Chapter 7

Reverse Osmosis

Objectives

The objective of this chapter is to present elements of membrane separation processes and to explain principles of membrane separation. The material also defines ranges for application of different membrane processes and summarizes performance parameters of membrane separation processes. In addition, an outline is made for different construction materials and module configurations. This also includes components of the RO desalination process.

7.1   Historical Background

Membranes are an intimate part of being alive. Several examples are simple to cite:
− The skin in all mammals is a very efficient and highly selective type of membrane controlling release of sweat to cool off the bodies through evaporation of tinny water droplets during hot weather. Skin selectivity as apparent, when its cut the fine blood cells and vessels that runs underneath the skin are broken and releases its blood content. A healthy and intact skin does not release blood.
− The lungs are also a good example of effective membranes, where fine cells within the lungs allow passage of oxygen from the inhaled air and release carbon dioxide into the same stream. The lungs as a membrane prevents permeation of the nitrogen in the inhaled air, irrespective of its high content.
− The kidney membranes regulate the water, salt ions, proteins, and other nutrient within the body. The kidneys are extremely efficient that a healthy body can survive with a quarter of both kidneys.
− On a much smaller scale, membrane walls in single cells within mammals, bacteria, and other microorganisms maintains the cell contents intact and regulate the input/output rates of nutrients or products.

Since the early days of civilization mankind have adopted simple forms of membranes. In early agriculture communities, household sieves were invented and developed to separate fin grain ground from coarse grain particles and shells. Similarly, cheesecloth was made from cotton fibers and used to manufacture cheese. Both forms of separation are based on differences in particle size. However, developments in membrane technology have focused on adoption of other separation mechanisms, such differences in solution and diffusion rates of various species across the membrane material.

Other than the sieve type membrane use of artificial membranes is rather new. Major landmarks in use of artificial membranes are summarized in the following points:

- In 1823, Dutrochet gave correct explanation of osmosis (passage of solvent across a membrane from low to high concentration) and dialysis (passage of solute across a membranes from high to low concentration).
- In 1867, Traube and Pfeffer performed one of the first quantitative studies on performance of artificial membranes.
- Moritz Taube, 1867, prepared the first synthetic membrane.
- In the late 1800's Graham discovered that arranging a membrane between a reservoir of pressurized air and another reservoir of unpressurized air could produce oxygen-enriched air.
- Early use of membranes was applied to recovery of NaOH by dialysis from wastewater containing hemicellulose from the viscose-rayon industry.
- Also, uranium isotopes (235 and 238) are separated in the vapor phase through porous membranes.

As for the RO membranes, their history started with the following two studies

- Reid and Breton, 1959, at the University of Florida developed cellulose acetate RO membranes.
- Loeb and Sourirajan, 1963, from the University of California, Los Angeles developed the first asymmetric cellulose acetate membrane, with higher salt rejection and water flux.

Subsequently, a huge amount of research studies were conducted with focus on development of new membrane materials and performance evaluation of these membranes. As for commercialization of the RO membranes it is summarized in the following points:

- In the late 1960s, the Gulf General Atomics and Aerojet General used Loeb-Sourirajan cellulose acetate membranes for constructing spiral wound modules.
- In 1971, Dupont introduced the Permasep B-9 permeator for brackish water desalination. The permeator contains millions of asymmetric aromatic polyamide (aramid) hollow fine fibers.
- In late 1973, Dupont introduced the Permasep B-10 permeator, also using asymmetric aramid fibers, capable of producing potable water from seawater in a single pass.
- In the mid-1970s, cellulose triacetate hollow fiber permeators were introduced by Dow Chemical Company, followed by Toyobo of Japan
- During the same period, Fluid Systems and FilmTec introduced the spiral wound polyamide thin film composite membranes.
- Throughout the 1980s, improvements were made to these membranes to increase water flux and salt rejection with both brackish water and seawater.
- Today the predominate membrane materials are still aramids, polyamides, and cellulose acetate and triacetate in spiral wound and hollow fiber configurations.

- Applications of the RO membranes include potable water production, waste recovery, food applications, kidney dialysis, high-purity water for boiler feed, and ultrapure water electronics applications.
- In 2000, the RO technology was used to treat more than two billion gallons of water per day, and this market is expected to continue growing during the first half of the 21st century.

7.2   Elements of Membrane Separation

A number of membrane-based desalination processes are used on industrial scale. As is shown in Fig. 1, the membrane-based processes include reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. Differences among these processes is shown in Fig. 1, where
- Microfiltration operates on a particle size range of 0.15 μm to 0.15 μm.
- Ultrafiltration operates on a particle size range of 0.15 μm to 5×10^{-2} μm
- Nanofiltration operates on a particle size range of 5×10^{-2} μm to 5×10^{-3} μm
- Reverse osmosis operates on a particle size range of 5×10^{-3} μm to 10^{-4} μm.

There is an inherent difference in the separation mechanism in all filtration processes and the reverse osmosis process. In filtration, separation is made by a sieving mechanism, where the membrane passes smaller particles and retains larger ones. In osmosis or reverse osmosis processes the membrane permeates only the solvent and retains the solute. Further distinction of the four membrane processes is shown in Fig. 1. As is shown, the microfiltration, ultrafiltration, and nanofiltration processes are used to separate the suspended material. On the other hand, the reverse osmosis process is used to separate dissolved solids. Nanofiltration is used for partial softening of brackish water.

A schematic for the osmosis and reverse osmosis phenomenon are shown in Fig. 2. In this configuration, the direction of solvent flow is determined by its chemical potential, which is a function of pressure, temperature, and concentration of dissolved solids. Pure water in contact with both sides of an ideal semi-permeable membrane at equal pressure and temperature has no net flow across the membrane because the chemical potential is equal on both sides. If a soluble salt is added on one side, the chemical potential of this salt solution is reduced. Osmotic flow from the pure water side across the membrane to the salt solution side will occur until the equilibrium of chemical potential is restored. Equilibrium occurs when the hydrostatic pressure differential resulting from the volume changes on both sides is equal to the osmotic pressure. This is a solution property independent of the membrane. Application of an external pressure to the salt solution side equal to the osmotic pressure will also cause equilibrium. Additional pressure will raise the chemical potential of the water in the salt solution and cause a solvent flow to the pure water side, because it now has a lower chemical potential.
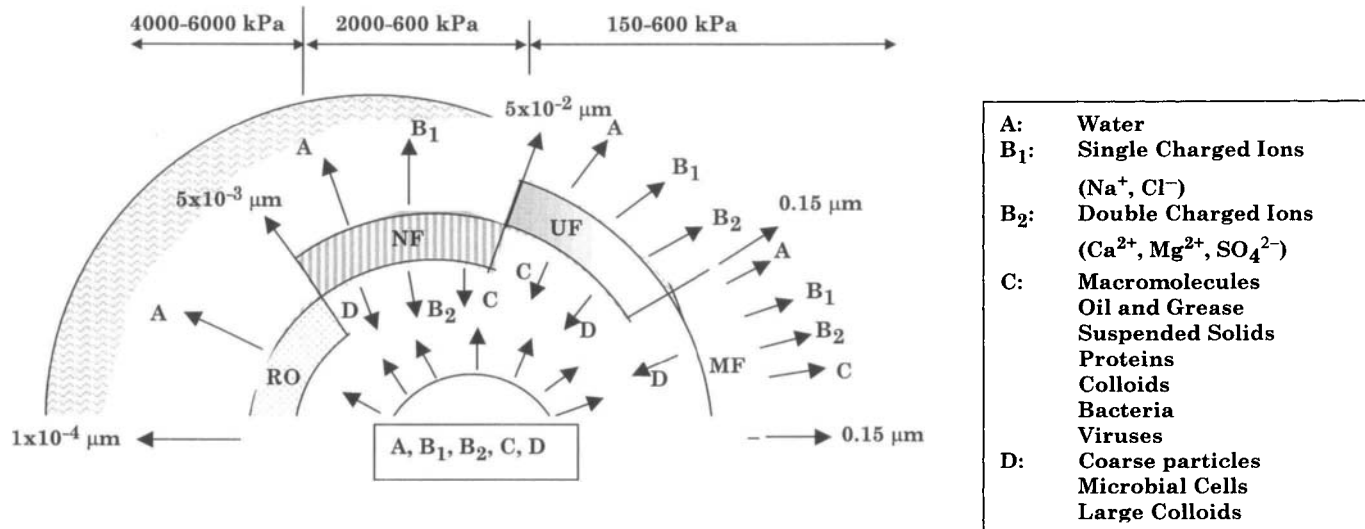
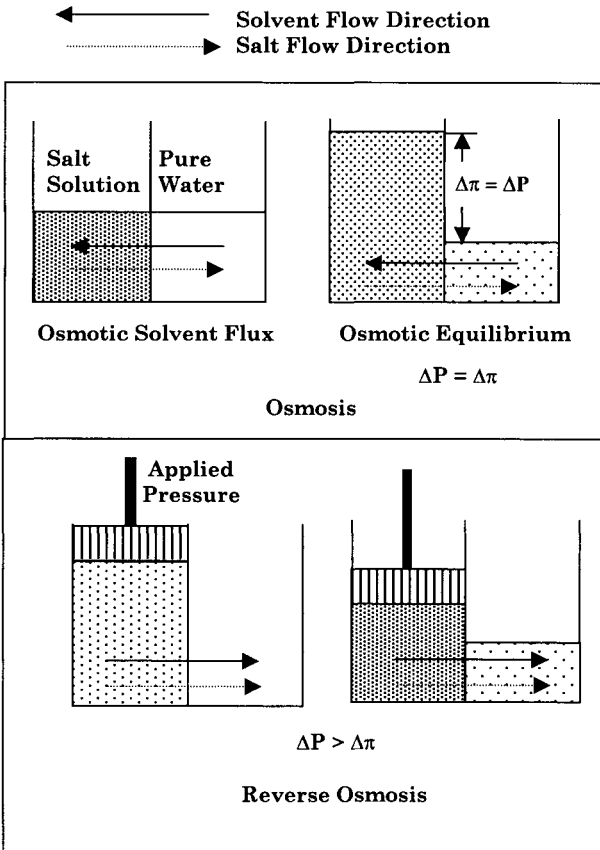Fig. 1. Membrane separation processes and corresponding particle sizes

Fig. 2. Osmosis and reverse osmosis processes.

7.3   Performance Parameters

        The RO process is defined in terms of a number of variables, which includes:
–   Osmotic and operating pressure
–   Salt rejection
–   Permeate recovery
Membrane manufacturing companies define system specifications in terms of the feed quality, which includes salinity and temperature.

7.3.1 Osmotic and Operating Pressure

The osmotic pressure, π, of a solution can be determined experimentally by measuring the concentration of dissolved salts in the solution. The osmotic pressure is obtained from the following equation

$$\pi = R\,T\,\sum X_i \tag{1}$$

where

π is the osmotic pressure (kPa).
T is the temperature (K).
R is the universal gas constant, 8.314 kPa m^3/kgmol K
$\sum X_i$ is the concentration of all constituents in a solution (kgmol/m^3).

An approximation for π may be made by assuming that 1000 ppm of Total Dissolved Solids (TDS) equals to 75.84 kPa of osmotic pressure.

Operating pressure is adjusted to overcome the adverse effects of the following:
– Osmotic pressure
– Friction losses
– Membrane resistance
– Permeate pressure
If the operating pressure is set equal to the sum of the above resistances the net permeate flow rate across the membrane would be minimal or equal to zero; therefore, the operating pressure is set at higher value in order to maintain economical permeate flow rate.

7.3.2 Salt Rejection

Salt rejection is defined by

$$SR = 100\%\,(1 - (X_p/X_f)) \tag{2}$$

where SR is the salt rejection. For example, a feed seawater with 42,000 ppm and a permeate with a salinity of 150 ppm gives a percentage salt passage of 99.64%. Similarly, for a brackish water feed with salinity of 5000 ppm and a permeate salinity of 150 ppm gives a percentage salt passage of 97%. The two cases indicate the dramatic difference between the seawater and brackish water desalination membranes. Current membrane technology provides salt rejection values above 99% for both seawater and brackish water membranes.

7.3.3 Permeate Recovery

Permeate recovery is another important parameter in the design and operation of RO systems. Recovery or conversion rate of feed water to product (permeate) is defined by

$$R = 100\% \ (M_p/M_f) \tag{3}$$

where R is recovery rate (in %), M_p is the permeate water flow rate, and M_f is the feed water flow rate. The recovery rate affects salt passage and product flow. As the recovery rate increases, the salt concentration on the feed-brine side of the membrane increases, which causes an increase in salt flow rate across the membrane. Also, a higher salt concentration in the feed-brine solution increases the osmotic pressure, reducing the ($\Delta P-\Delta \pi$) and consequently reducing the product water flow rate.

Membrane recovery for RO systems have increased over the years from lower values of 10-20% to current higher values up to 50%. This is achieved in part by proper system design and use of multiple modules of spiral wound membranes within the same pressure vessel. As for the hollow fiber membranes it common to use a single module within the same pressure vessel.

7.4   RO Membranes

Features of the RO membranes include the following:
− The membranes are formed of thin film of polymeric material several thousand Angstroms thick cast on polymeric porous material.
− Commercial membranes have high water permeability and a high degree of semi-permeability; that is, the rate of water transport must be much higher than the rate of transport of dissolved ions.
− The membrane must be stable over a wide range of pH and temperature, and have good mechanical integrity.
− The life of commercial membranes varies between 3-5 years. On average annual membrane replacement rates stand at 5-15%; this depends on the feed water quality, pretreatment conditions, and stability of operation.
− Major types of commercial reverse osmosis membranes include cellulose acetate (CA) and polyamide (PA).
− It should be noted that membrane choice is often governed by compatibility considerations rather than separation performance and flux related characteristics.

7.4.1 Cellulose Acetate Membranes

The original CA membrane, developed in the late 1950's by Loeb and Sourirajan, was made from cellulose diacetate polymer. Current CA membrane is usually made from a blend of cellulose diacetate and triacetate. The membrane preparation process includes thin film casting, cod bath leaching, and high temperature annealing. The casting process is associated with partial removal of the solvent material by evaporation. The cold bath process removes the remaining solvent and other leachable compounds. The annealing process is made in a hot water bath at a temperature of 60-90°C. The annealing step improves the semipermeability of the membrane with a decrease of water transport and a significant decrease of salt passage.

The CA membranes have an asymmetric structure with a dense surface layer of about 1000-2000 A (0.1-0.2 micron) which is responsible for the salt rejection property. The rest of the membrane film is spongy and porous and has high water permeability. Salt rejection and water flux of a cellulose acetate membrane can be controlled by variations in temperature and duration of the annealing step.

7.4.2 Composite Polyamide Membranes

The composite polyamide membranes are formed of two layers, the first is a porous polysulfone support and the second is a semi-permeable layer of amine and carboxylic acid chloride functional groups. This manufacturing procedure enables independent optimization of the distinct properties of the membrane support and salt rejecting skin. The resulting composite membrane is characterized by higher specific water flux and lower salt passage than cellulose acetate membranes.

Polyamide composite membranes are stable over a wider pH range than CA membranes. However, polyamide membranes are susceptible to oxidative degradation by free chlorine, while cellulose acetate membranes can tolerate limited levels of exposure to free chlorine. Compared to a polyamide membrane, the surface of cellulose acetate membrane is smooth and has little surface charge. Because of the neutral surface and tolerance to free chlorine, cellulose acetate membranes will usually have a more stable performance than polyamide membranes in applications where the feed water has a high fouling potential, such as with municipal effluent and surface water supplies.

7.5   Membrane Modules

The two major membrane module configurations used for reverse osmosis applications are hollow fiber and spiral wound. Other configurations, which include tubular and plate and frame, are used in the food and dairy industry.

7.5.1 Hollow Fine Fiber

This configuration uses membrane in the form of hollow fibers, which have been extruded from cellulosic or non-cellulosic material. The fiber is asymmetric in structure and is as fine as a human hair, about 42 µm ID and 85 µm OD, Fig. 3. Millions of these fibers are formed into a bundle and folded in half to a length of approximately 120 cm. A perforated plastic tube, serving as a feed water distributor is inserted in the center and extends the full length of the bundle. The bundle is wrapped and both ends are epoxy sealed to form a sheet-like permeate tube end and a terminal end which prevents the feed stream from bypassing to the brine outlet.

The hollow fiber membrane bundle, 10 cm to 20 cm in diameter, is contained in a cylindrical housing or shell approximately 137 cm long and 15-30 cm in diameter. The assembly has the highest specific surface area, defined as the total area per unit volume, among all module configurations. The pressurized feed water enters the permeator feed end through the center distributor tube, passes through the tube wall, and flows radially around the fiber bundle toward the outer permeator pressure shell. Water permeates through the outside wall of the fibers into the hollow core or fiber bore, through the bore to the tube sheet or product end of the fiber bundle, and exits through the product connection on the feed end of the permeator.

In a hollow fiber module, the permeate water flow per unit area of membrane is low, and therefore, the concentration polarization is not high at the membrane surface. The net result is that hollow fiber units operate in a non-turbulent or laminar flow regime. The hollow fine fiber membrane must operate above a minimum reject flow to minimize concentration polarization and maintain even flow distribution through the fiber bundle. Typically, a single hollow fiber permeator can be operated at up to 50-percent recovery and meet the minimum reject flow required. The hollow fiber unit allows a large membrane area per unit volume of permeator that results in compact systems. Hollow fiber perimeters are available for brackish and seawater applications.

Membrane materials are cellulose acetate blends and polyamide type material. Because of very close packed fibers and tortuous feed flow inside the

module, hollow fiber modules require feed water of better quality (lower concentration of suspended solids) than the spiral wound module configuration.

7.5.2 Spiral Wound

In a spiral wound configuration two flat sheets of membrane are separated with a permeate collector channel material to form a leaf. This assembly is sealed on three sides with the fourth side left open for permeate to exit. A feed/brine spacer material sheet is added to the leaf assembly. A number of these assemblies or leaves are wound around a central plastic permeate tube. This tube is perforated to collect the permeate from the multiple leaf assemblies. The typical industrial spiral wound membrane element is approximately 100 or 150 cm long and 10 or 20 cm in diameter, Fig. 4.

The feed/brine flow through the element is a straight axial path from the feed end to the opposite brine end, running parallel to the membrane surface. The feed channel spacer induces turbulence and reduces concentration polarization. Manufacturers specify brine flow requirements to control concentration polarization by limiting recovery (or conversion) per element to 10 – 20%.

Therefore, recovery (or conversion) is a function of the feed-brine path length. In order to operate at acceptable recoveries, spiral systems are usually staged with three to six membrane elements connected in series in a pressure tube. The brine stream from the first element becomes the feed to the following element, and so on for each element within the pressure tube.

The brine stream from the last element exits the pressure tube to waste. The permeate from each element enters the permeate collector tube and exits the vessel as a common permeate stream. A single pressure vessel with four to six membrane elements connected in series can be operated at up to 50-percent recovery under normal design conditions. The brine seal on the element feed end seal carrier prevents the feed/brine stream from bypassing the following element.

Spiral wound elements are most commonly manufactured with flat sheet membrane of either a cellulose diacetate and triacetate (CA) blend or a thin film composite. A thin film composite membrane consists of a thin active layer of one polymer cast on a thicker supporting layer of a different polymer. The composite membranes usually exhibit higher rejection at lower operating pressures than the cellulose acetate blends. The composite membrane materials may be polyamide, polysulfone, polyurea, or other polymers.
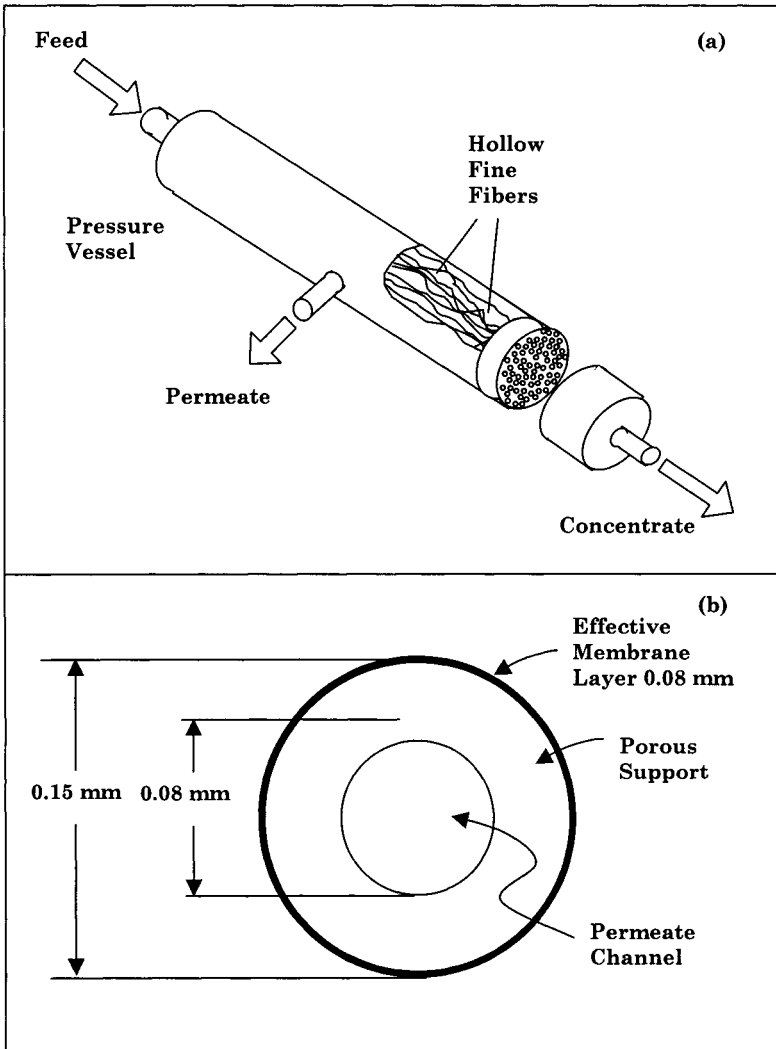
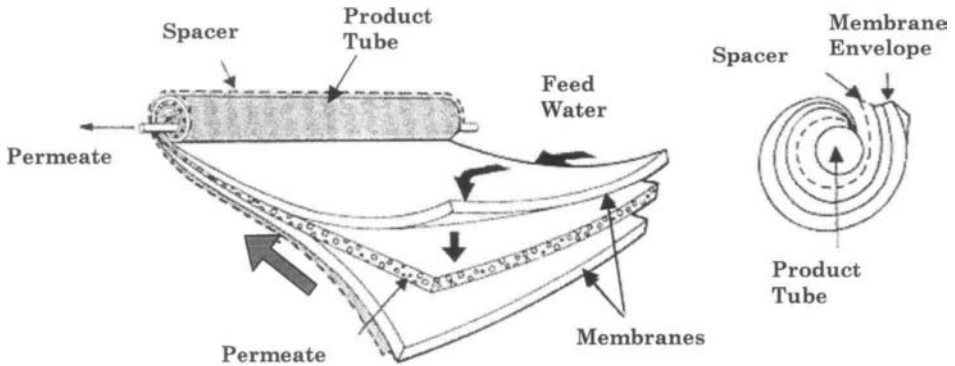Fig. 3. Hollow fiber membrane modules. (a) Assembly. (b) Fiber dimensions

Fig. 4. Spiral wound membrane modules

7.6   RO Systems

The RO systems may consist of the following basic components:
–   Feed water supply unit
–   Pretreatment system
–   High pressure pumping unit
–   Membrane element assembly unit
–   Instrumentation and control system
–   Permeate treatment and storage unit
–   Cleaning unit

Figure 5 shows a typical process diagram for the RO process. It should be noted that the system in Fig. 5 is only an example, where the level of feed pretreatment depends strongly on the quality of the feed water. Features of the RO process includes the following:
–   Large particles are removed from the feed water using mesh strainers or traveling screens. Mesh strainers are used in well water supply systems to stop and remove sand particles, which may be pumped from the well. Traveling screens are used mainly for surface water sources, which typically have large concentrations of biological debris.
–   It is common practice to disinfect surface feed water in order to control biological activity. Biological activity in well water is usually very low, and in majority of cases, well water does not require chlorination. In some cases, chlorination is used to oxidize iron and manganese in the well water before filtration. Well water containing hydrogen sulfide should not be chlorinated or

exposed to air. In presence of an oxidant, the sulfide ion can oxidize to elemental sulfur, which eventually may plug membrane elements.

– Settling of surface water in a detention tank results in some reduction of suspended particles. Addition of flocculants, such as iron or aluminum salts, results in formation of corresponding hydroxides; these hydroxides neutralize surface charges of colloidal particles, aggregate, and adsorb to floating particles before settling at the lower part of the clarifier. To increase the size and strength of the flock, a long chain organic polymer can be added to the water to bind flock particles together. Use of lime results in increase of pH, formation of calcium carbonate and magnesium hydroxide particles. Lime clarification results in reduction of hardness and alkalinity, and the clarification of treated water.

– Well water usually contains low concentrations of suspended particles, due to the filtration effect of the aquifer. The pretreatment of well water is usually limited to screening of sand, addition of scale inhibitor to the feed water, and cartridge filtration.

– Surface water may contain various concentrations of suspended particles, which are either of inorganic or biological origin. Surface water usually requires disinfection to control biological activity and removal of suspended particles by media filtration. The efficiency of filtration process can be increased by adding filtration aids, such as flocculants and organic polymers. Some surface water may contain high concentrations of dissolved organics. Those can be removed by passing feed water through an activated carbon filter. Depending on composition of the water, acidification and addition scale inhibitor may be required. The flow diagram of pretreatment system for surface water is shown below.

– Cartridge filters, almost universally used in all RO systems prior to the high pressure pump, serve as the final barrier to water born particles. The nominal rating commonly used in RO applications is in the range of 5 - 15 microns. Some systems use cartridges with micron ratings as low as 1 micron. There seems to be little benefit from lower micron rated filters as such filters require a high replacement rate with relatively small improvement in the final feed water quality.

– Recently, new pretreatment equipment has been introduced to the RO market. It consists of backwashable capillary microfiltration and ultrafiltration membrane modules. This new equipment can operate reliably at a very high recovery rates and low feed pressure. The new capillary systems can provide better feed water quality than a number of conventional filtration steps operating in series. The cost of this new equipment is still very high compared to the cost of an RO unit.
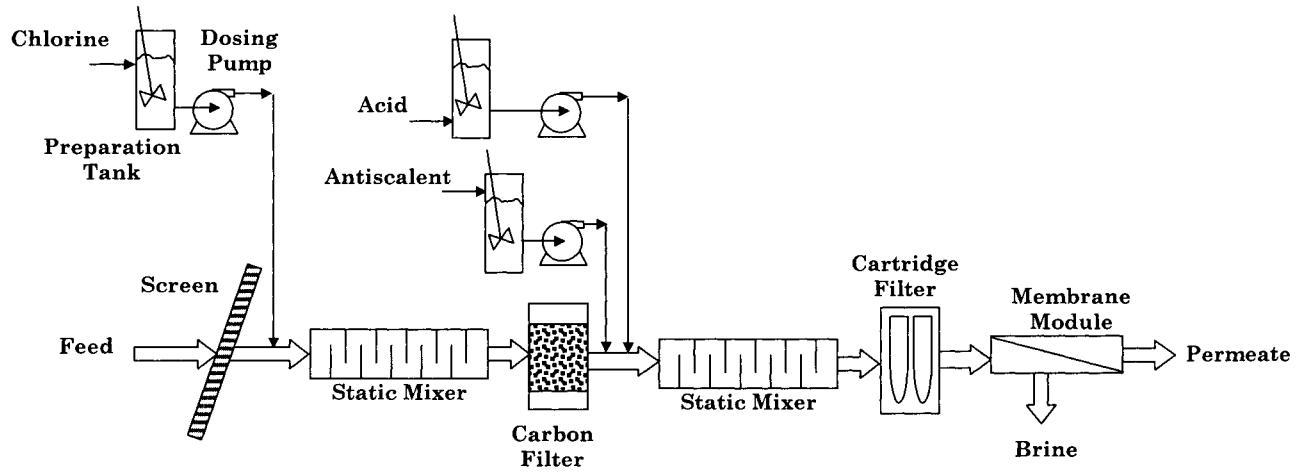
Fig. 5. Typical RO process with screening, chlorination, filtration, acidification and scale inhibition

7.7   RO Model and System Variables

The RO process is defined in terms of a number of variables, which includes:
- Osmotic pressure
- Water transport
- Salt transport
- Salt passage
- Salt rejection
- Permeate recovery
- Concentration polarization

The following sections include the equations and terms forming the RO simple model. The model is based on the following assumptions:
- Steady state and isothermal operation.
- Permeability coefficients of various salt ions or water are independent of temperature and concentration.
- Similar permeability coefficient for various salt ions.
- The salt flow rate across the membrane is negligible in comparison with the water permeate flow rate.
- Complete mixing within the permeate compartment.
- Salt concentration within the feed compartment varies linearly along the membrane area.

7.7.1 Permeator Mass and Salt Balances

The permeator mass and salt balances are given by the following relations:

$$M_f = M_p + M_b \tag{4}$$

$$X_f M_f = X_p M_p + X_b M_b \tag{5}$$

where
M_f is the feed flow rate, kg/s.
M_p is the permeate flow rate, kg/s
M_b is the brine flow rate, kg/s
X_f is the feed salinity, kg/m^3
X_p is the permeate salinity, kg/m^3.
X_b is the brine salinity, kg/m^3.

7.7.2 Water Transport

The following relation defines the rate of water passage through a semipermeable membrane

$$M_p = (\Delta P - \Delta\pi)\, K_w\, A \tag{6}$$

where

M_p is the rate of water flow through the membrane, m^3/s.
$\Delta\pi$ is the osmotic pressure differential across the membrane, kPa.
K_w is the water permeability coefficient, $m^3/m^2\, s\, kPa$
A is the membrane area, m^2.

In Eq. (6) the terms ΔP and $\Delta\pi$ represent the net hydraulic and osmotic pressure differential across the membrane, respectively, or

$$\Delta P = \overline{P} - P_p \tag{7}$$

$$\Delta\pi = \overline{\pi} - \pi_p \tag{8}$$

where

P_p and π_p are the permeate hydraulic and osmotic pressure, respectively.
$\overline{P}$ and $\overline{\pi}$ are the average hydraulic and osmotic pressures on the feed side and are given by:

$$\overline{P} = 0.5\,(P_f + P_b) \tag{9}$$

$$\overline{\pi} = 0.5\,(\pi_f + \pi_b) \tag{10}$$

where P_f and π_f are the hydraulic and osmotic pressures of the feed stream, respectively. While P_b and π_b are the hydraulic and osmotic pressures of the reject stream, respectively.

7.7.3 Salt Transport

The rate of salt flow through the membrane is defined by

$$M_s = (\overline{X} - X_p)\, K_s\, A \tag{11}$$

where

M_s is the flow rate of salt through the membrane, kg/s.

K_s is the membrane permeability coefficient for salt, m^3/m^2 s.

Xp is the permeate total dissolved solids concentration, kg/m^3.

A is the membrane area, m^2.

In Eq. (11) the term $\overline{X}$ is defined by

$$\overline{X} = (M_f\, X_f + M_b\, X_b)/(M_f + M_b) \tag{12}$$

where X_f and X_b are the feed and reject salt concentrations, respectively.

Equations 6 and 11 show that for a given membrane:
- Rate of water flow through a membrane is proportional to net driving pressure differential $(\Delta P - \Delta \pi)$ across the membrane.
- Rate of salt flow is proportional to the concentration differential across the membrane $(\overline{X} - Xp)$ and is independent of applied pressure.

Salinity of the permeate, Xp, depends on the relative rates of water and salt transport through reverse osmosis membrane:

$$Xp = M_s/M_d \tag{13}$$

The fact that water and salt have different mass transfer rates through a given membrane creates the phenomena of salt rejection. No membrane is ideal in the sense that it absolutely rejects salts; rather the different transport rates create an apparent rejection. Equations 6 and 11 show that increasing the operating pressure will increase water flow without changing salt flow, thus resulting in lower permeate salinity.

7.7.4 Semi-Empirical Models

Several approaches are adopted in evaluation of experimental models, which includes the following:
- Irreversible thermodynamic model.
- Frictional model.
- Solution-diffusion model.
- Solution-diffusion-imperfection model.
- Preferential adsorption capillary flow model.
- Diffusion viscous flow model
- Finely porous model.

All these models are special cases of the statistical-mechanical model, Mason and Lonsdale (1990).

The statistical-mechanical model includes the following equations:
Salt rejection

$$SR = (C_1 \frac{1}{(M_p / A)} + C_2)^{-1} \tag{14}$$

Permeate Flux

$$M_p / A = (D_1\ c_w + D_2)(\Delta p - \sigma \Delta \pi) \tag{15}$$

Membrane wall concentration

$$c_w = c_b + (c_b - c_d)(e^{M_p / Ak} - 1) \tag{16}$$

Variables in the above model are defined as follows:
– C_1, C_2, D_1, and D_2 are the fitting constants of Eqs. 14 and 15 with experimental data.
– SR is the salt reject.
– Mp is the permeate flow rate, m^3/s.
– A is the membrane area, m^2.
– ΔP is the pressure difference across the membrane, kPa.
– $\Delta \pi$ is the osmotic pressure difference across the membrane, kPa.
– cw is the salt concentration in the membrane wall, kg/m^3.
– c_b is the salt concentration in the bulk of the feed compartment, kg/m^3.
– cd is the salt concentration in the permeate stream, kg/m^3.
– k is the mass transfer coefficient, m/s.
– σ is the reflection coefficient.

The finely-porous model includes the following equations:
– Salt rejection

$$SR = 1 - (A_1 - (1 - A_1)\ e^{(-A_2 M_p /(AD_{sw}))})^{-1} \tag{17}$$

– Permeate Flux

$$M_p / A = \frac{\Delta p - \sigma \Delta \pi}{B_1 c_d + B_2\ \mu} \tag{18}$$

– Membrane wall concentration

$$c_w = c_b + (c_b - c_d)(e^{M_p / Ak} - 1) \tag{19}$$

The variables in the above model are similar to those of the statistical mechanical model, except for the following:

- A_1, A_2, B_1, and B2 are the fitting constants of Eqs. 17 and 18 with experimental data.
- μ is the water dynamic viscosity, kg/m s.
- D_{sw} is the solute diffusion coefficient in solution, m^2/s.

Both models are nonlinear and it requires iterative solution to determine the permeate flow rate, salt rejection, and membrane wall concentration.

7.7.5 Concentration Polarization

As water flows through the membrane and the membrane rejects salts, a boundary layer is formed near the membrane surface in which the salt concentration exceeds the salt concentration in the bulk solution. This increase of salt concentration is called concentration polarization. The effect of concentration polarization is to reduce actual product water flow rate and salt rejection versus theoretical estimates. The effects of concentration polarization are as follows:

- Greater osmotic pressure at the membrane surface than in the bulk feed solution, $\Delta\pi$, and reduced Net driving pressure differential across the membrane ($\Delta P - \Delta\pi$).
- Reduced water flow across membrane (M_d).
- Increased salt flow across membrane (M_s).
- Increased probability of exceeding solubility of sparingly soluble salts at the membrane surface, and the distinct possibility of precipitation causing membrane scaling.

The Concentration Polarization Factor (CPF) can be defined as a ratio of salt concentration at the membrane surface (C_s) to bulk concentration (C_b), where

$$CPF = C_s/C_b \tag{20}$$

An increase in permeate flux will increase the delivery rate of ions to the membrane surface and increase C_s. An increase of feed flow increases turbulence and reduces the thickness of the high concentration layer near the membrane surface. Therefore, the CPF is directly proportional to permeate flow (M_d), and inversely proportional to average feed flow (M_f), where

$$CPF = K_3 \exp(M_d/M_f) \tag{21}$$

where K_3 is a proportionality constant depending on system geometry.

Using the arithmetic average of feed and concentrate flow as average feed flow, the CPF can be expressed as a function of the permeate recovery rate a of membrane element (R):

$$CPF = K_3 \exp(2R/(2-R)) \tag{22}$$

The value of the Concentration Polarization Factor of 1.2, corresponds to 18% permeate recovery.

7.8   Case Studies

Example on Mathematical Model

Design a single stage RO desalination system by calculating the permeate salinity, the brine salinity, the brine flow rate, and the membrane area.

Data

Water permeability is 2.05×10^{-6} m^3/m^2 s kPa
Salt permeability is 2.03×10^{-5} m^3/m^2 s
Feed salinity is 42,000 ppm
Feed flow rate: 2.5 kg/s
Permeate flow rate: 1 kg/s
Feed pressure: 8000 kPa
Reject pressure: 7800 kPa
Permeate pressure: 101 kPa

Solution

The material balance on the permeator is given by

$$M_b = M_f - M_d$$
$$= 2.5 - 1$$
$$= 1.5 \text{ kg/s}$$

The remaining model equations include the salt balance and the water and salt permeation. Solution of these equations is iterative because of the

dependence of the osmotic pressure on the salinity of the permeate and brine streams. The iteration sequence is as follows:

– Assume salinity of the permeate stream is equal to 145 ppm or 0.145 kg/m^3.
– This value is used to calculate the brine salinity by solving the salt balance equation, which is given by

$$M_f\, X_f = M_b\, X_b + M_d\, X_d$$

which gives

$(2.5)(42) = (1.5)(X_b) + (1)(0.145)$
or $X_b = 69.903$ kg/m^3

– The average salinity on the feed side is calculated

$$\overline{X} = (M_f\, X_f + M_b\, X_b)/(M_f + M_b)$$
$$= ((2.5)(42) + (1.5)(69.903))/(2.5+1.5)$$
$$= 52.46 \text{ kg/m}^3$$

– The salinity of various streams is used to calculate the osmotic pressure of each stream

$$\pi_f = 75.84\ X_f = (75.84)(42) = 3185.28$$

$$\pi_b = 75.84\ X_b = (75.84)(69.903) = 5301.452 \text{ kPa}$$

$$\pi_p = 75.84\ X_p = (75.84)(0.145) = 10.9968 \text{ kPa}$$

– The average osmotic pressure on the feed side is then calculated

$$\overline{\pi} = 0.5\ (\pi_f + \pi_b) = 0.5\ (3185.28 + 5301.452) = 4243.366 \text{ kPa}$$

– Therefore, the net osmotic pressure across the membrane is given by

$$\Delta\pi = \overline{\pi} - \pi_p = 4243.366 - 10.9968 = 4232.3 \text{ kPa}$$

– The net pressure difference across the membrane is given by

$$\Delta p = 0.5(P_f + P_b) - P_p = (0.5)(8000 + 7800) - 101 = 7799 \text{ kPa}$$

– The permeate flux equation is used to calculate the membrane area, or,

$M_d = A\, k_w\, (\Delta P - \Delta \pi)$

$(1) = A\, (2.05 \times 10^{-6})\, (7799 - 4232.3)$

which gives $A = 136.76\ \mathrm{m}^2$

–   The average salinity on the feed side is calculated from

$\overline{X} = (M_f\, X_f + M_b\, X_b)/(M_f + M_b)$
  $= ((2.5)(42) + (1.5)(69.903))/(2.5 + 1.5)$
  $= 52.46\ \mathrm{kg/m}^3$

–   The salt transport equation is used to calculate the permeator area

$M_s = A\, k_s\, (\Delta X - X_p)$

$(1)(0.145) = A\, (2.03 \times 10^{-5})\, (52.46 - 0.145)$

which gives $A = 136.5\ \mathrm{m}^2$

The difference in the areas obtained by the two flux equations is small, which implies correctness of the initial assumption.

Example on Manufacturer Specifications

Design a single stage RO desalination system by calculating the permeate salinity, the brine salinity, the brine flow rate, and the membrane area.

Module Data

Membrane recovery ratio:	10%
Membrane module area:	$2.6\ \mathrm{m}^2$
Salt rejection:	99.5%
Module pressure drop:	69 kPa
Maximum applied pressure:	5500 kPa
Maximum feed flow rate:	$32.7\ \mathrm{m}^3/\mathrm{d}$
Permeate flow rate:	$1.5\ \mathrm{m}^3/\mathrm{d}$
Minimum brine flow rate:	$7.5\ \mathrm{m}^3/\mathrm{d}$

Design Data

Feed salinity is 42,000 ppm
Permeate flow rate: 5000 m^3/d
Permeate pressure: 101 kPa

Solution

The solution includes the following steps:
- The salt rejection definition is used to calculate the product salinity, where

$SR = 1 - X_p/X_f$
$0.995 = 1 - X_p/42000$

which gives $X_p = 210$ ppm

- The permeate recovery equation is used to calculate the feed flow rate for each module, or

$R = Q_d/Q_f$

Where Q_d and Q_f are the module flow rates for permeate and feed streams. This gives

$0.1 = 1.5/Q_f$
or $Q_f = 15$ m^3/d

This value is lower than the maximum limit per module, which is equal to 32.7 m^3/d

- Therefore the total amount of feed seawater is obtained by performing a simple balance on the total production capacity and the module production rate, where

$M_f = (M_d/Q_d)(Q_f)$
  $= (5000/1.5)(15)$
  $= 50000$ m^3/d

Also this gives the total number of modules, which is given by

$N = 5000/1.5$
  $= 3333$ modules

- The feed and permeate flow rates per module are used to calculate the brine flow rate, where

$Q_f = Q_d + Q_b$

$15 = 1.5 + Q_b$

which gives $Q_b = 13.5$ m^3/d. This value is higher than minimum brine flow rate per module, or 7.5 m^3/d.

– The salt balance for each module gives the salinity in the brine stream, where

$Q_f X_f = Q_d X_d + Q_b X_b$
$(15) (42000) = (1.5) (210) + (13.5)(X_b)$

which gives $X_b = 46643.3$ ppm

– The salinity of various streams is used to calculate the osmotic pressure of each stream

$\pi_f = 75.84 \, X_f = (75.84)(42) = 3185.28$ kPa

$\pi_b = 75.84 \, X_b = (75.84)(46.6433) = 3537.4$ kPa

$\pi_p = 75.84 \, X_p = (75.84)(0.21) = 15.9264$ kPa

– The resulting average osmotic pressure on the feed side is then calculated

$\bar{\pi} = 0.5 \, (\pi_f + \pi_b) = 0.5 \, (3185.28 + 3537.4) = 3361.3$ kPa

– Therefore, the net osmotic pressure across the membrane is given by

$\Delta\pi = \bar{\pi} - \pi_p = 3361.3 - 15.9264 = 3345.4$ kPa

– Assuming that the feed pressure is equal to the maximum module pressure, or 5500 kPa. Also, considering the module pressure drop gives a pressure of 5431 kPa in the brine stream.
– The net pressure difference across the membrane is given by

$\Delta p = 0.5(P_f + P_b) - P_p = 0.5(5500 + 5431) - 101 = 5364.5$ kPa

which is higher than the exerted osmotic pressure

Example on Semi-Empirical Model

Use the statistical mechanical model to obtain the permeate flow rate and membrane area at the following conditions:
- Membrane constants C_1, C_2, D_1, and D_2 with

$C_1 = -3.01 \times 10^{-1}$

$C_2 = 1.195164$

$D_1 = -1.56 \times 10^{-4}$

$D_2 = 1 \times 10^{-2}$

- Other data includes:
  Membrane salt rejection = 99%
  Feed salinity = 34,000 ppm
  Feed flow rate = 1000 m^3/d
  Permeate flow rate = 325 m^3/d
  Feed pressure = 6000 kPa
  Pressure of brine reject = 5900 kPa
  Permeate pressure = 101 kPa
  Salt concentration in membrane = 1.76 C_f

- The salt rejection definition is used to calculate the product salinity, where

$SR = 1 - X_p/X_f$
$0.99 = 1 - X_p/34000$

which gives X_p = 340 ppm

- From the above the pressure drop across the membrane is given by

$\Delta P = 0.5\ (Pf + Pb) - Pp$
$\quad = 0.5\ (6000 + 5900) - 101$
$\quad = 5849$ kPa

- The osmotic pressure is calculated for the feed, brine, and permeate

$\pi_f = 75.84\ X_f = (75.84)(34) = 2578.6$ kPa

$\pi_b = 75.84\ X_b = (75.84)(50.2) = 3806.3$ kPa

$\pi_p = 75.84\ X_p = (75.84)(0.34) = 25.8$ kPa

–   The resulting average osmotic pressure on the feed side is then calculated

$\overline{\pi} = 0.5\ (\pi_f + \pi_b) = 0.5\ (2578.6 + 3806.3) = 3192.4$ kPa

–   Therefore, the net osmotic pressure across the membrane is given by

$\Delta\pi = \overline{\pi} - \pi_p = 3192.4 - 25.8 = 3166.7$ kPa

–   The permeator area is calculated from the following equation

$M_p / A = (D_1\ c_w + D_2)(\Delta p - \sigma \Delta \pi)$

$325 / A = (-0.000156\ (60.2) + 0.01)(5849 - 3166.6)$

$A = 199\ m^2$

–   The salt rejection is then calculated from the following relation

$$SR = (C_1\ \frac{1}{(M_p / A)} + C_2)^{-1}$$

$$= ((-0.301)\frac{1}{(325/199)} + 1.19514)^{-1}$$

$$= 0.99$$

Problems

Problem 1

Design a single stage RO desalination system by calculating the permeate salinity, the brine salinity, the brine flow rate, and the membrane area. Analyze the following cases:

Data

Water permeability is $2.05 \times 10^{-6}\ m^3/m^2$ s kPa
Salt permeability is $2.03 \times 10^{-5}\ m^3/m^2$ s
Feed salinity is 34,000 ppm

Feed flow rate: 2.5 kg/s
Permeate flow rate: 1 kg/s
Feed pressure: 6000 kPa
Reject pressure: 5800 kPa
Permeate pressure: 101 kPa

Problem 2

The following module data are those for the DuPont B-10 permeator

Membrane recovery ratio:	35%
Salt rejection:	99.2%
Maximum applied pressure:	6895 kPa
Minimum brine flow rate:	1.584 m^3/d
Maximum brine flow rate:	14.256 m^3/d
Permeate flow rate:	2.46 m^3/d

Design Data

Feed salinity is 42,000 ppm
Permeate flow rate: 5000 m^3/d
Permeate pressure: 101 kPa

Design a single stage system by calculating the number of modules, osmotic pressure, permeation pressure difference, flow rates, and stream salinity.

Problem 3

A three stage RO system is designed using the following module data of the Osmonics permeator

Module Data

Membrane recovery ratio:	7%
Salt rejection:	99.5%
Maximum applied pressure:	5500 kPa
Minimum brine flow rate:	1.584 m^3/d
Maximum brine flow rate:	14.256 m^3/d
Permeate flow rate:	1.43 m^3/d

Design Data

Feed salinity is 34,000 ppm
Plant capacity: 24000 m^3/d

Permeate pressure: 101 kPa

Calculate the number of modules in each stage for the following configuration, flow rates and salinity of all stream, and the specific power consumption.
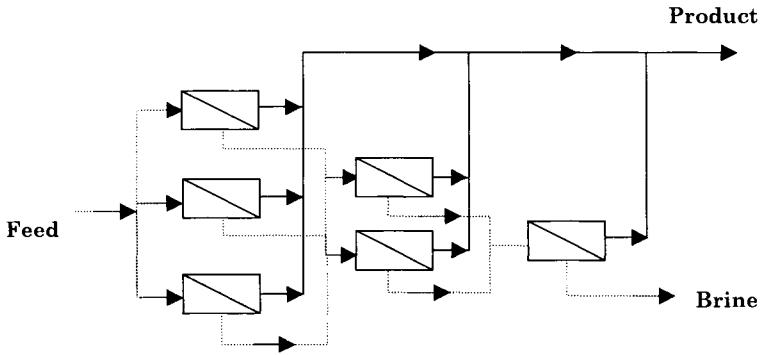
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Chapter 8

Reverse Osmosis Feed Treatment, Biofouling, and Membrane Cleaning

Objectives

The objective of this chapter is to outline characteristics of major features in RO operation, which includes feed pretreatment, biofouling, and membrane cleaning. The analysis include description of processes, procedures, troubleshooting, selection criteria

8.1   Need for Pretreatment Processes in RO

The RO feed water may contain various concentrations of suspended solids and dissolved matter. Suspended solids may consist of the following:
– Inorganic particles.
– Colloids.
– Biological matter, which includes microorganisms and algae.
On the other hand, Dissolved matter may consist of highly soluble salts, such as chlorides, and sparingly soluble salts, such as carbonates, sulfates, and silica.

Reduction in the feed water volume during the RO process results in increase of the concentration of suspended particles and dissolved ions. Settling of the suspended particles or scale formation from the sparingly soluble salts would result in the following:
– Blocking of the flow channels that would increase the pressure drop in the feed channels in the membrane module. This would require increasing the pumping power, which is limited by the original design value that takes into account clean operation in addition to some finite level of blockage.
– Reducing the permeation rate across the membrane and increase in the amount of salt passage through the membrane. This is caused by scale formation on the membrane surface.

In addition to physical masking of the membrane surface area and blockage of the membrane module, membrane damage can be caused by system operation at excessively low pH values, high chlorine concentration, or presence of other aggressive chemical compounds that would react and destruct the membrane material.

Depending on the raw water quality, the pretreatment process may consists of all or some of the following treatment steps:

– Removal of large particles using a coarse strainer.
– Water disinfection with chlorine or other biocides.
– Media filtration.
– Reduction of alkalinity by pH adjustment.
– Addition of scale inhibitor.

– Reduction of free chlorine using sodium bisulfite or activated carbon filters.
– Final removal of suspended particles using cartridge filters.

This chapter provides a summary for a large number of studies found in literature that covers the period from 1980 to 2001, see references on page 452.

8.2   *Testing Methods*

Testing methods of feed water include the following:
– Ionic constituents.
– Turbidity.
– Suspended solids.
– Total organic carbon.
– Silt Density Index (SDI).
– Dissolved gases such as CO_2, O_2, and Cl_2.
– PH.
– Temperature.

The RO operators use the SDI test as measure of the feed quality and operation ease. The guidelines for RO operation using the SDI test is as follows:
– SDI < 1, implies high quality feed water that would provide trouble free operation for years.
– 1 < SDI < 3, implies moderate to low quality feed water that would allow for few months of operation before need for membrane cleaning.
– 3 < SDI < 5 implies low quality feed water, which would require frequent cleaning.
– SDI > 5 implies very poor water quality and operation at these conditions is not acceptable.

The SDI test involves filtration of the water sample. A schematic of the SDI test unit is shown in Fig. 1. As is shown, the system includes the following elements:
– Feed pressure line.
– Pressure regulator.
– Filter paper assembly.
– Sample collection.
– Pressure gauge.
– Stop watch.

The SDI test procedure includes the following:
– A 500 ml (or 100 mℓ) volume feed water is forced through a standard filter under specified test conditions.

– After 15 min (or 5 min for the 100 mℓ sample) the test is repeated using the same filter.
– The filtration times t_1 and t_2 are used to determine the SDI, where

$$SDI = \frac{(1 - \frac{t_1}{t_2})\,(100)}{T} \qquad\qquad (1)$$

where, T is 5 (or 15 minutes for 100 mℓ sample).

   Other test conditions include the following:
– Applied pressure difference across the membrane is 2 bar.
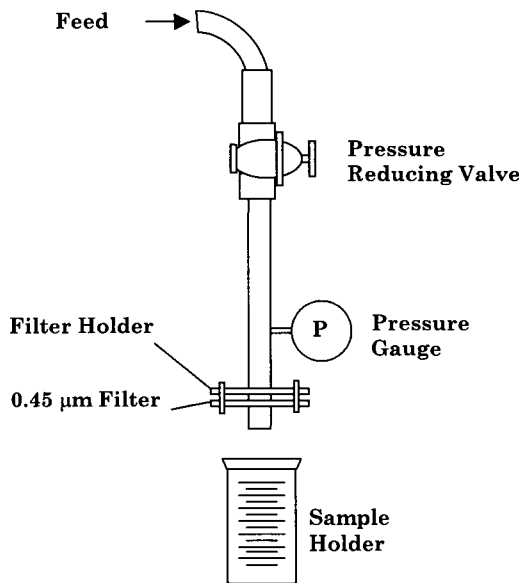– Filter pore diameter is 45 μm.
– Filter area is 1350 mm^2.

Fig. 1. SDI System.

8.3   *Suspended Solids and Silt Reduction*

   Typical examples of suspended solids include the following:
– Mud and silt
– Organic colloids
– Iron corrosion products
– Precipitated iron

- Algae
- Bacteria
- Rocks
- Silica/Sand
- Precipitated Manganese
- Precipitated Hardness
- Aluminum hydroxide flock

8.3.1 Media Filters

Features of media filters include the following:
- Formed of single- or multi-layered particles.
- The layers contain gravel, activated carbon or anthracite.
- The top layer of the bed consists of coarsely graded material, whereas the finely graded material is layered on the bottom
- The thickness of the filter layer is about 1-3 m.
- Compressed air or water is used for back-flushing.
- The particle size of the filter material is 0.5 – 3 mm.
- The filtration rate is 10-20 m h^{-1}.
- Most of the filtration process takes place in the top layer of the bed.

8.3.2 Cartridge Filters

Features of cartridge filters include the following:
- Cartridge filters are used in various RO configurations.
- The last pretreatment step prior to the RO process.
- The most common size is the 5 µm filter.
- The separation media can be made of polymer materials, such as polypropylene. Use of fiber shedding compounds, such as cotton and hemp, is not recommended since it may
- Combination of media and cartridge filters may be the most optimum and economic solution for particle removal.

8.4   Fouling and Scale Control

Scale forming compounds, in order of occurrence, include the following:
- Calcium carbonate
- Calcium sulfate
- Silica complexes
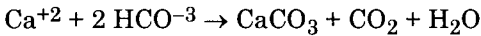- Barium sulfate
- Strontium sulfate

– Calcium fluoride

It should be stressed that the formed scale is made of several compounds. This is because that the first compound being precipitated would provide nucleation sites for other compounds.

8.4.1 Calcium Carbonate

The calcium carbonate equilibrium reaction is given by:

$$Ca^{+2} + 2\ HCO^{-3} \rightarrow CaCO_3 + CO_2 + H_2O$$

Precipitation of calcium carbonate is favored by:
– Increasing calcium or bicarbonate concentration.
– Decreasing the carbon dioxide concentration.
– Increasing the temperature.
– Increasing the pH (more alkaline solution).

Common methods to prevent calcium carbonate scaling include the following:
– Removal of all or some of the bicarbonate alkalinity by feeding acid.
– Use of scale-control agents

The choice between acid dosing and anti-scale control depends on:
– Type of membrane, especially compatibility for long-term operation at low pH.
– Process economics, which would optimize the purchasing cost of antiscalent and acid as well as the capital of handling and dosing equipment for the acid and the antiscalent. In this regard, sulfuric acid is very inexpensive when compared to other acids or antiscalent compounds. However, its use should be handled properly. Otherwise, the presence of the sulfate group in the acid may enhance formation of the calcium, barium, or strontium sulfate scale.
– Final selection would depend on the feed salinity and product quality, which may call for use of each method separately or the combined use of both techniques. For example, seawater desalination would call for simultaneous use of acid and antiscalent dosing.
– Another problem related to acid dosing is the generation of large amounts of CO_2. As a result, the CO2 concentration increases in the permeate water because of its high permeability of CO_2 across various types of RO membranes. This reduces the permeate pH and imposes an overload on ion exchange units used for polishing of the boiler makeup water.

8.4.2 *Calcium Sulfate*

Various forms $CaSO_4$ crystals include the following:
- Dehydrate calcium sulfate, $CaSO_4.2H_2O$.
- Anhydrous calcium sulfate, $CaSO_4$.
- Hemihydrate calcium sulfate, $CaSO_4.1/2H_2O$.

All of these compounds have reverse solubility, where it precipitates at high temperature. However, increase in the ionic concentration of Ca^{2+} and SO_4^{2-} beyond the solubility limit ions in the brine stream may result in severe scaling.

Prevention of $CaSO_4$ scaling in RO includes the following:
- Addition of antiscaling agents, which includes polyphosphates, polycarboxylates or sodium hexametaphosphate to prevent precipitation of $CaSO_4$. Proper dosing would allow for safe operation even if the brine stream has higher concentration than the saturation limit.
- Lowering the permeate recovery rate to prevent increase in the concentration beyond the saturation limit.

8.4.3 *Silica*

Silica scaling has the following features:
- The solubility of silica depends on the system pH and temperature.
- Low temperature operation, i.e., below 10 °C, and silica saturation below 120 ppm allows for operation with brine solutions supersaturated in silica with little or no silica scaling.
- Operation at higher concentrations or temperature enhances the silica scaling process.
- Silica forms complex precipitates with iron, aluminum, and magnesium hydroxides.
- The most effective method to prevent silica scaling is to maintain its concentration below the saturation limit, which is strongly affected by the system temperature.

8.4.4 *Organics*

A wide range of organic compounds can be found in the RO feed water. This depends on the water source and if it has been contaminated with industrial, municipal, or agricultural effluents. Variations in the organics physical and chemical properties give different effects on the RO process, which includes the following:

- Organic compounds reacts differently with the membrane separation process, where the membrane may reject or permeate the compound. Also, rejected or permeating organics may foul the membrane and reduce its performance.
- Organic compounds can be removed from the feed water through degasification of low boiling compounds, adsorption on activated carbon, coagulation and filtration, or removal by ion exchange resins.
- Final selection of the pretreatment process requires measuring the TOC of the feed water and chemical analysis to identify major compounds.

8.5   Biofouling in RO

Biofouling in RO is combined result of the following factors:
- Presence of microorganisms in the feed water.
- Availability of the membrane surface area, which can be colonized by the microorganisms.
- The RO membrane rejects all microorganisms found in the feed water. As a result, part of the rejected cells remains adhered to the membrane and initiates the process of biofilm formation.
- All pretreatment operations prior to the RO module may provide sufficient surface area for microorganisms and bacterial growth. For example, the large surface areas found in media filters, activated carbon beds, or even pipelines connecting various units.
- The biofilm growth mode, on the membrane surface or any other surface, requires the minimum possible amount of nutrients in the feed water. In addition, diffusion and penetration of biocides from the feed water bulk into the bacterial film is less effective than attacking single cells suspended in the feed water.

8.5.1 Effects of Biofouling on RO Performance

Biofouling effects on RO performance are characterized by gradual deterioration in the system performance. This includes a period of rapid decline followed by an asymptotic limit. Performance deterioration includes the following:
- Decrease in the permeate flux.
- Increase in pressure drop.
- Decrease in salt rejection.

The results of the above effects on the overall performance include the following:
- Increased cleaning and maintenance costs. This is necessary to maintain economic operation that calls for a specific range for production rate and

product quality. Membrane cleaning restores the system production rate within the specified limits as well as the product quality

– Reduction in membrane lifetime. This is a complex phenomenon, since exposure of the membrane to biofilm formation would result in several side effects, which includes increase in the pressure drop, increase in the flow velocity, exposure of the membrane to extracellular compounds, entrapment of settled solids in the biofilm, precipitation of scaling compounds on the membrane and within the biofilm.

– Other than reducing the flow area, the biofilm may increase friction and drag. Both factors increase the pressure drop within the system, which in turn increase the demand load on the high pressure feed pumps. This is necessary to maintain sufficient feed pressure and permeation rate.

– Uneven growth of the biofilm is also quiet common and that results in uneven flow within the system. As results, sections with lower flow rate may result in enhancement of scaling and settling of solids.

8.5.2 Biofouling Mechanism

The biofouling mechanism is formed of the following elements:

– Bifouling potential depends on feed water conditions, system design, and operating conditions. Feed water temperature is a very important parameter; where in the Gulf and equatorial regions the seawater temperature during the long summer period remains close to 30 °C. Such condition would highly favor bacterial growth and biofilm formation. In addition, presence of dead ends, rough piping, or non-disinfected water tanks in the system would enhance the biofilm formation process. Poor housekeeping may also contribute to microbial contamination and formation of the biofilm.

– Formation of the conditioning film, which involves adsorption of macromolecules on the membrane surface. This step may last for few seconds to minutes after the membrane is exposed to the feed water. The conditioning film has different surface properties than the original membrane surface. Therefore, the electrostatic charge of the conditioning film may considerably affect microbial adhesion.

– Microbial adhesion is achieved by hydrodynamic forces, motility, and diffusion. The microbial layer is protected to a large extent from the shearing forces of the bulk flow because of the small thickness of the biofilm in comparison with the boundary layer thickness. In addition, the RO membranes reject all the bacterial cells and microorganisms arriving at membrane surface. The adhesion process is also affected by the number of cells in the bulk, nutrient concentration, temperature, pH, flow hydrodynamics, and surface charge. Recent membrane development focus on construction of membranes with surface charge that inhibit microbial adhesion and formation of the conditioning film.

– Biofil 8.2.4 Assessment of Biofouling Potential   ; are irreversibly attached
to the membrane surface. As mentioned before, the biofilm formation is
favored since it is protected against biocide effects (because of diffusion
limitations) and it consumes much smaller amounts of nutrients than cells in
suspension. Therefore, the biofilm grows rapidly until it reaches an
asymptotic limit, where the growth rate (controlled by nutrient concentrations
and temperature) reaches equilibrium with the removal rate by shear forces.

8.5.3 Biofouling Assessment

Biofouling is recognized by indirect effects on the system performance:
permeate decline, decrease of salt rejection, or increase of the pressure drop on
the feed-side. Further assessment of membrane biofouling is achieved by any of
the following techniques:

– Analysis of the pretreatment filter media for biofouling. Presence of biofouling
  in these systems may give strong indication for membrane biofouling.
– Use of on-line membrane testing elements, which have smaller size than the
  actual membrane module. These elements can be removed and replaced on
  frequent basis. The removed elements are then dismantled and properly
  tested for biofouling and other forms scaling.

8.5.4 Biofouling Treatment

Addition of biocides to the feed water at an appropriate dosing rate would
kill the microorganisms and bacterial cells suspended in the water and forming
the biofilm on various parts of the system. Biocide treatment would prevent
further growth of existing biofilms or formation of new biofilms. However,
existing biofilms, formed of dead bacterial cells, would remain to affect the
system performance in various aspects, i.e., higher pressure drop, lower recovery,
lower salt rejection, etc. In other words, biocide treatment kills the
microorganisms and bacteria forming the biofilm, but has no effect on removal of
the biofilm. Moreover, a dead biofilm might become a substrate for new bacterial
cells, which may get attached to the dead biofilm and consume its nutrient
content. The same concept applies for the dead and suspended cells in the feed
stream, which may ends up being attached to the membrane surface and causes
reduction in recovery rate and salt rejection. Features of the biofouling treatment
processes are summarized below:

– Effectiveness of the biocide depends on several operating and design factors,
  which includes; type of biocide, concentration of biocide, side-reactions of
  biocide and compounds other than bacteria or microorganisms, pH,
  temperature, residence time, type of microorganism, growth state, physical
  nature of the biofilm

- Increase in the biocide concentration, temperature, and residence time would increase the percent kill of the microorganisms.
- Chlorine is one of the most effective and common biocide agents. However, it requires a de-chlorination unit placed ahead of the RO to protect membranes sensitive to chlorine attack. Another disadvantage of chlorine use is the safety precautions required for storage and handling.
- Other biocides include formaldehyde, ozone, peracetic acid, hydrogen peroxide, etc. Use of these is found much smaller scale than chlorine. In addition, some these have lower efficiency than chlorine and have harmful effects on the environment.

8.6   Membrane Cleaning

Membrane cleaning is dictated by increase in pressure drop, decrease in permeate recovery, and decrease in salt rejection. It should be stressed that normalized data should be used to correct for temperature effects on system performance. In addition, identification of foulants as well as analysis of feed and outlet water are important factors in determining the proper cleaning solution. The following is a summary of cleaning methods of various fouling and scaling compounds.

Calcium Carbonate and Metal Oxides Scale: Clean with low pH water. The water pH is adjusted to 3-4 and sulfuric, hydrochloric, or citric acids are used.

Calcium Sulfate Scale: Clean with a solution that include sodium tripoly phosphate or sodium salt of ethylene diamine tetra acetic acid.

Silica: Detergents and hydraulic cleaning.

Organics and biofouling: similar solution to calcium sulfate cleaning. In addition, use of detergents and biocides are recommended.

8.6.1 Membrane Cleaning Procedure

Generally, low pH solutions are used to clean metallic scales while alkaline solutions are used to clean biological and organic fouling. Relatively high flow with low pressure is recommended. System cleaning follows the following basic steps:

- Preparation of the cleaning solution and adjustment of temperature and pH.
- Displacement of the solution in RO modules by pumping the cleaning solution.
- Recycling and soaking of the element. Soaking time may vary from few hours to overnight depending on the fouling level.

– Flushing the unit with RO permeate water. The flushing procedure continues
  until foaming disappears and the pH and conductivity of the effluent solution
  approach those of the feed water.

Other features of the cleaning process include the following:

– Use of chlorine or other strong oxidants on polyamide membranes can cause
  irreversible damage to the membrane.
– Warm water at a temperature of 32 ℃ to 37 ℃ gives better cleaning results
  than lower temperature solutions.
– If the pH of an acid solution increases during recirculation, add more acid to
  return the pH back to the target value. This is because of acid consumption in
  dissolving inorganic scale.
– Use of sulfuric acid in low pH solutions may result in forming sulfate scale.
– Permeate water is preferred for mixing cleaning solutions.
– Use of filtered tap water for high pH solutions can result in carbonate fouling
  if the water is hard.

8.6.2 Membrane Sterilization

Membrane sterilization is necessary if the system is shut down for period
of more than 2 days. Sterilization compounds include the following:

– Hydrogen peroxide (0.25 wt %).
– Sodium bisulfite/glycerin (0.2 to 1 wt %/16 to 20 wt %).
– Sodium bisulfite (0.5 to 1 wt %).
– Formaldehyde (0.25 to 1 wt%).
– Copper sulfate (0.1 to 0.5 ppm)

Procedure for membrane sterilization includes: preparation of the
sterilizing solution, initial flushing with RO permeate water, circulation of the
sterilizing solution, drainage, and tight closure during the storage period. Placing
a sterilized unit back into operation requires flushing permeate water.

8.6.3 Cleaning System Specifications

The RO cleaning system is formed of a tank, 5 μm cartridge filter, pumping
unit, and instrumentation, Fig. 2. Cleaning solution is pumped from the tank
through the cartridge filter to the RO array. Solution is then recycled back to the
tank. The volume of solution should be sufficient to fill the volume of the vessels,
filters and piping. Instrumentation includes pH, temperature, flow rate,
pressure, and level controllers.

Choice of the construction material for the cleaning system includes the following:

– Tank: Fiberglass reinforced plastic or polypropylene. Tank should have a removable cover.
– Piping: PVC schedule 80 or Nylon reinforced flex hose.
– Valves: Stainless Steel.
– Pump: Stainless Steel or Non-metallic composite polyesters. Pump should be centrifugal type.

Material selection should be made to withstand extremes in pH, temperatures up to (45 ºC), and electrical sources/switches should be protected and well grounded.
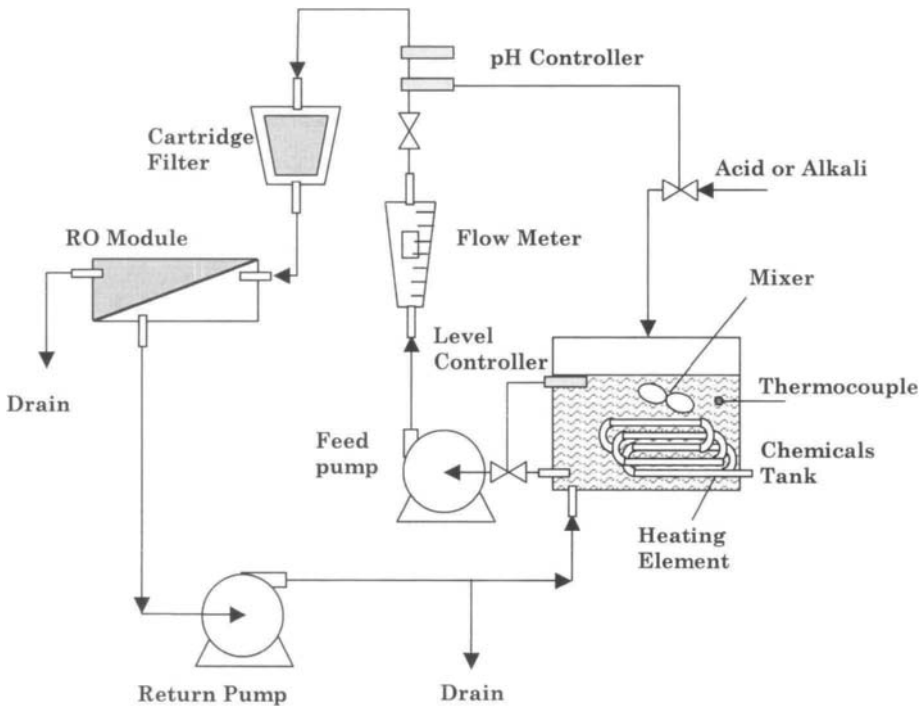

Fig. 2. RO cleaning system.

8.7 *Membrane Storage*

Various forms of membrane storage include the following:

– Short-term storage of membrane elements in place inside the pressure tubes.

- Long-term storage of membrane elements in place inside the pressure tubes.
- Dry storage of membrane elements as spares or before start-up of the plant.

Short-term storage ranges between 5 to 30 days. On the other hand the long term storage remains for more than 30 days. For both modes of storage, the membrane elements remain in place inside the pressure tubes. Both storage modes have similar sequence and are summarized below:

- Cleaning of the membrane elements.
- Flushing the membrane element with acidified water to prevent precipitation of scaling material.
- A suitable biocide is added to the flushing water to prevent microorganism growth.
- The pressure tubes are filled with the above solution.
- The cleaning, flushing, and filling sequence is repeated on frequent basis subject to the effectiveness of the biocide.
- Before, returning the system to service, the membrane elements are flushed with feed water. The flushing process starts at low pressure and then proceeds to high pressure operation. During the flushing process, the brine and product streams are rejected. Also, water samples are collected from both streams to check for presence of biocides.

Storage of membrane elements during transportation or prior to installation should provide protection from direct sunlight. The elements should be stored in a cool, dry place, and at a temperature range of 20°C to 35°C.

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