



Introduction to Reverse Osmosis Desalination

A SunCam online continuing education course

1. Desalination Status Overview

Reverse osmosis (RO) desalination is a treatment process for production of fresh, low-salinity potable water from saline water source (seawater or brackish water) via membrane separation. The mineral/salt content of the water is usually measured by the water quality parameter named total dissolved solids (TDS), concentration of which is expressed in milligrams per liter (mg/L), or parts per thousand (ppt). The World Health Organization and the United States Environmental Protection Agency (US EPA) under the Safe Drinking Water Act have established a maximum TDS concentration of 500 mg/L as a potable water standard. This TDS level can be used as a classification limit to define potable (fresh) water.

Typically, water of TDS concentration higher than 500 mg/L and lower or equal to 15,000 mg/L (15 ppt) is classified as brackish. Natural water sources such as sea, bay and ocean waters which have TDS concentration higher than 15,000 mg/L are generally classified as seawater. For example, Pacific Ocean seawater along the West Coast of the United States has average TDS concentration of 35,000 mg/L. This concentration can actually be in a range of 33,000 to 36,000 mg/L at various locations and depths along the Pacific Ocean coast.

Approximately 97.5 % of the water on our planet is located in the oceans and therefore, is classified as seawater. Of the 2.5 % of the planet's fresh water, approximately 70 % is in the form of polar ice and snow, and 30 % is groundwater, river and lake water, and air moisture. So even though the volume of the earth's water is vast, less than 2.6 million cubic miles of the 333 million cubic miles of water on the planet are of low salinity and are suitable for use after applying conventional water treatment only. Desalination provides means for tapping the world's main water resource – the ocean.

Over the past thirty years, desalination technology has made great strides in many arid regions of the world such as the Middle East and the Mediterranean. Today, desalination plants operate in more than 120 countries worldwide and some desert states, such as Saudi Arabia and the United Arab Emirates, rely on desalinated water for over 70 percent of their water supply. According to the 2009-10 IDA Desalination Yearbook prepared by the International Desalination Association, by the end of 2008 worldwide there were 14,754 desalination plants with total installed production capacity of 15,830 million gallons per day (MGD) which is approximately 1.5 % of the world's current drinking water supply.

Sea or brackish waters are typically desalinated using two general types of water treatment technologies – thermal evaporation (distillation) and membrane separation. Currently, approximately 60 % of the world's desalination systems use membrane separation technologies, most of which are reverse osmosis (RO) plants. This percentage has been increasing steadily over the past 10 years due to the remarkable advances in the membrane separation and energy recovery technologies, and associated reduction of the overall water production costs.

At present, in the US there are over 220 brackish desalination plants with fresh water production capacity of 25,000 gallons/day or more, over 75 % of which are located in three states: Florida, California and Texas. The largest seawater desalination plant in the US has been in operation in Tampa, Florida since 2007 (see Figure 1) and has fresh water production capacity of 25 MGD. Currently, more than two dozen new large reverse osmosis seawater desalination plants are under development in California, Florida and Texas as well as other states. Most of these plants are projected to be operational in the next 5 to 7 years.

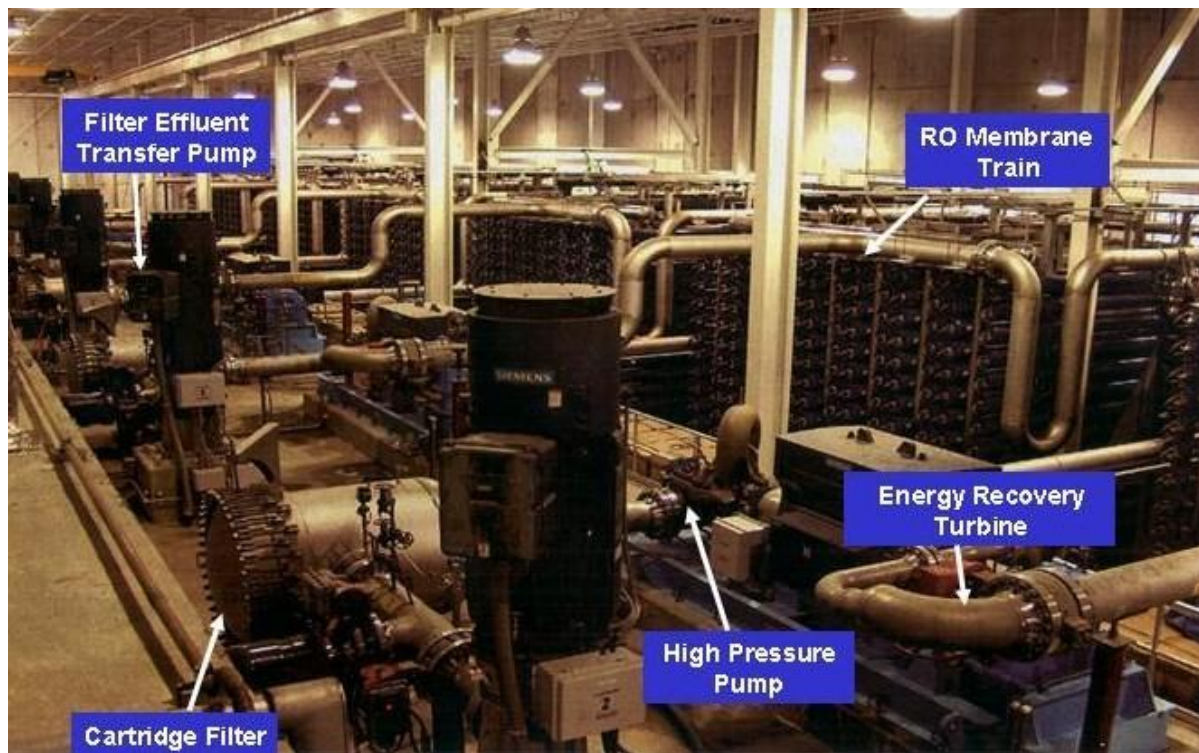


Figure 1 – 25 MGD Tampa Bay Seawater Desalination Plant, Florida

Until recently, desalination has been limited to the desert-climate dominated regions of the World. Technological advances and associated decrease in water production costs over the past decade have expanded its use in areas traditionally supplied with fresh water resources. While at

present desalination provides a relatively small portion of the water supply in the US, it is expected that in the next decade the construction of new desalination plants would grow exponentially due to the ever changing climate patterns triggered by global warming combined with population growth pressures, limited availability of new and inexpensive terrestrial water sources and dramatic advances in membrane technology which are projected to further reduce cost and energy use needed for desalination.

A large portion of the new capacity growth is expected to come from the development of seawater desalination plants. While brackish water sources, especially brackish aquifers, are limited in capacity and rate of recharging, the ocean has two unique and distinctive features as a water supply source – it is drought proof and is practically limitless. Over 50 % of World's population lives in urban centers bordering the ocean. In many arid parts of the world such as the Middle East, Australia, Northern Africa and Southern California, the population concentration along the coast exceeds 75 %. Usually coastal zones are the highest population growth “hot-spots” as well. Therefore, seawater desalination provides the logical solution for a sustainable, long-term management of the growing water demand pressures in coastal areas. Brackish desalination is expected to also increase in capacity, especially in the inland Southwestern and Central United States.

2. Brackish and Seawater Quality Characterization

Introduction

Reverse osmosis is a process where water containing inorganic salts (minerals), suspended solids, soluble and insoluble organics, aquatic microorganisms, and dissolved gases (collectively called source water constituents or contaminants) is forced under pressure through a semi-permeable membrane. Semi-permeable refers to a membrane that selectively allows water to pass through the membrane at much higher rate than any the transfer rate of any other constituents contained in it. Depending on their size and electric charge, most water constituents are retained (rejected) on the feed side of the RO membrane and the purified water (permeate) passes through the membrane (Figure 2).

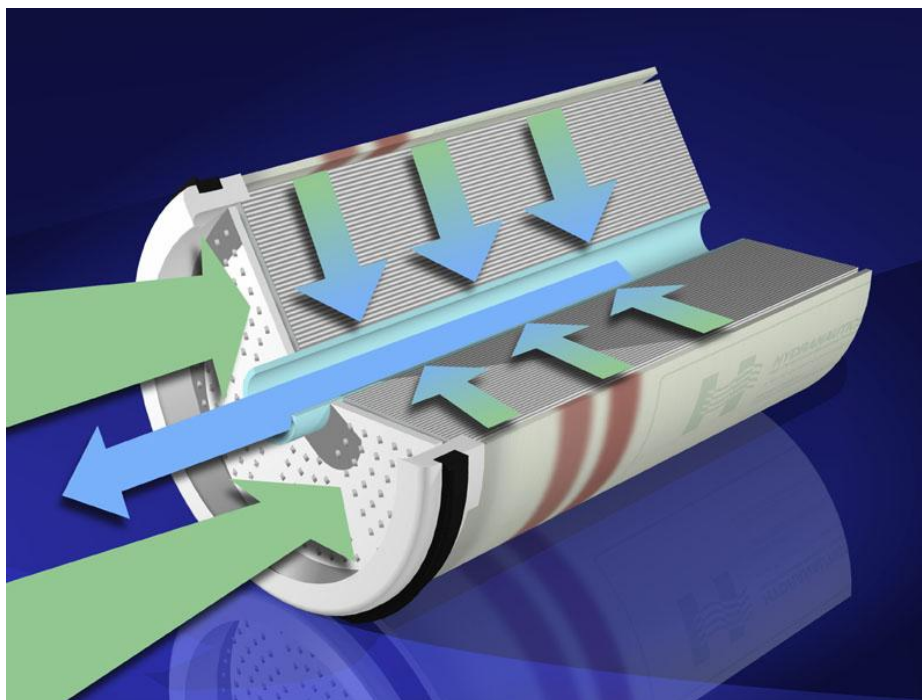


Figure 2 – Membrane Separation

Reverse osmosis membranes can reject particulate and dissolved solids of practically any size. However, they do not reject well gases because of their small molecular size. Usually RO membranes remove over 90 % of compounds of weight of 200 Daltons or more. One Dalton (Da) is equal to 1.666054×10^{-24} grams. In terms of physical size, RO membranes can reject well solids larger than 1 Angstrom. This means that they can remove practically all suspended solids, protozoa (i.e., Giardia and Cryptosporidium), bacteria, viruses, and other human pathogens contained in the source water (see Figure 3).

While RO membranes can retain both particular and dissolved solids, they are designed to primarily reject soluble compounds (mineral ions). The RO membrane structure and configuration is such that these membranes cannot store and remove from their surface large amounts of suspended solids. If left in the source water, the solid particulates would accumulate and quickly plug (foul) the surface of the RO membranes, not allowing the membranes to maintain a continuous steady state desalination process. Therefore, the suspended solids (particulates) contained in source water used for desalination have to be removed before they reach the RO membranes. The treatment of source water prior to desalination is termed pretreatment (see Figure 3). Membrane pretreatment technologies widely used today include both granular media filtration of surface loading rates comparable to these of filters used in conventional fresh water treatment, as well as membrane ultrafiltration (UF) and microfiltration (MF) membranes. Granular media filtration is the dominating pretreatment technology at present, which pressure driven filters used for small and medium size plants and gravity media filters applied for large desalination plants.

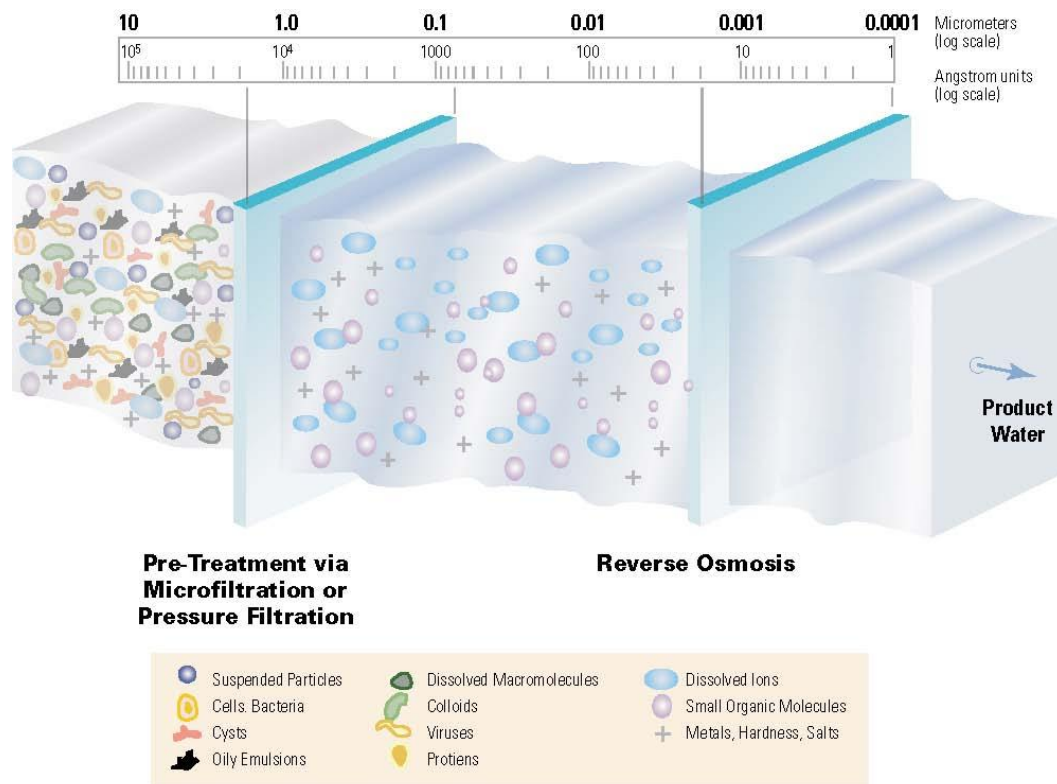


Figure 3 – RO Membrane Removal and Pretreatment

The constituents contained in source water used for desalination can be classified in four main groups: (1) dissolved minerals and gases; (2) colloids and suspended solids; (3) organics; (4) microorganisms. Each of these groups of constituents in seawater and brackish water as well as their rejection by RO membranes are discussed below.

Dissolved Minerals and Gasses

The primary purpose of RO desalination is to remove dissolved minerals (salts) contained in the source water. As indicated previously, a commonly used measure of the content of dissolved minerals is the concentration of total dissolved solids (salinity). This parameter encompasses all ions in the source water, including sodium, potassium, bromide, boron, calcium, magnesium, chloride, sulfate, bicarbonate, nitrate, metals, etc. Key ion content and TDS concentration of typical Pacific Ocean water and of permeate produced by seawater reverse osmosis (SWRO) membrane separation from this water, are shown in Table 1. Concentrations in this table are expressed both in milligrams per liter (mg/L) and in milli-equivalents per liter (meq/L).

Table 1 – Typical Pacific Ocean Water Quality

Parameter	TDS Concentration mg/L		TDS Concentration meq/L	
	Raw Water	Permeate	Raw Water	Permeate
Cations				
Calcium	403	0.6	20.1	0.03
Magnesium	1,298	1.3	106.2	0.11
Sodium	10,693	88	464.9	3.82
Potassium	387	4.3	12.9	0.14
Boron	4.6	0.8	1.5	0.26
Bromide	74	0.7	0.9	0.01
Total Cations	12,859.6	95.7	606.5	4.37
Anions				
Bicarbonate	142	2.2	2.24	0.03
Sulfate	2,710	7.5	56.6	0.16
Chloride	19,284	150	542.9	4.22
Fluoride	1.3	0.0	0.07	0.00
Nitrate	0.00	0.0	0.0	0.00
Total Anions	22,215.4	149.3	601.8	4.41
TDS (mg/L)	35,000	250	1,208	8.8

The milligrams per liter (mg/L) parameter, indicates the ratio of ion weight to solution volume. The milli-equivalent per liter (meq/L) designation reflects the capacity of ions to react with one another. The atomic or formula weight of an ion divided by its valence (number of +/- charges) is called the equivalent weight (eq) of this ion. A 1,000-th of this weight is termed milli-equivalent (meq). For example the meq/L concentration of calcium in Table 1, can be calculated as follows:

1. Calcium has a molecular weight of 40.08 grams/mole;
2. Calcium has a valence of +2;
3. The equivalent weight of calcium is = (40.08grams/mole)/(2 equivalents/mole) = 20.04 grams/eq (or mg/milliequivalent);
4. Since the seawater sample in Table 1 contains 403 mg Ca/L, then the concentration of calcium in meq/L is = Meq Ca/L = (403 mg Ca/L)/ (20.04 mg/meq) = 20.1 meq Ca/L.

The main reason of why the TDS concentration is often measured in meq/L, instead of only of mg/L is to check the accuracy of the TDS concentration measurement of the water for which analysis is completed. When added together, the meq/L concentrations of cations (positively charged ions) contained in the water should approximately equal the total meq/L concentrations of anions (negatively charged ions) in the solution. These two values are usually not exactly equal since other ions are present in the water. If the difference between total cation and anion content exceeds 5 to 10 %, than the accuracy of the laboratory analysis is inadequate or other ions are present in the water which may not have been reported or are not typically contained of water of the particular type of source.

Analysis of Table 1 indicates that sodium chloride contributes over 85 % of the total TDS concentration of Pacific Ocean water. The three other large contributors to TDS are sulfate (8 %), magnesium (4 %), and calcium (1 %). All other ions in seawater contribute only 2 % of the TDS in the water.

The ion make up of seawater at the same location may vary seasonally – typically within 10 %. However, seawater salinity varies in much wider range in different parts of the world. Table 2 shows typical salinity and temperature of seawater in various arid areas throughout the world - the highest salinity seawater occurs in the Middle East (the Arabian Gulf and Red Sea). This table also contains the typical values of another key source water quality factor for RO desalination – temperature. Warmer water has lower viscosity (i.e., water is less dense) which in turn increases the production rate of the RO membranes and vice versa.

Table 2 – Seawater TDS and Temperature of Various Ocean Sources

Seawater Source	Typical TDS Concentration (mg/L)	Temperature (⁰C)
Pacific/Atlantic Ocean	35,000	9 – 26 (avg. 18)
Caribbean	36,000	16 to 35 (avg. 26)
Mediterranean	38,000	16 to 35 (avg. 26)
Gulf of Oman, Indian Ocean	40,000	22 to 35 (avg. 30)
Red Sea	41,000	24 to 32 (avg. 28)
Arabian Gulf	45,000	16 to 35 (avg. 26)

Note: Seawater TDS and temperature may be outside the table ranges for a site-specific location.

Table 3 presents the TDS content of several brackish water sources located in the US. Analysis of this table indicates that brackish water TDS content may vary significantly from one location to another and that sodium and chloride may not always be the main contributors to the TDS content of the water. Usually, brackish water has higher content of silica and nitrates than seawater which often requires additional pretreatment.

Table 3 – Brackish Water Quality of Several Sources

Parameter		Orange County, California	Rio Grande, Texas	Tularosa, New Mexico	Cape Hatteras, North Carolina
Cations					
Calcium	mg/L	140	163	420	545
Magnesium	mg/L	10	51	163	1,398
Sodium	mg/L	300	292	114	4,961
Potassium	mg/L	35	0.0	2.3	99
Boron	mg/L	0.8	0.0	0.14	1.2
Bromide	mg/L	7.4	4.5	0.7	12.5
Total Cations	mg/L	493.2	510.5	700.14	7,016.7
Anions					
Bicarbonate	mg/L	275	275	270	223
Sulfate	mg/L	350	336	1,370	173
Chloride	mg/L	350	492	170	6,696
Fluoride	mg/L	0.8	0.08	0.0	1.0
Silica	mg/L	10	35	22	22
Nitrate	mg/L	1.0	1.5	10	1.0
Total Anions	mg/L	986.8	1,139.58	1,842	6,943
TDS (mg/L)	mg/L	1,480	1,650	2,542	13,960

Because the existing standard method for measurement of TDS concentration of water involves collection and evaporation of a discrete water sample at 105 °C and weighting of the solids remaining after evaporation, this parameter can only be measured discretely. On the other hand, the continuous monitoring of source water and product water TDS concentrations is essential for the cost effective and efficient operation of RO systems. Therefore, in practice TDS concentration is often monitored continuously by measurement of the electrical conductivity (EC) of the water. Electrical conductivity (also known as Specific Conductance) is a measure of

a solution's ability to conduct electricity. Conductivity level is expressed in micro-Siemens/meter ($\mu\text{S/m}$).

The ratio between TDS and EC in source water is site-specific and usually varies in a range between 0.67 and 0.70. For example, seawater with TDS concentration of 35,000 mg/L would typically have conductivity of 50,000 to 52,000 $\mu\text{S/m}$. The ratio between TDS and EC depends on the content of sodium chloride in the water and temperature. If TDS is made of 100 % sodium chloride, the TDS/EC ratio is typically 0.5. This ratio increases as the content in sodium chloride decreases (i.e., ions other than sodium and chloride have measurable contribution to salinity). Since product water TDS consists of over 91 % of sodium chloride (as compared to source seawater where sodium chloride contributes only 86 % of the salinity), the typical ratio of TDS to EC in permeate is 0.5.

The TDS of the source water is the most important water quality parameter in RO desalination for two main reasons. This parameter is a main factor in determining the feed pressure and therefore energy needed to produce fresh water from a given saline water source. Every 100 mg/L of TDS in the source water create approximately 1 psi of osmotic pressure which will need to be overcome by the pressure applied to the saline water fed to the RO membranes. For example, seawater that contains 35,000 mg/L of TDS will create approximately 350 psi of osmotic pressure. In addition, TDS concentration of the source water is a key factor in determining the expected product water quality since RO membranes reject a given percentage of the feed water TDS.

Besides sodium and chloride, which need to be removed in order to produce fresh water, other key inorganic constituents of TDS are various minerals (mainly salts of calcium and magnesium). These bivalent salts can precipitate on the surface of the membrane and form a thin layer of crystalline scale (see Figure 4), which in turn can plug membrane surface and reduce significantly membrane productivity.

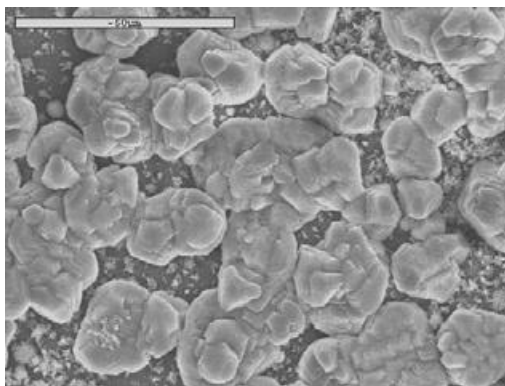


Figure 4 – Crystalline Scale on RO Membrane Surface

All minerals contained in the saline source water are concentrated during the process of membrane salt separation. As their concentration increases during the desalination process, ions of calcium, magnesium, barium, strontium, sulfate and carbonate can form sparingly insoluble salts which could precipitate on the RO membrane surface. The mineral scales that typically form during desalination are these of calcium carbonate, calcium and magnesium sulfate, and barium and strontium sulfate.

Formation of mineral scales on the membrane surface is balanced by the high salinity of the source water which tends to increase the solubility of all salts. This means that the higher the salinity of the source water the less likely it is a mineral scale to form on the membrane surface. Therefore, mineral scaling is usually a challenge for brackish water reverse osmosis systems. In typical seawater desalination systems, mineral scale fouling is usually not as challenging, unless source seawater pH would need to be increased to 8.8 or more in order to enhance boron removal of the RO membranes. Calcium carbonate and magnesium hydroxide are the most common causes for seawater RO membrane scaling, when source seawater pH is increased for enhanced boron removal. Scale formation in this case can be prevented by addition of antiscalant/dispersant to the source seawater. It is important to note that although source water temperature usually has limited influence on scale formation, when this temperature exceeds 35 °C, calcium carbonate scale would form at accelerated rate.

Other mineral foulants that may be contained in saline water are metal oxides and hydroxides. The metal foulants most frequently encountered during desalination are iron, manganese, copper, zinc and aluminum. Typically, open ocean seawater contains very low levels of these metal foulants and therefore, if such fouling is encountered on the membrane elements, the usual sources are overdosing of coagulant (iron salt) or corrosion of pipes, fittings, tanks and other metal equipment located upstream of the SWRO system. Iron and manganese fouling occurs more often when brackish water sources are used for desalination.

Iron and manganese fouling may also occur if source seawater is collected via subsurface intake from a coastal aquifer which is under the influence of fresh groundwater that contains high levels of these metals in reduced form (iron of more than 2 mg/L (as ferrous) and manganese of more than 0.5 mg/L). This type of scaling problem has been observed in desalination plants with beach well intakes collecting seawater from alluvial coastal aquifers, which are located near the entrance of a river or a creek into the ocean.

If iron and manganese are in a reduced form and they are below 1.0 mg/L and 0.1 mg/L respectively, than they can be removed by the RO membranes without causing accelerated fouling. However, if iron and manganese are in oxidized form, their levels should be reduced below 0.05 mg/L and 0.02 mg/L, respectively to prevent mineral fouling of the RO membranes. Such fouling will occur in a very high rate.

Another mineral fouling compound frequently encountered in fresh surface water and brackish aquifers is silica. Open ocean seawater contains silica of less than 20 mg/L and therefore, this compound is not a typical cause of SWRO membrane mineral fouling. Silica content above this level usually indicates that the source seawater quality is influenced by a fresh water discharge or coastal aquifer of high silica content located near the desalination plant intake area. Silica however, is often a challenge when surface brackish water is used as source water for desalination.

Both seawater and brackish water often contain various dissolved gases. The most common gases are oxygen, carbon dioxide, sodium bisulfite, and ammonia. All of the gases listed above pass through the RO membranes and therefore, desalination is typically not a suitable technology for degasification of brackish and seawater for drinking water production. Ocean seawater and desalinated water originating from it are usually supersaturated with dissolved oxygen (DO). The DO concentration of these waters typically varies between 5 and 8 mg/L. For comparison, most brackish waters originating from groundwater aquifers have a very low content of oxygen (0.5 mg/L or less). Because of its high oxygen content, seawater does not contain sodium bisulfite. This gas is however, frequently encountered in source waters from deep brackish aquifers.

Colloids and Suspended Solids

Both brackish and seawater can contain colloids and suspended solids. The content of these compounds depends on the source of saline water (brackish or seawater) and on the type of intake used for source water collection (subsurface intake (i.e., wells or infiltration gallery) or open intake). While colloids and suspended solids are easily rejected by all RO membranes, these membranes are not designed for steady-state continuous removal of colloids and suspended solids, and such compounds, if present in large quantities, tend to accumulate on the surface of the RO membranes and foul it to the extent that precludes these membranes from competing their main function – removal of dissolved solids.

Colloidal foulants are inorganic and organic compounds that naturally exist in suspension and may be concentrated by the RO separation process, and precipitate on the membrane surface thereby causing RO membrane productivity decline over time. Colloidal solids have particle size of 0.001 to 1 μm . For prevention of colloidal fouling, RO membrane manufacturers usually recommend RO membrane feed turbidity of less than 0.1 NTU, zeta potential higher than - 30 microvolts (mV) and SDI_{15} less than 4. The parameter SDI_{15} is also known as standard silt density index and is a measure of fine particulates contained in the saline water.

The two most common culprits of this type of fouling are colloidal silica and iron. Typically, seawater collected via open ocean intake does not contain significant amounts of iron and silica in colloidal form and this type of fouling usually does not present a challenge in seawater

desalination systems with open ocean intakes, especially if the intakes are not under influence of river water or fresh groundwater. Stability of colloids is reduced with the increase in source water salinity, and typical seawater with TDS concentration in a range of 30,000 to 45,000 mg/L, would contain silica and iron in dissolved and precipitated form rather than in colloidal form. For comparison, brackish water can contain large amounts of colloidal silica and iron.

If source seawater is collected via subsurface well intake which is under the influence of brackish coastal aquifer with high content of colloidal silica and/or iron, or it is collected near an area where silt-laden river enters into the ocean, than colloidal fouling may become a challenge for SWRO separation. Colloidal foulants could be removed by coagulation, flocculation and filtration.

In addition to naturally occurring colloidal matter, iron colloidal fouling on the surface of the RO membranes may be caused by corrosion of upstream piping and equipment, or by overdosing and/or poor mixing of iron-based coagulant used for conditioning of the source saline water. If the source water contains chlorine, this colloidal iron tends to catalyze the oxidation process caused by chlorine which in terms enhances the damage of the RO membranes even when residual chlorine in the source water is in very small dosages.

Another common source of colloidal fouling is caused by overdosing or poor mixing of polymer used for conditioning of the sources seawater prior to filtration. Such problem usually occurs when the source water contains fine particulates of relatively low quantity and electric charge (i.e., the water is of very low turbidity – typically below 0.5 NTU) and polymer is added to enhance flocculation of such particles.

Most common organic colloidal foulants are oil and grease, and oil-product based hydrocarbons. Such compounds are not contained naturally in open-ocean seawater, surface brackish water or brackish water aquifers, and their occurrence indicates that the saline water intake is under influence of man-made source/s of contamination – typically a discharge from wastewater treatment plant, from storm drains collecting surface runoff from urban areas (parking lots, industrial sites, etc.) or from waste discharges/oil leaks from ships/boats in port areas or oil tanks and landfills for brackish groundwater. Even in very small quantities (0.02 mg/L or more) oil and grease can cause an accelerated fouling of RO membranes.

Suspended solids are organic and inorganic particles contained in the source water such as fine debris, plankton, detritus and silt, which cannot pass through the RO membranes. All suspended solids which naturally occur in insoluble form, if not removed by pretreatment, would be retained on the feed side of the RO membranes and depending on the hydrodynamic conditions on the membrane surface, as well as the size and charge of these particles, they would either migrate along the membrane surface and ultimately exit with the concentrate, or would be

trapped on the membrane surface and would begin to accumulate there causing loss of membrane productivity over time. This type of foulants can be effectively removed by pre-filtering of the source seawater prior to RO membrane separation.

Particulate foulants in raw source water vary in size. However, most of them, including pico-phytoplankton in seawater, are larger than 0.1 micrometer or micron (μm). Usually, over 90 % of the particulate foulants are larger than 1 μm . A well designed and operating pretreatment system will produce permeate that does not contain particles larger than 20 μm . Typically, solids larger than 100 μm are settleable and can be removed by clarification of the source water prior to filtration.

Organic and Microbial Content

Depending on its origin all saline waters can contain naturally occurring or man-made organic compounds and aquatic microorganisms. Since all microorganisms and most organic molecules are relatively large in size, they are well rejected by the RO membranes. However, some of the organic compounds and aquatic species may accumulate on the membrane surface and form a cake layer that may significantly hinder membranes' main function – rejection of dissolved solids. Depending on the main source of the fouling cake layer, these RO membrane foulants are typically divided into two separate groups: natural organic foulants and microbiological foulants (or biofoulants).

Natural organic matter (NOM) is typically contained in surface saline waters (brackish or open ocean seawater) and includes compounds which are produced by naturally decaying algal and other aquatic vegetation and fauna (i.e., proteins, carbohydrates, oils, pigments (i.e., tannins), humic and fulvic substances (acids)). High content of NOM in the source water used for production of drinking water is undesirable because it causes discolorization of the water, forms carcinogenic disinfection byproducts (DBPs) when disinfected with chlorine, and results in complexation with heavy metals, which in turn causes an accelerated membrane fouling.

Typical surface saline water does not contain a large quantity of NOM that presents significant challenge to the desalination plant operations. High content of NOM is usually observed during algal blooms and/or when the desalination plant intake is located near the confluence with river or other fresh water source, or near wastewater treatment plant discharge.

Humic acids are polymeric (poly-hydroxy aromatic) substances which have the ability to form helates with metal ions in the seawater, such as iron. This feature of humic acids is very important for seawater or surface brackish water pretreatment systems using iron coagulants, because they can form a gel-like layer of helates on the surface of the membrane, which would cause fouling. Typically, such fouling layer can be dissolved at pH of 9 or more, at which condition both the membranes and the humic substances carry a negative charge. This feature is

used for membrane cleaning. Humic substances are hydrophobic and therefore, hydrophilic membranes are less prone to fouling by humic acids.

Most NOM in seawater and surface brackish water consists of compounds of relatively large molecular weights (500 to 3000 Daltons) and therefore, they are completely rejected by RO membranes. Humic acids in their natural state are not a food source for most aquatic organisms. However, when oxidized with chlorine or other oxidants, humic acids could become easily biodegradable and serve as food source for aquatic bacteria growing on the RO membrane surface. Therefore, continuous chlorination of source water containing large amount of humic acids often causes more membrane biofouling problems than it solves.

Negatively charged NOM, which dominates in surface brackish or seawater, has the tendency to adhere to the surface of thin-film composite RO membranes which typically have slightly positive charge. Once adsorption occurs, the NOM begins to form cake/gel on the membrane surface and to affect membrane performance.

This NOM can be removed with very little (typically less than 2 mg/L) or no coagulant addition to the source water. However, if the source seawater is influenced by surface runoff or large amount of alluvial organics contributed by a river entering the ocean near the intake or alluvial brackish aquifer is used for water supply, the NOM properties and ability to cause significant membrane productivity loss may increase dramatically. Under these circumstances, the efficient removal of NOM may require very high dosages of coagulant (usually over 20 mg/L).

Microbial foulants are aquatic microorganisms and organic compounds excreted by them (i.e., extracellular polysaccharides (EPS), proteins and lipids) which are deposited on the RO membrane surface. The phenomenon of accumulation of aquatic organisms and their metabolic products on the membrane surface is known as biological fouling or biofouling. The biofilm formed on the membrane surface (see Figure 5) contributes additional resistance (pressure headlosses) to the osmotic pressure that needs to be overcome in order to maintain steady production of fresh water by the membrane elements.

Recent research indicates that biofilm formed on RO membrane surface can cause performance decline by increasing the hydraulic resistance of the membranes and by a “cake enhanced osmotic pressure (CEOP)” effect. Therefore, if a microbial cake layer is formed on the surface of the RO membranes, then membrane productivity declines and membrane salt passage increases over time. In order to compensate for loss of productivity due to biofouling, the feed pressure of the SWRO membrane system would need to be increased, which in turn would result in elevated energy use to produce the same volume of fresh water.

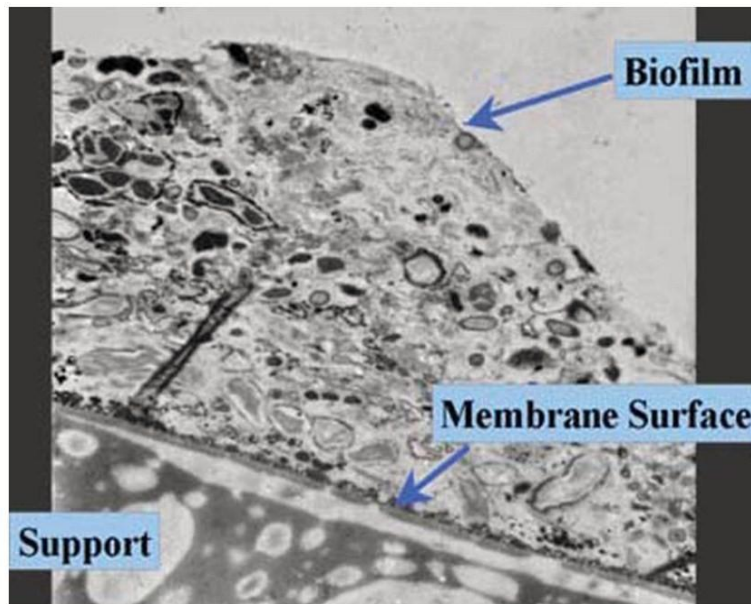


Figure 5 – Biofilm on RO Membrane Surface

Although bacteria constitute the majority of the membrane biofilm, other microorganisms such as fungi, algae and protozoa can also attach to the membrane surface and contribute to biofilm formation. Usually the most predominant bacteria causing biofouling are: *Pseudomonas*, *Bacillus*, *Arthobacter*, *Corynebacterium*, *Flavobacterium* and *Aeromonas*. Other microorganisms such as fungi (i.e., *Penicillium*, *Trichoderma*, *Mucor*, *Fusarium*, and *Aspergillus*) are typically present in the membrane biofilm in significantly lower levels than bacteria.

Biofouling is usually a mayor challenge for seawaters of naturally elevated organic content and temperature (such as these in the Middle East region) or is exhibited in many other parts of the world during conditions when the content of biodegradable organics in the source seawater increases significantly. Such conditions for example are intense algal blooms (i.e., red tides) or periods when surface runoff form rain precipitation or nearby river water of high organic content enter the seawater intake.

The biological fouling (biofouling) potential of a given source water would depend on many factors such as: (1) the concentration and speciation of microorganisms contained in the source water; (2) the content of easily biodegradable compounds in the water; (3) the concentration of nutrients and the balance (ratio) between organic compounds and the biologically available nitrogen and phosphorus in the source water; (4) the source water temperature.

Bacteria contained in brackish water or seawater typically exist in two states – metabolically active and inactive. The active state of bacteria cells is characterized with fast growth and

formation of extracellular material and bacterial colonies that could accumulate on the RO membrane surface. The inactive state of existence of marine bacteria is characterized with low metabolic and growth rates, and bacterial cell appearance in the form of single cells or small cell clusters that behave as micro-particles and have protective cellular cover which allows them to survive unfavorable environmental conditions, such as low content of food and oxygen, or high content of harmful substances such as chlorine and other biocides. At any given time some of the marine bacteria naturally occurring in the ocean are always in active state and other are in inactive state.

The predominant state of aquatic bacteria (active or inactive) would depend of how favorable the ambient environment is for bacterial survival and growth. Most of aquatic bacteria would transfer from inactive to active state under favorable environmental conditions, such as red tide in events in seawater, when high concentrations of easily biodegradable organics released from the decaying algal biomass, which serve as food to these bacteria, are readily available in the seawater. Since the bacteria can attach on the membrane surface and grow colonies there at a very high rate, red tide or other intense algal bloom events are usually the most frequent cause of RO membrane biofouling, especially in seawater desalination plants.

Membrane biofouling process (i.e., formation of microbial cake layer on the surface of the RO membranes) usually follows several key steps: (1) formation of primary organic conditioning film; (2) colonizing bacteria attachment; (3) formation of biopolymer matrix; (4) establishment of mature secondary biofilm; (5) biofilm equilibrium and die-off. The organic conditioning film is a micro-thin layer on the surface of the membrane which is rich in nutrients and easily biodegradable organics, and which creates suitable condition for bacteria to convert from inactive (particulate-like) state into active state when they are capable of producing extracellular polymers, which allow bacteria to attach to the membrane surface.

While during the first step of the biofilm formation process active bacteria adsorb to only 10 to 15 % of the membrane surface, these bacteria multiply in an exponential rate and within five to fifteen days they colonize the entire membrane surface and form a biofilm matrix layer that is several μm thick. The mucus-like biopolymer matrix formed on the membrane surface entraps organic molecules, colloidal particles, suspended solids and cells of other microorganisms (fungi, microalgae, etc.) over time to form a thicker cake of higher permeate flow resistance.

3. Reverse Osmosis – Basic Principles and Parameters

Reverse Osmosis Separation Process

If water of high salinity is separated from water of low salinity via semi-permeable membrane, a natural process of transfer of water will occur from the low-salinity side to the high-salinity side of the membrane until the salinity on both sides reaches the same concentration. This natural process of water transfer through a semi-permeable membrane driven by salinity gradient occurs

in every living cell and is known as osmosis. The hydraulic pressure applied on the membrane by the water during its transfer from the high-salinity to the low-salinity side of the membrane is termed osmotic pressure. Osmotic pressure is a natural force similar to gravity and is proportional to the difference in TDS concentration on both sides of the membrane, the source water temperature, and the type of ions that form the TDS content of the source water. This pressure is independent of the type of membrane itself.

In order to remove fresh (low salinity) water from a high salinity source water using membrane separation, the natural osmosis-driven movement of water will have to be reversed – i.e., the fresh water has to be transferred from the high salinity to the low salinity side of the membrane. For this reversal of the natural direction of fresh water flow to occur, the high-salinity source water will need to be pressurized at a level higher than the naturally occurring osmotic pressure (see Figure 6).

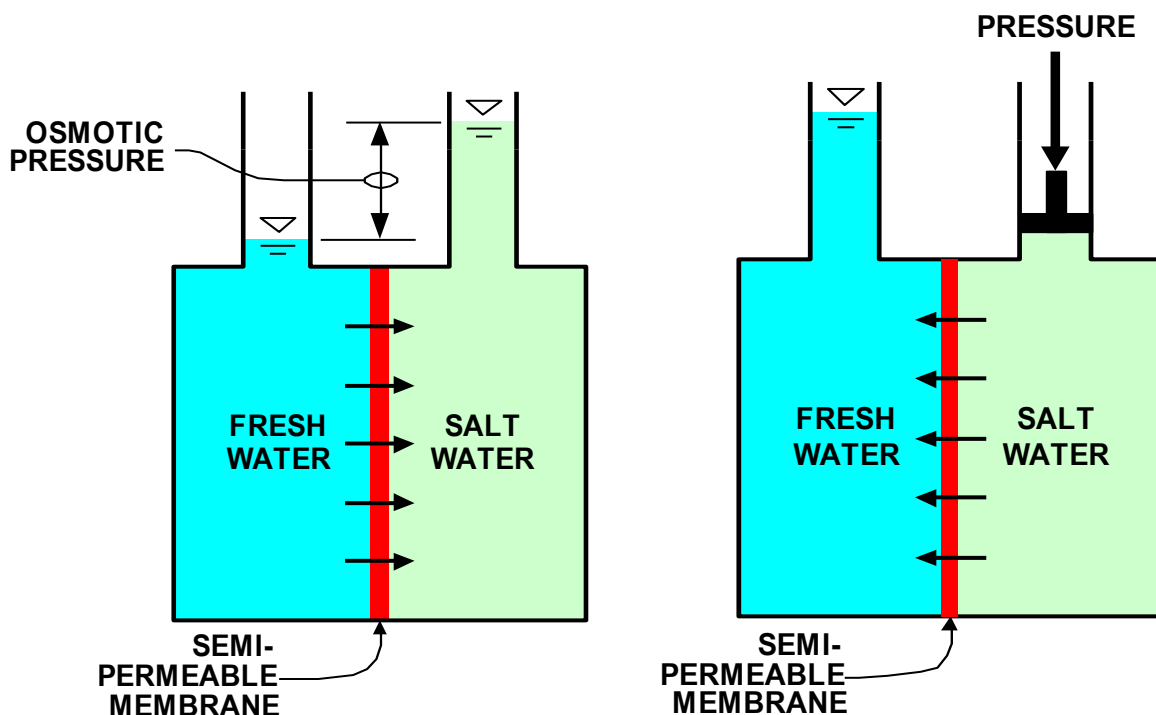


Figure 6 – Osmosis and Reverse Osmosis

If the high salinity source water is continuously pressurized at level higher than the osmotic pressure, a steady-state flow of fresh water from the high salinity to the low salinity side of the membrane will occur, resulting in a process of salt rejection and accumulation on one side of the membrane and fresh water production on the other side of the membrane. This process of forced movement of water through a RO membrane in an opposite direction to the salinity gradient driven osmotic force is known as reverse osmosis (RO). The RO process results in two streams –

one of fresh water of low salinity (permeate) and one of feed source water of elevated salinity (concentrate or retentate) - Figure 7.

While semi-permeable RO membranes reject all suspended solids, they are not an absolute barrier to dissolved solids (minerals and organics alike). Some passage of dissolved solids will accompany the passage of fresh water through the membrane. However, the key feature of semi-permeable membranes is that they pass water at a much higher rate than they do dissolved solids. The rates of water and salt passage are the two key performance characteristics of each RO membrane.

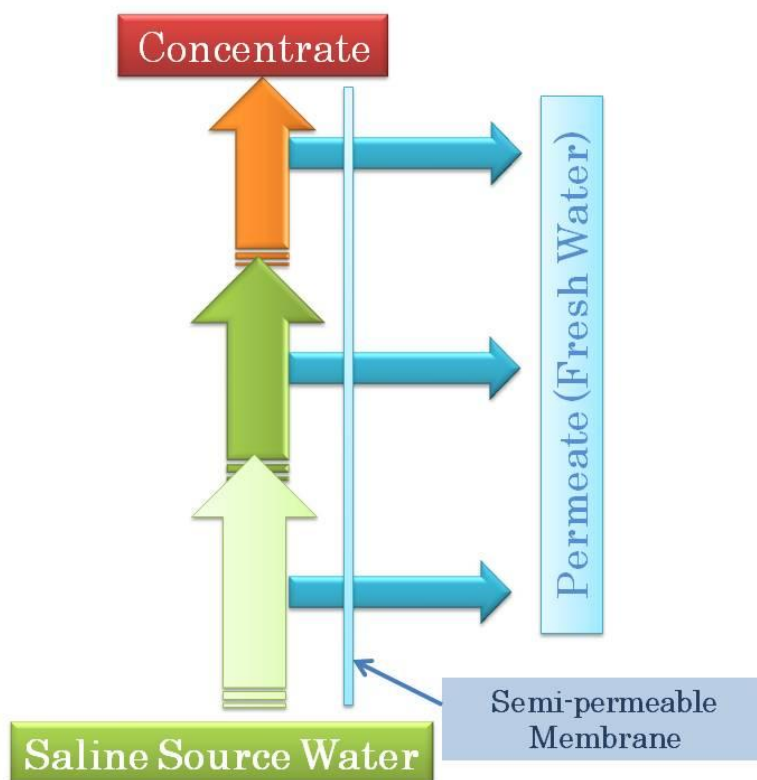


Figure 7 – Reverse Osmosis Process

Key Reverse Osmosis Process Parameters

In full-scale installations reverse osmosis membranes are configured in standard size membrane elements and assembled in modules and the feed water is applied to the membranes at pressure adequate to overcome the osmotic pressure of the saline water and the energy losses associated with the separation process. A general schematic of a RO system is shown on Figure 8. Key parameters associated with the performance of reverse osmosis systems are discussed below.

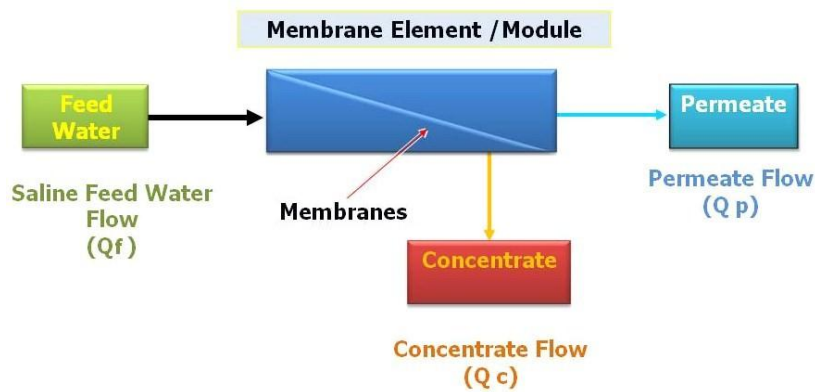


Figure 8 – General Schematic of RO System

Osmotic pressure of given saline water, P_o , is calculated by measuring the molar concentrations of the individual dissolved salts in this solution and applying the following formula:

$$P_o = R (T + 273) \sum (m_i) \quad (1)$$

Where P_o is the osmotic pressure of the saline water (in bars – 1 bar = 14.2 pounds per square inch or psi), R is the universal gas constant (0.082 L.atm/mol °K), T is the water temperature in °C, and $\sum (m_i)$ is the sum of the molar concentrations of all constituents in the saline water. An example of calculation of the osmotic pressure of the Pacific Ocean seawater of TDS concentration of 35,000 mg/L (Table 1) is given below. Table 4 shows the estimate of the molar concentration of all salts in the source Pacific Ocean seawater.

Based on formula (1), the osmotic pressure of the Pacific Ocean seawater at 25 °C is calculated as:

$$P_o = 0.082 (25 + 273) 1.1243 = 27.5 \text{ bars (391.2 psi)}$$

The relative osmotic pressure per 100 mg/L of TDS of Pacific Ocean water is: 27.5 bars/ (35,000 mg/L/100 mg/L) = 0.08 bars (1.12 psi)/100 mg/L. This estimate is consistent with the general “rule of thumb” often used in the desalination industry, which states that every 100 mg/L of salinity results in 1 psi (0.07 bars) of osmotic pressure.

Since this rule of thumb was derived for 100 % sodium chloride solution, its validity is questionable in source waters where compounds other than sodium and chloride are the main contributors to the TDS of the source water. For example, in the case of the brackish water of the Tularosa, New Mexico source presented in Table 3, where calcium sulfate contributes to over 70% of the TDS concentration and sodium chloride is only 11 % of TDS, the actual osmotic pressure of the source water will be significantly lower than the one estimated using the rule of

thumb presented above. For example, if the calculations shown on Table 4 are completed for the Tularosa, New Mexico brackish water shown in Table 3, the osmotic pressure of this water will be only 1.12 bars (16 psi), while the rule of thumb will result in an osmotic pressure estimate of $(1 \text{ psi} \times 2,542 \text{ mg/L}/100 \text{ mg/L}) = 25 \text{ psi}$, which is approximately 60 % higher than the actual value.

Table 4 – Calculation of Molar Concentration of Pacific Ocean Water Salts

Seawater Constituents	Concentration (mg/L)	Number of Milligrams per Mole	Molar Concentration m_i (moles/L)
Cations			
Calcium	403	40,000	0.0101
Magnesium	1,298	24,300	0.0534
Sodium	10,693	23,000	0.4649
Potassium	387	39,100	0.0099
Boron	4.6	10,800	0.0004
Bromide	74	79,900	0.0009
Total Cations	12,859.6	-	0.5396
Anions			
Bicarbonate	142	61,000	0.0023
Sulfate	2,710	96,100	0.0392
Chloride	19,284	35,500	0.5432
Fluoride	1.3	19,000	0.0000
Nitrate	0.00	62,000	0.0000
Total Anions	22,215.4	-	0.5847
Total	TDS = 35,000 mg/L		$\sum (m_i) = 1.1243 \text{ mol/L}$

Permeate Recovery Rate

Due to mineral scaling, concentrate polarization standard equipment and facility constraints, only a portion of the saline source water flow fed to the RO membrane system can be converted into fresh water (permeate). The portion of the feed source water flow converted into fresh water flow (Q_f) is defined as permeate recovery rate (P_r) and is measured as a percent of the saline feed flow (Q_f) – see Figure 9.

$$P_r = (Q_p/Q_f) \times 100 \% \quad (2)$$

As illustrated on Figure 9, for typical seawater reverse osmosis (SWRO) system the recovery rate is 40 % to 65 %. Most SWRO plants are designed around 50 % recovery, which means that it takes two gallons of seawater to produce one gallon of fresh water. Brackish water desalination plants are designed and operated at higher recoveries (typically 65% to 85 %).

The TDS of the concentrate (TDS_c) can be calculated based on the RO system permeate recovery rate P_r , in percent; the actual concentration of the permeate (TDS_p) and feed water TDS (TDS_f) using the following formula:

$$TDS_c = (TDS_f - P_r/100 \times TDS_p)/(1-P_r/100) \quad (3)$$

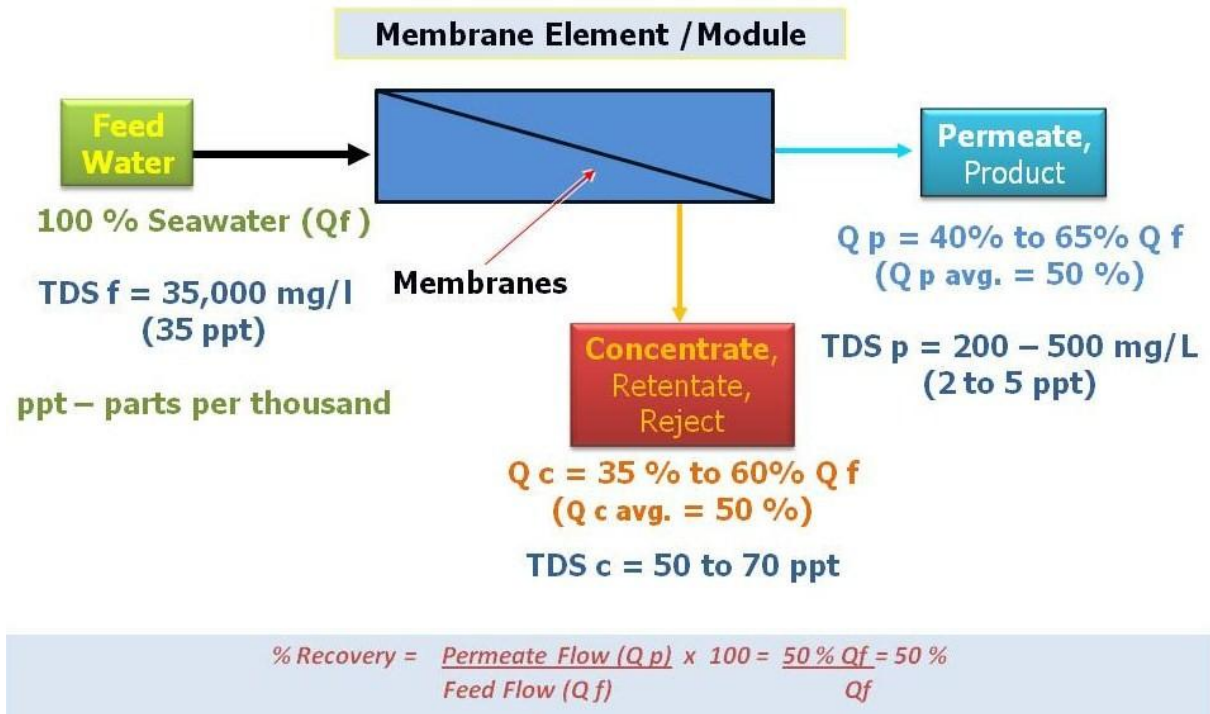


Figure 9 – Recovery of Typical SWRO System

For the example on Figure 9, the TDS of the concentrate, assuming recovery rate of 50 % and permeate salinity of 200 mg/L, is calculated as follows:

$$TDS_c = (35,000 \text{ mg/L} - 50\%/100 \times 200 \text{ mg/L})/(1-50\%/100) = 69,800 \text{ mg/L}$$

Net Driving Pressure (Trans-membrane Pressure)

Net driving pressure (NDP) also known as the trans-membrane pressure (TMP) is the actual pressure that drives the transport of fresh water from the feed side to the fresh water side of the

membrane. The average NDP of a membrane system is defined as a difference between the applied feed pressure of the saline water to the membrane (F_p) minus all other forces that counter the movement of permeate through the membrane, including: the average osmotic pressure on the feed/concentrate side of the membrane (O_{pfc}); the permeate pressure (P_p) and the pressure drop across the feed/concentrate side of the RO membrane (P_d). The NDP can be calculated as follows:

$$NDP = F_p - (O_{pfc} + P_p + 0.5 P_d) \quad (4)$$

The applied feed pressure F_p is controlled by the RO system operator and delivered through high pressure feed pumps. The average osmotic pressure on the feed/concentrate side of the membrane (O_{pfc}) is determined by the salinity and the temperature of the source seawater, and the concentrate. The permeate pressure (also known as product water back pressure) is a variable that is controlled by the RO plant operator and is mainly dependent on the energy needed to convey permeate to the downstream treatment and/or delivery facilities. Typically, permeate pressure is set at 15 to 30 psi (1 to 2 bars). The osmotic pressure of the permeate is usually very small because the salinity of this stream is low. Therefore, for practical purposes typically it is omitted from the calculations of the NDP.

The pressure drop across the feed/concentrate side of the RO membrane depends mainly of the membrane fouling and the RO membrane and system configuration. This pressure drop is usually between 35 psi and 95 psi (2.5 to 6.5 bars).

For the example on Figure 9, assuming SWRO system recovery of 50 %, saline water feed pressure of $F_p = 800$ psi (56 bars); P_p = permeate pressure of 20 psi (1.4 bar), and pressure drop across the RO system of $P_d = 45$ psi (3.2 bars), the NDP at which this RO system operates is determined as follows:

1. Calculate the Average Salinity on the Feed/Concentrate Side of the RO Membrane:

$$TDS_{fc} = (TDS_f + TDS_c)/2 = (35,000 \text{ mg/L} + 69,800 \text{ mg/L})/2 = 52,400 \text{ mg/L};$$

2. Calculate the Average Osmotic Pressure of the Saline Water on the Feed/Concentrate Side:

$$O_{pfc} = (1.12 \text{ psi/100 mg/L TDS}) \times 52,400 \text{ mg/L} = 587 \text{ psi (41 bars)};$$

3. Calculate NDP:

$$NDP = F_p - (O_{pfc} + P_p + 0.5 P_d) = 800 \text{ psi} - (587 \text{ psi} + 20 \text{ psi} + 0.5 \times 45 \text{ psi}) = 170 \text{ psi (12 bars)}.$$

Membrane Salt Passage and Salt Rejection

Salt passage (S_p) of a membrane is defined as the ratio between the concentration of salt in the permeate (TDS_p) to that is the saline feed water (TDS_f) (see Figure 8) and is indicative of the amount of salts that remain in RO permeate after desalination:

$$S_p = (TDS_p/TDS_f) 100\% \quad (5)$$

Salt rejection (S_r) in turn is a relative measure of how much of the salt that was initially in the source water was retained by the RO membrane:

$$S_r = 100\% - S_p = [1 - (TDS_p/TDS_f)] 100\% \quad (6)$$

For the seawater desalination example shown on Figure 9, the TDS passage of the SWRO membrane for the high end of performance of the RO membrane ($TDS_p = 200 \text{ mg/L}$) is $S_p = (200 \text{ mg/L}/35,000 \text{ mg/L}) 100\% = 0.57\%$. The total dissolved salt rejection of this RO membrane is $S_r = 100\% - 0.57\% = \underline{99.43\%}$.

It should be pointed out that salt passage and rejection can be applied not only to the total dissolved solids contained in the source water as a whole, but also to individual ions contained in this water. Not all ions are rejected equally by the same RO membrane. Usually the larger the ions and the higher their electrical charge the better rejected they are. This means for example that bivalent ions such as calcium and magnesium will be rejected better than monovalent ions such as sodium and chloride. Also, low-charge monovalent ions such as boron will be rejected at a lower rate than higher-charge monovalent ions such as chloride and sodium. This is a very important feature of the RO membranes because, often for practical purposes RO membrane structure can be modified to selectively reject specific ions better than the rest. For example, RO membrane material can be modified to have a “looser” structure, and remove mainly bivalent ions when the key goal of water treatment is water softening (i.e., removal of calcium and magnesium). Such membranes are often referred to as nanofiltration (NF) membranes. The NF membranes usually reject less than 30 % of the TDS (as compared to RO membranes which reject over 90 % of the TDS), but they retain over 99% of calcium and magnesium.

Since the weight and valence of the rejected ions are very important factors influencing RO membrane salt passage and rejection, and since the source water ion make up can vary significantly from one location to another, in order to be able to compare the salt rejection ability of different membranes, sodium chloride or sodium bisulfate are typically used as “standard” salts against which the rejection of commercial RO membranes is measured. Membrane rejection is tested against a standard salt feed solution of predetermined salinity and testing is competed at standard test feed pressure and feed flow rate. For example, for most commercial SWRO membranes, the salt rejection is determined using standard test solution of sodium chloride at salinity concentration of 32,000 mg/L; test feed pressure of 800 psi (55.2 bars); and

test recovery rate of 10 %. Salt rejection for most commercially available SWRO membranes at these test conditions is 99.60% to 99.85 %.

Please note that when used to desalinate actual seawater, the commercially available RO membrane elements usually have lower overall TDS concentration rejection (higher salt passage) than their standard level reported in manufacturer specifications – typically in a range of 99 to 99.5 % mainly because not all ions contained in the saline source water are rejected as well as sodium and chloride.

Membrane Permeate Flux

Membrane permeate flux is defined as the permeate flow a membrane produces per unit membrane area. Membrane element permeate flux (F_p), which is also referred to as membrane flux, is calculated by dividing the flowrate of permeate (Q_p) produced by a RO membrane element [usually expressed in gallons per day (gpd) or liters per hour (lph)] by the total membrane area of this element (S) [in square feet (sq ft) or meters (sq m)]. The flux unit is therefore, gal/sq ft/day (also referred to as gfd) and l/sq m/hour (also known as lmh).

$$F_p = Q_p / S \quad (7)$$

Since a full-scale RO system consists of a number of membrane elements, the average permeate flux of this system is calculated by dividing the total flow of permeate produced by all membranes by the total surface area of these membranes.

Specific Membrane Permeability (Specific Flux)

Specific membrane permeability (SMP), also known as specific membrane flux, is a parameter which characterizes the resistance of the membrane to water flow and is expressed as the membrane permeate flux (F_p) divided by the net driving pressure (NDP):

$$SMP = F_p / NDP \quad (8)$$

The standard specific permeability of a given membrane is typically determined for a feed temperature of 25 °C and is presented in gfd/psi or lmh/bar. For example, most commercially available seawater desalination RO membranes at present have SMP of 0.04 to 0.06 gfd/psi (1.0 to 1.4 lmh/bar). For comparison, brackish water RO membranes have significantly higher specific permeability (0.2 to 0.35 gfd/psi or 4.9 to 8.3 lmh/bar).

Nanofiltration membranes which have a “looser” membrane structure have even higher specific permeability than brackish and seawater RO membranes (0.3 to 0.6 gfd/psi or 7.4 to 15.8 lmh/bar). Usually, membranes of lower specific permeability also have higher salt rejection, so there is a trade-off between lower production and higher water quality. The specific membrane permeability is determined by the chemical and physical nature of the membrane.

Concentration Polarization Factor

A very important factor that may have a significant impact on the extent and type of membrane fouling and the overall RO system recovery is referred to as concentration polarization. This phenomenon entails formation of a boundary layer along the RO membrane feed surface, which has salt concentration significantly higher than that of the feed water. Because the high salinity layer increases the osmotic pressure at the membrane surface, it reduces the actual permeate flow produced by the RO system as well as decreases membrane salt rejection. In addition, if salt concentration in the high salinity boundary layer exceeds the solubility of sparingly soluble salts (such as calcium sulfate) in the source water, these salts would begin precipitating on the membrane surface and would form mineral scale.

For a given membrane, the magnitude of concentration polarization is driven by two key factors: (1) permeate flux; (2) feed flow. Increase in permeate flux increases the quantity of salt ions conveyed to the boundary layer and therefore, exacerbates concentrate polarization. Increase in feed flow however, intensifies turbulence along the surface of the RO membrane and as a result decreases the thickness and concentration of this layer. Since permeate flux is a measure of the permeate flow through a given membrane, and the ratio between the membrane permeate flow and feed flow is defined as recovery, concentrate polarization is directly related to the recovery at which a given RO system is operated.

As the recovery rate increases, the magnitude of concentrate polarization increases as well. For seawater reverse osmosis systems using standard membrane elements, operation at recovery rate of 50 %, would typically result in approximately 1.2 to 1.5 times higher salinity concentration of the boundary layer than that of the source seawater. Beyond 75 % recovery, this concentration ratio (also known as concentration factor) would exceed 2, which would have a significant impact on the efficiency of the membrane separation process. In addition, at recovery rate above 75 % and ambient salinity pH of 7.8 to 8.3, many of the salts in seawater would begin precipitating on the membrane surface, which would require the addition of large amounts of antiscalant (scale-inhibitor) and would make RO desalination impractical. Since scaling is pH dependent, an increase in pH to 8.8 or more (which often is practiced for enhanced boron removal from seawater), may result in scale formation at significantly lower SWRO recovery (50 to 55 %). In brackish water RO membrane systems, the source water TDS concentration is significantly lower, which in turn allows to operate these systems at significantly higher recoveries.

Membrane Performance Factors and Considerations

Reverse osmosis membrane separation process is closely related to two key features of the membranes: their ability to transport water and to transport salts. Desalination is possible

because the rate of water transfer RO membranes have is significantly higher than their rate of salt transport.

The water transport rate (Q_w) of RO membranes is proportional to their water transfer (water permeability) coefficient (A), which is a unique constant for each membrane material; the total membrane area (S), and the net driving pressure (NDP):

$$Q_w = A \times S \times \text{NDP} \quad (9)$$

The salt transport rate (Q_s) is proportional to the salt transfer coefficient (B), which similar to the water transfer coefficient is also unique for each membrane type; the surface area of the membrane (S), and the salt concentration gradient (ΔC), which collectively for all salts will be measured as the difference between the TDS levels of the concentrate and the permeate:

$$Q_s = B \times S \times \Delta C \quad (10)$$

These two equations provide key insights regarding the impact of various factors on membrane performance. Increased feed pressure results in elevated permeate flux, because the NDP increases. Since salt transport rate stays constant with increase in feed pressure in accordance with Equation 10, and permeate volume is increased, the product water quality of the permeate improves – i.e., operating at higher pressure yields higher fresh water production and better water. However, because it also consumes most energy, this type of operation is not practiced often.

Effect of Salinity on RO Performance

Figure 10 illustrates the effect of source water salinity fed to the RO system on its productivity of fresh water (permeate flux) and product water quality (salt rejection). Higher feed water salinity reduces the net driving pressure (assuming that the system is operating at the same feed pressure and recovery), which in turn decreases permeate flux (fresh water production). In terms of salt transport, increase in feed water salinity increases the salt concentration gradient (ΔC in formula 10) which results in accelerated salt transport through the membrane and therefore, in lower salt rejection (deteriorating product water quality).

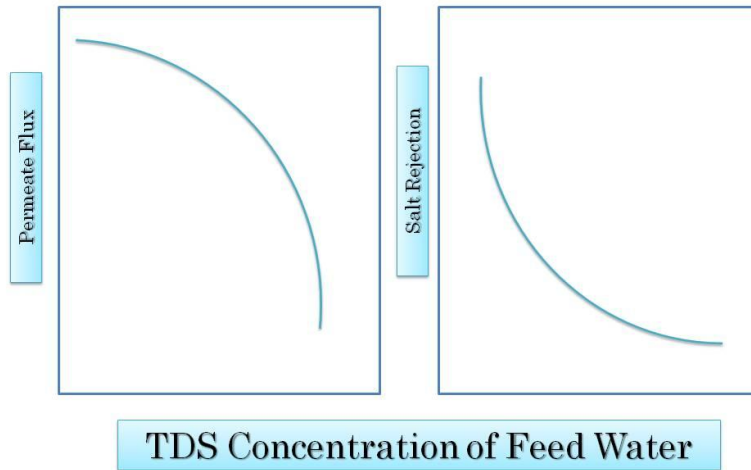


Figure 10 – Effect of Salinity on RO System Performance

Effect of Recovery on RO Performance

As indicated on Figure 11, recovery has limited effect on permeate flux and salt rejection until it reaches high concentration polarization levels and/or triggers precipitation of sparingly soluble salts (membrane salt scaling), after which the membrane performance deteriorates abruptly.

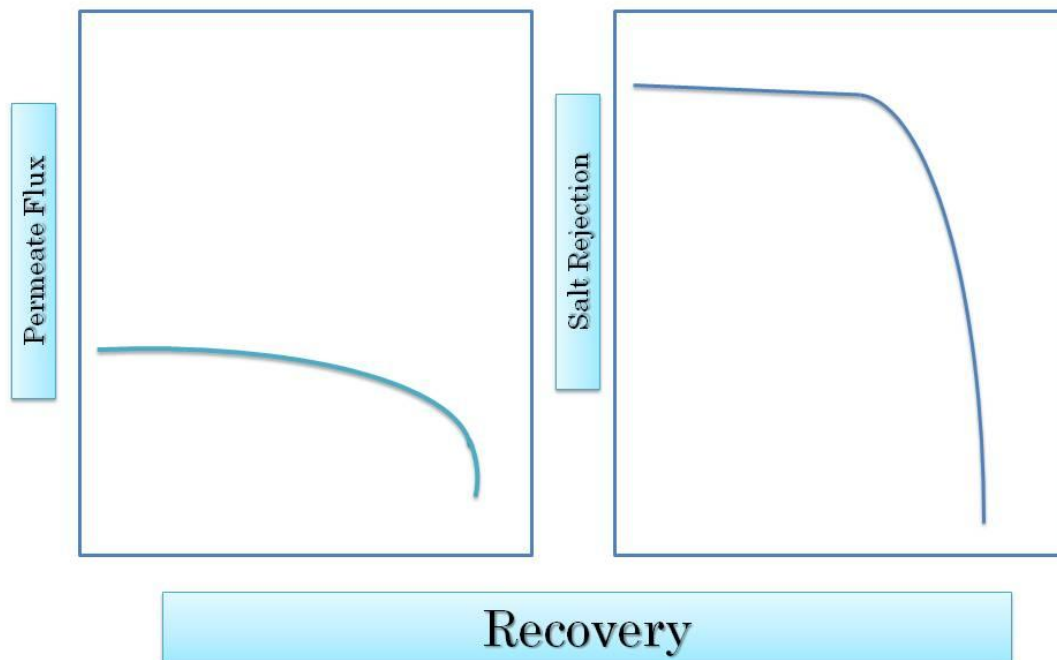


Figure 11 – Effect of Recovery on RO Performance

Effect of Temperature on RO Performance

Use of warmer water reduces saline water viscosity, which in turn increases the feed water NDP. Increase of NDP elevates the membrane flux (see Figure 12). As a rule of thumb, the permeate flux increases with 3% for every 1 °C of temperature increase. However, because most RO membranes are made of plastic materials (polymers), warmer temperatures result in loosening up of the membrane structure, which in turn increases salt passage (i.e., deteriorates slightly permeate water quality). It should be pointed out that as seen on Figure 12, the rate of permeate flux gain is typically much higher than the rate of deterioration of product water quality. Therefore, often operation at warmer seawater temperatures is beneficial.

In full scale membrane RO plants, the main operation strategy is usually to produce steady, near constant permeate flowrate rather than to increase permeate flux. In this case, use of warmer water allows to reduce RO system feed pressure and still maintain the same NDP. As a result, warmer water yields lower total energy use for desalination. Figure 13 shows the relationship between RO system energy use for desalination of Pacific Ocean seawater and temperature.

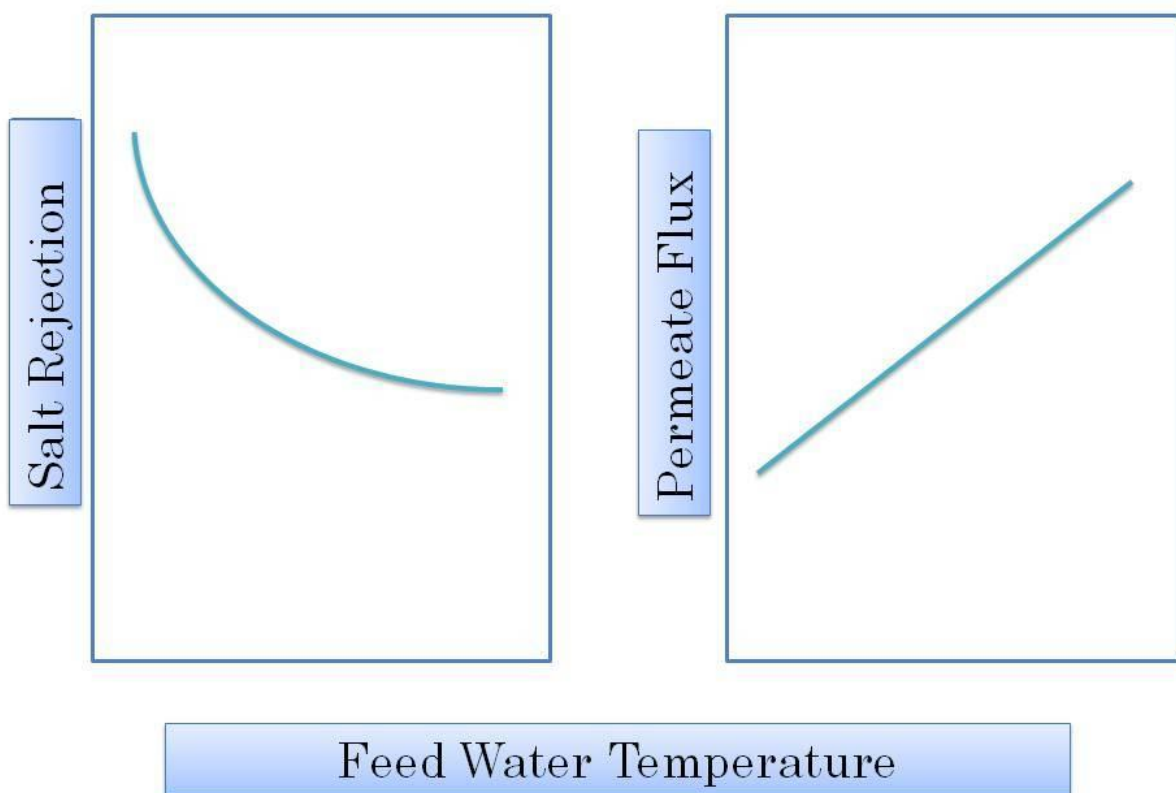


Figure 12 – Effect of Temperature on RO System Performance

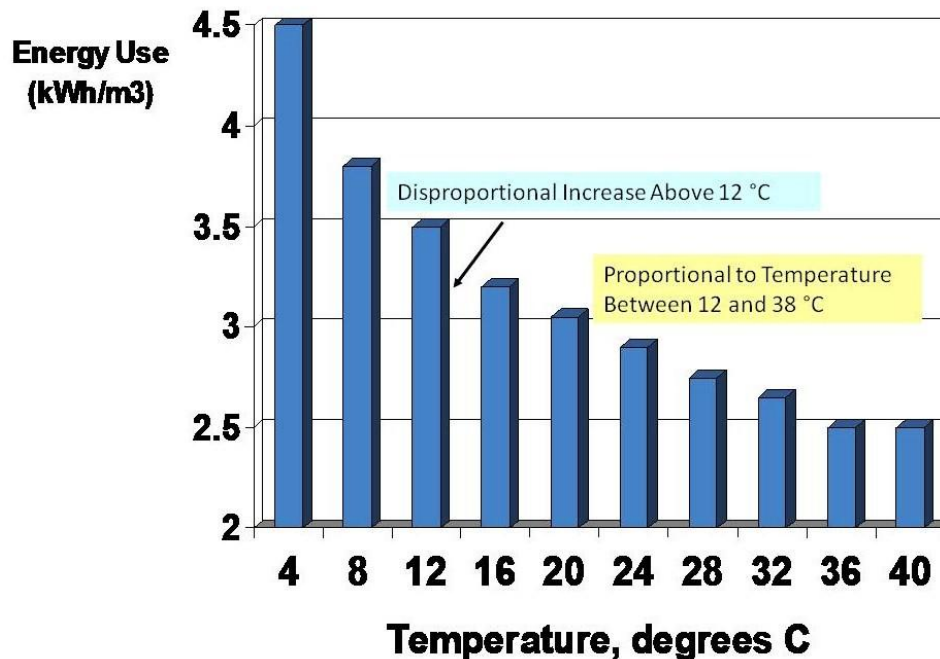


Figure 13 – SWRO System Power Use as a Function of Temperature

Analysis of Figure 13 illustrates several important trends: (1) typically between 12 and 28 °C, the RO system energy use is linearly proportional to the temperature – every 5 °C of temperature increase in this range result in 5 % of energy use reduction; (2) energy use increases almost exponentially when source water temperature decreases below 12 °C due to the curvilinear relationship between temperature and density/viscosity of the water below this temperature, and the “shrinkage” of the membrane polymer structure which results in reduced membrane permeability; (3) increasing seawater temperature above 36 °C is not beneficial because the high temperature results in deformation of the membrane material and accelerated bio-growth which in turn hinder long-term membrane productivity.

Reverse Osmosis Membranes – Structure and Materials

RO and NF membranes used today are composed of a semi-permeable thin film made of either aromatic polyamide (PA) or cellulose acetate (CA), which film is supported by a 0.25 to 0.50 mm micro-porous layer which in turn is casted on a layer of reinforcing fabric (See Figure 14). The 0.2 µm ultra thin polymeric film is the feature that gives the RO membrane its salt rejection abilities and characteristics. The main functions of the two support layers underneath the thin film are to reinforce the membrane structure and to maintain membrane integrity and durability.

The dense semi-permeable polymer film is of a random structure (matrix) which does not have pores. Water molecules are transported through the membrane film by diffusion and travel on a multi-dimensional curvilinear path within the randomly structured molecular polymer film matrix.

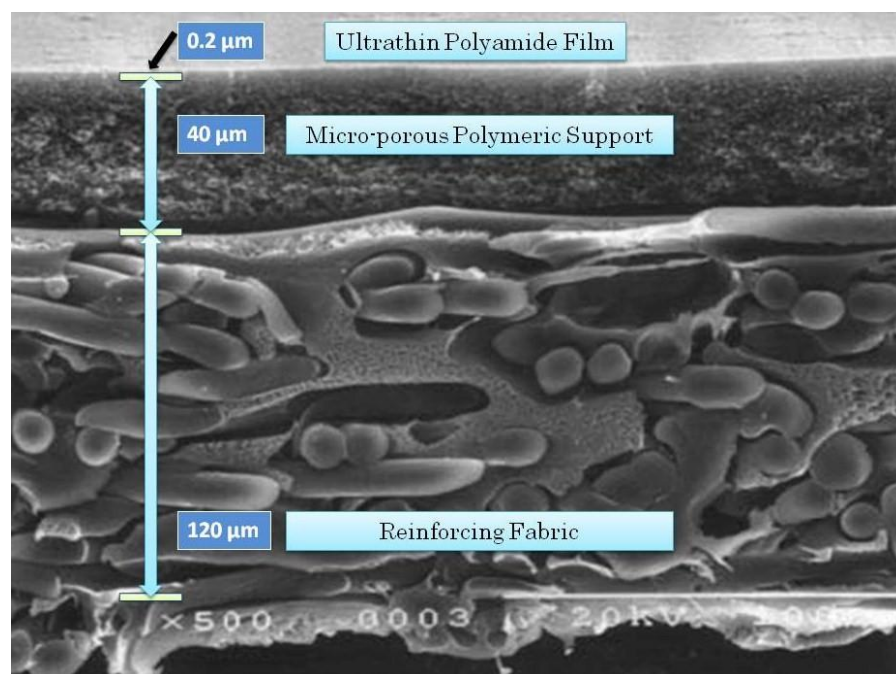
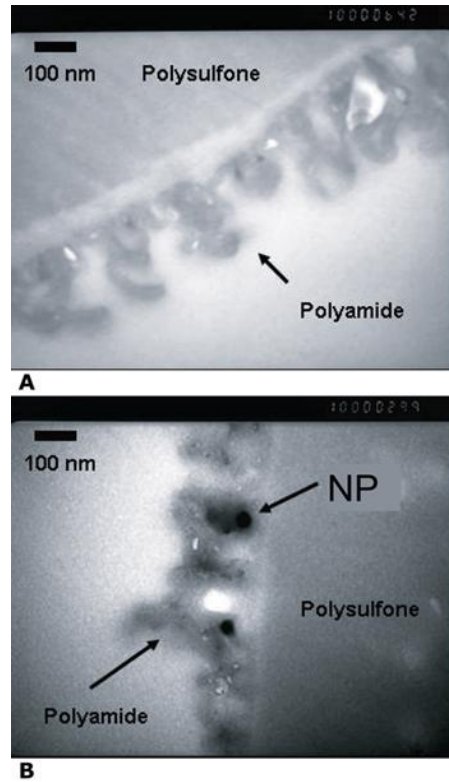


Figure 14 – Structure of Typical RO Membrane

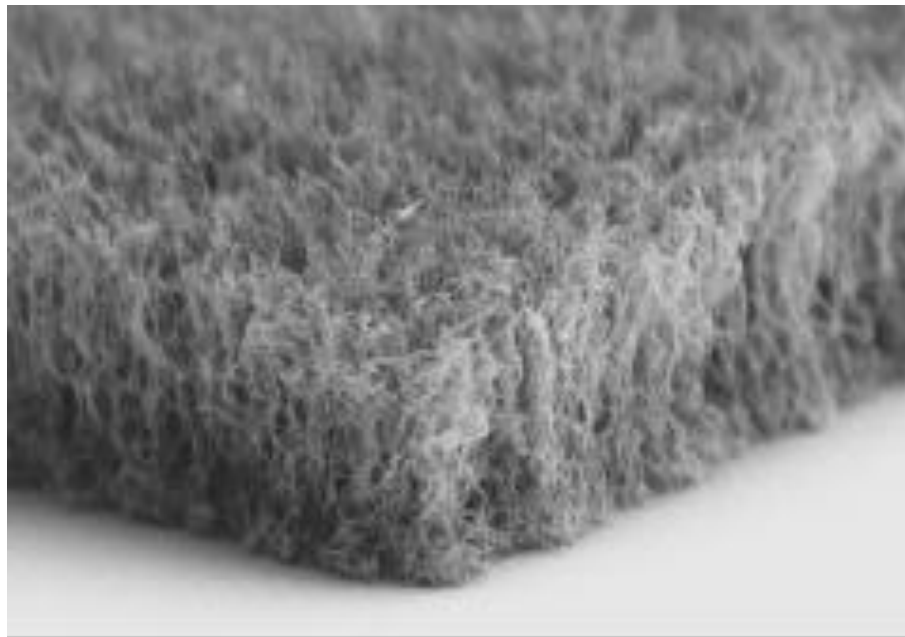
While the thin film RO membrane of conventional random matrix-based structure shown on Figure 14 is the type of membrane which dominates the desalination industry at present, new thin-film membranes of more porous-like structure are currently under development in research centers worldwide. Recently developed nano-structured membranes either incorporate inorganic nano-particles within the traditional membrane polymeric film (see Figure 15) or a made of highly-structured porous film which consists of densely packed array of nanotubes (Figure 16). On Figure 15, the upper picture denoted as (A) shows the thin film of conventional PA membrane, supported by the polysulfone support layer. The lower picture in this figure, denoted as B, shows the same type of membrane with embedded nano-particle (NP).

The nanostructured membranes reportedly have much higher specific permeability than conventional RO membranes at practically the same high salt rejection. In addition, nanostructured membranes have comparable or lower fouling rate than conventional thin-film composite RO membranes operating at the same conditions, and they can be designed for enhanced rejection selectivity of specific ions. If membrane material science evolves to a point when the membrane structure could be made of completely uniform size tubes, theoretically the same membrane surface area could produce up to 20 times more water per unit surface area than the RO membranes commercially available on the market today. Because of the significant potential that membrane material science has, the further development of the RO desalination membrane technology has the potential to measurable savings in terms of water production costs in the future.



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Figure 15 – Polyamide RO Membrane with Nanoparticles



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Figure 16 – RO Membrane with Carbon Nanotubes

Cellulose Acetate (CA) Membranes

The thin semi-permeable film of the first RO membranes developed in the 1950's in the University of California Los Angeles was made of cellulose acetate polymer. While the CA membranes have a three-layer structure similar to that of PA membranes, the main structural difference is that the first top two membrane layers (the ultrathin film and the micro-porous polymeric support) are made of different forms of the same CA polymer. In PA membranes these two layers are made of completely different polymers – the thin semi-permeable film is made of polyamide, while the micro-porous support is made of polysulfone.

The CA membranes have a number of limitations associated with their ability to perform only within a narrow range of pH (4 to 8) and their accelerated deterioration in the presence of microorganisms capable of producing cellulose enzyme and bio-assimilating the membrane material. Because of their high tolerance to oxidants (chlorine, peroxide, etc.) as compared to PA membranes, the CA membranes are used in municipal applications for saline waters of very high fouling potential (mainly in the Middle East and Japan), and for ultrapure water production in pharmaceutical and semiconductor industries.

Aromatic Polyamide (PA) Membranes

This is the most widely used type of RO membranes today. PA membranes have found numerous applications for both potable and industrial water production. The thin polyamide film of this type of semi-permeable membranes is formed on the surface of the micro-porous polysulfone support layer (Figure 14) by interfacial polymerization of monomers containing amine and carboxylic acid chlorine functional groups.

The PA membranes operate at lower NDP, have higher specific flux and lower salt passage than CA membranes, which are the main reasons why they have found a wider application at present. While CA membranes have neutral charge, at pH greater than 5, the PA membranes have negative charge, which amplifies co-ion repulsion and results in higher overall salt rejection of PA membranes as compared to CA membranes. However, it should be noted that at pH lower than 4, the PA membrane charge changes to positive and their rejection below this pH is reduced significantly, and is lower than that of CA membranes.

Another key advantage of PA membranes is that they can operate effectively in much wider pH range (2 to 12), which allows easier maintenance and cleaning. In addition, PA membranes are not biodegradable and usually have longer useful life – 5 to 7 years vs. 3 to 5 years. Aromatic polyamide membranes are used to produce brackish water, seawater and nanofiltration membrane elements.

It should be noted that PA membranes are highly susceptible to degradation by oxidation of chlorine, and other strong oxidants. For example, exposure to chlorine longer than 1,000 mg/L-

hour can cause a permanent damage of the membrane thin-film structure and can significantly and irreversibly reduce membrane performance in terms of salt rejection. Oxidants are widely used for biofouling control of RO and NF membranes, and therefore the feed water to PA membranes has to be dechlorinated prior to separation.

4. Membrane Elements

Classification

The CA and PA membranes described in the previous section are configured into commercially available membrane elements which pack a large surface membrane area and have standard size and performance. The two most widely used membrane element configurations at present are spiral-wound and hollow-fiber type. While until the mid nineties hollow-fiber membranes were the prevalent technology, today's market place is dominated by the spiral wound type RO membrane elements. Other membrane element configurations, such as tubular and plate-and-frame, have found application mainly in food and dairy industries but are practically never used in conventional municipal brackish or seawater desalination plants because of their higher costs and equipment space requirements.

Hollow-fiber Membrane Elements

In hollow fiber membrane elements, the thin semi-permeable film is applied as a coating to the surface of hollow fibers of diameter comparable to that of human hair (42 μm internal diameter/85 μm external diameter). The hollow fibers are assembled in bundles and folded in a half to a length of approximately 48 inches (120 cm).

The hollow-fiber bundle is 4 to 8 inches in diameter and is located inside a cylindrical housing which is 6 to 12 inches in diameter and is 54 inches long. Both ends of the bundle are epoxy-sealed to encapsulate the water introduced in the tube in a way that allows all of the concentrate generated in the tube to exit from only one location – the back end of the membrane. The feed water is introduced in the membrane element through a plastic perforated tube (feed water distributor) which extends over the entire length of the membrane and is located in the center of the bundle (membrane element). The feed water flows radially, permeates through the thin membrane film of the hollow fibers and the salts and impurities contained in this water are collected on the outer side of the fibers and evacuated through the concentrate pipe at the back end of the membrane element. Permeate is collected in the inner tubes of the hollow fibers and conveyed to the product water connection which is located on the back and/or feed end of the membrane element.

As compared to spiral-wound membrane configuration, which will be described in the next sections, the hollow-fiber membrane configuration allows to pack over three times more membrane surface per cubic foot of membrane volume. This higher surface area results in a proportionally lower permeate flux for the same volume of processed water, which in turns

reduces concentration polarization and associated scaling potential when the source seawater is of high mineral content. These features make hollow-fiber membrane elements very suitable for high-salinity waters of elevated scaling potential such as these or the Arabian Gulf, the Gulf of Oman (Indian Ocean) and the Red Sea. Therefore, this type of membrane element configuration has found a wider application in the Middle East than in other parts of the world.

Because of the lower permeate flux, and high membrane surface area, the feed water flow regime in the hollow-fiber membrane elements is laminar (as compared to nearly-turbulent flow which occurs in the spiral-wound elements). This low-energy laminar flow results in little to no “scrubbing effect” on the feed flow on the surface of the membranes. This low membrane surface velocity allows solids and biofilm to attach to and accumulate more easily on the membranes, which in turn makes the hollow-fiber membranes more susceptible to particulate fouling and biofouling. For comparison, the turbulent flow on the surface of the spiral-wound membrane elements makes this membrane configuration more resistant to particulate fouling and biofouling, but because of the higher permeate flux and concentration polarization, this configuration is more prone to mineral scaling.

Spiral Wound Membrane Elements

Spiral wound membrane elements are made of individual flat membrane sheets which have the three-layer structure described in the previous section (i.e., ultrathin CA or PA film; microporous polymeric support; and reinforcing fabric). A typical 8-inch diameter spiral wound RO membrane element has 40 to 42 flat membrane sheets.

The flat sheets are assembled into envelopes, each of which consists of two sheets separated by thin plastic net called permeate spacer to form a channel that allows to evacuate permeate separated from the saline source water by the flat sheets (permeate carrier). The three of the four sides of the two-membrane flat sheet envelope are sealed with glue and the fourth side is left open. Pressurized feed saline water is applied on the outside surface of the envelope and permeate is collected in the space between the two sheets and is directed towards the fourth open end of the envelope, which is connected to a central permeate collector tube (see Figure 17). This collector tube receives desalinated water (permeate) from all flat sheet leaves (envelopes) contained in the membrane element and evacuates it out of the element.

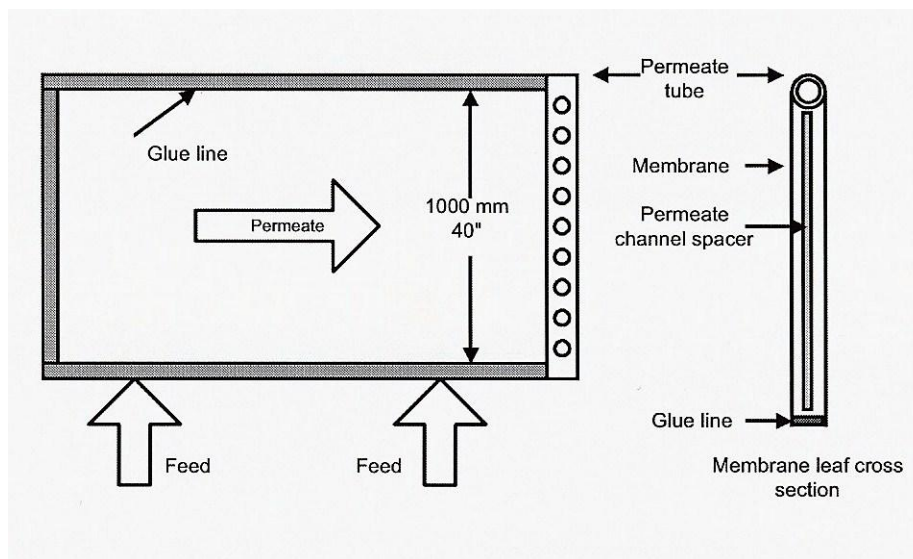


Figure 17 – Flat-sheet Membrane Envelope

The assembly of flat sheet membrane leafs and separating spacers is wrapped (rolled) around the permeate collector tube. The membrane leafs are kept in the spiral-wound assembly with a tape wrapped around them and contained by an outer fiberglass shell. The two ends of the RO element are finished with plastic caps called anti-telescoping devices or seal carriers. The plastic caps are perforated in a pattern that allows even distribution of the feed saline flow among all membrane leafs in the RO element. The plastic caps are often referred to as seal carriers, because one of the functions of these plastic caps is to carry a chevron-type u-cup style brine seal which closes the space between the membrane and the vessel in which the membrane is installed, which seal prevents the feed water from by-passing the RO element.

The source seawater flow is introduced from one end of the element and travels in a straight path along the length of the membrane element. A portion of the feed flow permeates through the membrane and is collected on the other side of the membrane as fresh water. The separated salts remain on the feed side of the membrane and are mixed with the remaining feed water. As a result, the salinity of the feed water increases as this water travels from one end of the membrane element to the other. The rejected mix of feed water and salts exits at the back end of the membrane element as concentrate (brine).

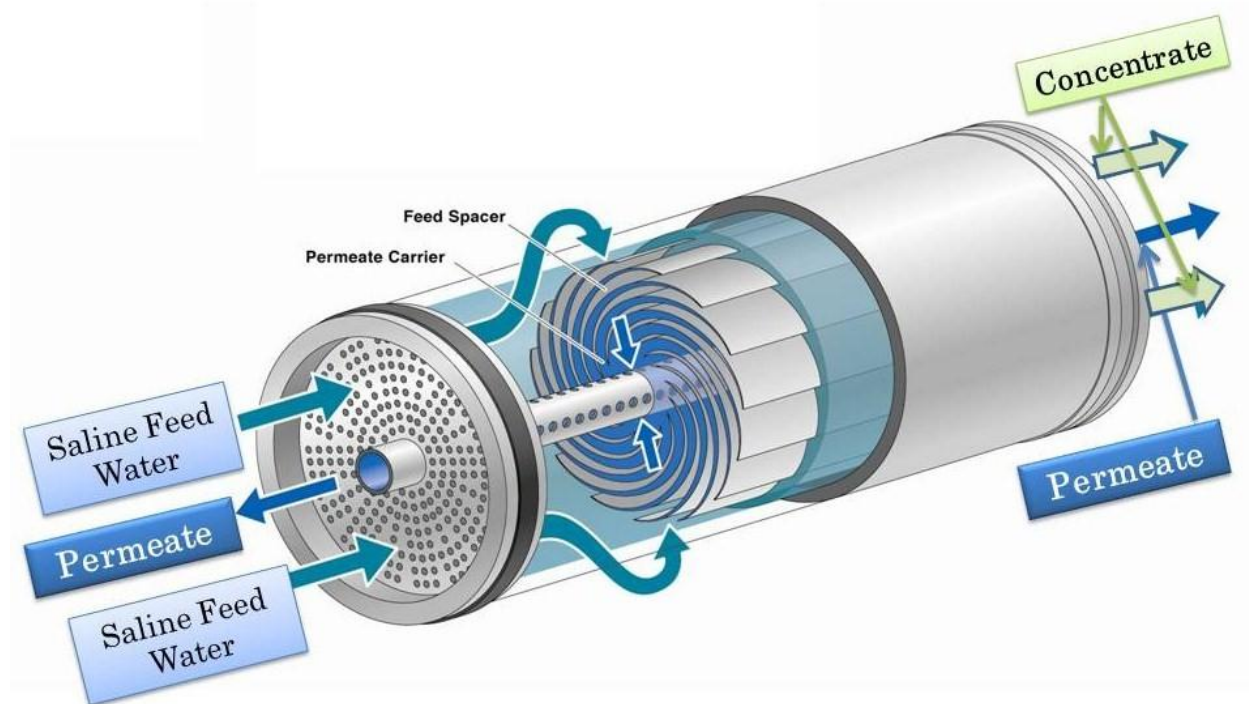


Fig 18 – Flow Patterns in Spiral Wound Membrane Element

A picture of a typical 8-inch RO membrane element is shown on Figure 19. Commercially available RO membrane elements are standardized in terms of diameter and length and usually are classified by diameter. Spiral wound RO membranes are available in 2.5-inch, 4-inch, 6-inch, 8-inch, 16-inch and 18-inch sizes. The most widely used size RO element is 8-inch. This element has a standard length of 40 inches.



Figure 19 – Typical 8-inch Membrane Element

Larger, 16-inch and 18-inch RO brackish and seawater membrane elements have become commercially available over the past 5 years and so far have received a very limited full-scale application. While 8-inch and smaller elements can be handled manually by a single person (Figure 20), larger size RO elements can only be loaded and unloaded by special equipment because of their significant weight.



Figure 20 – Unloading of RO Membrane Element from Pressure Vessel

Key Performance Parameters of Spiral Wound Membrane Elements

Commercially available membrane RO elements have standardized diameters and length, and salt rejection efficiency. Standard membrane elements have limitations with respect to a number of performance parameters such as: maximum feed water temperature (45 °C); pH (minimum of 3 and maximum of 10); silt density index (less than 4); chlorine content (not tolerant to chlorine in measurable amounts); and feed water pressure (maximum of 80 to 100 bars for SWRO membranes elements).

Membrane performance tends to naturally deteriorate over time due to combination of material wear-and-tear and irreversible fouling of the membrane elements. Typically membrane elements have to be replaced every 3 to 7 years to maintain their performance in terms of water quality and power demand for salt separation. Improvements of membrane element polymer chemistry and production process have made the membranes more durable and have extended their useful life. Use of elaborate granular media pretreatment technologies and ultra and micro-filtration (UF & MF) membrane pretreatment systems prior to RO desalination is expected to allow extending the membrane useful life to seven years and beyond, thereby reducing the costs for their replacement and the overall cost of water.

5. Overview of a Typical RO Desalination System

Figure 21 depicts a typical configuration of a large spiral wound membrane RO system. The membrane elements described in the previous section are installed in membrane vessels (Figure 20), which in turn are configured in RO membrane trains or racks. Each membrane vessel typically contains 6 to 8 individual membrane elements. An individual membrane train can have a little as one vessel and for large plants typically contains 100 to 200 vessels. The largest size SWRO trains used today have 5.5 MGD of production capacity and are located at the 36 MGD Point Lisas Seawater Desalination Plant in Trinidad. Usually individual RO trains are fed with saline water by dedicated high pressure feed pumps. However, recently used RO system configurations include a single high pressure pump feeding two or more RO trains.

As indicated previously, prior to membrane separation the source seawater has to be pretreated in order to remove particulate and biofouling constituents and control the solubility of scaling constituents in the source seawater below level at which they begin to form mineral deposits (scale) on the surface of the membrane. The level and type of pretreatment technologies and source water conditioning depend on the source water quality. Usually, most pretreatment systems include granular media or UF or MF membrane filtration followed by cartridge filtration.

The filtered water produced by the plant's pretreatment system is typically conveyed by transfer pumps from a filtrate water storage tank through cartridge filters into the suction pipe of the high pressure RO feed pumps. The main purpose of the cartridge filters is to protect the RO membranes from damage by filtration media, small particles of rust or other particulates that occasionally can be contained in the filtered water. The high pressure feed pumps are designed to deliver the source water to the RO membranes at pressure required for membrane separation of the fresh water from the salts. The actual required feed pressure is site-specific and is mainly determined by the source water salinity and the configuration of the RO system.

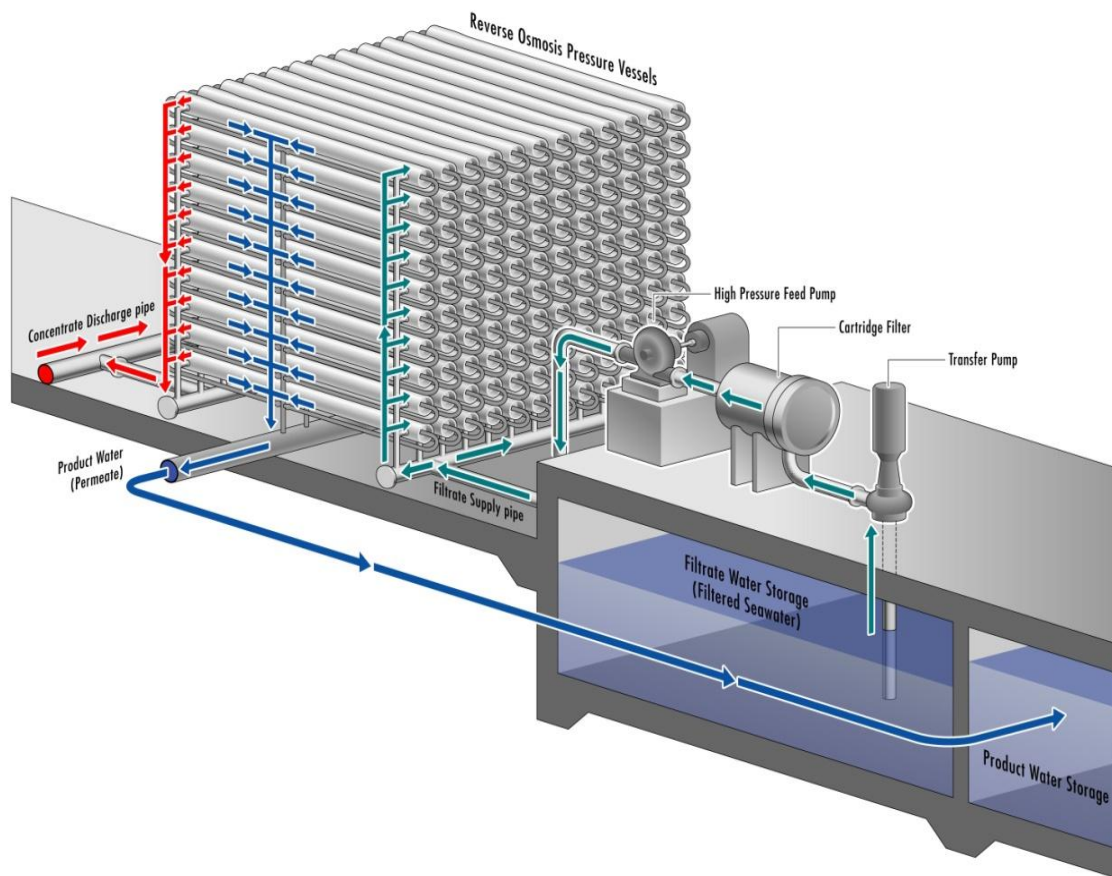


Figure 21 – Typical RO Membrane System Configuration

As shown on Figure 22, the SWRO membrane elements are connected in series inside a pressure vessel. A recent design trend is to use 7 or 8 elements per vessel. Traditionally, all of the feed seawater is introduced at the front of the membrane vessel and all permeate and concentrate are collected at the back end. As a result, the first (front) membrane element is exposed to the entire vessel feed flow and operates at flux significantly higher than that of the subsequent membrane elements. With a typical configuration of seven elements per vessel and ideal uniform flow distribution to all RO elements, each membrane element would produce one-seventh (14.3 %) of the total permeate flow of the vessel.

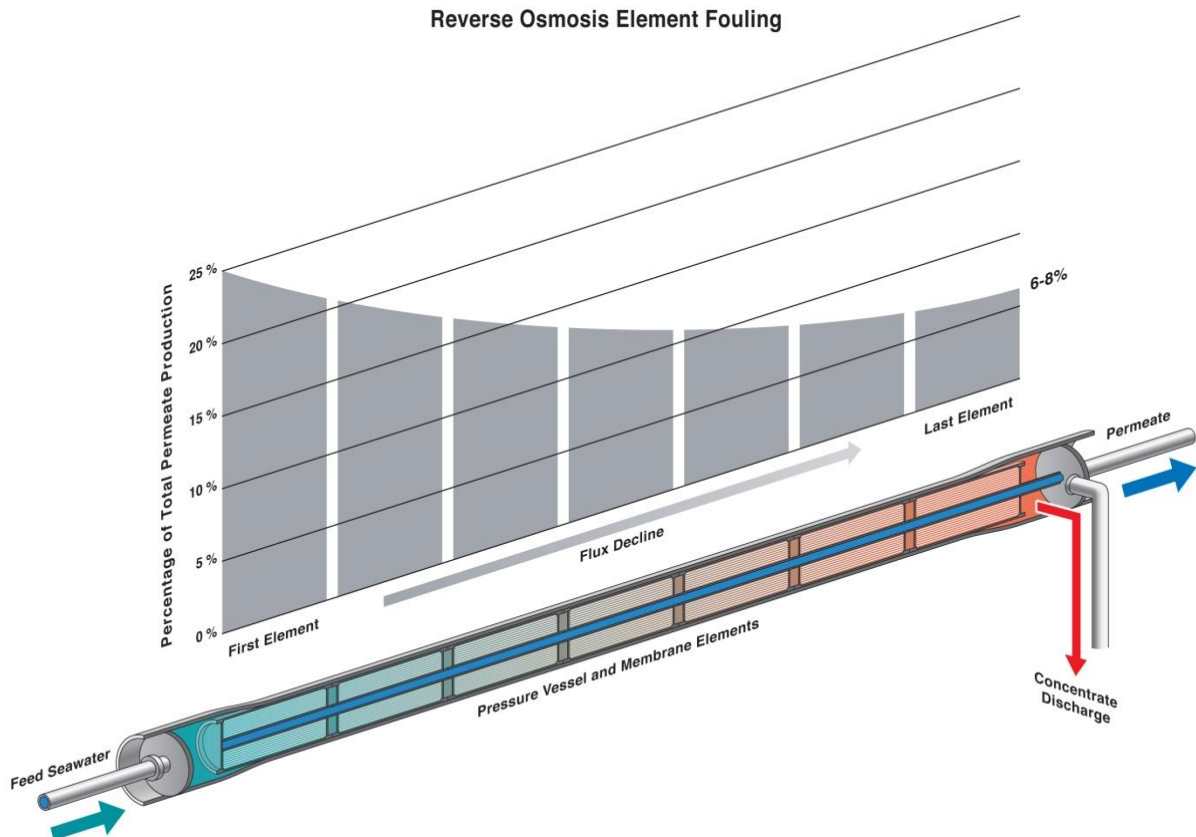


Figure 22 – Membrane Fouling and Flux Distribution in Membrane Vessel

However, in actual spiral wound RO systems, the flow distribution in a vessel is uneven and the first membrane element usually produces over 25 % of the total vessel permeate flow, while the last element only yields 6 to 8 % of the total vessel permeate (see Figure 22). The decline of permeate production along the length of the membrane vessel is mainly due to the increase in feed salinity and associated osmotic pressure as the permeate is removed from the vessel while the concentrate rejected from all elements remains in the vessel until it exits the last element.

Since the first element processes the largest portion of the feed flow it also receives and retains the largest quantity of the particulate and organic foulants contained in the source seawater, and is most impacted by biofouling. The remainder of the feed water that does not pass through the first RO element combines with the concentrate from this element and enters the feed channels of the second RO element of the vessel. This element therefore, is exposed to higher salinity feed water and lower feed pressure (energy), because some of the initially applied pressure (energy) has already been used in the first RO element of the vessel to produce permeate.

As a result, the permeate flow rate (flux) of the second element is lower and the concentrate polarization on the surface of this element is higher than that of the first RO element. The

subsequent membrane elements are exposed to increasingly higher feed salinity concentration and elevated concentrate polarization, which results in progressive reduction of their productivity (flux). As flux through the subsequent elements is decreased, accumulation of particulate and organic foulants on these elements diminishes and biofilm formation is reduced. However, the possibility for mineral scale formation increases because the concentration of salts in the boundary layer near the membrane surface increases. Therefore, in RO systems fouling caused by accumulation of particulates, organic matter and biofilm formation is usually most pronounced on the first and second membrane elements of the pressure vessels, while the last two RO elements are typically more prone to mineral scaling than the other types of fouling.

The flux distribution pattern in a RO vessel described above can be altered significantly by the membrane fouling process itself. If the source seawater contains a large amount of foulants of persistent occurrence, as the first element if completely fouled its permeability (flux) over time will be reduced below its typical level ($\pm 25\%$) and the flux of the second RO element will be increased instead. After the fouling of the second RO element reaches its maximum, a larger portion of the feed flow will be redistributed down to the third RO element, until all elements in the vessel begin to operate at a comparable lower flux.

Flux redistribution caused by particulate fouling, NOM deposition and/or biofouling can trigger scale formation of the last RO element, which would not occur under normal flow distribution pattern (non-fouling conditions) shown on Figure 22. The main reason for this phenomenon is that the concentrate polarization on the surface of the last RO element typically increases over two times as a result of this flux redistribution. As indicated previously, in a typical 7-element-per-vessel configuration and non-fouling conditions, the last element would operate at flux that is only 6 to 8 % of the average vessel flux. Under fouling-driven flux redistribution in the membrane vessel, the flux of the last element will increase to 12 to 14 % (i.e., would be approximately two times higher than usual). Since membrane polarization is exponentially proportional to flux, if the RO system is operated at the same recovery, the likelihood for scale formation on the last one or two RO elements increases dramatically.

In addition to increasing the potential for mineral fouling (scaling) on the last one or two membrane elements, the long term operation of fouled RO system is not advisable also because of the higher feed pressure (energy) needed to overcome the decreased membrane permeability if the system is operated to produce the same permeate flow. As the RO system feed pressure reaches certain level (i.e., 75 to 85 bars in seawater RO systems), the external membrane fouling would be compounded by internal fouling due to the physical compaction of the membrane structure which could cause irreversible damage to the membranes. Therefore, understanding of the causes and mechanisms of RO membrane fouling are of critical importance for the successful design and operation of SWRO desalination plants.