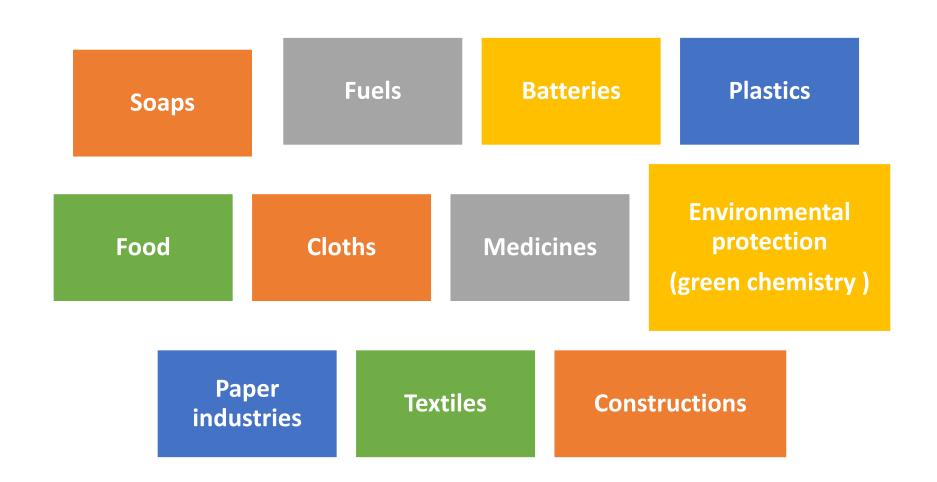




Chemistry in daily life





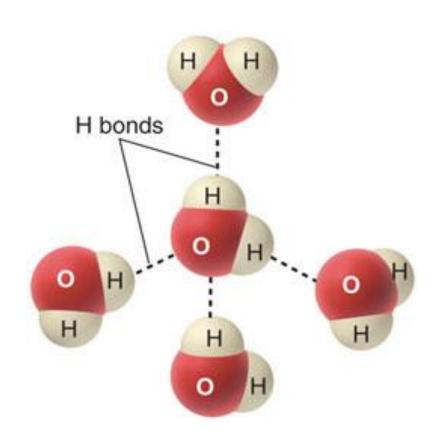
Water Technology





Chemistry of Water

- Universal Solvent
- Polar Molecule
- High Dielectric constant
- High Specific Heat
- High Heat of Vaporization
- Hydrogen bonding
- High Surface Tension
- Capillary Action
- Adhesion
- Cohesion





WHO Specifications for Drinking Water

Parameter	Values (ppm) except pH	
рН	6.5 - 8.5	
Hardness	300	
Chloride	250	
DO	5	
Nitrate	50	
Turbidity	5	
Fluoride	1.5	
TDS	500	



Impurities in water

- Suspended Impurities
- Dissolved Impurities
- Colloidal Impurities
- Biological Impurities



Water Analysis

- Hardness
- Alkalinity
- Chlorides and sulphates
- Dissolved oxygen



Hardness of Water

- Soap consuming capacity of water sample
- Due to dissolved salts of Ca & Mg
- Expressed in terms of ppm of CaCO₃

$$2C_{17}H_{35}COONa + CaCl_2$$
 $(C_{17}H_{35}COO)_2Ca \downarrow + 2NaCl$ Sodium stearate Curd like ppt



Temporary Hardness

- Also known as Carbonate or alkaline hardness
- Due to presence of Ca(HCO₃)₂ & Mg(HCO₃)₂
- Hardness can be removed by boiling hard water



$$Ca(HCO_3)_2$$
 $CaCO_3 \downarrow +CO_2 \uparrow +H_2O_3$



Permanent Hardness

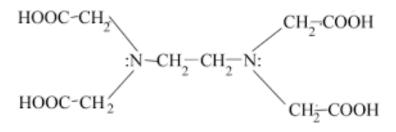
- Also known as non carbonate or non alkaline hardness
- Due to Chlorides, Nitrates & sulphates of Ca & Mg
- Can not be removed by boiling

Total hardness = Temporary Hardness + Permanent Hardness



Determination of Hardness by EDTA Method

- EDTA -EthyleneDiamineTetraAceticAcid
- Chelating agent
- Hexadentate ligand
- Na₂EDTA is preferred as it is more soluble in water



structure of EDTA



Determination of Hardness by EDTA Method

- Complexometric titration
- EBT is used as indicator
- •pH 10 is maintained by Buffer (NH₄Cl + NH₄OH)

Hardness = B.R x Molarity of EDTA x100 x 1000 / V

V is volume of sample used for titration

Procedure

Part-A: Standardization of Na₂EDTA by ZnSO₄

Part-B: Determination of total hardness using Std. Na₂EDTA



Reactions involved in Hardness

$$M^{2+}$$
 + EBT \rightarrow M-EBT + 2H⁺ Wine red



Numerical on Hardness

1. 20 ml standard hard water contain 14 gm CaCO₃ per lit. 20 ml of this required 22 ml EDTA for the end point. 100 ml of water sample required 15 ml EDTA solution. The same sample after boiling required 10 ml of EDTA solution Calculate carbonate and noncarbonate hardness of water.



Hardness of water

2.Calculate temporary Hardness total hardness and Permanent hardness in terms of CaCO₃ for sample with composition

a)Ca
$$(HCO_3)_2 = 6.4$$

b) Mg
$$(HCO3)_2 = 8.2$$

c)
$$MgSO_4 = 5.6$$

d)
$$MgCl_2 = 4.2$$

e)
$$CaSO_4 = 12.3$$

f)
$$Na_2SO_4 = 6.5$$



Alkalinity

- Acid Neutralizing Capacity of Water Sample
- Significance of alkalinity determination
- Determined By an acid-base Titration
- Phenolphthalein And Methyl Orange Are Used As Indicators



Alkalinity Types

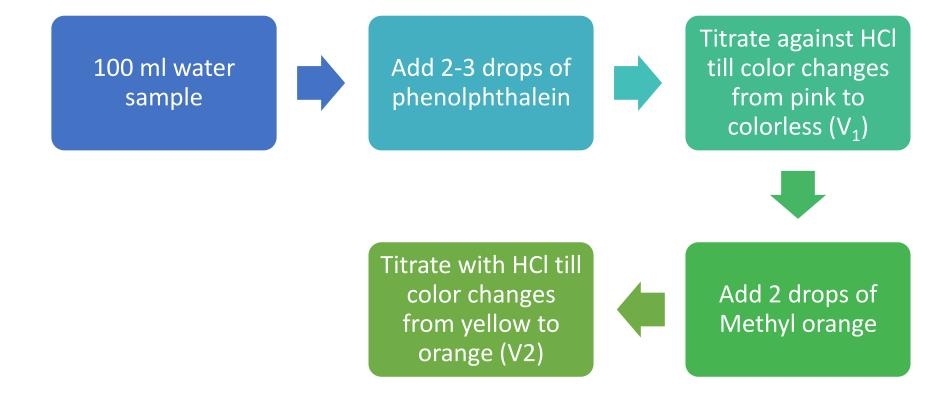
- Only HO
- Only CO₃²-
- Only HCO₃-
- OH- & CO₃²⁻ together
- CO₃²⁻ & HCO₃- together



Reactions Involved

 $O H^- + H^+ \rightarrow H_2O$ $\overline{\text{CO}_3^{2-}}$ + $\overline{\text{H}^+}$ \rightarrow $\overline{\text{HCO}_3^-}$ $HCO_3^- + H^+ \rightarrow H_2O + CO_2\uparrow$

Alkalinity Procedure





Computing Alkalinity

Phenolphthalein alkalinity (P)

$$P = (V_1 \times Z \times 50 \times 1000) / V$$
 ppm of CaCO₃ equivalents.

Methyl orange alkalinity (M) OR Total alkalinity

$$\mathbf{M} = (V_2 \times Z \times 50 \times 1000) / V \text{ ppm of CaCO}_3$$
 equivalents



Alkalinity Interpretation

Relation between P & M	OH-	CO ₃ ²⁻	HCO ₃ -
P = 0	0	0	M
P = M	P/M	0	0
P=1/2 M	0	2P	0
P>1/2M	2P-M	2(M-P)	0
P<1/2M	0	2P	M-2P



Numericals

- 50 ml water sample requires 4.5 ml of N/50 H₂SO₄ upto phenolphthalein end point and another 6 ml upto methyl orange end point, compute alkalinity result.
- water sample is not alkaline to phenolphthalein
 .100ml of sample on titration with N/50 HCl required
 17.5 ml to get methyl orange end point. compute
 alkalinity result.



Mohr's Method

- Chloride ion concentration is determined by titration of water sample with AgNO₃ in neutral or alkaline media
- Highly alkaline pH leads to formation of Silver Hydroxide (AgOH)
- At Low pH Chromate may transformed into dichromate leading to inaccurate result ($CrO_4^{2-} \Longrightarrow Cr_2O_7^{2-}$)
- Desired pH can be achieved by adding CaCO₃



Mohr's Method

 At the start chloride ions react with silver ions forming white ppt of Silver Chloride

 After all chloride are used up Ag⁺ reacts with chromate forming brick red precipitate







Chloride ions Concentration Calculation

1 mole of AgNO₃ = 1 mole of Cl⁻

1000 ml 1NAgNO₃ = 35.5 gm Cl⁻

amount of chloride = $N1 \times V1/V2 \times 35.5$

gm/lit.

N1 = Normality of AgNO₃

 $V1 = Volume of AgNO_3$

V2 = Volume of water sample

Chloride ion concentration above 250 ppm is not acceptable



Dissolved Oxygen

- Measurement gives idea about status of water system (
 Aerobic /Anaerobic)
- Indicator of water pollution
- DO level can give idea about survival of aquatic life
- DO is important factor causing corrosion of boiler material
- Possibility of aerobic biological processes for transforming biodegradable organic contaminants



Steps in Winkler's Method

O₂ Fixation

 Conversion Mn (II) to Mn(IV) State forming Brown ppt of Basic Manganic oxide

$$2Mn(OH)_2 + O_2 \qquad \qquad \qquad 2MnO(OH)_2 \downarrow \quad (Brown)$$

Conversion of Mn (IV) to Mn(II) on Acidification

$$MnO(OH)_2 + H_2SO_4$$
 $MnSO_4 + 2H_2O + (O)$



Winkler's Method

Oxidation of KI into I₂ by Nascent oxygen

$$2KI + H_2SO4 + O \longrightarrow K_2SO_4 + H_2O + I_2$$

Titration of liberated iodine with sodium thiosulphate using starch indicator

$$I_2 + Na_2S_2O_3$$
 $Na_2S_4O_6 \downarrow + 2NaI$



Outline Of Winkler Dissolved Oxygen Procedure

Carefully Collect Sample In 300 mL **BOD Bottle**



Add 2 mL MnSO₄ Soln. and 2 mL Alkali-iodide-azide Reagent



D.O. Present



Yellow

To

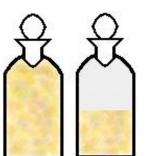
Brown

Floc,



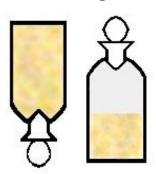
White Floc, No D.O.

Mix By Inverting and **Allow To Settle**



3 Repeat Mixing and

Settling



Add 2 mL H₂SO₄ and **Mix**

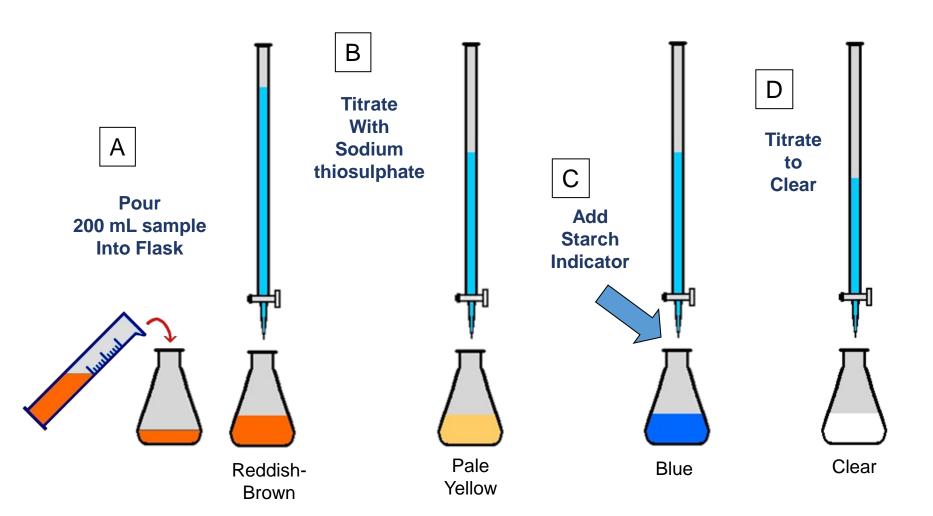
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Titration of Iodine Solution





Winkler's Method

 Nitrate ion interference may be avoided by adding sodium azide

```
DO = (X x N1 x 8)/200 (water sample taken ) x 1000 = .....mg/lit.
```

N1 = Normality of Sodium thiosulphate

X = Burette Reading



Ill effects of Hard Water In Boiler

- A) Priming & foaming (carryover)
- **B)** Caustic embrittlement
- **C) Boiler Corrosion**
- D) Scales & Sludges



Priming

Wet Steam formation inside boiler

Causes

- Very high level of boiler feed water
- Presence of excessive foam
- High speed of steam generation
- Faulty boiler design.



Prevention of Priming

- Avoiding rapid changes in steaming rate
- Maintaining low level of water
- Better Boiler Design
- Removing impurities from water



Foaming

Formation of continuous foam or bubbles on the surface of water

Causes:

- High conc. of dissolved salts in boiler feed water
- Presence of oil droplets and alkalies
- Presence of Finely dispersed suspended material
- Violent agitation of boiler feed water



Prevention of Foaming

- Use of antifoaming agents
- Removal of oil and greases using sodium aluminates
- Removal of silica using ferrous sulphate
- By using soft water



Disadvantages of priming and foaming

- Actual height of water column cannot be judged well due to foaming
- Because of priming, the salts present in the droplets enter in the part of machineries.
- The dissolved salts in droplet of wet steam get deposited on evaporation of water
- Foaming causes wet steam formation



Caustic Embrittlement

Boiler material gets brittle due to exposure to caustic solution at high pressure and high temperature condition

$$Na_2CO_3 + H_2O \implies 2NaOH + CO_2$$

Galvanic cell formation or Concentration cell



Prevention

- Use of Sodium phosphate instead of Na₂CO₃
- Addition of Tannin or Lignin
- Adjustment of pH between 8-9
- Adding Na₂SO₄



Boiler Corrosion

1.Dissolved oxygen

• 2Fe +
$$2H_2O + O_2 \longrightarrow 2Fe(OH)_2 \downarrow$$

• 2Fe(OH)₂ +1/2O₂
$$\longrightarrow$$
 Fe₂O₃.2H₂O (Rust)

Removal of oxygen

•
$$Na_2SO_3 + 1/2O_2 \longrightarrow Na_2SO_4$$

•
$$N_2H_4+O_2$$
 \longrightarrow $N_2\uparrow+2H_2O_2$









Corrosion in Boiler

Hydrolysis of salts

•
$$MgCl_2 + 2H_2O \longrightarrow 2Mg(OH)_2 + 2HCl$$

•
$$FeCl_2 + 2H_2O$$
 Fe(OH)₂ + 2HCl

Disadvantages

- Reducing the life of boiler
- Leakage of joints and rivets
- Increased cost of repairs & maintenance



Scales & Sludges formation

- Scales :Hard adherent deposit formed after saturation point inside boiler
- Due to presence of
 CaSO₄, MgCl₂, silicates
 of Ca & Mg







Scale formation

Causes -

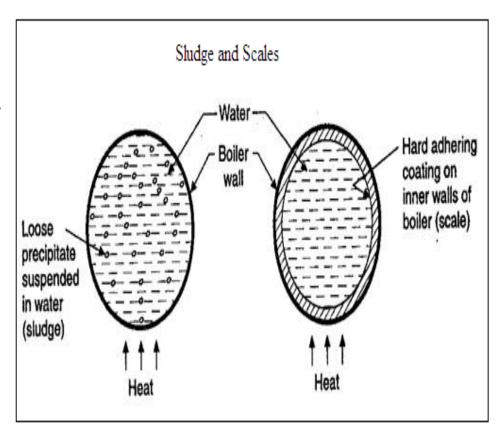
- i) Decomposition of bicarbonates
- ii) Hydrolysis of magnesium salts
- iii) Presence of silica
- iv) Decreased solubilities of CaSO₄ at high temperature





Disadvantages of Scale Formation

- Wastage of Fuel
- Over heating of boiler
- Boiler safety
- Danger of explosion





Sludge

Disadvantages

- Bad conductor of heat (Wastage of Fuel)
- Reduces boiler efficiency
- Reduces the flow rate of water in boiler.

Prevention

- Use of water containing very low quantity of total dissolved solids.
- Frequently making blow down operation.



Prevention of Scale formation

- Use of softened water
- Phosphate conditioning
- Adding sodium aluminates
- Adding organic chemicals like tannin.



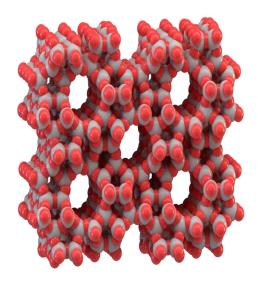
Water treatments

- Zeolite process
- Ion exchange method



Zeolite

- Naturally occurring hydrated aluminosilicates
- Also known as Permutit
- Porous Material
- Insoluble in water
- Works on Ion exchange
 Process

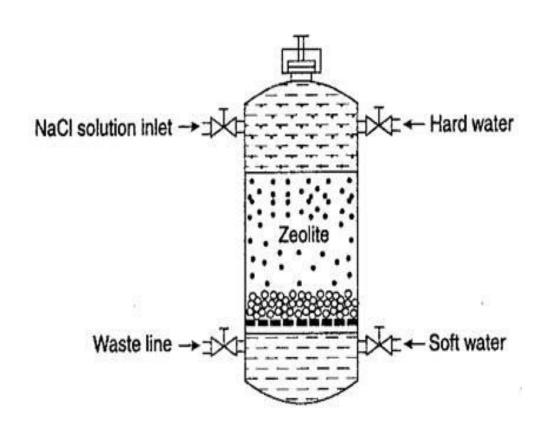






Zeolite

•Zeolite can trap
Ca²⁺, Mg²⁺ from
hard water and
releases Na⁺ ions
into water





Zeolite process

Process

Zeolite capture cations and releases equivalent Nations into water

$$Na_2 Ze + Ca^{2+} \rightarrow CaZe + 2Na^+$$

Regeneration

Brine solution is used



Limitations of Zeolite

- The effective concentration of sodium salt increases
- Mineral acid may disintegrate Zeolite bed
- Highly turbid water can not be treated
- Boiler feed Water with Fe⁺² and Mn⁺² can not be treated properly
- Capable of removing only Cations
- Hot water dissolves Zeolite



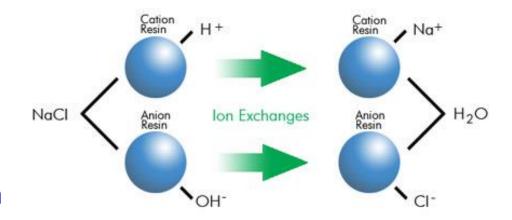
Numericals

- 1. A zeolite bed was exhausted on softening of 4000 litre of water requires 10 litres of 15 % NaCl solution for regeneration. Calculate hardness of water sample.
- 2. A Zeolite softner was completely exhausted and was regenerated by passing 100 litre of NaCl containing 120 gm/litre of NaCl. How many litre of sample of water having hardness 500 ppm can be soften by this softner?



Ion Exchange Method

- Resin are used for water softening
- Resin have either acidic or Basic Functional group with loosely bound ions
- Cation Exchange and anion exchange resins are used



Cation Exchange Resin (RCOOH)

RCOOH + Ca²⁺ \longrightarrow n [(RCOO)₂Ca²⁺] +2H⁺



Key Points – Ion Exchange Method

- Cation exchange resin allow only cation exchange
- Anion exchange resin allow only anion exchange
- Net result is demineralised water
- Cation Exchange resin are regenerated by dilute HCl
- Anion exchange resin are regenerated by dilute NaOH

Anion Exchange Resin $n [R - N^+ (CH_3)_3 OH^-] + Cl^- \longrightarrow n[R - N^+ (CH_3)_3]Cl^- + OH^-$

Regeneration of resin

- Process of regeneration is reversal of reaction for ion exchange process
- Regeneration of <u>cation Exchange resin</u>

$$(RCOO)_2M^{2+} + 2H^+$$
 RCOOH + M^{2+}

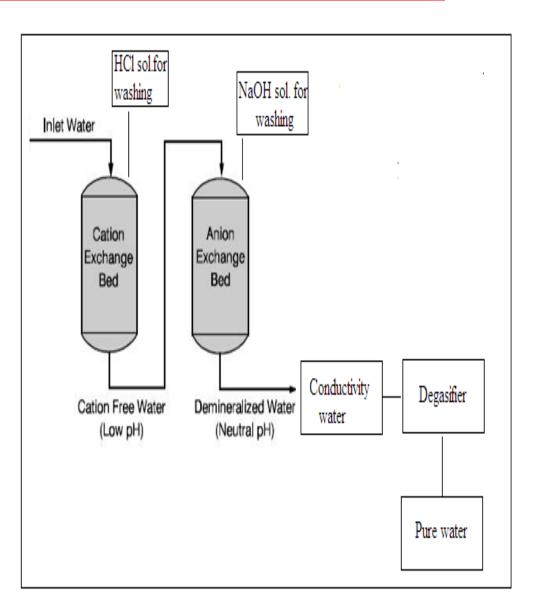
Regeneration of <u>anion Exchange resin</u>

$$[RN^{+}(CH_{3})_{3}]CI^{-} + OH^{-}$$
 $[RN^{+}(CH_{3})_{3}]OH^{-} + CI^{-}$



Ion Exchange Process

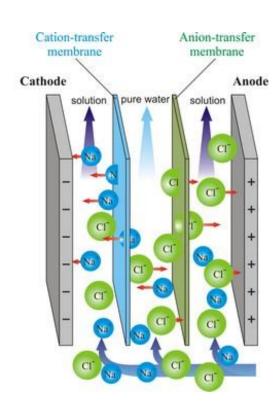
- Works well for variation of hardness of water
- Apparatus occupiessmall space
- Process is easy to operate
- Highly acidic or highly alkaline water can be treated effectively





Electrodialysis

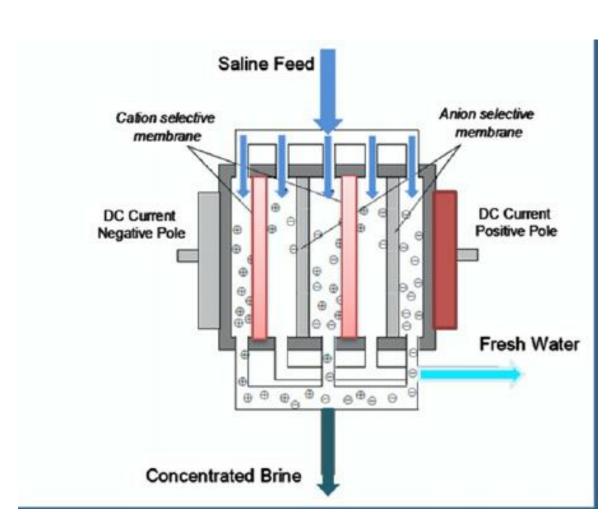
- The process of removing ionic pollutants from water using membranes and electric field is known as Electro dialysis.
- Ion selective membranes are used
- Cation selective membrane allow passage of cations only
- Anion Selective Membrane allow passage of anions only





Electrodialysis

- Under influence of electric field ions migrate towards
 Electrode with opposite sign
- •Concentrated and dilute solution are created in alternate compartment





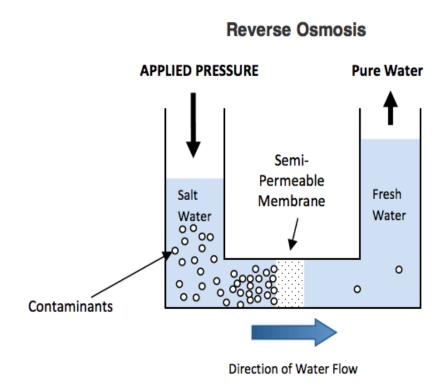
Applications of Electrodialysis

- Removal of ionic pollutants from treated industrial waste.
- Removal of salt from water
- Removal of limited quantity of salts from sea water.



Reverse Osmosis

- In RO process Solvent
 molecules travelled from high
 region of solute concentration
 to low Solute concentration
 through SPM
- External pressure is applied through high solute concentration compartment





Reverse Osmosis

- External applied pressure is greater than osmotic pressure
- Semi permeable membrane made up from polymeric materials like acrylics, polyamides, aramids
- Membrane allow only passage of water molecules (Selective Porosity) by which other impurities are rejected
- water gets separated from contaminants



Advantages of RO Process

- Ionic, colloidal, non-ionic impurities removed from water.
- Pure water for high pressure boiler can be obtained.
- Used to obtain drinking mineral water.
- Simple to operate.
- Low cost process.