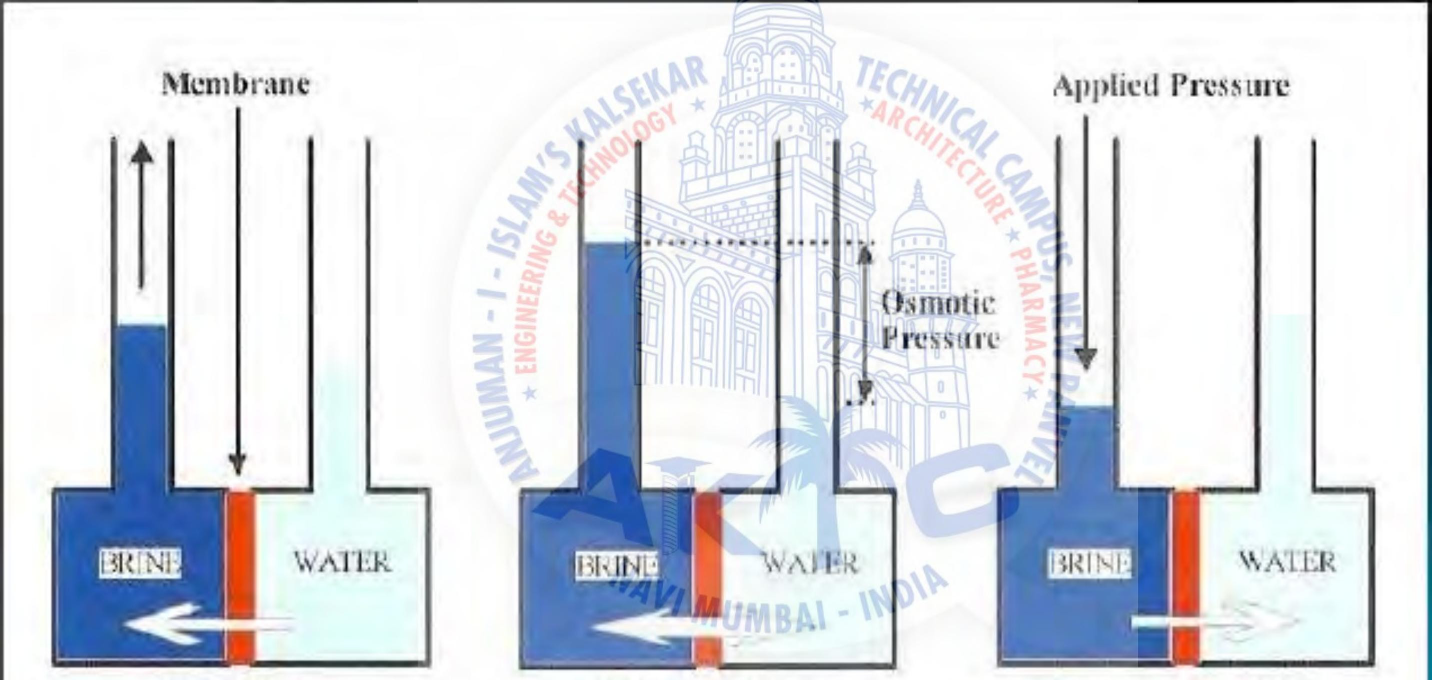
- Consist of three compartments containing

1. Sea Water 2. Pair of electrodes 3. Semi permeable membrane

- As current applied Na^+ ions moves towards cathode and Cl^- moves towards anode
- As result brine concentration decreases in the middle compartment.
- Pure water is removed from the central compartment.
- Conc. Brines are replaced by fresh brine water.
- Much more effective separation **Ion selective membranes** are used



Reverse Osmosis (RO)



OSMOSIS

WATER FLOWS TO HIGHER CONCENTRATION SOLUTION (BRINE IN THIS CASE)

EQUILIBRIUM

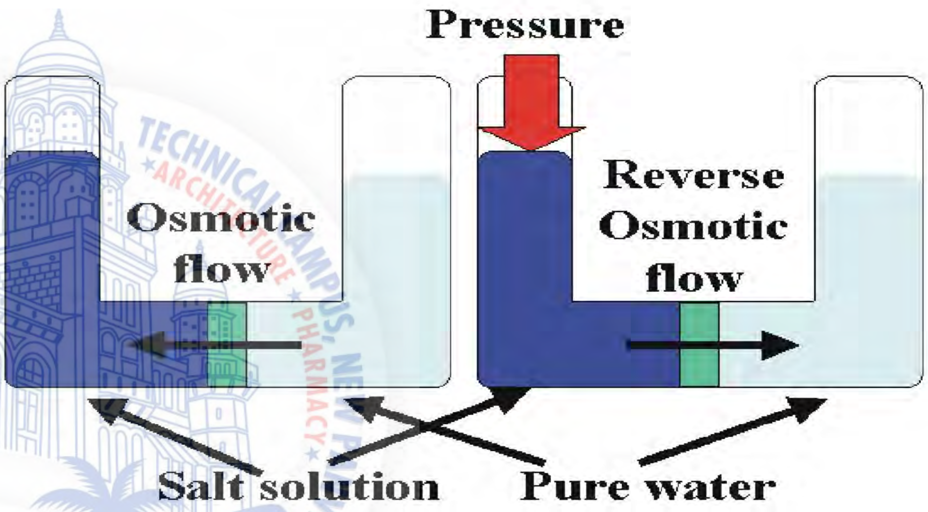
FLOW STOPS WHEN THE DIFFERENCE IN LEVELS EQUALS THE OSMOTIC PRESSURE

REVERSE OSMOSIS

FLOW IS REVERSED IF A PRESSURE GREATER THAN THE OSMOTIC PRESSURE IS APPLIED

Reverse Osmosis (or) Super Filtration (or) Hyper Filtration

Movement of solvent molecule from concentrated side to diluted side.
If only pressure is higher than that of osmotic pressure. Osmotic pressure is proportional to TDS of water and a pressure of at least twice the osmotic pressure is required to achive an economically Feasible flow.



Membranes:
Cellulose Acetate, Polymide, Polymethylmethaacrylate

Thickness: 0.0005 to 0.0000002 µm

Advantages:

Removes both ionic and non ionic and colloidal matters
Maintenance cost is low
Membrane replacement can be done with in few minutes.

Freezing Method

- The method is based on the principle that on lowering the temperature of sea water, it freezes and ice crystals formed are theoretically free from the saline constituents of the water. The crystals can be separated and melted to yield fresh water.

Fe and Mn in Water

Iron and manganese salts are found dissolved in water as invisible dissolved load, when exposed to the air these reduced forms slowly transform to insoluble visible oxidized ferric iron and compounds of manganese.

When their concentration exceeds about 0.3mg/l and 0.5 mg/l for iron and manganese respectively they become objectionable because-

- **They cause discoloration of clothes washed in such water due to deposition of red/brown coloured oxides of iron/manganese.**
- **They cause incrustation of water mains due to deposition of ferric Hydroxides and manganese oxides.**
- **They make the water unpleasant in taste.**
- **Periodic flushing of small distribution pipes may be effective in removing accumulations of rust particles.**

Removal of Fe and Mn from water

The iron and manganese may be present in water either in combination with organic matter or without such combination. When present without organic matter they can be easily removed by Aeration. By this technique the dissolved iron is oxidized to ferric oxide which is insoluble in water.

Dissolved Manganese compounds are converted to insoluble manganese compounds. The precipitated flock can settle down in settling tank or can be further removed by gravity or pressure filter.

The following reaction takes place-

$$4Fe + O_2 + 10H_2O = 4\,Fe\,(OH)_3 \downarrow + 8H$$

Hence 4x56 mg of Fe requires 2x16 mg of O2

1 mg of Fe requires o.14 mg of O_2

A reaction period of about 5 minutes or less at a pH of 7-7.5 and 0.14 mg of O_2 is required to convert 1mg of ferric iron to ferric oxide.

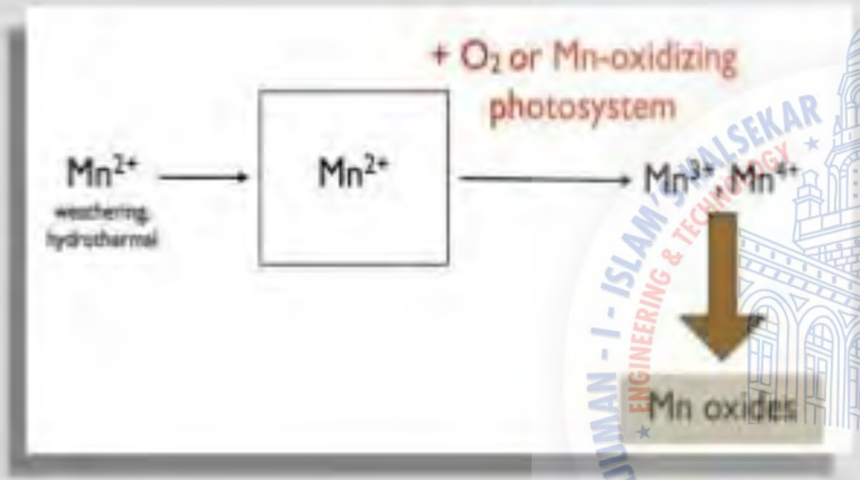
When iron is present as ferrous bicarbonate the following reactions take place:

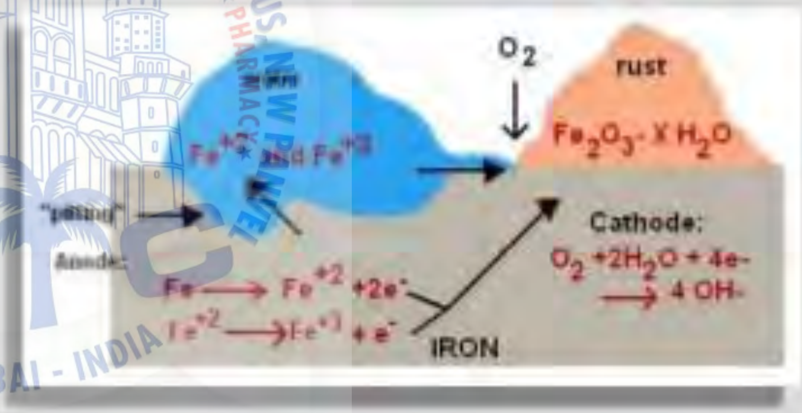
$$Fe(HCO_3)_2 + 2H_20 = FeO + 2CO_2 + 3H_2O$$

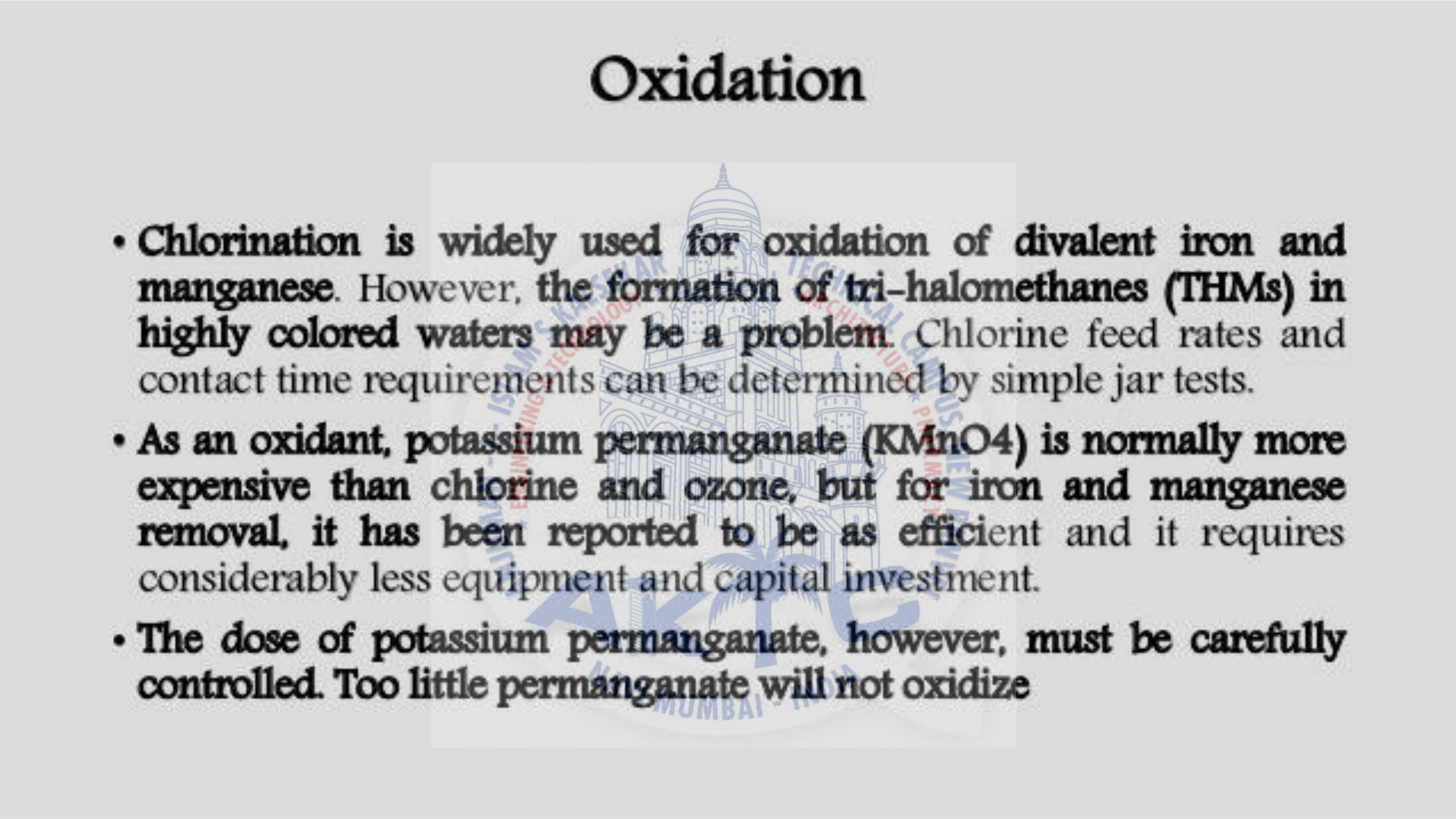
$$4FeO + O_2 = 2Fe_2O_3$$

$$Fe_2O_3 + 3H_2O = 2Fe(OH)_3$$

Oxidation


+ O₂ or Mn-oxidizing photosystem
Mn²⁺
weathering, hydrothermal
Mn²⁺
Mn³⁺, Mn⁴⁺
Mn oxides


O₂
rust
Fe₂O₃ · X H₂O
Fe⁺² and Fe⁺³
"pitting"
Anode:
Fe → Fe⁺² +2e⁻
Fe⁺² → Fe⁺³ + e⁻
IRON
Cathode:
O₂ +2H₂O + 4e⁻ → 4 OH⁻



Oxidation

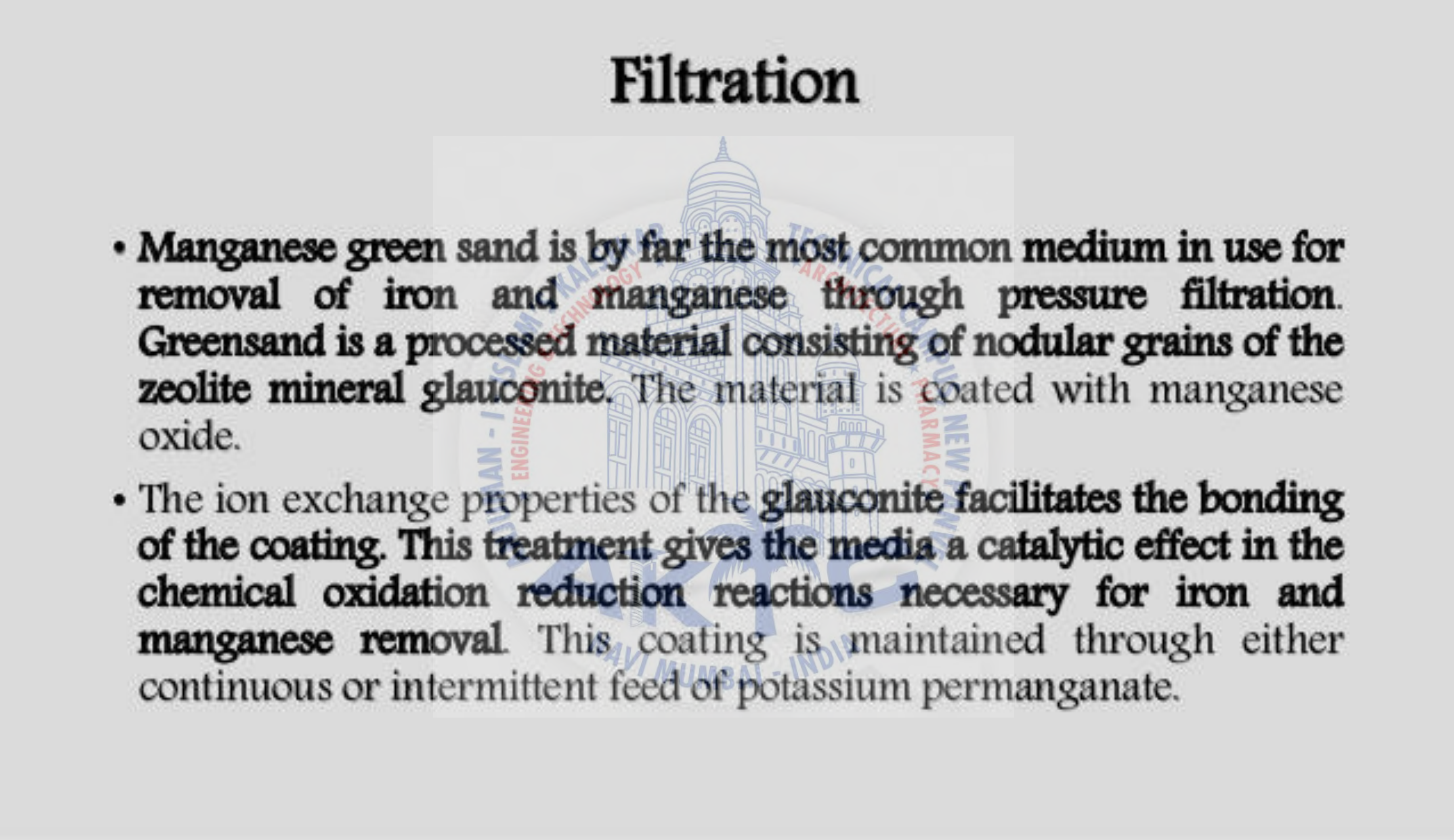
- **Chlorination is widely used for oxidation of divalent iron and manganese**. However, **the formation of tri-halomethanes (THMs) in highly colored waters may be a problem**. Chlorine feed rates and contact time requirements can be determined by simple jar tests.
- **As an oxidant, potassium permanganate (KMnO4) is normally more expensive than chlorine and ozone, but for iron and manganese removal, it has been reported to be as efficient** and it requires considerably less equipment and capital investment.
- **The dose of potassium permanganate, however, must be carefully controlled. Too little permanganate will not oxidize**

When iron and manganese are present in combination with organic matter, it becomes difficult to break the bond between them and to cause their removal.

This bond may be removed either by adding lime and thereby increasing the pH value of water to about 8.5 to 9 or by adding chlorine or potassium permanganate.

Manganese Zeolite- Natural green sand coated with manganese dioxide can be used to remove soluble iron and mangnese from solution. Manganese zeolite can be rejuvenated by Backwashing with potassium permangnate.

Greensand (Gluconite)



Filtration

- Manganese green sand is by far the most common medium in use for removal of iron and manganese through pressure filtration. Greensand is a processed material consisting of nodular grains of the zeolite mineral glauconite. The material is coated with manganese oxide.
- The ion exchange properties of the glauconite facilitates the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation reduction reactions necessary for iron and manganese removal. This coating is maintained through either continuous or intermittent feed of potassium permanganate.

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