

التقنيات المتقدمة لمعالجة المياه اللازمة للغلايات الصناعية العملاقة

Advanced technologies of water treatment required for huge industrial steam boilers

Prepared by

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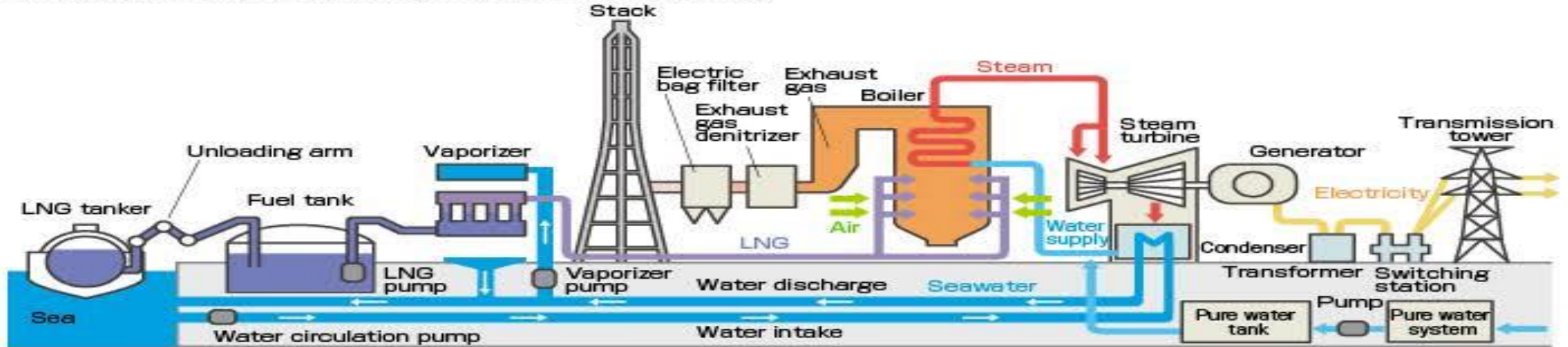
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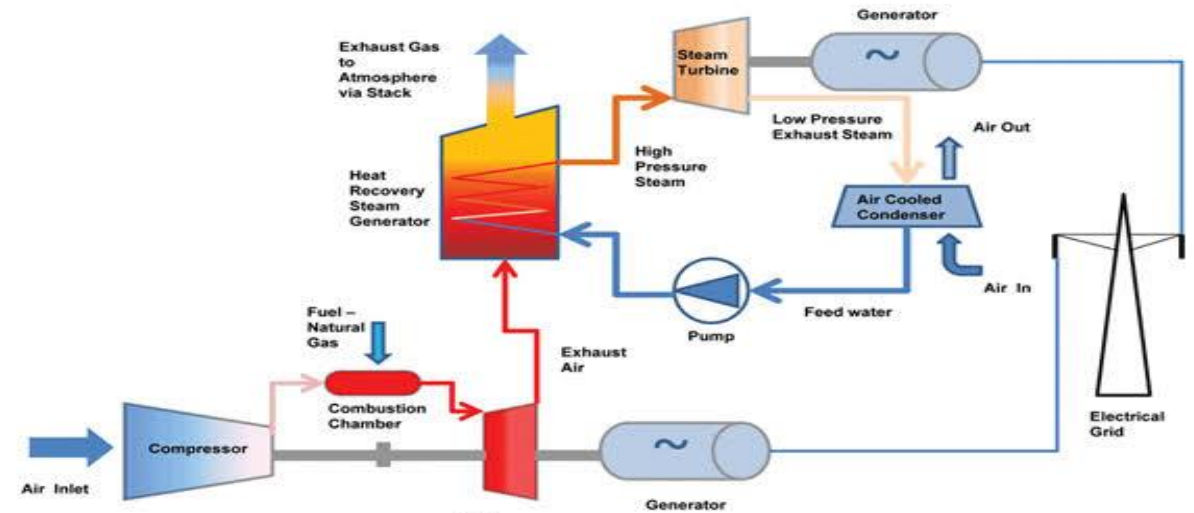
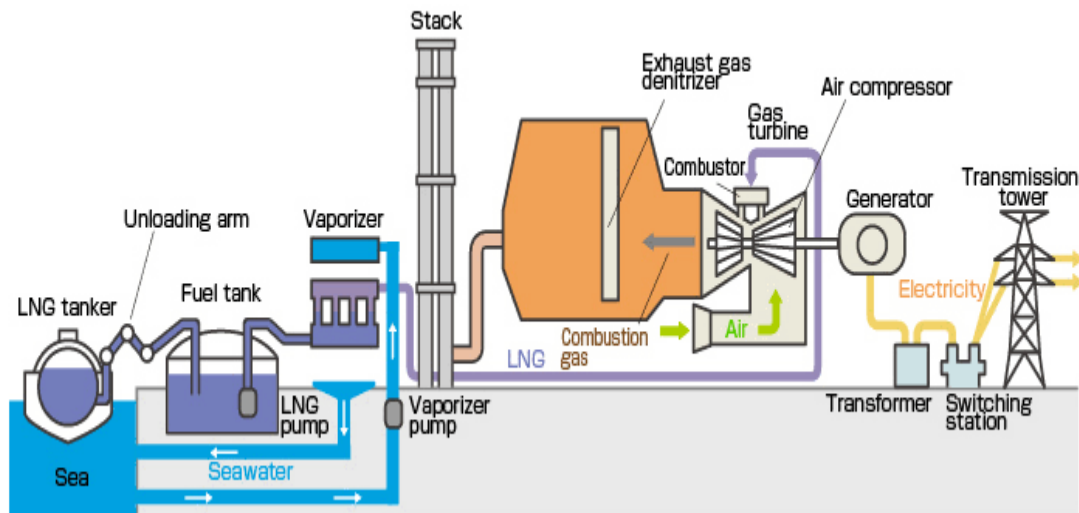
- **A simplified idea about the types of power stations.**
- **Introduction about types of thermal steam boilers which used in power generation.**
- **Major Chemical problems and its effect on high pressure boilers.**
- **Types of chemical treatments required for high pressure boilers.**
- **Permissible chemical specification rates for high pressure boilers.**
- **Methods of water treatment of feed boilers with RO &UF & DM and CEDI systems.**
- **Newest Chemical treatment methods required for internal water &steam circuit of boilers AVT and OT**

Types of electrical power station

Steam power generation (conceptual diagram)

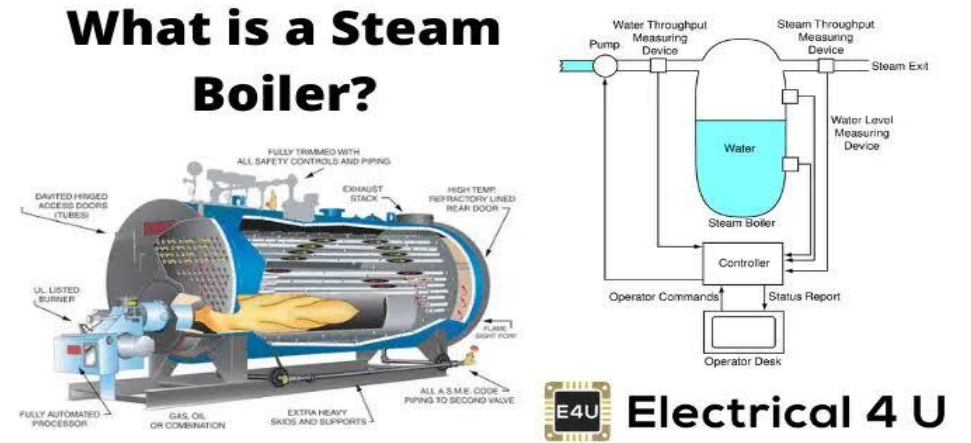
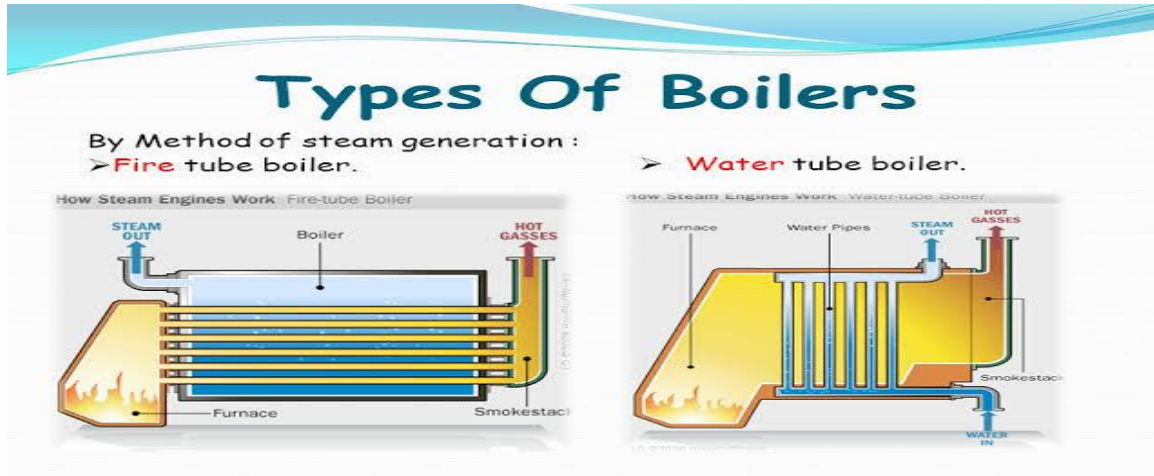


Gas turbine power generation (conceptual diagram)



Steam generator (thermal boiler)

Steam boiler can be defined as A device for converting water to steam under controlled conditions of temperature & pressure.”



Classification of boilers based on fuels

Gaseous Fuel A steam boiler is fired by gas may be natural gas, propane gas, or any other liquid petroleum gas. This type has Good efficiency of combustion, low cost fuel but High cost for the construction of pipelines

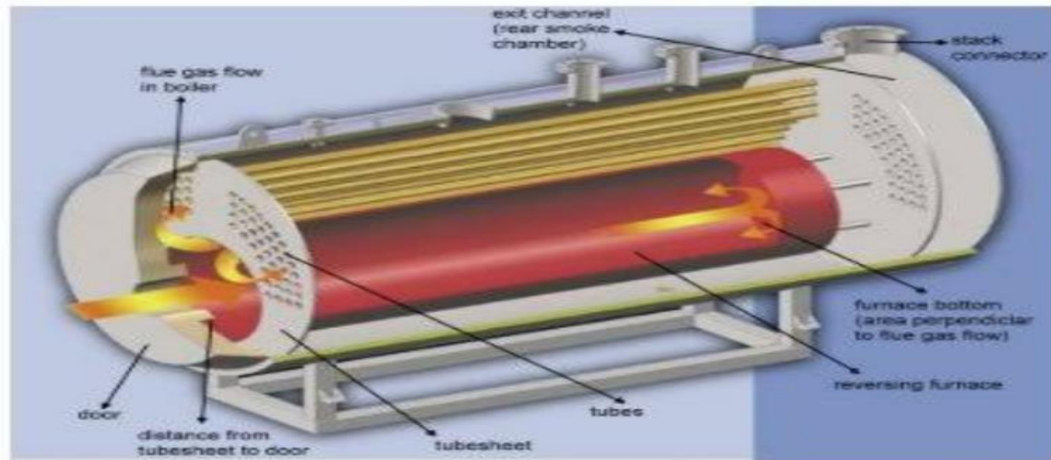
Liquid Fuel A steam boiler is fired by liquid fuel. The liquid used for the boiler may be heavy liquid oil, HSD or Light Diesel oil. This type easily cleaned and the Residue of combustions are not numerous but high cost fuel and High cost for the construction / storage

Solid Fuel A steam boiler is fired by solid fuel. The solid used for the boiler may be coal, coke, peat, wood this type Low cost of fuel but Residue of combustions are hardly cleaned and difficult to find good material

Boilers must be designed in such a way that avoided the formation of steam out of the water wall tubes. The circulation of water and steam in the boiler occurs because Difference of density between water and steam and the existence of mixture of water and steam.

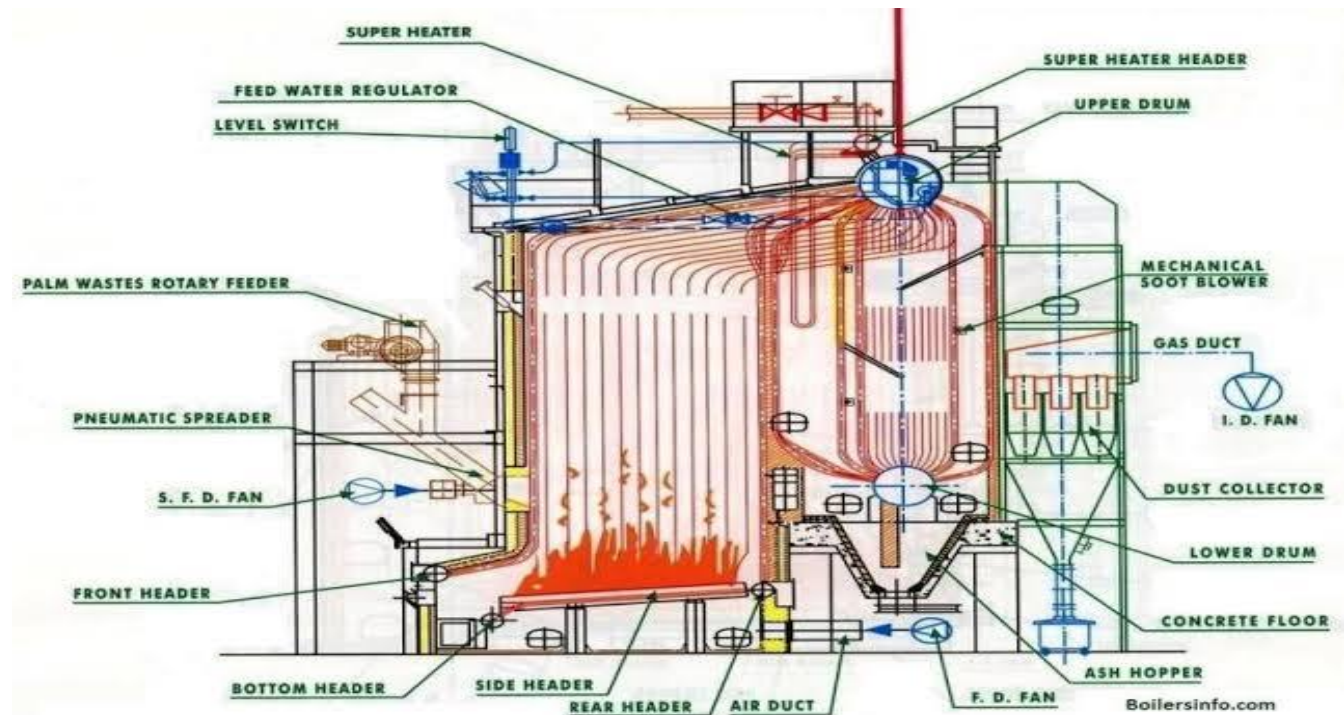
Fire tube boilers

which products of combustion pass through tubes which are surrounded by water, this type is **Easy to Clean, Relatively inexpensive, Compact in size, Well suited for industrial applications, Operates with oil, gas or solid fuels but it can generate steam only up to 24.5 bar and rate of steam generation is low up to 9 tons/ hrs). Over all efficiency is only 75% (not suitable for use in huge power generation plant)**

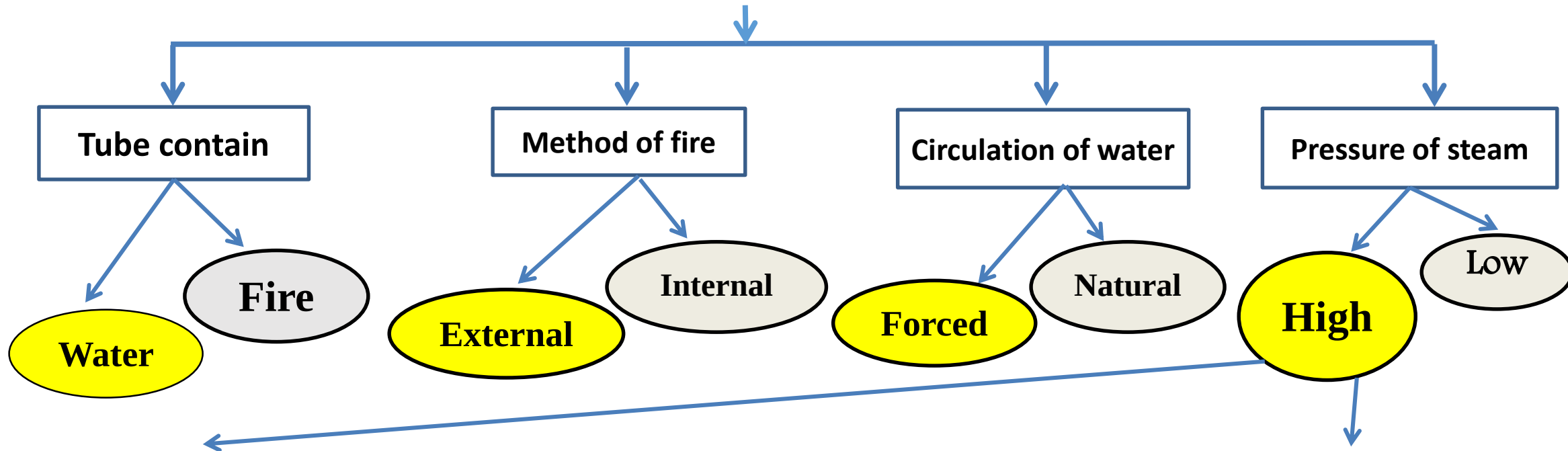


Water tube boilers

A steam boiler in which the water passes through the tubes and products of combustion surrounded the tubes, this type is **Available in larger capacities of Able to handle higher pressures, faster response to changing loads Able to reach very high temperatures, provide an adequate furnace to ensure complete combustion but it can generate steam with higher pressure up to 165 bar and rate of steam generation is low up to 450 tons/ hrs). Over all efficiency is only 90 % but High initial capital cost, Cleaning is difficult due to design structure, no commonality between tubes, huge in physical size, Lower tolerance for water quality and needs water treatment plant. (suitable for use in huge power generation plant)**



Thermal Steam boiler



Sub-boilers

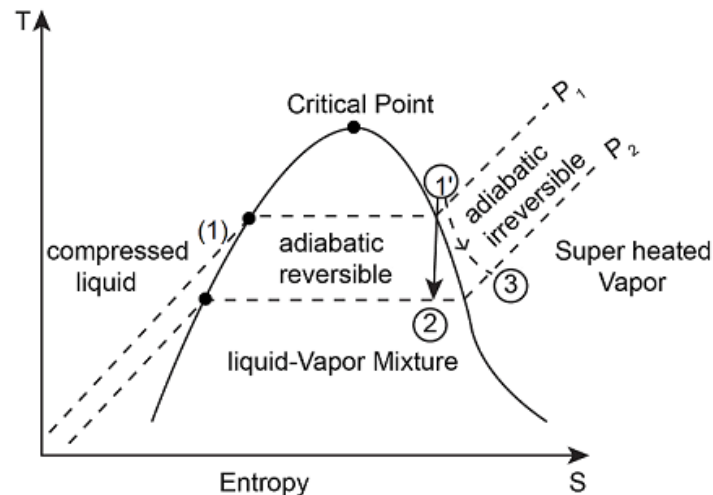
P (80 ---180 bar)

T >500 °C

Steam capacity (200 —250) kg/sec

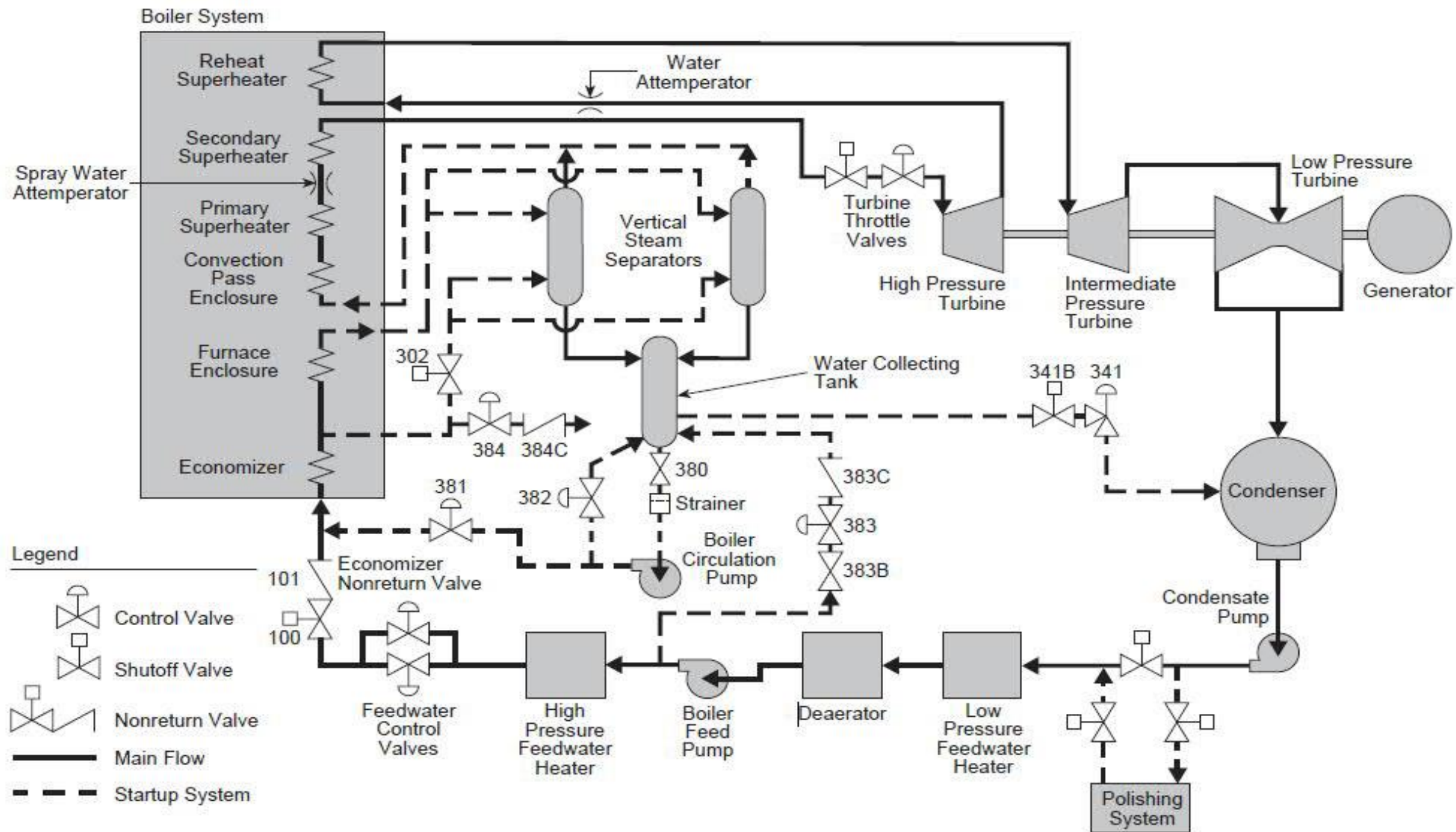
Must have drum in its design

This types with a lot of different design and load used in power plants in Egypt from 1895 till now.



Super critical -boilers

- **P (must be > 250 bar)**
- **T >500 °C**
- **Steam capacity (>500) kg/sec**
- **At full load all water converted to steam in once through without need to drum (which separated vapor out of liquid)**
- **This type used in power plants in Egypt from 2015.**



Major problems caused by impurities of water to the boiler

Scales formation

Scale Forming Ions

Ca ++, Mg ++, CO₃--
, HCO₃ --, SiO₃

- OVER HEATING OF TUBES
- REDUCTION OF HEAT TRANSFER
- CALLS FOR SHUT DOWN
- RESTRICTION OF WATER FLOW

Corrosion

Low pH Dissolved Oxygen

METAL LOSS, PITTING
LOSS OF PROTECTIVE OXIDE FILM
(DESIRED PROTECTIVE FILM IN BOILER
IS MAGNETIC IRON OXIDE, Fe₃O₄. OXYGEN
DESTRUCTS THE PROTECTIVE OXIDE FILM)
 $\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6 \text{Fe}_2\text{O}_3$

High Caustic Alkalinity

CAUSTIC CORROSION / EMBRITTLEMENT
 $\text{Fe}_3\text{O}_4 + 4\text{NaOH} = 2 \text{NaFeO}_2 + \text{Na}_2\text{FeO}_2 + \text{H}_2\text{O}$
(Sodium ferrate)
 $\text{Fe} + \text{NaOH} = \text{Na}_2\text{FeO}_2 (\text{Sodium Ferrite}) + \text{H}_2$

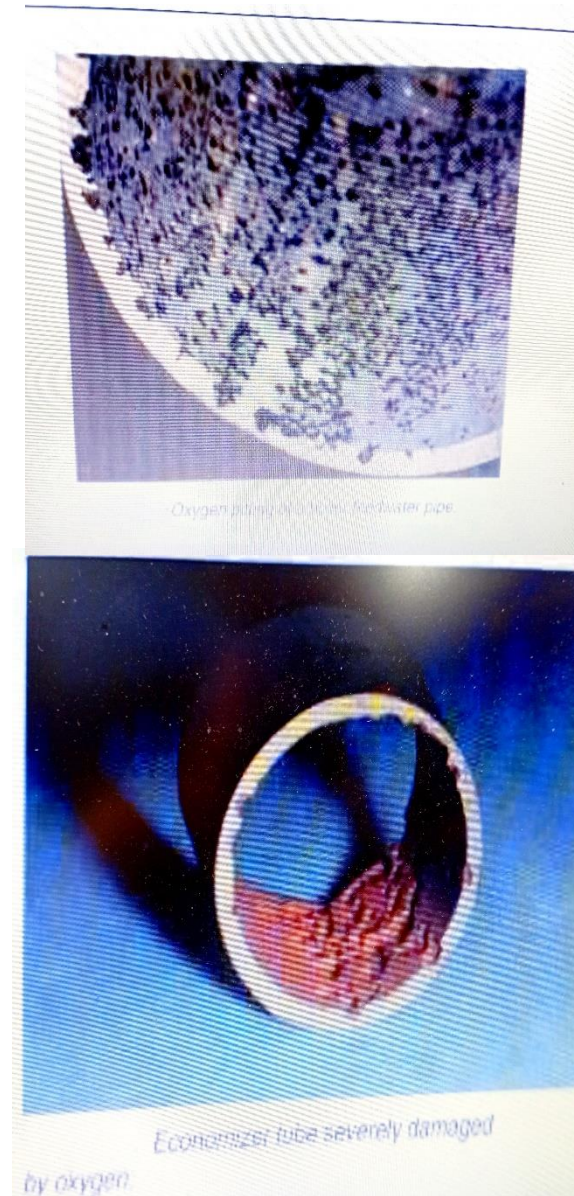
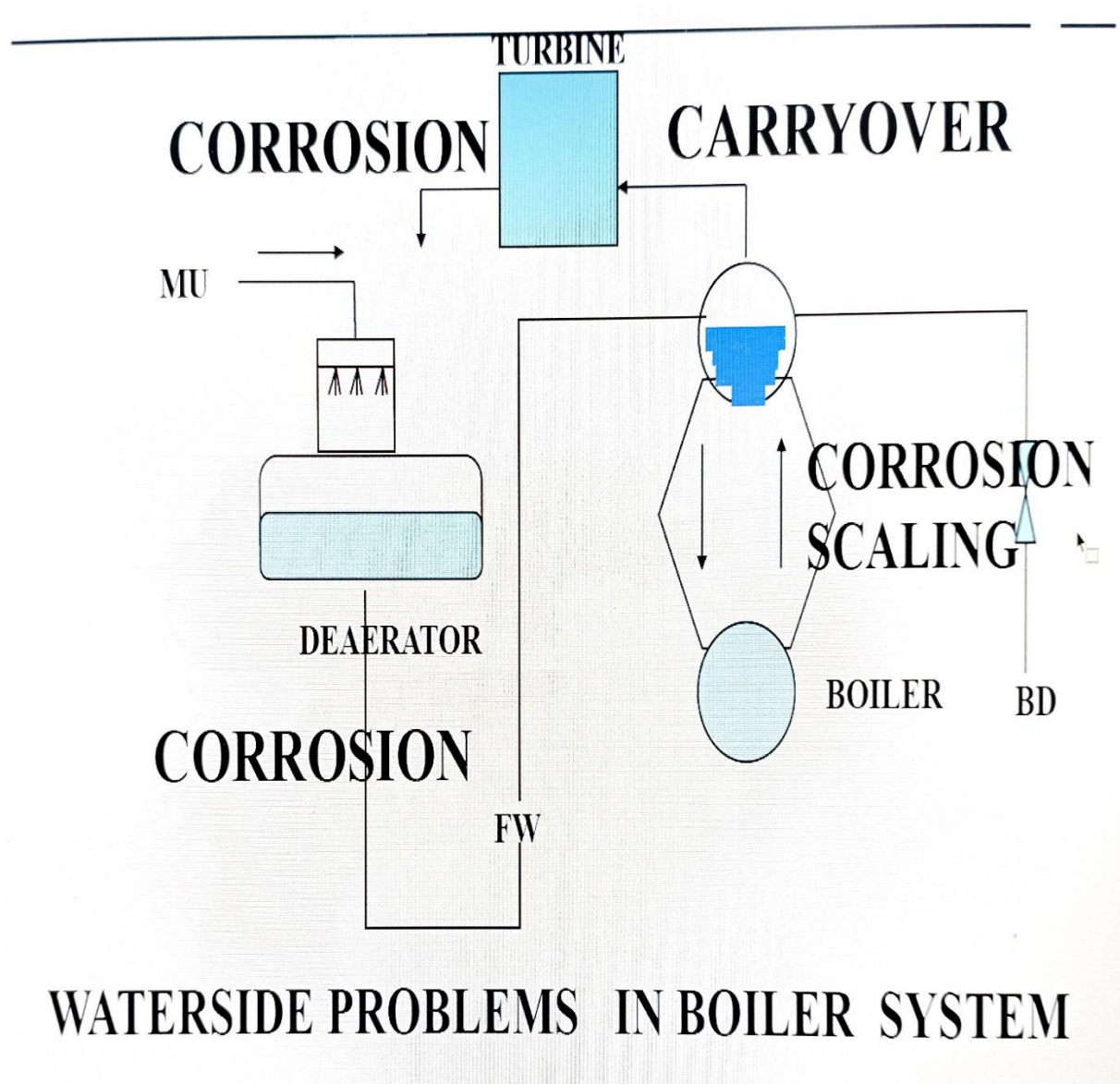
Carbon Dioxide

CONDENSATE CORROSION
BICARBONATES + HEAT CO₂
 $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ (CARBONIC ACID)
 $\text{Fe} + \text{H}_2\text{CO}_3 \rightarrow \text{Fe}(\text{CO}_3)_2$

Carryover steam

- Loss of water feed
 - incomplete separation of steam & water
 - Uneven fire distribution
 - boiler load Fluctuations
- After boiler deposits, Plugged valves, Deposition on turbine Blades cause unbalance

Water- impurities related problems in Boiler

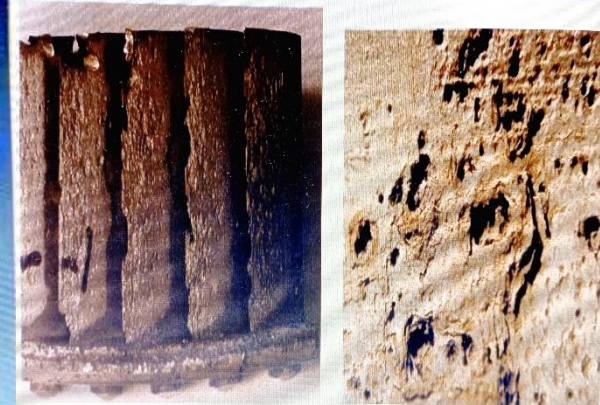


SCALING



Location - Boiler water tubes

TURBINE DEPOSITS



Benefits of Chemical Treatments in general

- Protect equipment from corrosion and extend equipment lifetime.
- Reduce fuel, operating and maintenance costs
- Minimize maintenance and decrease the shutdown time
- Increase boiler efficiency

The properties of the demineralized water (ultra pure water) required for supercritical boiler to be stored in the boiler feed tank is as follow:

- Specific conductivity @ 25 °C ≤ 0.1 mS/cm
 - Total Silica ≤ 10 ppb
 - Sodium ≤ 3 ppb
 - Sulphate ≤ 3 ppb
 - Chloride ≤ 3 ppb
 - Total Organic Carbon ≤ 100 ppb
 - pH 6.5 – 7.5

Types of Chemical treatment systems required for high pressure boilers

- 1) Chemical treatment for boiler before initial startup.
- 2) Chemical treatment for boiler through outage period.
- 3) External water treatment (Applied outside the boiler).
- 4) Internal water treatment (Applied internal the boiler).

(1) Chemical treatment for boiler before initial star up

known by chemical cleaning method for high pressure boilers (target of this treatment is to removal all impurities and deposits from the boiler metal with chemical solutions and formation of chemical passivation layer on surface of metal boiler to keep it from corrosion after start up. (in details in another lec.)

(2) Chemical treatment for boiler through outage period.

known by chemical preservation method for boilers (target of this treatment is to keep the boiler metal passivation layer from corrosion through the outage or shutdown or maintenance periods). . (in details in another lec.)

Impurities of raw water

Dissolved Matter

Inorganic

- Cations (Ca^{2+} , Mg^{2+} , Na^{+})
- Anions (Cl^{-} , SO_4^{2-})

Organic

- Benzoate $\text{C}_6\text{H}_5\text{COO}^{-}$
- Acetate $\text{CH}_3\text{COO}^{-}$
- etc...

Dispersed Matter

Inorganic

- Silica SiO_2
- Carbon dioxide CO_2
- Ammonia NH_3

Organic

- polymers
- oil

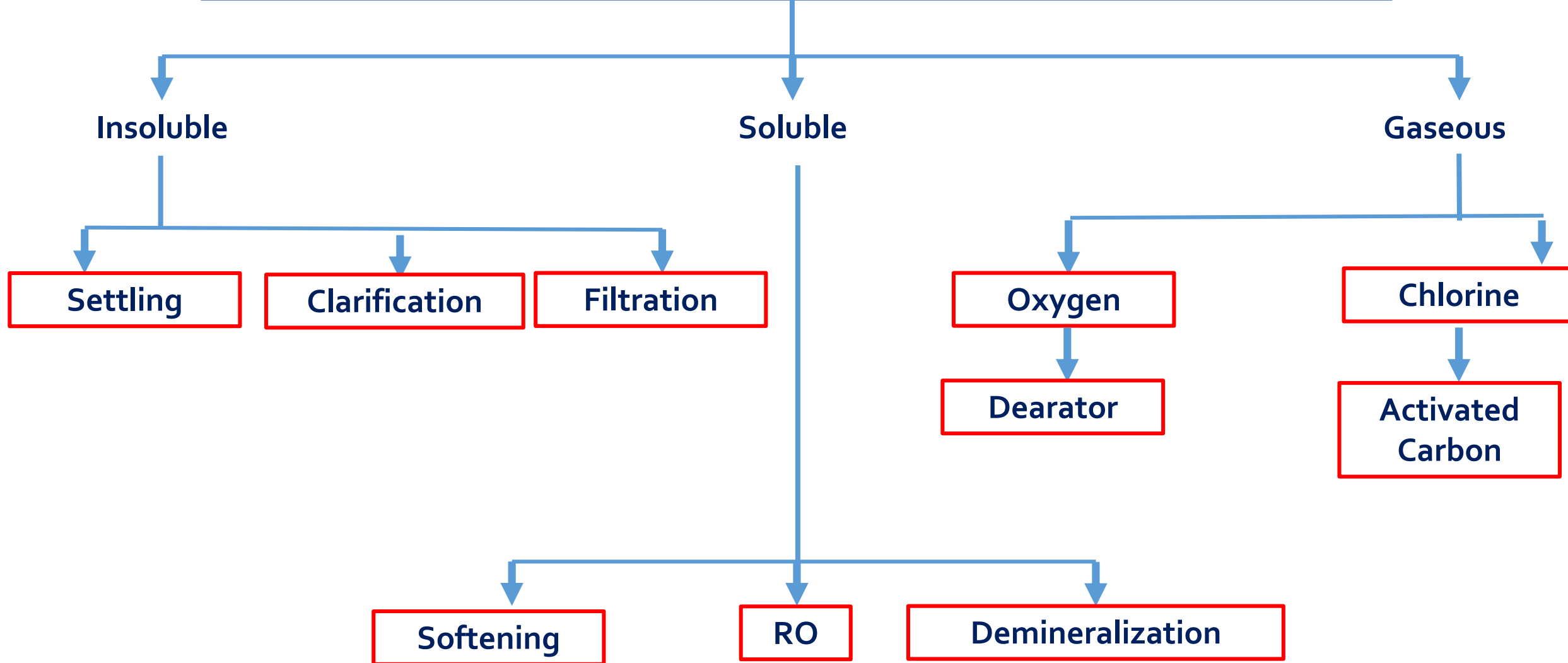
Non dissolved Matter

- Suspended solids
- Colloids
- Bacteria

Constituent	Chemical Formula	Difficulties Caused	Means of Treatment
Turbidity	non-expressed in analysis as units	imparts unsightly appearance to water; deposits in water lines, process equipment, etc.; interferes with most process uses	coagulation, settling, and filtration
Hardness	calcium and magnesium salts, expressed as CaCO_3	chief source of scale in heat exchange equipment, boilers, pipe lines, etc.; forms curds with soap, interferes with dyeing, etc.	softening; demineralization; internal boiler water treatment; surface active agents
Alkalinity	bicarbonate(HCO_3^-), carbonate(CO_3^{2-}), and hydroxide(OH^-), expressed as CaCO_3	foam and carryover of solids with steam; embrittlement of boiler steel; bicarbonate and carbonate produce CO_2 in steam, a source of corrosion in condensate lines	lime and lime-soda softening; acid treatment; hydrogen zeolite softening; demineralization dealkalization by anion exchange
Free Mineral Acid	H_2SO_4 , HCl , etc., expressed as CaCO_3	corrosion	neutralization with alkalis
Carbon Dioxide	CO_2	corrosion in water lines, particularly steam and condensate lines	aeration, deaeration, neutralization with alkalis
PH	hydrogen ion concentration defined as: $\text{pH} = \log \frac{1}{[\text{H}^+]}$	pH varies according to acidic or alkaline solids in water; most natural waters have a pH of 6.0-8.0	pH can be increased by alkalis and decreased by acids
Sulfate	SO_4^{2-}	adds to solids content of water, but in itself is not usually significant, combines with calcium to form calcium sulfate scale	demineralization, reverse osmosis, electro dialysis, evaporation
Chloride	Cl^-	adds to solids content and increases corrosive character of water	demineralization, reverse osmosis, electro dialysis, evaporation
Nitrate	NO_3^-	adds to solids content, but is not usually significant industrially: high concentrations cause methemoglobinemia in infants; useful for control of boiler metal embrittlement	demineralization, reverse osmosis, electro dialysis, evaporation
Fluoride	F^-	cause of mottled enamel in teeth; also used for control of dental decay: not usually significant industrially	adsorption with magnesium hydroxide, calcium phosphate, or bone black; alum coagulation
Sodium	Na^+	adds to solids content of water: when combined with OH^- , causes corrosion in boilers under certain conditions	demineralization, reverse osmosis, electro dialysis, evaporation

Silica	SiO_2	scale in boilers and cooling water systems; insoluble turbine blade deposits due to silica vaporization	hot and warm process removal by magnesium salts; adsorption by highly basic anion exchange resins, in conjunction with demineralization, reverse osmosis, evaporation
Iron	Fe^{2+} (ferrous) Fe^{3+} (ferric)	discolors water on precipitation; source of deposits in water lines, boilers. etc.; interferes with dyeing, tanning, papermaking, etc.	aeration; coagulation and filtration; lime softening; cation exchange; contact filtration; surface active agents for iron retention
Manganese	Mn^{2+}	same as iron	same as iron
Aluminum	Al^{3+}	usually present as a result of floc carryover from clarifier; can cause deposits in cooling systems and contribute to complex boiler scales	improved clarifier and filter operation
Oxygen	O_2	corrosion of water lines, heat exchange equipment, boilers, return lines, etc.	deaeration; sodium sulfite; corrosion inhibitors
Hydrogen Sulfide	H_2S	cause of "rotten egg" odor; corrosion	aeration; chlorination; highly basic anion exchange
Ammonia	NH_3	corrosion of copper and zinc alloys by formation of complex soluble ion	cation exchange with hydrogen zeolite; chlorination; deaeration
Dissolved Solids	none	refers to total amount of dissolved matter, determined by evaporation; high concentrations are objectionable because of process interference and as a cause of foaming in boilers	lime softening and cation exchange by hydrogen zeolite; demineralization, reverse osmosis, electrodialysis, evaporation
Suspended Solids	none	refers to the measure of undissolved matter, determined gravimetrically; deposits in heat exchange equipment, boilers, water lines, etc.	subsidence; filtration, usually preceded by coagulation and settling
Total Solids	none	refers to the sum of dissolved and suspended solids, determined gravimetrically	see "Dissolved Solids" and "Suspended Solids"

(3) External water treatment (required to boiler feed water).

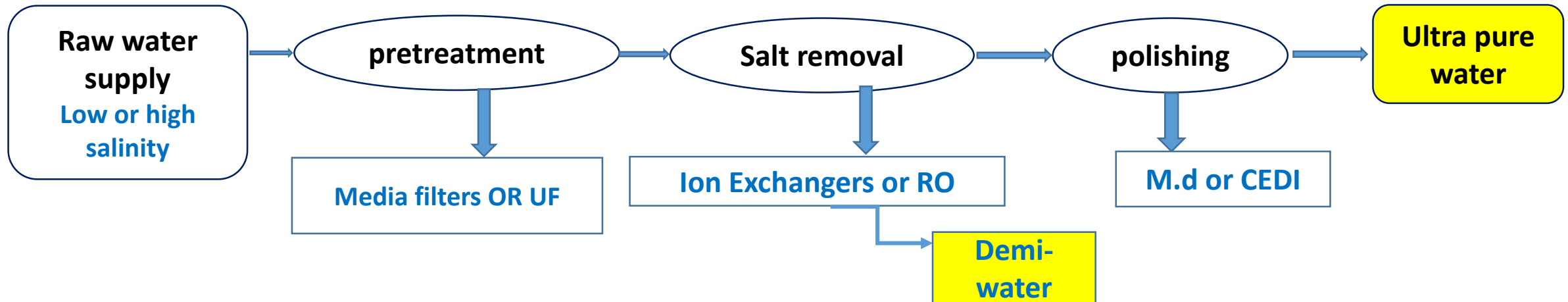


Classification of Water Treatment Systems

Water treatment in high pressure steam boilers which used in power generation plants can be classified into:

- **External Treatment Systems**

Refer to treatment of water before it enters the cycle



- **Internal Treatment Systems**

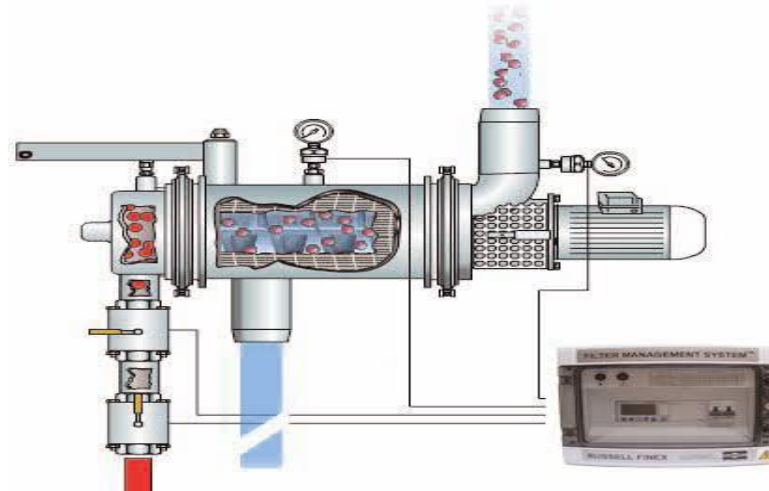
Refer to treatment of water inside the cycle

Both internal and external treatments are required for most of power generation facilities

Water Systems (Pretreatment)

Course particle (up to cm range) shall be removed to protect downstream equipment using one or combination of the following:

- Bar screens (trash racks) : *2-8 cm opening*
- Travelling screens : *3-10 mm opening mesh*
- Cartridge filters : *1-50 micron*
- Self cleaning filters : *micron range “automated”*



External treatment :

Includes all processes required to remove undesirable elements from raw water in order to meet make-up water requirements (**DEMI WATER**).

This includes :

- Removal of suspended solids (**pretreatment**)
- Removal of dissolved minerals (**demineralization**)

Makeup (MU)	
Conductivity, $\mu\text{S/cm}$	< 0.1
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 0.1
SiO_2 , $\mu\text{g/kg}$	< 10

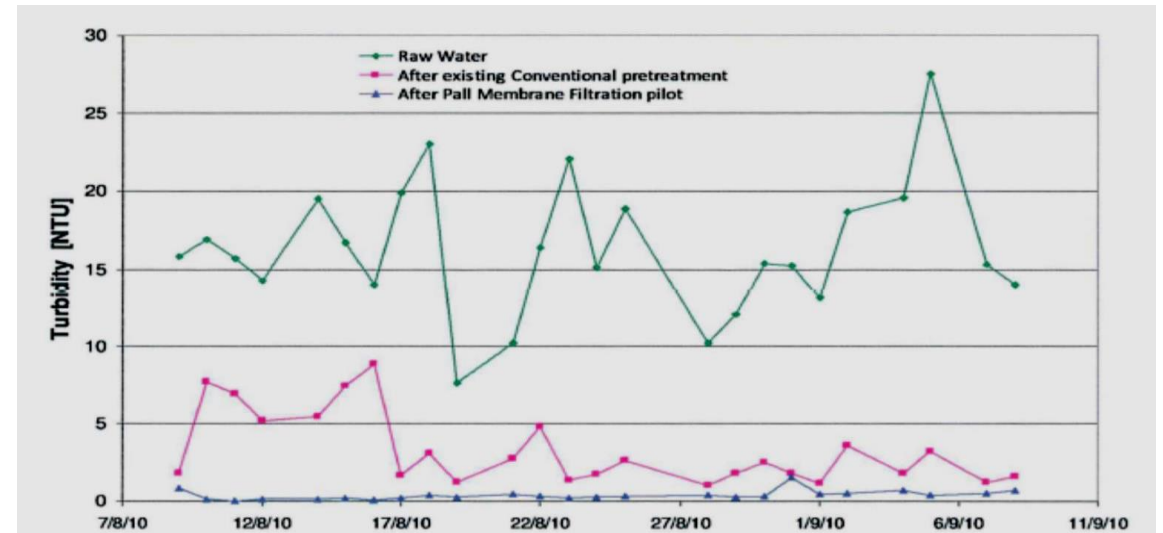
Low-salinity Water Systems Pretreatment

■ Conventional Technology

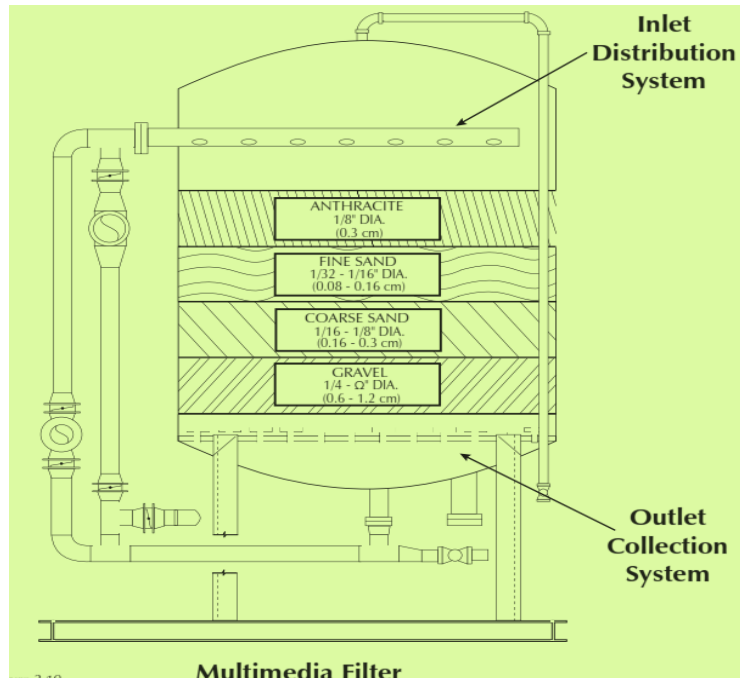
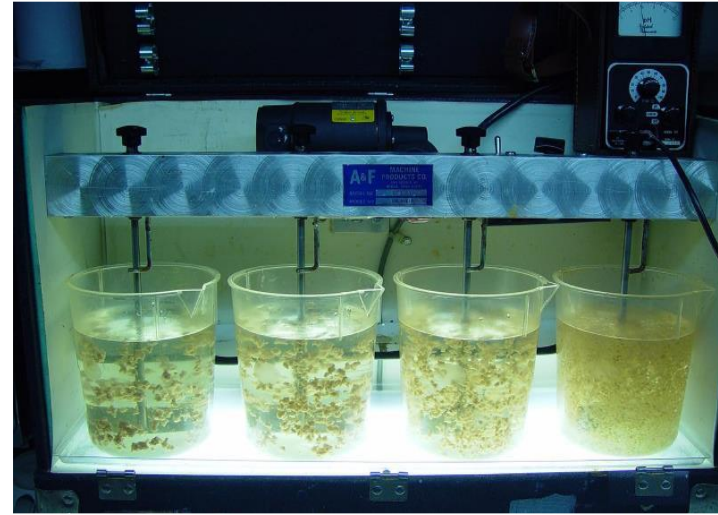
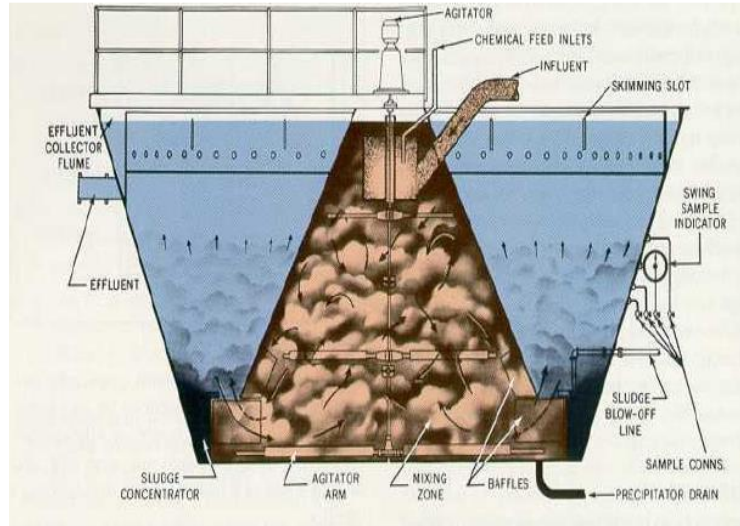
Clarification/MMF

■ Modern Technology

Ultra Filtration (UF)



Conventional Technology Clarification/MMF

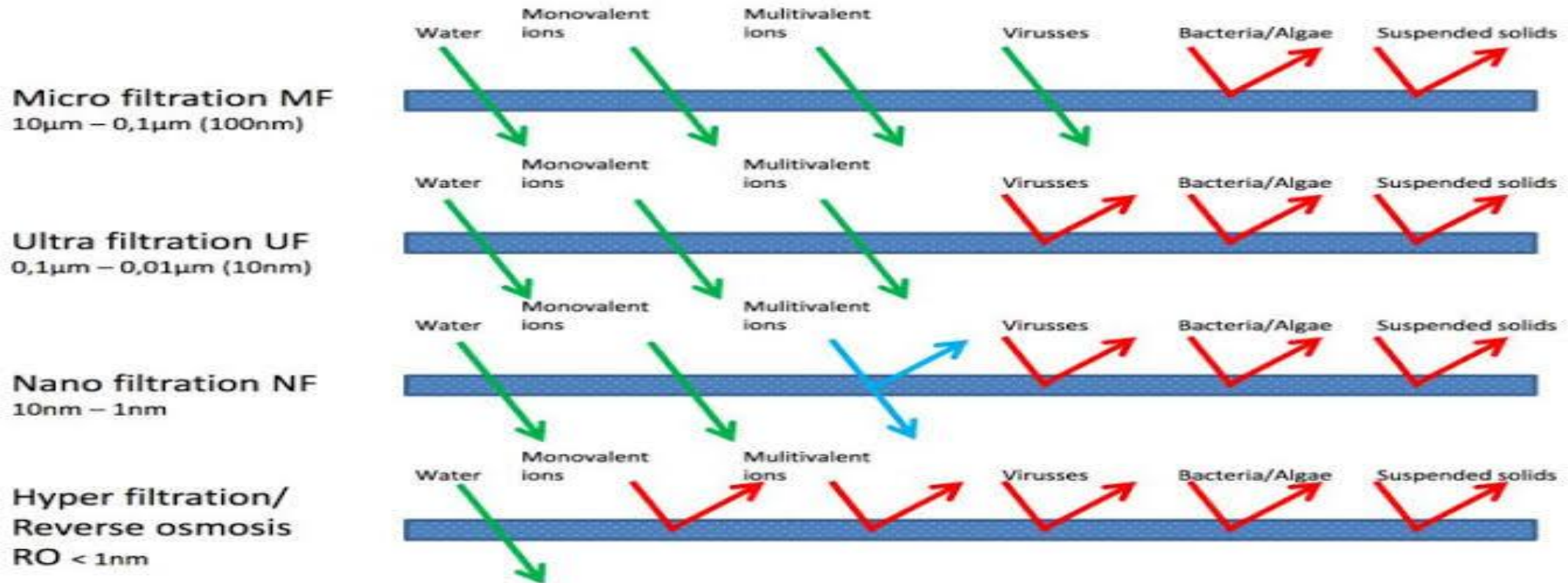


1. Screening
2. Chlorination (disinfection)
3. Mixing tank (clarifier) coagulants
4. Flocculation tank (settling)---- press filter
5. Multi media filters (open or close type)
To produce filtered (TDS < 1000 & PH 6.5-8.5 & turbidity < 5 total hardness < 500 water as feed of demineralized plant system or feed of drinking water system as type of coagulants
6. Carbon filter + ion exchangers unit ---- demi

Modern Technology for water treatment

UF system (Ultra Filtration)

Ultrafiltration is a membrane-based process that depends on the particle size to get rid of particles, Bacteria, a wide range of colloids and viruses, pathogens as well as the high molecular weight species and some of dissolved organics (DOC). However, it cannot treat salts!



UF membranes' industry based on the following aspects:

Membrane configuration, Membrane material, Operation mode, Pore size, Orientation ,Cleaning optimization

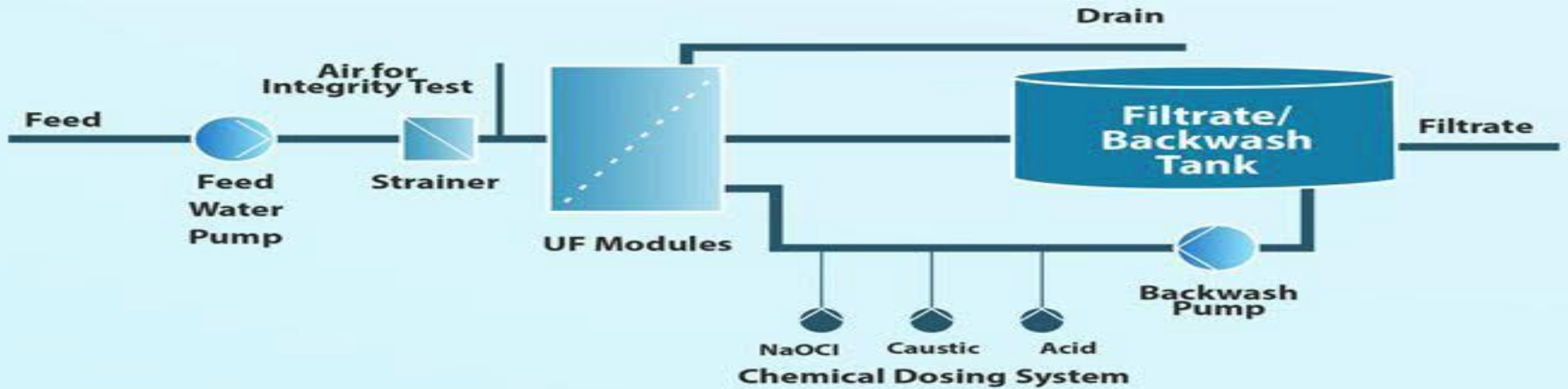
Ultrafiltration(UF) Water Purifier Technology

horizontal arrays



Ultrafiltration Membrane System



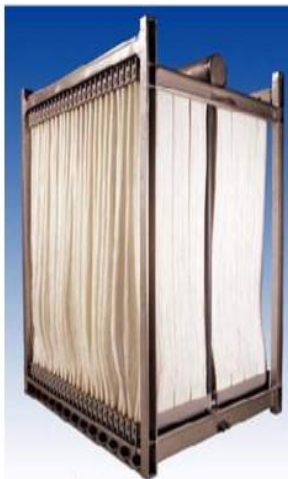


Ultra Filtration Process

Membrane configurations



Submerged hollow fiber



Flat Sheets



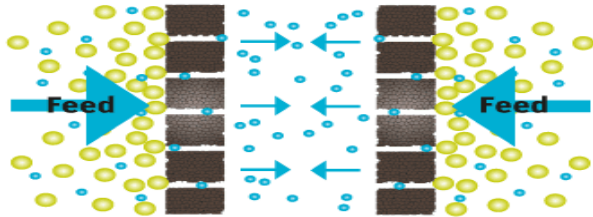
Pressurized hollow fiber



Tubular

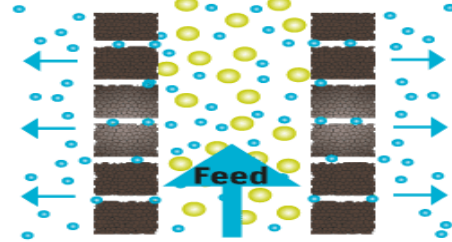
Flow modes

Outside-In Filtration

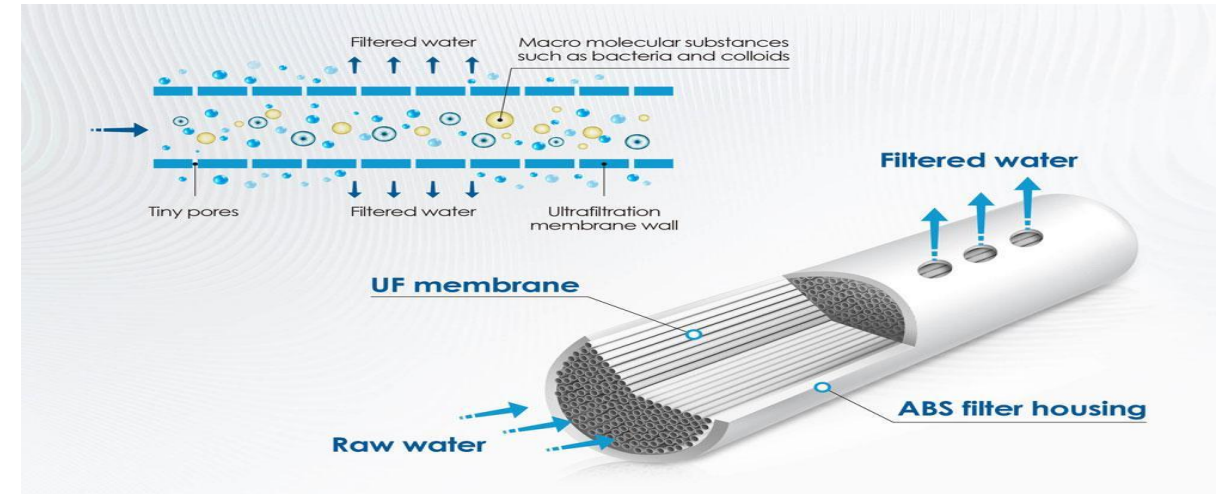


- Higher fouling
- Lower flux
- Harder to clean

Inside-Out Filtration



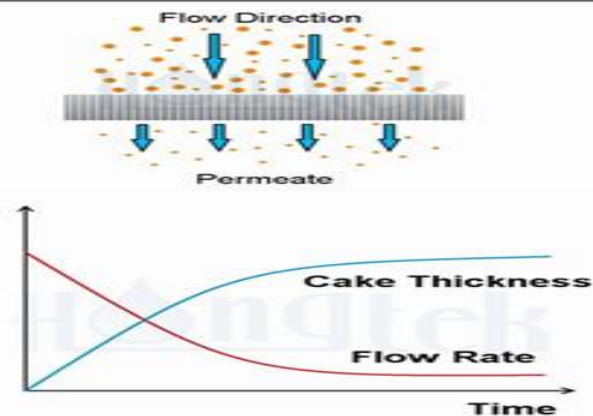
- Superior fouling resistance
- Higher sustainable flux
- Easier to clean



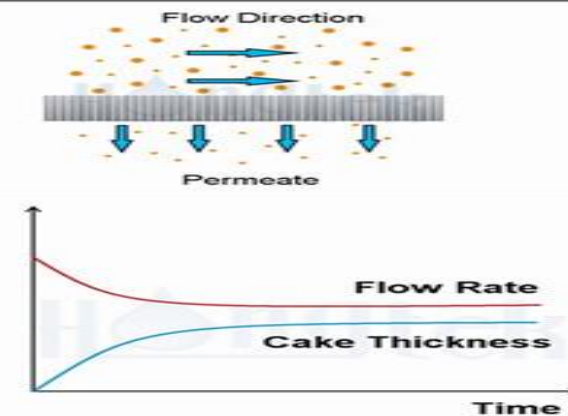
Operations Modes

Dead End filtration : Flow is perpendicular to the filtration surface, the particles are retained over the filter surface.

Cross flow filtration : Flow is tangential to the filtration surface, the particles are continuously flushed to the reject.



Dead End Filtration



Cross Flow Filtration

Flow modes

	Inside-Out	Outside-in
Submerged UF	Na	√
Pressurized UF	√	√
High suspended solids size	Na	√
Hydraulics	Best distribution	Good distribution
Turbulence operation and air scouring	Na	√
Material	Mostly PES	Mostly PVDF

Fibers Materials

	PES (Polyether Sulfone)	PVDF (Polyvinylidene Difluoride)	PP (Polypropylene)
Wettability with aqueous solutions	Hydrophilic	Hydrophobic	Hydrophobic
Strength	strong	Very strong	Very strong
Flow	High flow	Normal flow	
Thermal stability	normal	High	Very high
Chlorine exposure	High (250-300,000 ppm-hr)	Very high (up to 750,000 ppm-hr)	Very high



UF Plant

Schematic Process

Ultra filtration Plant

0:09 / 1:30



268



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Performance Parameters of UF plant

(1) Flux :

is filtrate flow rate per unit area of membrane.
Flux is a system design parameter that has a direct correlation with membrane fouling rate.

$$J = \frac{Q}{A_m}, [\text{lmh}]$$

where

J - filtrate flux, [liters/m²/hour].

Q - filtrate flow, [liters/hr].

A_m - effective membrane area, [m²].

Clean membrane → high filtrate Flux (J)

fouled membrane → low filtrate flux (J)

A_m- Specific for type of membrane

Q- filtered water flow (product of UF)

6 vessels (4 membrane) , all unit 24 membrane

A_m for every membrane A_m 80 m², All Unit A_m

1920 m², Q- filtered water flow measure for final product found =125000 l/hour

J=125000/1920= 65.1 lmh

For UF, the flux can be up to 90 lmh (some UF manufactures claim more~100lmh)

(2) Trans Membrane Pressure TMP

or the Net Driving Pressure NDP on the membrane. This is the effective pressure for forcing water through the membrane.

(pressure drop across membrane barrier)

A clean membrane mean → low TMP

fouled membrane → high TMP

In Cross flow design

$$TMP = (P_{\text{feed}} + P_{\text{concentrate}}) / 2 - P_{\text{filtered}}$$

in dead end flow design

$$TMP = (P_{\text{feed}} + \dots) / 1 - P_{\text{filtered}}$$

Note: TMP differ from Differential pressure →

Represent pressure drop across membrane module or unit from feed inlet to concentrate (all unit)

(3) Permeability or (TCSF)

Also called (Temperature Corrected Specific Flux) or NWP (normalized water permeability)

$$NWP \text{ or } TCSF = \frac{J \times TCF}{TMP}$$

TCF → Tempr. Correction factor Measure by (viscosity of water at measured (T) / viscosity of water @ 25° C) be constant as type of membrane test in manufacture .

NMP → very important parameter for comparison between pre and post use membrane.

Increase of flux (J) should be balanced by high (TMP) and vice versa.

Increase of TMP with constant flux (i.e. due to fouling) → means decrease of TCSF.

Increase of flux (J) with low (TMP) → means mechanical/chemical damage in fibers.

UF backwash

With out chemicals (only back wash with filtered water) after every cycle of operation (such as after every 40min of operation cycle) automatic back wash cycle done or as manual recommendation.

Chemical UF backwash CEB

Acid

Typically HCl or H₂SO₄ @ approx. 500 mg/L (target pH 2)

Frequency is typically every 72 hours or when necessary.

Removes colloids and inorganic salt plugging both inside and outside of membrane.

Alkali

NaOH @ approx. 500 mg/L (target pH 12)
Generally combined with NaOCl @ approx. 350 mg/L

Frequency is typically every 12-24 hours or when necessary.

Removes organics and biofoulants from membrane.

UF (CIP) chemicals

Acid

Typically HCl or H₂SO₄(target pH 2)

- Frequency is typically every 3 months or when necessary.
- Removes **colloids** and **inorganic** salt plugging both inside and outside of membrane.
- Nitric acid is the recommended acid for polymeric fouling

Alkali

- NaOH (target pH 12)
- Generally combined with NaOCl @ approx. 350 mg/L
- Frequency is typically every 3 months or when necessary.
- Removes **organics**, **Silica scaling** and **bio- foulants** from membrane.

Citric acid or Ascorbic acid

- Normally 1%w/w
- Frequency is typically every 3 months or when necessary.
- Acts as reducers to remove **Ferric** and/or **manganese**.

Citric Acid/EDTA

- Frequency is typically every 3 months or when necessary.
- Acts as complexing agents to remove **inorganic** salt from membrane.

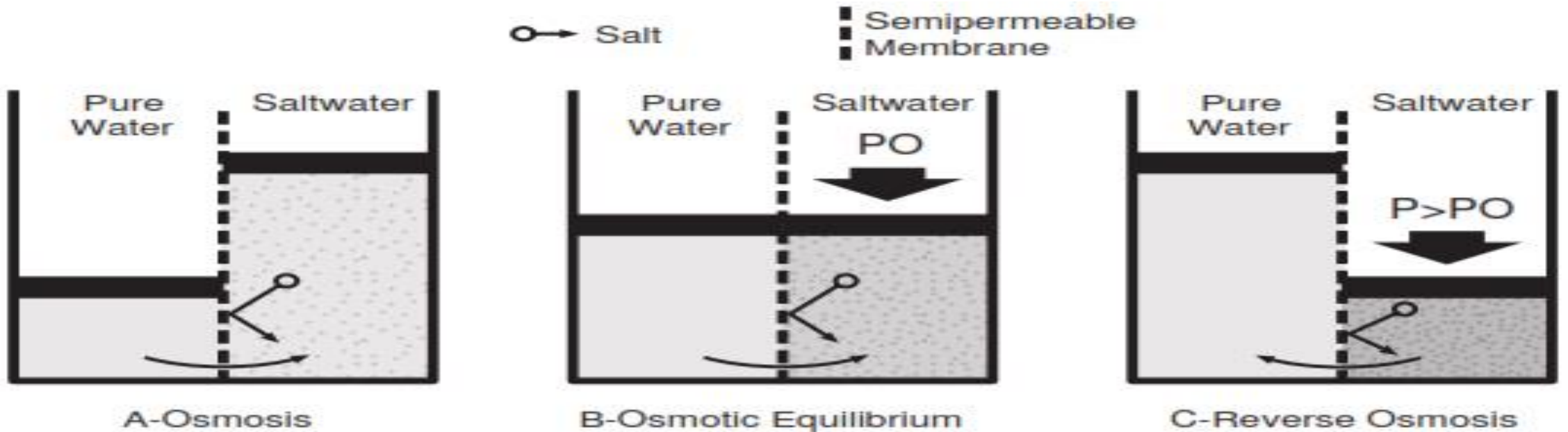
Oxidizing agents

- Normally Sodium hypochlorite (200-500 ppm free chlorine)
- Frequency is typically every 3 months or when necessary.
- Acts as oxidative agent to remove **Biofoulants** from membrane

Oxalic acid

- Oxalic Acid is not recommended for water with high hardness, as it will form irreversible calcium oxalate.
- Frequency is typically every 3 months or when necessary.
- Acts as reducer agent to remove **Ferric** and/or **manganese** from membrane.
- Oxalic acid (1%w/w) will be combined with ascorbic acid (0.25 %w/w), however o prevent oxalate forming make sure to first dissolve ascorbic acid before adding oxalic acid

Reverse osmosis (RO)



A - In the normal osmotic process, pure water flows across the semipermeable membrane, dashed line, to the brine chamber. The membrane does not allow the solute to permeate through to the pure water side.

B - Phase equilibrium is attained by applying a pressure equal to the osmotic pressure P_O to the brine.

C - In RO, the high pressure applied to the brine compartment forces the water to flow through the membrane from the brine side to the pure water side.

Theory of Osmosis

$$\text{Osmotic pressure (PSI)} = \text{TDS}/100$$

$$\text{Osmotic Pressure (bar)} = \text{TDS}/1400$$

Fluid pressure law → Measure pressure of liquid inside tube or tank with known height

$$P(\text{bar}) = \text{density (kg/m}^3) \times h \times g \text{ (m/s}^2) \text{ water}$$

$$P(\text{bar}) = 977 \times 9.81 \times h$$

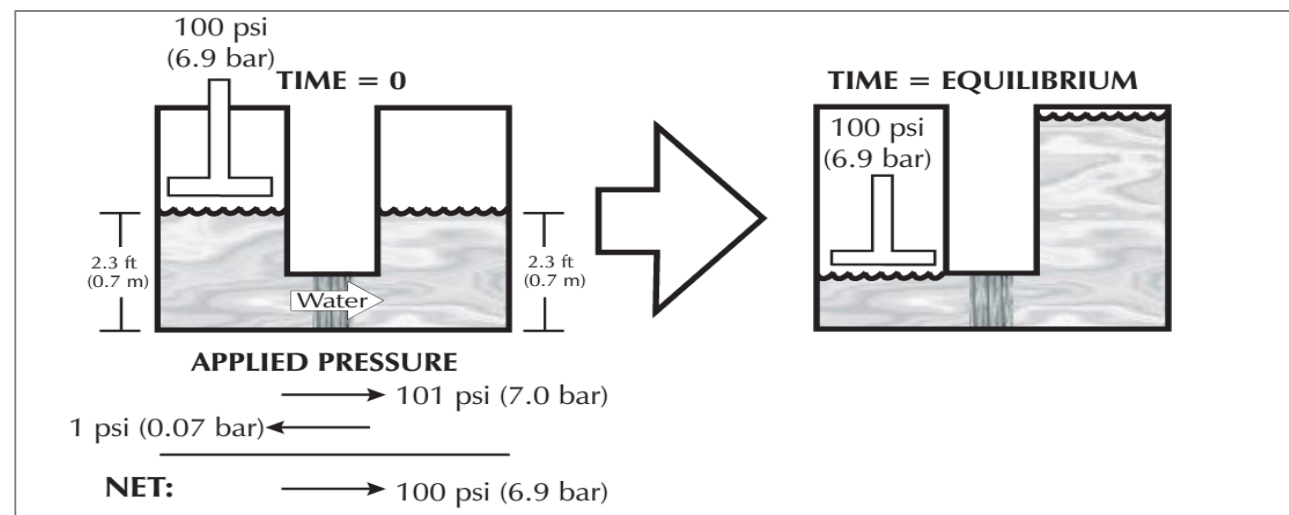
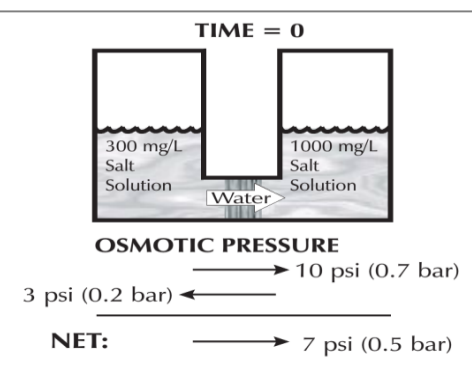
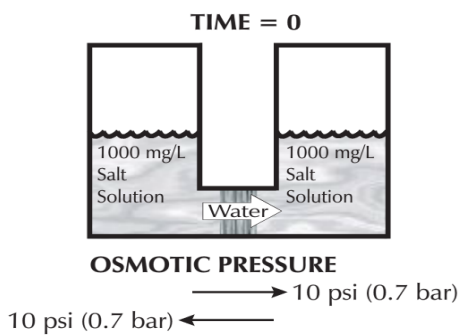
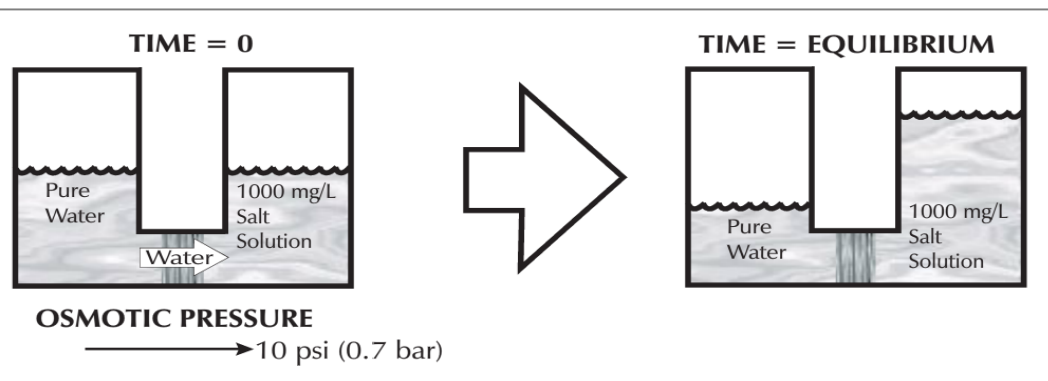
NET= difference betn. Osmotic pressure

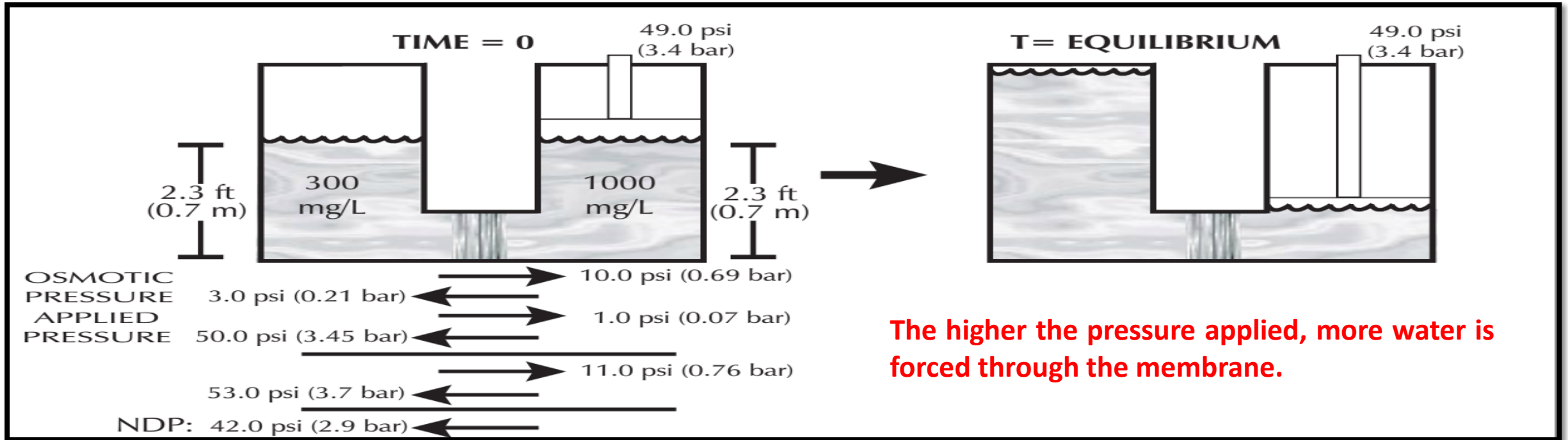
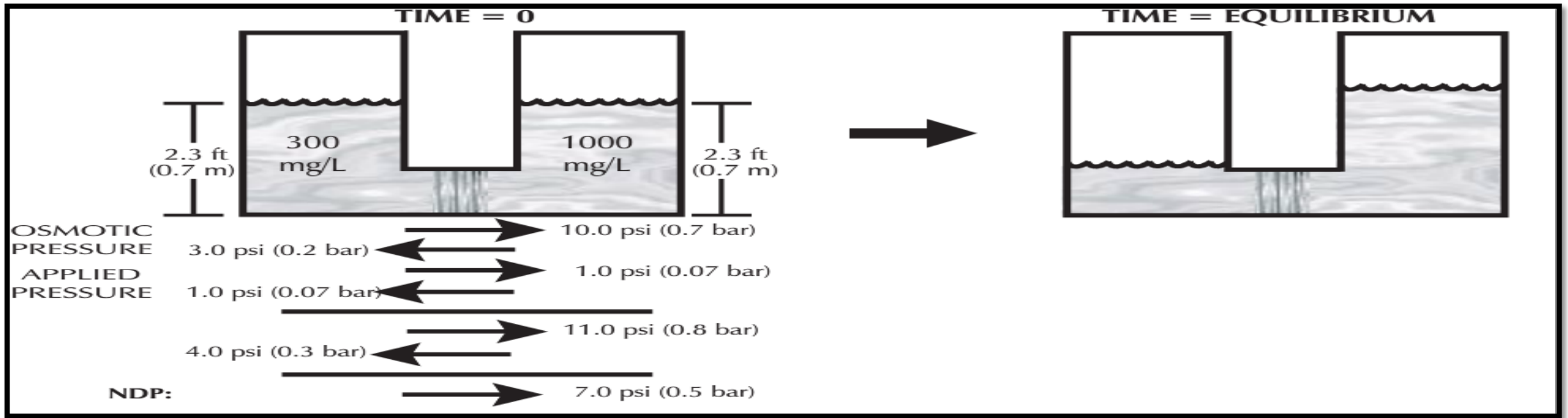
NDP= net driving pressure required for flow transfer through semi membrane = the sum of all pressures acting on either side of an RO membrane. $(OP+AP)_a - (OP+AP)_b$

Definition :

Reverse Osmosis is the passage of water in the opposite (reverse) direction of that which the natural osmosis process produce.

Applied Pressure : is the pressure applied to an RO membrane by hydrostatic head and/or by a pump.



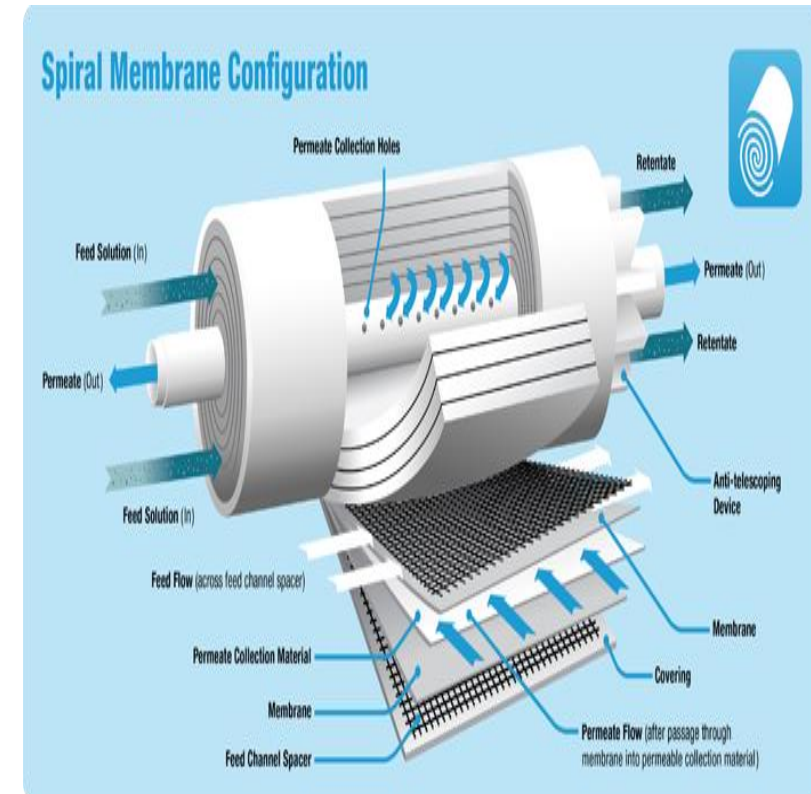
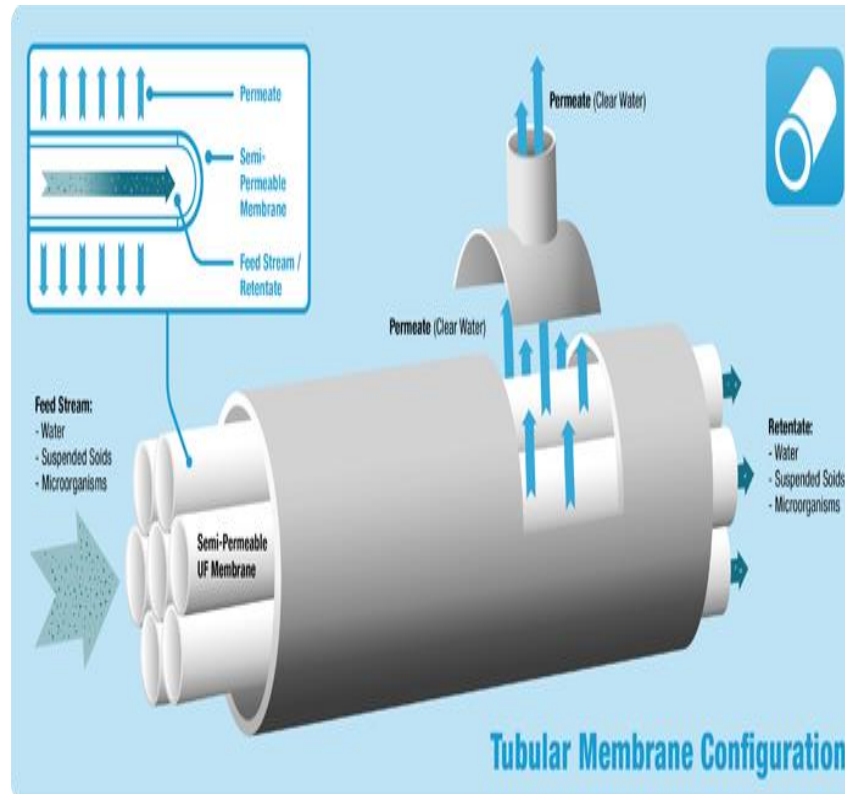
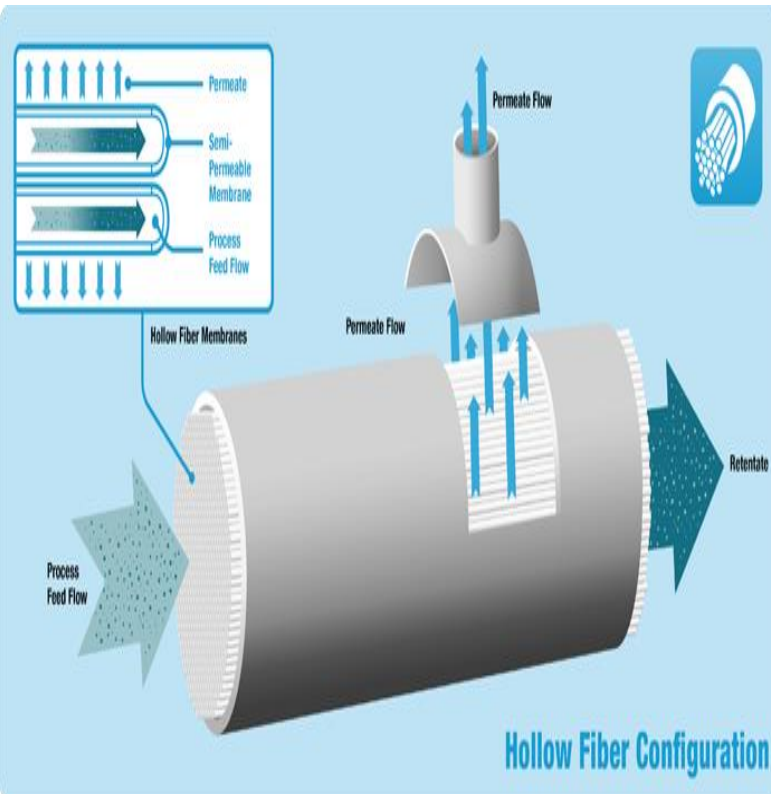


The higher the pressure applied, more water is forced through the membrane.

There are three main types of RO membranes

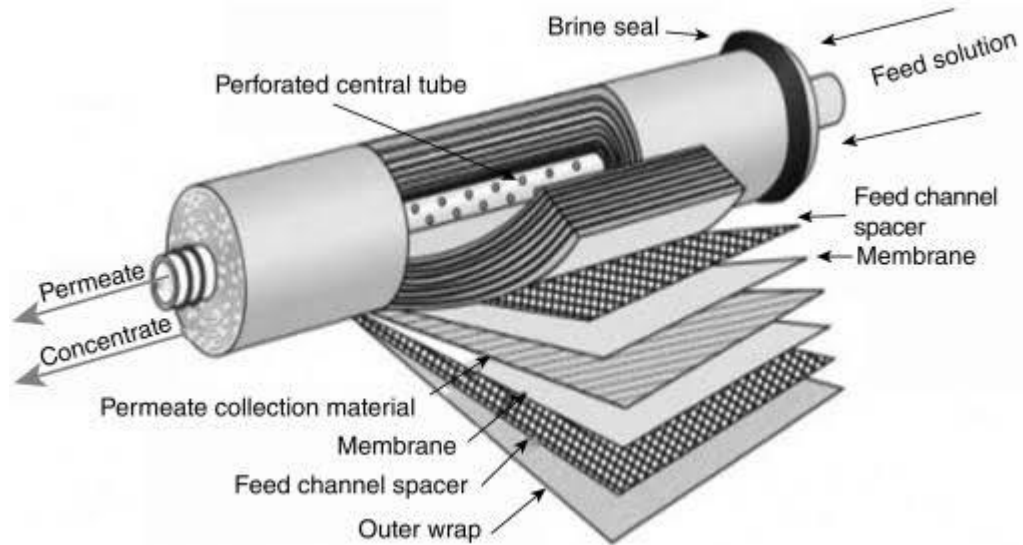
- Spiral wound
- Hollow fibers
- Tubular

All use flat sheet membrane, the difference is the manufacture techniques

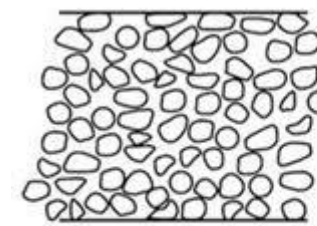
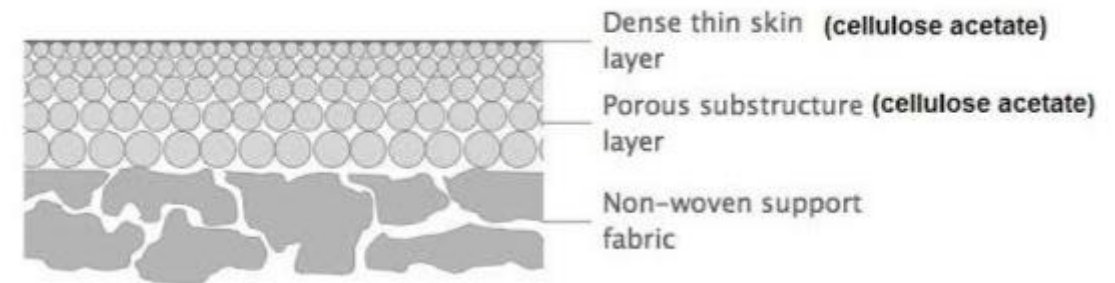


Membrane element types and configurations

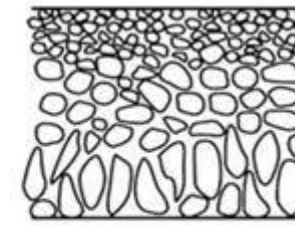
Thin film composite (TFC) membrane consisting of three layers (polyester support web, microporous poly sulfone interlayer and an ultra thin polyamide barrier layer on the top surface)



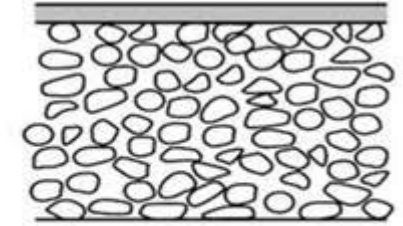
Cellulose acetate (asymmetric) membrane



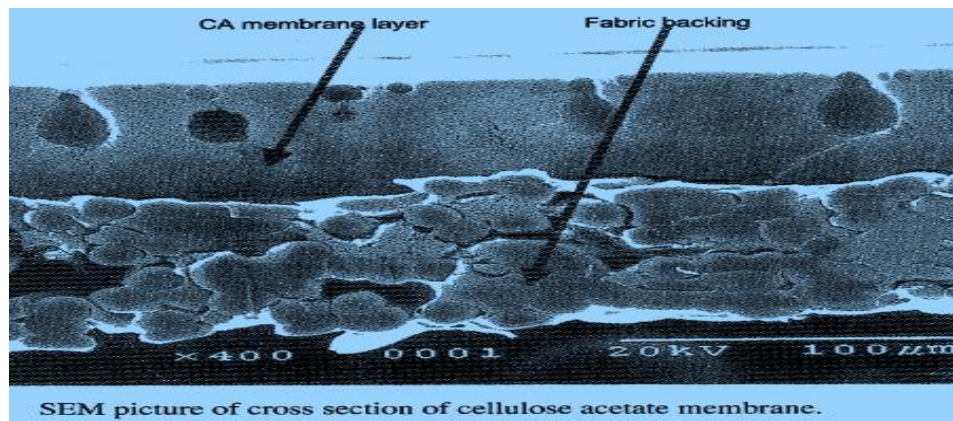
(a) Symmetric



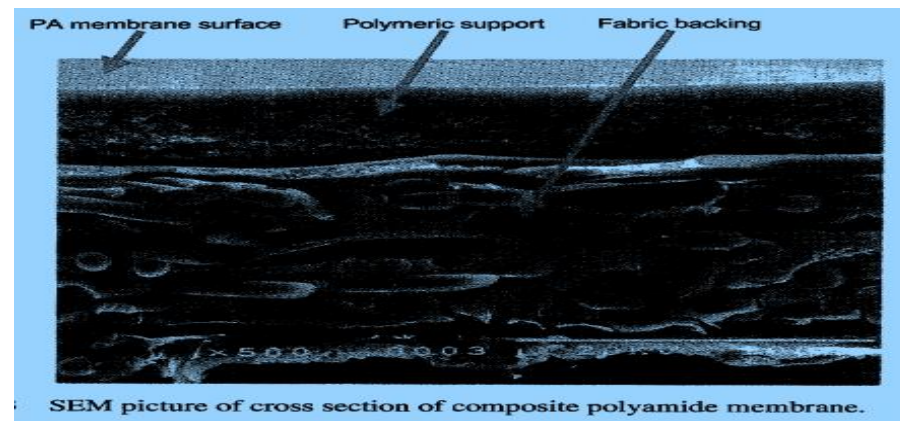
(b) Asymmetric



(c) Thin-film composite asymmetric membrane



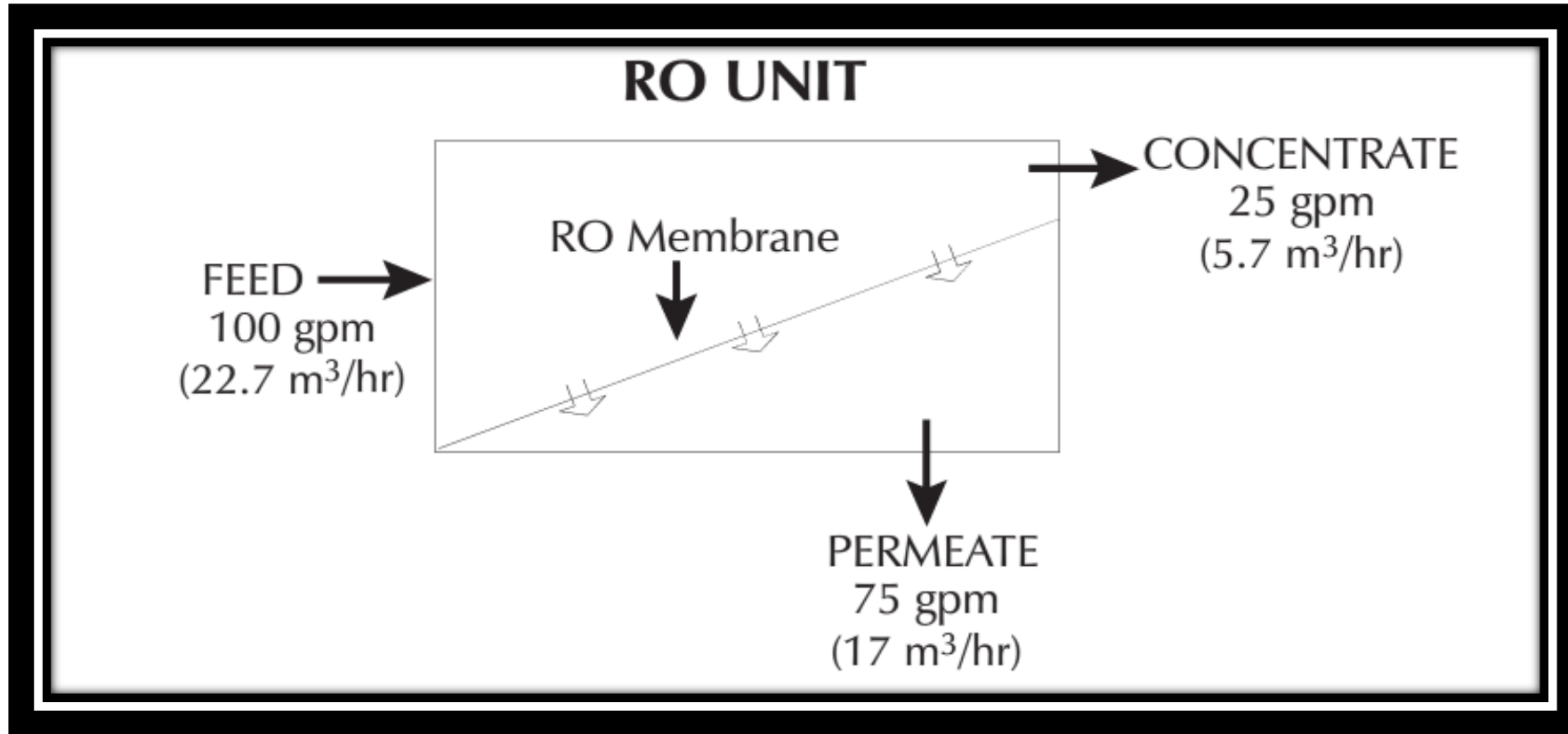
SEM picture of cross section of cellulose acetate membrane.



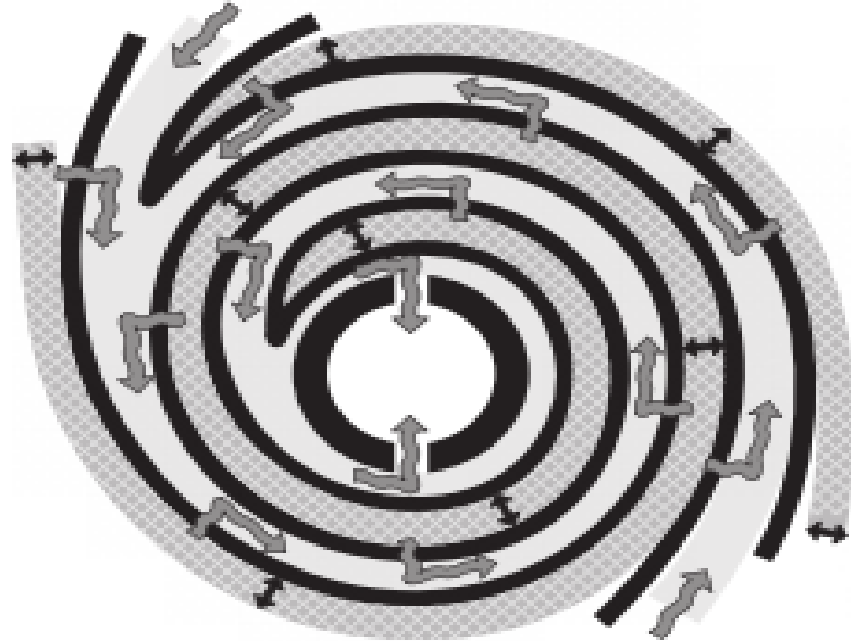
SEM picture of cross section of composite polyamide membrane.

Parameter	Polyamide Membranes	Cellulose Acetate Membranes
Salt rejection	High (> 99.5%)	Lower (up to 95%)
Feed pressure	Lower (by 30 to 50%)	High
Surface charge	Negative (limits use of cationic pretreatment coagulants)	Neutral (no limitations on pretreatment coagulants)
Chlorine tolerance	Poor (up to 1000 mg/L-hours); feed dechlorination needed	Good; continuous feed of 1 to 2 mg/L of chlorine is acceptable
Maximum temperature of source water	High (40 to 45°C; 104 to 113°F)	Relatively low (30 to 35°C; 86 to 95°F)
Cleaning frequency	High (weeks to months)	Lower (months to years)
Pretreatment requirements	High (SDI < 4)	Lower (SDI < 5)
Salt, silica, and organics removal	High	Relatively low
Biogrowth on membrane surface	May cause performance problems	Limited; not a cause of performance problems
pH tolerance	High (2 to 12)	Limited (4 to 6)

RO unit has one inlet stream (FEED) and two outlet streams (Permeate and Concentrate).



Cross-Section End View

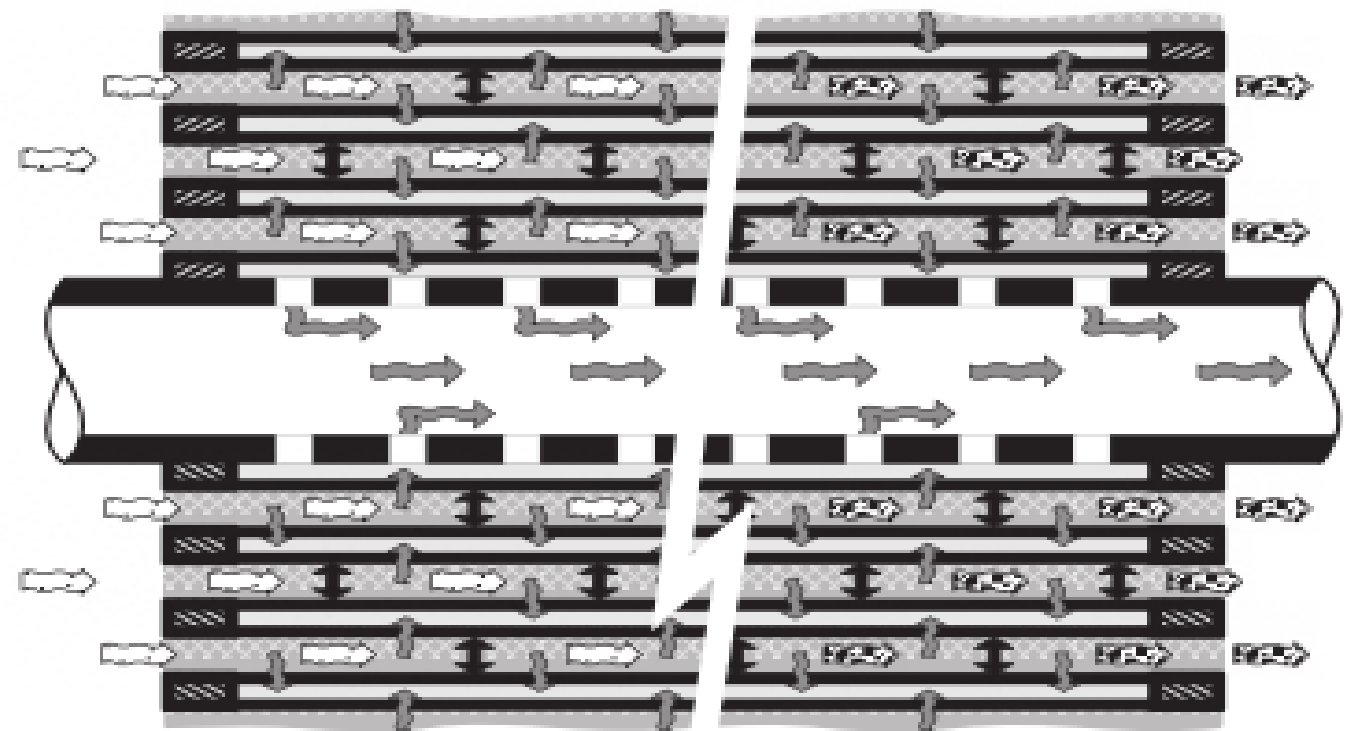


Feed And Concentrate Flow Arrows. The Left Arrow Indicates The Feed Solution With Less Solute And The Right Arrow The More Concentrated Solute.



Pressure On The Membrane. Denotes Equal Pressure From The Solution On All Of The Membrane.

Cross-Section Side View



Permeate Flow Arrow Indicates Flow Of Pure Water That Passes Through The Membrane And Spirals Through The Permeate Carrier To The Permeate Tube.

Note:

Only The First Three Wraps Of Membrane Around The Permeate Tube Are Depicted Here. The Separator Has Many Times This Number Of Wraps. The Typical Dimension Between Layers Of Membrane On The Feedwater Sides 0.03 Inches (0.76mm).

RO Membrane performance

(1) Water flux

It is dependent upon:

- ❖ **NDP** : Net Driving Pressure (Normalized differential pressure)
- ❖ **Temperature** : due to change of viscosity
Every 1.0 °C up or down about 3% change in flux.
- ❖ **Membrane type** : The thin film membranes (polyamide) requires generally half of the pressure of Asymmetric membranes (cellulose acetate)

Temperature Effect Equation

$$TCF = e^u \left(\frac{1}{T^\circ + 273} - \frac{1}{298} \right)$$

Where u = A constant which differs for each membrane type.

T° = Degrees Celsius

TCF = Temperature Correction Factor

(2) Salt flux (Salt passage)

- ❖ **Salt concentration gradient**
- ❖ **Temperature**
- ❖ **Ion charge** The higher the negative charge, the greater salt rejection (lower salt flux)

In general, the larger the molecule is , the greater the rejection.

Water has MW = 18 will pass through membrane and also any uncharged molecule close to water.

MW	Rejection
< 50	Zero to poor
50-100	Poor to good
100-200	Good to excellent
>200	Excellent

Performance of RO system can be observed from two main parameters:

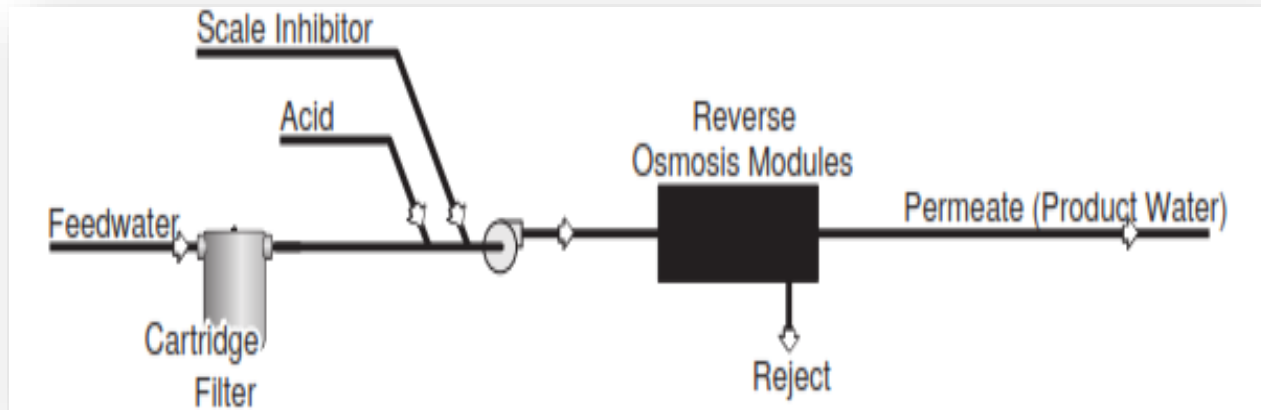
- ❖ Permeate flux
- ❖ Salt Flux (salt rejection)

The factors affecting the performance of RO system :

- ❖ Pressure
- ❖ Temperature
- ❖ Feed Salinity (Salt concentration)
- ❖ Recovery
- ❖ pH

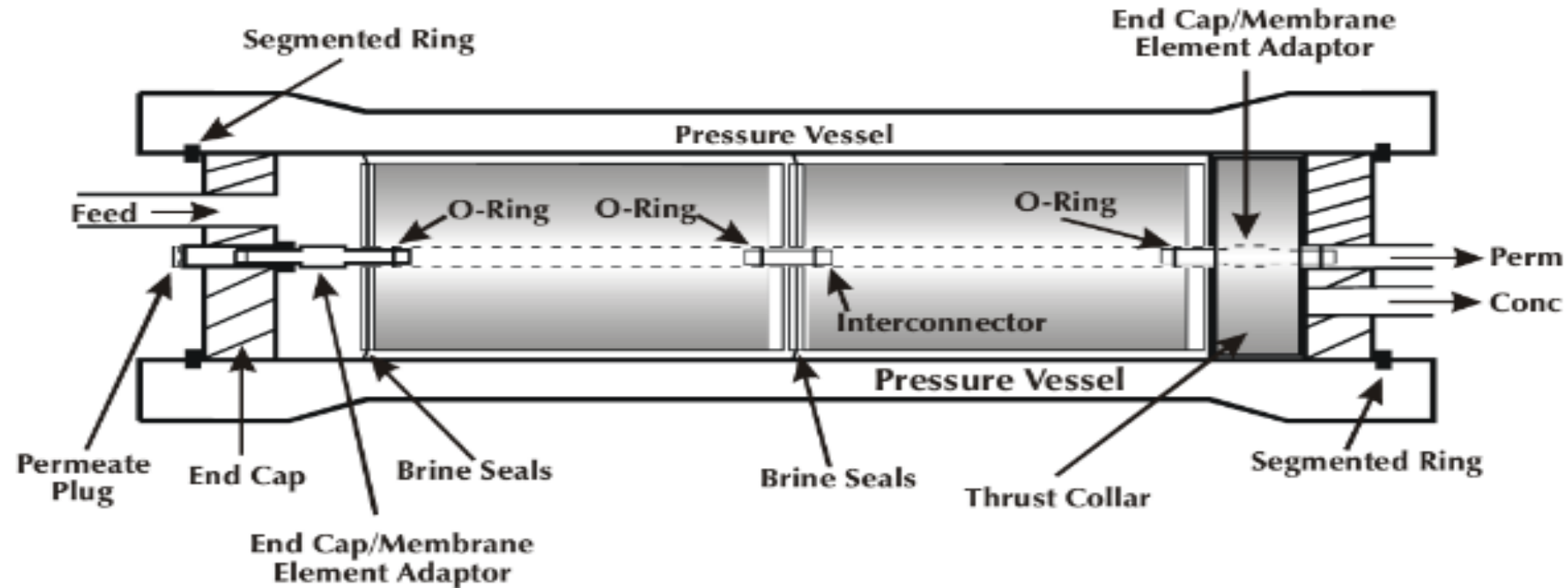
Generally the RO system is configured of the following equipment components:

- Feed water supply
- Pretreatment (cartridge)
- High pressure pumping
- RO membrane unit
- Instrumentation and control system
- Power supply system
- Cleaning unit



SDI (silt density index) is important parameter to evaluate efficiency of the pretreatment system SDI between 3-5 is desired upstream RO system

RO Vessel configuration

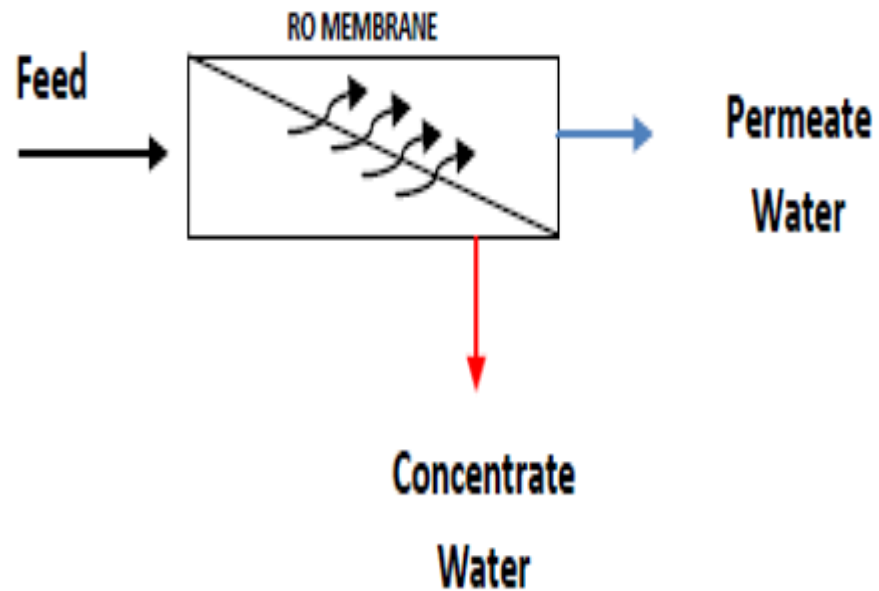


Pressure Vessel: is a component which houses RO elements and allow pressurized feed water to flow through RO elements .

RO System Configurations

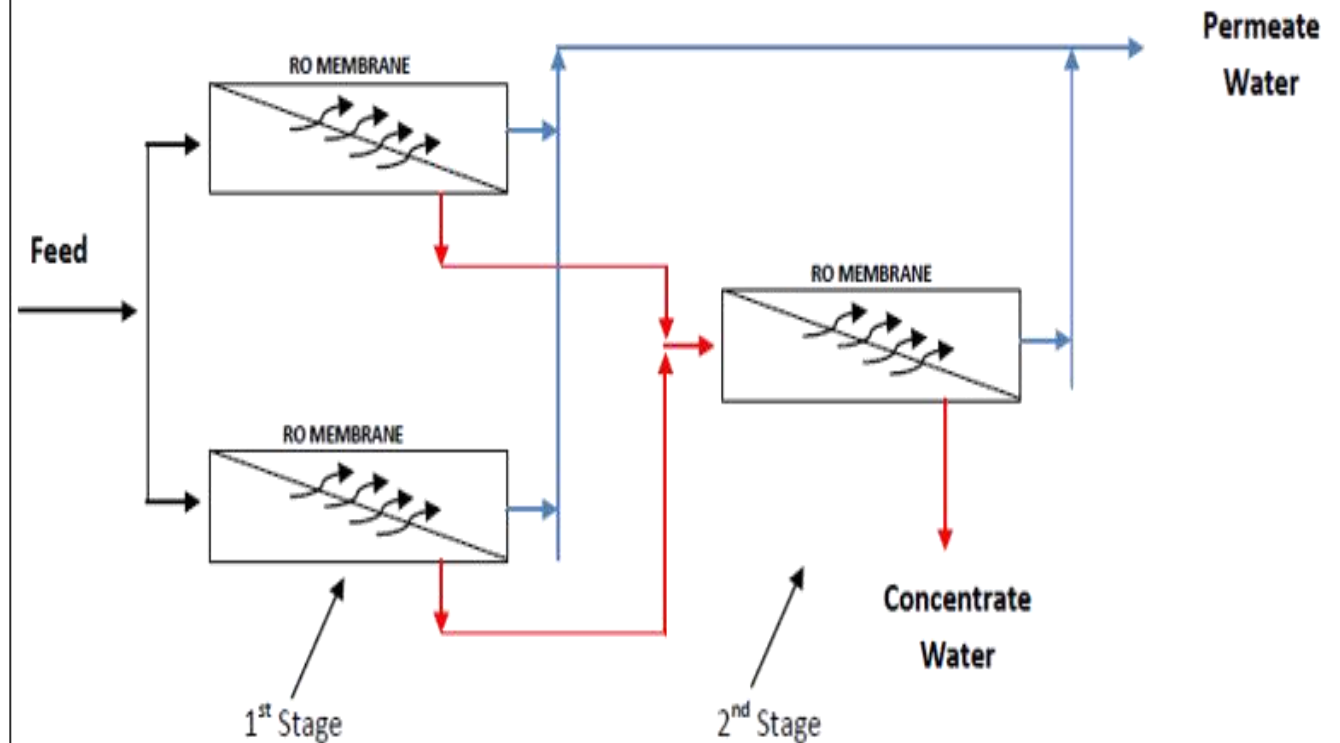
1 stage RO system

- Feed Water
- Permeate Water
- Concentrate Water

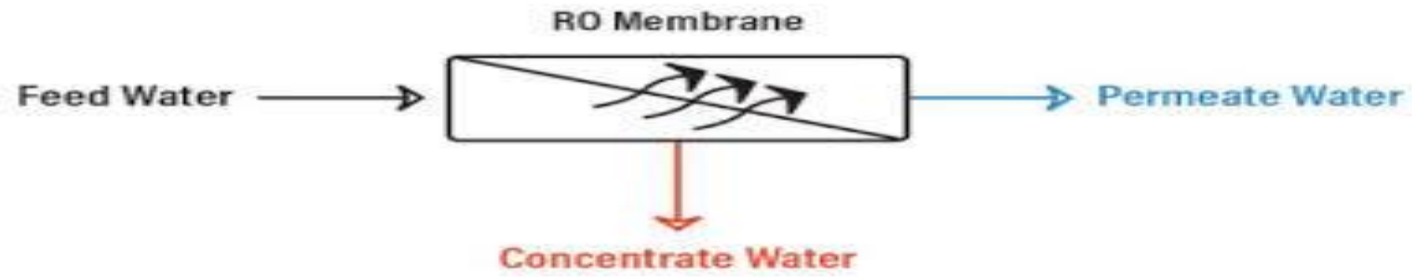


2 stage RO system

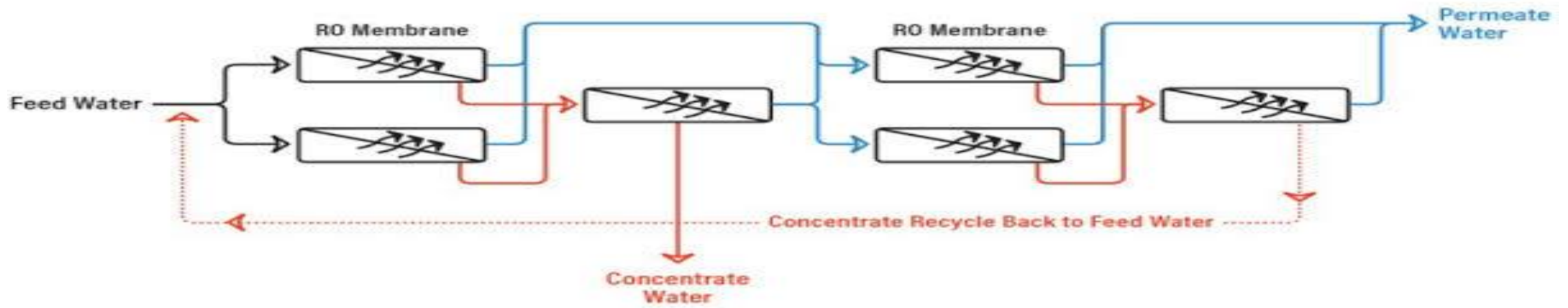
- Feed Water
- Permeate Water
- Concentrate Water



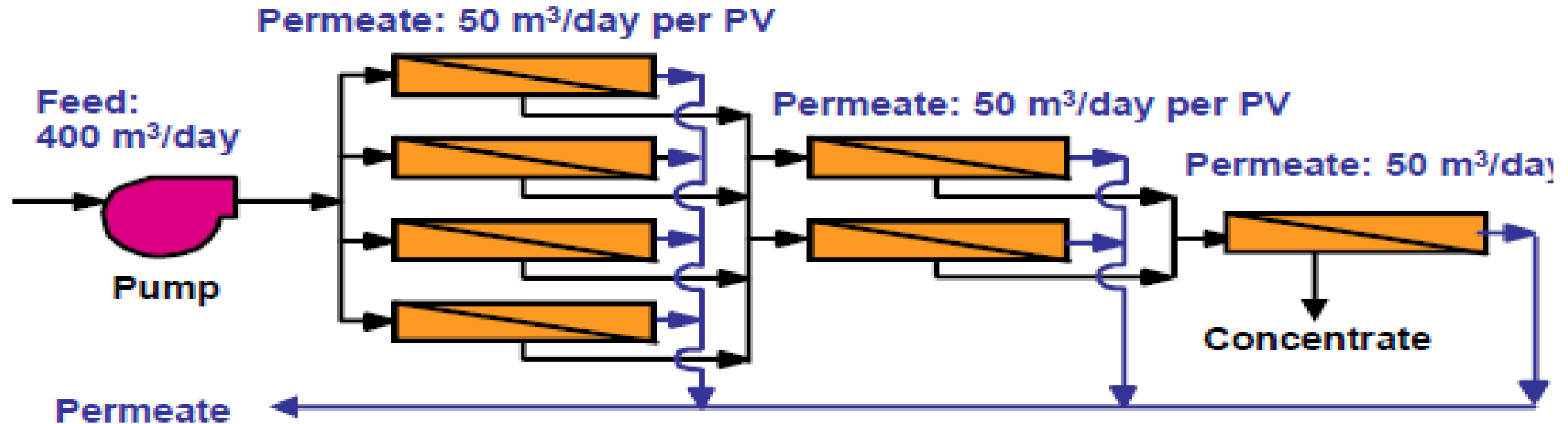
Single Pass RO



Double Pass RO



Three Stage System



$$\text{Recovery} = \frac{\text{Permeate Flow}}{\text{Feed Flow}} = \frac{200 + 100 + 50}{400} > 85\%$$

- Use for higher recovery
- Typical 85% recovery with 6-elements vessels
- Up to 90% depending on the feed water quality

In general about RO & UF systems used in power generation projects in Egypt

(RO system 3 units) Design configuration : Two stages (single pass) Recovery 75%

100% digital control operation system

(1) First stage contain 5 vessels each contain (4 RO membrane elements)

(2) Second stage contain 2 vessels each contain (4 RO membrane elements)

The reject of first stage is the feed of second stage

Total feed for the unit $67 \text{ m}^3 / \text{hour}$ (permeate $50 \text{ m}^3 / \text{hour}$ & reject $17 \text{ m}^3 / \text{hour}$)

Total capacity production of unit $1200 \text{ m}^3 / \text{day}$

In normal operation 2units in service and 1 unit stand by.

(UF system 3 units) Design configuration : Dead end filtration (inside-out filtration)

100% digital control operation system

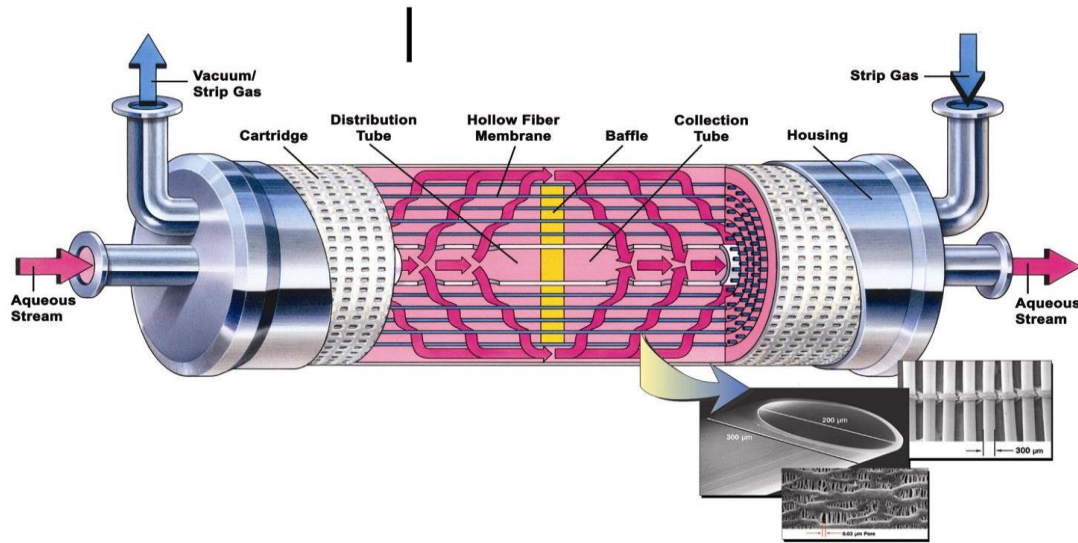
Every unit contain 9 vessels (with 4 UF membrane elements)

Total feed for the unit $130 \text{ m}^3 / \text{hour}$ (at full load) but by adjustment flux value (Auto) in normal operation unit work at $100 \text{ m}^3 / \text{hour}$, Back wash process auto after (cycle 40 min) , CEB after 12 cycle

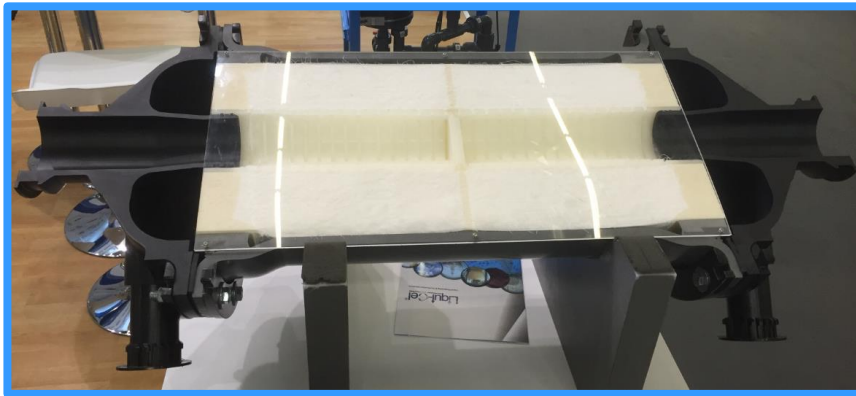
Total capacity production of unit $3000 \text{ m}^3 / \text{day}$

In normal operation 2units in service and 1 unit stand by.

Membrane Degassing (MD)

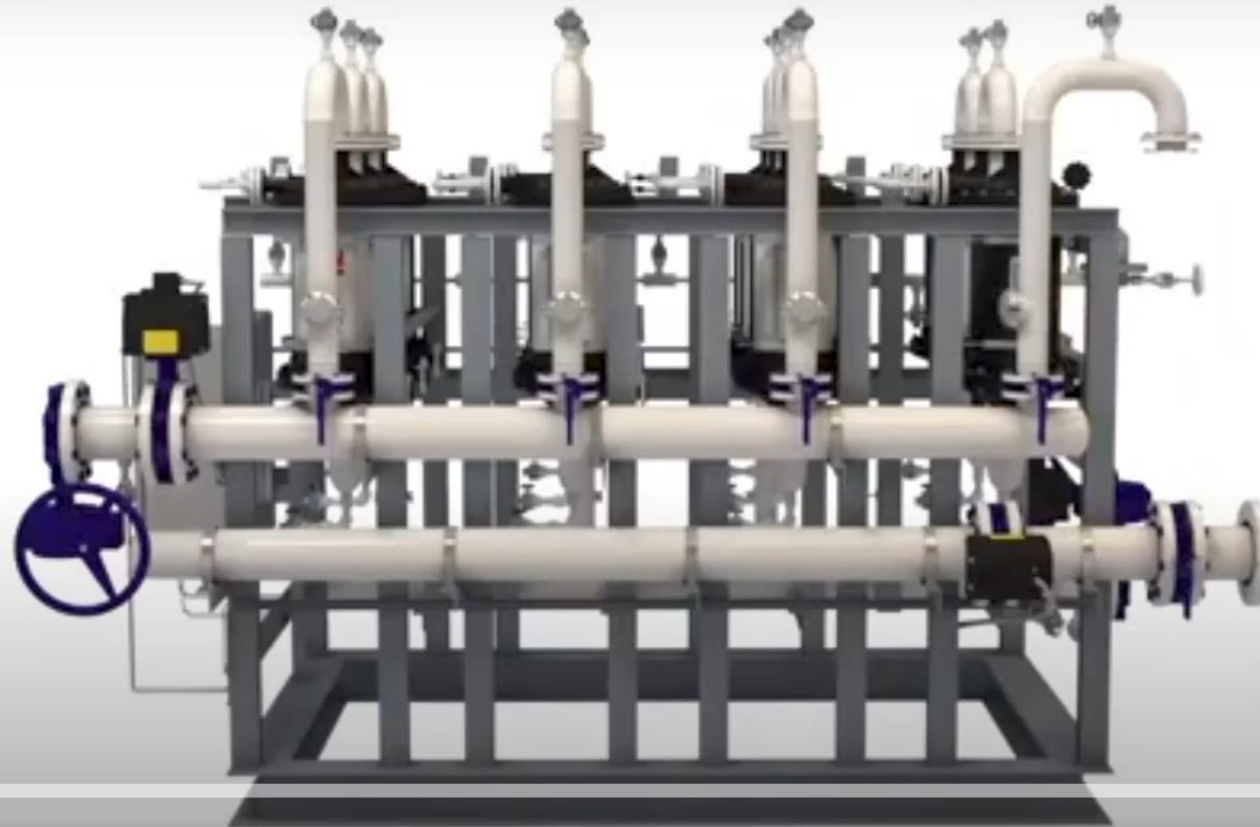


The Membrane Degassing (MD) contactors make possible to remove gasses from liquids (water). The liquid phase and the gas phase come into contact with each other (mass transfer) without mixing → this is possible by use of membranes! Hydrophobic hollow fiber. Typically used for degassing (CO₂ and O₂ reduction) and de-bubbling.





Membrane Degassing



0:05 / 1:39



YouTube



CEDI (continuous Electro Deionization system)

CEDI is water treatment process that uses combination of **ion exchange resins** (mixed anion, cation resins) And **direct current** to continuously deionized water.

Why?

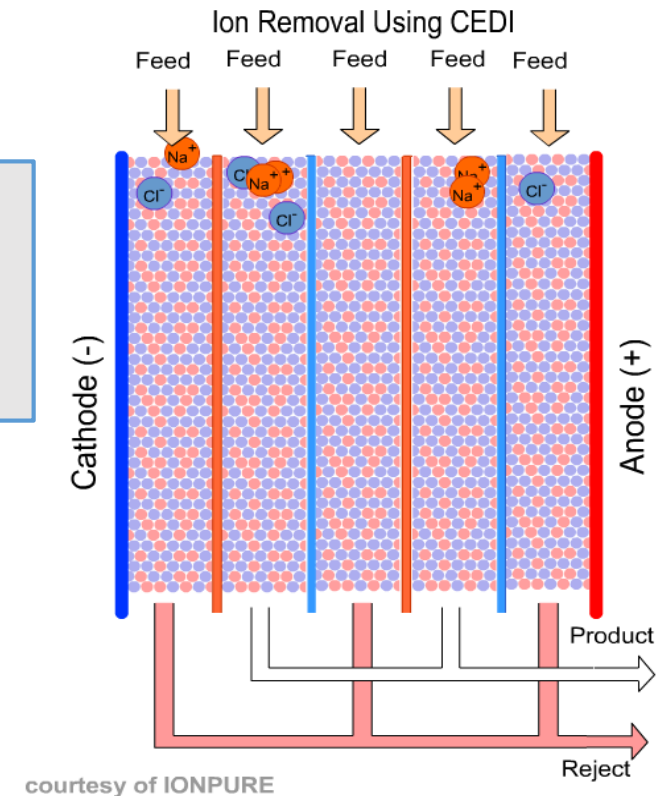
No regeneration Chemicals
Limited maintenance
Limited CAPEX and Low OPEX

What Does CEDI Remove?

❖ Ions	99 - 99,9%
❖ Sodium	99 - 99,9%
❖ Chloride	99 - 99,9%
❖ Silica	90 - 99,5%
❖ Boron	90 - 99,5%

Feed water Specification, std. series

Conductivity Equivalent	< 40 $\mu\text{S}/\text{cm}$ (incl. CO_2)
Temperature	5 - 45 °C (optimum 15 - 25)
Pressure	≤ 7 Bar (≤ 5 Bar for MX)
Chlorine	< 0,02 ppm Cl_2
Iron, manganese	< 0,01 ppm
Sulfide	< 0,01 ppm S^-
pH	4 - 11
Hardness*	< 1 ppm as CaCO_3 (opt. < 0,1)
Organics (TOC)	< 0,5 ppm as C
Silica	< 1 ppm SiO_2 (opt. < 0,1)



The process of Electrodeionisation (EDI)

**Electrodeionisation removes ions
(impurities) from water**

An EDI module contains...

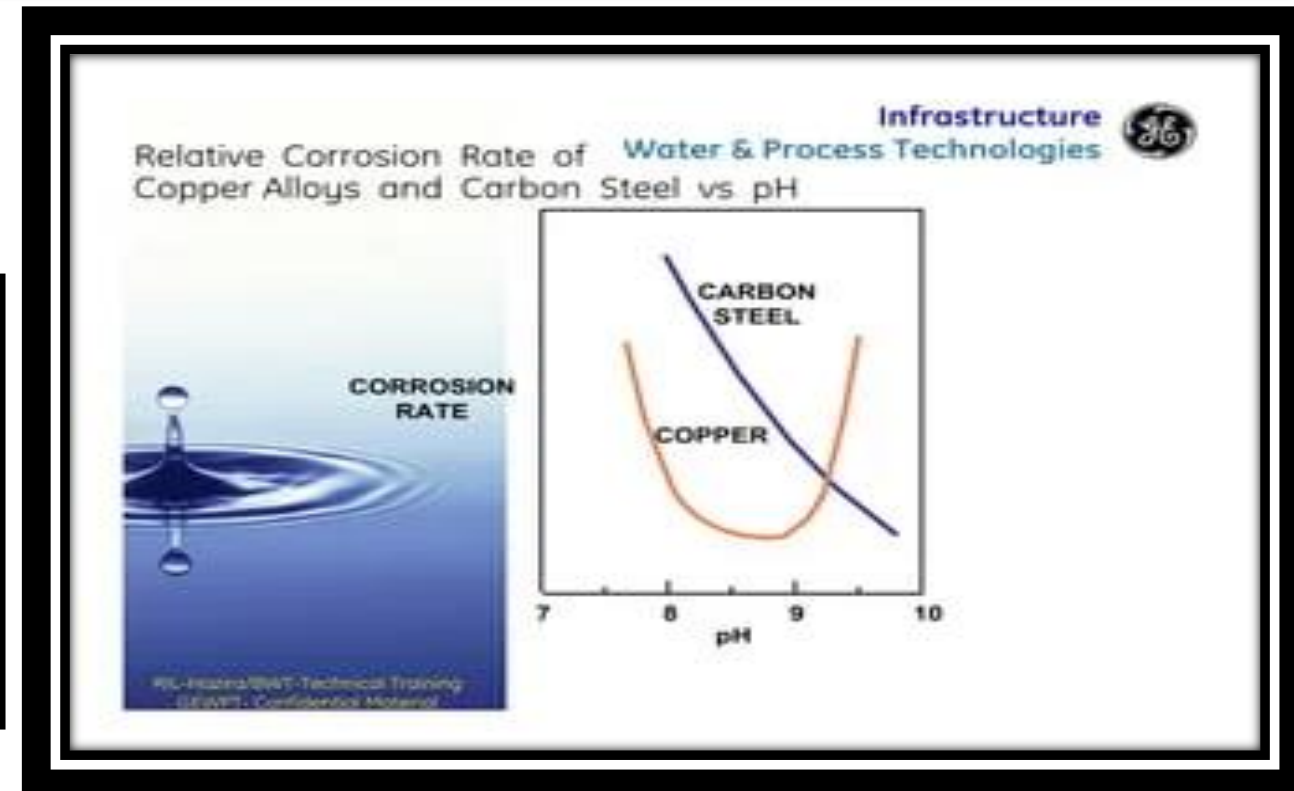
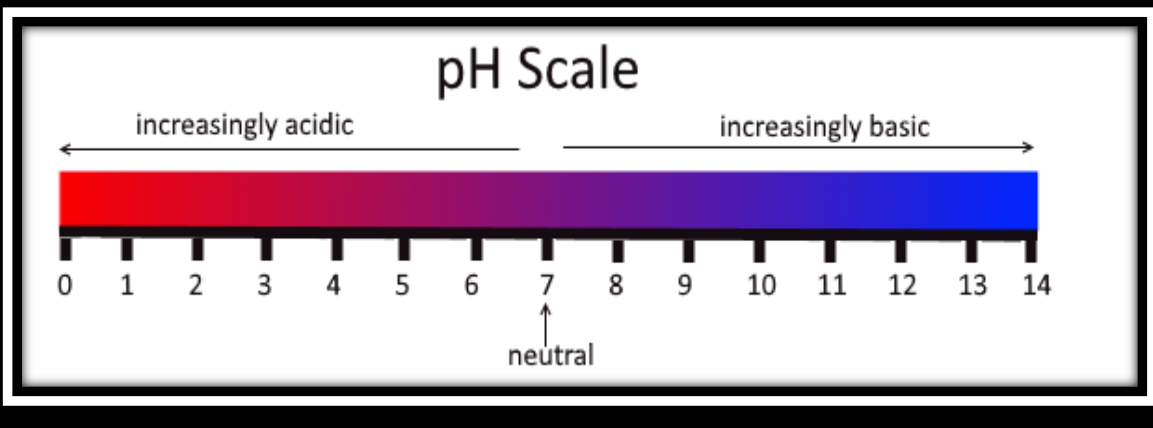
iontech

Internal Boiler water Treatment

Purpose of Internal boiler water treatment (steam-water analysis treatment systems)

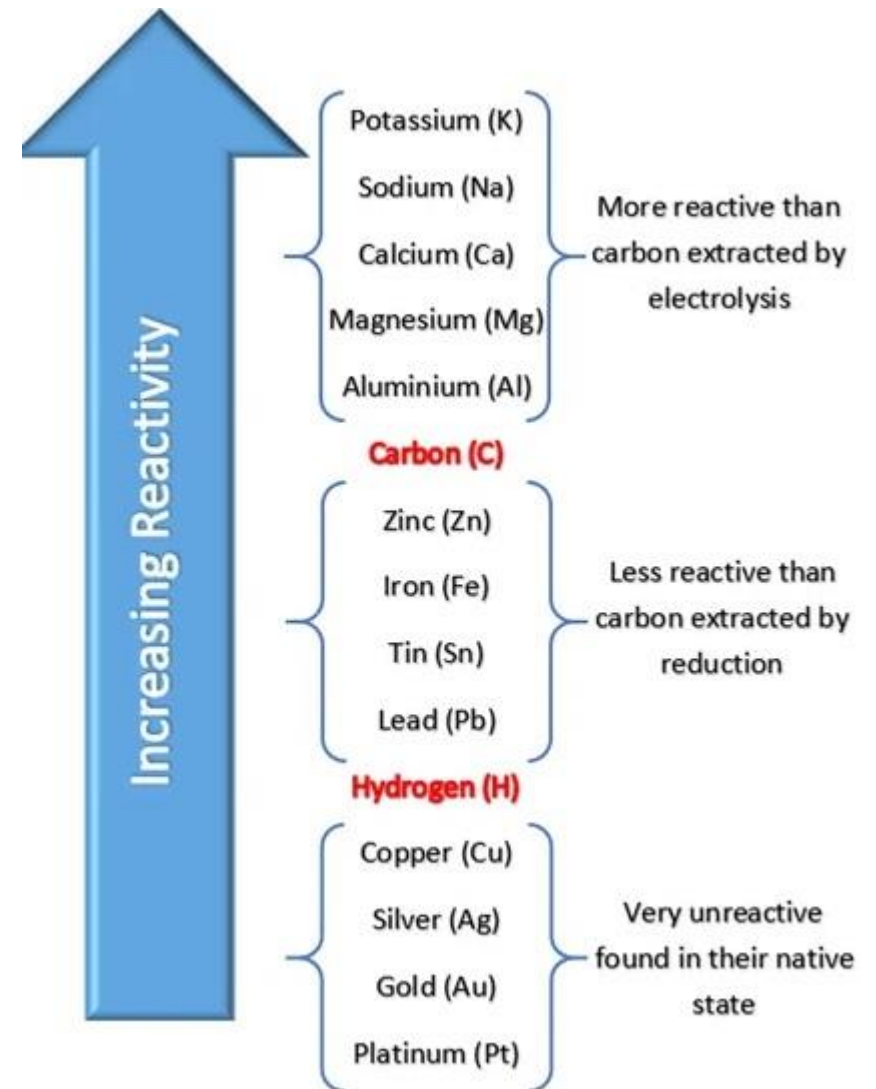
- Keep the internal boiler pipe protection layer (magnetite passivation layer) from corrosion... but how ?
- by removing all chemical causes which may be reacted or affected on this layer
- Note : the problems of corrosion, scale deposition increase with increasing the pressure and temperature of operation condition and so carryover problems.

Factors of Corrosion (1) pH

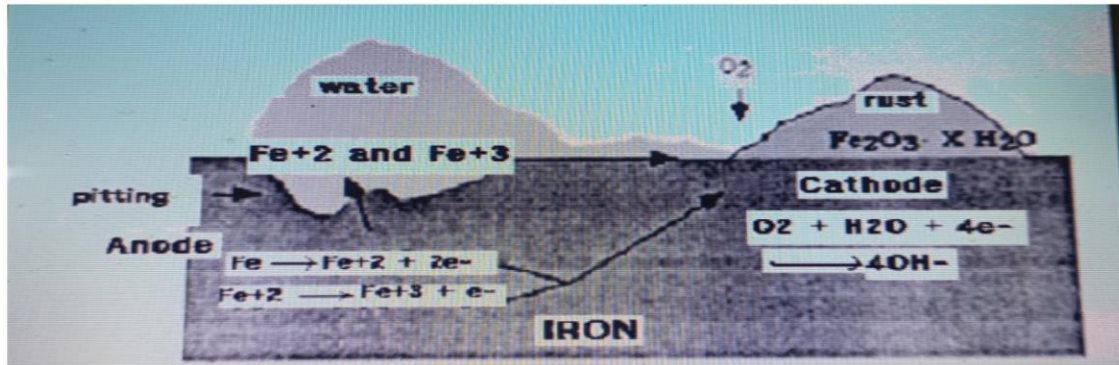


General information about corrosion of iron (metal of boiler)

- (1) The ability of different metals to undergo oxidation reactions according to the electromagnetic series
- (2) galvanic cells which occur on metal surface of boiler which called differential aeration cells (metal (low Conc. of O_2) Anode and high Conc of O_2 Cathode).
- (3) some dissolved ions such as chlorides, Aluminum and copper affect directly on the magnetite layer (prevent it to formation and destroying it), adsorption and oxidation with highly corrosive for magnetite layer.
high velocity of the solution with chlorides, Al and Cu ion act as role of sanding paper on surface of metal.
- (4) increasing in (tempr & pressure) condition cause (increase rate of all chemical reactions, changing in rate of solubility of some salts, increase in viscosity and motion water particles, Expel dissolved gases from water will be insoluble then release with steam.



Factors of corrosion (2) dissolved gases (O₂ & CO₂ and H₂)



CO₂ dissolved

Carbon dioxide damages the metal in a boiler

The corrosion mechanism (not a direct cause of corrosion)

$CO_2 + H_2O \rightarrow H_2CO_3$ Carbonic acid which reduces pH
Acid attack occur

Condensate pipe material mostly from copper alloy which corrode with forming **copper amino complexes** in presence of **CO₂ & O₂ in alkaline media (pH 9.2-9.6)** make corrosion for condensate pipe, and after increase in copper ion in water **make galvanic corrosion** with iron (different electronegativity) (further corrosion of iron)

O₂ dissolved

The iron gives up its electrons

$Fe \rightarrow Fe^{++} + 2e^-$ iron give iron ion +electron

The electrons combine with oxygen and water

$2e^- + \frac{1}{2} O_2 + H_2O \rightarrow 2OH^-$

The iron ion then combines with the hydroxyl ions

$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$

Ferrous hydroxide combines with water and oxygen

$2Fe(OH)_2 + H_2O + \frac{1}{2} O_2 \rightarrow 2Fe(OH)_3$

Ferric hydroxide decomposes

$2Fe(OH)_3 \rightarrow 3H_2O + Fe_2O_3 \text{ (III)}$

Ferric hydroxide Water Ferric oxide (Rust)

H₂ dissolved at high Temp. adsorbed on surface of magnetite and reduced it to (FeO) cathodic corrosion
 $H_2 + Fe_3O_4 = 3FeO + H_2O(g)$

Deposit (Scale) Problem

■ Common contaminants forming deposits

- Ca, Mg, Fe, Cu, Al, SiO₂, (Silt & Oil)

Scales Formed by salts that have limited solubility but are not totally insoluble in boiler water

Accumulation of solids that precipitate in the boiler water formed (sludge)

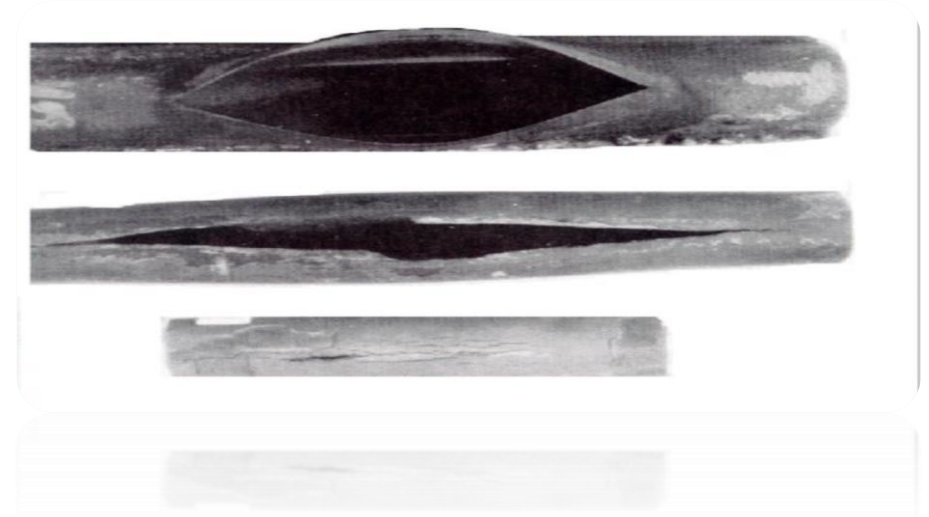
Deposits reduce heat transfer rate from boiler tube to boiler water, and increase the tube metal Temperature. Tube metal overheating and tube rupture can occur.

Scale problems in a boiler

- 1) reduce the efficiency of the boiler
- 2) lead directly to tube failure

■ Scale formation is minimized by

- 1) proper water treatment procedures
- 2) Chemical cleaning



Physical appearance of over heating failure

Carry-over Problem

a process which suspended and dissolved solids are picked up by the steam leaving the drum or super heat steam

- ❑ priming : the surging of water into the steam outlet (by too high a water level)
- ❑ foaming : the frothing of small steam bubbles that rise through the steam outlet (by excessive dissolved and suspended solids, by high alkalinity, and organic matters)
- ❑ vaporization : a material becomes a gas

ex) Silica in a high pressure boiler becomes a gas due to high Pr. and Temp.) Carry over with the steam leaving the boiler , Gaseous silica reaches the turbine blade, Gaseous silica changes to its solid form (due to low Pr. and Temp.) SiO₂ build-up (TBN) causing problems - restricting the steam flow

➤ The silica plates out as a glassy substance

Efficiency of the turbine drops

Prevention

2) Careful monitoring control of the level of water in the boiler drum (to prevent priming)

3) Reduce certain types of impurities (to prevent foaming)

- alkaline
- oil
- excessive amounts of dissolved solids

- The aim of internal treatment is to precipitate the all impurities present in the boiler to get harmless salts or sludge.
- Chemicals are added to the boiler water through all operation period react with dissolved salts to convert them into harmful sludge which can stay in the boiler water without creating any harm to the boiler tube .
- Chemicals which can adjustment pH value approximately 8.2-10 as recommendation of material manufacture.
- Chemicals which can scavengers the oxygen or any dissolved gasses.
- The main target is to protect the magnetite layer to keep the boiler metal.

Methods of boiler water treatment

(1) Soda Ash (sodium carbonate), Caustic Soda (NaOH) treatment

Used only in small boilers (react with dissolved chlorides, sulphates, magnesium to form insoluble sludge which can be removed from the boiler

(2) Phosphate treatment (used in drum boiler)

Na₃PO₄ or Na₂HPO₄ • To control impurities • To maintain pH without free hydroxides ion

• To prevent scale formation (consider good soluble agent for silica salts and so decrease its volatility with steam)

■ Trisodium phosphate is the most widely used chemical to remove hardness salts and convert them to a sludge (can be removed by blowdown)



Calcium Trisodium + Tricalcium Sodium → carbonate phosphate + phosphate carbonate (hardness salt) (sludge)

■ pH control $\text{Na}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{HPO}_4 + \text{NaOH}$

Trisodium phosphate + Water → Disodium phosphate + Sodium hydroxide (caustic)

phosphate In high pressure boiler recommended by keep residual phosphate as limit amount

All Volatile Treatment (Volatile chemicals) AVT (R)

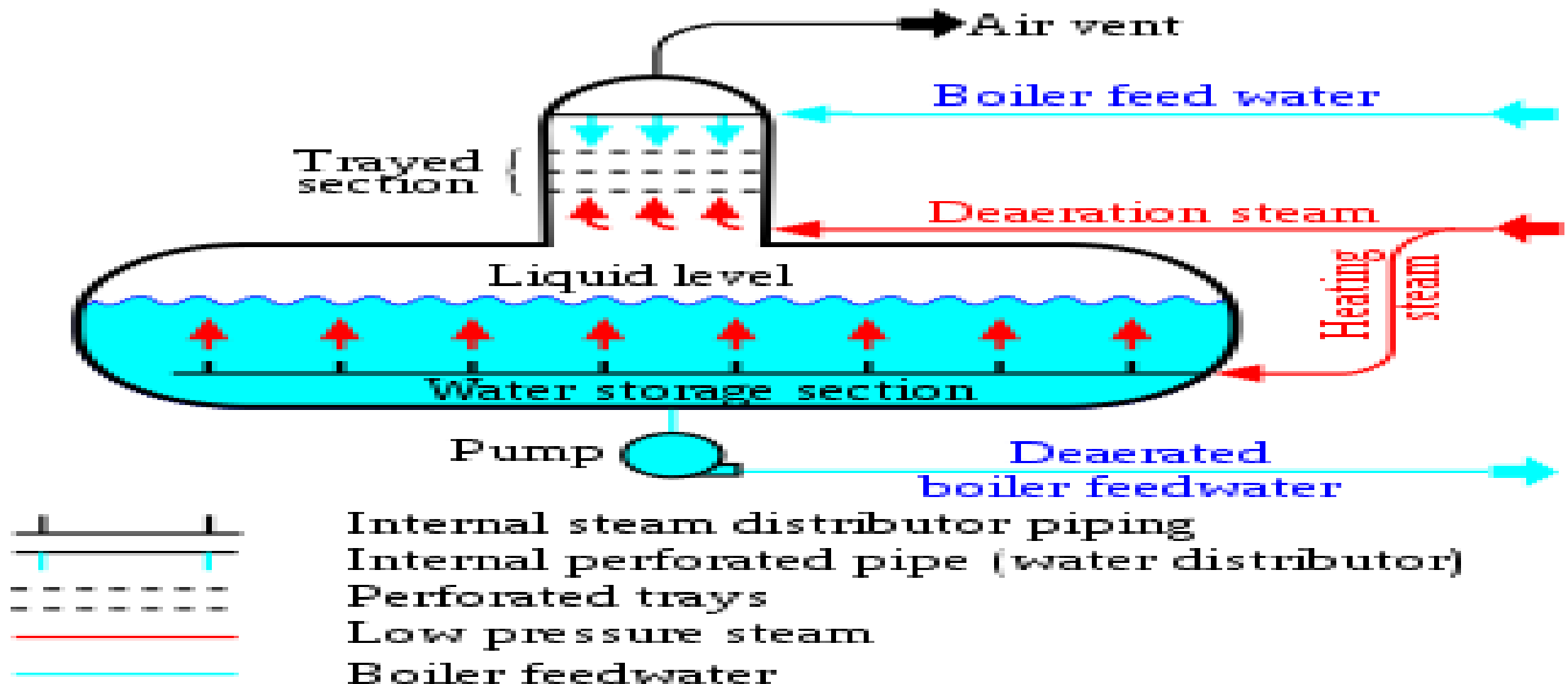
Oxygen scavenger : Hydrazine N_2H_4

- Convert iron oxide (rust) to magnetic layer
- React with dissolved oxygen converted to water and nitrogen
- Excess hydrazine in high temperature converted to Ammonia and nitrogen (help for pH adjustment)

Ammonium hydroxide : NH_4OH or morpholine but (lower volatile properties)

- pH control agents : *ammonia*, etc.
- Advantages : not build up in the boiler as impurities
- Disadvantages : any accidental in-leakage of impurities could be Dangerous
- React with carbonic acid found as result of CO_2 gas so keep the pH of water give ammonia gas which volatile with steam then condensate and circulated in cycle
- Disadvantages : excess ammonia cause corrosion with copper in heat exchangers .

Mechanical method for remove dissolved gasses O_2 & CO_2 (Deaerator)



Newest type of internal treatment of boiler water

The method of AVT (R) always used in sub boilers (boiler with drum) and also using phosphate treatment or not according to design of treatment or water quality needed This method target is to increase the thickness of magnetite layer (protection the boiler)

But in the last 15 years in Egypt newest type of steam boiler appear with high pressure steam capacity > 250 bar known as (super critical boiler) (once throw) (without drum) Found that the as the increase in thickness of magnetite layer that make pressure drop So it used newest type of internal treatment known as AVT(O) in start up and low load of its capacity and after that used Oxygenated treatment (OT)

All Volatile Treatment without oxygen scavenger (AVT(O))

- The AVT(O) method is to be applied during normal start-up and shut down period.
- Oxygen concentration will be minimized through the deaerator, and hydrazine is not used
- pH is maintained at the desired range by ammonia.

Oxygenated water treatment (OT)

- OT treatment shall be applied during normal operation.
- Oxygen concentration is strictly controlled by oxygen injection in the boiler feed water pump suction header

Difference between (AVT) and (OT)

(1) (AVT) All volatile Treatment

Magnetite Layer (Fe_3O_4) consists of an inner (topotatic) and outer (epitatic) layers. Fe (II) & Fe (III) ions.

Inner layer (dense) topotatic layer (more porous)

Outer layer (thin) epitatic layer. In lower T & P

So Fe(II) ions are easily transported through the porous magnetite layer from the steel surface, to the oxide/water phase boundary.

In AVT condition (pH 9.2 – 9.8), contributes the conversion of the mass-diffused Fe(II) ions to $\text{Fe}(\text{OH})_2$, which transforms in lower temperature regions (relatively slowly), to Fe_3O_4 according equation:



(2) (OT) oxygenated treatment

is newest technique used to reduce corrosion in a boiler and its associated feed water system in flow-through boilers.

- **Oxygen is injected into the feed water to keep the oxygen level between 30-50 ppb and (pH 8.8 – 9.2). Or between 30-150 ppb and (pH 8.0 -8.5) as type of boiler and manufacture recommendation and the ferrous ion concentration in feedwater is < 2.0 ppb under OT conditions. When OT is used, cation conductivity at the economizer inlet must be maintained below 0.15 μ S/cm this can be achieved by the use of a full-flow condensate polisher.**

OT programs are most commonly used in supercritical power boilers.

"Common injection points are just after the condensate polisher (C.P.P) and again at the deaerator outlet (Suction of Turbine Boiler Feed Pumps)."

This forms a thicker protective layer of hematite (Fe_2O_3) on top of the magnetite. This is a denser, flatter film (vs. the undulation scale with OT) so that there is less resistance to water flow compared to AVT. Also, OT reduces the risk of flow-accelerated corrosion.

Water Quality Boiler Limit

Parameter	Unit	Action Level	AVT (O)	AVT (R)	OT
pH	-	N	9.2 ÷ 9.6	9.0 ÷ 9.3	8.0 ÷ 8.5
		AL1	< 9.2 / > 9.6	< 9.0 / > 9.3	< 8.0 / > 8.5
		AL2	-	-	-
		AL3	-	-	-
Cationic conductivity	µS/cm	N	≤ 0.2	≤ 0.2	≤ 0.15
		AL1	≤ 0.4	≤ 0.4	≤ 0.3
		AL2	≤ 0.8	≤ 0.8	≤ 0.6
		AL3	> 0.8	> 0.8	> 0.6
Oxygen (O ₂)	g/kg	N	< 10	≤ 5	30 ÷ 150
		AL1	> 10	≤ 10	-
		AL2	-	≤ 20	-
		AL3	-	> 20	-
Silica (SiO ₂)	µg/kg	N	≤ 10	≤ 10	≤ 10
		AL1	> 10	> 10	> 10
		AL2	-	-	-
		AL3	-	-	-
Iron (Fe)	µg/kg	N	≤ 2	≤ 2	≤ 2
		AL1	> 2	> 2	> 2
		AL2	-	-	-
		AL3	-	-	-
Sodium (Na)	µg/kg	N	≤ 3	≤ 3	≤ 2
		AL1	≤ 6	≤ 6	≤ 4
		AL2	≤ 12	≤ 12	≤ 8
		AL3	> 12	> 12	> 8

To follow up water and steam quality limits for all parts of boiler in power plant (used SWAS system) Steam water analysis system (online chemical analyzers devices) connected by samples from all parts of plant Condensate, Dearator , Economizer, boiler storage tank , main steam , super heated steam and hot reheated steam if found in boiler design as show in figure.



Na , pH , dissolved oxygen, ORP,
Specific conductivity, cationic
conductivity, total iron , iron (II)
silica, Degassed cationic
conductivity





**Thank
you,...**

