

# Fundamentals of Membranes for Water Treatment

Alyson Sagle and Benny Freeman<sup>1</sup>

## Introduction

Membranes emerged as a viable means of water purification in the 1960s with the development of high performance synthetic membranes. Implementation of membranes for water treatment has progressed using more advanced membranes made from new materials and employed in various configurations. An increasing scarcity in fresh water sources fueled a push towards alternative resources such as ocean water. In the 1970s, exploration began into using membranes for water desalination. Proving successful at producing purified water from salt water, membranes became a viable alternative to evaporation-based technologies in the water treatment market. Over the years, purified water standards have become more stringent, and a plethora of new applications have appeared. However, membranes have risen to the challenge and continue to perform efficiently and effectively<sup>1</sup>.

## Background

**Types of membranes.** Water treatment processes employ several types of membranes<sup>1</sup>. They include microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) membranes (Figure 1)<sup>2</sup>. MF membranes have the largest pore size and typically reject large particles and various microorganisms. UF membranes have smaller pores than MF membranes and, therefore, in addition to large particles and microorganisms, they can reject bacteria and soluble macromolecules such as proteins. RO membranes are effectively non-porous and, therefore, exclude particles and even many low molar mass species such as salt ions, organics, etc.<sup>2</sup> NF membranes are relatively new and are sometimes called “loose” RO membranes. They are porous membranes, but since the pores are on the order of ten angstroms or less, they exhibit performance between that of RO and UF membranes<sup>3</sup>.

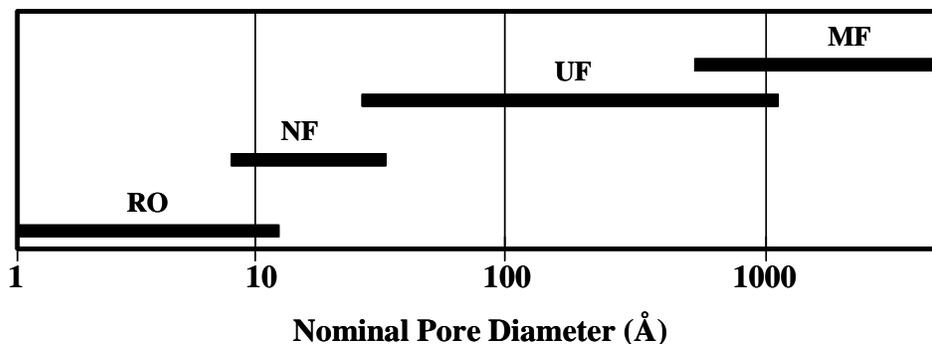
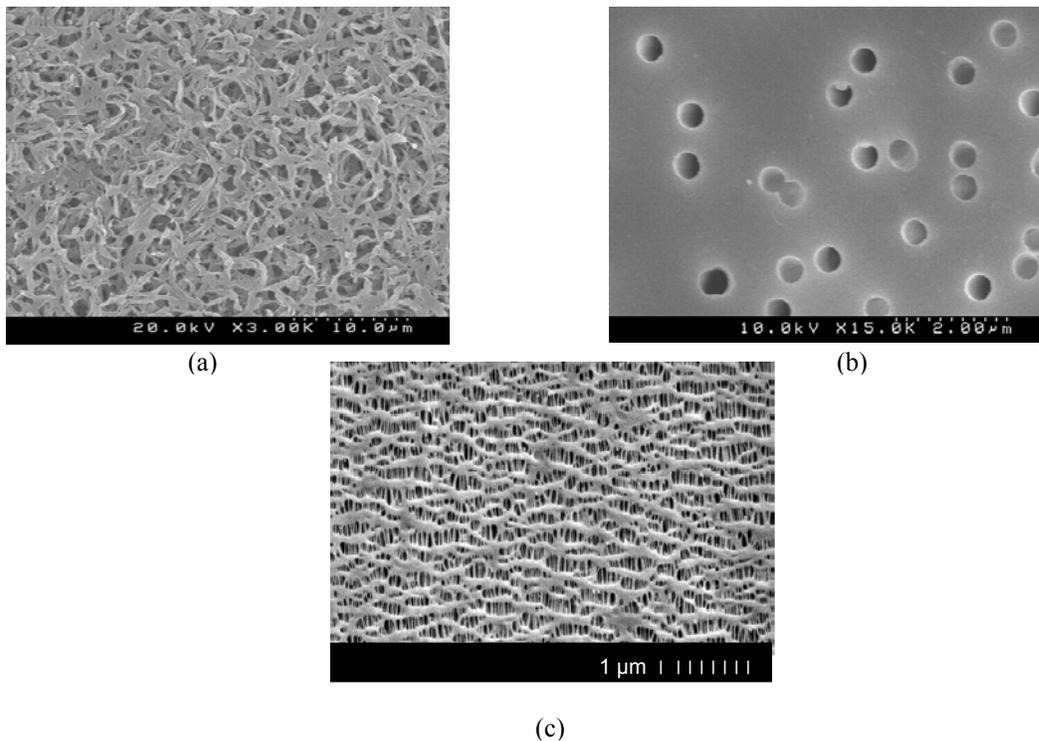


Figure 1. Range of nominal membrane pore sizes<sup>2</sup>.

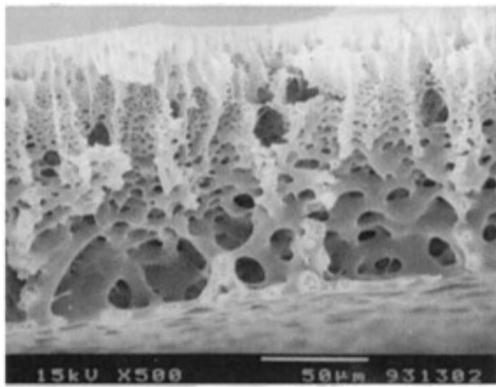
<sup>1</sup> University of Texas at Austin

**Membrane Characteristics.** Membranes are generally classified as isotropic or anisotropic. Isotropic membranes are uniform in composition and physical nature across the cross-section of the membrane. Anisotropic membranes are non-uniform over the membrane cross-section, and they typically consist of layers which vary in structure and/or chemical composition.

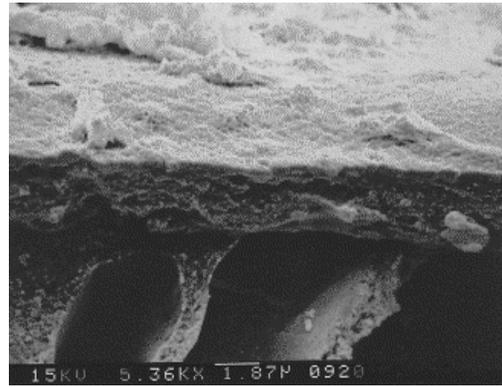
Isotropic membranes can be divided into various subcategories. For example, isotropic membranes may be microporous. Microporous membranes are often prepared from rigid polymeric materials with large voids that create interconnected pores<sup>3</sup>. The most common microporous membranes are phase inversion membranes (Figure 2a)<sup>3</sup>. These are produced by casting a film from a solution of polymer and solvent and immersing the cast film in a nonsolvent for the polymer. Most polymers used in such applications are hydrophobic, so water is the most common nonsolvent<sup>4</sup>. Upon contact with water, the polymer precipitates to form the membrane. Another type of microporous membrane is the track-etched membrane (Figure 2b)<sup>3</sup>. This type of membrane is prepared by irradiating a polymer film with charged particles that attack the polymer chains, leaving damaged molecules behind. The film is then passed through an etching solution, and the damaged molecules dissolve to produce cylindrical pores, many of which are perpendicular to the membrane surface. A less common microporous membrane is an expanded-film membrane (Figure 2c)<sup>3</sup>. Expanded film membranes are oriented crystalline polymers with voids created by an extrusion and stretching process. First, the material is extruded near its melting temperature using a rapid draw-down rate. Then, the extruded material is cooled, annealed, and stretched up to 300% of its original length. This stretching process creates slit-like pores ranging in size from 200 to 2500 Å. Isotropic membranes can also be dense films which either lack pores or contain pores that are so small as to render the membrane effectively non-porous<sup>3</sup>. These films are prepared by solution casting followed by solvent evaporation or melt extrusion.



**Figure 2.** SEM images showing top surfaces of a) a phase inversion membrane<sup>5</sup>, b) a track-etched membrane<sup>5</sup>, and c) an expanded film membrane<sup>6</sup>.



(a)

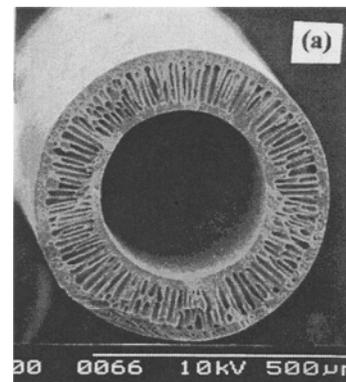


(b)

**Figure 3.** SEM images of a) cross-section of an anisotropic microporous membrane<sup>7</sup> and b) cross-section of a thin-film composite membrane<sup>8</sup>.

There are two main types of anisotropic membranes: phase separation membranes and thin film composite membranes. Anisotropic phase separation membranes are often called Loeb-Sourirajan membranes, referring to the people who are credited with initially developing them<sup>3</sup>. These phase-separated membranes are homogeneous in chemical composition but not in structure. Loeb-Sourirajan membranes are produced via phase inversion techniques such as those described above, except that the pore sizes and porosity vary across the membrane thickness (Figure 3a). Loeb-Sourirajan membranes often consist of a rather dense layer of polymer on the surface of an increasingly porous layer. Thin film composite membranes are both chemically and structurally heterogeneous (Figure 3b)<sup>3</sup>. Thin film composites usually consist of a highly porous substrate coated with a thin dense film of a different polymer. They can be made via several methods including interfacial polymerization, solution coating, plasma polymerization or surface treatment<sup>3</sup>.

The descriptions above of isotropic and anisotropic membranes refer to flat sheet configurations. However, membranes can also be produced as hollow fibers<sup>3</sup>. Like flat sheets, these fibers can either be isotropic or anisotropic. They also can be dense or porous. Common fibers used in industry today are anisotropic with a dense outer layer around a porous tube (Figure 4). One advantage of hollow fiber membranes is that they have more surface area per unit volume than flat sheet membranes<sup>3</sup>.

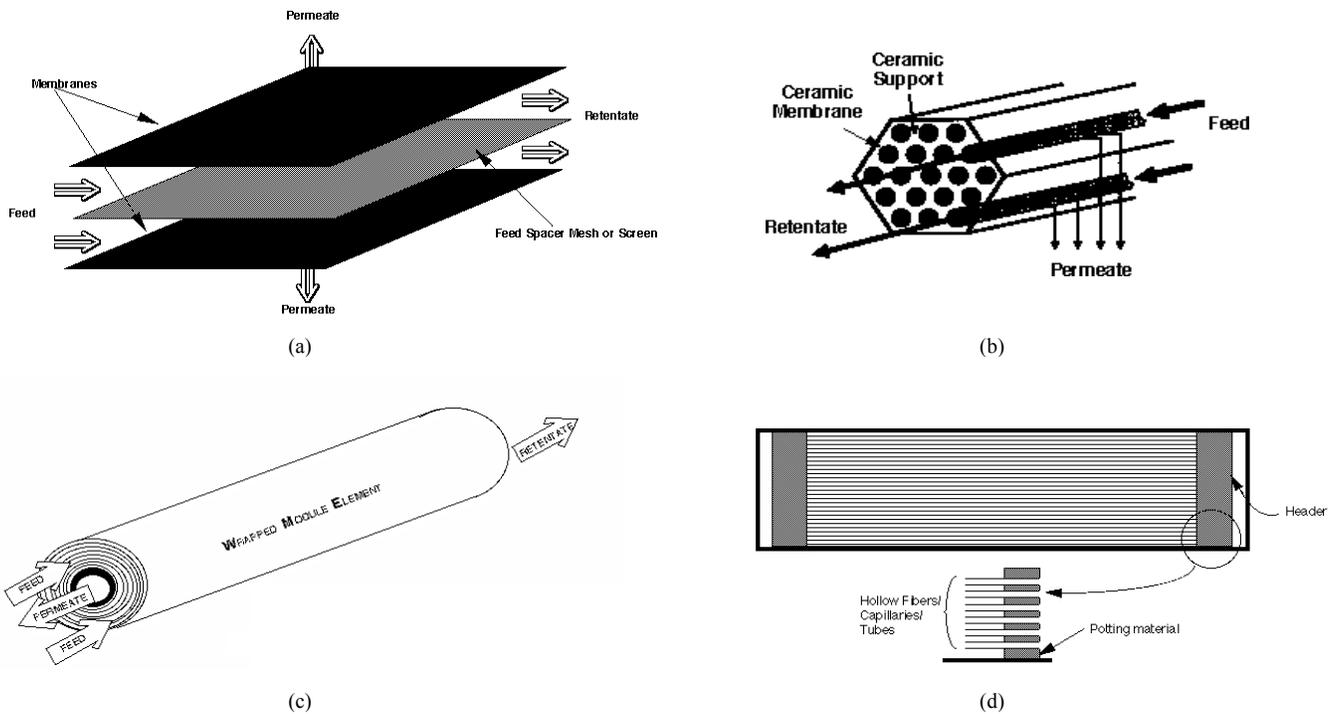


**Figure 4.** SEM image of hollow fiber cross-section<sup>9</sup>.

**Membrane Materials.** Most MF, UF, RO, and NF membranes are synthetic organic polymers. MF and UF membranes are often made from the same materials, but they are prepared under different membrane formation conditions so that different pore sizes are produced<sup>4</sup>. Typical MF and UF polymers include poly(vinylidene fluoride), polysulfone, poly(acrylonitrile) and poly(acrylonitrile)-poly(vinyl chloride) copolymers<sup>3</sup>. Poly(ether sulfone) is also commonly used for UF membranes<sup>3</sup>. MF membranes also include cellulose acetate-cellulose nitrate blends, nylons, and poly(tetrafluoroethylene)<sup>3</sup>. RO membranes are typically either cellulose acetate or polysulfone coated with aromatic polyamides<sup>3</sup>. NF membranes are made from cellulose acetate blends or polyamide composites like the RO membranes, or they could be modified forms of UF membranes such as sulfonated polysulfone<sup>10</sup>.

Membranes can also be prepared from inorganic materials such as ceramics or metals<sup>3</sup>. Ceramic membranes are microporous, thermally stable, chemically resistant, and often used for microfiltration<sup>3</sup>. However, disadvantages such as high cost and mechanical fragility have hindered their wide-spread use. Metallic membranes are often made of stainless steel and can be very finely porous. Their main application is in gas separations, but they can also be used for water filtration at high temperatures or as a membrane support<sup>11</sup>.

**Membrane Modules.** There are four main types of modules: plate-and-frame, tubular, spiral wound, and hollow fiber (Figure 5)<sup>3</sup>. The plate-and-frame module is the simplest configuration, consisting of two end plates, the flat sheet membrane, and spacers. In tubular modules, the membrane is often on the inside of a tube, and the feed solution is pumped through the tube. The most popular module in industry for nanofiltration or reverse osmosis membranes is the spiral wound module. This module has a flat sheet membrane wrapped around a perforated permeate collection tube<sup>3</sup>. The feed flows on one side of the membrane. Permeate is collected on the



**Figure 5.** Schematic of a) plate and frame, b) tubular, c) spiral wound and d) hollow fiber modules<sup>12</sup>.

other side of the membrane and spirals in towards the center collection tube.

Hollow fiber modules used for seawater desalination consist of bundles of hollow fibers in a pressure vessel<sup>3</sup>. They can have a shell-side feed configuration where the feed passes along the outside of the fibers and exits the fiber ends. Hollow fiber modules can also be used in a bore-side feed configuration where the feed is circulated through the fibers<sup>3</sup>. Hollow fibers employed for waste water treatment and in membrane bioreactors are not always used in pressure vessels. Bundles of fibers can be suspended in the feed solution, and the permeate is collected from one end of the fibers<sup>13</sup>.

## Theory

The theory governing fluid transport through membranes is often expressed as follows<sup>14</sup>:

$$\vec{N}_A = \rho_A \vec{v} - D_{AB} \vec{\nabla} \rho_A \quad (1)$$

where  $N_A$  is the mass flux of component A through the membrane (mass per time per area),  $\rho_A$  is the mass density of component A,  $\vec{v}$  is the mass average velocity of the fluid through the membrane,  $D_{AB}$  is the effective diffusion coefficient of component A in the membrane, and  $\vec{\nabla} \rho_A$  is the mass density gradient. In membranes where pore flow contributes significantly to flux, Darcy's Law is often used to characterize the mass average velocity<sup>14</sup>:

$$\vec{v} = -\frac{\kappa}{\mu} (\vec{\nabla} p - \rho \vec{g}) \quad (2)$$

where  $\kappa$  is the Darcy Law permeability of the medium,  $\mu$  is the fluid viscosity,  $\vec{\nabla} p$  is the pressure gradient (i.e., the rate of pressure change with respect to position),  $\rho$  is the solution density and  $\vec{g}$  is the gravity vector. Introducing Eq. 2 into Eq. 1, restricting transport to only the x-direction, which would typically be the direction perpendicular to the membrane surface, and neglecting gravity, yields:

$$N_{Ax} = \frac{\rho_A \kappa}{\mu} \frac{dp}{dx} - D_{AB} \frac{d\rho_A}{dx} \quad (3)$$

The first term in Eq. 3 represents mass flux due to pressure-driven convection through pores, and the second term represents flux due to diffusion. Diffusion through porous membranes is typically negligible relative to convection. In this case, the flux is directly proportional to the pressure gradient across the membrane. The applied pressure difference across the membrane, often called the transmembrane pressure difference, is the driving force governing transport of liquid through a porous membrane.

In applying the convective term of Eq. 3 to transport through UF and MF membranes, the permeability,  $\kappa$ , depends, often in a complex way, on factors such as the porosity and the tortuosity of the membrane. Tortuosity,  $\tau$ , is the ratio of the average length of the "tortuous" path that the fluid must travel to pass through the membrane to the membrane thickness. For example, a cylindrical pore perpendicular to the surface has a tortuosity of one. Most phase

inversion membranes have tortuosities from 1.5 to 2.5<sup>3</sup>. Porosity,  $\epsilon$ , is the void fraction of the membrane. UF and MF membrane porosity typically ranges from 0.3 to 0.7<sup>3</sup>.

Since RO membranes are effectively non-porous, the transport of a molecule across the membrane is diffusion controlled. This means that the second term of Eq. 3 controls the flux across the membrane. Water molecules sorb into the upstream face of the membrane, diffuse down the chemical potential gradient across the membrane, and desorb from the downstream face of the membrane. The second step, diffusion through the membrane, is the rate-determining step in water transport across the membrane. This mechanism of mass transport across membranes is commonly referred to as the “solution- diffusion” model<sup>14</sup>. Beginning with the more general model of mass transport being driven by chemical potential gradients rather than concentration gradients, the solution-diffusion transport equation for reverse osmosis can be derived<sup>14,15</sup>:

$$N_{Aw} = L(\Delta p - \Delta \pi) \quad (4)$$

where  $N_{Aw}$  is the water flux through the membrane,  $\Delta p$  is the transmembrane pressure difference,  $\Delta \pi$  is the difference in osmotic pressure between the feed and the permeate, and  $L$  is a constant describing the physical characteristics of the membrane itself. Within the context of the solution-diffusion model used to describe transport in nonporous films,  $L$  is given by<sup>15</sup>:

$$L = \frac{DSV}{RTl} \quad (5)$$

where  $D$  is the water diffusivity in the membrane,  $S$  is the water solubility in the membrane,  $V$  is the molar volume of water,  $R$  is the ideal gas constant,  $T$  is the ambient temperature, and  $l$  is the membrane thickness. A complete derivation can be found in the Baker and Wijmans review of the solution-diffusion model<sup>15</sup> and in Paul’s recent re-examination of the solution-diffusion model for reverse osmosis<sup>16</sup>.

As seen from Eq. 4, osmotic pressure of the feed and permeate solutions plays a role in the separation. Osmotic pressure is the pressure needed to cause a solvent (water) to leave a solution (seawater, waste water, etc.) and permeate through the membrane. For an ideal solution, with complete dissociation of salt ions, osmotic pressure is defined as<sup>17</sup>:

$$\pi = CRT \quad (6)$$

where  $\pi$  is the osmotic pressure,  $C$  is the salt ion concentration,  $R$  is the ideal gas constant, and  $T$  is the solution temperature. The salt ion concentration,  $C$ , is given by the number of ions in solution per gram of water divided by the specific volume of water. Table I presents the osmotic pressure for several solutions pertinent to water treatment applications.

Table I. Typical osmotic pressure values for solutions at 25°C<sup>17</sup>

Solute	Concentration (mg/L)	Osmotic Pressure (psi)
NaCl	2,000	23
NaCl	35,000	397
Brackish water	2,000-5,000	15-39
Seawater	32,000	339

In reverse osmosis, salt transport across a membrane is as important as water transport. However, unlike water flux, which is driven by both applied transmembrane pressure and osmotic pressure, the salt flux is only a function of salt concentration<sup>3</sup>:

$$N_s = B(C_{feed} - C_{permeate}) \quad (7)$$

where  $N_s$  is the salt flux through the membrane,  $B$  is the salt permeability constant describing the physical characteristics of the membrane,  $C_{feed}$  is the salt concentration in the feed solution, and  $C_{permeate}$  is the salt concentration in the permeate solution. Analogous to  $L$  in the solution-diffusion equation,  $B$  is given by<sup>3</sup>:

$$B = \frac{D_s K_s}{l} \quad (8)$$

where  $D_s$  is the salt diffusivity in the membrane,  $K_s$  is the salt partition coefficient, and  $l$  is the membrane thickness. However, instead of reporting salt flux values, most membrane performance specifications provide salt rejection values. Salt rejection,  $R$ , is defined as follows<sup>3</sup>:

$$R = \left( 1 - \frac{C_{permeate}}{C_{feed}} \right) \times 100\% \quad (9)$$

Futhermore, water flux and salt flux depend on each other. Eq. 10 relates the water flux,  $N_{Aw}$ , and the salt flux,  $N_s$ <sup>18</sup>:

$$\frac{C_w}{C_{permeate}} = \frac{N_{Aw}}{N_s} \quad (10)$$

where  $C_w$  is the water concentration in the permeate and  $C_{permeate}$  is the salt concentration in the permeate. By substituting Eq. 4 and Eq. 7 into Eq. 10 and rearranging terms, the following expression for rejection may be derived<sup>18</sup>:

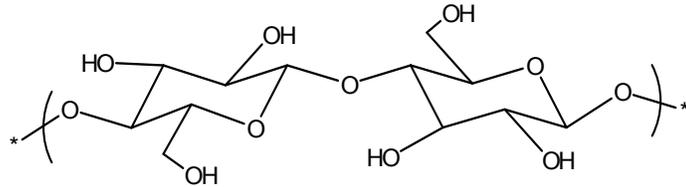
$$R = \left( \frac{\frac{L}{B}(\Delta p - \Delta \pi)}{1 + \frac{L}{B}(\Delta p - \Delta \pi)} \right) \times 100\% \quad (11)$$

Eq. 11 relates salt rejection to the physical properties of the membrane (which influence L and B), the applied transmembrane pressure difference, and the osmotic pressure difference between the permeate and the feed. Eq. 11 allows one to predict the salt rejection of the membrane based on the experimental conditions and the membrane properties.

## Reverse Osmosis Membranes

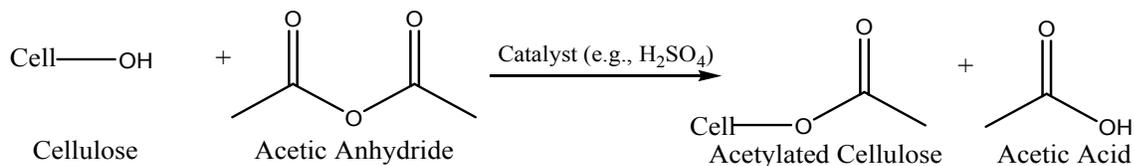
**History.** The first recorded synthetic membrane was prepared in 1867 by Moritz Traube<sup>19</sup>. His most successful membrane was a precipitated film of copper ferrocyanide which he used to study osmosis. His initial success spawned several decades of investigations into the theory behind the thermodynamics and kinetics of the diffusion process. In 1963, Loeb and Sourirajan demonstrated asymmetric cellulose acetate membranes which exhibited relatively high flux and good salt rejection<sup>20</sup>. RO membranes made their commercial debut when Gulf General Atomics and Aerojet General employed the Loeb-Sourirajan cellulose acetate (CA) membranes in spiral wound modules to purify water<sup>1</sup>.

**Cellulose-Based Membranes.** The initial leader in the RO membrane market was the Loeb-Sourirajan CA membrane. These CA membranes were asymmetric and exhibited NaCl rejection values of approximately 99.5% using a feed solution of 52,500 mg/L NaCl and flux values from 5 to 11 gallons per square foot per day (GFD) (9 to 19



**Figure 6.** Chemical structure of a cellulose repeat unit<sup>21</sup>.

LMH) at feed pressures ranging from 1500 to 2000 psig<sup>20</sup>. CA membranes are made from acetylated cellulose. Cellulose (Figure 6) is a naturally occurring polymer found in plants such as cotton<sup>22</sup>. It is a linear, rod-like material that is relatively inflexible, which renders CA membranes mechanically robust. Acetylation of the cellulose occurs via the following reaction<sup>21</sup>:



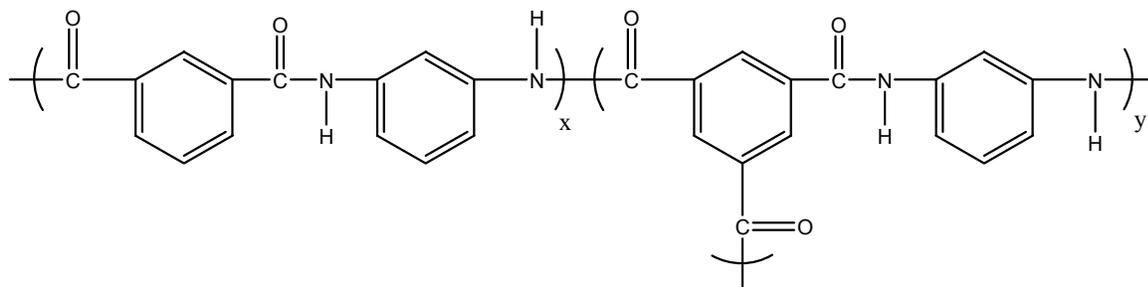
The degree of acetylation describes how many of the pendant OH groups on the cellulose (see Figure 6) are replaced with acetyl groups, CH<sub>3</sub>COO. The degree of acetylation can range from 0 to 3 where 0 represents unreacted cellulose and 3 corresponds to completely substituted cellulose, also called cellulose triacetate (CTA). The degree of acetylation has a large effect on the resulting membrane properties. A high degree of acetylation gives high salt selection but low permeability<sup>22</sup>. Lower degrees of acetylation yield membranes with lower rejection but higher

flux<sup>22</sup>. Commercial CA membranes used for reverse osmosis have a degree of acetylation of about 2.7. This composition provides a good balance between salt rejection and permeate flux. Some membranes also use blends of CA and CTA. Blending CA with CTA increases the mechanical stability and resistance to hydrolysis but decreases the permeability. One example of a commercial CA blend membrane exhibits a flux of 22 GFD at 425 psi ( $\Delta p$ ) and an average NaCl rejection of 97.5% from a 2000 mg/L NaCl feed solution<sup>23</sup>.

CA membranes offer several advantages over other RO membranes on the market today. They are relatively easy to make and they have excellent mechanical properties. They are also relatively resistant to attack by chlorine. CA membranes can tolerate up to 5 ppm of free chlorine, which is much higher than the tolerance shown by other membranes such as those based on aromatic polyamides<sup>22</sup>.

CA membranes also possess shortcomings which new membranes have tried to address. CA membranes tend to hydrolyze over time, which decreases their selectivity<sup>22</sup>. Also, they are extremely sensitive to changes in pH and are stable only in pH ranges of 4 to 6<sup>3</sup>. Salt rejection of CA membranes decreases as temperature increases. Therefore, feed water temperature typically does not exceed 35°C<sup>3</sup>.

**Thin Film Composite Membranes.** Cellulose acetate membranes were the dominant choice for RO membranes until the advent of thin film composite (TFC) RO membranes in 1972. Based on aromatic polyamides, TFC membrane fluxes and rejections surpassed those of CA. For example, a CA-based membrane has a flux of 22 GFD at 425 psig feed pressure and an average NaCl rejection of 97.5% using a 2000 mg/L NaCl feed solution at 77°F and pH 7.5. A polyamide TFC membrane with the same feed solution exhibits a flux of 27 GFD at only 225 psig feed pressure and an average rejection of 99.5%<sup>23</sup>. Most TFC membranes are made with a porous, highly permeable support such as polysulfone, which is coated with a cross-linked aromatic polyamide thin film<sup>3</sup>. The coating provides the salt rejection properties of the membrane. The first TFC RO membrane was developed by John Cadotte at North Star Research<sup>24</sup>. He used interfacial polymerization to create a polyamide coating on a support. This polyamide coating was based on the reaction between *m*-phenyl diamine and trimesoyl chloride<sup>24</sup>. Variations of this chemistry are still used today to produce cross-linked membranes for commercial RO membranes (Figure 7). Cadotte's TFC showed a NaCl rejection of 99% and a flux of 18 GFD (31 LMH) for a feed solution of 35,000 mg/L NaCl and a feed pressure of 1500 psi<sup>3</sup>. Today's membranes have improved even further, and a typical membrane exhibits NaCl rejections of 99.5 % and permeate fluxes of 30 GFD (51 LMH) for a feed solution of 35,000 mg/L NaCl at 800 psi<sup>3</sup>.



**Figure 7.** Representative chemical structure of commercial polyamide membranes used as the separation layer in thin film composite membranes<sup>24</sup>.

In addition to high rejection and high flux, TFC membranes offer other advantages over CA membranes. For one, they can also reject some low molecular weight organics<sup>3</sup>. They are also stable over a larger pH range and at higher temperatures than CA<sup>3</sup>.

However, one drawback of TFC membranes is their sensitivity to chlorine. TFC membranes are highly susceptible to attack by chlorine. The polyamide is believed to undergo ring chlorination, which disrupts hydrogen bonding between the chains and degrades the polymer matrix<sup>25</sup>. This phenomenon results in a drastic reduction in salt rejection. Unfortunately, most TFC membranes can only tolerate up to 1000 ppm-hrs of chlorine exposure<sup>3</sup>. This limit is far less than the CA tolerance and means that additional pre-treatment steps to remove chlorine must be taken before feed water is exposed to polyamide TFC membranes.

**Membrane Fouling.** A major problem shared by both CA and TFC membranes is fouling<sup>1</sup>. In general, fouling occurs either on the surface of a membrane or within its pores, and it causes a decrease in flux<sup>1</sup>. There are four major types of fouling: biofouling, scaling, organic, and colloidal<sup>1</sup>. Biofouling results from microbial contamination of feed water and produces a biofilm on the surface of the membrane, which increases the resistance to water permeation through the membrane. Scaling arises from the precipitation and deposition of salts on the membrane surface. Organic fouling comes from substances such as hydrocarbons which coat the surface and/or plug pores in the porous support layer. Colloidal fouling mainly stems from particles, such as clay or silica, accumulating on the surface of the membrane. Fouling can be controlled to some extent by adding disinfectants, anti-scaling agents, and other pre-treatment steps. However, these are not remedies to the problem, and fouling remains a key area in definite need of improvement for RO membranes<sup>1</sup>.

**Reverse Osmosis Membrane Market.** The RO market is dominated by only a few companies (Table II). In 1998, RO membrane and module sales were more than \$4 billion, and the market growth rate was projected to be 8-10% per year<sup>26</sup>. In 2000, membrane sales for desalination were more than \$350 million, and membrane sales for waste water purification were approximately \$400 million<sup>26</sup>.

**Table II. Domestic RO manufacturers**

Name	Location
Applied Membranes Inc.	San Marcos, CA
Dow Chemical/The FilmTec Corp.	Midland, MI
GE Osmonics	Minnetonka, MN
Hydranautics	Oceanside, CA
Trisep Corporation	Goleta, CA
Toray Membrane America, Inc.*	Watertown, MA

\*Toray Membrane America, Inc. is a partnership between Toray, Mitsui USA, and Ionics.

## Desalination

Currently, there are over 12,500 industrial-scale desalination plants throughout the world, and they produce fresh water from seawater and brackish water<sup>27</sup>. On average, seawater contains approximately 35,000 mg/L of salt, but this value can vary anywhere from 24,000 to 42,000 mg/L based on location<sup>28</sup>. Brackish water has lower salinity than seawater, often ranging between 2,000-5,000 mg/L. However, drinking water standards require salinity levels below 250 mg/L<sup>29</sup>. For feed water containing 35,000 mg/L of salt, membranes having a minimum salt rejection of 99.3% are required to produce drinking water from seawater in a single pass<sup>3</sup>.

There are several technologies currently used for desalination. Among the most popular are multi-effect distillation (MED) (also called multiple-effect evaporation), multi-stage flash (MSF), and reverse osmosis (RO)<sup>30</sup>. MED is the oldest technique, first being used around the middle of the 19<sup>th</sup> century to desalinate water<sup>30</sup>. The basic design involves heat transfer between steam and seawater through numerous stages. MED normally results in a high ratio of water produced to steam consumed. The high ratio means that the process is optimized to produce the maximum amount of water for a minimum amount of energy input to the process<sup>30</sup>.

MSF is an improved, simpler version of MED and is the most popular and most common technique used today<sup>30</sup>. MSF consists of a series of flash chambers where seawater is heated and the pure condensate is collected. While the technique is easy and reliable, it also requires more energy than MED, making it more expensive<sup>30</sup>.

RO for desalination emerged in the 1960s with the treatment of brackish water<sup>1</sup>. In the 1980s RO became more competitive with current desalination technologies for seawater purification<sup>30</sup>. The major advantage of RO is the lower energy consumption due to the absence of an evaporation step.

There are a few other desalination techniques that are not as widely used. One of these is electrodialysis (ED), where separation is achieved by using an electric potential to pass saltwater through a series of stacked anionic and cationic membranes<sup>30</sup>. This method is not very efficient for highly concentrated salt solutions. Another method, also based on electrochemistry, is capacitive deionization (CDI)<sup>31</sup>. In this method, ion removal occurs by electrosorption onto charged porous electrodes. CDI offers many advantages including good mechanical properties, easy cleaning, low cost, and reduced electrolysis of water. A major disadvantage of CDI is the lack of data for large scale use. One other technique is mechanical vapor compression (MVC)<sup>30</sup>. This technique is very similar to MSF and MED in that it uses steam to vaporize the feed water. The difference between the traditional methods and MVC is that MVC uses a mechanical compressor instead of a cooling unit to condense the vapor to the pressure and temperature desired in the output stream. The energy recovered from the compression process is then recycled to heat the feed. This is an efficient process; however, it is only used in small-scale production because it is technically more complex and requires better process control than the traditional methods of MED and MSF.

**Energy Demands.** One of the major considerations in desalination is the energy consumption of the process. Lower energy consumption translates into lower product cost. RO has an advantage over MSF and MED because RO does not require heating to desalinate water<sup>27</sup>. For RO, the main energy costs come from the electric power needed to run the process pumps. MSF

and MED require electric energy for pumps, but they also require heat for evaporation. This thermal energy often comes from steam generated from low or medium-pressure turbine lines.

The feed water salinity content also plays a role in determining the energy requirements of the system. Lower salinity leads to a higher purity product with less effort, which allows the plant to operate at a lower overall specific power level<sup>27</sup>. RO processes are more directly affected than other desalination processes by salinity content because feed osmotic pressure is directly proportional to feed salt content. Higher salt content means higher osmotic pressure, which requires a greater transmembrane pressure difference to cause the feed to permeate through the membrane. Higher transmembrane pressure differences require more electrical power, thus increasing overall energy consumption. However, despite this factor, economic studies of RO, MSF, and MED desalination methods have shown that RO has the lowest overall energy requirements. Table III outlines results from one such study<sup>32</sup>.

**Table III. Energy Comparison of Desalination Processes**

Desalination Process	Unit Energy Cost (\$/m <sup>3</sup> )
MSF	1.10
MED	1.15
RO	0.63

These calculations are based on a plant capacity of 32,000 m<sup>3</sup>/day and a total dissolved solids (TDS) concentration of 42,000 mg/L. \$0.053/kWh is used as the energy cost<sup>32</sup>

**Costs.** Energy costs and fixed charges (interest on loans, rental costs, etc.) are the two main factors in unit cost calculations<sup>27</sup>. Additional charges such as chemical costs and labor are less important than the energy and fixed costs. The cost to desalinate a unit volume of water for the three desalination methods discussed previously is recorded in Table IV, and RO is significantly less than the others<sup>33</sup>.

**Table IV. Cost comparison for produced water**

Desalination Process	Water Cost (\$/m <sup>3</sup> )
MSF	1.04
MED	0.95
RO	0.82

These calculations are based on a plant capacity of 31,822 m<sup>3</sup>/day and a TDS concentration of 37,000 mg/L. Energy costs are estimated as \$1.5/Gigajoule (GJ).<sup>33</sup>

Also, the cost of desalinated water via RO has decreased over the last decade and will continue to decrease<sup>34</sup>. In the early 90s, a survey of various RO desalination plants around the world found that, on average, it cost approximately \$1 to desalinate one cubic meter of seawater via reverse osmosis. By the end of the decade that average cost had dropped to about 70 cents. The cost is expected to decrease by another 20% over the next 5 to 10 years<sup>34</sup>. Some of the cost reduction can be attributed to more efficient water pre-treatment and more advanced membranes.

Another important aspect is the capital cost of desalination plant construction. An MSF or MED plant with a capacity of 27,000 m<sup>3</sup>/day costs approximately \$40 million. An RO plant with a much higher capacity, approximately 100,000 m<sup>3</sup>/day, would cost around \$50 million. So, initially a higher cost would be required for an RO plant, but the end result would be a significantly higher production rate<sup>27</sup>.

***Environmental Impact.*** One other aspect in the implementation of a desalination process is its impact on the surroundings. There are two main issues: the atmospheric emissions related to mechanical or thermal energy input and the brine discharge<sup>30</sup>. As discussed above, RO has the lowest energy requirements of the three main desalination processes, which means that a power plant supporting an RO process would have lower atmospheric emissions than power plants supporting MSF and MED<sup>30</sup>.

The overall impact of brine discharge is determined by its temperature, salinity, and chemical content<sup>30</sup>. It is detrimental to the environment to introduce heated brine to a water source because it negatively affects the water oxygen content, which, in turn, affects the water ecosystem. Here, RO has an advantage because no additional heating is involved; the brine exits the process at essentially the same temperature as the feed. However, MED and MSF employ heating, and, therefore, the brine is at least 10°C warmer than the feed stream<sup>30</sup>.

Salt content also negatively affects the oxygen content of water<sup>30</sup>. Since RO processes typically have a larger capacity and produce more desalinated water per day than the other processes, the RO process results in the highest rate of brine discharge. However, all of the processes are ultimately removing the same amount of salt and returning it to the original source, just at different rates. So, the effects of all three processes are approximately the same<sup>30</sup>.

Finally, any chemical additives to the water should be considered in assessing environmental impact. All three processes can employ biocides which are discharged<sup>30</sup>. RO processes can also require anti-scaling additives to enhance membrane performance<sup>30</sup>. On the other hand, the distillation processes use anti-foaming agents<sup>30</sup>. Therefore, none of the three methods are clear cut winners when it comes to reduced chemical impact on the environment. RO, MED, and MSF brine discharges all have high salinity and chemical additives, but when it comes to discharge temperature, RO is the least destructive to the surroundings. This fact, coupled with reduced emissions due to lower power consumption, makes RO a more environmentally friendly option<sup>30</sup>.

## **Future Prospects for Membranes**

With the proven success of membranes in the water treatment arena, membrane technology continues to advance. Major problems still needing attention are membrane fouling and membrane chemical stability. Reduced fouling would make membranes even more cost effective by extending their operational lifetime and lowering their energy requirements. Work in this area has focused on surface modification of membranes and increasing the pretreatment of the feed water before it reaches the membranes. The chemical stability of membranes is also being studied<sup>35</sup>. Improving the polyamide TFC membrane's tolerance to chlorine would reduce operation costs by eliminating pre-treatment dechlorination steps.

In addition to waste water treatment and desalination, new applications of membranes for water purification are being pursued. One example is the purification of produced water, which is

water generated during gas and oil production<sup>36</sup>. This water is contaminated with oils and salts, rendering it unsuitable for beneficial use in many cases. Membranes able to remove hydrocarbons and salt could turn produced water into an excellent source of water in the often arid regions where oil and gas production is most prevalent<sup>37</sup>.

Overall, the membrane field has advanced immensely. Being economical, environmentally friendly, versatile, and easy to use, membranes are a leading choice for water purification applications and should continue to be for many years to come.

## Acknowledgements

We would like to thank Dr. Michelle Chapman from the U.S. Bureau of Reclamation, Dr. Steve Kloos from GE Osmonics, and Dr. Rich Salinaro from Pall Corporation for their kind suggestions. We would also like to acknowledge the Office of Naval Research and the Department of Energy for their partial support of our research in the area of membranes for water treatment.

## References

1. Amjad, Z., Ed. Reverse Osmosis: Membrane Technology, Water Chemistry, and Industrial Applications; Van Nostrand Reinhold: New York, 1993.
2. Perry, R. H.; Green, D. W., Eds. Perry's Chemical Engineers' Handbook, 7th ed.; McGraw-Hill: New York, 1997.
3. Baker, R. W. Membrane Technology and Applications, 2<sup>nd</sup> ed.; John Wiley & Sons, Ltd.: Chichester, 2004.
4. Pinnau, I.; Freeman, B. D. In Formation and Modification of Polymeric Membranes; Pinnau, I.; Freeman, B. D., Eds.; ACS Symposium Series 744; American Chemical Society: Washington D.C., 2000; pp 1-22.
5. SEM images kindly provided by Jason Morehouse and Leah Worrel, University of Texas at Austin.
6. SEM image taken from "Product Properties: Celgard<sup>®</sup> 2320 Microporous Membrane"  
[www.celgard.com/documents/Celgard%202320.pdf](http://www.celgard.com/documents/Celgard%202320.pdf)
7. SEM image from: Di Luccio, M.; Norbrega, R.; Borges, C.P. "Microporous anisotropic phase inversion membranes from bisphenol A polycarbonate: effect of additives to the polymer solution," Journal of Applied Polymer Science, 86 (2002) 3085-3096.
8. Reprinted from Journal of Membrane Science, 143, Trushinski, B.J.; Dickson, J.; Smyth, T.; Childs, R.F.; McCarry, B.E. "Polysulfonamide thin-film composite reverse osmosis membranes", 181-188, Copyright 1998, with permission from Elsevier.
9. Reprinted with permission from D. Wang, K. Li, and W. K. Teo, "Preparation of Poly(ethersulfone) and Poly(ether imide) Hollow Fiber Membranes for Gas Separation: Effect of Internal Coagulant", In Membrane Formation and Modification; Pinnau, I.; Freeman, B. D., Eds.; ACS: Washington D.C., 2000; Vol. 744, pp 96-109. Copyright 2000

American Chemical Society.

10. Nunes, S. P.; Peinemann, K. V. *Membrane Technology in the Chemical Industry*; Wiley-VCH: Weinheim, 2001.
- Product Information: Pall Corporation Inorganic membranes, <http://www.pall.com/AccuSep.asp>, (2004).
12. Pelligrino, J.; Sikdar S.K. *Membrane Technology Fundamentals for Bioremediation*. <http://www.membranes.nist.gov>, (2004).
13. Product Information: Zenon ZeeWeed<sup>®</sup> 500, <http://www.zenonenv.com/products/500.shtml>, (2004).
14. Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*, 2nd ed.; John Wiley & Sons, Inc.: New York, 2002.
15. Baker, R.W.; Wijmans, J.G. "The solution-diffusion model: A review", *Journal of Membrane Science*, 107 (1995) 1-21.
16. Paul, D.R. "Reformulation of the solution-diffusion theory of reverse osmosis", *Journal of Membrane Science*, 241 (2004) 371-386.
17. Freeman, B. D. "Osmosis", In *Encyclopedia of Applied Polymer Physics*, 1995; Vol. 13, pp 59-71.
18. R. J. Riley, H. K. Lonsdale, C. R. Lyons, and U. Merten, "Preparation of Ultrathin Reverse Osmosis Membranes and the Attainment of Theoretical Salt Rejection", *Journal of Applied Polymer Science*, 11 (1967) 2143-2158.
19. Mason, E. A. "From pig bladders and cracked jars to polysulfones: an historical perspective on membrane transport", *Journal of Membrane Science*, 60 (1991) 125-145.
20. Loeb, S.; Sourirajan, S. "Seawater demineralization by means of an osmotic membrane", *Advances in Chemistry Series*, 38 (1963) 117-132.
21. Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1999.
22. Kesting, R. E. In *Reverse Osmosis and Synthetic Membranes: Theory- Technology- Engineering*; Sourirajan, S., Ed.; National Research Council Canada: Ottawa, 1977; pp 89-110.
23. Product Information: GE Osmonics AG and CE Desal Membranes, <http://www.desal.com>, (2004).
24. Cadotte, J. E. In *Materials Science of Synthetic Membranes*, 269 ed.; Lloyd, D. R., Ed.; American Chemical Society: Washington D.C., 1985; pp 273-294.
25. Alvonitis, S.; Hanbury, W.T; Hodgkeiss, T. "Chlorine Degradation of Aromatic Polyamides", *Desalination*, 85 (1992) 321-334.

26. Strathmann, H. "Membrane Separation Processes: Current Relevance and Future Opportunities", *AIChE Journal*, 47 (2001) 1077-1087.
27. Ettouney, H. M.; El-Sessouky, H. T.; Faibish, R. S.; Gowin, P. J. "Evaluating the Economics of Desalination." In *Chemical Engineering Progress*, 2002; Vol. 98, pp 32-39.
28. Riley, R. L. In *Membrane Separation Systems: Recent Developments and Future Directions*; Baker, R. W.; Cussler, E. L.; Eykamp, W.; Koros, W. J.; Riley, R. J.; Strathmann, H., Eds.; Noyes Data Corporation: Park Ridge, 1991; pp 276-328.
29. Mallevalle, J.; Odendaal, P. E.; Wiesner, M. R., Eds. *Water Treatment: Membrane Processes*; McGraw-Hill: New York, 1996.
30. Van der Bruggen, B.; Vandecasteele, C. "Distillation vs. membrane filtration: overview of process evolutions in seawater desalination", *Desalination*, 143 (2002) 207-218.
31. Ryoo, M.-W.; Kim, J.-H.; Seo, G. "Role of titania incorporated on activated carbon cloth for capacitive deionization of NaCl solution", *Journal of Colloid and Interface Science*, 264 (2003) 414-419.
32. Wade, N. M. "Technical and economic evaluations of distillation and reverse osmosis desalination processes", *Desalination*, 93 (1993) 343-363.
33. Wade, N. M. "Distillation plant development and cost update", *Desalination*, 136 (2001) 3-12.
34. Glueckstern, P.; Priel, M. "Potential cost reduction of seawater desalination", *Water Science and Technology: Water Supply*, 3 (2003) 39-47.
35. Konagaya, S.; Kuzumoto, H.; Watanabe, O. "New reverse osmosis membrane materials with higher resistance to chlorine", *Journal of Applied Polymer Science*, 75 (2000) 1357-1364.
36. Produced water discharges to the North Sea: Fate and Effects in the water column, Summary Report, [www.olf.no/static/en/rapporter/producedwater/2.html](http://www.olf.no/static/en/rapporter/producedwater/2.html), (1998)
37. Rawn-Schatzinger, V.; Arthur, D.; Langhus, B. "Coalbed Natural Gas Resources: Beneficial Use Alternatives." In *GasTIPS*, 2004; Vol. 10, pp 9-14.

## Glossary

$\kappa$	Darcy's Law permeability coefficient
$\pi$	osmotic pressure
$\rho$	mass density (mass per volume)
$\varepsilon$	porosity
$\tau$	tortuosity
$\mu$	viscosity of liquid
$C$	concentration
$C_{\text{feed}}$	solute concentration in feed solution
$C_{\text{permeate}}$	solute concentration in permeate solution
$D$	water diffusivity coefficient
$D_s$	salt diffusivity coefficient

$K_s$	salt sorption coefficient
$l$	membrane thickness
$N_A$	mass flux of component A
$N_s$	salt flux
$N_{Aw}$	water flux
$p$	pressure
$R$	ideal gas constant
R	salt rejection
S	water solubility coefficient
T	temperature
V	molar volume of water
$v$	mass average velocity
CA	cellulose acetate membranes; first high performance reverse osmosis membrane in industry
CDI	capacitive deionization; desalination technique utilizing electrosorption to remove ions from solution
CTA	cellulose triacetate; derivative of cellulose acetate used in reverse osmosis membranes
ED	electrodialysis; desalination technique using both positive and negative-charged membranes and an applied electric potential to remove ions from feed solution
Feed	water solution input to a membrane
Flux	performance characteristic of membranes, measured in either mass of material permeated per unit time per unit area of membrane or volume of material permeated per unit time per unit area of membrane
GFD	gallons per square foot per day, English flux units
LMH	liters per meter squared per hour, metric flux units
MED	multi-effect distillation, desalination technique where seawater is evaporated via direct contact with a heat transfer surface through a series of several stages and the vapor is condensed to obtain the purified product
MF	microfiltration; membranes that reject large particles and microorganisms
MSF	multi-stage flash; desalination technique in which seawater is vaporized in a series of flash chambers with progressively lower pressures and then condensed to obtain purified water
MVC	mechanical vapor compression; desalination technique similar to MSF but uses a mechanical compressor to condense evaporated seawater
NF	nanofiltration; membranes with characteristics falling between those of ultrafiltration and reverse osmosis membranes
Permeate	stream that has passed through a membrane
ppm	parts per million, mass fraction unit; 1 ppm is 1 gram solute per million grams of solution *ppm is often incorrectly interchanged with mass per volume (concentration) values. This is approximately true, but not 100% accurate because solvent density is used as the solution density to calculate the volume from the mass of solution. To avoid this misuse, this paper expresses most concentrations in terms of mg/L.
Rejection	salt separation performance characteristic for reverse osmosis membranes
RO	reverse osmosis membranes; membranes that reject most particles and many low molar mass species such as salt ions
SEM	Scanning Electron Microscopy; technique used to capture magnified views of membranes
TDS	total dissolved solids; concentration (e.g., mass of salt / volume of solution)
TFC	thin film composite; the most popular type of reverse osmosis membranes
UF	ultrafiltration, membranes that reject soluble macromolecules in addition to large particles and microorganisms